Synthetic Inorganic Models for Biological Activation and Reduction of Nitrous Oxide and Carbon Dioxide

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THESIS

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This thesis is dedicated to my husband, Ali Mohamadi, without his love, support, and encouragement it would have been a much longer road to success.

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List of abbreviations

Å	Angstrom
Ar	Aryl
Cat	Catalyst
CODH	Carbon monoxide dehydrogenase
Cp	Cyclopentadienyl
Cp*	Pentamethylcycopentadienyl
Cy	Cyclohexyl
D	Doublet
DCM	Dichloromethane
DFT	Density Functional Theory
equiv	equivalent
Fp	$FeCp(CO)_2$
FT-IR	Fourier Transform Infra-Red
h	hours
HOMO	Highest Occupied Molecular Orbital
IMe	*N*, *N*'-dimethylimidazol-2-ylidene
IMes	*N, N'*-bis(2,4,6-trimethylphenyl) imidazol-2-ylidine
IPr	*N*, *N*'-bis(2,6-diisopropylphenyl)-imidazol-2-ylidine
IPr*	1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl) imidazo- 2-ylidene)
IR	Infra-Red

List of abbreviations (Continued)

J	NMR coupling constant
K	Kelvin
kcal	Kilocalorie
L	Ligand
LUMO	Lowest Unoccupied Molecular Orbital
M	Metal
Me	Methyl
Mes	Mesityl
MHz	Mega Hertz
mL	mililiter
Mp	$MoCp(CO)_3$
NHC	N-heterocyclic carbene
NHis	Histidine
NMR	Nuclear magnetic resonance
NO_2OR	Nitrous oxide reductase
o-	ortho
p-	para
Ph	Phenyl
pin	pinacol
py	pyridine
RT	Room Temperature
s	singlet

List of abbreviations (Continued)

s^{-1}	per second
^{t}Bu	tertbutyl
THF	Tetrahydrofuran
TMS	Trimethylsilane
TS	Transition State
UV	Ultra Violet
Wp	$WCp(CO)_3$
◦	degree
‡	Transition State
δ	Chemical shift
v	Frequency

Summary

Synthetic inorganic models for biological activation and reduction of nitrous oxide and carbon dioxide is presented in this thesis. Chapter one discusses reduction and conversion of nitrous oxide and carbon dioxide gases to control their impacts on the earth atmosphere by nitrous oxide reductase and CO dehydrogenase. In this chapter we also discuss the important role of bimetallic cooperative effect in both multimetallic nitrous oxide and reductase CO dehydrogenase enzymes in the activation and reduction of N_2O and CO_2, respectively. Chapter two examines the small-molecule activation by Hillhouse's carbene-supported [Cu_2(μ-S)] complex as a model of Cu_Z site to add further insight into possible roles of tetranuclearity in Cu_Z and its effect on unsupported sulfide ligand in the active site. Chapter three investigates a tunable bimetallic effect on product selectivity in catalytic CO_2 reduction by using N-heterocyclic carbene-ligated Cu complexes. Introducing a bimetallic effect with analogous Cu−Fe, Cu−W, and Cu−Mo catalysts produces mixtures of formate and CO. Within a series of isosteric catalysts, the selectivity of CO versus formate can be controlled by tuning the electronic nature of the Cu/M (M= Fe, W, Mo) pairing.

Chapter four discusses catalytic hydroboration of ketones and aldehydes by readily available copper carbene complex, (IPr)CuOtBu, at very low catalyst loadings (0.1 mol%), in some cases with turnover frequencies exceeding 6000 h^{-1}. The hydroboration of ketones and aldehydes occurs selectively in the presence of other reducible functional groups including alkenes, nitriles, esters, and alkyl chlorides.

Chapter 1: Introduction

1. Introduction

1.1 Impact of CO_2 and N_2O on climate change as greenhouse gases

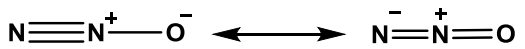
Greenhouse gases (GHG) are the gases in the atmosphere that absorb radiation and they are mainly responsible for the greenhouse effect. The greenhouse effect is one of the leading causes of global warming. Greenhouse gas emissions to the atmosphere and their influence on global climate are one of the significant environmental concerns of present times. Anthropogenic activities have caused unprecedented increases in GHG emissions to the atmosphere. Greater concentrations of greenhouse gases mean more solar radiation is trapped within the earth's atmosphere, making temperatures increase. Two of the most common and worrying greenhouse gases are N_2O and CO_2. N_2O is released during the terminal step of bacterial denitrification. Also, modern agricultural practices, livestock waste management, and the use of nitrogen-rich fertilizers contribute significantly to nitrous oxide emissions. A single nitrous oxide molecule has 300 times the global warming potential of a carbon dioxide molecule, making it a powerful GHG which contributes approximately 6% to global climate change. Nitrous oxide also reacts with ozone in the stratosphere causing depletion of stratospheric ozone which subsequently increases the risk of harmful ultraviolet radiation reaching the earth.

CO_2, is emitted whenever coal, oil, natural gas, and other carbon-rich fossil fuels are burned. Although carbon dioxide is not the most powerful greenhouse gas, it is the largest contributor to climate change.[1]

1.2. Nitrous Oxide (N_2O)

1.2.1 Chemistry of Nitrous Oxide

Nitrous oxide, also known as dinitrogen oxide or dinitrogen monoxide is a colorless, odorless and non-toxic gas with the formula N_2O. It is commonly known as laughing gas because of the euphoric effects of inhaling it. The nitrous oxide molecule is a linear chain of three atoms: a nitrogen atom bound to a second nitrogen atom that in turn is bound to an oxygen atom. Its electronic and geometrical structure can be described by the valence bond resonance forms (eq. 1):



(1)

N_2O is a minor component of the earth's atmosphere, however, it has been identified as a major environmental concern. Nitrous oxide impacts the climate in two different ways: The global warming potential (GWP) of N_2O considered over a range of 100 years is 12 times stronger than of CH_4 and exceeds CO_2 by a factor of almost 300 because of its long lifetime of approximately 114 years.[2] Besides its effect on global warming, it is also highly potent in stratospheric ozone depletion.[2,3] Upon emission into the troposphere, nitrous oxide is transported into the stratosphere, where it is converted into nitrogen oxides (NO_X) that catalyze ozone depletion (eq. 2).[2,4]

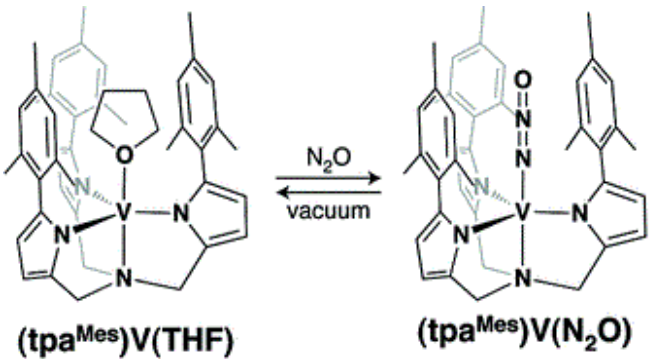
(eq. 2)

$$N_2O + h\nu \longrightarrow N_2 + O^{\bullet}$$
$$N_2O + O^{\bullet} \longrightarrow 2NO^{\bullet}$$

$$NO^{\bullet} + O_3 \longrightarrow NO_2 + O_2$$
$$NO_2 + O^{\bullet} \longrightarrow NO^{\bullet} + O_2$$

The origin of about 70% of the atmospheric amount of N_2O is from microbial processes as a by-product in nitrification and as an intermediate during denitrification.[4] However, the main sources for the increase in atmospheric N_2O concentration are of anthropogenic activities, such as burning of fossil fuels, wastewater treatment[5], and most of all agriculture.[3] Especially the increasing N input to agricultural soils by fertilization leads to an exponentially rising concentration of N_2O in the atmosphere.[6]

N_2O has been long considered an inert molecule because, despite being thermodynamically a potent oxidant, it is kinetically very stable toward decomposition and reduction. These kinetic barriers can be overcome through binding and activation by metal ions. Yet N_2O is in general a poor ligand to transition metals owing to its weak σ-donating and π-accepting properties, and there is only one X-ray crystal structure of a metal N_2O complex reported by Chang and coworkers (Scheme 1).[7] They represented a vanadium-pyrrolide system that reversibly binds N_2O at room temperature and provided the first single crystal X-ray structure of a complex.



Scheme 1. Reaction of (tpa^{Mes})V(THF) with N_2O reported by Chang and coworkers.[7](Reprinted with permission from reference 7 Copyright 2011 American Chemical Society).

1.2.2 Nitrous oxide reductase

Bacterial denitrification is the dissimilatory conversion of nitrate, NO_3^-, in four reductive steps via nitrite, NO_2^-, nitric oxide, NO, and nitrous oxide, N_2O, to yield the inert and stable product dinitrogen, N_2 (eq. 3).[8,9]

$$NO_3^- \xrightarrow{\text{Nar}} NO_2^- \xrightarrow{\text{Nir}} NO \xrightarrow{\text{Nr}} N_2O \xrightarrow{N_2\text{OR}} N_2 \quad (3)$$

To carry out these four reductions, a variety of enzyme systems have evolved. Nitrous oxide reductase is a copper-containing metalloenzyme that catalyzes the last step of denitrification which is a two-electron reduction of N_2O to N_2 (eq. 4). Although the reaction is highly exergonic due to the stability of the product dinitrogen, N_2O is rather inert at room temperature and its transformation requires an effective catalyst.

$$N_2O + 2e^- + 2H^+ \longrightarrow N_2 + H_2O \quad (4) \qquad \Delta G^\circ = -81 \text{ kcal/ mol}$$

1.2.2.1 Structure of nitrous oxide reductase (N_2OR)

N_2OR enzyme has been isolated and biochemically characterized from different classes of Proteobacteria that perform the complete denitrification pathway. N_2OR is a homodimer, each monomer is formed of two domains, N-terminal and C-terminal domain (Figure 1A).[10] The structure of the N-terminal domain has a seven-bladed β-propeller fold and binds the tetranuclear copper monosulfide or "Cu_Z center" which is the catalytic center. The smaller C-terminal domain has a cupredoxin fold and binds the binuclear "Cu_A center," the electron transferring center and its ligated equatorially by two bridging cysteine (Cys) and two histidine (His) residues (Figure 1B).[11] The arrangement of the two monomers is such that the Cu_A center from one monomer is located at 10 Å from the Cu_Z center of the other subunit, making N_2OR a functional dimer, as the two copper centers in one subunit are 40 Å apart, a distance that would hinder intramolecular electron transfer in a monomer.

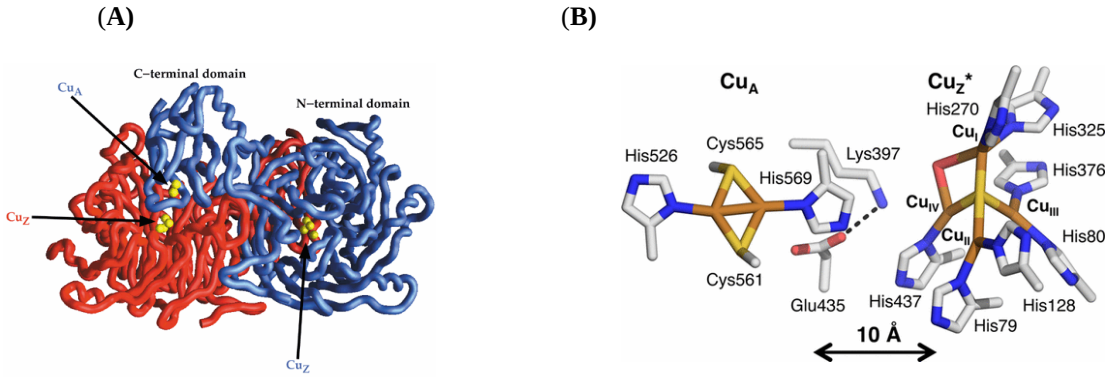


Figure 1. N_2OR is a homodimer. One monomer is shown in red and the other is shown in blue. The copper ions in the CuA and CuZ sites are represented as yellow sphere (A)10 X-ray crystallographic structure of the copper sites of nitrous oxide reductase from Paracoccusdenitrificans (B).[11] (Reprinted with permission from reference 10 Copyright 2004 John Wiley and Sons and reference 11 Copyright 2017 American Chemical Society).

1.2.2.2 Active site in N_2OR

The active site of the nitrous oxide reductase enzyme is a unique tetranuclear copper site with a μ_4-bridging sulfide ligand and it is ligated by 7 His residues.[12] The active site has been purified in two different conditions. The electronic structure of the active site purified in the presence of oxygen known as Cu_Z^* (Figure 2A). The resting redox state of Cu_Z^* is the $3Cu^I1Cu^{II}$ (1-hole) state,[13,14] and a slow reductive activation using the reductant, reduced methyl viologen, is required to access the $4Cu^I$ (fully reduced) redox state of Cu_Z^*, which is its active state in N_2O reduction. A different structural form of the active site in the enzyme purified in the absence of oxygen, is known as Cu_Z (Figure 2B).[15,14] The Cu_Z contains a second sulfur ligand bound on the Cu_I–Cu_{IV} edge of the tetranuclear copper site. The resting redox state of the Cu_Z is the $2Cu^I2Cu^{II}$ (2-hole) and it can progress to $3Cu^I1Cu^{II}$ (1-hole) redox state by reductive activation. The Cu_Z^* reacts with N_2O at a rapid rate required for catalytic turnover, however 1-hole Cu_Z reacts with N_2O at a very slow rate.

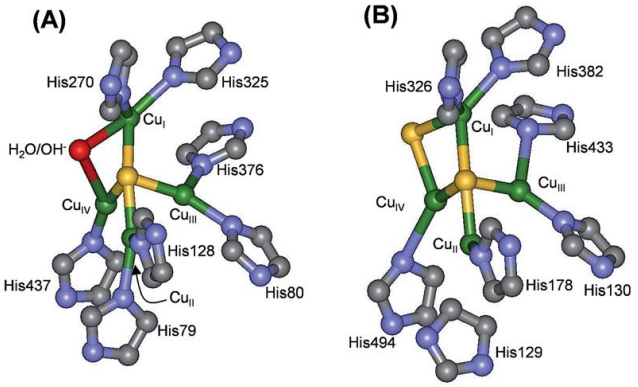


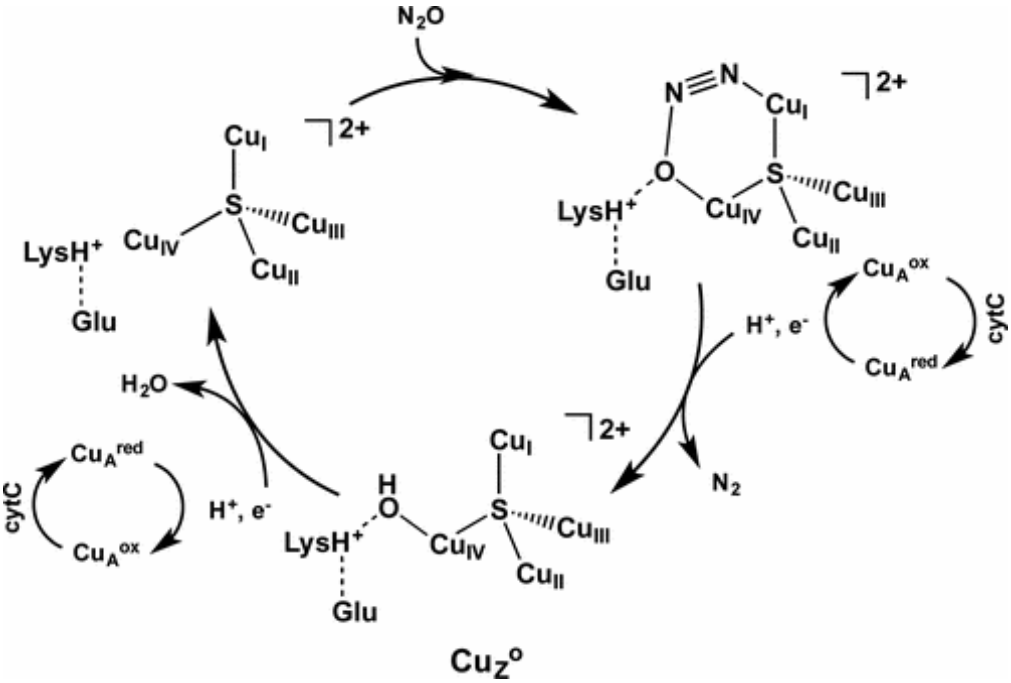
Figure 2. Crystal structures of Cu_Z^* derived from aerobically prepared N_2OR (A) and Cu_Z derived from anaerobically prepared N_2OR (B). Copper shown in green, sulfur yellow, carbon gray, oxygen red, and nitrogen blue.[14] (Reprinted with permission from reference 14 Copyright 2014 Royal Society of Chemistry).

1.2.2.3 Mechanism of N_2O reduction by nitrous oxide reductase enzyme

As mentioned, the $4Cu^I$ state of the Cu_4S cluster is the only form of the N_2OR active site that can reduce N_2O at a rate that is catalytically competent for turnover.[12] The in vitro reconstruction of the activity requires a slow activation in the presence of the artificial electron donor, reduced methyl or benzyl viologen, and not physiologically relevant reductants, such as cytochrome c_{552}, necessary to reduce Cu_Z^* from a resting non-active state ($1Cu^{II}/3Cu^I$) to the fully reduced state $4(Cu^I)$, in contrast to the turnover cycle, which is very fast.

In the recent proposed mechanism for N_2O reduction (Scheme 2),[11] the reaction begins with the fully reduced state Cu_4S and N_2O coordinates to the fully reduced cluster in a linear mode with N-coordinated to Cu_I. Then N−O bond elongates by 0.1−0.2 Å. The structure then rearranges to form a μ-1,3 coordination geometry with the O of N_2O coordinating to Cu_{IV} and hydrogen-bonded to Lys_{397}. The backbonding from Cu_I and Cu_{IV} into the N_2O π^* orbital in the μ-1,3 isomer lowers the energy of the N_2O π^* orbital that will receive two electrons involved in N−O bond cleavage.

In the next step, N−O bond cleaves to form Cu_Z^o intermediate as the product. The hydrogen bonding of the Lys_{397} from the second sphere to the terminal hydroxide coordinated at Cu_{IV} stabilizes the 1-hole Cu_Z^o intermediate. Thus, the Cu_Z^o intermediate is a kinetic product of turnover which decay to the thermodynamically favored resting 1-hole form of Cu_Z^*. The higher energy of metastable $Cu_Z°$ relative to resting 1-hole Cu_Z^* provides the driving force necessary for the rapid reduction of $Cu_Z°$ via electron transfer from Cu_A in turnover. This excludes the inactive resting 1-hole Cu_Z^* state from the catalytic cycle.



Scheme 2. Mechanism of N_2O reduction by the Cu_4S active site of N_2OR proposed by Solomon and coworers.[11](Reprinted with permission from reference 11 Copyright 2017 American Chemical Society).

Cu_Z^o is the only intermediate in this catalytic cycle that its structure has been confirmed experimentally and the structure of the N_2O bridged intermediates is proposed by DFT calculations.

In the proposed mechanism, only two Cu centers, Cu_I and Cu_{IV}, participate directly in N_2O binding and reductive N-O cleavage. The other two Cu centers, Cu_{II} and Cu_{III}, do not interact with the N_2O substrate according to this model and the roles of these two Cu centers have not been discussed in the function of N_2OR.

1.2.3 Bio-inspired approach toward replicating nitrous oxide reductase (N_2OR) activity

Since the importance of the N_2O reduction, several research groups have studied the activation of N_2O by different clusters to obtain insight into the mechanism of the nitrous oxide by the nitrous oxide reductase enzyme.

A unique mixed-valent tricopper cluster bridged by disulfide ligand (Figure 3) reduces N_2O to N_2 at a low temperature.[16] This cluster has a distorted tetrahedral geometry with Cu1 and Cu2 in the +1-oxidation state and a five-coordinate Cu3 in the +2-oxidation state.

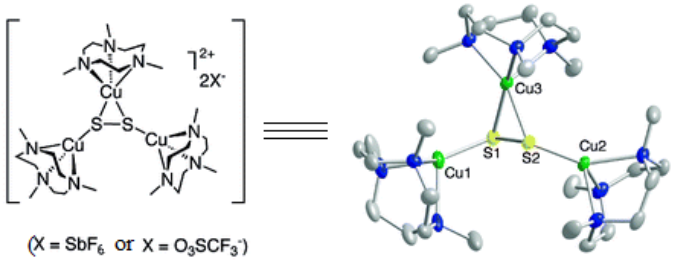


Figure 3. Structure of sulfide bridging tricopper cluster synthesized by Tolman and coworkers.[16](Reprinted with permission from reference 16 Copyright 2009 American Chemical Society).

It loses a [LCu(I)] (X) (L =1,4,7-trimethyltriazacyclononane, X = $O_3SCF_3^-$ or SbF_6^-) fragment easily to yield $[L_2Cu_2S_2]^+$ upon warming to a high temperature (eq. 5).

$$\left[L_3Cu_3S_2\right]^{2+} \rightleftharpoons \left[L_2Cu_2S_2\right]^{+} + \left[LCu(I)\right]^{+} \qquad (5)$$

The formation of N_2 by GC/MS was confirmed upon dissolving the cluster in CH_2Cl_2 and exposing to N_2O at -80°C. Also, an addition of ~7-fold excess [LCu(CH_3CN)] (SbF_6) to the

solution of trinuclear cluster in CH_2Cl_2 inhibited both the decomposition of trinuclear cluster in the absence of N_2O and its reaction with N_2O to form N_2. These results indicating the feasibility of $[L_2Cu_2S_2]^+$ formation, are consistent with a pre-equilibrium step (eq. 5) that generates $[L_2Cu_2S_2]^+$ as the active species in the N_2O activation process with added LCu(I) shifting the equilibrium to the presumably less reactive trinuclear cluster.

In 2010 Torelli and coworkers reported the preparation of the first MV (mixed-valent) copper complex $[1\text{-}(CF_3SO_3)_2]$ with a $\{Cu_2S\}^{2+}$ motif which two copper atoms bridged by the thiophenolate-type moiety (Figure 4A).[17] This complex was unreactive towards N_2O, probably due to the poor ligating ability of the substrate and the saturated copper coordination sphere.

In 2014 this research group synthesized a dissymmetric MV dicopper (II,I) complex $[2.\ (H_2O)\ (OTf)]^+$ with labile triflate and water molecules at the copper centers (Figure 4B). They also reported the reduction of N_2O by this dinuclear dissymmetric copper complex.[14]

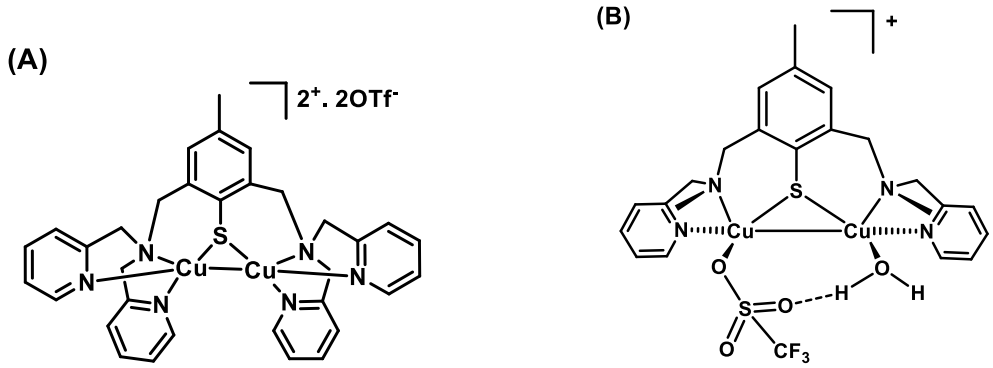
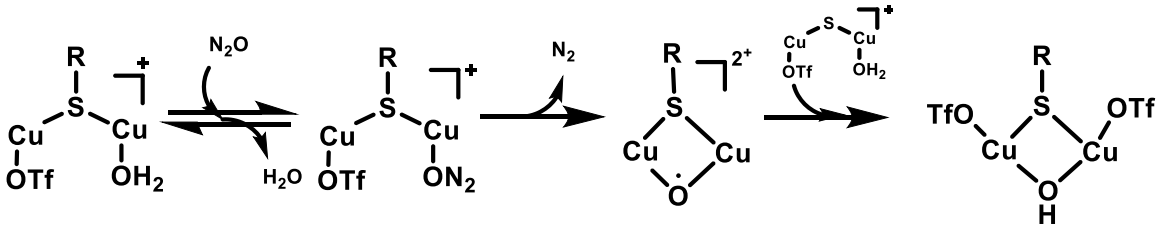


Figure 4. Structure of $[1\text{-}(CF_3SO_3)_2]$ and (A) and $[2.\ (H_2O)\ (OTf)]^+$ (B) complexes synthesized by Torelli and coworkers.[17]

When N_2O was bubbled into an acetone solution of $[2.\ (H_2O)\ (OTf)]^+$, under an Ar atmosphere at room temperature, the formation of N_2 was confirmed by analyzing the headspace of the reaction

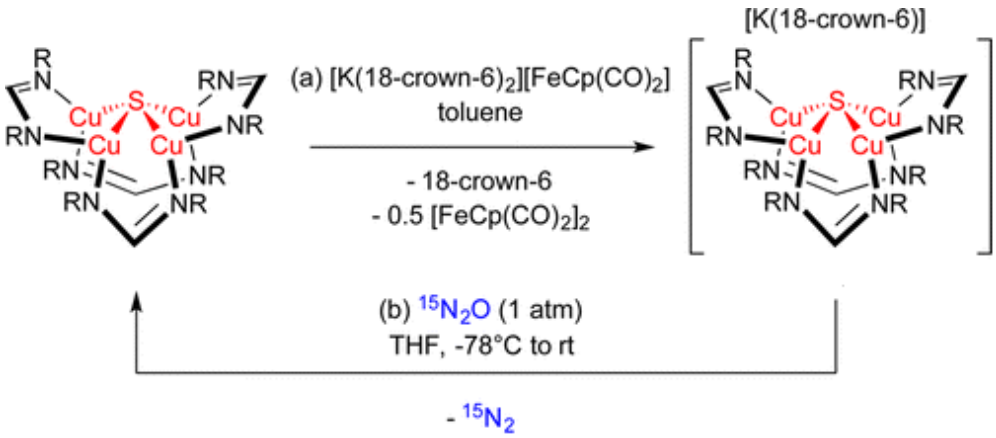
by GC-MS. The structure of the final product showed the presence of a binuclear entity in which the two copper centers are bridged by the sulfur atom from the ligand and by a hydroxo ion. The binding mode of the N_2O was investigated by DFT calculation and η^1-O N_2O binding mode was proposed. Also, the N_2O reduction mechanism by this dinuclear copper complex was explored. The reaction initiates with binding a N_2O to the complex (Scheme 3). The reaction involves an equilibrium between [2. (H_2O) (OTf)] $^+$ and [2. (N_2O) (OTf)] $^+$. After N_2 evolution from [2. (N_2O) (OTf)]$^+$, intermediate HV (high-valent) forms which can be reduced by starting complex to provide [3. (μ-OH) $(OTf)_2$].



Scheme 3. Proposed reaction pathway for N_2O reduction by [2. (H_2O) (OTf)] $^+$.

Mankad and coworkers reported a two-hole state [Cu_4(μ$_4$-S)] cluster supported by nitrogenous amidinate ligands.[18] Recently, they studied the synthesis and characterization of its one-electron reduction product.[19] They chemically reduced a two-hole complex with [K(18-crown-6)$_2$] [Fp] (Fp = $FeCp(CO)_2$) to produce a 1-hole complex, as its [K(18-crown-6)]$^+$ salt. This one-hole complex reduces N_2O stoichiometrically producing a two-hole complex plus N_2 and completing a synthetic cycle for N_2O reduction (Scheme 4). When they exposed the solution of a 1-hole complex to N_2O at -78°C the reaction was observed. They confirmed the evolution of N_2 as detected by headspace GC-MS analysis. Also, ^{1}HNMR analysis indicated that a one-hole complex had been oxidized to a two-hole complex in up to 89% yield. They added electrophiles Me_3SiCl or PhC(O)Cl to the

final product mixtures and observed the formation of $(Me_3Si)_2O$ or PhC(O)OC(O)Ph, confirmed the presence of nucleophilic O^{2-}.



Scheme 4. Synthetic Cycle for N_2O reduction by 1-hole complex reported by Mankad and coworkers.[19] (Reprinted with permission from reference 19 Copyright 2016 American Chemical Society).

Based on their hypothesis, two molecules of a one-hole complex cooperate to reduce N_2O by two electrons with one cluster activating the N_2O substrate and the other acting as a sacrificial reductant.

Productive N_2O reduction is possible with the dicopper model complexes reported by Tolman and Torelli because neither of them feature unprotected sulfide (S^{2-}) ligands that might be susceptible to oxidation. The only N_2O activation by a true copper-sulfide model is Mankad group result.

1.3 Carbon dioxide

As mentioned before, carbon dioxide is another greenhouse gas released by both natural and artificial processes. It is also a necessary material for the growth of all earth's plants and for many industrial processes. In an ideal scenario, the CO_2 produced on earth should be balanced with what is consumed, so that the level of CO_2 remains constant to maintain environmental stability. Unfortunately, with the escalation of human industrial activities, this balance has gradually been disrupted, leading to more CO_2 production and making global warming as a serious issue. Therefore, converting CO_2 into valuable materials seems to be essential, indeed critical, for environmental protection.

1.3.1 Chemistry of carbon dioxide

Carbon dioxide is an odorless, colorless, inert, nontoxic, and incombustible gas. It is the final product of the complete oxidation of carbon. Carbon dioxide is a linear molecule with a very short C-O bond distance, since it is centrosymmetric it has no electrical dipole and the entire molecule is nonpolar. However, it contains polar bonds due to the differences in electronegativity between C and O.

Two vibrational bands are observed in the IR spectrum an antisymmetric stretching mode at 2349 cm^{-1} and a degenerate pair of bending modes at 667 cm^{-1}. There is also a symmetric stretching mode at 1388 cm^{-1} which is only observed in the Raman spectrum.[20] The CO_2 molecule is highly inert and low activity of this molecule causes remarkable challenges to the utilization of carbon dioxide in industrial applications.

In the reduction of the carbon dioxide, the first step involves activation of CO_2, which is a decrease of the C-O bond orders and the bending of the molecule. Bent CO_2 interacts with electrophiles and

nucleophiles through its frontier orbitals. The feasibility of the interaction between nucleophile and CO_2 is by simplifying the transfer of electron density from the nucleophile into the lowest unoccupied molecular orbital (LUMO). The highest occupied molecular orbital (HOMO) with its strongly localized electron density as oxygen in-plane lone pairs is favorable to interactions with electrophiles.

1.3.2 Enzymatic conversion of carbon dioxide

In nature, enzymes have been identified that catalyze the reversible reduction of CO_2 to CO (CO dehydrogenase) or CO_2 to formate (formate dehydrogenase). The active site of the CO dehydrogenase enzyme contains a metal cluster to assist in CO_2 activation and electron transfer.

Based on the formate dehydrogenase (FDHs) metal-content, they can be divided into two major classes. First class which is metal-independent FDHs, belongs to the D-specific dehydrogenases of 2-oxyacids family having no metal ions or other redox cofactors. The other class known as the metal-dependent FDHs and they are from prokaryotic organisms which are members of the dimethyl sulfoxide reductase family of mononuclear molybdenum-containing and tungsten-containing enzymes.

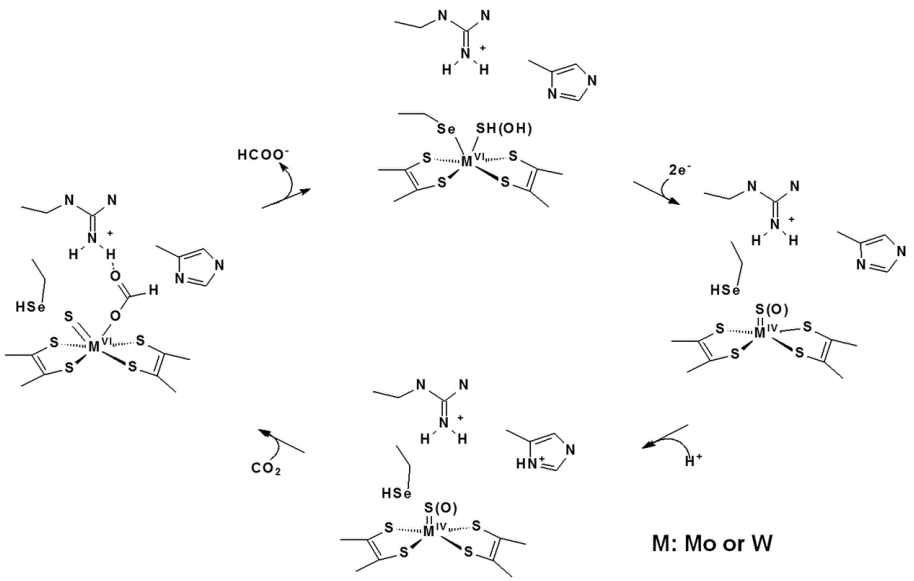
1.3.2.1 Reversible interconversion of CO_2 and formate by metal-dependent formate dehydrogenase

Metal-dependent formate dehydrogenase contains molybdenum or tungsten centers in their active sites. These enzymes are highly oxygen sensitive and can catalyze reversible two-electron oxidation of formate to carbon dioxide (eq. 6).

$$\mathbf{HCOO^- \rightleftharpoons CO_2 + 2e^- + H^+} \qquad \mathbf{(6)}$$

In the oxidized state of these enzymes, the active site contains Mo(VI) and W(VI) ion hexacoordinated in a distorted trigonal prismatic geometry to four sulfur atoms from two pyranopterin molecules, one selenium atom from selenocysteine (SeCy) and one sulfur atom. Two arginine and histidine residues are near the metal center and play a key role in the catalysis.

Based on the proposed mechanism for the reduction of CO_2, the catalytic cycle starts with the oxidized form of the active site with two conserved arginine and histidine residues close to the metal ion (Scheme 5).[21] Firstly, two electrons are transferred to the molybdenum or tungsten center and then Mo(VI) or W(VI) ion are reduced to the Mo(IV) or W(IV) ion. The selenocysteine ligand is simultaneously liberated from the active site. Subsequently, one H^+ ion is transferred to the N atom of the imidazole ring to form an intermediate used as a proton donor in the subsequent step. Once CO_2 is connected to the active site, a C-H bond is formed and a C=O bond is cleaved into a C-O bond and a formate is formed. The formation of the C-H bond is the rate-determining step and the role of the arginine residue during the formation of the C-H bond process is to assist in orienting the formate ligand for the proton removal/delivery by the histidine residue. This C-H bond formation/cleavage step involves a coupled two-electron/one-proton transfer to different sites.



Scheme 5. The proposed mechanism for the reduction of CO_2 to formate by molybdenum- or tungsten-containing $F_{ate}DH$.[21] (Reprinted with permission from reference 21 Copyright 2015 Royal Society of Chemistry).

1.3.2.2 Reversible interconversion of CO_2 and CO by carbon monoxide dehydrogenase (CODHs)

Reduction of carbon dioxide to carbon monoxide is another way for carbon dioxide fixation. Carbon monoxide dehydrogenase (CODHs) are the biological catalysts for the reversible oxidation of CO to CO_2, with water as the source of oxygen (eq. 7) and they are the only catalysts kinetically and thermodynamically optimized to equilibrate CO_2 and CO at room temperature.

$$\mathbf{CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^-} \qquad \mathbf{(7)}$$

Two main types of CODHs have been reported varying in their cofactor composition, structure, and stability in the presence of dioxygen: the anaerobic bacteria and archaea use oxygen-sensitive

Ni- and Fe-containing CODHs, whereas the aerobic, carboxydotrophic bacteria use a Cu-, Mo-, and Fe active site.

1.3.2.2.1. Carbon dioxide activation at the Ni, Fe-cluster of anaerobic carbon monoxide dehydrogenase

The active site in anaerobic CODHs isolated from *Carboxydothermus hydrogenoformans* has been described as an asymmetrical heteronuclear [$NiFe_4S_5$] cluster (Figure 5). The metal ions of the cluster are covalently bound to the protein by five cysteine residues and one histidine residue. The Ni ion is coordinated by four S atoms and shares two inorganic μ_3-S atoms and one μ_2-S atom with four Fe atoms of the active site. Cys_{526} donates the fourth S-ligand to the Ni ion and completes the slight tetrahedrally distorted square-planar geometry. The proximity of the Ni and Fe atoms and the obvious vacant coordination site on Ni suggests the likelihood of cooperative interactions between the two metal centers during catalysis.[22]

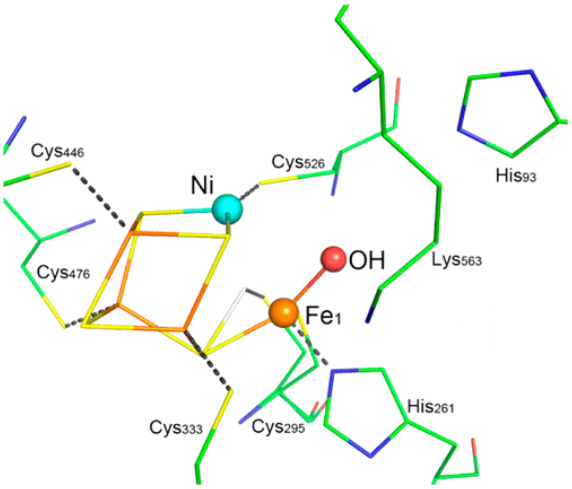
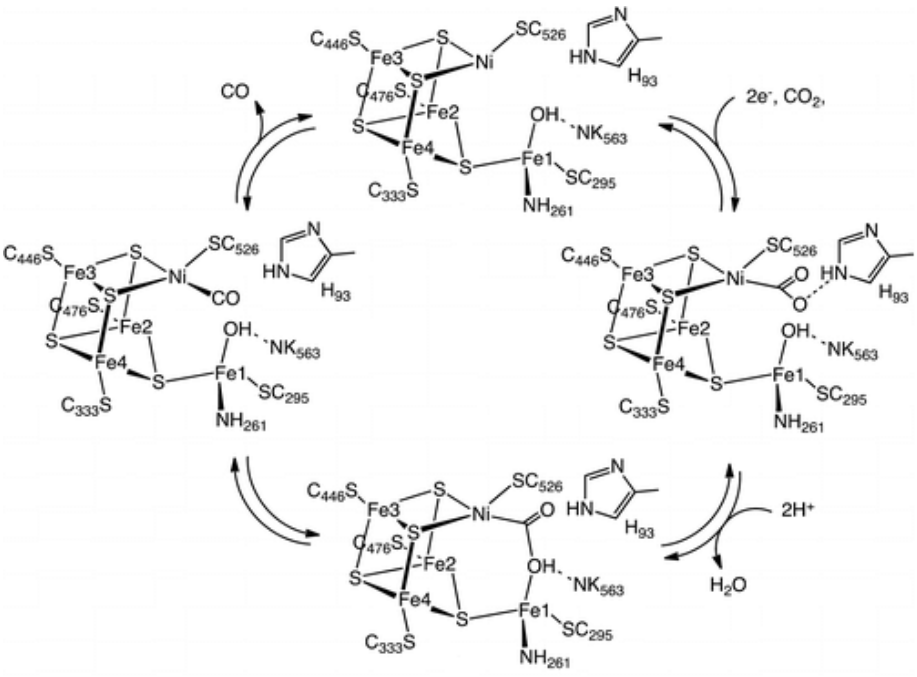


Figure 5. The active site of [NiFe] CO dehydrogenase.[22] (Reprinted with permission from reference 22 Copyright 2013 American Chemical Society).

In the proposed mechanism for CO_2 reduction by [NiFe] CODH (Scheme 6) insertion of CO_2 to the active site forms metallocarboxylate. The resulting CO_2 adduct is stabilized by hydrogen-bonding interactions with a protonated histidine residue. Loss of water from CO_2 adduct complex and the binding of one oxygen of the CO_2 molecule to iron in resulting complex induces the weakening and subsequent cleavage of the carboxylate C-O single bond generating CO and H_2O.



Scheme 6. Proposed mechanism for the reduction of CO_2 to CO by [NiFe] CODH.[22] (Reprinted with permission from reference 22 Copyright 2013 American Chemical Society).

1.3.2.2.2 Carbon dioxide activation at the Mo, Cu-cluster of aerobic carbon monoxide dehydrogenase

An aerobic carbon monoxide dehydrogenaos (CODH) is found in the aerobic bacterium *Oligotropha carboxido*V*orans.* The active site of oxidized CODH contains [CuSMo(=O) OH] metal cluster that is consist of a Cu ion and a Mo-oxo_hydroxo group (Figure. 6).[23] The metals are bridged by a μ-sulfido ligand. The cluster is covalently linked to the large subunit of CODH through interactions of the Cu ion with the S atom of Cys_{388}. The Mo ion is coordinated by the $S_7$and S_8 of the molybdopterin cytosine dinucleotide cofactor, which is noncovalently bound to the large subunit. The ligands around Mo form a distorted square pyramidal geometry. The dithiolate group of MCD is positioned in the equatorial plane together with a hydroxo- and sulfido-group. The oxo-group is positioned in the axial plane. The μ-sulfido ligand and the Sγ atom of Cys_{388} is

ligated to the Cu ion in a distorted linear geometry. The Mo-Cu distance is 3.70 Å in the oxidized form and increases to 4.23 Å upon reduction.

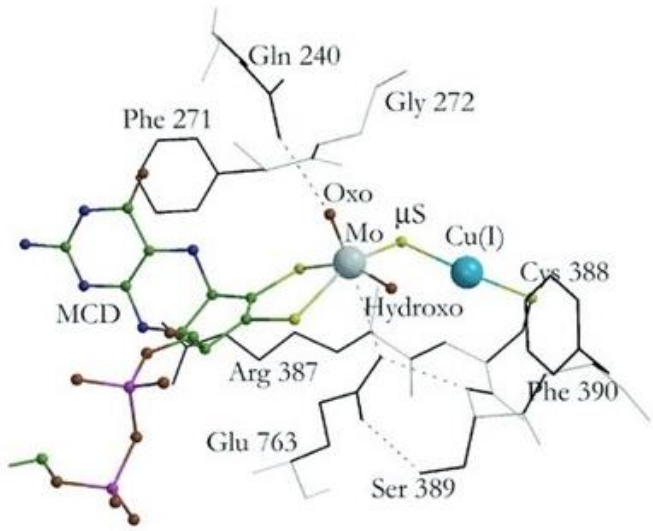


Figure 6. Active site in the Mo, Cu-Cluster of aerobic carbon monoxide dehydrogenase.[23] (Reprinted with permission from reference 23 Copyright 2002 National Academy of Sciences)

For the reversible oxidation of CO by Mo-Cu-CODH, several mechanisms have been proposed. The first mechanism is inspired from the crystal structure of the n-butylisocyanide-inhibited CODH.[23] This mechanism is based on a 1.1 Å resolution crystal structure of the binding of an inhibitor, n-butylisocyanide, to the active site of the oxidized enzyme (Figure 7). The structure shows the n-butylisocyanide integrated between the bridging sulfur and copper but still bound to the molybdenum equatorial oxygen, making a bridging thiocarbamate derivative. CO is suggested to take the place of the CN in the mechanism.

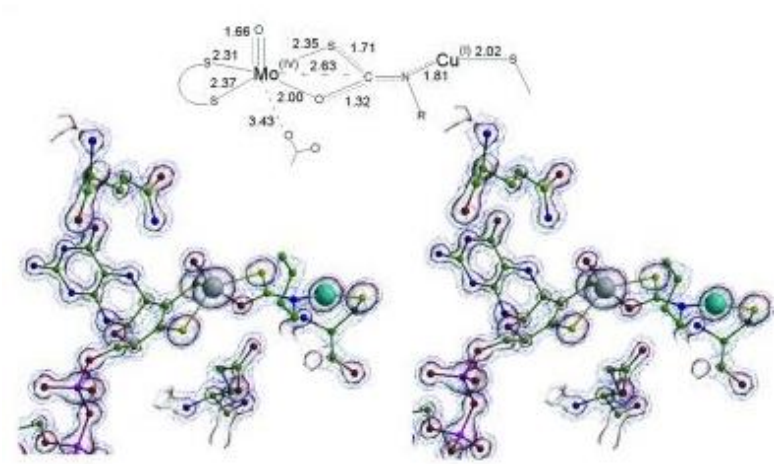
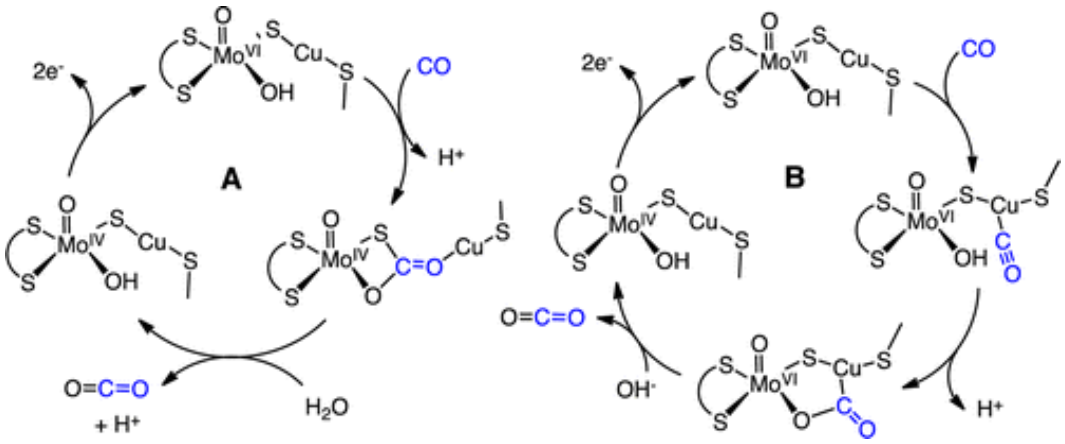


Figure 7. The n-butylisocyanide-containing active site.[23] (Reprinted with permission from reference 23 Copyright 2002 National Academy of Sciences)

This mechanism starts in the oxidized Mo(VI)–Cu(I) state. The substrate CO reaches the cluster through the substrate channel. Since the inhibitor n-butylisocyanide shows the formation of a thiocarbamate derivative, this type of structure with a sulfur–carbon bond is suggested also when the CO molecule is inserted into the Cu-S bond. The coordinated hydroxyl group then attacks the CO, forms CO_2 which leaves the molecule. Released electrons are transferred via the sulfido ligand to yield the reduced Mo (IV) state. The oxidation state Cu (I) do not change during the mechanism. Then catalytic cycle is closed by addition of a hydroxyl ligand derived from a water molecule and oxidation of the Mo (IV) to Mo(VI) through electron transfer from the active site Mo to external redox partners like cytochrome b561 (Scheme 7A).

The second mechanism proposed by DFT calculations suggests a large geometry change is unfavorable during insertion of CO into the Cu–S bond. Based on these calculations, CO binds directly to Cu(I).[24] Coordination of CO to Cu(I) of the binuclear center also confirmed experimentally.[25] Then, the hydroxyl attacks the carbon of CO, subsequently CO_2 is released

followed by reoxidation of Mo(IV) to Mo(VI) with an addition of a hydroxyl ligand. An important role of the polypeptide in this enzyme was confirmed by both the X-ray and DFT studies. X-ray data suggests a nearby glutamate is essential for stabilization of the Mo(VI) state. DFT studies propose the attack of CO by the hydroxyl ligand is more favorable after deprotonation, likely facilitated by a nearby conserved glutamate residue (Scheme 7B). The mechanism proposed by DTF studies is favored due to the recent direct observation of the Cu(I)-CO intermediate in the enzyme by spectroscopic methods.[25]



Scheme 7. Proposed mechanism of MoCu-CODH from (a) X-ray data by Dobbek and coworkers and (b) DFT calculations by Hoffmann and coworkers.[23] (Reprinted with permission from reference 23 Copyright 2002 National Academy of Sciences)

As discussed, mononuclear formate dehydrogenase enzyme catalyzes reversible two-electron oxidation of formate to carbon dioxide (eq. 6) and binuclear CO dehydrogenase enzyme catalyzes reversible oxidation of CO to CO_2 (eq. 7). Apparently the nuclearities of the metalloenzymatic active sites play an important role in selectivity of the products during biological CO_2 reduction. In the active site of the both formate dehydrogenase and aerobic CO dehydrogenase enzymes,

oxidized Mo(VI) ion has the distorted square-pyramidal coordination geometry with an apical Mo=O and two sulfurs from a pyranopterin cofactor. The active site of the enzyme in aerobic CO dehydrogenase however, consists of a Cu ion bridged by a μ-sulfido ligand to Mo ion.

1.3.3. Synthetic Models of [MoCu] CO dehydrogenases

Model studies of the active site of the [MoCu]-CODH have been designed to gain additional knowledge about the structure and function of this system. The most important feature of the model complex would be to achieve the nearly linear and unsupported Mo-μ_2-S-Cu bridge.[26] To date, several model complexes were reported by different research groups, however no reactivity towards CO or any other substrates was reported for any of these complexes. The very first model complex, [Tp^{iPr} MoO(OAr)(μ-S) Cu(Me_3tacn)] (Tp^{iPr} = hydrotris(3-isopropylpyrazol-1-yl)borate; OAr = OC_6H_3 $^tBu_2$-3,5; Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), was introduced by Young and coworkers (Figure 8, complex a) which is the only model complex reported having an unsupported Mo-μ_2-S-Cu bridge.[27] In this complex, Mo lacks the dithiolene type coordination which is a close mimic of MCD observed in the active site and Cu(I) is coordinated by a tridentate N-donor ligand, tacn (1,4,7-triazacyclononane), instead of a thiolate ligation. The next structural model complex, $(Et_4N)_2$[(bdt)Mo(O)S_2Cu(SPh)] (bdt = 1,2-benzene dithiolate), were reported by Tatsumi and coworkers (Figure 8b).[28] This binuclear complex could not mimic the reaction of [MoCu]-CODH with isocyanide and CO because of the disulfide-bridged geometry in this molecule which leads to a shorter Mo-Cu distance (2.596 Å) than seen in the active site (3.70 Å). R. H. Holm and coworkers adopted a different strategy which used monodithiolene W(VI) complexes in place of its molybdenum analogue (Figure 8, complexes c, d, and e).[29] The synthesis

of $[PPh_4]_2[(bdt)W(O)(S_2)Cu\text{-}(SC_6H_4S\bullet)]$ (Figure 8, complex f) (bdt = benzenedithiolate) was developed by Sarkar and coworkers.[30]

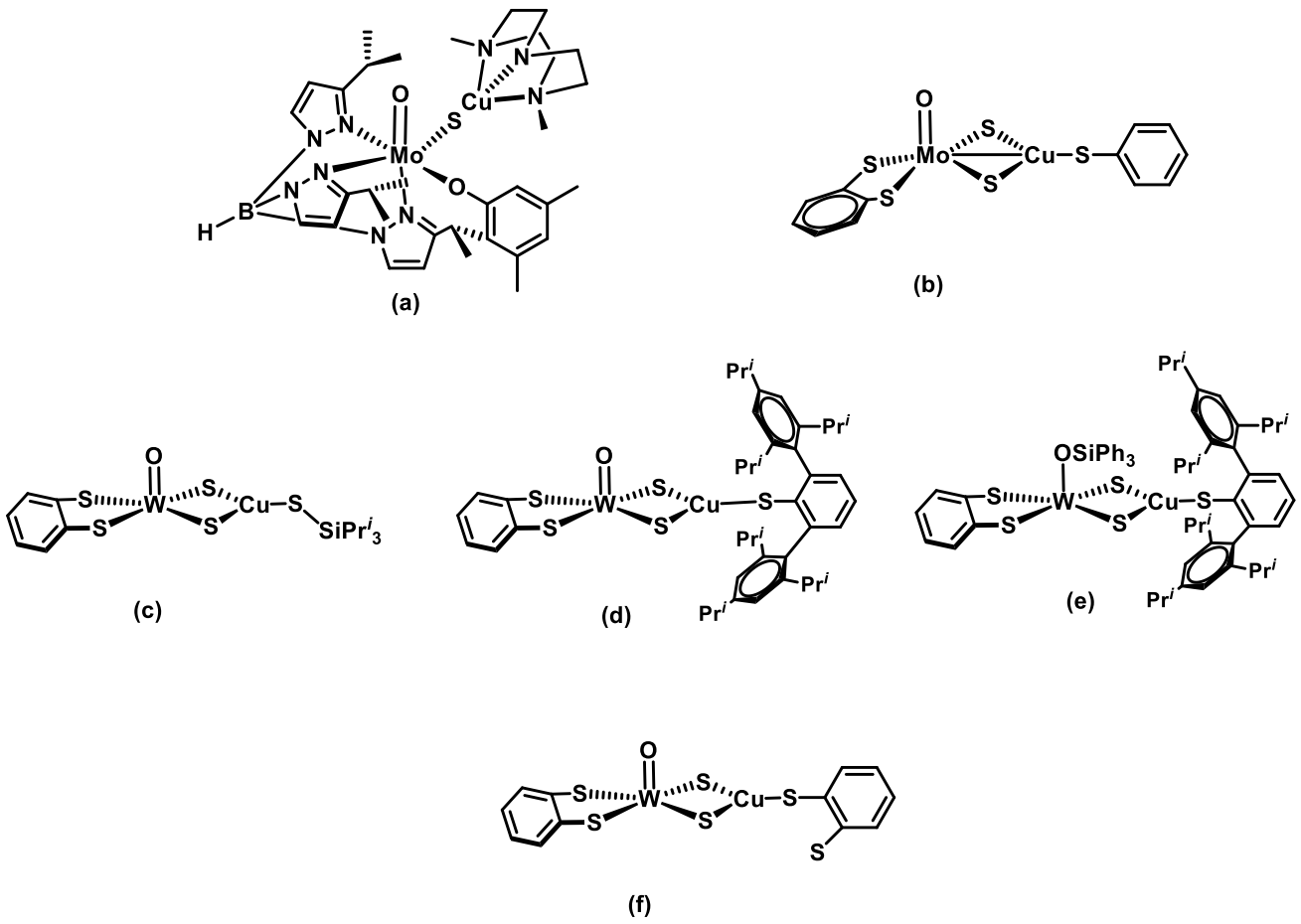


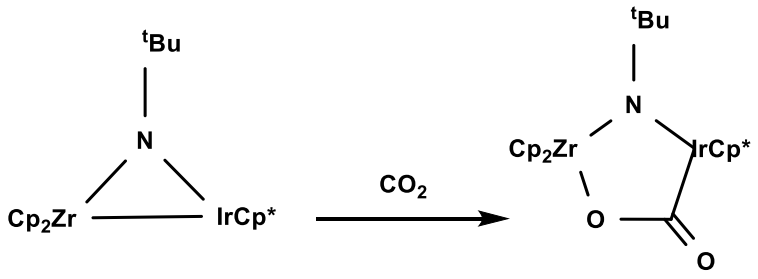
Figure 8. Selected model complexes for the active site of [MoCu]-CODH.

1.3.4. Reaction of CO_2 with heterobimetallic complexes

Carbon dioxide is a very stable molecule and large energy input requires to split the O=C(O) bond and generate carbon monoxide. Activation of CO_2 by simultaneous interaction with electron-rich and electron- deficient metal centers has been of continuous interest since the concept of

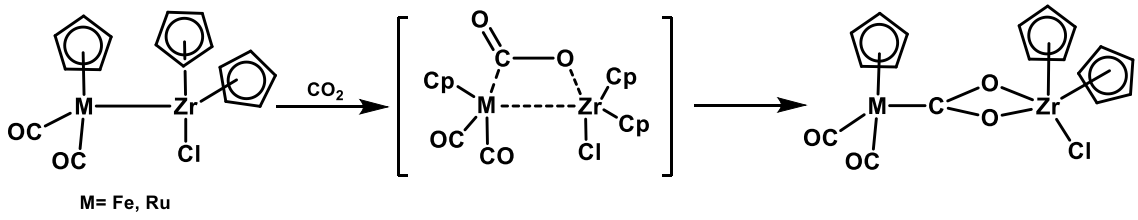
bifunctional CO_2 activation was first introduced by Floriani and coworkers in 1974.[31-33]

Later, Bergman and coworkers published a report demonstrating the reaction between $Cp_2Zr(\mu\text{-}N^tBu)$ IrCp* (Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl) and CO_2 by direct addition of a carbon dioxide C=O bond across the Zr-Ir bond, leading to the unique simple heterobimetallacyclic complex (Scheme 8).[34]



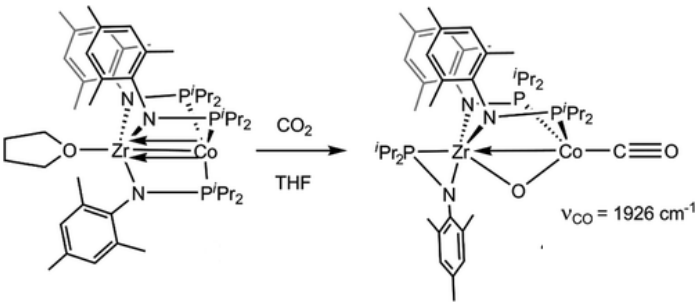
Scheme 8. CO_2 activation by an early–late heterobimetallic Zr–Ir complex.

Cutler and coworkers had shown direct insertion of CO_2 into the early–late transition metal bond. The insertion of CO_2 into the M–Zr bond (M= Fe, Ru) of $[Cp(CO)_2M–Zr(Cl)Cp_2]$ formed the μ-η^1(C): η^2(O, O') compounds $[Cp(CO)_2M–CO_2–Zr(Cl)Cp_2]$ which involves a bifunctional CO_2 activation step, as shown in Scheme 9.[35]



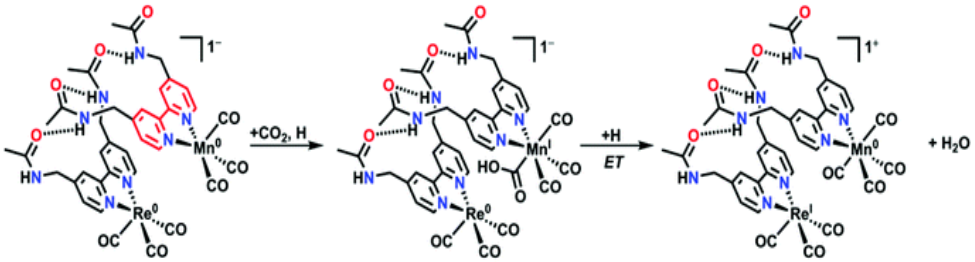
Scheme 9. Insertion of CO_2 into the M–Zr bond in $[Cp(CO)_2M–Zr(Cl)Cp_2]$ complex.

The highly polar metal- metal multiple bonds in reduced Co ($^{i}Pr_2PNMes)_3Zr(THF)$ complex facilitate oxidative addition of the C=O bond in CO_2 leads to clean formation of (OC)Co $(iPr_2PNMes)_2(\mu\text{-}O)Zr(iPr_2PNMes)$ with a terminal CO and bridging Zr-O-Co oxo unit (Scheme 10).[36]



Scheme 10. Oxidative addition of the C=O bond in CO_2 to the highly polar metal- metal multiple bonds in reduced Zr/Co complexe by Thomas and coworkers.[36] (Reprinted with permission from reference 36 Copyright 2011 American Chemical Society).

The use of hydrogen-bonding interactions in the non-covalent assembly of a heterobimetallic supramolecular system with Re and Mn bipyridine-based electrocatalysts is introduced by Kubiak and coworkers.[37] Under catalytic conditions, the formation of hydrogen bonds generates a catalyst system which promotes the reduction of CO_2 to CO and H_2O (Scheme 11).



Scheme 11. Proposed mechanism of CO_2 reduction by the hydrogen-bonded heterobimetallic active species by Kubiak and coworkers.[37] (Reprinted with permission from reference 37 Copyright 2016 Royal Society of Chemistry).

The system reported by Kubiak and coworkers is the only system that is able to achieve catalytic CO_2 reduction. The other systems were limited to stoichiometric CO_2 activation, thus motivating additional research into catalytic CO_2 reduction with bimetallic complexes.

1.4. Research goals

CO_2 and N_2O are isoelectronic and as discussed in the previous sections, reduction and conversion of theses greenhouse gases is an attractive and promising solution to control their impacts on the earth atmosphere. In nature, bimetallic cooperative effect in both multimetallic CO dehydrogenase and nitrous oxide reductase enzymes plays an important role in the activation and reduction of CO_2 and N_2O respectively. The active site of N_2O reductase has a [$Cu_4(\mu_4$-S)] structural core but studies indicate that only binuclear [Cu-S-Cu] center participate directly in N_2O binding and reductive N-O cleavage and the other two copper centers do not interact directly with N_2O. The active site in an aerobic CO dehydrogenase contains a unique dinuclear heterometal [CuSMo(=O)OH] cluster. In another word, bimetallic [Cu-S-Cu] and [Cu-S-Mo] cores play an important role in the nitrous oxide reductase and CO dehydrogenase enzymes, respectively. The Cu ion is common in these bimetallic cores, which is bridged to another metal center (Cu or Mo) by unsupported sulfide ligand.

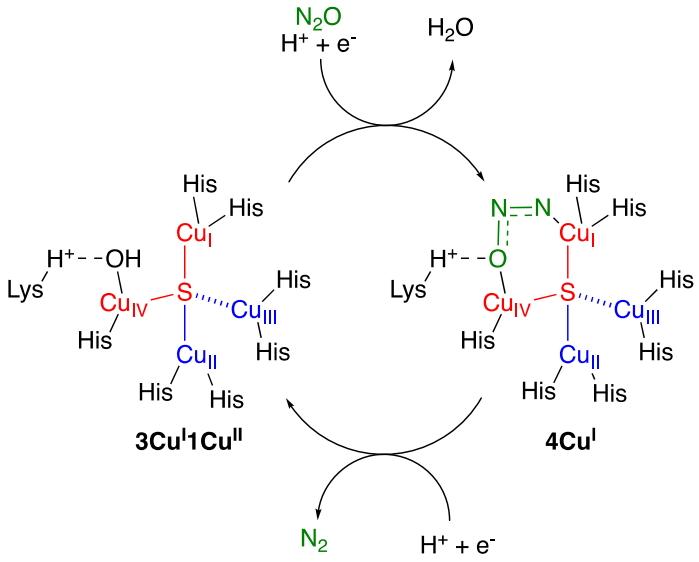
One the research goals explored in this dissertation is to study the small-molecule activation chemistry by Hillhouse's carbene-supported [$Cu_2(\mu$-S)] complex as a model of Cu_Z site to add further insight into possible roles of tetranuclearity in Cu_Z and its effect on unsupported sulfide ligand in the active site (chapter two).

Another research goals explored in this dissertation is to study bimetallic effect on product selectivity in catalytic CO_2 reduction by using N-heterocyclic carbene-ligated Cu complexes (chapter three).

Chapter 2: Activation of N_2O and CO_2 Induces Oxidation or Expulsion of the Sulfur in a $[Cu_2S]$ Complex: Insights into a Role of Tetranuclearity in the Cu_Z Site of Nitrous Oxide Reductase.

2.1. Introduction

Because nitrous oxide (N_2O) is harmful as a greenhouse gas and ozone layer destroyer,[38,39] it is critical to understand the mechanisms by which nature regulates its atmospheric concentrations. Notably, during the terminal step of bacterial denitrification, N_2O undergoes two-electron reduction catalyzed by nitrous oxide reductase (N_2OR), generating benign N_2 + H_2O as products (Chapter 1, eq. 4).[40] The active site for catalytic N_2O reduction in N_2OR is a tetranuclear copper cluster, Cu_Z.[41-43] The kinetically competent form of Cu_Z that participates in enzymatic catalysis has a $[Cu_4(\mu_4\text{-}S)]$ structural core,[44] which activates N_2O upon reduction to the $4Cu^I$ state.[45] Computational studies indicate that the reaction coordinate for N-O cleavage involves μ-1,3 binding between two of the Cu centers, labeled Cu_I and Cu_{IV} (Scheme 12), with crucial assistance from hydrogen bond donation by a protonated lysine residue in the secondary coordination sphere.[11] Thus, only two Cu centers, Cu_I and Cu_{IV}, participate directly in N_2O binding and reductive N-O cleavage. The other two Cu centers, Cu_{II} and Cu_{III}, do not interact directly with the N_2O substrate according to this model.



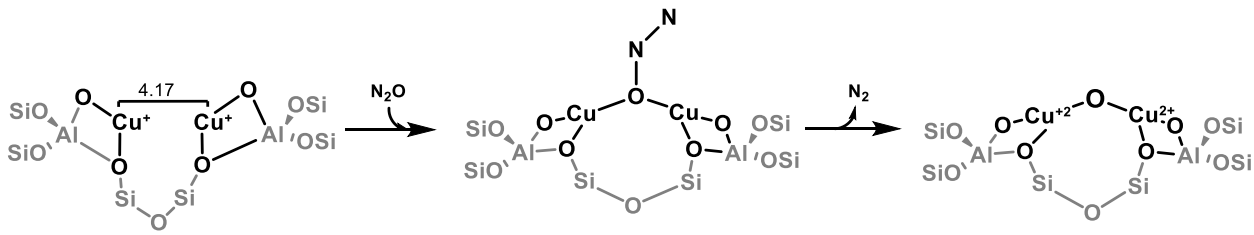
Scheme 12. N_2O binding and reduction at Cu_Z

Furthermore, within the synthetic copper-sulfur model literature, it is clear that dicopper species are capable of mediating two-electron reduction of N_2O. For example, Tolman and coworkers introduced a unique mixed-valent tricopper cluster bridged by disulfide ligand loses a [LCu(I)] (X) fragment easily to yield $[L_2Cu_2S_2]^+$ (Chapter 1, eq. 5) upon warming to a high temperature. $[L_2Cu_2S_2]^+$ is the active species in the N_2O activation and reduction to N_2.[16]

In another study Torelli and coworkers reported a dissymmetric mixed-valent (MV) dicopper (II, I) [**2**. (H_2O) (OTf)]$^+$ containing core with labile triflate and water molecules at the copper centers (Chapter 1, Figure 4) is reduces N_2O to N_2 (Chapter 1, Scheme 3).[14]

Solomon and coworkers reported the reaction between binuclear Cu(I) sites in the 10-membered rings Cu−ZSM-5 and N_2O generates the $[Cu_2O]^{2+}$ site (Scheme 13).[46] Thermodynamically, the most stable Cu(I) center prefers bidentate coordination with a close to linear bite angle. When the Cu−Cu distance is appropriately short (<4.2 Å), N_2O can bind in a "bridged" μ-1,1-O fashion and the oxo-transfer reaction is proceeding with a low activation energy barrier (2 kcal/mol). However, when the Cu−Cu distance is long (>5.0 Å), N_2O binds in a "terminal" η^1-O fashion to a single

Cu(I) site of the dimer and the resulting Ea for N_2O activation is significantly higher. Therefore, bridging N_2O between two Cu(I) centers is essential for its competent two-electron activation in $[Cu_2O]^{2+}$ active site formation.



Scheme 13. Reduction of N_2O by $[Cu_2O]^{2+}$ active site in Cu−ZSM-5 reported by Solomon and coworkers.[46]

Therefore, these three examples demonstrate that tetranuclearity is not a requirement for N_2O reduction with copper-sulfur clusters.[13]An intriguing question, then, is what are the roles of the "spectator" Cu_{II} and Cu_{III} centers in the function of N_2OR. In other words, why is the catalytic site of N_2OR tetranuclear as opposed to dinuclear if only two Cu centers are required for the two-electron reduction of N_2O? Two possible roles for Cu_{II} and Cu_{III} have been proposed in the literature. First, the two electrons that ultimately transfer from Cu_Z to N_2O are delocalized over all four Cu centers via the covalent μ_4-S^{2-} bridge, which serves to lower the energetic barrier for electron transfer.[11] Second, a computational study indicates that under reaction condition a putative $[Cu_2(\mu\text{-}S)]$ core would be protonated at the μ-S^{2-} atom and converted to the $[Cu_2SH]^+$ species. The latter binds the N_2O molecule. However, $[Cu_2SH\text{-}N_2O]^+$ has a much higher N-O cleavage barrier than the $[Cu_4S(im)_7N_2O]^{2+}$ complex and a smaller driving force for the reaction, which make the Cu_2SH cluster a less efficient catalyst than the tetranuclear Cu_Z cluster (Figure 9). The reason for the higher activation energy is significantly reduced charge transfer from the Cu_2SH fragment to the N_2O ligand in the transition state.[47] Thus, the conventional wisdom is that while the Cu_{II} and Cu_{III} sites do not interact directly with substrate and their participation in the N-O bond cleavage

of N_2O molecule is very limited, they serve to facilitate electron transfer and to protect against protonation.

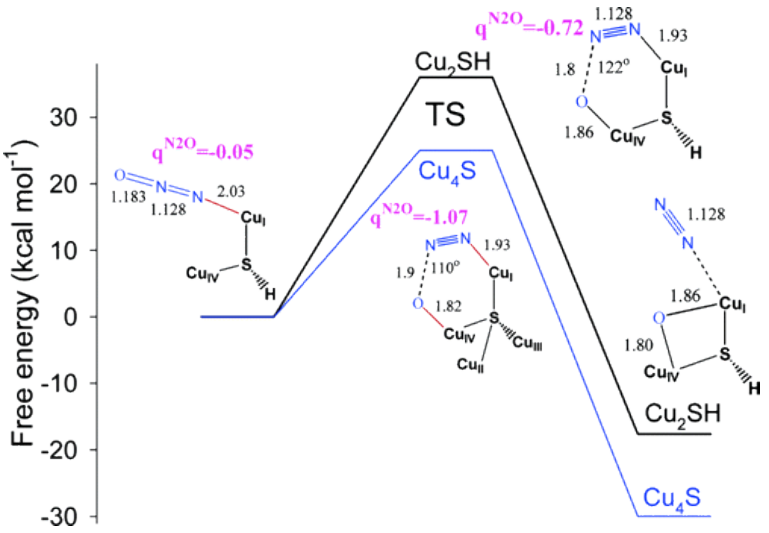
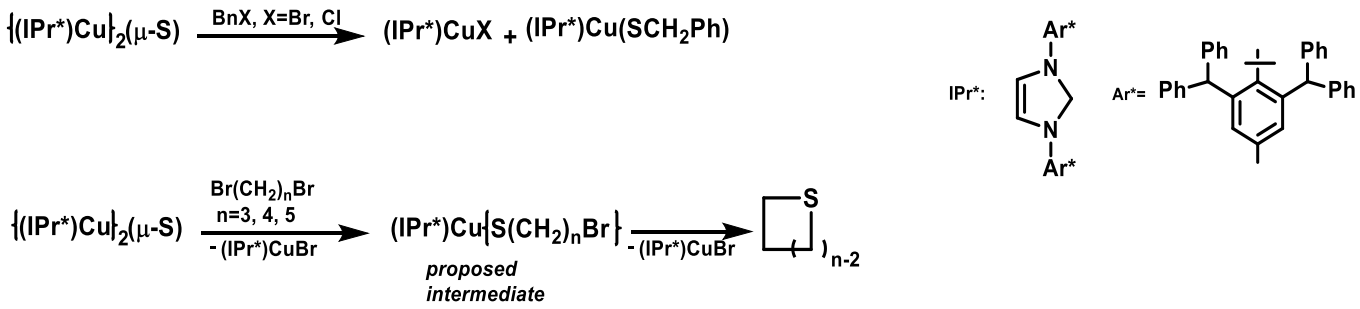


Figure 9. Reaction coordinate for N-O bond cleavage by the binuclear $[Cu_2SH(im)_3]^+$ (black) and teranuclear $[Cu_4S\ (im)_7]^{2+}$ (blue) clusters.[47] (Reprinted with permission from reference 47 Copyright 2006 American Chemical Society).

Studying the small-molecule activation chemistry of a model $[Cu_2(\mu\text{-}S)]$ complex could add further insight into possible roles of tetranuclearity in Cu_Z, requirements for this conversion and general strategies for efficient N_2O activation. An excellent candidate for such studies is the complex $[(IPr^*)Cu]_2(\mu\text{-}S)$, which was published posthumously by Hillhouse in 2015.[48] Reactivity studies of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with organic substrates established the nucleophilic character of its bridging S^{2-} ligand (Scheme 14), but no reactivity studies with small molecules such as N_2O were reported.



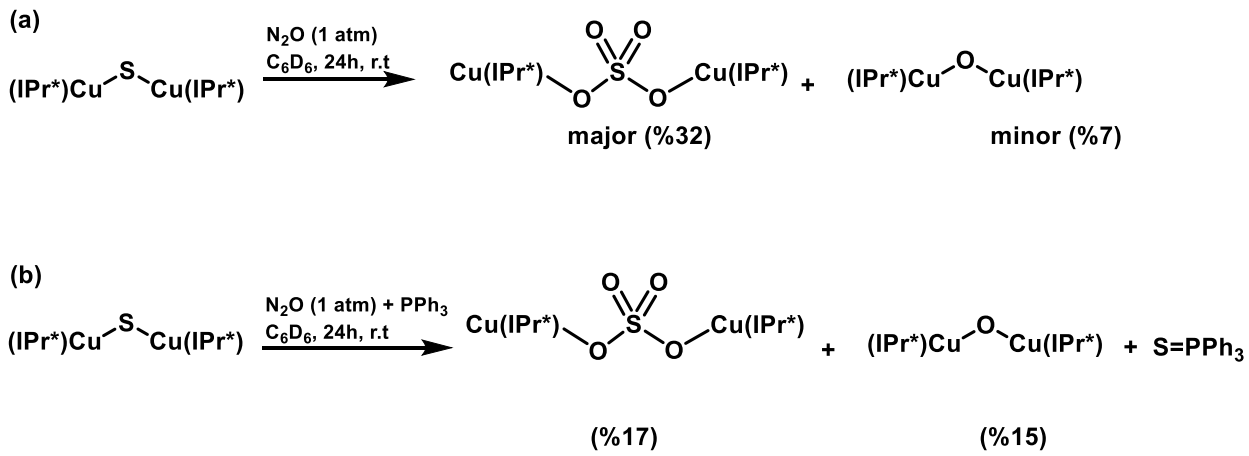
Scheme 14. The reaction of nucleophilic sulfido ligand in $[(IPr^*)Cu]_2(\mu\text{-}S)$ with haloalkyl electrophiles (benzyl halides and dibromoalkanes).[48]

2.2. Results & discussion

In this chapter, we have examined the small-molecule activation chemistry of $[(IPr^*)Cu]_2(\mu\text{-}S)$ towards N_2O and its isoelectronic analogue, CO_2. Our results lead us to propose that additional roles of tetranuclearity in Cu_Z that have not been appreciated before might include protection of the S^{2-} ligand against oxidation by N_2O and against expulsion from the active site during N_2O reduction.

2.2.1. Reaction of $[(IPr^*)\ Cu]_2(\mu\text{-}S)$ with nitrous oxide

Exposing $[(IPr^*)\ Cu]_2(\mu\text{-}S)$ to N_2O (1 atm, room temperature) resulted in a mixture of six different compounds, according to ^1H NMR analysis at 24 h (Scheme 15a). The major product of the reaction (32%) was found to be $[(IPr^*)Cu]_2(\mu\text{-}SO_4)$ (Table 1, entry 1).



Scheme 15. Reaction of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with N_2O in the absence (a) and in the presence (b) of PPh_3**.**

The identity of $[(IPr^*)Cu]_2(\mu\text{-}SO_4)$ was confirmed by generating it independently from $(IPr^*)CuCl$ + Ag_2SO_4, from observing the $[M+H]^+$ ion by ESI-MS, and by X-ray crystallography (Figure 10).

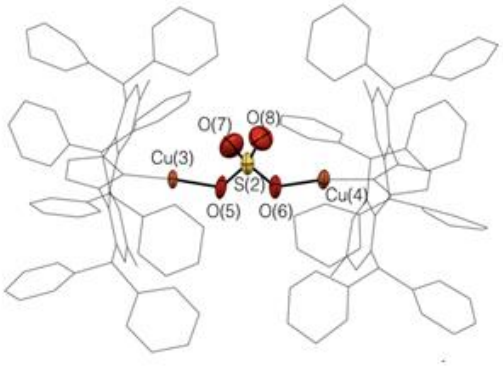


Figure 10. Solid-state structures of $[(IPr^*Cu)_2]$ $(\mu\text{-}SO_4)$ determined by X-ray crystallography. The IPr^* ligands are shown as wireframes, the inorganic cores are shown as 50%-probability thermal ellipsoids, hydrogens are omitted, and only one of two molecules from the asymmetric unit of $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ is shown. Selected bond distances (Å) and angles (°) for $[(IPr^*Cu)_2](\mu\text{-}SO_4)$: Cu(3)-O(5), 1.914(9); Cu(4)-O(6), 1.891(9); S(2)-O(5), 1.46(1); S(2)-O(6), 1.468(9); S(2)-O(7), 1.45(1); S(2)-O(8), 1.54(1).

A minor product was found to be $[(IPr^*)Cu]_2(\mu\text{-}O)$. The identity of $[(IPr^*)Cu]_2(\mu\text{-}O)$ is tentatively proposed by noting that it was generated independently from the dehydration of $(IPr^*)CuOH$ by heating over molecular sieves, and from observing the $[M+H]^+$ ion by ESI-MS. We have been unable to grow X-ray quality crystals of $[(IPr^*)Cu]_2(\mu\text{-}O)$ even after repeated attempts. A third species (Table 1, entry 3), yet unidentified, was determined to be an intermediate that converts to $[(IPr^*Cu)_2]$ $(\mu\text{-}SO_4)$ upon further reaction with N_2O. This conclusion was reached by observing that this species converted to $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ when the reaction was continued beyond 24 h to 60 h under N_2O (Figure 13), while no further conversion to $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ was evident even at 5 d when the N_2O atmosphere was replaced with N_2 at the 24 h time point.

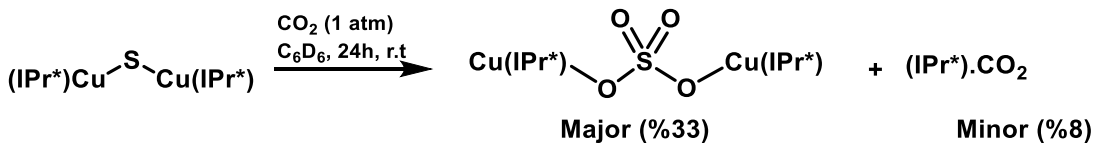
The other three components of the product mixture have not been identified but formed in only small quantities. These three products also formed when $[(IPr^*)\ Cu]_2(\mu\text{-}S)$ was exposed to air, but no formation of $[(IPr^*Cu)_2]$ $(\mu\text{-}SO_4)$ or $[(IPr^*)Cu]_2(\mu\text{-}O)$ from air was evident (Table 1, entry 4,5,6).

Interestingly, the products $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ and $[(IPr^*)Cu]_2(\mu\text{-}O)$ formed in roughly equimolar amounts (36% total) when N_2O was added to a mixture of $[(IPr^*)Cu]_2(\mu\text{-}S)$ and PPh_3 (Scheme 15b). The formation of $Ph_3P{=}S$ was detected by ^{31}P NMR analysis, indicating that the byproduct of $[(IPr^*)Cu]_2(\mu\text{-}S) + N_2O$ converting to $[(IPr^*)Cu]_2(\mu\text{-}O)$ is likely elemental sulfur. It is important to note that no reaction was observed between $[(IPr^*)Cu]_2(\mu\text{-}S)$ and PPh_3 under N_2, and that $Ph_3P{=}S$ was not observed when PPh_3 was added to the product mixture after 24 h of exposing $[(IPr^*)Cu]_2(\mu\text{-}S)$ to N_2O as opposed to having PPh_3 present from the beginning.

2.2.2. Reaction of $[(IPr^*)\ Cu]_2(\mu\text{-}S)$ with carbon dioxide

Exposing $[(IPr^*)Cu]_2(\mu\text{-}S)$ to CO_2 (1 atm, room temperature) provided similar results to the N_2O reaction (Scheme 16). Once again, the major product (33%) was $[(IPr^*Cu)_2](\mu\text{-}SO_4)$. The same

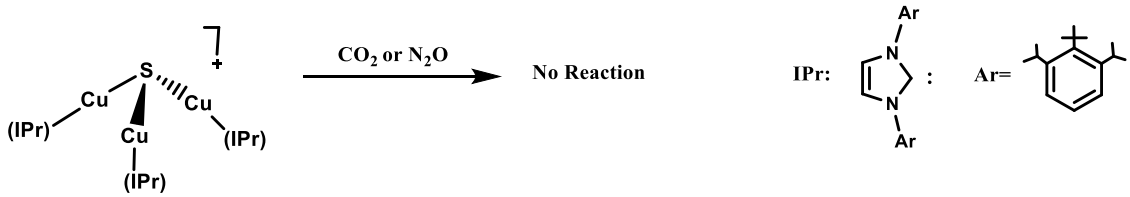
three unidentified byproducts formed in small quantities, although no obvious intermediate was observed. An additional minor product (8%) was the $(IPr^*)\cdot CO_2$ adduct, whose identity was established by independently exposing the free IPr^* carbene to CO_2 (1 atm, room temperature) as is well known for related carbenes.[49] Unlike in the N_2O case, the presence of PPh_3 in the reactant mixture did not impact the nature of the product distribution, and neither compound $[(IPr^*)\ Cu]_2(\mu\text{-}O)$ nor $Ph_3P{=}S$ were observed from CO_2 under any conditions we examined.



Scheme 16. Reaction of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with CO_2

2.2.3. Reaction of $[(IPr)Cu]_3(\mu_3\text{-}S)$ with nitrous oxide and carbon dioxide

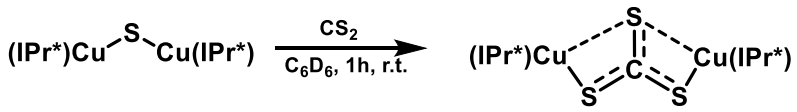
Exposing "protected" tricopper analogue of $[(IPr^*)Cu]_2(\mu\text{-}S)$, $[(IPr)Cu]_3(\mu_3\text{-}S)$,[50] was found to be inert towards N_2O and CO_2 under conditions (Scheme 17) where $[(IPr^*)Cu]_2(\mu\text{-}S)$ undergoes the reactions.



Scheme 17. Reaction of $[(IPr)Cu]_3(\mu_3\text{-}S)$ with N_2O and CO_2.

2.2.4. Reaction of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with carbon disulfide

To gain insight into the initial interaction between $[(IPr^*)Cu]_2(\mu\text{-}S)$ and N_2O/CO_2, we examined the reactivity of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with CS_2 as a model substrate. A rapid reaction was observed between $[(IPr^*)Cu]_2(\mu\text{-}S)$ and CS_2, generating pink-colored $[(IPr^*)Cu]_2(\mu\text{-}CS_3)$ quantitatively (Scheme 18). The identity of $[(IPr^*)Cu]_2(\mu\text{-}CS_3)$ was confirmed by X-ray crystallography (Figure 11) and by observation of the $[M+H]^+$ ion by ESI-MS.



Scheme 18. Activation of carbon disulfide by $[(IPr^*)Cu]_2(\mu\text{-}S)$.

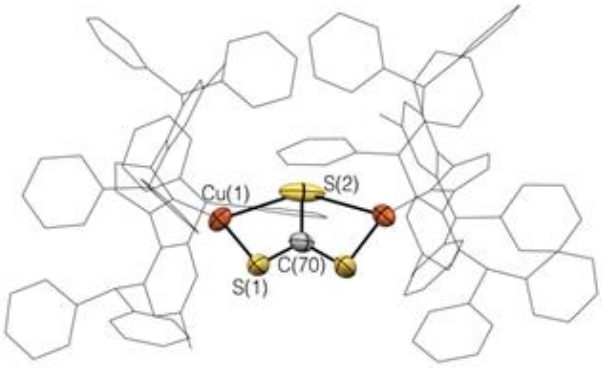


Figure 11. Solid-state structures of $[(IPr^*)Cu)_2](\mu\text{-}CS_3)$ determined by X-ray crystallography. The IPr^* ligands are shown as wireframes, the inorganic cores are shown as 50%-probability thermal ellipsoids, hydrogens are omitted. Selected bond distances (Å) and angles (°) for $[(IPr^*)\ Cu)_2]\ (\mu\text{-}CS_3)$: Cu(1)-S (1), 2.163(2); Cu(1)-S(2), 2.905(2); S(1)-C(70), 1.673(4); S(2)-C(70), 1.716(8); S(1)-C(70)-S(2), 119.2(2); S(1)-C(70)-S(1#), 121.7(5).

Using the structure of $[(IPr^*)Cu]_2(\mu\text{-}CS_3)$ as a starting point, we were able to optimize the structure of a DFT model, $[(IMe)Cu]_2(\mu\text{-}CS_3)$, whose $[Cu_2CS_3]$ core closely resembles the experimentally determined structure of $[(IPr^*)\ Cu]_2(\mu\text{-}CS_3)$ (IMe = *N*, *N*'-dimethylimidazol-2-ylidene). Then, using the $[(IMe)Cu]_2(\mu\text{-}CS_3)$, structure as a starting point, we located energy minima for the DFT models $[(IMe)Cu]_2(\mu\text{-}SCO_2)$ and $[(IMe)Cu]_2(\mu\text{-}SN_2O)$, which are shown in Figure 12. Unlike $[(IMe)Cu]_2(\mu\text{-}CS_3)$, the $[(IMe)Cu]_2(\mu\text{-}SCO_2)$ and $[(IMe)Cu]_2(\mu\text{-}SN_2O)$ structures exhibit unsymmetrical bridging within the dicopper core. In both cases, one Cu center is engaging in Lewis acid activation of an oxygen atom from the small molecule, with multiple bond character being evident from the optimized C-O/N-N bond distances distal to this Lewis acid activation. Loss of CO and N_2 from $[(IMe)Cu]_2(\mu\text{-}SCO_2)$ and $[(IMe)Cu]_2(\mu\text{-}SN_2O)$, respectively, would generate $[(IMe)Cu]_2(\mu\text{-}SO)$, which we also were able to optimize (Figure 12). The optimized structure of $[(IMe)Cu]_2(\mu\text{-}SO)$ places the sulfur and oxygen centers clearly within bonding distance (1.80 Å) and features an unsymmetrical, puckered $[Cu_2(\mu\text{-}SO)]$ core. We propose that $[(IMe)Cu]_2(\mu\text{-}SO)$ is a reasonable approximation for an early intermediate that ultimately is either exhaustively oxidized by the small-molecule oxidant to generate $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ or trapped by PPh_3 to generate $[(IPr^*)\ Cu]_2(\mu\text{-}O)$.

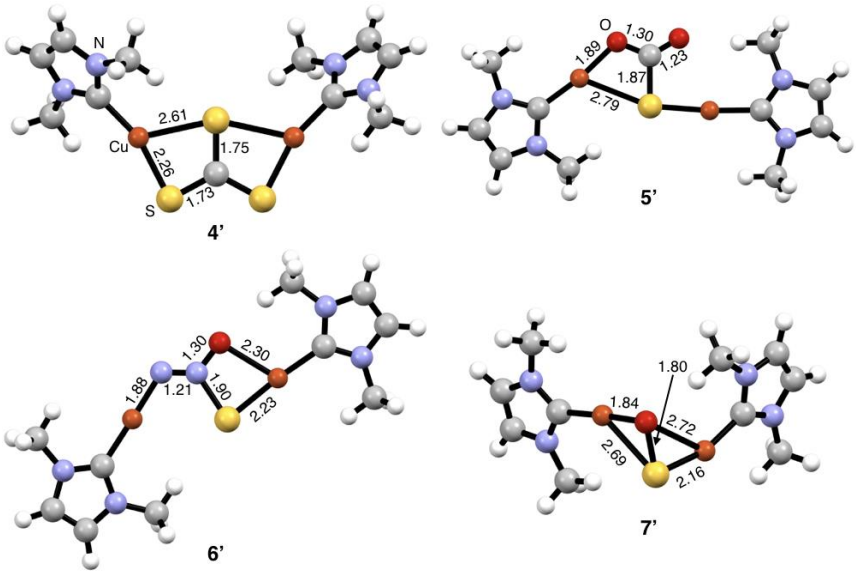
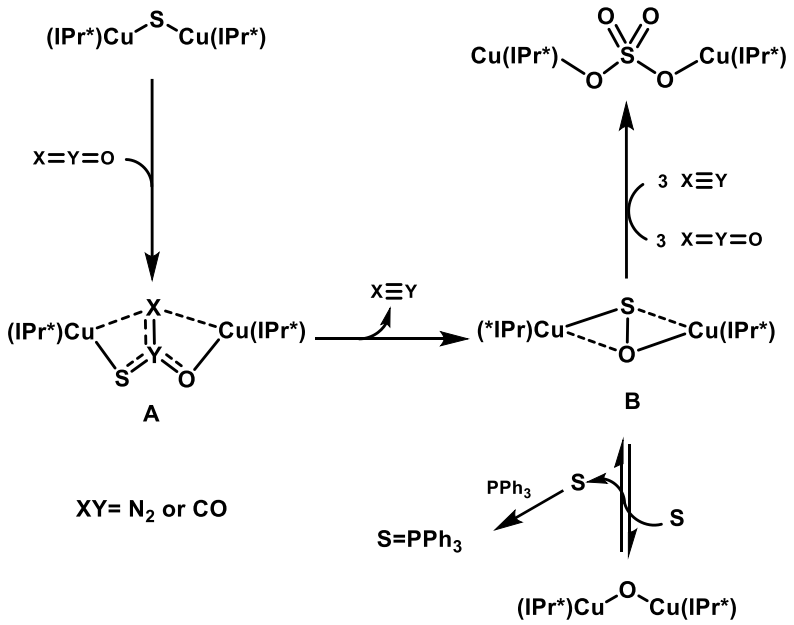


Figure 12. DFT-optimized structures (BVP86/LANL2TZ(f)/6-311+(d)) of dicopper complexes relevant to the small-molecule activation chemistry of $[(IPr^*)Cu]_2(\mu\text{-}S)$. Bond distance labels are in units of Å. Color code: C, gray; H, white; Cu, orange; N, blue; O, red; S, yellow.

2.3. Proposed Mechanism for the activation of small molecules by $[(IPr^*)Cu]_2(\mu\text{-}S)$

Based on the experimental and computational observations outlined above, our preliminary mechanistic proposal is outlined in Scheme 19. Initial insertion of the small-molecule heteroallene into a Cu-S bond of $[(IPr^*)Cu]_2(\mu\text{-}S)$ produces intermediate **A**, which in turn evolves N_2 or CO to generate intermediate **B**. From here, presumably there are two distinct pathways. One involves further oxidation of **B** by three sequential equivalents of the heteroallene oxidant to produce $[(IPr^*Cu)_2](\mu\text{-}SO_4)$. The other involves reversible expulsion of elemental sulfur to produce $[(IPr^*)Cu]_2(\mu\text{-}O)$. In the case of N_2O, the formation of $[(IPr^*)Cu]_2(\mu\text{-}O)$ can be accelerated by trapping the elemental sulfur with PPh_3. In the case of CO_2, the formation of $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ is sufficiently rapid that $[(IPr^*)Cu]_2(\mu\text{-}O)$ does not form even in the presence of PPh_3. Further studies will be required to understand the conversion of **A** to **B** and to elucidate how **B** is further oxidized by N_2O and CO_2.



Scheme 19. Hypothetical mechanism for the activation of small molecules by $[(IPr^{*})Cu]_2(\mu\text{-}S)$ complex.

2.4. Conclusion

These studies reveal the chemistry of a $[Cu_2(\mu_2\text{-}S)]$ core towards small molecules including N_2O. If one were to imagine the catalytic site of N_2OR having such a dinuclear core instead of a tetranuclear $[Cu_4(\mu_4\text{-}S)]$ core, productive catalysis would be hampered or prevented by oxidation and/or expulsion of the S^{2-} ligand. Thus, in addition to participating in electron delocalization and preventing protonolysis, another role of the two "spectator" Cu centers in Cu_Z may be to prevent these unproductive side reactions of the bridging S^{2-} ligand from competing with productive N_2O reductase reactivity.

2.5. Experimental procedures

2.5.1. General considerations

Unless otherwise specified, all reactions and manipulations were performed under purified N_2 in a glovebox or using standard Schlenk line techniques. Glassware was oven-dried prior to use. Reaction solvents (tetrahydrofuran, toluene and pentane) were sparged with argon and dried using a Glass Contour Solvent System built by Pure Process Technology, LLC, or purified by repeated freeze-pump-thaw cycles followed by prolonged storage over activated, 3-A molecular sieves (methanol and NMR solvents). N_2O and CO_2 gas were purchased from PRAXAIR at a purity of 99.999% (5.0 UHP grade) and purified further by running through an O_2 removing catalyst column (RCI GetterMax 133T) and a drying column (Drierite). Literature methods were used to synthesize (IPr*)CuCl,[51] the free IPr* carbene,[52] (IPr*)Cu-OtBu,[48] (IPr*)Cu-SH,[48] and $\{(IPr^*)Cu\}_2(\mu\text{-}S)$[48]. Unless otherwise specified, all other chemicals were purchased from commercial sources and used without further purification.

2.5.2. Physical measurements

NMR spectra were recorded at ambient temperature using Bruker Avance DPX-400 spectrometer. ^{1}HNMR chemical shifts were referenced to residual solvent peak. ^{31}P NMR chemical shifts were refrenced to external triphenylphosphine (-6.7 ppm). Elemental analyses were performed by Midwest Microlab, LLC in Indianapolis, IN. HRMS analyses were performed on Micromass 70 VSE mass spectrometer by the Mass spectroscopy Lab, SCS, University of Illinois. Single-crystal X-ray diffraction studies were performed using a Bruker PHOTON II diffractometer. Solution and refinement were accomplished with the SHELXTL suite of programs,[53] using standard methods,[54] and CIF files are included as Supporting Information.

2.5.3. Computational methods

All calculations were performed using Gaussian09, Revision B.01.[55] Density functional theory (DFT) calculations were carried out using a hybrid functional, BVP86, consisting of Becke's 1988 gradient corrected Slater exchange functional[56] combined with the VWNS local electron correlation functional and Perdew's 1986 nonlocal electron correlation functional.[57] Mixed basis sets were employed: the LANL2TZ(f) triple-ζ basis set[58-60] with effective core potential[61,62] was used for Cu, and the Gaussian09 internal 6-311+G(d) basis set was used for C, H, N, O and S. The bulky aryl groups of the IPr* (1,3-bis(2,6-bis(diphenylmethyl)-4-methylphenyl) imidazo- 2-ylidene) ligands were truncated to methyl groups to minimize computational time. Frequency calculations confirmed that the optimized structures corresponded to energy minima with zero imaginary vibrational frequencies. Optimized XYZ coordinates are provided as Supporting Information.

2.5.4. Generation of $[(IPr^*)Cu]_2(\mu\text{-}SO_4)$ from $(IPr^*)CuCl$

In a nitrogen filled glovebox a scintillation vial was charged with IPr^*CuCl (50 mg, 0.05 mmol) and Ag_2SO_4 (15 mg, 0.05 mmol). Toluene (4 mL) and methanol (2 mL) were then added. The reaction mixture was stirred at 65 ^oC temperature for 8h, and then it was filtered through Celite. Volatiles were removed from the filtrate under reduced pressure. Then white solid was dissolved in C_6D_6, and mesitylene (0.05 mmol, 6.9 μL) was added as an internal integration standard. ^1H-NMR integration indicated 3% conversion to $[(IPr^*Cu)_2](\mu\text{-}SO_4)$. Colorless single crystals suitable for X-ray diffraction studies were grown by diffusion of pentane vapors into a concentrated solution $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ in 2-methyltetrahydrofuran. Note: Due to a low yield of {(IPr^*)

$Cu\}_2(\mu\text{-}SO_4)$ in this reaction, the single crystals used for X-ray diffraction were actually grown from a reaction mixture from $[(IPr^*)Cu]_2(\mu\text{-}S) + CO_2$ (see below). ^{1}H-NMR (400 MHz, C_6D_6): δ 7.46 (s, 8H), 7.44 (s, 10H), 7.32 (s, 8H), 6.84 (s, b, 10H), 5.69 (s, 4H, NCH), 5.49 (s, 8H, CH Ph_2), 1.76 (s, 12H, CH_3).

2.5.5. Preparation of (IPr*)CuOH

Inside the glovebox a 20 mL scintillation vial was charged with stir bar, $(IPr^*)CuCl$ (0.4 g, 0.39 mmol), CsOH (0.177 g, 1.18 mmol) and THF (15 mL). The reaction mixture was stirred at room temperature for 12 h, then filtered through Celite. The solvent was removed from the filtrate under reduced pressure to yield a white powder (0.373 g, 94%). Colorless single crystals suitable for X-ray diffraction studies were grown by diffusion of pentane vapors into a concentrated solution of $(IPr^*)CuOH$ in THF. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.50 (s, 4H), 7.48 (s, 4H, CH phenyl), 7.17-7.19 (m, 6H), 6.99-7.03 (m, 30H), 5.68 (s, 4H, CH ph_2), 5.54 (s, 2H, NCH), 1.73 (s, 6H, CH_3). Anal. Calcd for $C_{69}H_{57}CuN_2O$: C, 83.4; H, 5.79; N, 2.82. Found: C, 81.25; H, 5.59; N, 2.84. Repeated attempts at obtaining satisfactory combustion analysis results (with %C within ±0.4% of the calculated value) gave results with a large degree of variance, indicating either that the spectroscopically pure samples were decomposed during shipping/handling or that the compound does not combust cleanly.

2.5.6. Preparation of $[(IPr^*)Cu]_2(\mu\text{-}O)$ from $(IPr^*)CuOH$

Inside the glovebox a 50-mL Schlenk flask was charged with stir bar, (IPr*)CuOH (0.7 g, 0.7 mmol), molecular sieves (3 g) and toluene (15 mL). The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The reaction mixture was stirred at 65°C for 6 h under N_2. After 6 h the reaction was cooled down to room temperature and was transferred inside the

glovebox. The reaction was filtered through plug of Celite. Solvent was removed from the filtrate under reduced pressure to yield a white powder (0.35 g, 25 %). ^{1}H-NMR (400 MHz, C_6D_6): δ 7.44 (s, 8H), 7.42 (s, 10H), 7.30 (t, J=7.6 Hz, 18H), 7.09 (t, J=7.3 Hz, 12H), 6.93-7.0 (m, 56H), 5.59 (s, 8H, CH ph_2), 5.43 (s, 4H, NCH), 1.78 (s, 12H, CH_3). HRMS (ESI) calcd. for $[C_{138}H_{112}N_4OCu+H]^+$: 1967.7506 Found: 1967.7472

2.5.7. Preparation of $[(IPr^*)Cu]_2(\mu\text{-}CS_3)$

In a nitrogen filled glovebox a scintillation vial was charged with $\{(IPr^*)Cu\}_2(\mu\text{-}S)$ (15 mg, 0.0075 mmol) and stir bar. Benzene-d_6 (3 mL) was added, followed by CS_2 (0.46 μL, 0.007mmol). The reaction mixture was stirred at room temperature for 1 h then ^{1}H-NMR was taken to confirm complete conversion to $\{(IPr^*)Cu\}_2(\mu\text{-}CS_3)$. Solvent was removed under reduced pressure to yield a pink powder (14 mg, 96 %). Pink single crystals suitable for X-ray diffraction studies were grown by diffusion of pentane vapors into concentrated solution of $\{(IPr^*)Cu\}_2(\mu\text{-}CS_3)$ in THF. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.54 (s, 6H), 7.52 (s, 10 H) 7.23-7.19 (m, 16H), 7.06 (s, 8H), 6.91-6.97 (m, 52), 5.69 (s, 8H, CH ph_2), 5.57 (s, 4H, NCH), 1.75 (s, 12H, CH_3). HRMS (ESI) calcd. for $[C_{139}H_{112}N_4S_3Cu_2+H]^+$: 2059.6719 Found: 2059.6707.

2.5.8. Reaction of IPr^*carbene with CO_2

In a nitrogen filled glovebox a 50 mL Schlenk flask was charged with IPr^* (40 mg, 0.044 mmol) and stir bar. Then C_6D_6 (4 mL) was added. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reaction mixture was stirred for 24 h at room temperature under

CO_2, and then volatiles were removed under reduced pressure. The resulting solid was analyzed by ^{1}H-NMR. ^{1}H-NMR (400 MHz, C_6D_6): δ 7.85 (d, J= 7.6 Hz, 8H), 7.22 (t, J= 7.7Hz, 8H), 7.04 (t, J= 7.4 Hz, 4H), 6.87-6.93 (m, 24H), 6.03 (s, 4H, $CHPh_2$), 5.02 (s, 2H, NCH), 1.60 (s, 6H, Me).

2.5.9. Reaction of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with N_2O

In a nitrogen filled glovebox, $[(IPr^*)Cu]_2(\mu\text{-}S)$ **(**50 mg, 0.025 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into a scintillation vial. This solution was transferred to a Schlenk flask. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freezepump- thaw cycles and backfilled with N_2O (1 atm). The reaction mixture was exposed to N_2O for 24 h at room temperature. ^{1}H-NMR analysis at this point showed that six different species had formed, with compound $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ as the main product of the reaction. The third component (Table 1 entry 3) was found to be an intermediate which can convert to compound $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ upon further exposure to N_2O. The presence of N_2O is necessary for this conversion, as established by observing that when the reaction was stopped after 24 h and then was stirred under N_2 for 5 days the conversion of intermediate to $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ was not observed.

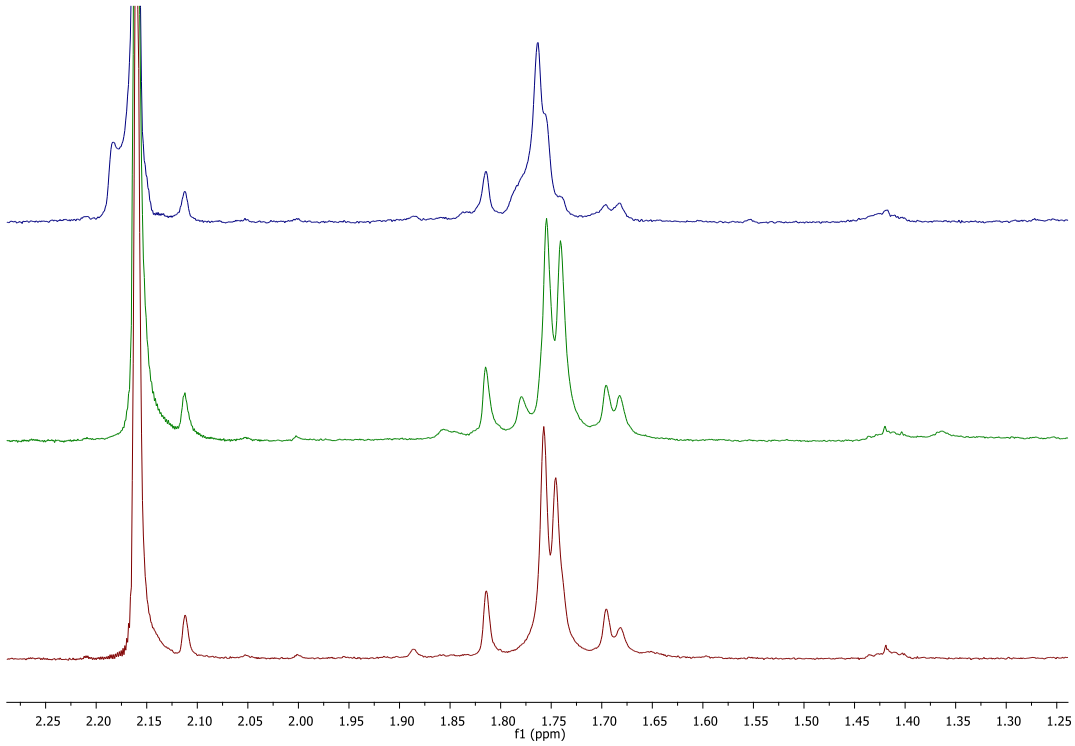
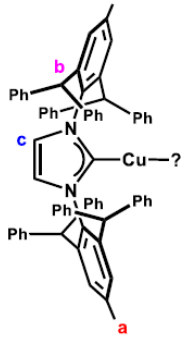


Figure 13. Comparison of ^{1}H NMR spectra resulting from reaction of $\{(IPr^{*})Cu\}_2(\mu\text{-}S)$ with nitrous oxide in three different conditions: 24 h under N_2O (red), 60 h under N_2O (blue), and 24 h under N_2O followed by stirring under N_2 for 5 days (green).



Identity	a	b	c
{(IPr*) Cu}$_2$(μ-SO$_4$)	1.76	5.49	5.69
{(IPr*) Cu}$_2$(μ-O)	1.78	5.44	5.59
Intermediate	1.75	5.58	5.62
Minor impurity	1.74	5.56	5.64
Minor impurity	1.68	5.53	5.55
Minor impurity	1.82	5.14	6.04

Table 1. ^{1}H NMR chemical shifts for different species formed in the N_2O reaction.

2.5.10. Reaction of [(IPr*)Cu]$_2$(μ-S) with N_2O in the presence of PPh_3

In a nitrogen filled glovebox a scintillation vial was charged with [(IPr*)Cu]$_2$(μ-S) (30 mg, 0.0151 mmol) and triphenyphosphine (4 mg, 0.0151 mmol), and then C_6D_6 (6 mL) was added. This solution was transferred to a 50-mL Schlenk flask. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freeze-pump-thaw cycles and backfilled with N_2O (1 atm). After 24 h the reaction flask was transferred into the glovebox and mesitylene (2 μL, 0.0151 mmol) was added as an internal integration standard. ^{1}H-NMR and ^{31}P

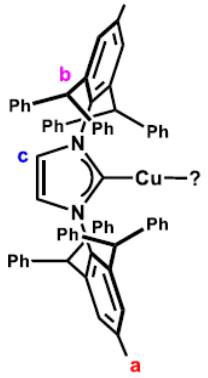
NMR spectra were taken. ^{1}H-NMR integration indicated 19% conversion to [(IPr*Cu)$_2$](μ-SO$_4$), 17% conversion to [(IPr*)Cu]$_2$(μ-O).

2.5.11. Reaction of [(IPr*)Cu]$_2$(μ-S) with N$_2$O and addition of PPh$_3$ after 24 h

In a nitrogen filled glovebox a scintillation vial was charged with [(IPr*)Cu]$_2$(μ-S) (30 mg, 0.0151 mmol), and then C_6D_6 (6 mL) was added. This solution was transferred to a 50-mL Schlenk flask. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freezepump-thaw cycles and backfilled with N2O (1 atm). The reaction mixture was exposed to N_2O for 24 h at room temperature. After 24 h the schlenk flask was transferred inside the glovebox and triphenyphosphine (4 mg, 0.0151 mmol) and mesitylene (2 μL, 0.0151 mmol) were added to the solution. The reaction was stirred under N_2 for 1h and then ^{1}H-NMR and ^{31}P-NMR spectra were taken.

2.5.12. Reaction of [(IPr*)Cu]$_2$(μ-S) with CO$_2$

In a nitrogen filled glovebox, [(IPr*)Cu]$_2$(μ-S) (50 mg, 0.025 mmol) was dissolved in C_6D_6 (6 mL) and pipette filtered through Celite into another scintillation vial. This solution was transferred to a 50-mL Schlenk flask. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reaction mixture was exposed to CO_2 for 24 h at room temperature. After 24 h five different species had formed according to ^{1}H-NMR analysis, with compound [(IPr*Cu)$_2$](μ-SO$_4$). as the main product of the reaction. ^{1}H-NMR integration indicated 33% conversion to [(IPr*Cu)$_2$] (μ-SO$_4$).



Identity	a	b	c
{(IPr*) Cu}$_2$(μ-SO$_4$)	1.76	5.49	5.69
(IPr)*CO$_2$	1.60	5.02	6.03
Intermediate	1.75	5.58	5.62
Minor impurity	1.74	5.56	5.64
Minor impurity	1.68	5.53	5.55
Minor impurity	1.82	5.14	6.04

Table 2. ^{1}H NMR chemical shifts for different species formed in the CO_2 reaction.

2.5.13. Reaction of [(IPr*)Cu]$_2$(μ-S) with CO_2 in the presence of PPh_3

In a nitrogen filled glovebox a scintillation vial was charged with [(IPr*)Cu]$_2$(μ-S) (30 mg, 0.0151 mmol) and triphenyphosphine (4 mg, 0.0151 mmol), and then C_6D_6 (6 mL) was added. This solution was transferred to a 50-mL Schlenk flask. The Schlenk flask was taken out of the glovebox and connected to a Schlenk line. The solution was degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reaction mixture was exposed to CO_2 for 24 h at room temperature. After 24 h ^{1}H-NMR and ^{31}P-NMR were taken.^{1}H-NMR integration indicated 31% conversion to [(IPr*Cu)$_2$](μ-SO$_4$).

2.5.14. Reaction of $[(IPr^*)Cu]_2(\mu\text{-}S)$ with PPh_3

In a nitrogen filled glovebox a scintillation vial was charged with $[(IPr^*Cu)_2](\mu\text{-}SO_4)$ (10 mg, 0.005 mmol) and triphenyphosphine (1.3 mg, 0.005 mmol) and then C_6D_6 (2 mL) was added. The reaction mixture was stirred at room temperature for 24 h then ^{1}H-NMR and ^{31}P-NMR were taken, which indicated that no reaction had occurred.

Chapter 3: Catalyst Control of Selectivity in CO_2 Reduction Using a Tunable Heterobimetallic Effect.

(This chapter was previously published as Bagherzadeh, S. Mankad, N. P. *J. Am. Chem. Soc.*, **2015**, 137 (34), 10898–10901).

3.1. Introduction

Motivation ranging from environmental remediation to energy storage to chemical synthesis have driven intense research into CO_2 reduction catalysis.[22] While several catalytic approaches have proven successful in overcoming the kinetic barrier associated with activating the inert CO_2 molecule, achieving control over product selectivity remains underdeveloped. For example, several homogeneous catalyst designs have been identified for the reduction of CO_2 with oxophilic silane or borane reagents. Corresponding HCO_2[E],[63-66] CO,[67] H_2CO,[68-69] H_3CO[E],[70-74] CH_4[75-78] reduction products or mixtures thereof[79-82] are observed ([E] = silyl or boryl), with the product selectivity being determined empirically rather than through rational design in most cases. However, nature has evolved to achieve exquisite efficiency, as well as selectivity control during biological CO_2 reduction, and apparently the nuclearities of the metalloenzymatic active sites play an important role (Figure 14).

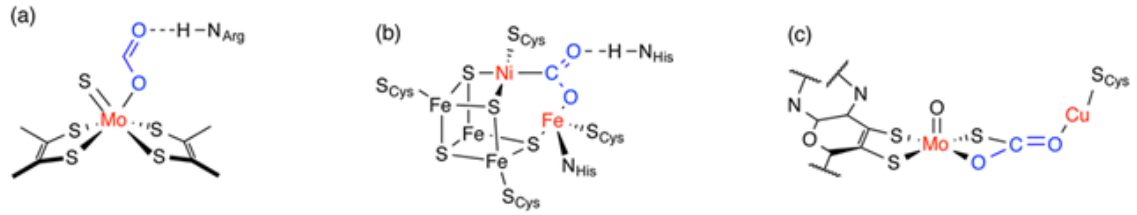
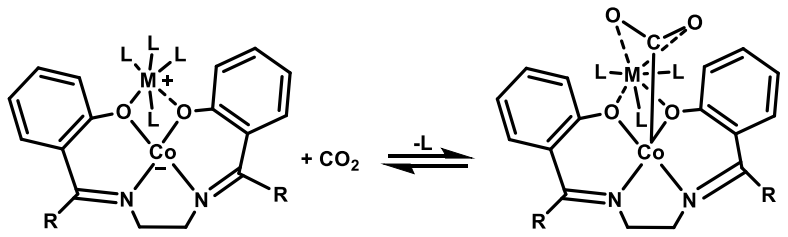


Figure 14. (a) Proposed monometallic CO_2 activation by a [Mo] formic acid dehydrogenase; proposed bimetallic CO_2 activation at the active sites of (b) [NiFe] and (c) [MoCu] carbon monoxide dehydrogenases.[83-85] (Reprinted with permission from reference 33. Copyright 2015 American Chemical Society).

The monometallic Mo and W active sites of formic acid dehydrogenases[83] interconvert CO_2

and formic acid selectively, while the heterobimetallic Ni/Fe[84] and Cu/Mo[85] active sites of the carbon monoxide dehydrogenases interconvert CO_2 and CO selectively. Similar synthetic bimetallic effects have been identified in stoichiometric CO_2 reactions.

The carbon dioxide fixation with bifunctional complexes holding in their structure a nucleophilic cobalt (I) and an alkali cation results in the anchoring mode of the CO_2, which binds cobalt through the carbon, while both oxygens interact with alkali cations (Scheme 20).[31] Therefore, both metal centers are involved in binding CO_2. The fixation of CO_2 by such systems displays different degrees of reversibility depending on the reaction solvent and the nature of the alkali cation.

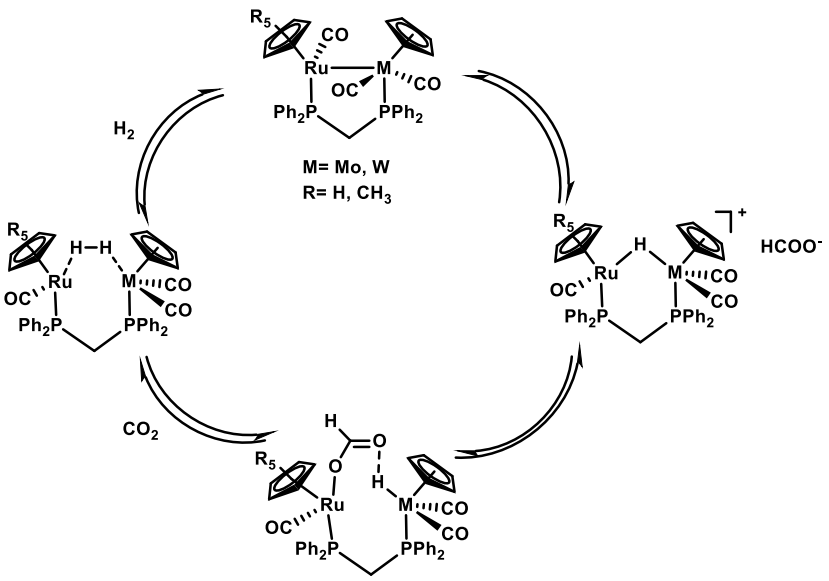


Scheme 20. Carbon dioxide fixation by "bifunctional complex" with nucleophilic cobalt(I) and an alkali cation.[31] (M = Li, Na, K, Cs; R= H, Et, n-Pr; L = THF, Py)

Thomas and coworkers demonstrated that the highly polar metal-metal multiple bonds in reduced $Co(^{i}Pr_2PNMes)_3Zr(THF)$ complex facilitate oxidative addition of the C=O bond in CO_2 leading to clean formation of $(OC)Co(iPr_2PNMes)_2(\mu\text{-}O)Zr(iPr_2PNMes)$ with a terminal CO and bridging Zr-O-Co oxo unit (Chapter 1, Scheme 10).[36] The hemilability of the phosphinoamide ligand framework is the key to this reactivity, as dissociation of a phosphine ligand from Co provides substrate access to the metal-metal bond. Although this heterobimetallic complex activates CO_2, the liberation of CO has not been observed in this reaction.

In 2003, Lau and coworkers reported synthesis of Ru–Mo and Ru–W bimetallic complexes. These complexes presented very low activity in the catalysis of CO_2 hydrogenation to formic acid and

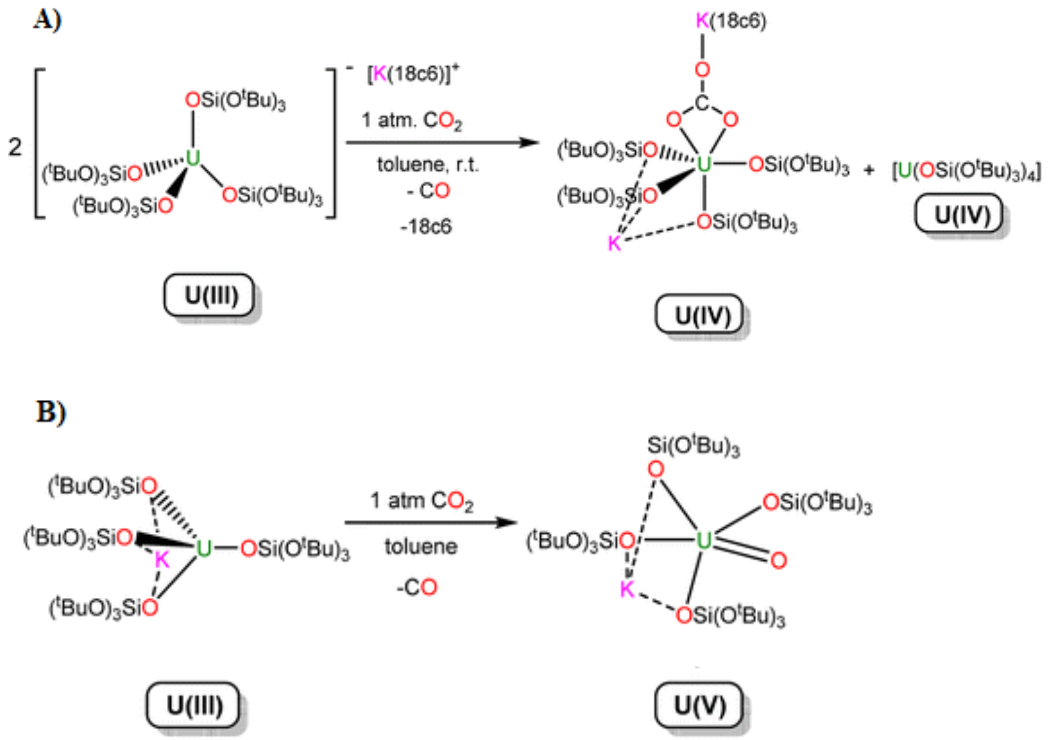
the reverse reaction. A reaction mechanism involves the formation of the dihydrogen-bonded dihydride species which is proposed to account for the catalytic reactions. The low reactivity of these complexes is related to their non-facile reactions with H_2 to generate the active dihydride species; on the other hand, the slowness of the catalytic formic acid decomposition by these bimetallic complexes is possibly due to the formation of a stable intermediate, which contains a strong Ru–H–M bridge (Scheme 21).[86]



Scheme 21. Proposed mechanism of CO_2 hydrogenation and decomposition of formic acid catalyzed by bimetallic Ru-M (M= Mo, W).

The presence of a cooperative effect of the two metal centers in the CO_2 transformation also studied by Mazzanti and coworkers.[87] The ion pair complex [K(18C6)] [U(OSi-(O^{t}Bu)$_3$)$_4$], encourages the selective reductive disproportionation of CO_2 to produce CO and the mononuclear uranium (IV) carbonate complex [U(OSi(O^{t}Bu)$_3$)$_4$(μ-κ^2:κ^1-CO_3)K_2(18C6)](Scheme 22A). However, the heterobimetallic complex [U(OSi(O^{t}Bu)$_3$)$_4$K], promotes the potassium-assisted two-electron

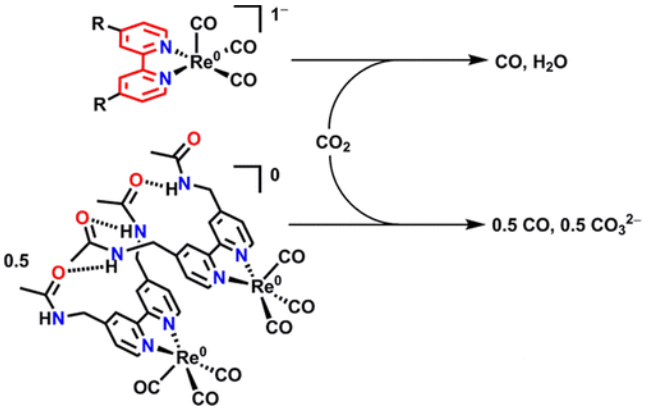
reductive cleavage of CO_2, yielding CO and the U(V) terminal oxo complex [UO(OSi(O^{t}Bu)$_3$)$_4$K] (Scheme 22B).



Scheme 22. Reaction of [K(18c6)] [U(OSi(O^{t}Bu)$_3$)$_4$] (A) and [U(OSi(O^{t}Bu)$_3$)$_4$K] (B) with CO_2.[28] (Reprinted with permission from reference 28 Copyright 2014 American Chemical Society).

Noncovalent self-assembly can modulate the catalytic properties of metal complexes by preferring alternative catalytic pathways. The Re^I(bpy) catalyst system has a high efficiency for the generation of CO in the presence of weak acids.[88-90] The reaction catalyzed is a two-proton/two electron (2 H^+/2 e^-) reduction of CO_2 to CO and H_2O, however they still do not approach the high kinetic and thermodynamic efficiencies (low overpotentials) of natural enzymes. Kubiak and coworkers introduced the addition of methyl acetamidomethyl groups at the 4,4′-positions of a 2,2′-bipyridyl ligand in Re^I fac-tricarbonyl chloride complexes to improve the rate of a bimolecular

reduction mechanism of CO_2.[91] The methyl acetamidomethyl groups cause a hydrogen-bond-driven association of 2 equivalent of the singly reduced complex, enhancing a bimolecular catalytic mechanism for the disproportionation of CO_2 to CO and CO_3^{2-}. This reaction operates at a lower potential than the unimolecular mechanism (Scheme 23).



Scheme 23. Electrocatalytic reduction of CO_2 with unimolecular and bimolecular Re^{I}(bpy) complexes.[91] (Reprinted with permission from reference 91 Copyright 2014 American Chemical Society).

Later in 2016, Kubiak and coworkers used the hydrogen-bonding interactions of the methyl acetamidomethyl groups of the dacbpy ligand to generate supramolecular heterobimetallic species containing Mn and Re bpy-based electrocatalysts.[37] Under these catalytic conditions, the formation of hydrogen bonds generates a catalyst system which promotes the reduction of CO_2 to CO and H_2O (Chapter 1, Scheme 11).

Bimetallic effects have rarely been studied systematically with respect to either reaction rate[86, 92-94] or product selectivity[91] in catalytic CO_2 reduction.

In 1995 DuBois and coworkers reported electrochemical reduction of CO_2 catalyzed by a dinuclear palladium complex containing a bridging hexaphosphine ligand in acidic DMF solution (Figure 15B).[93] In comparison to a mononuclear [Pd(triphosphine)(CH_3CN)] $(BF_4)_2$ complex (Figure

15A), they demonstrated higher CO_2 reduction rate with the dinuclear palladium complex. A cooperative interaction between the two palladium sites and CO_2 plays an important role in dramatically enhancing catalytic rates of CO_2 reduction (Scheme 23).

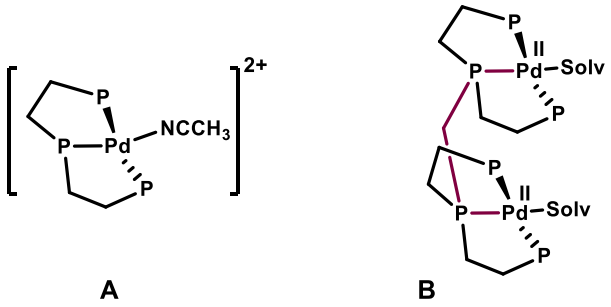
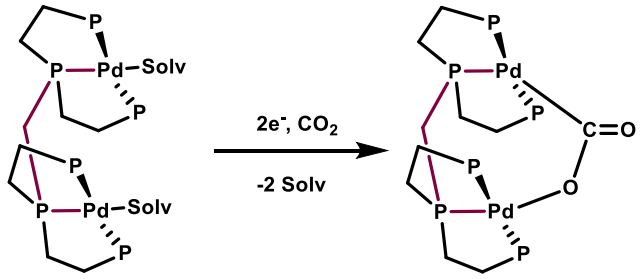


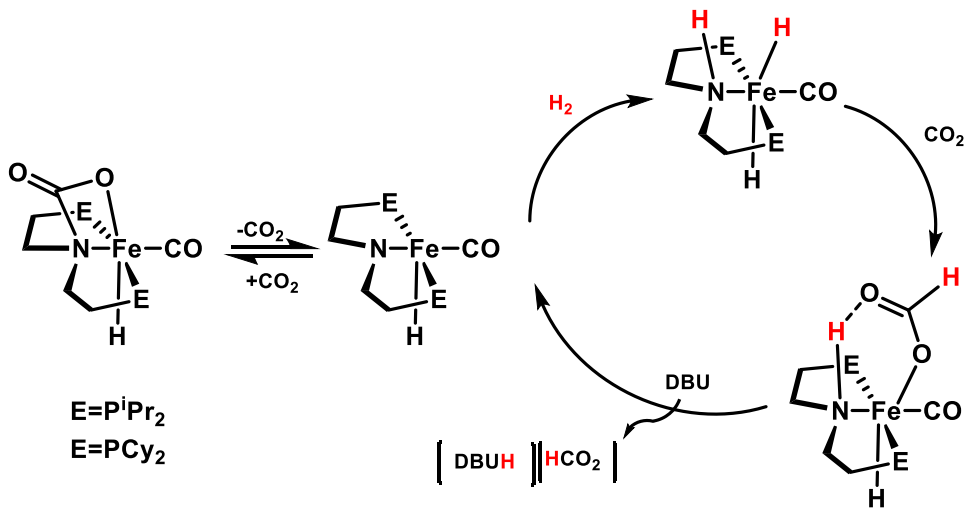
Figure 15. Mononuclear (A) and dinuclear (B) palladium complexes



Scheme 24. Interaction between two palladium sites and CO_2

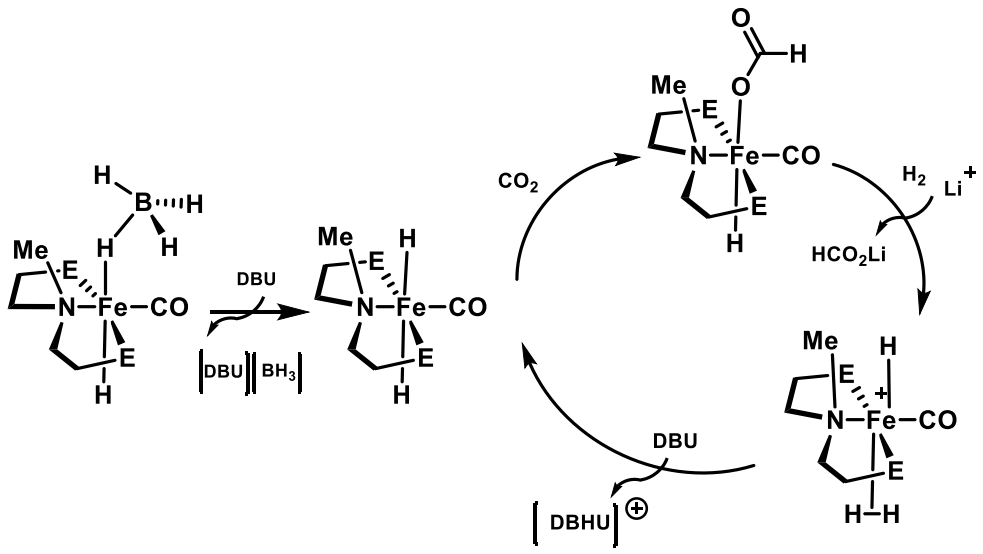
In 2015 Bernskoetter and Hazari et al. published a report demonstrating catalytic hydrogenation of CO_2 to formate with iron (II) carbonyl hydride complexes supported by PNP ligand with a secondary or a tertiary amine (Scheme 25).[94] They observed a notable improvement in catalytic activity upon the addition of Lewis acid (LA) co-catalysts in both cases. In systems with a secondary amine ligand, (^{R}PNP)Fe(H)CO(HCO_2) was identified as the catalyst resting state and

suggested a key role for LA was disrupting a stabilizing hydrogen bond between N–H and Fe–O_2CH moieties in this species.



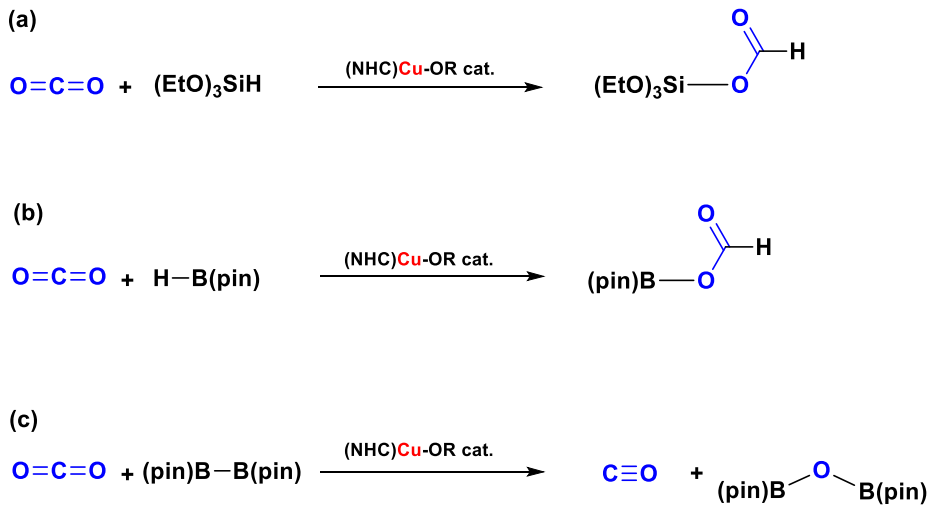
Scheme 25. Proposed mechanism for (^{R}PNP)Fe(H)CO/Li^+ catalyzed CO_2 hydrogenation.

In systems with tertiary amine, formate complex, (^{iPr}PN^{Me}P)Fe(H)CO(HCO_2), was identified as the catalytic resting state. The primary role of LA in this complex was its assistance in a formate for dihydrogen substitution which yields a transient cationic iron(II) dihydrogen complex (Scheme 26).

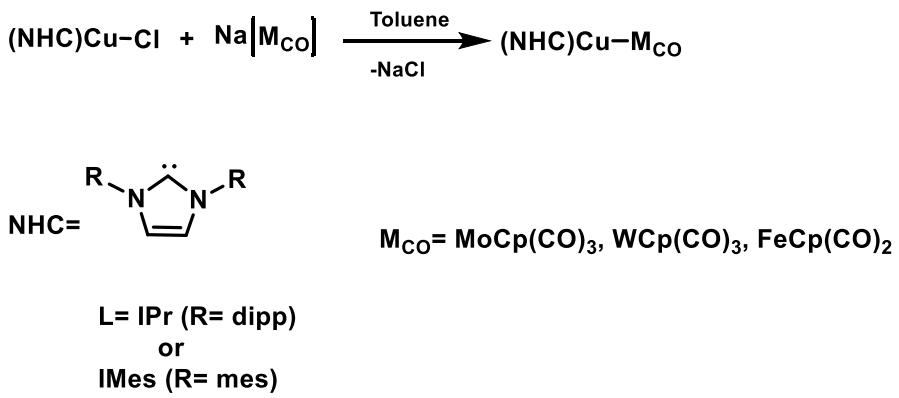


Scheme 26. Proposed pathway for catalytic CO_2 hydrogenation using ($^{iPr}PN^{Me}P$)Fe(H)CO(BH_4).

Similar bimetallic cooperative effects may be important in heterogeneous CO_2 catalysis, where well-defined mechanistic understanding is more elusive.[95]Catalysts based on Cu ligated by N-heterocyclic carbenes (NHCs) provide a convenient testing ground for this phenomenon: monometallic (NHC)Cu catalysts for CO_2 reduction are well established (Scheme 27),[96] and our group has developed the ability to synthesize heterobimetallic (NHC)Cu-[M] complexes with tunable steric and electronic properties ([M] =metal carbonyl anion) (Scheme 28).[97]



Scheme 27. Previously established reagent control of CO_2 reduction with (NHC)Cu catalysts.



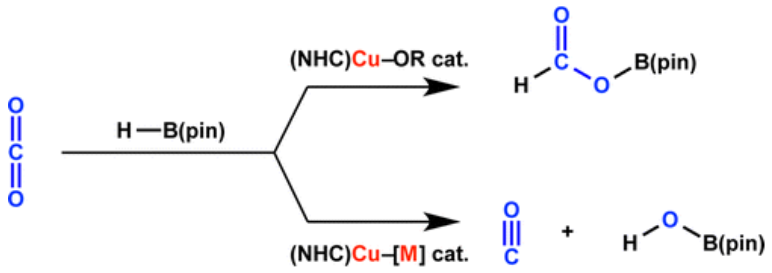
Scheme 28. General synthesis of heterobimetallic complexes.

Previously, it was known that reagent control over CO_2 reduction selectivity could be achieved with a single monometallic (NHC)Cu catalyst. Copper/N-heterocyclic carbene-catalyzed hydrosilylation and hydroboration of carbon dioxide with hydrosilane and pinacolborane reductants produce a formic acid derivative selectively (Scheme 27a and 27b),[64,65] however, bis(pinacolato)-diboron (pinB-Bpin), reductant selectively produces CO (Scheme 27c).[67]

3.2. Results & discussion

3.2.1. CO_2 reduction with (NHC)Cu-[M] catalysts

In this chapter, catalyst control over CO_2 reduction selectivity with (NHC)Cu-[M] catalysts is described (Scheme 29) with a single H-[B] reductant, selectivity for CO versus HCO_2[B] can be controlled by tuning the heterobimetallic catalyst through the nature of the Cu/M pairing.

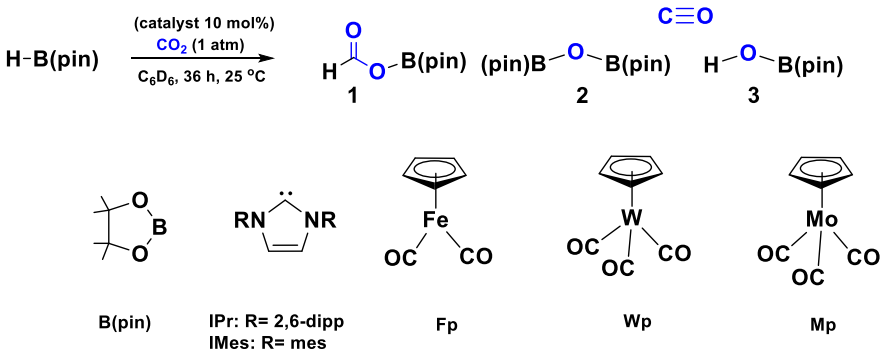


Scheme 29. Established catalyst control by introducing a heterobimetallic effect; [M] = metal carbonyl anion, NHC= N-heterocyclic carbene, pin = pinacolate.

During our group studies on heterobimetallic C−H borylation,[98] we proposed that pinacolborane, H-Bpin, is reversibly activated by (IPr)Cu-Fp (IPr = N,N′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; Fp = $FeCp(CO)_2$) to yield small concentrations of the pair 0.5 $[(IPr)Cu{-}H]_2$ + Fp-Bpin.[99] We also noted that exposure of this mixture to CO_2 produced both the formate product, HCO_2Bpin, and a boron oxygenate, pinB-O-Bpin , even though (IPr)Cu-Fp itself does not react with CO_2.[100] Product pinB-O-Bpin was presumed to result from CO_2 deoxygenation. (The direct product of CO_2 deoxygenation, HO-Bpin, if produced slowly would react with H-Bpin to generate pinB-O-Bpin and H_2.) Upon further examination, we found that (IPr)Cu-Fp is a catalyst for CO_2 reduction by H-Bpin, converting 72% of the H-Bpin to a ~ 0.7:1 mixture of pinB-O-Bpin and HCO_2Bpin under the conditions specified in Table 3 (Entry 1). At first, we presumed that these two products were derived from separated monometallic catalyst by $[(IPr)CuH]_2$ and Fp-Bpin. Indeed, $[(IPr)CuH]_2$ is already known to quantitatively catalyze CO_2 reduction to formate using silane or borane

reductants in different solvents (benzene, THF) and at different temperatures (25−100 °C);[64,65] one relevant data point is presented in Table 3 (Entry 2). However, to our surprise, exposing Fp-Bpin to the same conditions did not produce HO-Bpin or pinB-O-Bpin and, in fact, resulted in no reaction whatsoever (Table 3, Entry 3). Together, these results demonstrate that the deoxygenation of CO_2 by H-Bpin to produce CO requires both metal sites to be present and verifies the presence of a cooperative effect. Seeking to better understand this bimetallic selectivity effect, we then tested other (IPr)Cu-[M] complexes as catalysts under the same conditions. Use of (IPr)Cu-Wp (Wp = $WCp(CO)_3$) resulted in 76% conversion of H-Bpin with ∼2:1 CO/ HCO_2Bpin selectivity (Table 3, Entry 4). Use of (IPr)Cu-Mp (Mp =$MoCp(CO)_3$) resulted in 73% conversion of H-Bpin with ∼12:1 selectivity for CO over HCO_2Bpin (Table 3, Entry 5). Since the Fp, Wp, and Mp fragments represent electronically distinct metal carbonyl species (relative nucleophilicities: $[Fp]^-$, 7×10^7; $[Wp]^-$, 500; $[Mp]^-$, 67),[101] this series of experiments demonstrates that CO_2 reduction selectivity can be controlled by electronically tuning the bimetallic pairing.

We then examined the sterically less hindered (IMes)Cu-[M] catalysts (IMes = N,N′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), which might be expected to give higher concentrations of the catalytically active (NHC)CuH/[M]-Bpin pairs. All three of the catalysts exhibited high selectivity for CO over HCO_2Bpin (Table 3, Entries 6−8). The corresponding monometallic precatalyst, (IMes)Cu−O^{t}Bu, is known to give high yields of formate during CO_2 reduction with silane or borane reagents.[64,65]



entry	catalyst	% conversion[b]	equiv of 1[c]	equiv of 2[c]	equiv of 3[c]	CO/1[d]
1	(IPr)CuFp	72 ± 15	3.0 ± 1.0	0	2.1 ± 0.5	~ 0.7:1
2[e]	(IPr)CuOtBu	85	8.5	0	0	0
3	FpBpin	0	0	0	0	N/A
4	(IPr)CuWp	76 ±14	1.8 ± 0.5	1.3 ± 0.3	2.3 ± 0.7	~ 2:1
5	(IPr)CuMp	73 ± 21	0.3 ± 0.3	0	3.5± 1.0	~ 12:1
6	(IMes)CuFp	92 ± 30	0	2.4 ± 1.7	3.4± 1.2	³ 20:1
7	(IMes)CuWp	92 ± 4	0	n.d.[f]	n.d.[f]	³ 20:1
8	(IMes)CuMp	82 ± 21	0	0	4.1± 1.0	³ 20:1
9[g]	(IPr)CuOtBu + FpBpin	96 ± 3	0	n.d.[f]	n.d.[f]	³ 20:1

Table 3. Catalytic CO_2 Reduction Results with Pinacolborane (HBpin).[a] Determined by ^{1}H NMR integration against an internal standard (mesitylene). [b]Based on HBpin. [c]Based on catalyst. [d]Assumes 1 equiv of CO per HO-Bpin and 1 equiv of CO per pinB-O-Bpin. [e]Data from ref 4 (THF, 35 °C, 24 h). [f]Not determined due to peak overlap, but HO-Bpin and pinB-O-Bpin were the only [Bpin]-containing products observed. [g]Catalyst loading of 10 mol % was used for each cocatalyst.

We used two different methods to verify formation of CO during the reduction of CO_2. The first method was two-pot, three-phases CO trapping experiment reported by Cummins (Figure 18).[102] In this experiment Cp*RuCl(PCy_3) was used as a CO trapping reagent and volatile material (carbon monoxide) was transported in the vapor phase and facile CO binding by Cp*RuCl(PCy_3) was indicated by a dramatic color change from blue to yellow, as well as by clear ^{31}P NMR signatures (Figure 19). The second method used to confirm CO formation was GC−MS analysis of the reaction headspace (Figure 20).

We consider ^{1}H NMR integration of the nonvolatiles HO-Bpin and pinB-O-Bpin relative to HCO_2Bpin to be the more accurate method for determining CO: HCO_2Bpin selectivity. In some cases, individual yields of HO-Bpin and pinB-O-Bpin were not determined due to their similar ^{1}H and ^{11}B NMR spectra. We could verify their peak assignments by exposing one of the catalytic mixtures featuring both HO-Bpin and pinB-O-Bpin to additional H-Bpin after completion of the reaction: H_2 evolution was observed by ^{1}HNMR as the peaks for HO-Bpin shrank and the peaks for pinB-O-Bpin grew in both ^{1}H and ^{11}B-NMR.

Nonetheless, the resolution of HO-Bpin and pinB-O-Bpin by ^{1}H-NMR is highly dependent on spectral line widths, and sometimes we can only report overall conversion to HO-Bpin + pinB-O-Bpin.

3.2.3. Proposed mechanism for carbon dioxide reduction

Several observations lead us to a hypothetical mechanism. (1) Neither (NHC)Cu-Fp nor Fp-Bpin react with CO_2 independently, indicating that the CO_2 activating species must be $[(NHC)Cu{-}H]_2$. (2) Catalysis with $[(NHC)Cu{-}H]_2$ produces HCO_2Bpin but does not result in decarbonylation to either HO-Bpin or pinB-O-Bpin, indicating that the [M]-Bpin species act as catalysts/precatalysts for the decarbonylation of HCO_2Bpin. (3) Catalytic reactions that give high selectivity for CO at

full conversion contained large amounts of formate HCO_2Bpin at partial conversion. (4) Although HCO_2Bpin is known to be unstable toward isolation,[103] Fp-Bpin (10 mol %) was added to a preformed ~1:1 mixture of (HO-Bpin + pinB-O-Bpin)/ HCO_2Bpin under N_2, and no reaction was observed after 36 h. Replacing the N_2 atmosphere with a CO_2 atmosphere resulting in consumption of HCO_2Bpin and a ~4:1 mixture of (HO-Bpin + pinB-O-Bpin)/ HCO_2Bpin after 24 h; FpH was observed as a byproduct (Figure 16).

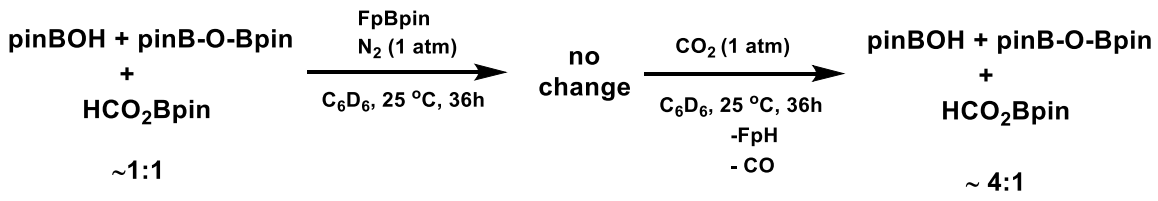


Figure 16. Observed decarbonylation activity of Fp-Bpin on formate HCO_2Bpin.

Collecting these observations together, a hypothetical mechanism is shown in Figure 17. Catalyst activation by HBpin produces 0.5 $[(NHC)CuH]_2$ + [M]Bpin. Hence, an autotandem reaction is used. First, copper-catalyzed hydroboration converts CO_2 to HCO_2Bpin. Formate HCO_2Bpin is then decarbonylated through rate-determining electrophilic activation by [M]-E (E = Bpin in the first turnover and then H throughout). Transfer of E^+ to HCO_2Bpin initiates decarbonylation via intermediate A, but this reversible activation must be driven forward through sequestration of [M]−by CO_2. Carboxylation of $[Fp]^-$ is known to be reversible,[104]and the acid-catalyzed decarbonylation of formate HCO_2Bpin through A is proposed in analogy to the known Brønsted or Lewis acid catalyzed decarbonylation of formic acid itself.[105,106]

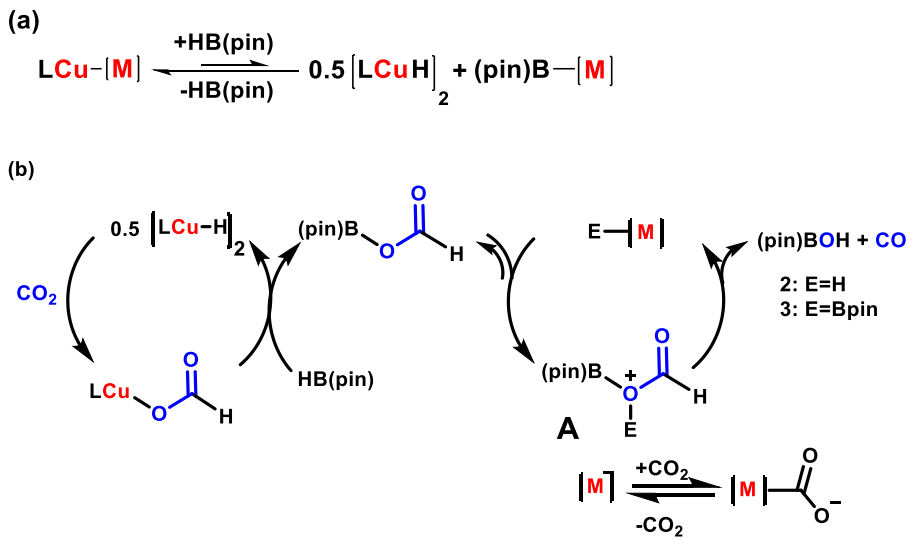


Figure 17. Hypothetical mechanism: (a) catalyst activation, followed by autotandem (b) CO_2 hydroboration, and (c) CO_2-assisted formate decarbonylation. E = B(pin) for the first turnover and then H throughout. L = IPr or IMes, [M] = Fp, Wp, or Mp, pin = pinacolate.

Consistent with this proposal, within the series of isosteric IPr-ligated complexes (Table 3, Entries 1, 4−5), the rate of decarbonylation is apparently related to the lability of [M]-Bpin, following the [M]− leaving group ability of $[Mp]^-$ > $[Wp]^-$> $[Fp]^-$ that also correlates with their relative pKa values.[101] Furthermore, catalysis with a 1:1 mixture of (IPr)Cu−OtBu +Fp-Bpin (Table 3, Entry 9) gave higher selectivity for CO than did (IPr)Cu-Fp, presumably because the metals need not be linked during productive catalysis and because the unfavorable[99]catalyst activation equilibrium was bypassed, giving higher effective concentration of the decarbonylation catalyst (much like for all IMes catalysts, vide supra). At this time, we cannot rule out that decarbonylation reactivity could also come from polarity inversion in the catalyst activation step yielding the pair, (NHC)CuBpin + [M]H, of which (NHC)CuBpin is established as a catalyst for CO_2 deoxygenation.[67] However, all experimental observations are consistent with the simpler mechanism shown in Figure 17.

3.3. Conclusion

These studies reveal a tunable bimetallic effect on selectivity control in catalytic carbon dioxide reduction using N-heterocyclic carbene-ligated Cu complexes. While the monometallic Cu-only system catalyzes hydroboration of CO_2 with pinacolborane to produce formate exclusively, introducing a bimetallic effect with analogous Cu−Fe, Cu−W, and Cu−Mo catalysts produces mixtures of formate and CO. Within a series of isosteric catalysts, the selectivity of CO versus formate was controlled by tuning the electronic nature of the Cu/M pairing, with high selectivity for CO being achieved using a Cu−Mo catalyst.

3.4. Experimental procedures

3.4.1. General considerations

All reactions and manipulations were conducted under purified N_2 using standard Schlenk line techniques or in a glovebox. Deuterated benzene (C_6D_6) was degassed by repeated freeze-pump-thaw cycles and stored over activated 3-Å molecular sieves prior to use. ^{1}H and ^{13}C NMR spectra were recorded using Bruker Avance 400-MHz NMR spectrometer.

NMR spectra were recorded at room temperature, and chemical shifts were referenced to residual solvent peak. ^{11}B NMR chemical shifts were referenced to external pinacolborane (29.0 and 27.6 ppm). The ^{1}H NMR and ^{11}B NMR data of PinBOCOH,[79] PinBOH,[107] and $(Pin)_2B_2O$[108], matched literature values. Literature methods were used to synthesize NaWp,[109] IMes·HCl, IPr·HCl,[110](IMes)CuCl, (IPr)CuCl,[51,111] (IMes)CuFp, (IPr)CuFp,[112] (IPr)CuMp, (IMes)CuMp, (IMes)CuWp, (IPr)CuWp,[97] Cp*RuCl(PCy3),[113] and FpBpin.[98]

3.4.2. Procedures for catalytic CO_2 reduction using heterobimetallic complexes as a catalyst

3.4.2.1. Catalytic reduction of CO_2 by (IMes)Cu-Mp

In a nitrogen filled glovebox, (IMes)Cu-Mp (18 mg, 0.029 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (42.6 μL, 0.29 mmol) and mesitylene (40.3 μL, 0.29 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.2.2. Catalytic reduction of CO_2 by (IMes)Cu-Wp

In a nitrogen filled glovebox, (IMes)Cu-Wp (18 mg, 0.026 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (37.2 μL, 0.26 mmol) and mesitylene (36.2 μL, 0.26 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.2.3. Catalytic reduction of CO_2 by (IMes)Cu-Fp

In a nitrogen filled glovebox, (IMes)Cu-Fp (18 mg, 0.033 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (47.9 μL, 0.33 mmol) and mesitylene (45.9 μL, 0.33mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.2.4. Catalytic reduction of CO_2 by (IPr)Cu-Mp

In a nitrogen filled glovebox, (IPr)Cu-Mp (18 mg, 0.026 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (37.7 μL, 0.26 mmol) and mesitylene (36.2 μL, 0.26 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.2.5. Catalytic reduction of CO_2 by (IPr)Cu-Wp

In a nitrogen filled glovebox, (IPr)Cu-Wp (18 mg, 0.023 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (33.4 μL, 0.23 mmol)

and mesitylene (32 μL, 0.23 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.2.6. Catalytic reduction of CO_2 by (IPr)Cu-Fp

In a nitrogen filled glovebox, (IPr)Cu-Fp (18 mg, 0.0286 mmol) was dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (41.5 μL, 0.286 mmol) and mesitylene (39.8 μL, 0.286 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.3. CO trapping experiment

In a nitrogen filled glovebox, (IMes)Cu-Fp (5 mg, 0.009 mmol) was dissolved in C_6D_6 (3 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (13 μL, 0.09 mmol) was added. This solution was transferred to 50mL Schlenk flask with two arms. The Schlenk flask was taken out of the glovebox and connected to the Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reaction was exposed to CO_2 for 3 h and stirred for 36 h at room temperature. After 36 h another two-arm Schlenk flask was

charged with Cp*RuCl(PCy_3) (50 mg, 0.09 mmol) and taken out of the glove box. The two flasks were connected by adaptor (Figure 18). The Cp*RuCl(PCy_3) containing flask was put under vacuum for 5 minutes and by opening the first flask, the CO gas and 2/3 of solution of this flask were transferred to the Cp*RuCl(PCy_3) flask. The mixture of Ru complex, CO and solution were stirred for 3 h. It was then reintroduced into the glovebox and analyzed by ^{31}P NMR. The ^{31}P NMR chemical shift had moved downfield by 11 ppm, consistent with what was observed by Cummins and coworkers (Figure 19).[102]

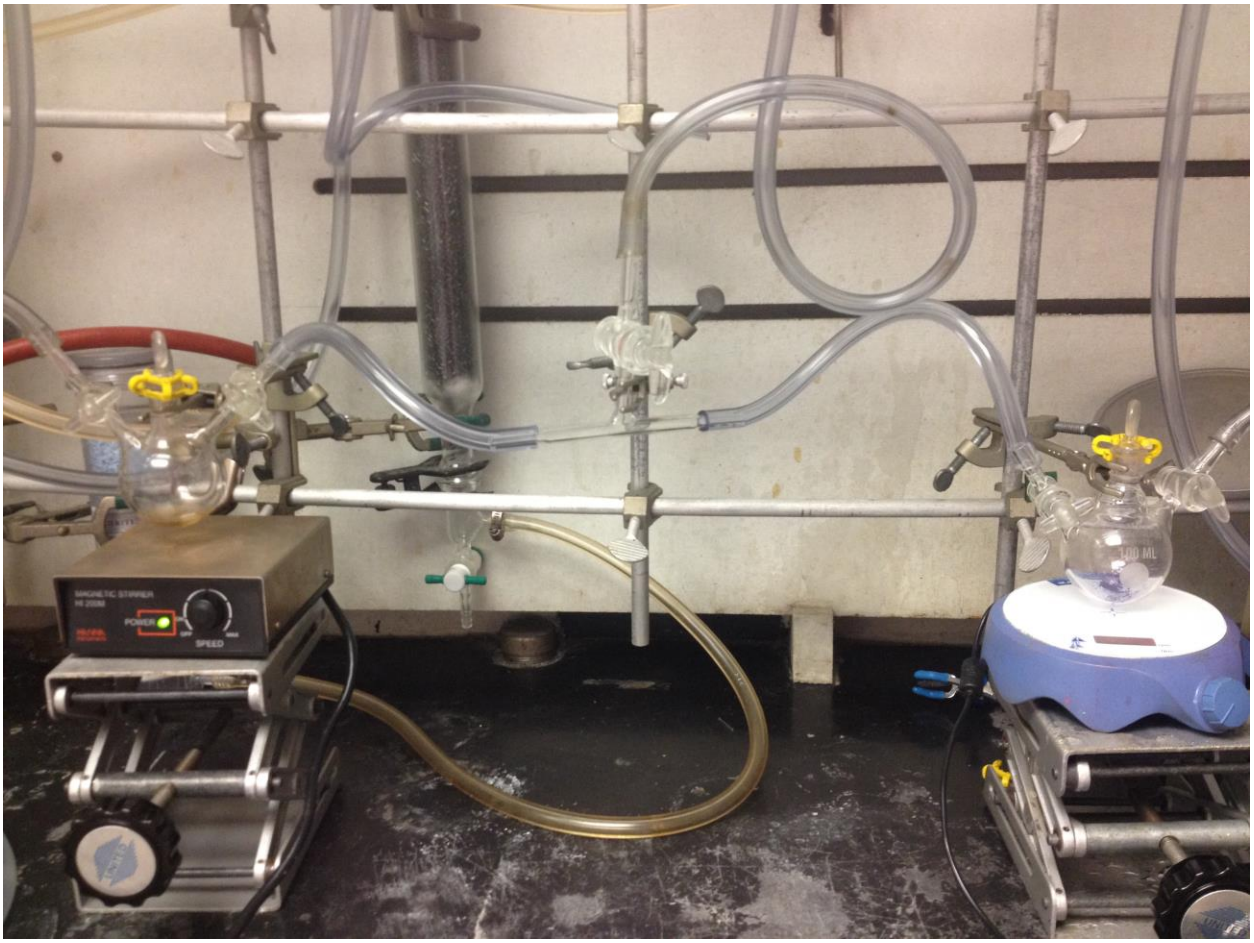


Figure 18. Experimental apparatus for CO trapping experiment. The flask on the left contains CO evolving reaction catalyzed by (IMes)Cu-Fp. The flask on the right contains the CO trapping Ru reagent.

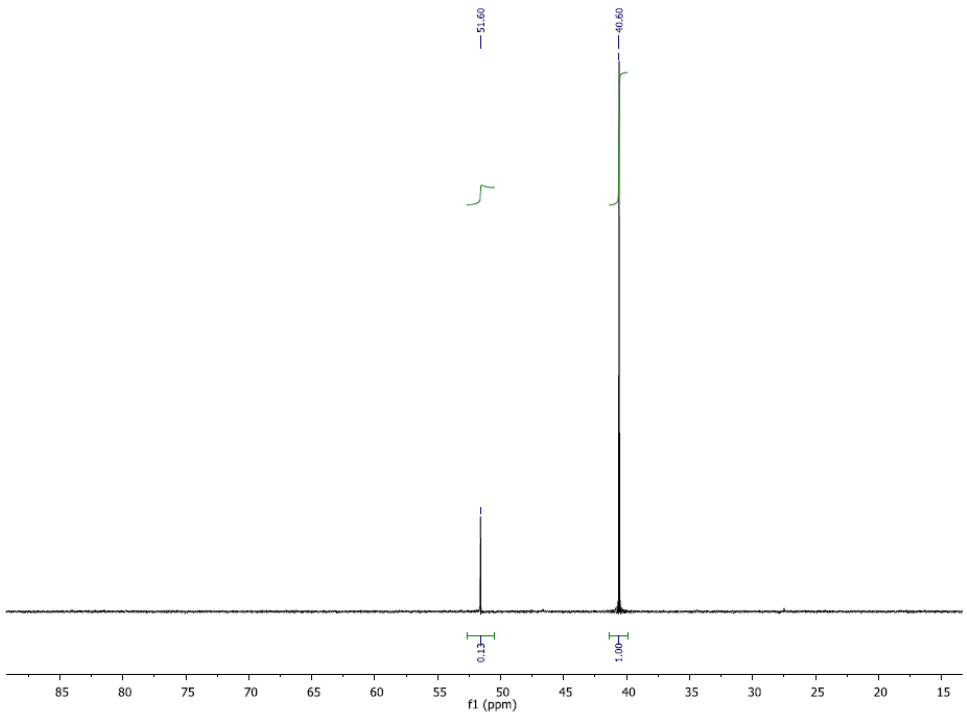
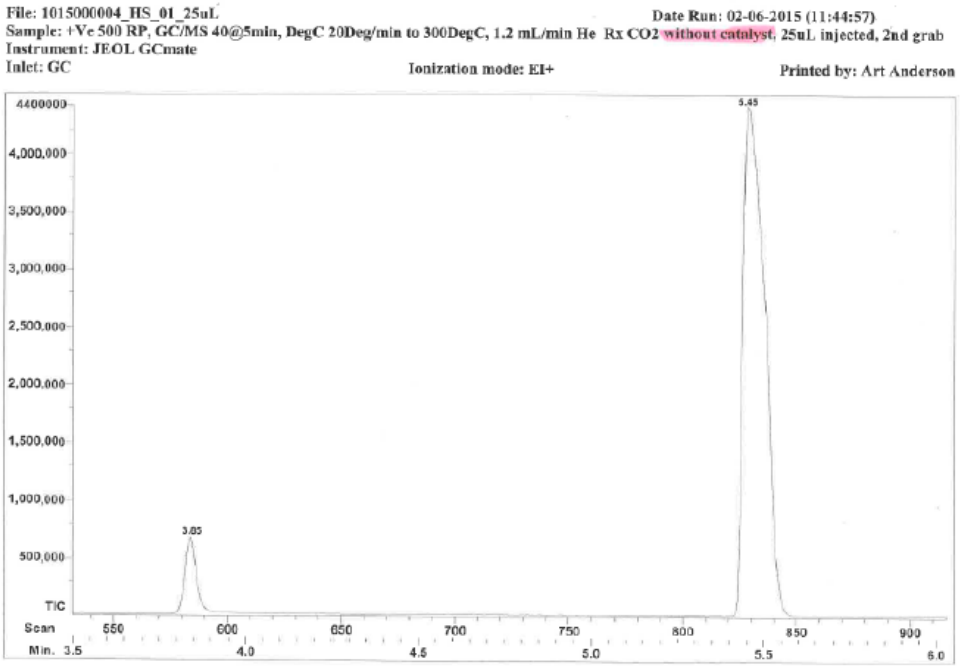


Figure 19. ^{31}P NMR spectra of the resulting mixture of Cp*RuCl(PCy_3) (40.6 ppm) and Cp*RuCl(PCy_3)(CO) (51.6 ppm) because of trapping CO from the catalytic reduction of CO_2 with (IMes)Cu-Fp.

3.4.4. GC-MS detection of CO

In a nitrogen filled glovebox, (IMes)Cu-Fp (18 mg, 0.033 mmol) was dissolved in C_6D_6 (4 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (47.9 μL, 0.33 mmol) and mesitylene (40.3 μL, 0.29 mmol) were added. This solution was transferred to 50 mL Schlenk flask. The flask was sealed with a fresh septum secured with copper wire and a Keck clip. The flask was taken out of the glovebox and connected to a Schlenk line. After three freeze-pump-thaw cycles the flask was backfilled with CO_2 and then it was closed. The reaction was stirred room temperature for 36 h hours, the gases in the reaction headspace were then analyzed by GC-MS. To serve as a blank, inside the glovebox a 50 mL round bottom Schlenk flask was charged with piacolborane and C_6D_6 and stir bar, then it was sealed using a fresh septum secured with

copper wire and a Keck clip. Then it was taken out of the glove box and connected to the Schleck line, after three freeze-pump-thaw cycles the flask was backfilled with CO_2 and then it was closed. The solution was stirred room temperature for 36h hours, the gases in the reaction headspace were then analyzed by GC-MS. (Figure 20).



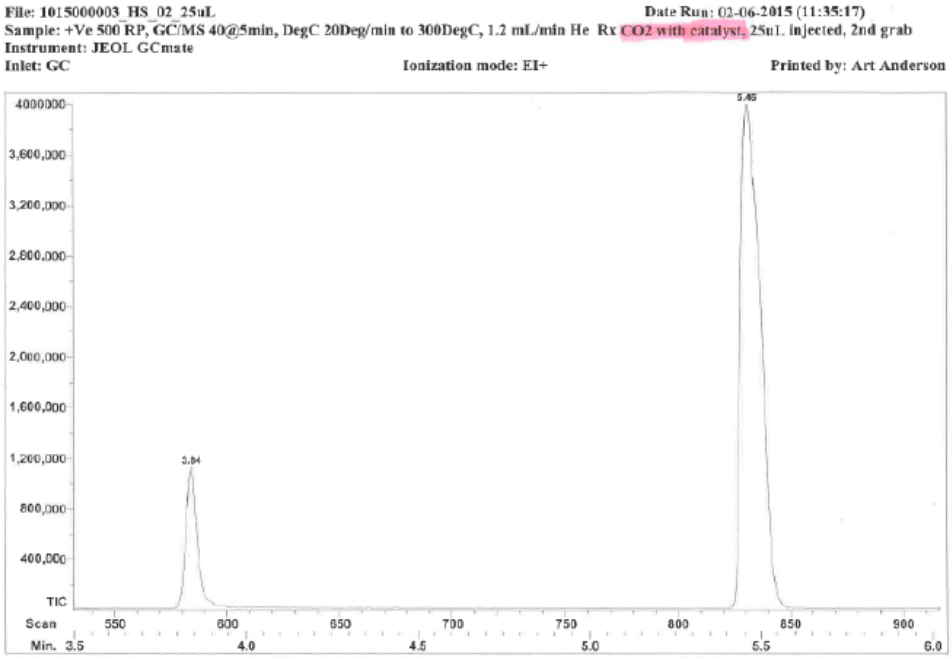


Figure 20. GC-MS analysis of CO_2 reduction without catalyst (top) and in the presence of catalyst (bottom)

3.4.5. Catalytic reduction of CO_2 by (IPr)CuOtBu and FpBpin

In a nitrogen filled glovebox, (IPr)CuOtBu (18 mg, 0.034 mmol) and FpBpin (10.4 mg, 0.034 mmol) were dissolved in C_6D_6 (6 mL) and pipette-filtered through Celite into another scintillation vial. Pinacolborane (49.7 μL, 0.34 mmol) and mesitylene (47.7 μL, 0.34 mmol) were added. This solution was transferred to three Schlenk flasks (2 mL of the solution in each Schlenk flask). The Schlenk flasks were taken out of the glove box and connected to a Schlenk line. The solutions were degassed by three freeze-pump-thaw cycles and backfilled with CO_2 (1 atm). The reactions were exposed to CO_2 for 36 h at room temperature. The conversion yields and error bars shown in Table 3 were calculated by ^{1}H NMR integration relative to the mesitylene internal standard, from an average of three independent reactions.

3.4.6. In situ generation of HCO_2Bpin, and its decarbonylation by FpBpin

To a typical product mixture containing a ~1:1 mixture of (pinBOH+pinB-O-Bpin): HCO_2Bpin generated by the typical catalytic procedure (see above), FpBpin (3.5 mg, 0.0114 mmol) was added under N_2 atmosphere. The reaction was analyzed by NMR spectroscopy at 8 h and 36 h. After 36 h, the solution was taken out of the glove box and connected to the Schlenk line and was exposed to the CO_2 for 24 h, then re-analyzed by NMR spectroscopy.

Chapter 4: Extremely Efficient Hydroboration of Ketones and Aldehydes by Copper Carbene Catalysis.

(This chapter was previously published as Bagherzadeh, S.; Mankad, N. P. *Chem. Commun.* **2016**, 52, 3844-3846.)

4. 1. Introduction

Reduction of carbonyl compounds is an effective strategy for synthesizing industrially important alcohols. Catalytic hydrosilylation and hydroboration represent methods that can be conducted under mild conditions as alternatives to using flammable and pressurized H_2 or hazardous metal-hydride reductants. In comparison to catalytic hydrosilylation, carbonyl hydroboration catalysis is surprisingly underdeveloped.[114]

Since silyl and boryl groups represent orthogonal alcohol protecting groups, further advancement of catalytic hydroboration would significantly add to the synthetic toolkit. Hydroboration of organic C=O groups with benign reagents, such as pinacolborane (HBpin) and catecholborane (HBcat) have been catalyzed with transition metals (Ti,[115-118] Zn,[119-123] and Ru[124,125]) and with main group elements (Mg,[126-128] P,[129] Ga, Ge, and Sn[130]). In selected cases, modest to good levels of enantioselectivity were achieved using chiral ligands,[116,117,119-121] although further development of stereoselectivity is needed.

4.1.1. Transition metal catalyzed hydroboration of carbonyl compounds

As mentioned, efficient conversion of carbonyl compounds into the corresponding alcohols is an important transformation in organic synthesis. Transition metal complexes of titanium, ruthenium, and zinc are reported to catalyze the hydroboration of carbonyl compounds.

4.1.1.1. Ti complex catalyzed hydroboration of C=O

Titanium alkoxides present the early examples of transition metal complexes applied in the catalytic hydroboration of carbonyl compounds. In 1994, DiMare and coworkers reported the reduction of acetophenone with HBcat or BH_3 in the presence of 5 mol% Ti(O*i*Pr)$_4$.[115] The reduction happened readily to give the corresponding alcohol in high yields. They also demonstrated the asymmetric reduction of acetophenone using Ti-TADDOL complex (Figure 21a)

as a catalyst. A poor ee of 24% was observed under this condition and they did not propose the mechanism for this hydroboration reaction.

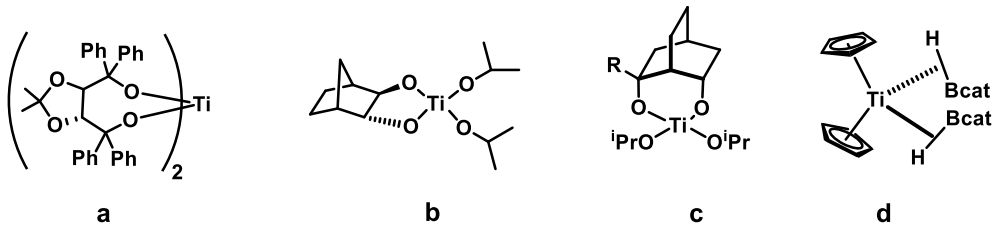
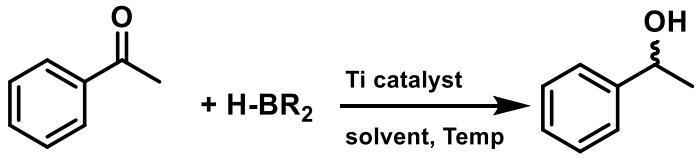


Figure 21. Ti-complexes used in catalytic hydroboration of ketones

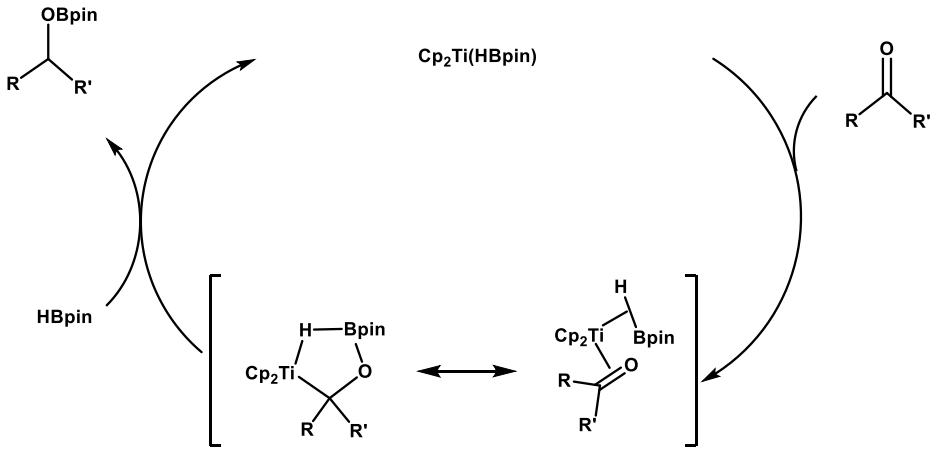
Wandrey and Frejd's groups independently discovered that titanium-alkoxide complexes (Figure 21b and 21c) can be generated in situ from the reaction of $Ti(OiPr)_4$ with TADDOL-analogous ligands. These Ti-alkoxide complexes were efficient in reduction of acetophenone to give 1-phenylethanol (Scheme 30).[116,117] With HBcat (1.1 equiv) in the presence of 21b (10 mol %), the reaction was completed within 1 h (100% conversion and 82% ee). Changing the reductant to the $BH_3 \cdot THF$ complex resulted in a significant decrease in ee values to 18%. Likewise, 21c (R = 2-anisyl, 10 mol %) and HBcat (2 equiv) were able to reduce acetophenone within 7.5 h (47% yield, 89% ee). For both cases, however, the structural characterization of these Ti-alkoxide complexes was not accomplished, and the actual active catalysts in the systems were indistinct.

In 2013, Muhoro and coworkers published a report representing catalytic hydroboration of ketones and aldehydes by Titanocene bis(catecholborane) complex (Figure 21d).[118] The catalytic reaction proceeded in the presence of 5 mol % of catalyst (Figure 21d) and HBpin. They also studied various substrate screens at room temperature. This reaction afforded the alkoxypinacolboronate esters in good yields (69−91%). They demonstrated that the rate of reaction for electron poor ketones was much faster than electron rich ketones.

The dissociation of HBcat and coordination of HBpin to the complex was proposed to be a key step in formation of the catalytically active species Cp_2Ti-(HBpin). The catalytic cycle starts with the coordination of ketone to Cp_2Ti-(HBpin) and formation of η^2-C=O π coordinated complex with a Ti(II) center. Coordination of HBpin to the intermediate would afford alkoxypinacolborane and regenerate Cp_2Ti(HBpin) (Scheme 31).



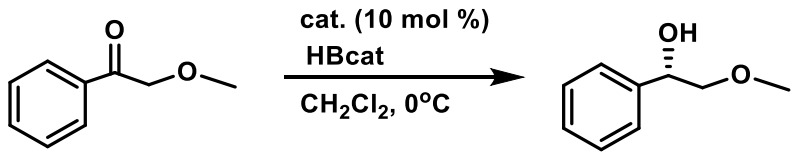
Scheme 30. DiMare: 21a (5 mol %), BH_3 or HBcat (1 equiv), CH_2CI_2, 20 °C. Wandrey: 21b (10 mol %), HBcat (1.1equiv), hexane, −30 °C (82% ee, S configuration). Frejd: 21c (R = 2-anisyl) (10 mol %), HBcat (1.5 equiv), hexane, −20 °C (96% ee, R configuration). [d]Muhoro: 21d (5 mol %), HBpin (1 equiv), C_6D_6, r.t.



Scheme 31. Proposed mechanism for $Cp_2Ti(HBcat)_2$-catalyzed hydroboration reaction

4.1.1.2. Zn complex catalyzed hydroboration of C=O

Umani-Ronchi and Cozzi et al. studied catalytic hydroboration of α-methoxyacetophenone in the presence of bis(oxazoline) Zn(II) complex (10 mol %) (Figure 22a).[119] This reaction afforded (S)-(+)-2-methoxy-1-phenylethanol with 78% yield and 82% ee (Scheme 32). They demonstrated that a two-point binding site to Zn center is essential for high ee values, therefore limiting the ketone substrates only to α-alkoxyketone derivatives.



Scheme 32. Hydroboration of α-methoxyacetophenone in the presence of bis(oxazoline) Zn(II) complex

Later in 2003, Cozzi and coworkers developed the Zn(II) complex supported by an iminooxazoline (IMOX) ligand (Figure 22b). They were able to improve the enantioselectivity in the hydroboration of a variety of ketones by using this complex as a catalyst.

Pyrazole-based chiral L-alaninemethylester Zn(II) complex (Figure 22c) and a trans-1, -2-diaminocyclohexane derivative Zn(II) complex (Figure 22d) were developed by Kim and Jeong et al.[121,120] Both complexes catalyzed hydroboration of acetophenone using HBcat in low ee values (21% and 48%) of the corresponding alcohol.

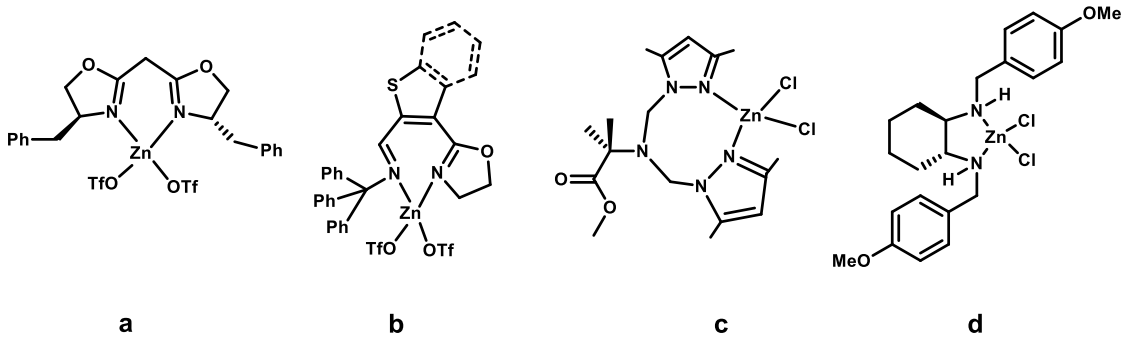
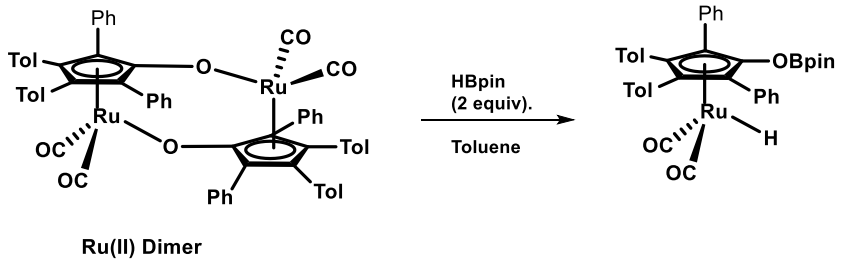


Figure 22. Zn complexes used in reduction of ketones.

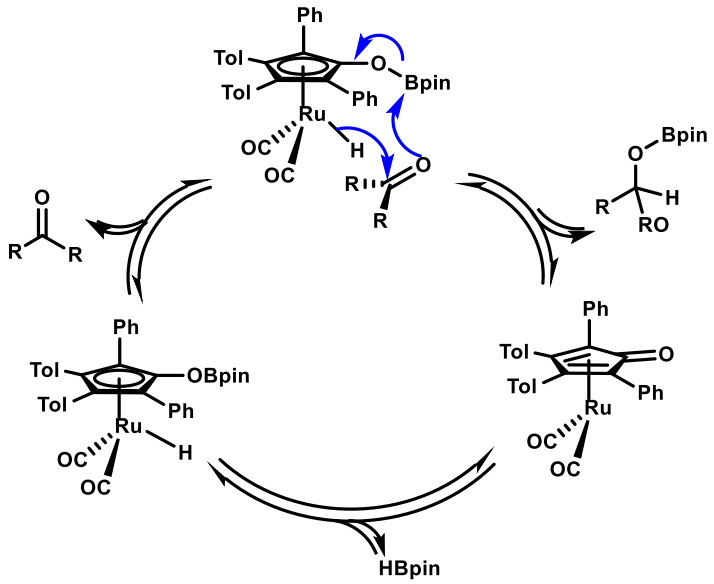
4.1.1.3. Ru complex catalyzed hydroboration of C=O

In 2009, Casey and Clark et al. published a report demonstrating synthesis of the boron-substituted Shvo's catalyst (Scheme 33) by oxidative addition of pinacolborane to ruthenium dimer.



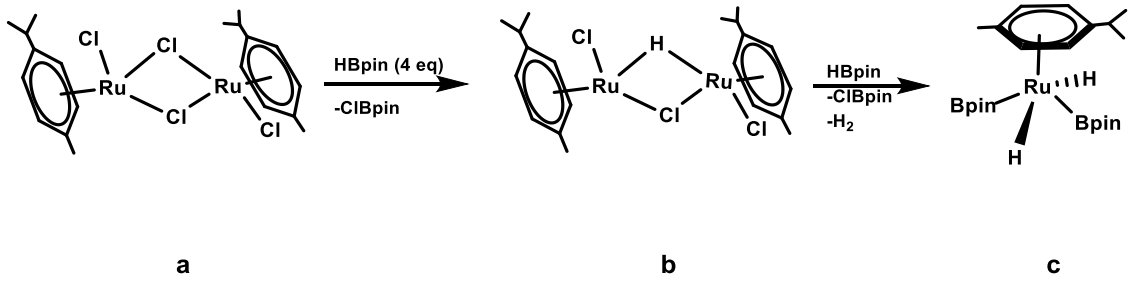
Scheme 33. Synthesis of the boron-substituted Shvo's catalyst

This compound is Lewis acidic enough to promote hydroboration of aldehydes and ketones through a ligand-metal bifunctional catalyst system.[125] Both electron rich and deficient aldehydes were tolerated with qualitatively faster reactions for electron-deficient aldehydes, but harsher reaction conditions were required for the ketones. The proposed reaction mechanism is shown in Scheme 34.



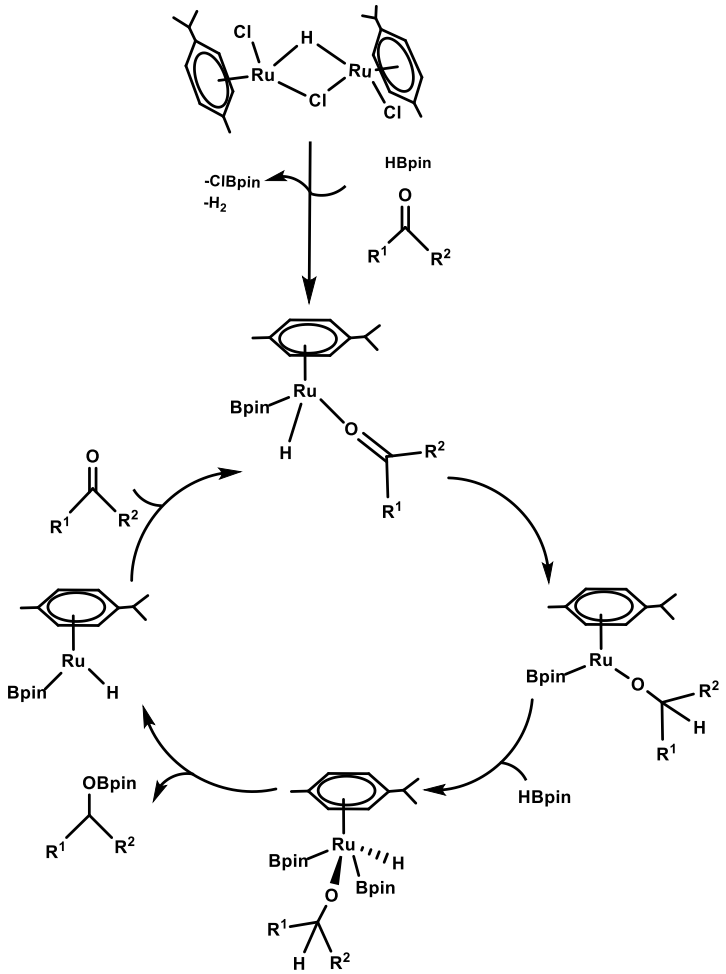
Scheme 34. Proposed catalytic cycle for hydroboration of carbonyl compounds catalyzed by boron-substituted Shvo's catalyst.

Highly efficient hydroboration of aldehydes, ketones, and chemoselective hydroboration of aldehydes under mild conditions using the [Ru(p-cymene) $Cl_2]_2$ (Scheme 33a) as a precatalyst was reported by Gunanathan and coworkers.[124] Mechanistic studies revealed that the reaction of pinacolborane with [Ru(p-cymene)$Cl_2]_2$ provides [{(η^6-p-cymene)RuCl}$_2$(μ-H-μ-Cl)] (Scheme 33b). Additional oxidative addition of pinacolborane may generate the catalytically active mononuclear Ru species (Scheme 35c).



Scheme 35. Reaction of [Ru(p-cymene) $Cl_2]_2$ with pinacolborane

The catalytic cycle consists of 1,3-hydride transfer from the metal center to the carbonyl group, and reductive elimination of boronate esters from a Ru(IV) intermediate was suggested (Scheme 36).



Scheme 36. Plausible mechanism for the hydroboration of carbonyl compounds with $[Ru(p\text{-cymene})Cl_2]_2$

4.1.2. Main group compounds in catalytic hydroboration of C=O

Main group compounds could participate in hydroboration reactions as catalysts. Corey−Bakashi−Shibata (CBS) catalyst (Figure 23a) is one of the well-known metal-free catalysts for hydroboration. This catalyst is used for the asymmetric reduction of ketones.[131,132]

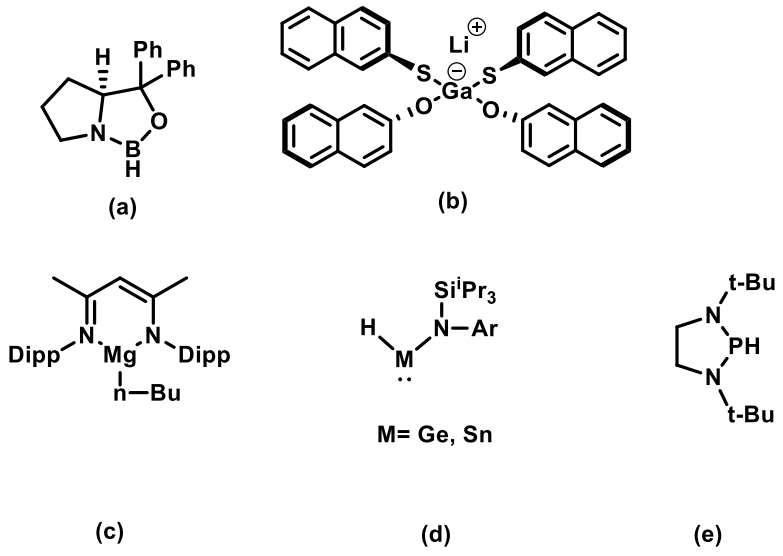
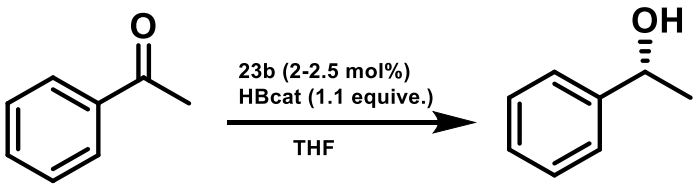


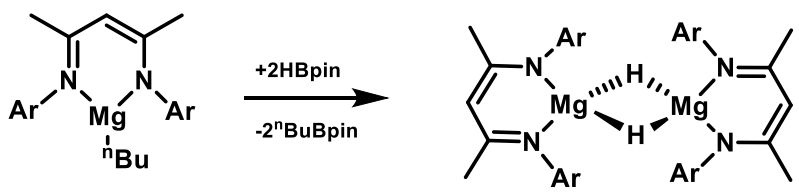
Figure 23. Selected examples of main group catalysts for hydroboration aldehydes and ketones

Woodward and coworkers reported synthesis of $LiGa(MTB)_2$ catalyst (Figure 23b) which catalyze the enantioselective reduction of prochiral ketones.[133] In the catalytic reaction, $LiGa(MTB)_2$ catalyst and ketone substrate were mixed in THF, subsequently addition of HBcat (1.1 equiv) produced the corresponding secondary alcohol in good yields and ee values (Scheme 36).



Scheme 37. Enantioselective reduction of prochiral ketones catalyzed by $LiGa(MTB)_2$

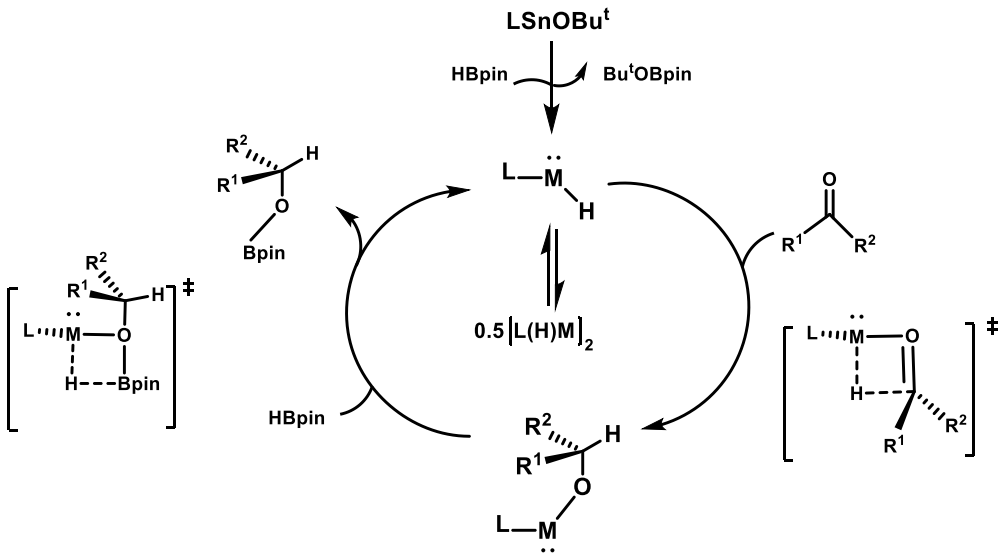
Hill and coworkers published a report demonstrating hydroboration of aldehyde and ketones by using (^{Dip}Nacnac)Mg^{n}Bu [^{Dip}Nacnac = (DipNCMe] $_2CH^-$, Dip = 2,6-^{i}Pr2C_6H_3) as a precatalyst (Figure 23c).[127] The active form in the catalytic cycle was determined to be a dimeric species, $[(DipNacnac)MgnH]_2$, formed by reaction of HBpin with 23a (Scheme 36).



Scheme 38. Formation of $[(DipNacnac)MgnH]_2$ by reaction between HBpin and $(^{Dip}Nacnac)Mg^{n}Bu$.

In 2014, Jones et al. reported the bulky, two-coordinate germanium(II) and tin(II) hydride complexes, L (H)M: (M = Ge or Sn, L = −N(Ar)($SiPri_3$), Ar = C_6H_2\{C- (H)Ph_2\}$_2$Pri -2,6,4), which act as an efficient catalyst for hydroboration of variety unactivated and bulky carbonyl compounds. Hydroboration of ketone substrates required a higher loading of catalyst, but still gave products in excellent yields (80−>99%) NMR yields.

The Ge- and Sn-catalyzed reactions mechanism initially includes attack of the O-center of the substrate at the two-coordinate metal center, with hydrometalation subsequently proceeding via a four-membered transition state. The monomeric, two-coordinate metal alkoxide intermediate then undergoes a σ-bond metathesis reaction with HBpin to generate the borate ester and return the catalyst (Scheme 39).



Scheme 39. Proposed cycle for the hydroboration of carbonyl compounds catalyzed by L MH (M = Ge or Sn).

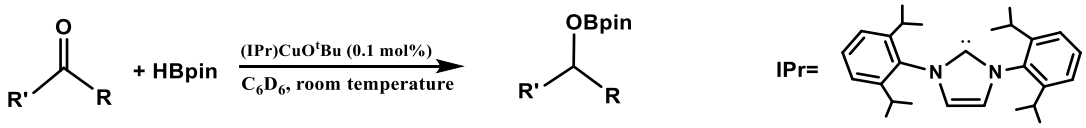
4.2. Results & discussion

Between the transition metal catalysts, readily available copper carbene[134] catalysts, such as (IPr)-CuO^{t}Bu[135] (IPr = N,N'-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) which can be generated in situ from air-stable (IPr)CuCl, have been extensively explored for hydrosilylation reactions.[111, 136-142] Furthermore, the same catalysts are active for hydroboration of CO_2 (Chapter 3, Scheme 28b)[65] and for diboration of aldehydes.[143] Therefore, we were surprised to find that no reports exist for hydroboration of carbonyl compounds by copper carbene catalysis. During our on-going studies of bimetallic reduction reactions of small molecules,[144] we have discovered that (IPr)CuO^{t}Bu is an extremely efficient catalyst for hydroboration of ketones and aldehydes with HBpin. In this chapter, we highlight the impressive catalyst loadings (0.1 mol%) and turnover frequencies (>6000 h^{-1}) that can be achieved for various ketone and aldehyde substrates in the presence of other reducible functional groups. Given the recent development of chiral copper carbenes by several

research groups,[136,145-149] this chapter provides the basis for future development of C=O hydroboration reactions that are both efficient and stereoselective.

During the course of studying our group's bimetallic hydroboration catalysts,[144] we discovered 10 mol% loading of (IPr)CuO^{t}Bu catalyses ketone hydroboration to quantitative conversion within minutes. Using the acetophenone derivative as a test substrate (Table 4), we tried lower catalyst loadings and ultimately determined that quantitative hydroboration with HBpin was achieved within 10 min even at 0.1 mol% loading. Using the same conditions, (room temperature, 10 min, 0.1 mol% catalyst, 1.0 eq. HBpin) we tested various other ketone substrates. The more electron deficient acetophenone derivative 2 also underwent quantitative hydroboration, while the more electron rich acetophenone derivative 3 produced the hydroboration product in lower yields. Similarly, the more sterically hindered ketones 4 and 5 gave moderate yields under these conditions. Interestingly, aldehyde 6 also underwent hydroboration with moderate yields. Since the reaction time was not optimized for each individual substrate, these yields likely reflect relative reaction rates rather than maximum yields.

As evidence for this, we note that all reactions approached quantitative conversion when reaction times were increased to 1 h (Table 4). Gratifyingly, even the ortho-substituted arylcarbonyl complexes 7 and 8 underwent hydroboration to high conversions under these conditions (Table 4). As this method produces no byproducts and utilizes catalyst loadings below the detection limits of NMR spectroscopy, the reduction products can be isolated in spectroscopically pure form simply by removal of volatiles in vacuo. However, selectivity between ketones and aldehydes is poor, as evidenced by the reduction of 4-acetylbenzaldehyde, which reacted efficiently but was unselective for ketone vs. aldehyde hydroboration.



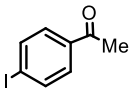
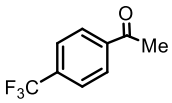
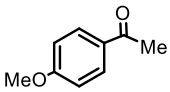
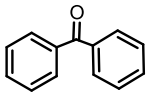
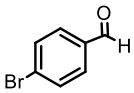
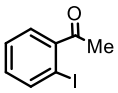
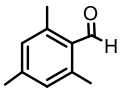
Substrate	Yield(%) at 10 min	Yield(%) at 1h
 1	98	>99
 2	94	>99
 3	46	95
 4	55	94
5	49	94
 6	62	87
 7	92	94
 8	87	96

Table 4. Hydroboration of carbonyl compounds by copper carbene catalysis. [a]Determined by ^{1}H NMR integration against an internal standard (mesitylene).

4.3. Mechanism of hydroboration of ketones and aldehydes

A σ-bond metathesis type mechanism[114] is likely operative here (Figure 24), proposed in analogy to the accepted mechanism for hydrosilylation by copper carbene catalysis.[111, 136-141, 150] First, the (IPr)CuO^{t}Bu precatalyst reacts with HBpin to generate a copper– hydride intermediate, which takes the dimeric form $[(IPr)Cu]_2(\mu\text{-}H)_2$ in the solid state[135] and may be either monomeric[141] or dimeric[99] in solution under the reaction conditions. Second, the carbonyl substrate inserts into the Cu–H bond via transition state TS1 to generate the corresponding copper–alkoxide intermediate. Finally, reaction with HBpin via σ-bond metathesis transition state TS2 produces the alkoxyboronate ester product and regenerates the copper-hydride species for further reaction. In the related hydrosilylation catalysis with copper carbenes, TS1 is thought to be primarily under steric control, the Si analogue of TS2 under electronic control, and the two barrier heights are generally similar enough that the rate-determining step changes based on the natures of the silane reductant and the carbonyl substrate.[141] Both sterically hindered substrates and electron-rich substrates give slow catalytic rates for the hydroboration reaction (Table 4), and further studies are necessary to determine whether TS1, TS2, or both are rate determining and responsible for these observed effects.

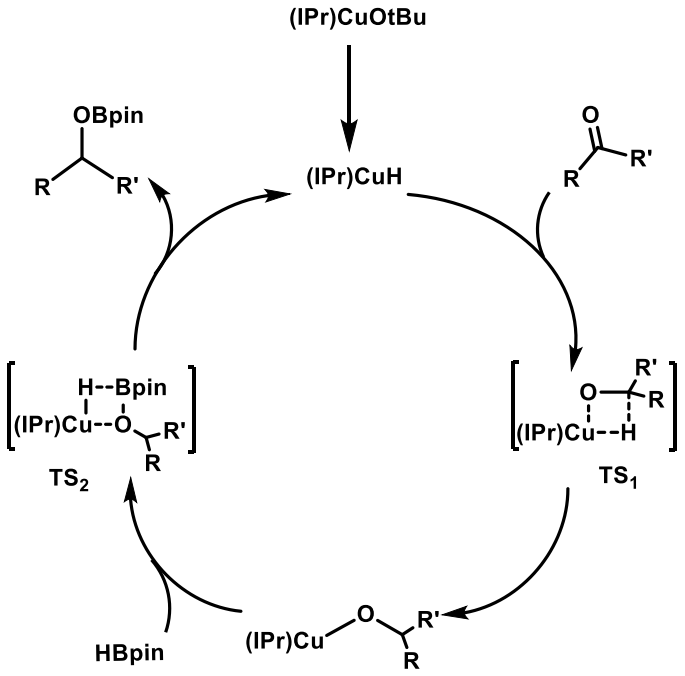
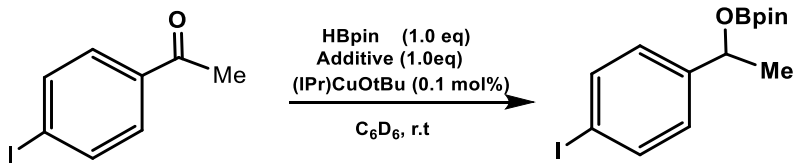


Figure 24. Proposed mechanism for hydroboration by copper carbene catalysis

4.4. Additive screen in hydroboration reaction

To determine whether carbonyl groups can undergo hydroboration in the presence of other reducible functional groups, we conducted a brief additive screen as pioneered by Glorius.[151] Substrate 1 was subjected to the standard reaction conditions in the presence of different additives (1.0 eq.) as indicated in Table 5. Hydroboration of the carbonyl group in 1 was observed in the presence of alkene, nitrile, ester, and alkyl chloride functional groups. In these cases, the additive was detected in the product mixture and had not been reduced.



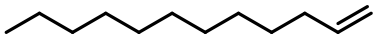
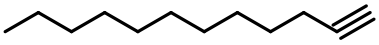
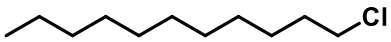
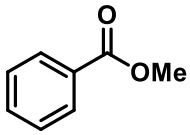
Additive	(Yield %) at 10 min	(Yield %) at 1 h
	81	>99
	7	16
	81	87
	71	84
	46	99
Me−C≡N	70	90

Table 5. Robustness of ketone hydroboration towards reducible functional groups. [a] Determined by ^{1}H NMR integration against an internal standard (mesitylene).

On the other hand, the presence of an alkyne functional group poisoned the carbonyl reduction. Alkyne hydroboration[152,153] by copper carbene catalysis apparently outcompetes even the highly efficient ketone hydroboration reaction reported here. Additives with coordinating functional groups – especially pyridine – slow the rate of catalysis but do not prevent the reaction from reaching high conversions at longer reaction times (Table 5).

4.5. Conclusion

The studies in this chapter reveal extremely efficient hydroboration of ketones and aldehydes with readily available copper carbene complex, (IPr)CuO^{t}Bu, at very low catalyst loadings (0.1 mol%) with high turnover frequencies. This method produces no byproducts and the reaction products can be isolated by removal of volatiles in vacuo. Also,the reduction of carbonyl groups occurs selectivitily in the presence of other reducible functional groups including alkenes, nitriles, esters, and alkyl chlorides.

4.6. Experimental

4.6.1. General considerations

All reactions were conducted under purified N_2 using in a glovebox and a Schlenk line. Deuterated benzene (C_6D_6) was degassed by repeated freeze-pump-thaw cycles and stored over activated 3-Å molecular sieves prior to use. ^{1}H and ^{11}B NMR spectra were recorded using Bruker Avance 400-MHz NMR spectrometer. NMR spectra were recorded at room temperature, and chemical shifts were referenced to residual solvent peak. ^{11}B NMR chemical shifts were referenced to external pinacolborane (29.01 and 27.6 ppm). Literature methods were used to synthesize (IPr)CuO^{t}Bu.[135] All other reagents were purchased from commercial vendors and used without further purification.

4.6.2. General catalytic procedure

In the glovebox, a scintillation vial was charged with (IPr)CuO^{t}Bu (1.5 mg, 0.00285 mmol), and C_6D_6 (6 mL) was added. Another 20-mL scintillation vial was charged with a stir bar and substrate (0.952 mmol). The substrate was dissolved in C_6D_6 (5 mL), and then pinacolborane (138 μL, 0.952 mmol), mesitylene (132.6 μL, 0.952 mmol) and in some cases additives (0.952 mmol) were added to this solution. Then, an aliquot of the (IPr)CuO^{t}Bu stock solution (2 mL) was added to the reaction vial, and the resulting mixture was stirred at room temperature for 10 min and 1 h (as

indicated in the manuscript). Aliquots of the reaction solution was transferred to NMR tubes, and ^{1}H and ^{11}B NMR spectra (see below) were taken to monitor reaction progress. Separate catalytic runs performed by multiple researchers were reproduced to within ±2%.

4.6.3. Isolation of 2-(1-(4-iodophenyl) ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In the glovebox, a scintillation vial was charged with (IPr)CuO^{t}Bu (1 mg, 0.002 mmol), and was dissolved in C_6D_6 (2 mL). Another 20-mL scintillation vial was charged with a stir bar and 4-iodoacetophenone (0.234 g, 0.952 mmol). The substrate was dissolved in C_6D_6 (2 mL), and then pinacolborane (138 μL, 0.952 mmol) was added to this solution. Then an aliquote of the catalyst stock solution (1 mL) was added to the solution to the reaction vial, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed to afford the product: 0.25 g, 70%.

4.6.4. Isolation of 2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

In the glovebox, a scintillation vial was charged with (IPr)CuO^{t}Bu (1 mg, 0.002 mmol), and was dissolved in C_6D_6 (2 mL). Another 20-mL scintillation vial was charged with a stir bar and benzophenone (0.173 g, 0.952 mmol). The substrate was dissolved in C_6D_6 (2 mL), and then pinacolborane (138 μL, 0.952 mmol) was added to this solution. An aliquot of the catalyst stock solution (1 mL) was added to the solution to the reaction vial, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed to afford the product: 0.20 g, yield: 68%.

References:

1. Munoz, C.; Paulino, L.; Monreal, C.; Zagal, E. *Chil J Agr Res* **2010**, *70* (3), 485-497.

2. Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. *Science* **2009**, *326* (5949), 123-125.

3. Crutzen, P. J.; Mosier, A. R.; Smith, K. A.; Winiwarter, W. *Atmos Chem Phys* **2008**, *8* (2), 389-395.

4. Conrad, R. *Microbiol Rev* **1996**, *60* (4), 609-612.

5. Dickinson, R. E.; Cicerone, R. J. *Nature* **1986**, *319* (6049), 109-115.

6. Skiba, U. M.; Sheppard, L. J.; MacDonald, J.; Fowler, D. *Atmos Environ* **1998**, *32* (19), 3311-3320.

7. Piro, N. A.; Lichterman, M. F.; Harman, W. H.; Chang, C. J. *J Am Chem Soc* **2011**, *133* (7), 2108-2111.

8. Einsle, O.; Kroneck, P. M. H. *Biol Chem* **2004**, *385* (10), 875-883.

9. Huang, L.; Gao, X.; Guo, J. S.; Ma, X. X.; Liu, M. *Environ Earth Sci* **2013**, *68* (8), 2171-2180.

10. Rosenzweig, A. C. *Nat Struct Biol* **2000**, *7* (3), 169-71.

11. Johnston, E. M.; Carreira, C.; Dell'Acqua, S.; Dey, S. G.; Pauleta, S. R.; Moura, I.; Solomon, E. I. *J Am Chem Soc* **2017**, *139* (12), 4462-4476.

12. Johnston, E. M.; Dell'Acqua, S.; Ramos, S.; Pauleta, S. R.; Moura, I.; Solomon, E. I. *J Am Chem Soc* **2014**, *136* (2), 614-617.

13. Chen, P.; Cabrito, I.; Moura, J. J. G.; Moura, I.; Solomon, E. I. *J Am Chem Soc* **2002**, *124* (35), 10497-10507.

14. Esmieu, C.; Orio, M.; Torelli, S.; Le Pape, L.; Pecaut, J.; Lebrun, C.; Menage, S. *Chem Sci* **2014**, *5* (12), 4774-4784.

15. Pomowski, A.; Zumft, W. G.; Kroneck, P. M. H.; Einsle, O. *Nature* **2011**, *477* (7363), 234-U143.

16. Bar-Nahum, I.; Gupta, A. K.; Huber, S. M.; Ertem, M. Z.; Cramer, C. J.; Tolman, W. B. *J Am Chem Soc* **2009**, *131* (8), 2812-2820.

17. Torelli, S.; Orio, M.; Pécaut, J.; Jamet, H.; Le Pape, L.; Ménage, S. *Angew. Chem. Int. Ed.* **2010**, *49* (44), 8249-8252.

18. Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Mankad, N. P. *Chem Commun* **2015**, *51* (59), 11860-11863.

19. Johnson, B. J.; Antholine, W. E.; Lindeman, S. V.; Graham, M. J.; Mankad, N. P. *J Am Chem Soc* **2016**, *138* (40), 13107-13110.

20. Atkins, P. W.; De Paula, J. *Atkins' Physical chem*. Oxford, Oxford University Press, 2006.

21. Shi, J. F.; Jiang, Y. J.; Jiang, Z. Y.; Wang, X. Y.; Wang, X. L.; Zhang, S. H.; Han, P. P.; Yang, C. *Chem Soc Rev* **2015**, *44* (17), 5981-6000.

22. Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem Rev* **2013**, *113* (8), 6621-6658.

23. Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *P Natl Acad Sci USA* **2002**, *99* (25), 15971-15976.

24. Hofmann, M.; Kassube, J. K.; Graf, T. *J Biol Inorg Chem* **2005**, *10* (5), 490-495.

25. Shanmugam, M.; Wilcoxen, J.; Habel-Rodriguez, D.; Cutsail Iii, G. E.; Kirk, M. L.; Hoffman, B. M.; Hille, R. *J Am Chem Soc* **2013**, *135* (47), 17775-17782.

26. Majumdar, A. *Dalton Trans* **2014**, *43* (32), 12135-12145.

27. Gourlay, C.; Nielsen, D. J.; White, J. M.; Knottenbelt, S. Z.; Kirk, M. L.; Young, C. G. *J Am Chem Soc* **2006**, *128* (7), 2164-2165.

28. Takuma, M.; Ohki, Y.; Tatsumi, K. *Inorg Chem* **2005**, *44* (17), 6034-6043.

29. Groysman, S.; Majumdar, A.; Zheng, S.-L.; Holm, R. H. *Inorg Chem* **2010**, *49* (3), 1082-1089.

30. Bose, M.; Moula, G.; Begum, A.; Sarkar, S. *Inorg Chem* **2011**, *50* (9), 3852-3854.

31. Gambarotta, S.; Arena, F.; Floriani, C.; Zanazzi, P. F. *J Am Chem Soc* **1982**, *104* (19), 5082-5092.

32. Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J Am Chem Soc* **1978**, *100* (23), 7405-7407.

33. Floriani, C.; Fachinetti, G. *Chem Commun* **1974**, (15), 615-616.

34. Hanna, T. A.; Baranger, A. M.; Bergman, R. G. *J Am Chem Soc* **1995**, *117* (45), 11363-11364.

35. Pinkes, J. R.; Steffey, B. D.; Vites, J. C.; Cutler, A. R. *Organometallics* **1994**, *13* (1), 21-23.

36. Krogman, J. P.; Foxman, B. M.; Thomas, C. M. *J Am Chem Soc* **2011**, *133* (37), 14582-14585.

37. Machan, C. W.; Kubiak, C. P. *Dalton Trans* **2016**, *45* (40), 15942-15950.

38. Thomson, A. J.; Giannopoulos, G.; Pretty, J.; Baggs, E. M.; Richardson, D. *J Biol Sci* **2012**, *367* (1593), 1157-1168.

39. Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. *Science* **2009**, *326* (5949), 123-125.

40. Pauleta, S. R.; Dell'Acqua, S.; Moura, I. *Coordin Chem Rev* **2013**, *257* (2), 332-349.

41. Brown, K.; Tegoni, M.; Prudencio, M.; Pereira, A. S.; Besson, S.; Moura, J. J.; Moura, I.; Cambillau, C. *Nature Struct Biol* **2000**, *7* (3), 191-195.

42. Pomowski, A.; Zumft, W. G.; Kroneck, P. M. H.; Einsle, O. *Nature* **2011**, *477* (7363), 234-237.

43. Solomon, E. I.; Heppner, D. E.; Johnston, E. M.; Ginsbach, J. W.; Cirera, J.; Qayyum, M.; Kieber-Emmons, M. T.; Kjaergaard, C. H.; Hadt, R. G.; Tian, L. *Chem Rev* **2014**, *114* (7), 3659-3853.

44. Johnston, E. M.; Dell'Acqua, S.; Ramos, S.; Pauleta, S. R.; Moura, I.; Solomon, E. I. *J Am Chem Soc* **2014**, *136* (2), 614-617.

45. Ghosh, S.; Gorelsky, S. I.; Chen, P.; Cabrito, I.; Moura; MouraMoura, I.; Solomon, E. I. *J Am Chem Soc* **2003**, *125* (51), 15708-15709.

46. Tsai, M.-L.; Hadt, R. G.; Vanelderen, P.; Sels, B. F.; Schoonheydt, R. A.; Solomon, E. I. *J Am Chem Soc* **2014**, *136* (9), 3522-3529.

47. Gorelsky, S. I.; Ghosh, S.; Solomon, E. I. *J Am Chem Soc* **2006**, *128* (1), 278-290.

48. Zhai, J.; Filatov, A. S.; Hillhouse, G. L.; Hopkins, M. D. *Chem Sci* **2016**, *7* (1), 589-595.

49. Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem Commun* **2003**, (1), 28-29.

50. Zhai, J.; Hopkins, M. D.; Hillhouse, G. L. *Organometallics* **2015**, *34* (19), 4637-4640.

51. Santoro, O.; Collado, A.; Slawin, A. M. Z.; Nolan, S. P.; Cazin, C. S. J. *Chem Commun* **2013**, *49* (89), 10483-10485.

52. Berthon-Gelloz, G.; Siegler, M. A.; Spek, A. L.; Tinant, B.; Reek, J. N. H.; Marko, I. E. *Dalton Trans* **2010**, *39* (6), 1444-1446.

53. Sheldrick, G. *Acta Crystallogr A* **2008**, *64* (1), 112-122.

54. Müller, P. *Crystallogr Rev* **2009**, *15* (1), 57-83.

55. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision B.01. Wallingford CT, 2009.

56. Becke, A. D. *Physical Rev A* **1988**, *38* (6), 3098-3100.

57. Perdew, J. P. *Phys. Rev. B* **1986**, *33* (12), 8822-8824.

58. Hay, P. J.; Wadt, W. R. *J. Chem. Phys* **1985**, *82* (1), 299-310.

59. Roy, L. E.; Hay, P. J.; Martin, R. L. *J. Chem. Theory Comput* **2008**, *4* (7), 1029-1031.

60. Ehlers, A. W.; Böhme, M.; Dapprich, S.; Gobbi, A.; Höllwarth, A.; Jonas, V.; Köhler, K. F.; Stegmann, R.; Veldkamp, A.; Frenking, G. *J. Chem. Phys* Lett **1993**, *208* (1), 111-114.

61. Hay, P. J.; Wadt, W. R. *J. Chem. Phys* **1985**, *82* (1), 270-283.

62. Wadt, W. R.; Hay, P. J. *J. Chem. Phys* **1985**, *82* (1), 284-298.

63. Lalrempuia, R.; Iglesias, M.; Polo, V.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Angew. Chem. Int. Ed* **2012**, *51* (51), 12824-12827.

64. Zhang, L.; Cheng, J.; Hou, Z. *Chem Commun* **2013**, *49* (42), 4782-4784.

65. Shintani, R.; Nozaki, K. *Organometallics* **2013**, *32* (8), 2459-2462.

66. Jiang, Y.; Blacque, O.; Fox, T.; Berke, H. *J Am Chem Soc* **2013**, *135* (20), 7751-7760.

67. Laitar, D. S.; Müller, P.; Sadighi, J. P. *J Am Chem Soc* **2005**, *127* (49), 17196-17197.

68. Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *J Am Chem Soc* **2014**, *136* (11), 4419-4425.

69. Jin, G.; Werncke, C. G.; Escudié, Y.; Sabo-Etienne, S.; Bontemps, S. *J Am Chem Soc* **2015**, *137* (30), 9563-9566.

70. Riduan, S. N.; Zhang, Y.; Ying, J. Y. *Angew. Chem. Int. Ed* **2009**, *48* (18), 3322-3325.

71. Chakraborty, S.; Zhang, J.; Krause, J. A.; Guan, H. *J Am Chem Soc* **2010**, *132* (26), 8872-8873.

72. Abdalla, J. A. B.; Riddlestone, I. M.; Tirfoin, R.; Aldridge, S. *Angew. Chem. Int. Ed.* **2015**, *54* (17), 5098-5102.

73. Pal, R.; Groy, T. L.; Trovitch, R. J. *Inorg Chem* **2015**, *54* (15), 7506-7515.

74. Courtemanche, M.-A.; Légaré, M.-A.; Maron, L.; Fontaine, F.-G. *J Am Chem Soc* **2013**, *135* (25), 9326-9329.

75. Matsuo, T.; Kawaguchi, H. *J Am Chem Soc* **2006**, *128* (38), 12362-12363.

76. Berkefeld, A.; Piers, W. E.; Parvez, M. *J Am Chem Soc* **2010**, *132* (31), 10660-10661.

77. Park, S.; Bézier, D.; Brookhart, M. *J Am Chem Soc* **2012**, *134* (28), 11404-11407.

78. Wehmschulte, R. J.; Saleh, M.; Powell, D. R. *Organometallics* **2013**, *32* (22), 6812-6819.

79. Bontemps, S.; Vendier, L.; Sabo-Etienne, S. *Angew. Chem. Int. Ed.* **2012**, *51* (7), 1671-1674.

80. Schäfer, A.; Saak, W.; Haase, D.; Müller, T. *Angew. Chem. Int. Ed.* **2012**, *51* (12), 2981-2984.

81. Wang, T.; Stephan, D. W. *Chem Commun* **2014**, *50* (53), 7007-7010.

82. Scheuermann, M. L.; Semproni, S. P.; Pappas, I.; Chirik, P. J. *Inorg Chem* **2014**, *53* (18), 9463-9465.

83. Reda, T.; Plugge, C. M.; Abram, N. J.; Hirst, J. *Proc Natl Acad Sci* **2008**, *105* (31), 10654-10658.

84. Jeoung, J.-H.; Dobbek, H. *Science* **2007**, *318* (5855), 1461-1464.

85. Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc Natl Acad Sci* **2002**, *99* (25), 15971-15976.

86. Man, M. L.; Zhou, Z.; Ng, S. M.; Lau, C. P. *Dalton Trans* **2003**, (19), 3727-3735.

87. Cooper, O.; Camp, C.; Pecaut, J.; Kefalidis, C. E.; Maron, L.; Gambarelli, S.; Mazzanti, M. *J Am Chem Soc* **2014**, *136* (18), 6716-6723.

88. Smieja, J. M.; Kubiak, C. P. *Inorg Chem* **2010**, *49* (20), 9283-9289.

89. Hawecker, J.; Lehn, J.-M.; Ziessel, R. *Helv. Chim. Acta* **1986**, *69* (8), 1990-2012.

90. Smieja, J. M.; Benson, E. E.; Kumar, B.; Grice, K. A.; Seu, C. S.; Miller, A. J. M.; Mayer, J. M.; Kubiak, C. P. *Proc Natl Acad Sci* **2012**, *109* (39), 15646-15650.

91. Machan, C. W.; Chabolla, S. A.; Yin, J.; Gilson, M. K.; Tezcan, F. A.; Kubiak, C. P. *J Am Chem Soc* **2014**, *136* (41), 14598-14607.

92. Sampson, M. D.; Nguyen, A. D.; Grice, K. A.; Moore, C. E.; Rheingold, A. L.; Kubiak, C. P. *J Am Chem Soc* **2014**, *136* (14), 5460-5471.

93. Steffey, B. D.; Curtis, C. J.; DuBois, D. L. *Organometallics* **1995**, *14* (10), 4937-4943.

94. Zhang, Y.; MacIntosh, A. D.; Wong, J. L.; Bielinski, E. A.; Williard, P. G.; Mercado, B. Q.; Hazari, N.; Bernskoetter, W. H. *Chem Sci* **2015**, *6* (7), 4291-4299.

95. Matsubu, J. C.; Yang, V. N.; Christopher, P. *J Am Chem Soc* **2015**, *137* (8), 3076-3084.

96. Zhang, L.; Hou, Z. *Chem Sci* **2013**, *4* (9), 3395-3403.

97. Banerjee, S.; Karunananda, M. K.; Bagherzadeh, S.; Jayarathne, U.; Parmelee, S. R.; Waldhart, G. W.; Mankad, N. P. *Inorg Chem* **2014**, *53* (20), 11307-11315.

98. Mazzacano, T. J.; Mankad, N. P. *J Am Chem Soc* **2013**, *135* (46), 17258-17261.

99. Parmelee, S. R.; Mazzacano, T. J.; Zhu, Y.; Mankad, N. P.; Keith, J. A. *ACS Catalysis* **2015,** *5* (6), 3689-3699.

100. Jayarathne, U.; Parmelee, S. R.; Mankad, N. P. *Inorg Chem* **2014**, *53* (14), 7730-7737.

101. King, R. B. *Accounts Chem Res* **1970**, *3* (12), 417-427.

102. Silvia, J. S.; Cummins, C. C. *J Am Chem Soc* **2010**, *132* (7), 2169-2171.

103. Chakraborty, S.; Patel, Y. J.; Krause, J. A.; Guan, H. *Polyhedron* **2012**, *32* (1), 30-34.

104. Lee, G. R.; Cooper, N. J. *Organometallics* **1985**, *4* (4), 794-796.

105. Zieliński, M.; Zielińska, A.; Papiernik-Zielińska, H. *J. Radioanal. Nucl. Chem* **1994**, *183* (2), 301-311.

106. Halpern, J.; Kemp, A. L. W. *J Am Chem Soc* **1966**, *88* (22), 5147-5150.

107. Sueki, S.; Kuninobu, Y. *Org. Lett.***2013**, *15* (7), 1544-1547.

108. Hawkeswood, S.; Stephan, D. W. *Dalton Trans.* **2005**, (12), 2182-2187.

109. Behrens, U.; Edelmann, F. *J. Organomet. Chem.* **1984**, *263* (2), 179-182.

110. Jafarpour, L.; Stevens, E. D.; Nolan, S. P. *J. Organomet. Chem.* **2000**, *606* (1), 49-54.

111. Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23* (5), 1157-1160.

112. Jayarathne, U.; Mazzacano, T. J.; Bagherzadeh, S.; Mankad, N. P.*Organometallics* **2013**, *32* (14), 3986-3992.

113. Campion, B. K.; Heyn, R. H.; Tilley, T. D. *Chem. Commun* **1988**, (4), 278-280.

114. Chong, C. C.; Kinjo, R. *ACS Catalysis* **2015**, *5* (6), 3238-3259.

115. Lindsley, C. W.; DiMare, M. *Tetrahedron Lett* **1994**, *35* (29), 5141-5144.

116. Giffels, G.; Dreisbach, C.; Kragl, U.; Weigerding, M.; Waldmann, H.; Wandrey, C. *Angew. Chem. Int. Ed* **1995**, *34* (18), 2005-2006.

117. Almqvist, F.; Torstensson, L.; Gudmundsson, A.; Frejd, T. *Angew. Chem. Int. Ed.* **1997**, *36* (4), 376-377.

118. Oluyadi, A. A.; Ma, S.; Muhoro, C. N. *Organometallics* **2013**, *32* (1), 70-78.

119. Bandini, M.; Cozzi, P. G.; de Angelis, M.; Umani-Ronchi, A. *Tetrahedron Lett* **2000**, *41* (10), 1601-1605.

120. Roh, S. G.; Yoon, J. U.; Jeong, J. H. *Polyhedron* **2004**, *23* (12), 2063-2067.

121. Roh, S.-G.; Park, Y.-C.; Park, D.-K.; Kim, T.-J.; Jeong, J. H. *Polyhedron* **2001**, *20* (15–16), 1961-1965.

122. Lummis, P. A.; Momeni, M. R.; Lui, M. W.; McDonald, R.; Ferguson, M. J.; Miskolzie, M.; Brown, A.; Rivard, E. *Angew. Chem. Int. Ed.* **2014**, *53* (35), 9347-9351.

123. Locatelli, M.; Cozzi, P. G. *Angew. Chem. Int. Ed.* **2003**, *42* (40), 4928-4930.

124. Kaithal, A.; Chatterjee, B.; Gunanathan, C. *Org Lett* **2015**, *17* (19), 4790-4793.

125. Koren-Selfridge, L.; Londino, H. N.; Vellucci, J. K.; Simmons, B. J.; Casey, C. P.; Clark, T. B. *Organometallics* **2009**, *28* (7), 2085-2090.

126. Lampland, N. L.; Hovey, M.; Mukherjee, D.; Sadow, A. D. *ACS Catalysis* **2015**, *5* (7), 4219-4226.

127. Arrowsmith, M.; Hadlington, T. J.; Hill, M. S.; Kociok-Kohn, G. *Chem Commun* **2012**, *48* (38), 4567-4569.

128. Mukherjee, D.; Ellern, A.; Sadow, A. D. *Chem Sci* **2014**, *5* (3), 959-964.

129. Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed.* **2015**, *54* (1), 190-194.

130. Hadlington, T. J.; Hermann, M.; Frenking, G.; Jones, C. *J Am Chem Soc* **2014**, *136* (8), 3028-3031.

131. Corey, E. J.; Bakshi, R. K.; Shibata, S. *J Am Chem Soc* **1987**, *109* (18), 5551-5553.

132. Corey, E. J.; Shibata, S.; Bakshi, R. K. *J. Org. Chem.***1988**, *53* (12), 2861-2863.

133. Blake, A. J.; Cunningham, A.; Ford, A.; Teat, S. J.; Woodward, S. *Chem-Eur J* **2000**, *6* (19), 3586-3594.

134. Díez-González, S.; Nolan, S. P. *Synlett* **2007**, *2007* (14), 2158-2167.

135. Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23* (14), 3369-3371.

136. Albright, A.; Gawley, R. E. *J Am Chem Soc* **2011**, *133* (49), 19680-19683.

137. Díez-González, S.; Kaur, H.; Zinn, F. K.; Stevens, E. D.; Nolan, S. P. *J. Org. Chem.* **2005**, *70* (12), 4784-4796.

138. Díez-González, S.; Scott, N. M.; Nolan, S. P. *Organometallics* **2006**, *25* (9), 2355-2358.

139. Diez-Gonzalez, S.; Escudero-Adan, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans* **2010**, *39* (32), 7595-7606.

140. Díez-González, S.; Stevens, E. D.; Scott, N. M.; Petersen, J. L.; Nolan, S. P. *Chem. Eur. J* **2008**, *14* (1), 158-168.

141. Vergote, T.; Nahra, F.; Merschaert, A.; Riant, O.; Peeters, D.; Leyssens, T. *Organometallics* **2014**, *33* (8), 1953-1963.

142. Vergote, T.; Nahra, F.; Peeters, D.; Riant, O.; Leyssens, T. *J. Organomet. Chem.* **2013**, *730* (Supplement C), 95-103.

143. Laitar, D. S.; Tsui, E. Y.; Sadighi, J. P. *J Am Chem Soc* **2006**, *128* (34), 11036-11037.

144. Bagherzadeh, S.; Mankad, N. P. *J Am Chem Soc* **2015**, *137* (34), 10898-10901.

145. Van Veldhuizen, J. J.; Campbell, J. E.; Giudici, R. E.; Hoveyda, A. H. *J Am Chem Soc* **2005**, *127* (18), 6877-6882.

146. Albright, A.; Eddings, D.; Black, R.; Welch, C. J.; Gerasimchuk, N. N.; Gawley, R. E. *The J. Org. Chem.* **2011**, *76* (18), 7341-7351.

147. Park, J. K.; Lackey, H. H.; Rexford, M. D.; Kovnir, K.; Shatruk, M.; McQuade, D. T. *Organic Lett* **2010**, *12* (21), 5008-5011.

148. Selim, K. B.; Matsumoto, Y.; Yamada, K.-i.; Tomioka, K. *Angew. Chem. Int. Ed.* **2009**, *48* (46), 8733-8735.

149. Takatsu, K.; Shintani, R.; Hayashi, T. *Angew. Chem. Int. Ed.* **2011**, *50* (24), 5548-5552.

150. Yun, J.; Kim, D.; Yun, H. *Chem Commun* **2005**, (41), 5181-5183.

151. Collins, K. D.; Glorius, F. *Nat Chem* **2013**, *5* (7), 597-601.

152. Lipshutz, B. H.; Bošković, Ž. V.; Aue, D. H. *Angew. Chem. Int. Ed.* **2008**, *47* (52), 10183-10186.

153. Semba, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Eur. J* **2012**, *18* (14), 4179-4184.

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They are only intended as comments.
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Cu3 Cu 0.58955(6) 0.17492(6) 0.74110(6) 0.0419(5) Uani 1 1 d . U . . .
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O6 O 0.4368(4) 0.2650(4) 0.7444(4) 0.065(2) Uani 1 1 d . U . . .
O7 O 0.5364(5) 0.2694(5) 0.8153(4) 0.106(3) Uani 1 1 d . U . . .
O8 O 0.5230(5) 0.3383(4) 0.7530(4) 0.102(3) Uani 1 1 d . U . . .
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C6 C 0.9821(6) 1.0122(6) 0.7006(5) 0.054(3) Uani 1 1 d . U . . .
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C8 C 1.0133(6) 1.0361(6) 0.7967(5) 0.050(3) Uani 1 1 d . U . . .
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C10 C 0.9044(6) 1.0654(7) 0.7462(5) 0.080(4) Uani 1 1 d . U . . .
H10A H 0.9105 1.0998 0.7784 0.119 Uiso 1 1 calc R U . . .
H10B H 0.8737 1.0337 0.7463 0.119 Uiso 1 1 calc R U . . .
H10C H 0.8885 1.0804 0.7134 0.119 Uiso 1 1 calc R U . . .
C11 C 1.1198(6) 1.0174(5) 0.8534(4) 0.045(2) Uani 1 1 d . U . . .
H11 H 1.1542 0.9914 0.8454 0.054 Uiso 1 1 calc R U . . .
C12 C 1.1502(7) 1.0806(7) 0.8807(5) 0.061(3) Uani 1 1 d . U . . .
C13 C 1.1207(7) 1.1324(6) 0.8837(5) 0.066(3) Uani 1 1 d . U . . .
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C14 C 1.1531(8) 1.1934(7) 0.9105(6) 0.083(3) Uani 1 1 d . U . . .
H14 H 1.1306 1.2296 0.9117 0.100 Uiso 1 1 calc R U . . .
C15 C 1.2131(8) 1.1964(8) 0.9326(7) 0.093(4) Uani 1 1 d . U . . .
H15 H 1.2354 1.2359 0.9489 0.112 Uiso 1 1 calc R U . . .
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H17 H 1.2357 1.0516 0.8998 0.114 Uiso 1 1 calc R U . . .
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C19 C 1.0934(6) 1.0138(6) 0.9377(5) 0.055(3) Uani 1 1 d . U . . .
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C20 C 1.0694(6) 0.9848(6) 0.9714(5) 0.062(3) Uani 1 1 d . U . . .
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C21 C 1.0495(8) 0.9243(7) 0.9529(6) 0.092(3) Uani 1 1 d . U . . .
H21 H 1.0360 0.9024 0.9747 0.111 Uiso 1 1 calc R U . . .
C22 C 1.0495(8) 0.8960(7) 0.9016(6) 0.108(4) Uani 1 1 d . U . . .
H22 H 1.0381 0.8529 0.8885 0.130 Uiso 1 1 calc R U . . .
C23 C 1.0658(8) 0.9285(7) 0.8667(6) 0.096(3) Uani 1 1 d . U . . .
H23 H 1.0583 0.9096 0.8292 0.116 Uiso 1 1 calc R U . . .
C24 C 1.0550(6) 0.9606(6) 0.6491(5) 0.054(2) Uani 1 1 d . U . . .
H24 H 1.1008 0.9529 0.6605 0.065 Uiso 1 1 calc R U . . .
C25 C 1.0510(8) 1.0095(7) 0.6157(5) 0.073(3) Uani 1 1 d . U . . .
C26 C 1.1068(8) 1.0427(7) 0.6219(5) 0.083(3) Uani 1 1 d . U . . .
H26 H 1.1455 1.0339 0.6451 0.100 Uiso 1 1 calc R U . . .
C27 C 1.1066(8) 1.0900(7) 0.5936(6) 0.091(3) Uani 1 1 d . U . . .
H27 H 1.1443 1.1141 0.5990 0.110 Uiso 1 1 calc R U . . .
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H28 H 1.0523 1.1290 0.5399 0.111 Uiso 1 1 calc R U . . .
C29 C 0.9941(8) 1.0651(7) 0.5526(6) 0.092(3) Uani 1 1 d . U . . .
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C30 C 0.9965(8) 1.0165(7) 0.5802(5) 0.079(3) Uani 1 1 d . U . . .
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C37 C 1.2412(5) 0.8384(5) 0.7541(5) 0.041(2) Uani 1 1 d . U . . .
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C39 C 1.3013(6) 0.7695(6) 0.7988(5) 0.059(3) Uani 1 1 d . U . . .
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C41 C 1.2711(6) 0.7441(6) 0.7025(6) 0.069(3) Uani 1 1 d . U . . .
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H43B H 1.3725 0.6794 0.7781 0.164 Uiso 1 1 calc R U . . .
H43C H 1.3380 0.6548 0.7142 0.164 Uiso 1 1 calc R U . . .
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C46 C 1.3043(8) 0.8415(8) 0.6246(6) 0.101(3) Uani 1 1 d . U . . .
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C52 C 1.1743(8) 0.7472(8) 0.5549(6) 0.105(4) Uani 1 1 d . U . . .
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C58 C 1.3224(9) 0.9114(7) 0.8822(6) 0.092(3) Uani 1 1 d . U . . .
C59 C 1.3787(8) 0.9088(8) 0.8694(6) 0.102(4) Uani 1 1 d . U . . .
H59 H 1.3838 0.8755 0.8416 0.123 Uiso 1 1 calc R U . . .
C60 C 1.4273(9) 0.9540(8) 0.8965(7) 0.117(4) Uani 1 1 d . U . . .
H60 H 1.4648 0.9537 0.8861 0.140 Uiso 1 1 calc R U . . .
C61 C 1.4210(10) 0.9959(9) 0.9356(8) 0.126(4) Uani 1 1 d . U . . .
H61 H 1.4554 1.0265 0.9523 0.151 Uiso 1 1 calc R U . . .
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C63 C 1.3157(9) 0.9579(7) 0.9291(6) 0.106(4) Uani 1 1 d . U . . .
H63 H 1.2780 0.9570 0.9390 0.127 Uiso 1 1 calc R U . . .
C64 C 1.2511(8) 0.8372(7) 0.8914(6) 0.095(3) Uani 1 1 d D U . . .
C65 C 1.2948(9) 0.8230(6) 0.9359(5) 0.105(4) Uani 1 1 d D U . . .
H65 H 1.3382 0.8327 0.9411 0.125 Uiso 1 1 calc R U . . .

C66 C 1.2803(10) 0.7951(7) 0.9746(6) 0.126(4) Uani 1 1 d D U . . .
H66 H 1.3098 0.7861 1.0054 0.151 Uiso 1 1 calc R U . . .
C67 C 1.2164(10) 0.7838(9) 0.9593(8) 0.147(4) Uani 1 1 d D U . . .
H67 H 1.2039 0.7580 0.9788 0.176 Uiso 1 1 calc R U . . .
C68 C 1.1644(10) 0.8005(9) 0.9220(7) 0.146(4) Uani 1 1 d D U . . .
H68 H 1.1214 0.8005 0.9216 0.176 Uiso 1 1 calc R U . . .
C69 C 1.1913(9) 0.8171(8) 0.8855(7) 0.131(4) Uani 1 1 d D U . . .
H69 H 1.1626 0.8137 0.8504 0.157 Uiso 1 1 calc R U . . .
C70 C 0.8301(5) 0.6103(5) 0.7399(4) 0.0242(18) Uani 1 1 d . U . . .
C71 C 0.7859(5) 0.5213(5) 0.7447(4) 0.023(2) Uani 1 1 d . U . . .
H71 H 0.7817 0.4795 0.7463 0.028 Uiso 1 1 calc R U . . .
C72 C 0.7409(5) 0.5598(5) 0.7418(4) 0.021(2) Uani 1 1 d . U . . .
H72 H 0.6991 0.5524 0.7427 0.025 Uiso 1 1 calc R U . . .
C73 C 0.7364(5) 0.6702(5) 0.7375(4) 0.0253(18) Uani 1 1 d . U . . .
C74 C 0.7406(5) 0.7104(5) 0.7866(4) 0.042(2) Uani 1 1 d . U . . .
C75 C 0.7087(5) 0.7660(5) 0.7863(4) 0.044(2) Uani 1 1 d . U . . .
H75 H 0.7105 0.7948 0.8195 0.053 Uiso 1 1 calc R U . . .
C76 C 0.6756(6) 0.7770(6) 0.7380(5) 0.050(3) Uani 1 1 d . U . . .
C77 C 0.6699(5) 0.7363(5) 0.6893(4) 0.040(2) Uani 1 1 d . U . . .
H77 H 0.6465 0.7458 0.6564 0.048 Uiso 1 1 calc R U . . .
C78 C 0.6984(5) 0.6805(5) 0.6880(4) 0.033(2) Uani 1 1 d . U . . .
C79 C 0.6460(6) 0.8402(6) 0.7394(5) 0.072(4) Uani 1 1 d . U . . .
H79A H 0.6306 0.8459 0.7025 0.108 Uiso 1 1 calc R U . . .
H79B H 0.6781 0.8737 0.7621 0.108 Uiso 1 1 calc R U . . .
H79C H 0.6107 0.8410 0.7547 0.108 Uiso 1 1 calc R U . . .
C80 C 0.6978(5) 0.6364(5) 0.6347(4) 0.037(2) Uani 1 1 d . U . . .
H80 H 0.7077 0.5956 0.6434 0.045 Uiso 1 1 calc R U . . .
C81 C 0.6315(6) 0.6256(5) 0.5932(5) 0.044(2) Uani 1 1 d . U . . .
C82 C 0.5896(6) 0.5816(6) 0.5985(5) 0.061(3) Uani 1 1 d . U . . .
H82 H 0.6014 0.5607 0.6268 0.073 Uiso 1 1 calc R U . . .
C83 C 0.5280(7) 0.5698(7) 0.5590(5) 0.081(3) Uani 1 1 d . U . . .
H83 H 0.4974 0.5427 0.5625 0.097 Uiso 1 1 calc R U . . .
C84 C 0.5128(7) 0.5969(7) 0.5164(6) 0.080(3) Uani 1 1 d . U . . .
H84 H 0.4720 0.5881 0.4906 0.096 Uiso 1 1 calc R U . . .
C85 C 0.5556(6) 0.6363(6) 0.5108(5) 0.064(3) Uani 1 1 d . U . . .
H85 H 0.5449 0.6555 0.4814 0.077 Uiso 1 1 calc R U . . .
C86 C 0.6141(6) 0.6477(5) 0.5480(5) 0.052(3) Uani 1 1 d . U . . .
H86 H 0.6446 0.6727 0.5420 0.062 Uiso 1 1 calc R U . . .
C87 C 0.7460(6) 0.6510(6) 0.6111(5) 0.049(2) Uani 1 1 d . U . . .
C88 C 0.7618(5) 0.6053(6) 0.5722(4) 0.045(2) Uani 1 1 d . U . . .
H88 H 0.7424 0.5646 0.5630 0.054 Uiso 1 1 calc R U . . .
C89 C 0.8048(6) 0.6172(6) 0.5464(5) 0.059(3) Uani 1 1 d . U . . .
H89 H 0.8163 0.5844 0.5217 0.071 Uiso 1 1 calc R U . . .
C90 C 0.8313(7) 0.6770(7) 0.5566(6) 0.089(3) Uani 1 1 d . U . . .
H90 H 0.8614 0.6859 0.5397 0.107 Uiso 1 1 calc R U . . .
C91 C 0.8115(7) 0.7244(7) 0.5932(6) 0.092(3) Uani 1 1 d . U . . .

H91 H 0.8249 0.7665 0.5986 0.110 Uiso 1 1 calc R U . . .
C92 C 0.7722(7) 0.7084(7) 0.6211(6) 0.077(3) Uani 1 1 d . U . . .
H92 H 0.7635 0.7397 0.6487 0.093 Uiso 1 1 calc R U . . .
C93 C 0.7795(6) 0.6956(6) 0.8402(5) 0.058(2) Uani 1 1 d . U . . .
H93 H 0.8098 0.6653 0.8304 0.070 Uiso 1 1 calc R U . . .
C94 C 0.7395(8) 0.6639(7) 0.8634(6) 0.076(3) Uani 1 1 d . U . . .
C95 C 0.6779(8) 0.6711(7) 0.8579(6) 0.087(3) Uani 1 1 d . U . . .
H95 H 0.6565 0.6972 0.8360 0.105 Uiso 1 1 calc R U . . .
C96 C 0.6446(9) 0.6417(8) 0.8832(6) 0.101(3) Uani 1 1 d . U . . .
H96 H 0.6015 0.6493 0.8794 0.121 Uiso 1 1 calc R U . . .
C97 C 0.6703(10) 0.6057(8) 0.9107(7) 0.111(4) Uani 1 1 d . U . . .
H97 H 0.6452 0.5851 0.9258 0.133 Uiso 1 1 calc R U . . .
C98 C 0.7339(9) 0.5936(8) 0.9206(7) 0.111(4) Uani 1 1 d . U . . .
H98 H 0.7531 0.5660 0.9418 0.134 Uiso 1 1 calc R U . . .
C99 C 0.7668(9) 0.6263(7) 0.8964(6) 0.100(3) Uani 1 1 d . U . . .
H99 H 0.8109 0.6220 0.9033 0.119 Uiso 1 1 calc R U . . .
C100 C 0.8192(7) 0.7515(6) 0.8796(5) 0.065(3) Uani 1 1 d . U . . .
C101 C 0.8067(7) 0.7830(6) 0.9253(5) 0.073(3) Uani 1 1 d . U . . .
H101 H 0.7692 0.7707 0.9317 0.087 Uiso 1 1 calc R U . . .
C102 C 0.8438(8) 0.8301(7) 0.9616(6) 0.088(4) Uani 1 1 d . U . . .
H102 H 0.8325 0.8515 0.9926 0.106 Uiso 1 1 calc R U . . .
C103 C 0.9009(8) 0.8474(7) 0.9528(6) 0.094(4) Uani 1 1 d . U . . .
H103 H 0.9303 0.8786 0.9792 0.112 Uiso 1 1 calc R U . . .
C104 C 0.9123(7) 0.8189(8) 0.9065(6) 0.101(4) Uani 1 1 d . U . . .
H104 H 0.9481 0.8333 0.8989 0.121 Uiso 1 1 calc R U . . .
C105 C 0.8740(7) 0.7694(7) 0.8697(6) 0.082(3) Uani 1 1 d . U . . .
H105 H 0.8846 0.7481 0.8384 0.099 Uiso 1 1 calc R U . . .
C106 C 0.8993(5) 0.5264(5) 0.7500(4) 0.0304(19) Uani 1 1 d . U . . .
C107 C 0.9160(5) 0.5016(5) 0.7028(4) 0.042(2) Uani 1 1 d . U . . .
C108 C 0.9723(6) 0.4770(6) 0.7079(5) 0.053(3) Uani 1 1 d . U . . .
H108 H 0.9842 0.4600 0.6763 0.063 Uiso 1 1 calc R U . . .
C109 C 1.0125(6) 0.4760(7) 0.7576(5) 0.064(3) Uani 1 1 d . U . . .
C110 C 0.9965(6) 0.5019(6) 0.8032(5) 0.055(3) Uani 1 1 d . U . . .
H110 H 1.0258 0.5024 0.8375 0.066 Uiso 1 1 calc R U . . .
C111 C 0.9403(5) 0.5273(5) 0.8021(4) 0.038(2) Uani 1 1 d . U . . .
C112 C 1.0775(6) 0.4498(8) 0.7625(5) 0.100(5) Uani 1 1 d . U . . .
H11A H 1.1039 0.4618 0.8005 0.150 Uiso 1 1 calc R U . . .
H11B H 1.0980 0.4664 0.7401 0.150 Uiso 1 1 calc R U . . .
H11C H 1.0720 0.4046 0.7500 0.150 Uiso 1 1 calc R U . . .
C113 C 0.9214(5) 0.5528(5) 0.8525(4) 0.0384(19) Uani 1 1 d . U . . .
H113 H 0.8774 0.5655 0.8400 0.046 Uiso 1 1 calc R U . . .
C114 C 0.9182(6) 0.5042(5) 0.8825(4) 0.042(2) Uani 1 1 d . U . . .
C115 C 0.8596(6) 0.4786(6) 0.8793(5) 0.052(3) Uani 1 1 d . U . . .
H115 H 0.8212 0.4909 0.8586 0.062 Uiso 1 1 calc R U . . .
C116 C 0.8600(7) 0.4340(6) 0.9080(5) 0.057(3) Uani 1 1 d . U . . .
H116 H 0.8203 0.4157 0.9056 0.068 Uiso 1 1 calc R U . . .

C117 C 0.9112(7) 0.4148(6) 0.9385(5) 0.059(3) Uani 1 1 d . U . . .
H117 H 0.9082 0.3847 0.9578 0.071 Uiso 1 1 calc R U . . .
C118 C 0.9671(6) 0.4394(6) 0.9412(5) 0.053(3) Uani 1 1 d . U . . .
H118 H 1.0046 0.4252 0.9614 0.064 Uiso 1 1 calc R U . . .
C119 C 0.9719(6) 0.4866(5) 0.9142(4) 0.047(2) Uani 1 1 d . U . . .
H119 H 1.0120 0.5054 0.9184 0.056 Uiso 1 1 calc R U . . .
C120 C 0.9622(6) 0.6112(6) 0.8879(5) 0.048(2) Uani 1 1 d . U . . .
C121 C 0.9585(6) 0.6325(6) 0.9411(5) 0.056(3) Uani 1 1 d . U . . .
H121 H 0.9346 0.6089 0.9551 0.068 Uiso 1 1 calc R U . . .
C122 C 0.9910(7) 0.6897(6) 0.9734(6) 0.074(3) Uani 1 1 d . U . . .
H122 H 0.9877 0.7062 1.0088 0.088 Uiso 1 1 calc R U . . .
C123 C 1.0273(7) 0.7207(7) 0.9530(6) 0.080(3) Uani 1 1 d . U . . .
H123 H 1.0516 0.7576 0.9754 0.096 Uiso 1 1 calc R U . . .
C124 C 1.0294(6) 0.7005(6) 0.9022(6) 0.072(3) Uani 1 1 d . U . . .
H124 H 1.0543 0.7239 0.8890 0.086 Uiso 1 1 calc R U . . .
C125 C 0.9963(6) 0.6463(6) 0.8684(5) 0.056(3) Uani 1 1 d . U . . .
H125 H 0.9972 0.6335 0.8319 0.068 Uiso 1 1 calc R U . . .
C126 C 0.8686(6) 0.4981(6) 0.6464(4) 0.053(2) Uani 1 1 d . U . . .
H126 H 0.8404 0.5322 0.6526 0.063 Uiso 1 1 calc R U . . .
C127 C 0.8243(8) 0.4383(7) 0.6240(5) 0.071(3) Uani 1 1 d . U . . .
C128 C 0.8529(9) 0.3818(7) 0.6204(6) 0.092(3) Uani 1 1 d . U . . .
H128 H 0.8973 0.3790 0.6317 0.111 Uiso 1 1 calc R U . . .
C129 C 0.8027(9) 0.3227(8) 0.5953(6) 0.099(4) Uani 1 1 d . U . . .
H129 H 0.8155 0.2818 0.5873 0.119 Uiso 1 1 calc R U . . .
C130 C 0.7431(10) 0.3342(9) 0.5865(7) 0.109(4) Uani 1 1 d . U . . .
H130 H 0.7149 0.2980 0.5737 0.131 Uiso 1 1 calc R U . . .
C131 C 0.7152(9) 0.3848(8) 0.5917(6) 0.105(4) Uani 1 1 d . U . . .
H131 H 0.6707 0.3862 0.5843 0.126 Uiso 1 1 calc R U . . .
C132 C 0.7604(8) 0.4414(8) 0.6108(5) 0.086(3) Uani 1 1 d . U . . .
H132 H 0.7439 0.4808 0.6138 0.104 Uiso 1 1 calc R U . . .
C133 C 0.8992(6) 0.5131(7) 0.6081(5) 0.058(2) Uani 1 1 d . U . . .
C134 C 0.8872(6) 0.4804(7) 0.5543(5) 0.065(3) Uani 1 1 d . U . . .
H134 H 0.8598 0.4436 0.5404 0.078 Uiso 1 1 calc R U . . .
C135 C 0.9153(7) 0.5017(7) 0.5206(6) 0.075(3) Uani 1 1 d . U . . .
H135 H 0.9096 0.4783 0.4845 0.090 Uiso 1 1 calc R U . . .
C136 C 0.9519(7) 0.5575(8) 0.5406(6) 0.088(3) Uani 1 1 d . U . . .
H136 H 0.9697 0.5714 0.5166 0.106 Uiso 1 1 calc R U . . .
C137 C 0.9650(7) 0.5962(8) 0.5952(6) 0.086(3) Uani 1 1 d . U . . .
H137 H 0.9878 0.6356 0.6072 0.104 Uiso 1 1 calc R U . . .
C138 C 0.9411(7) 0.5700(7) 0.6277(6) 0.077(3) Uani 1 1 d . U . . .
H138 H 0.9524 0.5900 0.6653 0.092 Uiso 1 1 calc R U . . .
C139 C 0.6518(5) 0.1163(5) 0.7478(4) 0.0267(18) Uani 1 1 d . U . . .
C140 C 0.7406(5) 0.0695(5) 0.7519(4) 0.028(2) Uani 1 1 d . U . . .
H140 H 0.7830 0.0627 0.7527 0.033 Uiso 1 1 calc R U . . .
C141 C 0.6994(5) 0.0299(5) 0.7542(4) 0.031(2) Uani 1 1 d . U . . .
H141 H 0.7062 -0.0115 0.7565 0.037 Uiso 1 1 calc R U . . .

C142 C 0.5840(5) 0.0308(5) 0.7515(4) 0.0284(19) Uani 1 1 d . U . . .
C143 C 0.5724(5) 0.0333(5) 0.7999(4) 0.037(2) Uani 1 1 d . U . . .
C144 C 0.5172(5) 0.0058(5) 0.7992(4) 0.044(3) Uani 1 1 d . U . . .
H144 H 0.5085 0.0084 0.8326 0.053 Uiso 1 1 calc R U . . .
C145 C 0.4725(5) -0.0264(6) 0.7504(5) 0.046(3) Uani 1 1 d . U . . .
C146 C 0.4875(5) -0.0281(5) 0.7041(4) 0.047(3) Uani 1 1 d . U . . .
H146 H 0.4581 -0.0493 0.6706 0.056 Uiso 1 1 calc R U . . .
C147 C 0.5440(5) -0.0003(5) 0.7026(4) 0.039(2) Uani 1 1 d . U . . .
C148 C 0.4127(5) -0.0545(6) 0.7502(4) 0.066(4) Uani 1 1 d . U . . .
H14A H 0.3774 -0.0345 0.7304 0.099 Uiso 1 1 calc R U . . .
H14B H 0.4119 -0.0491 0.7877 0.099 Uiso 1 1 calc R U . . .
H14C H 0.4087 -0.0987 0.7324 0.099 Uiso 1 1 calc R U . . .
C149 C 0.5556(5) -0.0003(5) 0.6496(4) 0.042(2) Uani 1 1 d . U . . .
H149 H 0.5929 0.0301 0.6595 0.050 Uiso 1 1 calc R U . . .
C150 C 0.5769(7) -0.0623(6) 0.6231(5) 0.058(2) Uani 1 1 d . U . . .
C151 C 0.5485(7) -0.1186(7) 0.6158(6) 0.079(3) Uani 1 1 d . U . . .
H151 H 0.5139 -0.1227 0.6292 0.094 Uiso 1 1 calc R U . . .
C152 C 0.5720(8) -0.1733(7) 0.5868(6) 0.086(4) Uani 1 1 d . U . . .
H152 H 0.5487 -0.2124 0.5746 0.103 Uiso 1 1 calc R U . . .
C153 C 0.6255(8) -0.1657(8) 0.5786(6) 0.089(4) Uani 1 1 d . U . . .
H153 H 0.6430 -0.2019 0.5637 0.107 Uiso 1 1 calc R U . . .
C154 C 0.6576(8) -0.1139(8) 0.5886(6) 0.092(4) Uani 1 1 d . U . . .
H154 H 0.6953 -0.1114 0.5789 0.110 Uiso 1 1 calc R U . . .
C155 C 0.6346(7) -0.0632(7) 0.6139(6) 0.080(3) Uani 1 1 d . U . . .
H155 H 0.6604 -0.0255 0.6260 0.096 Uiso 1 1 calc R U . . .
C156 C 0.5041(7) 0.0234(7) 0.6110(6) 0.073(3) Uani 1 1 d . U . . .
C157 C 0.4083(8) 0.0052(9) 0.5278(7) 0.137(5) Uani 1 1 d D U . . .
H157 H 0.3775 -0.0257 0.5027 0.164 Uiso 1 1 calc R U . . .
C158 C 0.4018(9) 0.0710(9) 0.5387(7) 0.130(5) Uani 1 1 d . U . . .
H158 H 0.3735 0.0897 0.5136 0.155 Uiso 1 1 calc R U . . .
C159 C 0.4390(8) 0.1037(9) 0.5875(8) 0.130(5) Uani 1 1 d . U . . .
H159 H 0.4373 0.1473 0.5956 0.155 Uiso 1 1 calc R U . . .
C160 C 0.4803(7) 0.0787(7) 0.6276(7) 0.102(4) Uani 1 1 d . U . . .
H160 H 0.4912 0.0996 0.6650 0.122 Uiso 1 1 calc R U . . .
C161 C 0.6194(5) 0.0726(5) 0.8547(4) 0.042(2) Uani 1 1 d . U . . .
H161 H 0.6434 0.1039 0.8452 0.050 Uiso 1 1 calc R U . . .
C162 C 0.6674(6) 0.0334(6) 0.8822(5) 0.053(3) Uani 1 1 d . U . . .
C163 C 0.6621(7) -0.0300(6) 0.8714(5) 0.068(3) Uani 1 1 d . U . . .
H163 H 0.6262 -0.0522 0.8439 0.081 Uiso 1 1 calc R U . . .
C164 C 0.7080(7) -0.0629(7) 0.8997(6) 0.083(4) Uani 1 1 d . U . . .
H164 H 0.7059 -0.1067 0.8902 0.099 Uiso 1 1 calc R U . . .
C165 C 0.7574(7) -0.0274(7) 0.9430(6) 0.084(4) Uani 1 1 d . U . . .
H165 H 0.7882 -0.0487 0.9638 0.100 Uiso 1 1 calc R U . . .
C166 C 0.7636(7) 0.0340(7) 0.9566(6) 0.071(3) Uani 1 1 d . U . . .
H166 H 0.7977 0.0567 0.9859 0.085 Uiso 1 1 calc R U . . .
C167 C 0.7175(6) 0.0626(6) 0.9255(5) 0.058(3) Uani 1 1 d . U . . .

H167 H 0.7207 0.1065 0.9350 0.070 Uiso 1 1 calc R U . . .
C168 C 0.5839(6) 0.1085(6) 0.8927(5) 0.046(2) Uani 1 1 d . U . . .
C169 C 0.5780(6) 0.0882(6) 0.9367(5) 0.052(3) Uani 1 1 d . U . . .
H169 H 0.5962 0.0516 0.9441 0.063 Uiso 1 1 calc R U . . .
C170 C 0.5449(6) 0.1222(6) 0.9701(5) 0.062(3) Uani 1 1 d . U . . .
H170 H 0.5411 0.1096 1.0008 0.074 Uiso 1 1 calc R U . . .
C171 C 0.5179(6) 0.1748(7) 0.9573(5) 0.070(3) Uani 1 1 d . U . . .
H171 H 0.4937 0.1977 0.9783 0.084 Uiso 1 1 calc R U . . .
C172 C 0.5264(6) 0.1938(7) 0.9140(5) 0.070(3) Uani 1 1 d . U . . .
H172 H 0.5097 0.2310 0.9067 0.084 Uiso 1 1 calc R U . . .
C173 C 0.5584(6) 0.1603(6) 0.8814(5) 0.056(3) Uani 1 1 d . U . . .
H173 H 0.5626 0.1735 0.8510 0.067 Uiso 1 1 calc R U . . .
C174 C 0.7406(5) 0.1801(5) 0.7450(5) 0.034(2) Uani 1 1 d . U . . .
C175 C 0.7348(6) 0.1919(5) 0.6969(5) 0.052(2) Uani 1 1 d . U . . .
C176 C 0.7638(6) 0.2469(5) 0.6951(5) 0.050(3) Uani 1 1 d . U . . .
H176 H 0.7626 0.2552 0.6613 0.060 Uiso 1 1 calc R U . . .
C177 C 0.7950(6) 0.2894(5) 0.7447(5) 0.047(3) Uani 1 1 d . U . . .
C178 C 0.8011(5) 0.2766(5) 0.7922(4) 0.034(2) Uani 1 1 d . U . . .
H178 H 0.8237 0.3058 0.8247 0.041 Uiso 1 1 calc R U . . .
C179 C 0.7746(5) 0.2207(5) 0.7951(4) 0.033(2) Uani 1 1 d . U . . .
C180 C 0.8269(7) 0.3505(6) 0.7415(5) 0.072(4) Uani 1 1 d . U . . .
H18A H 0.8448 0.3772 0.7782 0.108 Uiso 1 1 calc R U . . .
H18B H 0.7952 0.3721 0.7196 0.108 Uiso 1 1 calc R U . . .
H18C H 0.8607 0.3404 0.7247 0.108 Uiso 1 1 calc R U . . .
C181 C 0.7837(5) 0.2055(5) 0.8501(4) 0.0409(19) Uani 1 1 d . U . . .
H181 H 0.7523 0.1700 0.8427 0.049 Uiso 1 1 calc R U . . .
C182 C 0.8467(6) 0.1817(6) 0.8689(5) 0.044(2) Uani 1 1 d . U . . .
C183 C 0.9035(6) 0.2109(6) 0.8709(4) 0.047(2) Uani 1 1 d . U . . .
H183 H 0.9018 0.2459 0.8562 0.056 Uiso 1 1 calc R U . . .
C184 C 0.9631(6) 0.1906(6) 0.8939(5) 0.065(3) Uani 1 1 d . U . . .
H184 H 1.0012 0.2122 0.8964 0.078 Uiso 1 1 calc R U . . .
C185 C 0.9636(7) 0.1372(7) 0.9128(6) 0.078(3) Uani 1 1 d . U . . .
H185 H 1.0029 0.1206 0.9258 0.094 Uiso 1 1 calc R U . . .
C186 C 0.9105(7) 0.1083(7) 0.9134(5) 0.075(3) Uani 1 1 d . U . . .
H186 H 0.9128 0.0739 0.9289 0.090 Uiso 1 1 calc R U . . .
C187 C 0.8505(7) 0.1301(6) 0.8902(5) 0.061(3) Uani 1 1 d . U . . .
H187 H 0.8129 0.1090 0.8894 0.074 Uiso 1 1 calc R U . . .
C188 C 0.7669(6) 0.2565(6) 0.8902(5) 0.050(2) Uani 1 1 d . U . . .
C189 C 0.8093(7) 0.2905(6) 0.9383(5) 0.062(3) Uani 1 1 d . U . . .
H189 H 0.8527 0.2826 0.9453 0.074 Uiso 1 1 calc R U . . .
C190 C 0.7922(7) 0.3362(7) 0.9777(6) 0.074(3) Uani 1 1 d . U . . .
H190 H 0.8221 0.3614 1.0091 0.089 Uiso 1 1 calc R U . . .
C191 C 0.7267(8) 0.3404(7) 0.9658(6) 0.089(4) Uani 1 1 d . U . . .
H191 H 0.7121 0.3686 0.9917 0.107 Uiso 1 1 calc R U . . .
C192 C 0.6790(7) 0.3055(7) 0.9171(6) 0.086(3) Uani 1 1 d . U . . .
H192 H 0.6355 0.3127 0.9104 0.103 Uiso 1 1 calc R U . . .

C193 C 0.6995(7) 0.2608(7) 0.8804(6) 0.075(3) Uani 1 1 d . U . . .
H193 H 0.6701 0.2339 0.8499 0.090 Uiso 1 1 calc R U . . .
C194 C 0.7019(8) 0.1449(7) 0.6440(6) 0.082(3) Uani 1 1 d . U . . .
H194 H 0.6810 0.1121 0.6545 0.099 Uiso 1 1 calc R U . . .
C195 C 0.7455(9) 0.1144(8) 0.6188(6) 0.114(3) Uani 1 1 d D U . . .
C196 C 0.7768(8) 0.0641(8) 0.6121(7) 0.144(4) Uani 1 1 d D U . . .
H196 H 0.7705 0.0438 0.6379 0.173 Uiso 1 1 calc R U . . .
C197 C 0.8138(9) 0.0262(10) 0.5868(7) 0.155(5) Uani 1 1 d D U . . .
H197 H 0.8279 -0.0125 0.5924 0.186 Uiso 1 1 calc R U . . .
C198 C 0.8251(11) 0.0569(9) 0.5525(8) 0.163(5) Uani 1 1 d D U . . .
H198 H 0.8547 0.0408 0.5342 0.196 Uiso 1 1 calc R U . . .
C199 C 0.7966(10) 0.1122(9) 0.5405(8) 0.152(4) Uani 1 1 d D U . . .
H199 H 0.7987 0.1300 0.5119 0.182 Uiso 1 1 calc R U . . .
C200 C 0.7643(9) 0.1355(9) 0.5809(7) 0.137(4) Uani 1 1 d D U . . .
H200 H 0.7531 0.1765 0.5809 0.165 Uiso 1 1 calc R U . . .
C201 C 0.6527(9) 0.1710(8) 0.6118(7) 0.124(4) Uani 1 1 d D U . . .
C202 C 0.6244(8) 0.1405(9) 0.5592(7) 0.178(5) Uani 1 1 d D U . . .
H202 H 0.6414 0.1040 0.5440 0.214 Uiso 1 1 calc R U . . .
C203 C 0.5695(9) 0.1618(9) 0.5256(8) 0.200(6) Uani 1 1 d D U . . .
H203 H 0.5495 0.1393 0.4892 0.240 Uiso 1 1 calc R U . . .
C204 C 0.5462(10) 0.2169(10) 0.5482(8) 0.191(6) Uani 1 1 d D U . . .
H204 H 0.5108 0.2319 0.5259 0.230 Uiso 1 1 calc R U . . .
C205 C 0.5710(10) 0.2486(9) 0.5988(8) 0.165(5) Uani 1 1 d D U . . .
H205 H 0.5575 0.2869 0.6145 0.198 Uiso 1 1 calc R U . . .
C206 C 0.6188(9) 0.2188(8) 0.6258(8) 0.141(5) Uani 1 1 d D U . . .
H206 H 0.6314 0.2361 0.6639 0.170 Uiso 1 1 calc R U . . .
C207 C 0.3292(5) 0.3955(5) 0.7476(4) 0.0256(18) Uani 1 1 d . U . . .
C208 C 0.2811(5) 0.4831(5) 0.7513(4) 0.035(2) Uani 1 1 d . U . . .
H208 H 0.2737 0.5249 0.7513 0.042 Uiso 1 1 calc R U . . .
C209 C 0.2400(5) 0.4408(5) 0.7544(4) 0.031(2) Uani 1 1 d . U . . .
H209 H 0.1992 0.4473 0.7583 0.038 Uiso 1 1 calc R U . . .
C210 C 0.2428(4) 0.3301(5) 0.7541(4) 0.0221(18) Uani 1 1 d . U . . .
C211 C 0.2165(5) 0.2851(5) 0.7062(4) 0.0271(19) Uani 1 1 d . U . . .
C212 C 0.1900(5) 0.2294(5) 0.7129(5) 0.040(2) Uani 1 1 d . U . . .
H212 H 0.1706 0.1975 0.6813 0.048 Uiso 1 1 calc R U . . .
C213 C 0.1913(6) 0.2200(5) 0.7626(5) 0.045(2) Uani 1 1 d . U . . .
C214 C 0.2193(5) 0.2679(5) 0.8081(4) 0.037(2) Uani 1 1 d . U . . .
H214 H 0.2213 0.2620 0.8428 0.044 Uiso 1 1 calc R U . . .
C215 C 0.2441(5) 0.3227(5) 0.8060(4) 0.0301(19) Uani 1 1 d . U . . .
C216 C 0.1648(7) 0.1617(6) 0.7669(5) 0.078(4) Uani 1 1 d . U . . .
H21A H 0.1227 0.1509 0.7403 0.117 Uiso 1 1 calc R U . . .
H21B H 0.1614 0.1666 0.8036 0.117 Uiso 1 1 calc R U . . .
H21C H 0.1925 0.1288 0.7596 0.117 Uiso 1 1 calc R U . . .
C217 C 0.2738(5) 0.3735(5) 0.8578(4) 0.039(2) Uani 1 1 d . U . . .
H217 H 0.2904 0.4076 0.8458 0.047 Uiso 1 1 calc R U . . .
C218 C 0.2271(6) 0.4009(5) 0.8851(4) 0.049(2) Uani 1 1 d D U . . .

C219 C 0.1673(6) 0.3805(6) 0.8767(5) 0.071(3) Uani 1 1 d D U . . .
H219 H 0.1506 0.3444 0.8484 0.085 Uiso 1 1 calc R U . . .
C220 C 0.1286(7) 0.4069(6) 0.9052(5) 0.089(4) Uani 1 1 d D U . . .
H220 H 0.0873 0.3880 0.8968 0.107 Uiso 1 1 calc R U . . .
C221 C 0.1466(6) 0.4586(7) 0.9447(6) 0.090(4) Uani 1 1 d D U . . .
H221 H 0.1187 0.4771 0.9639 0.108 Uiso 1 1 calc R U . . .
C222 C 0.2047(6) 0.4833(7) 0.9562(6) 0.090(4) Uani 1 1 d D U . . .
H222 H 0.2194 0.5208 0.9833 0.109 Uiso 1 1 calc R U . . .
C223 C 0.2436(6) 0.4534(6) 0.9279(5) 0.075(3) Uani 1 1 d D U . . .
H223 H 0.2861 0.4704 0.9389 0.090 Uiso 1 1 calc R U . . .
C224 C 0.3315(6) 0.3524(5) 0.8957(5) 0.046(2) Uani 1 1 d . U . . .
C225 C 0.3253(6) 0.3339(5) 0.9398(5) 0.052(3) Uani 1 1 d . U . . .
H225 H 0.2854 0.3321 0.9461 0.062 Uiso 1 1 calc R U . . .
C226 C 0.3825(6) 0.3167(6) 0.9771(5) 0.066(3) Uani 1 1 d . U . . .
H226 H 0.3809 0.3043 1.0085 0.079 Uiso 1 1 calc R U . . .
C227 C 0.4369(7) 0.3194(6) 0.9646(6) 0.068(3) Uani 1 1 d . U . . .
H227 H 0.4739 0.3074 0.9875 0.081 Uiso 1 1 calc R U . . .
C228 C 0.4414(6) 0.3385(6) 0.9206(6) 0.065(3) Uani 1 1 d . U . . .
H228 H 0.4805 0.3405 0.9131 0.079 Uiso 1 1 calc R U . . .
C229 C 0.3871(6) 0.3546(6) 0.8878(5) 0.058(3) Uani 1 1 d . U . . .
H229 H 0.3899 0.3683 0.8573 0.069 Uiso 1 1 calc R U . . .
C230 C 0.2104(5) 0.2962(5) 0.6520(4) 0.0398(19) Uani 1 1 d . U . . .
H230 H 0.2484 0.3238 0.6572 0.048 Uiso 1 1 calc R U . . .
C231 C 0.1541(6) 0.3305(6) 0.6310(5) 0.052(2) Uani 1 1 d . U . . .
C232 C 0.0941(6) 0.3135(6) 0.6305(5) 0.061(3) Uani 1 1 d . U . . .
H232 H 0.0883 0.2781 0.6431 0.073 Uiso 1 1 calc R U . . .
C233 C 0.0427(7) 0.3452(7) 0.6127(6) 0.073(3) Uani 1 1 d . U . . .
H233 H 0.0019 0.3314 0.6122 0.088 Uiso 1 1 calc R U . . .
C234 C 0.0506(7) 0.3962(7) 0.5957(5) 0.076(3) Uani 1 1 d . U . . .
H234 H 0.0150 0.4183 0.5832 0.091 Uiso 1 1 calc R U . . .
C235 C 0.1112(7) 0.4175(7) 0.5962(6) 0.082(3) Uani 1 1 d . U . . .
H235 H 0.1167 0.4532 0.5840 0.098 Uiso 1 1 calc R U . . .
C236 C 0.1614(6) 0.3848(7) 0.6150(5) 0.068(3) Uani 1 1 d . U . . .
H236 H 0.2026 0.3994 0.6172 0.081 Uiso 1 1 calc R U . . .
C237 C 0.2144(6) 0.2362(6) 0.6102(5) 0.055(3) Uani 1 1 d . U . . .
C238 C 0.2662(7) 0.2000(6) 0.6215(6) 0.066(3) Uani 1 1 d . U . . .
H238 H 0.2975 0.2124 0.6559 0.079 Uiso 1 1 calc R U . . .
C239 C 0.2737(7) 0.1473(7) 0.5847(6) 0.082(3) Uani 1 1 d . U . . .
H239 H 0.3081 0.1227 0.5943 0.098 Uiso 1 1 calc R U . . .
C240 C 0.2312(8) 0.1324(8) 0.5356(6) 0.092(4) Uani 1 1 d . U . . .
H240 H 0.2354 0.0960 0.5102 0.110 Uiso 1 1 calc R U . . .
C241 C 0.1793(7) 0.1691(7) 0.5196(6) 0.089(4) Uani 1 1 d . U . . .
H241 H 0.1511 0.1582 0.4836 0.107 Uiso 1 1 calc R U . . .
C242 C 0.1707(7) 0.2215(7) 0.5577(5) 0.074(3) Uani 1 1 d . U . . .
H242 H 0.1364 0.2462 0.5482 0.089 Uiso 1 1 calc R U . . .
C243 C 0.3896(5) 0.4876(5) 0.7459(4) 0.0290(19) Uani 1 1 d . U . . .

C244 C 0.4387(5) 0.5130(5) 0.7935(4) 0.037(2) Uani 1 1 d . U . . .
C245 C 0.4897(5) 0.5449(5) 0.7886(4) 0.042(2) Uani 1 1 d . U . . .
H245 H 0.5227 0.5642 0.8204 0.050 Uiso 1 1 calc R U . . .
C246 C 0.4937(5) 0.5491(6) 0.7394(5) 0.045(2) Uani 1 1 d . U . . .
C247 C 0.4461(5) 0.5214(5) 0.6923(4) 0.039(2) Uani 1 1 d . U . . .
H247 H 0.4499 0.5232 0.6580 0.046 Uiso 1 1 calc R U . . .
C248 C 0.3928(5) 0.4909(5) 0.6949(4) 0.033(2) Uani 1 1 d . U . . .
C249 C 0.5484(6) 0.5882(6) 0.7342(5) 0.073(4) Uani 1 1 d . U . . .
H24A H 0.5637 0.6224 0.7667 0.109 Uiso 1 1 calc R U . . .
H24B H 0.5331 0.6048 0.7021 0.109 Uiso 1 1 calc R U . . .
H24C H 0.5831 0.5620 0.7304 0.109 Uiso 1 1 calc R U . . .
C250 C 0.3393(5) 0.4580(5) 0.6435(4) 0.039(2) Uani 1 1 d . U . . .
H250 H 0.3018 0.4518 0.6558 0.047 Uiso 1 1 calc R U . . .
C251 C 0.3198(6) 0.4974(6) 0.6039(5) 0.048(2) Uani 1 1 d . U . . .
C252 C 0.2758(6) 0.5398(6) 0.6098(5) 0.067(3) Uani 1 1 d . U . . .
H252 H 0.2579 0.5416 0.6384 0.080 Uiso 1 1 calc R U . . .
C253 C 0.2567(7) 0.5784(7) 0.5782(5) 0.077(3) Uani 1 1 d . U . . .
H253 H 0.2256 0.6062 0.5836 0.092 Uiso 1 1 calc R U . . .
C254 C 0.2833(7) 0.5767(7) 0.5373(6) 0.077(3) Uani 1 1 d . U . . .
H254 H 0.2696 0.6040 0.5144 0.093 Uiso 1 1 calc R U . . .
C255 C 0.3289(6) 0.5375(6) 0.5279(5) 0.063(3) Uani 1 1 d . U . . .
H255 H 0.3472 0.5374 0.4998 0.076 Uiso 1 1 calc R U . . .
C256 C 0.3466(6) 0.4975(6) 0.5627(4) 0.053(3) Uani 1 1 d . U . . .
H256 H 0.3779 0.4696 0.5578 0.064 Uiso 1 1 calc R U . . .
C257 C 0.3571(5) 0.3920(6) 0.6190(4) 0.039(2) Uani 1 1 d . U . . .
C258 C 0.3123(5) 0.3572(5) 0.5713(4) 0.040(2) Uani 1 1 d . U . . .
H258 H 0.2746 0.3748 0.5556 0.048 Uiso 1 1 calc R U . . .
C259 C 0.3226(6) 0.2982(6) 0.5474(5) 0.046(3) Uani 1 1 d . U . . .
H259 H 0.2934 0.2762 0.5141 0.056 Uiso 1 1 calc R U . . .
C260 C 0.3742(6) 0.2711(6) 0.5713(5) 0.053(3) Uani 1 1 d . U . . .
H260 H 0.3801 0.2295 0.5555 0.063 Uiso 1 1 calc R U . . .
C261 C 0.4183(6) 0.3038(6) 0.6187(5) 0.050(3) Uani 1 1 d . U . . .
H261 H 0.4545 0.2851 0.6357 0.060 Uiso 1 1 calc R U . . .
C262 C 0.4085(5) 0.3653(6) 0.6412(4) 0.039(2) Uani 1 1 d . U . . .
H262 H 0.4393 0.3885 0.6731 0.047 Uiso 1 1 calc R U . . .
C263 C 0.4344(6) 0.5085(6) 0.8478(4) 0.049(2) Uani 1 1 d . U . . .
H263 H 0.4025 0.4736 0.8412 0.058 Uiso 1 1 calc R U . . .
C264 C 0.4101(8) 0.5685(8) 0.8763(6) 0.079(3) Uani 1 1 d . U . . .
C265 C 0.4272(8) 0.6242(8) 0.8809(6) 0.092(3) Uani 1 1 d . U . . .
H265 H 0.4581 0.6306 0.8641 0.110 Uiso 1 1 calc R U . . .
C266 C 0.4062(9) 0.6760(9) 0.9073(7) 0.111(4) Uani 1 1 d . U . . .
H266 H 0.4256 0.7162 0.9135 0.133 Uiso 1 1 calc R U . . .
C267 C 0.3593(10) 0.6668(10) 0.9228(8) 0.132(4) Uani 1 1 d . U . . .
H267 H 0.3492 0.7011 0.9471 0.159 Uiso 1 1 calc R U . . .
C268 C 0.3223(10) 0.6155(10) 0.9097(8) 0.137(4) Uani 1 1 d . U . . .
H268 H 0.2805 0.6135 0.9120 0.164 Uiso 1 1 calc R U . . .

C269 C 0.3557(8) 0.5620(9) 0.8910(7) 0.121(4) Uani 1 1 d . U . . .
H269 H 0.3396 0.5218 0.8888 0.145 Uiso 1 1 calc R U . . .
C270 C 0.4955(6) 0.4951(6) 0.8850(5) 0.053(2) Uani 1 1 d . U . . .
C271 C 0.5226(7) 0.5256(7) 0.9367(5) 0.077(3) Uani 1 1 d . U . . .
H271 H 0.5022 0.5600 0.9510 0.092 Uiso 1 1 calc R U . . .
C272 C 0.5753(8) 0.5124(7) 0.9696(6) 0.101(4) Uani 1 1 d . U . . .
H272 H 0.5926 0.5367 1.0058 0.121 Uiso 1 1 calc R U . . .
C273 C 0.6049(8) 0.4607(7) 0.9486(6) 0.103(4) Uani 1 1 d . U . . .
H273 H 0.6404 0.4472 0.9721 0.123 Uiso 1 1 calc R U . . .
C274 C 0.5832(7) 0.4298(7) 0.8953(6) 0.083(3) Uani 1 1 d . U . . .
H274 H 0.6066 0.3986 0.8804 0.099 Uiso 1 1 calc R U . . .
C275 C 0.5283(7) 0.4439(6) 0.8640(5) 0.064(3) Uani 1 1 d . U . . .
H275 H 0.5109 0.4200 0.8277 0.076 Uiso 1 1 calc R U . . .
N1 N 1.1406(4) 0.9622(4) 0.7518(3) 0.0314(17) Uani 1 1 d . U . . .
N2 N 1.2108(4) 0.8941(4) 0.7525(3) 0.0297(17) Uani 1 1 d . U . . .
N3 N 0.7678(4) 0.6135(4) 0.7372(3) 0.0205(15) Uani 1 1 d . U . . .
N4 N 0.8400(4) 0.5516(4) 0.7450(3) 0.0224(16) Uani 1 1 d . U . . .
N5 N 0.6435(4) 0.0588(4) 0.7528(3) 0.0255(16) Uani 1 1 d . U . . .
N6 N 0.7121(4) 0.1226(4) 0.7481(3) 0.0244(16) Uani 1 1 d . U . . .
N7 N 0.2684(4) 0.3874(4) 0.7509(3) 0.0234(16) Uani 1 1 d . U . . .
N8 N 0.3358(4) 0.4555(4) 0.7482(3) 0.0267(16) Uani 1 1 d . U . . .

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Cu1 0.0464(10) 0.0400(10) 0.0561(11) 0.0144(8) 0.0206(8) -0.0148(8)
Cu2 0.0395(10) 0.0443(10) 0.0520(11) 0.0109(8) 0.0242(8) -0.0119(8)
Cu3 0.0335(9) 0.0308(9) 0.0697(12) 0.0161(8) 0.0252(8) 0.0115(7)
Cu4 0.0299(9) 0.0354(9) 0.0444(10) 0.0159(8) 0.0201(7) 0.0191(7)
O1 0.097(5) 0.117(5) 0.118(5) -0.009(5) 0.038(4) -0.075(4)
O2 0.110(5) 0.120(6) 0.116(5) 0.026(5) 0.021(4) -0.089(4)
O3 0.171(9) 0.153(6) 0.246(13) 0.046(7) 0.047(10) -0.051(7)
O4 0.255(13) 0.183(9) 0.068(4) 0.029(7) -0.007(6) -0.050(10)
O5 0.050(4) 0.065(4) 0.100(5) 0.010(4) 0.026(4) 0.035(3)
O6 0.057(3) 0.049(4) 0.093(5) 0.014(4) 0.031(4) 0.035(3)
O7 0.115(7) 0.102(8) 0.085(4) 0.032(5) -0.002(5) 0.030(7)
O8 0.113(7) 0.053(4) 0.131(8) 0.021(5) 0.027(7) 0.005(5)
S1 0.128(4) 0.140(4) 0.079(3) 0.021(3) 0.017(3) -0.106(3)
S2 0.055(2) 0.059(2) 0.084(3) 0.015(2) 0.015(2) 0.0347(19)
C1 0.037(4) 0.031(4) 0.034(4) 0.016(4) 0.018(4) -0.002(3)
C2 0.034(4) 0.034(4) 0.041(5) 0.014(5) 0.014(5) -0.006(3)

C3 0.042(4) 0.032(4) 0.047(5) 0.010(5) 0.027(5) -0.004(3)
C4 0.039(4) 0.038(5) 0.035(3) 0.014(4) 0.024(3) 0.005(4)
C5 0.051(5) 0.050(5) 0.035(3) 0.010(4) 0.019(3) 0.009(4)
C6 0.051(5) 0.065(6) 0.037(5) 0.003(5) 0.009(4) 0.015(5)
C7 0.050(5) 0.075(7) 0.047(5) 0.003(5) 0.017(4) 0.020(5)
C8 0.055(5) 0.064(6) 0.035(5) 0.003(5) 0.025(4) 0.021(5)
C9 0.047(4) 0.044(5) 0.037(3) 0.005(4) 0.025(3) 0.015(4)
C10 0.048(7) 0.124(12) 0.059(9) 0.007(8) 0.016(6) 0.028(7)
C11 0.054(5) 0.049(4) 0.035(4) 0.002(4) 0.024(3) 0.007(4)
C12 0.060(5) 0.058(5) 0.063(5) 0.008(5) 0.021(5) -0.011(4)
C13 0.079(6) 0.051(5) 0.068(7) 0.013(6) 0.022(6) -0.013(5)
C14 0.096(7) 0.057(5) 0.093(8) 0.018(6) 0.022(7) -0.021(6)
C15 0.093(7) 0.070(6) 0.108(8) 0.018(7) 0.020(7) -0.035(6)
C16 0.078(7) 0.084(7) 0.123(8) -0.001(7) 0.013(7) -0.027(5)
C17 0.070(6) 0.078(6) 0.114(8) -0.001(7) 0.011(6) -0.015(5)
C18 0.088(6) 0.053(5) 0.038(4) -0.002(4) 0.035(5) -0.010(5)
C19 0.081(7) 0.049(6) 0.035(5) 0.001(4) 0.025(5) -0.006(5)
C20 0.099(7) 0.057(6) 0.031(5) 0.008(5) 0.021(5) -0.013(6)
C21 0.155(8) 0.066(6) 0.050(6) 0.009(6) 0.028(7) -0.035(7)
C22 0.184(9) 0.066(7) 0.066(7) -0.008(5) 0.045(7) -0.051(7)
C23 0.163(8) 0.064(6) 0.059(6) -0.012(5) 0.051(6) -0.038(6)
C24 0.063(5) 0.064(5) 0.034(4) 0.004(3) 0.021(4) 0.005(4)
C25 0.100(6) 0.086(6) 0.034(5) 0.015(4) 0.022(5) 0.000(5)
C26 0.115(7) 0.087(7) 0.045(6) 0.021(5) 0.019(6) -0.013(6)
C27 0.126(8) 0.086(8) 0.057(7) 0.026(6) 0.012(6) -0.011(7)
C28 0.124(9) 0.092(8) 0.061(7) 0.028(6) 0.018(6) 0.002(7)
C29 0.120(8) 0.101(8) 0.059(7) 0.032(5) 0.024(6) 0.009(7)
C30 0.102(7) 0.096(7) 0.048(7) 0.027(5) 0.032(5) 0.021(6)
C31 0.068(6) 0.072(5) 0.037(5) 0.000(4) 0.018(5) 0.000(5)
C32 0.075(7) 0.081(7) 0.055(6) -0.001(5) 0.018(5) -0.017(5)
C33 0.089(7) 0.089(7) 0.076(7) -0.004(6) 0.008(6) -0.027(6)
C34 0.094(8) 0.084(7) 0.073(7) -0.016(6) -0.001(6) -0.025(6)
C35 0.093(8) 0.070(7) 0.050(6) -0.007(5) -0.003(6) 0.001(6)
C36 0.082(7) 0.067(6) 0.036(6) -0.003(4) 0.011(5) 0.001(6)
C37 0.043(5) 0.037(4) 0.049(3) 0.017(4) 0.018(4) 0.009(4)
C38 0.053(5) 0.042(5) 0.055(4) 0.030(3) 0.017(4) -0.002(4)
C39 0.066(6) 0.053(6) 0.055(5) 0.031(4) 0.001(5) 0.007(5)
C40 0.078(7) 0.062(6) 0.066(6) 0.015(5) 0.001(6) 0.022(5)
C41 0.075(7) 0.063(6) 0.054(5) 0.001(5) 0.007(6) 0.030(5)
C42 0.055(5) 0.060(5) 0.051(4) 0.011(4) 0.020(4) 0.024(4)
C43 0.119(12) 0.064(9) 0.099(11) 0.005(7) -0.026(9) 0.035(8)
C44 0.075(6) 0.079(6) 0.046(4) 0.013(4) 0.021(4) 0.035(4)
C45 0.103(7) 0.114(7) 0.061(6) 0.030(5) 0.031(5) 0.023(5)
C46 0.093(7) 0.127(8) 0.084(7) 0.022(7) 0.030(6) 0.006(6)
C47 0.102(8) 0.137(10) 0.108(8) 0.033(8) 0.035(7) 0.000(7)
C48 0.117(9) 0.148(10) 0.118(8) 0.049(8) 0.034(7) 0.006(8)

C49 0.126(9) 0.142(9) 0.112(8) 0.064(7) 0.036(8) 0.016(7)
C50 0.123(8) 0.128(8) 0.089(7) 0.058(6) 0.033(7) 0.022(6)
C51 0.085(7) 0.090(7) 0.060(5) -0.002(5) 0.014(5) 0.035(5)
C52 0.105(8) 0.118(8) 0.064(6) -0.020(6) 0.015(6) 0.019(6)
C276 0.118(8) 0.125(8) 0.077(7) 0.003(6) -0.023(6) 0.061(7)
C53 0.119(9) 0.130(10) 0.078(7) -0.029(7) 0.016(7) 0.011(7)
C54 0.125(9) 0.115(9) 0.086(7) -0.015(7) -0.002(8) 0.008(7)
C55 0.125(9) 0.116(9) 0.092(8) -0.006(7) 0.006(8) -0.001(6)
C56 0.108(8) 0.104(8) 0.081(7) -0.006(6) 0.013(6) 0.005(6)
C57 0.101(6) 0.062(6) 0.052(4) 0.022(4) 0.016(5) -0.005(4)
C58 0.129(7) 0.069(6) 0.070(6) 0.025(4) 0.013(6) -0.027(5)
C59 0.134(7) 0.089(8) 0.082(7) 0.032(6) 0.021(6) -0.044(7)
C60 0.153(8) 0.098(9) 0.096(9) 0.034(6) 0.023(7) -0.059(7)
C61 0.160(9) 0.083(8) 0.119(9) 0.028(6) 0.016(7) -0.051(8)
C62 0.161(9) 0.072(8) 0.103(8) 0.014(6) 0.010(7) -0.029(7)
C63 0.147(8) 0.068(7) 0.087(7) 0.015(5) 0.016(6) -0.026(6)
C64 0.138(7) 0.093(7) 0.057(5) 0.022(5) 0.031(5) -0.026(6)
C65 0.177(8) 0.083(8) 0.056(7) 0.026(6) 0.031(6) -0.012(7)
C66 0.204(10) 0.109(8) 0.071(7) 0.036(6) 0.039(8) -0.020(9)
C67 0.208(10) 0.139(9) 0.103(8) 0.046(7) 0.046(8) -0.042(9)
C68 0.180(9) 0.164(9) 0.107(9) 0.052(8) 0.047(7) -0.060(8)
C69 0.158(8) 0.151(9) 0.091(7) 0.039(7) 0.042(6) -0.049(8)
C70 0.027(4) 0.026(4) 0.027(4) 0.011(4) 0.016(4) 0.003(3)
C71 0.034(4) 0.025(4) 0.020(5) 0.016(4) 0.013(4) 0.009(3)
C72 0.025(4) 0.031(4) 0.019(5) 0.017(4) 0.016(4) 0.004(3)
C73 0.037(4) 0.029(4) 0.022(3) 0.013(3) 0.022(4) 0.012(3)
C74 0.059(5) 0.051(5) 0.024(3) 0.006(3) 0.027(4) 0.024(4)
C75 0.069(6) 0.051(5) 0.019(4) -0.001(4) 0.029(4) 0.025(4)
C76 0.068(6) 0.048(5) 0.027(4) -0.003(4) 0.011(5) 0.026(5)
C77 0.053(6) 0.045(5) 0.019(4) 0.007(4) 0.008(5) 0.025(4)
C78 0.046(5) 0.036(4) 0.023(3) 0.009(3) 0.015(3) 0.018(4)
C79 0.085(10) 0.061(8) 0.053(8) -0.004(6) 0.012(7) 0.043(7)
C80 0.058(4) 0.038(5) 0.021(4) 0.006(4) 0.020(3) 0.013(4)
C81 0.062(4) 0.044(5) 0.027(4) 0.007(4) 0.016(4) 0.007(4)
C82 0.074(6) 0.069(7) 0.037(6) 0.014(5) 0.012(5) -0.013(5)
C83 0.088(6) 0.082(7) 0.058(7) 0.022(5) -0.003(5) -0.029(6)
C84 0.084(7) 0.081(8) 0.057(7) 0.020(6) -0.007(6) -0.015(6)
C85 0.077(7) 0.061(7) 0.045(6) 0.019(5) -0.001(5) 0.001(6)
C86 0.070(6) 0.045(6) 0.039(5) 0.017(5) 0.008(4) 0.008(5)
C87 0.066(5) 0.056(5) 0.028(5) 0.000(4) 0.025(4) 0.002(5)
C88 0.059(6) 0.056(5) 0.028(6) 0.011(4) 0.024(4) 0.017(5)
C89 0.077(7) 0.071(6) 0.040(6) 0.010(5) 0.036(5) 0.003(6)
C90 0.103(7) 0.088(7) 0.080(7) -0.009(6) 0.057(6) -0.025(6)
C91 0.109(8) 0.080(6) 0.086(7) -0.016(6) 0.058(6) -0.032(6)
C92 0.095(7) 0.067(6) 0.066(7) -0.018(6) 0.046(5) -0.025(6)
C93 0.091(6) 0.060(5) 0.026(4) 0.008(3) 0.024(4) 0.032(4)

C94 0.121(6) 0.078(6) 0.045(5) 0.025(4) 0.040(5) 0.027(5)
C95 0.115(7) 0.099(8) 0.063(7) 0.035(5) 0.038(6) 0.009(6)
C96 0.127(8) 0.115(9) 0.080(8) 0.048(6) 0.040(7) 0.003(7)
C97 0.149(8) 0.112(9) 0.092(8) 0.053(6) 0.045(8) 0.004(8)
C98 0.158(9) 0.109(8) 0.095(8) 0.062(6) 0.050(8) 0.023(7)
C99 0.145(8) 0.102(8) 0.080(7) 0.051(5) 0.054(6) 0.037(6)
C100 0.094(6) 0.062(6) 0.032(5) 0.005(4) 0.016(4) 0.030(5)
C101 0.111(7) 0.068(7) 0.032(6) 0.000(4) 0.022(5) 0.006(6)
C102 0.114(8) 0.081(8) 0.046(6) -0.010(5) 0.009(6) 0.011(7)
C103 0.095(8) 0.090(8) 0.058(7) -0.024(6) -0.001(6) 0.007(6)
C104 0.087(7) 0.103(8) 0.078(7) -0.029(6) 0.013(6) 0.015(6)
C105 0.082(7) 0.085(7) 0.058(6) -0.021(5) 0.019(5) 0.025(5)
C106 0.035(4) 0.041(5) 0.030(3) 0.025(4) 0.020(3) 0.020(4)
C107 0.053(4) 0.065(5) 0.034(3) 0.041(4) 0.030(3) 0.035(4)
C108 0.056(5) 0.096(7) 0.036(4) 0.044(5) 0.037(4) 0.047(5)
C109 0.061(5) 0.115(7) 0.040(5) 0.045(5) 0.031(4) 0.055(5)
C110 0.051(5) 0.097(7) 0.035(4) 0.038(5) 0.022(4) 0.043(5)
C111 0.036(4) 0.061(5) 0.031(3) 0.029(4) 0.017(3) 0.024(4)
C112 0.085(8) 0.191(13) 0.059(9) 0.068(9) 0.043(6) 0.102(9)
C113 0.040(5) 0.053(5) 0.030(4) 0.019(3) 0.016(4) 0.011(4)
C114 0.057(5) 0.050(5) 0.028(5) 0.015(4) 0.020(4) 0.004(4)
C115 0.066(5) 0.062(6) 0.037(6) 0.014(4) 0.027(5) -0.001(5)
C116 0.073(6) 0.066(7) 0.040(6) 0.015(5) 0.029(5) -0.010(6)
C117 0.084(7) 0.061(7) 0.042(6) 0.020(5) 0.027(6) -0.004(6)
C118 0.076(6) 0.053(6) 0.040(6) 0.024(4) 0.023(5) 0.006(5)
C119 0.067(5) 0.056(6) 0.030(6) 0.022(4) 0.025(5) 0.010(5)
C120 0.052(5) 0.052(5) 0.043(5) 0.024(4) 0.010(4) 0.007(4)
C121 0.065(6) 0.057(6) 0.044(5) 0.015(4) 0.011(5) 0.005(5)
C122 0.088(7) 0.059(7) 0.062(6) 0.009(5) 0.011(6) 0.001(6)
C123 0.085(7) 0.061(7) 0.078(6) 0.012(6) 0.004(6) -0.013(5)
C124 0.066(7) 0.063(7) 0.082(7) 0.021(6) 0.013(6) -0.007(5)
C125 0.052(6) 0.061(6) 0.060(6) 0.026(5) 0.014(5) -0.001(5)
C126 0.073(5) 0.074(5) 0.030(4) 0.038(4) 0.023(3) 0.036(4)
C127 0.115(6) 0.081(5) 0.029(5) 0.028(5) 0.029(5) 0.015(5)
C128 0.148(8) 0.079(6) 0.055(6) 0.021(6) 0.034(7) 0.014(6)
C129 0.162(9) 0.083(6) 0.061(7) 0.021(6) 0.044(8) 0.002(7)
C130 0.157(8) 0.090(7) 0.069(7) 0.023(7) 0.012(8) -0.002(7)
C131 0.137(8) 0.092(8) 0.071(7) 0.027(7) 0.004(7) -0.010(6)
C132 0.115(6) 0.091(7) 0.045(6) 0.027(6) 0.005(7) -0.005(5)
C133 0.071(6) 0.090(6) 0.036(4) 0.046(5) 0.025(4) 0.041(4)
C134 0.089(7) 0.090(7) 0.043(5) 0.042(5) 0.038(5) 0.055(5)
C135 0.093(8) 0.110(8) 0.051(6) 0.041(6) 0.049(6) 0.056(6)
C136 0.081(7) 0.147(9) 0.064(6) 0.042(6) 0.050(6) 0.028(6)
C137 0.079(7) 0.141(8) 0.059(6) 0.047(6) 0.034(6) 0.009(6)
C138 0.077(7) 0.122(7) 0.050(5) 0.046(5) 0.028(5) 0.016(5)
C139 0.031(4) 0.018(4) 0.041(5) 0.005(4) 0.026(4) 0.010(3)

C140 0.031(4) 0.022(4) 0.047(5) 0.011(5) 0.036(5) 0.010(3)
C141 0.038(4) 0.021(4) 0.053(5) 0.017(4) 0.035(5) 0.009(3)
C142 0.029(4) 0.031(5) 0.032(3) 0.008(4) 0.020(3) -0.002(3)
C143 0.042(4) 0.041(5) 0.031(3) 0.005(4) 0.021(3) -0.014(4)
C144 0.052(5) 0.056(6) 0.028(4) 0.006(5) 0.020(4) -0.027(4)
C145 0.049(5) 0.062(6) 0.029(5) 0.007(5) 0.017(4) -0.027(5)
C146 0.051(5) 0.057(6) 0.027(4) 0.000(5) 0.013(4) -0.030(5)
C147 0.044(5) 0.041(5) 0.035(3) 0.003(4) 0.022(3) -0.013(4)
C148 0.057(7) 0.107(10) 0.026(7) 0.007(7) 0.008(5) -0.050(7)
C149 0.048(5) 0.051(5) 0.032(4) 0.011(4) 0.021(3) -0.006(4)
C150 0.079(6) 0.059(5) 0.041(5) 0.008(5) 0.030(5) 0.005(4)
C151 0.102(7) 0.058(5) 0.073(7) 0.007(6) 0.030(6) 0.007(6)
C152 0.105(8) 0.061(6) 0.079(7) 0.010(6) 0.014(7) 0.026(6)
C153 0.106(8) 0.080(7) 0.072(7) 0.010(7) 0.019(7) 0.035(7)
C154 0.097(8) 0.093(8) 0.079(7) -0.002(7) 0.035(6) 0.030(6)
C155 0.080(7) 0.087(6) 0.068(7) -0.005(6) 0.035(6) 0.018(5)
C156 0.075(6) 0.081(6) 0.055(5) 0.020(5) 0.007(5) 0.016(5)
C157 0.136(9) 0.127(8) 0.090(8) 0.004(7) -0.035(6) 0.062(8)
C158 0.134(9) 0.118(8) 0.104(8) 0.030(8) -0.016(7) 0.054(7)
C159 0.114(9) 0.094(8) 0.135(9) 0.025(7) -0.028(7) 0.034(7)
C160 0.093(8) 0.076(7) 0.104(7) 0.016(6) -0.014(6) 0.016(6)
C161 0.042(5) 0.044(5) 0.038(4) 0.004(4) 0.014(3) -0.009(3)
C162 0.050(5) 0.051(5) 0.049(5) -0.002(5) 0.012(4) 0.001(4)
C163 0.071(7) 0.052(5) 0.062(7) -0.003(5) 0.007(5) 0.018(5)
C164 0.080(7) 0.063(6) 0.078(7) -0.004(6) -0.001(6) 0.025(5)
C165 0.077(7) 0.071(6) 0.079(7) 0.004(6) -0.001(5) 0.021(6)
C166 0.062(6) 0.069(6) 0.065(7) 0.004(6) 0.006(5) 0.013(6)
C167 0.052(6) 0.063(6) 0.050(6) 0.002(5) 0.011(4) 0.006(5)
C168 0.056(5) 0.041(5) 0.033(4) -0.001(4) 0.011(4) -0.002(4)
C169 0.066(6) 0.054(6) 0.034(5) 0.001(4) 0.018(5) 0.006(5)
C170 0.070(7) 0.068(7) 0.049(6) 0.004(5) 0.027(5) 0.008(5)
C171 0.078(7) 0.076(7) 0.052(6) -0.002(6) 0.026(5) 0.023(5)
C172 0.083(7) 0.068(7) 0.050(6) 0.004(5) 0.017(5) 0.026(5)
C173 0.069(7) 0.056(6) 0.037(6) 0.003(5) 0.011(5) 0.013(5)
C174 0.048(5) 0.021(4) 0.043(3) 0.011(3) 0.025(4) -0.003(4)
C175 0.086(6) 0.037(5) 0.042(4) 0.012(3) 0.033(4) -0.017(4)
C176 0.081(6) 0.044(5) 0.033(4) 0.013(4) 0.029(5) -0.015(5)
C177 0.071(6) 0.039(5) 0.038(5) 0.011(4) 0.025(5) -0.018(5)
C178 0.043(5) 0.027(5) 0.032(4) 0.008(4) 0.011(5) -0.004(4)
C179 0.040(5) 0.022(4) 0.041(3) 0.015(3) 0.015(4) 0.004(4)
C180 0.116(11) 0.047(7) 0.058(8) 0.015(6) 0.032(8) -0.033(7)
C181 0.052(4) 0.034(5) 0.043(4) 0.019(3) 0.017(4) 0.006(4)
C182 0.059(4) 0.044(5) 0.035(5) 0.017(4) 0.018(4) 0.016(4)
C183 0.054(5) 0.053(6) 0.037(6) 0.004(5) 0.022(5) 0.018(5)
C184 0.061(5) 0.076(7) 0.054(6) 0.007(5) 0.019(5) 0.026(6)
C185 0.079(6) 0.088(7) 0.062(7) 0.022(6) 0.010(6) 0.036(6)

C186 0.090(7) 0.083(7) 0.057(6) 0.040(5) 0.012(6) 0.035(6)
C187 0.080(6) 0.070(6) 0.048(6) 0.038(5) 0.021(5) 0.025(5)
C188 0.065(5) 0.050(5) 0.049(4) 0.026(4) 0.029(4) 0.019(4)
C189 0.079(6) 0.059(7) 0.053(6) 0.014(4) 0.030(5) 0.017(5)
C190 0.097(6) 0.072(7) 0.063(6) 0.013(5) 0.042(6) 0.017(6)
C191 0.100(7) 0.085(8) 0.087(7) 0.006(6) 0.047(6) 0.032(7)
C192 0.082(6) 0.093(8) 0.093(8) 0.015(6) 0.047(5) 0.029(6)
C193 0.070(5) 0.082(7) 0.077(7) 0.014(5) 0.033(5) 0.022(6)
C194 0.135(7) 0.052(5) 0.050(4) 0.003(4) 0.020(4) -0.014(4)
C195 0.186(8) 0.083(7) 0.060(6) 0.000(5) 0.032(5) 0.036(6)
C196 0.208(9) 0.124(8) 0.086(7) 0.002(6) 0.041(6) 0.059(6)
C197 0.212(10) 0.147(9) 0.097(9) 0.005(7) 0.055(8) 0.071(7)
C198 0.215(10) 0.149(10) 0.124(9) 0.013(8) 0.066(7) 0.066(8)
C199 0.212(10) 0.138(10) 0.111(8) 0.004(7) 0.077(7) 0.056(8)
C200 0.201(9) 0.119(8) 0.096(7) 0.001(6) 0.071(6) 0.037(7)
C201 0.148(8) 0.095(8) 0.078(6) -0.026(6) -0.006(5) 0.020(5)
C202 0.181(10) 0.151(9) 0.105(7) -0.043(7) -0.042(7) 0.068(7)
C203 0.190(11) 0.169(10) 0.130(8) -0.047(8) -0.053(7) 0.080(8)
C204 0.178(10) 0.160(10) 0.136(9) -0.042(8) -0.040(8) 0.072(8)
C205 0.155(10) 0.140(10) 0.127(9) -0.032(8) -0.015(8) 0.047(7)
C206 0.151(10) 0.116(9) 0.105(8) -0.022(7) -0.002(7) 0.029(6)
C207 0.024(4) 0.028(4) 0.036(4) 0.016(4) 0.019(4) 0.013(3)
C208 0.035(5) 0.028(4) 0.053(6) 0.021(5) 0.021(5) 0.020(4)
C209 0.024(4) 0.037(4) 0.048(5) 0.026(5) 0.019(4) 0.023(4)
C210 0.015(4) 0.030(4) 0.035(3) 0.016(3) 0.020(4) 0.015(3)
C211 0.018(4) 0.036(4) 0.035(3) 0.008(3) 0.020(4) 0.011(4)
C212 0.045(6) 0.035(5) 0.037(4) 0.008(4) 0.011(5) 0.002(4)
C213 0.062(6) 0.035(5) 0.039(5) 0.016(4) 0.010(5) -0.004(4)
C214 0.054(6) 0.033(5) 0.036(4) 0.014(4) 0.027(5) 0.002(4)
C215 0.035(5) 0.034(4) 0.037(3) 0.016(3) 0.028(4) 0.006(4)
C216 0.116(11) 0.048(7) 0.073(9) 0.013(6) 0.034(8) -0.030(7)
C217 0.048(4) 0.038(5) 0.037(4) 0.014(3) 0.020(3) 0.000(4)
C218 0.056(5) 0.053(6) 0.038(5) 0.005(4) 0.019(4) 0.011(4)
C219 0.060(5) 0.081(7) 0.064(6) -0.013(5) 0.033(5) 0.013(5)
C220 0.067(6) 0.101(8) 0.084(7) -0.027(6) 0.038(6) 0.012(6)
C221 0.066(6) 0.099(8) 0.086(7) -0.032(6) 0.040(6) 0.013(6)
C222 0.076(7) 0.094(8) 0.086(7) -0.027(6) 0.042(6) 0.009(6)
C223 0.066(6) 0.077(7) 0.072(7) -0.014(5) 0.033(5) 0.010(5)
C224 0.047(4) 0.045(5) 0.051(5) 0.018(4) 0.019(4) 0.003(4)
C225 0.059(5) 0.060(6) 0.042(6) 0.016(5) 0.022(4) 0.021(5)
C226 0.072(6) 0.067(7) 0.052(6) 0.013(5) 0.012(5) 0.026(6)
C227 0.061(6) 0.065(7) 0.064(7) 0.007(5) 0.006(5) 0.023(6)
C228 0.051(5) 0.062(7) 0.079(7) 0.013(6) 0.016(5) 0.014(6)
C229 0.049(5) 0.065(6) 0.068(6) 0.025(5) 0.023(5) 0.006(6)
C230 0.033(4) 0.057(5) 0.036(3) 0.012(3) 0.020(4) 0.001(4)
C231 0.037(4) 0.074(5) 0.050(5) 0.027(4) 0.011(4) 0.005(4)

C232 0.039(5) 0.080(7) 0.070(6) 0.025(5) 0.022(5) 0.016(5)
C233 0.044(5) 0.097(8) 0.084(7) 0.032(6) 0.019(6) 0.021(5)
C234 0.052(5) 0.108(8) 0.072(7) 0.042(6) 0.009(6) 0.028(6)
C235 0.059(6) 0.109(7) 0.083(7) 0.059(6) 0.002(6) 0.017(6)
C236 0.046(5) 0.097(7) 0.067(6) 0.051(5) 0.004(5) 0.009(5)
C237 0.057(6) 0.074(6) 0.039(4) 0.003(4) 0.033(4) -0.002(4)
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C248 0.030(4) 0.048(5) 0.030(3) 0.020(4) 0.014(3) 0.008(4)
C249 0.070(8) 0.106(11) 0.042(8) 0.015(7) 0.020(6) -0.037(7)
C250 0.037(4) 0.055(5) 0.031(4) 0.010(3) 0.018(4) 0.009(3)
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C262 0.044(5) 0.062(5) 0.029(5) 0.019(4) 0.031(4) 0.021(4)
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C273 0.121(8) 0.080(8) 0.071(7) 0.017(6) -0.022(6) 0.021(6)
C274 0.097(7) 0.072(7) 0.064(7) 0.022(6) -0.002(6) 0.008(6)
C275 0.083(7) 0.062(7) 0.044(6) 0.022(5) 0.010(5) 0.002(5)
N1 0.037(3) 0.030(3) 0.036(4) 0.007(4) 0.025(3) 0.000(3)
N2 0.037(4) 0.030(3) 0.037(4) 0.017(3) 0.025(4) 0.000(3)

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N3 0.025(3) 0.024(3) 0.021(4) 0.013(3) 0.014(3) 0.007(3)
N4 0.027(3) 0.028(4) 0.018(4) 0.014(3) 0.008(3) 0.009(3)
N5 0.029(3) 0.022(4) 0.038(4) 0.015(3) 0.022(3) 0.003(3)
N6 0.031(3) 0.021(3) 0.034(4) 0.010(3) 0.027(4) 0.001(3)
N7 0.013(3) 0.029(3) 0.037(4) 0.024(3) 0.008(3) 0.012(3)
N8 0.027(3) 0.027(3) 0.038(4) 0.018(4) 0.021(3) 0.012(3)

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

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Cu3 O5 1.914(8) . ?
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Cu4 C207 1.892(10) . ?
O1 S1 1.378(10) . ?
O2 S1 1.239(9) . ?
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O4 S1 1.347(12) . ?
O5 S2 1.459(9) . ?
O6 S2 1.467(9) . ?
O7 S2 1.452(10) . ?
O8 S2 1.535(10) . ?
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C3 N1 1.377(12) . ?
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N6 C139 Cu3 128.5(8) . . ?
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H14B C148 H14C 109.5 . . ?
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H18A C180 H18C 109.5 . . ?
H18B C180 H18C 109.5 . . ?
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N7 C207 Cu4 125.4(8) . . ?
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H21A C216 H21C 109.5 . . ?
H21B C216 H21C 109.5 . . ?
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H24B C249 H24C 109.5 . . ?
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C274 C273 C272 120.9(16) . . ?
C274 C273 H273 119.5 . . ?
C272 C273 H273 119.5 . . ?
C275 C274 C273 119.2(16) . . ?

```
C275 C274 H274 120.4 . . ?
C273 C274 H274 120.4 . . ?
C274 C275 C270 120.7(14) . . ?
C274 C275 H275 119.7 . . ?
C270 C275 H275 119.7 . . ?
C1 N1 C3 107.4(9) . . ?
C1 N1 C4 124.2(9) . . ?
C3 N1 C4 128.1(9) . . ?
C1 N2 C2 109.9(9) . . ?
C1 N2 C37 126.3(9) . . ?
C2 N2 C37 123.5(9) . . ?
C70 N3 C72 113.0(8) . . ?
C70 N3 C73 122.7(8) . . ?
C72 N3 C73 123.7(8) . . ?
C70 N4 C71 111.7(8) . . ?
C70 N4 C106 122.8(8) . . ?
C71 N4 C106 125.6(9) . . ?
C139 N5 C141 108.5(8) . . ?
C139 N5 C142 124.5(9) . . ?
C141 N5 C142 126.8(8) . . ?
C139 N6 C140 110.6(8) . . ?
C139 N6 C174 122.5(9) . . ?
C140 N6 C174 126.9(8) . . ?
C209 N7 C207 111.1(9) . . ?
C209 N7 C210 125.7(8) . . ?
C207 N7 C210 123.0(8) . . ?
C207 N8 C208 109.7(8) . . ?
C207 N8 C243 127.2(9) . . ?
C208 N8 C243 123.1(9) . . ?

_refine_diff_density_max    1.061
_refine_diff_density_min   -0.771
_refine_diff_density_rms    0.119

_shelx_res_file
;

    cnmsb4_20170609p.res created by SHELXL-2014/7


TITL cnmsb4_20170609 in P-1
CELL 0.71073  22.19270  22.33520  26.58500 103.7126 107.0616  90.1052
ZERR    4.00   0.00190   0.00190   0.00230   0.0020   0.0019   0.0020
LATT 1
SFAC C  H  N  O  S  Cu
UNIT 552  448  16  16  4  8
```

```
L.S. 11
BOND $H
FMAP 2
PLAN 20
SIZE 0.200 0.200 0.300
OMIT 0 2 0
OMIT 1 1 1
OMIT -1 0 2
OMIT -4   2   3
OMIT 2   5   1
OMIT 0  -1   3
OMIT 6   4   2
OMIT -2  -3   6
OMIT -1  -3   3
OMIT -7   3   0
OMIT -7  -7   6
OMIT -6  -3   5
OMIT 0  -3   5
OMIT -6  -4   7
OMIT -5  -1   3
OMIT -9   0   5
OMIT 2   3   4
OMIT 6   1   3
OMIT -3   1   7
OMIT 4   4   3
OMIT 3  -2   6
OMIT 3  -2   2
OMIT 5   4   2
OMIT 3   1   4
OMIT 2   2   5
OMIT -3  -3   9
OMIT 4   4   4
OMIT -8   1   4
OMIT 7   1   5
OMIT -10   1   4
OMIT 3  -2   3
DFIX 1.4 C64 C65
DFIX 1.4 C65 C66
DFIX 1.4 C66 C67
DFIX 1.4 C67 C68
DFIX 1.4 C68 C69
DFIX 1.4 C64 C69
DFIX 1.4 C201 C202
DFIX 1.4 C202 C203
DFIX 1.4 C203 C204
DFIX 1.4 C204 C205
```

```
DFIX 1.4 C205 C206
DFIX 1.4 C201 C206
DFIX 1.4 C195 C196
DFIX 1.4 C196 C197
DFIX 1.4 C197 C198
DFIX 1.4 C198 C199
DFIX 1.4 C199 C200
DFIX 1.4 C195 C200
DFIX 1.4 C218 C219
DFIX 1.4 C219 C220
DFIX 1.4 C220 C221
DFIX 1.4 C221 C222
DFIX 1.4 C222 C223
DFIX 1.4 C218 C223
DFIX 1.4 C157 C276
FLAT C64 > C69
FLAT C201 > C206
FLAT C195 > C200
FLAT C218 > C223
DELU 0.005
SIMU 0.01
DELU 0.001 C75
SIMU 0.005 C75
ISOR
TEMP -173.500
ACTA
WGHT    0.100000
FVAR      0.28340
MOLE 1
CU1   6    1.087831    0.836457    0.738649    11.00000    0.04638    0.03996 =
      0.05610    0.01436    0.02059   -0.01484
CU2   6    0.886040    0.669548    0.735999    11.00000    0.03948    0.04435 =
      0.05198    0.01091    0.02418   -0.01187
CU3   6    0.589550    0.174917    0.741101    11.00000    0.03350    0.03079 =
      0.06970    0.01609    0.02523    0.01148
CU4   6    0.387201    0.333761    0.745310    11.00000    0.02991    0.03536 =
      0.04444    0.01587    0.02010    0.01909
O1    4    1.030770    0.767437    0.724277    11.00000    0.09667    0.11723 =
      0.11830   -0.00898    0.03823   -0.07494
O2    4    0.938576    0.730132    0.726555    11.00000    0.11049    0.11952 =
      0.11602    0.02608    0.02147   -0.08931
O3    4    1.020423    0.673254    0.750174    11.00000    0.17118    0.15265 =
      0.24572    0.04569    0.04674   -0.05131
O4    4    1.014962    0.776085    0.807673    11.00000    0.25540    0.18293 =
      0.06800    0.02902   -0.00696   -0.05037
O5    4    0.524846    0.228603    0.720238    11.00000    0.05037    0.06532 =
```

```
      0.10047    0.01007    0.02629    0.03492
O6    4    0.436850    0.264970    0.744431    11.00000    0.05674    0.04939 =
      0.09319    0.01424    0.03087    0.03529
O7    4    0.536417    0.269367    0.815252    11.00000    0.11509    0.10225 =
      0.08467    0.03159   -0.00168    0.02975
O8    4    0.522956    0.338293    0.752994    11.00000    0.11274    0.05279 =
      0.13138    0.02097    0.02700    0.00538
S1    5    0.991137    0.757142    0.753202    11.00000    0.12848    0.14015 =
      0.07873    0.02050    0.01694   -0.10612
S2    5    0.505923    0.274953    0.760378    11.00000    0.05485    0.05883 =
      0.08368    0.01547    0.01513    0.03470
C1    1    1.149190    0.901943    0.749162    11.00000    0.03747    0.03132 =
      0.03354    0.01616    0.01825   -0.00177
C2    1    1.243207    0.951722    0.760269    11.00000    0.03362    0.03423 =
      0.04133    0.01375    0.01431   -0.00577
AFIX  43
H2    2    1.286739    0.960100    0.764865    11.00000   -1.20000
AFIX   0
C3    1    1.198524    0.991499    0.759658    11.00000    0.04189    0.03151 =
      0.04704    0.01032    0.02737   -0.00448
AFIX  43
H3A   2    1.205688    1.034646    0.764087    11.00000   -1.20000
AFIX   0
C4    1    1.083281    0.988897    0.751408    11.00000    0.03940    0.03758 =
      0.03472    0.01370    0.02391    0.00466
C5    1    1.041216    0.989243    0.700757    11.00000    0.05058    0.05047 =
      0.03534    0.00972    0.01898    0.00898
C6    1    0.982087    1.012174    0.700582    11.00000    0.05071    0.06499 =
      0.03706    0.00291    0.00878    0.01505
AFIX  43
H6    2    0.951314    1.009895    0.666563    11.00000   -1.20000
AFIX   0
C7    1    0.966627    1.037758    0.747294    11.00000    0.04977    0.07543 =
      0.04651    0.00318    0.01737    0.01966
C8    1    1.013252    1.036079    0.796671    11.00000    0.05472    0.06429 =
      0.03497    0.00261    0.02501    0.02146
AFIX  43
H8    2    1.003140    1.049488    0.829705    11.00000   -1.20000
AFIX   0
C9    1    1.072498    1.015897    0.798896    11.00000    0.04738    0.04420 =
      0.03670    0.00490    0.02467    0.01473
C10   1    0.904365    1.065351    0.746229    11.00000    0.04801    0.12389 =
      0.05897    0.00700    0.01632    0.02846
AFIX 137
H10A  2    0.910455    1.099818    0.778351    11.00000   -1.50000
H10B  2    0.873731    1.033730    0.746288    11.00000   -1.50000
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```
H10C  2    0.888486    1.080420    0.713355    11.00000   -1.50000
AFIX   0
C11   1    1.119833    1.017365    0.853389    11.00000    0.05410    0.04943 =
      0.03476    0.00168    0.02362    0.00735
AFIX  13
H11   2    1.154191    0.991426    0.845429    11.00000   -1.20000
AFIX   0
C12   1    1.150154    1.080596    0.880680    11.00000    0.05959    0.05778 =
      0.06277    0.00811    0.02112   -0.01120
C13   1    1.120748    1.132420    0.883667    11.00000    0.07928    0.05071 =
      0.06822    0.01312    0.02217   -0.01337
AFIX  43
H13   2    1.076243    1.129515    0.867414    11.00000   -1.20000
AFIX   0
C14   1    1.153061    1.193396    0.910503    11.00000    0.09567    0.05730 =
      0.09266    0.01788    0.02228   -0.02128
AFIX  43
H14   2    1.130607    1.229619    0.911650    11.00000   -1.20000
AFIX   0
C15   1    1.213090    1.196369    0.932574    11.00000    0.09251    0.07020 =
      0.10823    0.01841    0.01980   -0.03475
AFIX  43
H15   2    1.235358    1.235881    0.948933    11.00000   -1.20000
AFIX   0
C16   1    1.246199    1.145056    0.933480    11.00000    0.07756    0.08425 =
      0.12350   -0.00083    0.01267   -0.02731
AFIX  43
H16   2    1.289825    1.147835    0.953193    11.00000   -1.20000
AFIX   0
C17   1    1.212510    1.087274    0.903622    11.00000    0.06956    0.07810 =
      0.11432   -0.00058    0.01140   -0.01466
AFIX  43
H17   2    1.235659    1.051607    0.899842    11.00000   -1.20000
AFIX   0
C18   1    1.092520    0.987185    0.888716    11.00000    0.08786    0.05307 =
      0.03813   -0.00215    0.03467   -0.00995
C19   1    1.093355    1.013848    0.937725    11.00000    0.08115    0.04924 =
      0.03495    0.00081    0.02471   -0.00613
AFIX  43
H19   2    1.110990    1.055357    0.952408    11.00000   -1.20000
AFIX   0
C20   1    1.069386    0.984825    0.971359    11.00000    0.09936    0.05707 =
      0.03053    0.00814    0.02118   -0.01286
AFIX  43
H20   2    1.067577    1.007661    1.005850    11.00000   -1.20000
AFIX   0
```

```
C21   1    1.049474    0.924333    0.952850    11.00000    0.15540    0.06622 =
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AFIX  43
H21   2    1.036016    0.902419    0.974705    11.00000   -1.20000
AFIX   0
C22   1    1.049470    0.896024    0.901589    11.00000    0.18442    0.06634 =
      0.06589   -0.00760    0.04519   -0.05116
AFIX  43
H22   2    1.038096    0.852868    0.888482    11.00000   -1.20000
AFIX   0
C23   1    1.065839    0.928468    0.866705    11.00000    0.16313    0.06392 =
      0.05898   -0.01159    0.05056   -0.03820
AFIX  43
H23   2    1.058307    0.909574    0.829203    11.00000   -1.20000
AFIX   0
C24   1    1.054970    0.960563    0.649065    11.00000    0.06296    0.06443 =
      0.03444    0.00449    0.02091    0.00546
AFIX  13
H24   2    1.100805    0.952930    0.660516    11.00000   -1.20000
AFIX   0
C25   1    1.050958    1.009544    0.615746    11.00000    0.09956    0.08631 =
      0.03421    0.01471    0.02193    0.00005
C26   1    1.106802    1.042676    0.621929    11.00000    0.11504    0.08708 =
      0.04534    0.02104    0.01857   -0.01297
AFIX  43
H26   2    1.145479    1.033926    0.645130    11.00000   -1.20000
AFIX   0
C27   1    1.106624    1.089985    0.593610    11.00000    0.12568    0.08568 =
      0.05715    0.02607    0.01230   -0.01094
AFIX  43
H27   2    1.144334    1.114089    0.598972    11.00000   -1.20000
AFIX   0
C28   1    1.052680    1.098979    0.560003    11.00000    0.12417    0.09204 =
      0.06078    0.02815    0.01831    0.00166
AFIX  43
H28   2    1.052333    1.128963    0.539872    11.00000   -1.20000
AFIX   0
C29   1    0.994150    1.065140    0.552552    11.00000    0.11990    0.10089 =
      0.05884    0.03222    0.02420    0.00919
AFIX  43
H29   2    0.955243    1.074563    0.530166    11.00000   -1.20000
AFIX   0
C30   1    0.996490    1.016463    0.580176    11.00000    0.10229    0.09639 =
      0.04832    0.02729    0.03230    0.02073
AFIX  43
H30   2    0.959952    0.989856    0.573170    11.00000   -1.20000
```

```
AFIX   0
C31   1    1.021006    0.896538    0.616414    11.00000    0.06782    0.07227 =
      0.03697    0.00021    0.01773    0.00042
C32   1    0.987522    0.864227    0.637893    11.00000    0.07540    0.08148 =
      0.05455   -0.00050    0.01759   -0.01727
AFIX  43
H32   2    0.982068    0.882468    0.672227    11.00000   -1.20000
AFIX   0
C33   1    0.960563    0.803461    0.609598    11.00000    0.08924    0.08894 =
      0.07613   -0.00398    0.00767   -0.02652
AFIX  43
H33   2    0.934921    0.781222    0.623092    11.00000   -1.20000
AFIX   0
C34   1    0.973183    0.778714    0.562402    11.00000    0.09356    0.08448 =
      0.07290   -0.01583   -0.00069   -0.02503
AFIX  43
H34   2    0.955321    0.738085    0.543098    11.00000   -1.20000
AFIX   0
C35   1    1.009923    0.807912    0.540222    11.00000    0.09308    0.07039 =
      0.05035   -0.00707   -0.00262    0.00115
AFIX  43
H35   2    1.018048    0.789008    0.507119    11.00000   -1.20000
AFIX   0
C36   1    1.033933    0.866968    0.570173    11.00000    0.08229    0.06723 =
      0.03550   -0.00292    0.01140    0.00050
AFIX  43
H36   2    1.061321    0.888390    0.557647    11.00000   -1.20000
AFIX   0
C37   1    1.241198    0.838440    0.754091    11.00000    0.04332    0.03667 =
      0.04871    0.01671    0.01755    0.00851
C38   1    1.268102    0.824009    0.802182    11.00000    0.05280    0.04199 =
      0.05456    0.03018    0.01710   -0.00154
C39   1    1.301258    0.769497    0.798817    11.00000    0.06592    0.05314 =
      0.05474    0.03064    0.00135    0.00695
AFIX  43
H39   2    1.325208    0.759497    0.831346    11.00000   -1.20000
AFIX   0
C40   1    1.299484    0.730936    0.749637    11.00000    0.07800    0.06203 =
      0.06640    0.01545    0.00053    0.02206
C41   1    1.271060    0.744053    0.702522    11.00000    0.07470    0.06316 =
      0.05402    0.00132    0.00732    0.03004
AFIX  43
H41   2    1.271425    0.716506    0.669370    11.00000   -1.20000
AFIX   0
C42   1    1.239558    0.800611    0.702114    11.00000    0.05451    0.05992 =
      0.05082    0.01073    0.02022    0.02411
```

```
C43   1    1.331546    0.671399    0.749707    11.00000    0.11907    0.06409 =
      0.09852    0.00457   -0.02559    0.03477
AFIX 137
H43A  2    1.304937    0.641345    0.756859    11.00000   -1.50000
H43B  2    1.372520    0.679378    0.778064    11.00000   -1.50000
H43C  2    1.337996    0.654819    0.714242    11.00000   -1.50000
AFIX   0
C44   1    1.204290    0.817514    0.649940    11.00000    0.07485    0.07893 =
      0.04630    0.01268    0.02110    0.03455
AFIX  13
H44   2    1.170983    0.844511    0.658684    11.00000   -1.20000
AFIX   0
C45   1    1.245420    0.856433    0.630220    11.00000    0.10262    0.11392 =
      0.06139    0.03006    0.03097    0.02332
C46   1    1.304336    0.841549    0.624621    11.00000    0.09327    0.12717 =
      0.08394    0.02154    0.03041    0.00624
AFIX  43
H46   2    1.321474    0.806782    0.636895    11.00000   -1.20000
AFIX   0
C47   1    1.341578    0.873713    0.602096    11.00000    0.10187    0.13734 =
      0.10802    0.03314    0.03485    0.00010
AFIX  43
H47   2    1.378654    0.859850    0.593516    11.00000   -1.20000
AFIX   0
C48   1    1.317671    0.922669    0.595552    11.00000    0.11745    0.14753 =
      0.11791    0.04905    0.03448    0.00559
AFIX  43
H48   2    1.342050    0.947385    0.582956    11.00000   -1.20000
AFIX   0
C49   1    1.266114    0.947849    0.602196    11.00000    0.12577    0.14229 =
      0.11160    0.06424    0.03556    0.01591
AFIX  43
H49   2    1.258323    0.988407    0.597839    11.00000   -1.20000
AFIX   0
C50   1    1.218554    0.910296    0.617189    11.00000    0.12292    0.12768 =
      0.08894    0.05780    0.03274    0.02179
AFIX  43
H50   2    1.177431    0.921620    0.617611    11.00000   -1.20000
AFIX   0
C51   1    1.169107    0.761223    0.605886    11.00000    0.08455    0.09005 =
      0.06046   -0.00243    0.01404    0.03507
C52   1    1.174309    0.747241    0.554857    11.00000    0.10529    0.11803 =
      0.06367   -0.02036    0.01547    0.01907
AFIX  43
H52   2    1.205018    0.768803    0.545865    11.00000   -1.20000
AFIX   0
```

```
C276  1    0.471409   -0.006298    0.562423    11.00000    0.11844    0.12476 =
      0.07669    0.00265   -0.02287    0.06106
AFIX  43
H276  2    0.490425   -0.040703    0.546352    11.00000   -1.20000
AFIX   0
C53   1    1.133281    0.700502    0.516533    11.00000    0.11918    0.12957 =
      0.07813   -0.02946    0.01582    0.01127
AFIX  43
H53   2    1.130851    0.695950    0.479528    11.00000   -1.20000
AFIX   0
C54   1    1.098213    0.662794    0.527430    11.00000    0.12499    0.11523 =
      0.08629   -0.01533   -0.00238    0.00843
AFIX  43
H54   2    1.076350    0.626353    0.501868    11.00000   -1.20000
AFIX   0
C55   1    1.095644    0.679191    0.576171    11.00000    0.12526    0.11650 =
      0.09230   -0.00572    0.00584   -0.00122
AFIX  43
H55   2    1.065405    0.655738    0.584073    11.00000   -1.20000
AFIX   0
C56   1    1.130586    0.726188    0.619043    11.00000    0.10792    0.10388 =
      0.08133   -0.00613    0.01274    0.00497
AFIX  43
H56   2    1.127347    0.732853    0.654769    11.00000   -1.20000
AFIX   0
C57   1    1.266612    0.866393    0.854265    11.00000    0.10055    0.06220 =
      0.05216    0.02188    0.01644   -0.00496
AFIX  13
H57   2    1.230621    0.892300    0.843576    11.00000   -1.20000
AFIX   0
C58   1    1.322404    0.911368    0.882229    11.00000    0.12879    0.06884 =
      0.06985    0.02460    0.01280   -0.02666
C59   1    1.378714    0.908826    0.869423    11.00000    0.13382    0.08934 =
      0.08212    0.03216    0.02117   -0.04424
AFIX  43
H59   2    1.383827    0.875490    0.841611    11.00000   -1.20000
AFIX   0
C60   1    1.427331    0.953991    0.896489    11.00000    0.15252    0.09849 =
      0.09555    0.03433    0.02284   -0.05883
AFIX  43
H60   2    1.464799    0.953694    0.886069    11.00000   -1.20000
AFIX   0
C61   1    1.420951    0.995903    0.935564    11.00000    0.16006    0.08337 =
      0.11868    0.02782    0.01636   -0.05064
AFIX  43
H61   2    1.455396    1.026454    0.952300    11.00000   -1.20000
```

```
AFIX   0
C62   1    1.365850    1.004848    0.960049    11.00000    0.16123    0.07205 =
      0.10304    0.01363    0.01017   -0.02921
AFIX  43
H62   2    1.365088    1.036453    0.990829    11.00000   -1.20000
AFIX   0
C63   1    1.315694    0.957899    0.929063    11.00000    0.14710    0.06818 =
      0.08659    0.01538    0.01622   -0.02572
AFIX  43
H63   2    1.277982    0.957017    0.938989    11.00000   -1.20000
AFIX   0
C64   1    1.251141    0.837237    0.891367    11.00000    0.13809    0.09276 =
      0.05669    0.02227    0.03076   -0.02593
C65   1    1.294752    0.822974    0.935931    11.00000    0.17679    0.08307 =
      0.05553    0.02586    0.03123   -0.01152
AFIX  43
H65   2    1.338169    0.832717    0.941052    11.00000   -1.20000
AFIX   0
C66   1    1.280250    0.795065    0.974638    11.00000    0.20359    0.10852 =
      0.07124    0.03606    0.03925   -0.01952
AFIX  43
H66   2    1.309810    0.786084    1.005390    11.00000   -1.20000
AFIX   0
C67   1    1.216382    0.783762    0.959306    11.00000    0.20754    0.13863 =
      0.10304    0.04648    0.04641   -0.04187
AFIX  43
H67   2    1.203890    0.758031    0.978848    11.00000   -1.20000
AFIX   0
C68   1    1.164364    0.800498    0.921958    11.00000    0.18034    0.16405 =
      0.10703    0.05237    0.04723   -0.06023
AFIX  43
H68   2    1.121423    0.800525    0.921570    11.00000   -1.20000
AFIX   0
C69   1    1.191288    0.817087    0.885537    11.00000    0.15760    0.15126 =
      0.09140    0.03851    0.04205   -0.04937
AFIX  43
H69   2    1.162574    0.813660    0.850364    11.00000   -1.20000
AFIX   0
C70   1    0.830108    0.610267    0.739928    11.00000    0.02735    0.02622 =
      0.02681    0.01128    0.01608    0.00320
C71   1    0.785937    0.521254    0.744676    11.00000    0.03424    0.02497 =
      0.01954    0.01566    0.01323    0.00873
AFIX  43
H71   2    0.781735    0.479460    0.746261    11.00000   -1.20000
AFIX   0
C72   1    0.740891    0.559776    0.741778    11.00000    0.02461    0.03093 =
```

```
      0.01911    0.01657    0.01551    0.00390
AFIX  43
H72   2    0.699093    0.552352    0.742656    11.00000   -1.20000
AFIX   0
C73   1    0.736423    0.670216    0.737494    11.00000    0.03653    0.02902 =
      0.02238    0.01289    0.02200    0.01150
C74   1    0.740560    0.710398    0.786592    11.00000    0.05917    0.05062 =
      0.02448    0.00630    0.02747    0.02390
C75   1    0.708659    0.766016    0.786334    11.00000    0.06935    0.05085 =
      0.01875   -0.00051    0.02873    0.02490
AFIX  43
H75   2    0.710542    0.794847    0.819488    11.00000   -1.20000
AFIX   0
C76   1    0.675626    0.776990    0.737957    11.00000    0.06779    0.04756 =
      0.02715   -0.00310    0.01116    0.02558
C77   1    0.669867    0.736252    0.689305    11.00000    0.05268    0.04476 =
      0.01883    0.00685    0.00765    0.02538
AFIX  43
H77   2    0.646502    0.745815    0.656401    11.00000   -1.20000
AFIX   0
C78   1    0.698394    0.680492    0.688005    11.00000    0.04564    0.03589 =
      0.02300    0.00913    0.01516    0.01755
C79   1    0.646022    0.840248    0.739442    11.00000    0.08509    0.06131 =
      0.05324   -0.00442    0.01180    0.04331
AFIX 137
H79A  2    0.630589    0.845907    0.702480    11.00000   -1.50000
H79B  2    0.678114    0.873659    0.762123    11.00000   -1.50000
H79C  2    0.610721    0.841016    0.754657    11.00000   -1.50000
AFIX   0
C80   1    0.697838    0.636356    0.634714    11.00000    0.05783    0.03842 =
      0.02123    0.00647    0.02032    0.01347
AFIX  13
H80   2    0.707669    0.595596    0.643373    11.00000   -1.20000
AFIX   0
C81   1    0.631475    0.625584    0.593206    11.00000    0.06206    0.04398 =
      0.02740    0.00686    0.01597    0.00674
C82   1    0.589563    0.581556    0.598531    11.00000    0.07436    0.06877 =
      0.03690    0.01435    0.01236   -0.01306
AFIX  43
H82   2    0.601442    0.560721    0.626839    11.00000   -1.20000
AFIX   0
C83   1    0.528018    0.569830    0.558979    11.00000    0.08839    0.08240 =
      0.05822    0.02180   -0.00303   -0.02877
AFIX  43
H83   2    0.497356    0.542713    0.562549    11.00000   -1.20000
AFIX   0
```

```
C84   1    0.512786    0.596863    0.516441    11.00000    0.08422    0.08106 =
      0.05651    0.01997   -0.00652   -0.01517
AFIX  43
H84   2    0.471952    0.588058    0.490565    11.00000   -1.20000
AFIX   0
C85   1    0.555555    0.636256    0.510815    11.00000    0.07748    0.06083 =
      0.04498    0.01928   -0.00072    0.00069
AFIX  43
H85   2    0.544877    0.655526    0.481438    11.00000   -1.20000
AFIX   0
C86   1    0.614060    0.647704    0.548003    11.00000    0.06978    0.04522 =
      0.03901    0.01719    0.00838    0.00782
AFIX  43
H86   2    0.644616    0.672717    0.541974    11.00000   -1.20000
AFIX   0
C87   1    0.745967    0.651006    0.611150    11.00000    0.06564    0.05603 =
      0.02806   -0.00040    0.02491    0.00161
C88   1    0.761799    0.605319    0.572180    11.00000    0.05888    0.05563 =
      0.02793    0.01146    0.02361    0.01714
AFIX  43
H88   2    0.742382    0.564643    0.563026    11.00000   -1.20000
AFIX   0
C89   1    0.804840    0.617205    0.546374    11.00000    0.07658    0.07066 =
      0.04009    0.00968    0.03620    0.00303
AFIX  43
H89   2    0.816295    0.584414    0.521687    11.00000   -1.20000
AFIX   0
C90   1    0.831285    0.677040    0.556554    11.00000    0.10297    0.08778 =
      0.07980   -0.00881    0.05722   -0.02462
AFIX  43
H90   2    0.861372    0.685912    0.539715    11.00000   -1.20000
AFIX   0
C91   1    0.811486    0.724440    0.593191    11.00000    0.10887    0.08016 =
      0.08589   -0.01565    0.05809   -0.03227
AFIX  43
H91   2    0.824888    0.766515    0.598553    11.00000   -1.20000
AFIX   0
C92   1    0.772151    0.708390    0.621149    11.00000    0.09485    0.06721 =
      0.06602   -0.01809    0.04622   -0.02467
AFIX  43
H92   2    0.763501    0.739746    0.648667    11.00000   -1.20000
AFIX   0
C93   1    0.779491    0.695595    0.840170    11.00000    0.09100    0.05995 =
      0.02570    0.00762    0.02406    0.03171
AFIX  13
H93   2    0.809844    0.665295    0.830411    11.00000   -1.20000
```

```
AFIX   0
C94   1    0.739517    0.663871    0.863432    11.00000    0.12051    0.07755 =
      0.04507    0.02468    0.04034    0.02679
C95   1    0.677873    0.671123    0.857911    11.00000    0.11518    0.09896 =
      0.06313    0.03537    0.03764    0.00868
AFIX  43
H95   2    0.656492    0.697191    0.836018    11.00000   -1.20000
AFIX   0
C96   1    0.644562    0.641735    0.883179    11.00000    0.12666    0.11492 =
      0.08029    0.04799    0.04046    0.00308
AFIX  43
H96   2    0.601537    0.649272    0.879403    11.00000   -1.20000
AFIX   0
C97   1    0.670297    0.605709    0.910666    11.00000    0.14932    0.11236 =
      0.09153    0.05324    0.04487    0.00431
AFIX  43
H97   2    0.645202    0.585123    0.925822    11.00000   -1.20000
AFIX   0
C98   1    0.733917    0.593635    0.920637    11.00000    0.15830    0.10892 =
      0.09453    0.06228    0.05020    0.02321
AFIX  43
H98   2    0.753109    0.566016    0.941773    11.00000   -1.20000
AFIX   0
C99   1    0.766794    0.626258    0.896406    11.00000    0.14550    0.10162 =
      0.07961    0.05050    0.05404    0.03708
AFIX  43
H99   2    0.810860    0.621967    0.903332    11.00000   -1.20000
AFIX   0
C100  1    0.819213    0.751538    0.879638    11.00000    0.09416    0.06210 =
      0.03208    0.00517    0.01617    0.02967
C101  1    0.806738    0.783042    0.925310    11.00000    0.11144    0.06841 =
      0.03216   -0.00029    0.02239    0.00619
AFIX  43
H101  2    0.769210    0.770705    0.931688    11.00000   -1.20000
AFIX   0
C102  1    0.843769    0.830061    0.961637    11.00000    0.11444    0.08091 =
      0.04621   -0.01028    0.00942    0.01138
AFIX  43
H102  2    0.832525    0.851498    0.992583    11.00000   -1.20000
AFIX   0
C103  1    0.900866    0.847377    0.952794    11.00000    0.09464    0.09021 =
      0.05795   -0.02351   -0.00113    0.00737
AFIX  43
H103  2    0.930313    0.878569    0.979200    11.00000   -1.20000
AFIX   0
C104  1    0.912287    0.818858    0.906537    11.00000    0.08688    0.10260 =
```

```
      0.07807   -0.02908    0.01293    0.01503
AFIX  43
H104  2    0.948099    0.833274    0.898856    11.00000   -1.20000
AFIX   0
C105  1    0.874011    0.769419    0.869726    11.00000    0.08159    0.08499 =
      0.05809   -0.02124    0.01872    0.02471
AFIX  43
H105  2    0.884639    0.748074    0.838434    11.00000   -1.20000
AFIX   0
C106  1    0.899344    0.526420    0.749999    11.00000    0.03539    0.04102 =
      0.02979    0.02501    0.01961    0.02030
C107  1    0.915963    0.501576    0.702835    11.00000    0.05279    0.06522 =
      0.03407    0.04105    0.02996    0.03535
C108  1    0.972259    0.476989    0.707933    11.00000    0.05635    0.09635 =
      0.03567    0.04394    0.03651    0.04663
AFIX  43
H108  2    0.984175    0.459977    0.676264    11.00000   -1.20000
AFIX   0
C109  1    1.012451    0.476020    0.757570    11.00000    0.06139    0.11467 =
      0.03960    0.04465    0.03140    0.05540
C110  1    0.996451    0.501934    0.803216    11.00000    0.05126    0.09652 =
      0.03453    0.03810    0.02184    0.04326
AFIX  43
H110  2    1.025778    0.502370    0.837510    11.00000   -1.20000
AFIX   0
C111  1    0.940294    0.527322    0.802075    11.00000    0.03631    0.06102 =
      0.03130    0.02861    0.01680    0.02371
C112  1    1.077499    0.449805    0.762492    11.00000    0.08462    0.19119 =
      0.05874    0.06795    0.04291    0.10181
AFIX 137
H11A  2    1.103901    0.461753    0.800517    11.00000   -1.50000
H11B  2    1.098022    0.466356    0.740121    11.00000   -1.50000
H11C  2    1.071960    0.404627    0.749970    11.00000   -1.50000
AFIX   0
C113  1    0.921374    0.552814    0.852542    11.00000    0.03968    0.05322 =
      0.03047    0.01885    0.01602    0.01105
AFIX  13
H113  2    0.877371    0.565520    0.840026    11.00000   -1.20000
AFIX   0
C114  1    0.918184    0.504249    0.882512    11.00000    0.05691    0.05018 =
      0.02768    0.01525    0.02010    0.00371
C115  1    0.859590    0.478568    0.879340    11.00000    0.06590    0.06170 =
      0.03717    0.01413    0.02697   -0.00091
AFIX  43
H115  2    0.821228    0.490910    0.858589    11.00000   -1.20000
AFIX   0
```

```
C116  1    0.860012    0.433969    0.908048    11.00000    0.07305    0.06617 =
      0.04033    0.01542    0.02893   -0.01047
AFIX  43
H116  2    0.820255    0.415676    0.905631    11.00000   -1.20000
AFIX   0
C117  1    0.911245    0.414799    0.938531    11.00000    0.08446    0.06101 =
      0.04155    0.01981    0.02674   -0.00411
AFIX  43
H117  2    0.908183    0.384659    0.957760    11.00000   -1.20000
AFIX   0
C118  1    0.967088    0.439352    0.941178    11.00000    0.07613    0.05334 =
      0.04021    0.02409    0.02348    0.00649
AFIX  43
H118  2    1.004607    0.425165    0.961435    11.00000   -1.20000
AFIX   0
C119  1    0.971858    0.486568    0.914230    11.00000    0.06705    0.05594 =
      0.02960    0.02202    0.02497    0.00954
AFIX  43
H119  2    1.012001    0.505438    0.918371    11.00000   -1.20000
AFIX   0
C120  1    0.962239    0.611174    0.887889    11.00000    0.05244    0.05174 =
      0.04253    0.02424    0.00954    0.00693
C121  1    0.958477    0.632478    0.941140    11.00000    0.06536    0.05716 =
      0.04386    0.01517    0.01068    0.00529
AFIX  43
H121  2    0.934579    0.608917    0.955085    11.00000   -1.20000
AFIX   0
C122  1    0.991045    0.689713    0.973420    11.00000    0.08822    0.05934 =
      0.06199    0.00886    0.01092    0.00098
AFIX  43
H122  2    0.987652    0.706232    1.008776    11.00000   -1.20000
AFIX   0
C123  1    1.027305    0.720703    0.952977    11.00000    0.08478    0.06105 =
      0.07759    0.01216    0.00418   -0.01261
AFIX  43
H123  2    1.051633    0.757589    0.975418    11.00000   -1.20000
AFIX   0
C124  1    1.029443    0.700469    0.902213    11.00000    0.06627    0.06273 =
      0.08185    0.02112    0.01308   -0.00711
AFIX  43
H124  2    1.054337    0.723884    0.888986    11.00000   -1.20000
AFIX   0
C125  1    0.996347    0.646309    0.868412    11.00000    0.05190    0.06098 =
      0.05967    0.02590    0.01356   -0.00119
AFIX  43
H125  2    0.997205    0.633485    0.831924    11.00000   -1.20000
```

```
AFIX   0
C126  1    0.868588    0.498107    0.646414    11.00000    0.07320    0.07379 =
      0.03003    0.03813    0.02333    0.03602
AFIX  13
H126  2    0.840424    0.532199    0.652575    11.00000   -1.20000
AFIX   0
C127  1    0.824308    0.438308    0.624048    11.00000    0.11536    0.08050 =
      0.02857    0.02767    0.02886    0.01504
C128  1    0.852859    0.381792    0.620397    11.00000    0.14786    0.07883 =
      0.05494    0.02074    0.03384    0.01446
AFIX  43
H128  2    0.897313    0.379015    0.631677    11.00000   -1.20000
AFIX   0
C129  1    0.802740    0.322695    0.595293    11.00000    0.16198    0.08253 =
      0.06133    0.02111    0.04384    0.00223
AFIX  43
H129  2    0.815456    0.281820    0.587281    11.00000   -1.20000
AFIX   0
C130  1    0.743051    0.334152    0.586460    11.00000    0.15663    0.09019 =
      0.06873    0.02329    0.01210   -0.00223
AFIX  43
H130  2    0.714854    0.297993    0.573670    11.00000   -1.20000
AFIX   0
C131  1    0.715178    0.384793    0.591726    11.00000    0.13669    0.09191 =
      0.07104    0.02725    0.00398   -0.00950
AFIX  43
H131  2    0.670713    0.386194    0.584307    11.00000   -1.20000
AFIX   0
C132  1    0.760429    0.441364    0.610832    11.00000    0.11541    0.09079 =
      0.04539    0.02693    0.00546   -0.00496
AFIX  43
H132  2    0.743888    0.480813    0.613824    11.00000   -1.20000
AFIX   0
C133  1    0.899231    0.513123    0.608133    11.00000    0.07103    0.08972 =
      0.03569    0.04572    0.02496    0.04142
C134  1    0.887167    0.480416    0.554282    11.00000    0.08854    0.08952 =
      0.04259    0.04157    0.03771    0.05493
AFIX  43
H134  2    0.859797    0.443648    0.540432    11.00000   -1.20000
AFIX   0
C135  1    0.915345    0.501714    0.520639    11.00000    0.09310    0.10985 =
      0.05109    0.04059    0.04894    0.05625
AFIX  43
H135  2    0.909555    0.478303    0.484490    11.00000   -1.20000
AFIX   0
C136  1    0.951898    0.557474    0.540640    11.00000    0.08124    0.14736 =
```

```
      0.06367    0.04246    0.04966    0.02814
AFIX  43
H136  2    0.969733    0.571362    0.516618    11.00000   -1.20000
AFIX   0
C137  1    0.965044    0.596200    0.595191    11.00000    0.07922    0.14081 =
      0.05945    0.04672    0.03445    0.00914
AFIX  43
H137  2    0.987849    0.635592    0.607214    11.00000   -1.20000
AFIX   0
C138  1    0.941109    0.570027    0.627676    11.00000    0.07718    0.12229 =
      0.04967    0.04639    0.02824    0.01591
AFIX  43
H138  2    0.952377    0.590042    0.665273    11.00000   -1.20000
AFIX   0
C139  1    0.651849    0.116252    0.747822    11.00000    0.03057    0.01782 =
      0.04057    0.00517    0.02555    0.00957
C140  1    0.740555    0.069544    0.751920    11.00000    0.03104    0.02157 =
      0.04736    0.01092    0.03580    0.00998
AFIX  43
H140  2    0.783022    0.062665    0.752726    11.00000   -1.20000
AFIX   0
C141  1    0.699445    0.029920    0.754231    11.00000    0.03759    0.02078 =
      0.05278    0.01733    0.03456    0.00934
AFIX  43
H141  2    0.706155   -0.011483    0.756488    11.00000   -1.20000
AFIX   0
C142  1    0.584046    0.030848    0.751500    11.00000    0.02931    0.03075 =
      0.03234    0.00752    0.02047   -0.00174
C143  1    0.572375    0.033329    0.799908    11.00000    0.04213    0.04117 =
      0.03145    0.00462    0.02146   -0.01368
C144  1    0.517160    0.005808    0.799186    11.00000    0.05173    0.05611 =
      0.02785    0.00586    0.02005   -0.02685
AFIX  43
H144  2    0.508528    0.008415    0.832559    11.00000   -1.20000
AFIX   0
C145  1    0.472543   -0.026388    0.750350    11.00000    0.04924    0.06234 =
      0.02859    0.00677    0.01676   -0.02652
C146  1    0.487511   -0.028055    0.704128    11.00000    0.05076    0.05697 =
      0.02705   -0.00043    0.01314   -0.03001
AFIX  43
H146  2    0.458102   -0.049280    0.670595    11.00000   -1.20000
AFIX   0
C147  1    0.544042   -0.000261    0.702588    11.00000    0.04432    0.04137 =
      0.03451    0.00345    0.02158   -0.01348
C148  1    0.412662   -0.054520    0.750207    11.00000    0.05698    0.10731 =
      0.02590    0.00710    0.00827   -0.05031
```

```
AFIX 137
H14A  2    0.377352   -0.034538    0.730433    11.00000   -1.50000
H14B  2    0.411910   -0.049082    0.787691    11.00000   -1.50000
H14C  2    0.408736   -0.098725    0.732403    11.00000   -1.50000
AFIX   0
C149  1    0.555631   -0.000285    0.649568    11.00000    0.04785    0.05141 =
      0.03225    0.01081    0.02131   -0.00581
AFIX  13
H149  2    0.592912    0.030103    0.659455    11.00000   -1.20000
AFIX   0
C150  1    0.576856   -0.062276    0.623123    11.00000    0.07882    0.05927 =
      0.04093    0.00835    0.03037    0.00525
C151  1    0.548522   -0.118597    0.615776    11.00000    0.10228    0.05798 =
      0.07304    0.00721    0.03008    0.00670
AFIX  43
H151  2    0.513905   -0.122702    0.629211    11.00000   -1.20000
AFIX   0
C152  1    0.571951   -0.173259    0.586786    11.00000    0.10491    0.06079 =
      0.07906    0.00985    0.01443    0.02597
AFIX  43
H152  2    0.548703   -0.212431    0.574597    11.00000   -1.20000
AFIX   0
C153  1    0.625498   -0.165726    0.578606    11.00000    0.10598    0.08038 =
      0.07207    0.01042    0.01885    0.03471
AFIX  43
H153  2    0.643048   -0.201934    0.563703    11.00000   -1.20000
AFIX   0
C154  1    0.657584   -0.113929    0.588646    11.00000    0.09673    0.09297 =
      0.07893   -0.00248    0.03453    0.02984
AFIX  43
H154  2    0.695255   -0.111404    0.578921    11.00000   -1.20000
AFIX   0
C155  1    0.634637   -0.063222    0.613853    11.00000    0.08047    0.08697 =
      0.06807   -0.00479    0.03509    0.01806
AFIX  43
H155  2    0.660406   -0.025484    0.626040    11.00000   -1.20000
AFIX   0
C156  1    0.504140    0.023405    0.610955    11.00000    0.07547    0.08086 =
      0.05500    0.01977    0.00701    0.01567
C157  1    0.408288    0.005227    0.527789    11.00000    0.13563    0.12705 =
      0.09032    0.00375   -0.03457    0.06210
AFIX  43
H157  2    0.377455   -0.025679    0.502654    11.00000   -1.20000
AFIX   0
C158  1    0.401782    0.070976    0.538737    11.00000    0.13435    0.11795 =
      0.10369    0.03015   -0.01561    0.05447
```

```
AFIX  43
H158  2    0.373522    0.089672    0.513572    11.00000   -1.20000
AFIX   0
C159  1    0.438979    0.103726    0.587490    11.00000    0.11381    0.09447 =
      0.13527    0.02533   -0.02773    0.03351
AFIX  43
H159  2    0.437291    0.147350    0.595607    11.00000   -1.20000
AFIX   0
C160  1    0.480292    0.078732    0.627584    11.00000    0.09299    0.07596 =
      0.10365    0.01560   -0.01430    0.01635
AFIX  43
H160  2    0.491228    0.099639    0.664963    11.00000   -1.20000
AFIX   0
C161  1    0.619434    0.072575    0.854741    11.00000    0.04187    0.04401 =
      0.03795    0.00380    0.01367   -0.00950
AFIX  13
H161  2    0.643402    0.103950    0.845213    11.00000   -1.20000
AFIX   0
C162  1    0.667418    0.033406    0.882161    11.00000    0.05004    0.05136 =
      0.04916   -0.00172    0.01178    0.00149
C163  1    0.662140   -0.029966    0.871442    11.00000    0.07086    0.05241 =
      0.06191   -0.00257    0.00719    0.01759
AFIX  43
H163  2    0.626166   -0.052181    0.843924    11.00000   -1.20000
AFIX   0
C164  1    0.708009   -0.062855    0.899726    11.00000    0.07955    0.06250 =
      0.07819   -0.00433   -0.00128    0.02491
AFIX  43
H164  2    0.705904   -0.106745    0.890204    11.00000   -1.20000
AFIX   0
C165  1    0.757424   -0.027405    0.943038    11.00000    0.07708    0.07078 =
      0.07851    0.00378   -0.00136    0.02078
AFIX  43
H165  2    0.788232   -0.048660    0.963842    11.00000   -1.20000
AFIX   0
C166  1    0.763629    0.033977    0.956617    11.00000    0.06171    0.06941 =
      0.06511    0.00430    0.00558    0.01265
AFIX  43
H166  2    0.797735    0.056690    0.985926    11.00000   -1.20000
AFIX   0
C167  1    0.717487    0.062630    0.925519    11.00000    0.05247    0.06277 =
      0.04957    0.00153    0.01052    0.00606
AFIX  43
H167  2    0.720656    0.106541    0.934968    11.00000   -1.20000
AFIX   0
C168  1    0.583851    0.108482    0.892659    11.00000    0.05619    0.04149 =
```

```
      0.03274   -0.00065    0.01099   -0.00226
C169  1    0.577978    0.088218    0.936693    11.00000    0.06558    0.05435 =
      0.03384    0.00124    0.01759    0.00624
AFIX  43
H169  2    0.596212    0.051592    0.944095    11.00000   -1.20000
AFIX   0
C170  1    0.544927    0.122229    0.970148    11.00000    0.06961    0.06774 =
      0.04915    0.00394    0.02693    0.00837
AFIX  43
H170  2    0.541110    0.109571    1.000836    11.00000   -1.20000
AFIX   0
C171  1    0.517943    0.174840    0.957288    11.00000    0.07757    0.07590 =
      0.05164   -0.00184    0.02648    0.02317
AFIX  43
H171  2    0.493715    0.197667    0.978274    11.00000   -1.20000
AFIX   0
C172  1    0.526430    0.193780    0.914036    11.00000    0.08324    0.06800 =
      0.05027    0.00408    0.01711    0.02569
AFIX  43
H172  2    0.509688    0.230989    0.906683    11.00000   -1.20000
AFIX   0
C173  1    0.558414    0.160297    0.881359    11.00000    0.06865    0.05570 =
      0.03652    0.00319    0.01080    0.01256
AFIX  43
H173  2    0.562638    0.173454    0.851016    11.00000   -1.20000
AFIX   0
C174  1    0.740596    0.180125    0.744972    11.00000    0.04797    0.02082 =
      0.04306    0.01136    0.02451   -0.00278
C175  1    0.734753    0.191878    0.696934    11.00000    0.08581    0.03705 =
      0.04223    0.01172    0.03320   -0.01696
C176  1    0.763828    0.246856    0.695056    11.00000    0.08138    0.04417 =
      0.03286    0.01291    0.02883   -0.01507
AFIX  43
H176  2    0.762574    0.255169    0.661349    11.00000   -1.20000
AFIX   0
C177  1    0.794954    0.289372    0.744710    11.00000    0.07129    0.03885 =
      0.03781    0.01133    0.02502   -0.01756
C178  1    0.801076    0.276623    0.792157    11.00000    0.04327    0.02686 =
      0.03193    0.00822    0.01096   -0.00353
AFIX  43
H178  2    0.823745    0.305761    0.824731    11.00000   -1.20000
AFIX   0
C179  1    0.774587    0.220686    0.795121    11.00000    0.03988    0.02239 =
      0.04096    0.01496    0.01467    0.00420
C180  1    0.826908    0.350504    0.741501    11.00000    0.11615    0.04656 =
      0.05795    0.01474    0.03166   -0.03253
```

```
AFIX 137
H18A  2    0.844793    0.377159    0.778201    11.00000   -1.50000
H18B  2    0.795224    0.372095    0.719589    11.00000   -1.50000
H18C  2    0.860668    0.340442    0.724710    11.00000   -1.50000
AFIX   0
C181  1    0.783740    0.205513    0.850064    11.00000    0.05241    0.03389 =
      0.04323    0.01897    0.01723    0.00569
AFIX  13
H181  2    0.752279    0.169968    0.842689    11.00000   -1.20000
AFIX   0
C182  1    0.846747    0.181682    0.868901    11.00000    0.05945    0.04433 =
      0.03466    0.01666    0.01807    0.01613
C183  1    0.903469    0.210924    0.870940    11.00000    0.05355    0.05257 =
      0.03700    0.00389    0.02241    0.01801
AFIX  43
H183  2    0.901767    0.245947    0.856238    11.00000   -1.20000
AFIX   0
C184  1    0.963127    0.190634    0.893901    11.00000    0.06075    0.07572 =
      0.05367    0.00736    0.01865    0.02552
AFIX  43
H184  2    1.001228    0.212243    0.896413    11.00000   -1.20000
AFIX   0
C185  1    0.963589    0.137217    0.912803    11.00000    0.07947    0.08809 =
      0.06193    0.02167    0.01016    0.03575
AFIX  43
H185  2    1.002913    0.120650    0.925771    11.00000   -1.20000
AFIX   0
C186  1    0.910454    0.108269    0.913366    11.00000    0.09019    0.08348 =
      0.05738    0.03973    0.01246    0.03451
AFIX  43
H186  2    0.912785    0.073870    0.928931    11.00000   -1.20000
AFIX   0
C187  1    0.850542    0.130070    0.890205    11.00000    0.07973    0.07012 =
      0.04789    0.03777    0.02096    0.02485
AFIX  43
H187  2    0.812866    0.109050    0.889356    11.00000   -1.20000
AFIX   0
C188  1    0.766918    0.256479    0.890223    11.00000    0.06483    0.05001 =
      0.04917    0.02622    0.02908    0.01936
C189  1    0.809304    0.290499    0.938301    11.00000    0.07936    0.05854 =
      0.05340    0.01388    0.02952    0.01666
AFIX  43
H189  2    0.852664    0.282643    0.945268    11.00000   -1.20000
AFIX   0
C190  1    0.792190    0.336222    0.977735    11.00000    0.09676    0.07160 =
      0.06312    0.01257    0.04150    0.01708
```

```
AFIX  43
H190  2    0.822077    0.361419    1.009060    11.00000   -1.20000
AFIX   0
C191  1    0.726687    0.340446    0.965778    11.00000    0.10000    0.08459 =
      0.08680    0.00632    0.04670    0.03176
AFIX  43
H191  2    0.712144    0.368624    0.991750    11.00000   -1.20000
AFIX   0
C192  1    0.678978    0.305451    0.917063    11.00000    0.08186    0.09268 =
      0.09337    0.01458    0.04724    0.02937
AFIX  43
H192  2    0.635507    0.312722    0.910430    11.00000   -1.20000
AFIX   0
C193  1    0.699545    0.260762    0.880428    11.00000    0.06990    0.08216 =
      0.07704    0.01448    0.03328    0.02239
AFIX  43
H193  2    0.670078    0.233903    0.849900    11.00000   -1.20000
AFIX   0
C194  1    0.701918    0.144871    0.644030    11.00000    0.13531    0.05202 =
      0.04991    0.00326    0.02017   -0.01379
AFIX  13
H194  2    0.681004    0.112110    0.654518    11.00000   -1.20000
AFIX   0
C195  1    0.745547    0.114387    0.618777    11.00000    0.18621    0.08275 =
      0.05985    0.00033    0.03189    0.03565
C196  1    0.776780    0.064130    0.612070    11.00000    0.20819    0.12374 =
      0.08595    0.00178    0.04097    0.05938
AFIX  43
H196  2    0.770460    0.043804    0.637924    11.00000   -1.20000
AFIX   0
C197  1    0.813770    0.026188    0.586792    11.00000    0.21204    0.14718 =
      0.09708    0.00543    0.05458    0.07083
AFIX  43
H197  2    0.827881   -0.012532    0.592368    11.00000   -1.20000
AFIX   0
C198  1    0.825095    0.056872    0.552504    11.00000    0.21546    0.14918 =
      0.12399    0.01270    0.06556    0.06623
AFIX  43
H198  2    0.854706    0.040764    0.534235    11.00000   -1.20000
AFIX   0
C199  1    0.796628    0.112233    0.540521    11.00000    0.21228    0.13797 =
      0.11081    0.00418    0.07738    0.05616
AFIX  43
H199  2    0.798657    0.129970    0.511865    11.00000   -1.20000
AFIX   0
C200  1    0.764305    0.135456    0.580863    11.00000    0.20119    0.11944 =
```

```
      0.09555    0.00108    0.07091    0.03696
AFIX  43
H200  2    0.753146    0.176509    0.580920    11.00000   -1.20000
AFIX   0
C201  1    0.652733    0.170951    0.611823    11.00000    0.14755    0.09543 =
      0.07844   -0.02558   -0.00577    0.01990
C202  1    0.624438    0.140481    0.559162    11.00000    0.18129    0.15120 =
      0.10541   -0.04270   -0.04189    0.06803
AFIX  43
H202  2    0.641434    0.104013    0.544021    11.00000   -1.20000
AFIX   0
C203  1    0.569475    0.161801    0.525623    11.00000    0.19012    0.16890 =
      0.12974   -0.04735   -0.05349    0.07959
AFIX  43
H203  2    0.549525    0.139261    0.489228    11.00000   -1.20000
AFIX   0
C204  1    0.546152    0.216907    0.548237    11.00000    0.17818    0.15996 =
      0.13631   -0.04157   -0.04007    0.07214
AFIX  43
H204  2    0.510823    0.231928    0.525884    11.00000   -1.20000
AFIX   0
C205  1    0.570962    0.248563    0.598834    11.00000    0.15538    0.14038 =
      0.12744   -0.03163   -0.01495    0.04667
AFIX  43
H205  2    0.557455    0.286913    0.614525    11.00000   -1.20000
AFIX   0
C206  1    0.618795    0.218839    0.625784    11.00000    0.15052    0.11554 =
      0.10539   -0.02151   -0.00187    0.02889
AFIX  43
H206  2    0.631402    0.236135    0.663912    11.00000   -1.20000
AFIX   0
C207  1    0.329162    0.395549    0.747575    11.00000    0.02395    0.02773 =
      0.03596    0.01601    0.01881    0.01276
C208  1    0.281119    0.483059    0.751327    11.00000    0.03458    0.02788 =
      0.05321    0.02124    0.02107    0.01962
AFIX  43
H208  2    0.273684    0.524921    0.751271    11.00000   -1.20000
AFIX   0
C209  1    0.240007    0.440789    0.754430    11.00000    0.02358    0.03666 =
      0.04786    0.02645    0.01933    0.02288
AFIX  43
H209  2    0.199156    0.447291    0.758343    11.00000   -1.20000
AFIX   0
C210  1    0.242795    0.330057    0.754131    11.00000    0.01470    0.02962 =
      0.03467    0.01629    0.01992    0.01539
C211  1    0.216474    0.285064    0.706234    11.00000    0.01822    0.03565 =
```

```
      0.03509    0.00834    0.02011    0.01061
C212  1    0.190016    0.229393    0.712889    11.00000    0.04517    0.03542 =
      0.03736    0.00788    0.01100    0.00242
AFIX  43
H212  2    0.170644    0.197463    0.681275    11.00000   -1.20000
AFIX   0
C213  1    0.191331    0.220043    0.762643    11.00000    0.06202    0.03469 =
      0.03940    0.01551    0.01004   -0.00374
C214  1    0.219349    0.267894    0.808099    11.00000    0.05375    0.03273 =
      0.03574    0.01360    0.02658    0.00225
AFIX  43
H214  2    0.221337    0.261959    0.842757    11.00000   -1.20000
AFIX   0
C215  1    0.244079    0.322670    0.805981    11.00000    0.03473    0.03382 =
      0.03704    0.01634    0.02787    0.00576
C216  1    0.164769    0.161725    0.766877    11.00000    0.11552    0.04771 =
      0.07256    0.01273    0.03356   -0.02993
AFIX 137
H21A  2    0.122712    0.150881    0.740285    11.00000   -1.50000
H21B  2    0.161407    0.166625    0.803554    11.00000   -1.50000
H21C  2    0.192487    0.128804    0.759613    11.00000   -1.50000
AFIX   0
C217  1    0.273784    0.373464    0.857797    11.00000    0.04783    0.03837 =
      0.03743    0.01407    0.02028    0.00049
AFIX  13
H217  2    0.290350    0.407576    0.845811    11.00000   -1.20000
AFIX   0
C218  1    0.227136    0.400927    0.885139    11.00000    0.05628    0.05268 =
      0.03827    0.00519    0.01923    0.01118
C219  1    0.167287    0.380483    0.876736    11.00000    0.06035    0.08113 =
      0.06393   -0.01300    0.03280    0.01264
AFIX  43
H219  2    0.150644    0.344372    0.848379    11.00000   -1.20000
AFIX   0
C220  1    0.128564    0.406918    0.905218    11.00000    0.06652    0.10084 =
      0.08402   -0.02717    0.03831    0.01228
AFIX  43
H220  2    0.087252    0.387987    0.896772    11.00000   -1.20000
AFIX   0
C221  1    0.146569    0.458626    0.944703    11.00000    0.06561    0.09928 =
      0.08612   -0.03183    0.03956    0.01251
AFIX  43
H221  2    0.118664    0.477139    0.963937    11.00000   -1.20000
AFIX   0
C222  1    0.204714    0.483257    0.956156    11.00000    0.07649    0.09392 =
      0.08647   -0.02734    0.04228    0.00873
```

```
AFIX  43
H222  2    0.219364    0.520776    0.983265    11.00000   -1.20000
AFIX   0
C223  1    0.243621    0.453352    0.927936    11.00000    0.06634    0.07688 =
      0.07164   -0.01413    0.03300    0.00998
AFIX  43
H223  2    0.286076    0.470405    0.938933    11.00000   -1.20000
AFIX   0
C224  1    0.331522    0.352359    0.895663    11.00000    0.04709    0.04510 =
      0.05120    0.01763    0.01855    0.00287
C225  1    0.325268    0.333854    0.939757    11.00000    0.05928    0.05962 =
      0.04227    0.01570    0.02199    0.02064
AFIX  43
H225  2    0.285389    0.332150    0.946051    11.00000   -1.20000
AFIX   0
C226  1    0.382459    0.316676    0.977111    11.00000    0.07213    0.06741 =
      0.05205    0.01344    0.01154    0.02561
AFIX  43
H226  2    0.380917    0.304289    1.008547    11.00000   -1.20000
AFIX   0
C227  1    0.436909    0.319365    0.964597    11.00000    0.06125    0.06475 =
      0.06375    0.00742    0.00596    0.02300
AFIX  43
H227  2    0.473939    0.307382    0.987514    11.00000   -1.20000
AFIX   0
C228  1    0.441418    0.338463    0.920614    11.00000    0.05074    0.06196 =
      0.07866    0.01326    0.01552    0.01398
AFIX  43
H228  2    0.480543    0.340477    0.913070    11.00000   -1.20000
AFIX   0
C229  1    0.387105    0.354594    0.887835    11.00000    0.04883    0.06467 =
      0.06803    0.02509    0.02322    0.00576
AFIX  43
H229  2    0.389856    0.368346    0.857337    11.00000   -1.20000
AFIX   0
C230  1    0.210405    0.296201    0.652034    11.00000    0.03297    0.05679 =
      0.03604    0.01193    0.01978    0.00142
AFIX  13
H230  2    0.248368    0.323830    0.657160    11.00000   -1.20000
AFIX   0
C231  1    0.154059    0.330453    0.630976    11.00000    0.03735    0.07375 =
      0.04967    0.02735    0.01089    0.00520
C232  1    0.094134    0.313457    0.630484    11.00000    0.03876    0.08044 =
      0.06975    0.02490    0.02184    0.01552
AFIX  43
H232  2    0.088263    0.278123    0.643081    11.00000   -1.20000
```

```
AFIX   0
C233  1    0.042654    0.345151    0.612673    11.00000    0.04426    0.09651 =
     0.08360    0.03198    0.01854    0.02081
AFIX  43
H233  2    0.001924    0.331421    0.612246    11.00000   -1.20000
AFIX   0
C234  1    0.050602    0.396228    0.595715    11.00000    0.05218    0.10771 =
     0.07176    0.04239    0.00938    0.02801
AFIX  43
H234  2    0.015024    0.418318    0.583215    11.00000   -1.20000
AFIX   0
C235  1    0.111245    0.417506    0.596242    11.00000    0.05912    0.10864 =
     0.08295    0.05927    0.00174    0.01742
AFIX  43
H235  2    0.116732    0.453209    0.584003    11.00000   -1.20000
AFIX   0
C236  1    0.161424    0.384828    0.614968    11.00000    0.04636    0.09659 =
     0.06737    0.05119    0.00429    0.00946
AFIX  43
H236  2    0.202595    0.399425    0.617207    11.00000   -1.20000
AFIX   0
C237  1    0.214418    0.236182    0.610166    11.00000    0.05674    0.07430 =
     0.03930    0.00255    0.03314   -0.00187
C238  1    0.266186    0.200043    0.621467    11.00000    0.07208    0.06744 =
     0.05814   -0.00479    0.03751    0.00439
AFIX  43
H238  2    0.297450    0.212358    0.655908    11.00000   -1.20000
AFIX   0
C239  1    0.273744    0.147325    0.584744    11.00000    0.08594    0.08957 =
     0.06541   -0.01332    0.04235    0.01070
AFIX  43
H239  2    0.308073    0.122661    0.594271    11.00000   -1.20000
AFIX   0
C240  1    0.231239    0.132356    0.535588    11.00000    0.09751    0.09729 =
     0.06614   -0.02370    0.03786    0.00101
AFIX  43
H240  2    0.235446    0.095971    0.510178    11.00000   -1.20000
AFIX   0
C241  1    0.179348    0.169086    0.519557    11.00000    0.09627    0.09120 =
     0.05939   -0.01980    0.02240   -0.00832
AFIX  43
H241  2    0.151122    0.158171    0.483618    11.00000   -1.20000
AFIX   0
C242  1    0.170723    0.221481    0.557674    11.00000    0.07635    0.08841 =
     0.04715   -0.00955    0.02481   -0.00796
AFIX  43
```

```
H242  2    0.136407    0.246186    0.548230    11.00000   -1.20000
AFIX   0
C243  1    0.389607    0.487634    0.745896    11.00000    0.02932    0.03386 =
      0.03444    0.02361    0.01357    0.00988
C244  1    0.438723    0.513047    0.793466    11.00000    0.04243    0.04460 =
      0.03109    0.02202    0.01031   -0.00159
C245  1    0.489674    0.544869    0.788551    11.00000    0.04069    0.06146 =
      0.02431    0.01603    0.00690   -0.00823
AFIX  43
H245  2    0.522694    0.564211    0.820423    11.00000   -1.20000
AFIX   0
C246  1    0.493657    0.549141    0.739410    11.00000    0.04176    0.06972 =
      0.02644    0.01288    0.01325   -0.00632
C247  1    0.446108    0.521386    0.692329    11.00000    0.04294    0.05702 =
      0.02308    0.01772    0.01499    0.00077
AFIX  43
H247  2    0.449937    0.523202    0.658046    11.00000   -1.20000
AFIX   0
C248  1    0.392782    0.490869    0.694891    11.00000    0.03022    0.04751 =
      0.03031    0.01970    0.01404    0.00753
C249  1    0.548429    0.588176    0.734190    11.00000    0.07004    0.10625 =
      0.04224    0.01473    0.02028   -0.03672
AFIX 137
H24A  2    0.563694    0.622376    0.766731    11.00000   -1.50000
H24B  2    0.533123    0.604768    0.702110    11.00000   -1.50000
H24C  2    0.583051    0.562030    0.730435    11.00000   -1.50000
AFIX   0
C250  1    0.339301    0.458047    0.643506    11.00000    0.03717    0.05473 =
      0.03141    0.01039    0.01787    0.00921
AFIX  13
H250  2    0.301757    0.451806    0.655754    11.00000   -1.20000
AFIX   0
C251  1    0.319823    0.497424    0.603915    11.00000    0.04846    0.05475 =
      0.03232    0.01189    0.00026    0.00188
C252  1    0.275824    0.539841    0.609780    11.00000    0.07144    0.06982 =
      0.04378    0.01295   -0.00408    0.02206
AFIX  43
H252  2    0.257922    0.541641    0.638426    11.00000   -1.20000
AFIX   0
C253  1    0.256732    0.578352    0.578172    11.00000    0.08807    0.07666 =
      0.05029    0.02008   -0.00492    0.02431
AFIX  43
H253  2    0.225625    0.606211    0.583645    11.00000   -1.20000
AFIX   0
C254  1    0.283280    0.576729    0.537323    11.00000    0.09402    0.07417 =
      0.04498    0.01801   -0.01023    0.00904
```

```
AFIX  43
H254  2    0.269554    0.603976    0.514389    11.00000   -1.20000
AFIX   0
C255  1    0.328915    0.537484    0.527918    11.00000    0.07942    0.06327 =
      0.03464    0.01830   -0.00594   -0.00796
AFIX  43
H255  2    0.347227    0.537441    0.499786    11.00000   -1.20000
AFIX   0
C256  1    0.346642    0.497488    0.562656    11.00000    0.06588    0.05809 =
      0.02754    0.01269   -0.00079   -0.00952
AFIX  43
H256  2    0.377935    0.469625    0.557783    11.00000   -1.20000
AFIX   0
C257  1    0.357119    0.392001    0.619041    11.00000    0.04246    0.05564 =
      0.02858    0.01492    0.02031    0.01337
C258  1    0.312287    0.357219    0.571340    11.00000    0.04731    0.05355 =
      0.03081    0.01540    0.02366    0.00172
AFIX  43
H258  2    0.274626    0.374844    0.555614    11.00000   -1.20000
AFIX   0
C259  1    0.322564    0.298174    0.547443    11.00000    0.05720    0.05976 =
      0.03054    0.00906    0.02736    0.00132
AFIX  43
H259  2    0.293407    0.276203    0.514061    11.00000   -1.20000
AFIX   0
C260  1    0.374199    0.271066    0.571312    11.00000    0.06562    0.06406 =
      0.04046    0.01091    0.03646    0.01430
AFIX  43
H260  2    0.380129    0.229541    0.555485    11.00000   -1.20000
AFIX   0
C261  1    0.418256    0.303833    0.618698    11.00000    0.05432    0.06286 =
      0.04359    0.01597    0.02887    0.02368
AFIX  43
H261  2    0.454469    0.285124    0.635705    11.00000   -1.20000
AFIX   0
C262  1    0.408480    0.365345    0.641250    11.00000    0.04423    0.06174 =
      0.02949    0.01935    0.03119    0.02079
AFIX  43
H262  2    0.439269    0.388451    0.673109    11.00000   -1.20000
AFIX   0
C263  1    0.434359    0.508470    0.847794    11.00000    0.06340    0.05873 =
      0.03360    0.02122    0.02131   -0.00691
AFIX  13
H263  2    0.402452    0.473576    0.841209    11.00000   -1.20000
AFIX   0
C264  1    0.410053    0.568503    0.876326    11.00000    0.10123    0.08226 =
```

```
      0.07243    0.01991    0.05480    0.01248
C265  1    0.427200    0.624249    0.880920    11.00000    0.12470    0.07398 =
      0.09612    0.02948    0.05498    0.03354
AFIX  43
H265  2    0.458146    0.630591    0.864074    11.00000   -1.20000
AFIX   0
C266  1    0.406233    0.676027    0.907287    11.00000    0.13869    0.08807 =
      0.12320    0.02896    0.06369    0.04428
AFIX  43
H266  2    0.425557    0.716188    0.913512    11.00000   -1.20000
AFIX   0
C267  1    0.359292    0.666805    0.922850    11.00000    0.15050    0.11707 =
      0.14296    0.01179    0.08183    0.03599
AFIX  43
H267  2    0.349245    0.701086    0.947098    11.00000   -1.20000
AFIX   0
C268  1    0.322303    0.615488    0.909697    11.00000    0.14449    0.13484 =
      0.14681   -0.00244    0.09646    0.02538
AFIX  43
H268  2    0.280467    0.613453    0.912006    11.00000   -1.20000
AFIX   0
C269  1    0.355735    0.562049    0.890956    11.00000    0.13358    0.11968 =
      0.12774   -0.00186    0.09369    0.01087
AFIX  43
H269  2    0.339626    0.521773    0.888789    11.00000   -1.20000
AFIX   0
C270  1    0.495452    0.495098    0.885039    11.00000    0.08321    0.05399 =
      0.02929    0.02796    0.01486   -0.00690
C271  1    0.522647    0.525627    0.936681    11.00000    0.11416    0.06570 =
      0.03842    0.02140   -0.00279    0.01148
AFIX  43
H271  2    0.502238    0.559954    0.951030    11.00000   -1.20000
AFIX   0
C272  1    0.575333    0.512440    0.969624    11.00000    0.12135    0.07985 =
      0.06309    0.00991   -0.02349    0.01725
AFIX  43
H272  2    0.592559    0.536722    1.005828    11.00000   -1.20000
AFIX   0
C273  1    0.604895    0.460664    0.948635    11.00000    0.12125    0.08038 =
      0.07102    0.01721   -0.02220    0.02057
AFIX  43
H273  2    0.640427    0.447160    0.972066    11.00000   -1.20000
AFIX   0
C274  1    0.583230    0.429791    0.895296    11.00000    0.09664    0.07187 =
      0.06428    0.02163   -0.00243    0.00789
AFIX  43
```

```
H274  2    0.606620    0.398641    0.880359    11.00000   -1.20000
AFIX   0
C275  1    0.528275    0.443934    0.863984    11.00000    0.08309    0.06222 =
      0.04443    0.02245    0.01023    0.00191
AFIX  43
H275  2    0.510869    0.420041    0.827661    11.00000   -1.20000
AFIX   0
N1    3    1.140647    0.962239    0.751802    11.00000    0.03679    0.03018 =
      0.03588    0.00710    0.02483   -0.00037
N2    3    1.210760    0.894098    0.752482    11.00000    0.03668    0.02968 =
      0.03669    0.01730    0.02474   -0.00001
N3    3    0.767783    0.613526    0.737168    11.00000    0.02458    0.02412 =
      0.02114    0.01298    0.01358    0.00744
N4    3    0.839952    0.551577    0.745022    11.00000    0.02680    0.02833 =
      0.01762    0.01409    0.00845    0.00937
N5    3    0.643539    0.058840    0.752818    11.00000    0.02865    0.02166 =
      0.03770    0.01482    0.02154    0.00252
N6    3    0.712109    0.122574    0.748145    11.00000    0.03097    0.02134 =
      0.03410    0.01017    0.02707    0.00069
N7    3    0.268431    0.387360    0.750872    11.00000    0.01324    0.02875 =
      0.03708    0.02400    0.00842    0.01239
N8    3    0.335839    0.455453    0.748243    11.00000    0.02724    0.02740 =
      0.03786    0.01771    0.02072    0.01180
HKLF 4

REM  cnmsb4_20170609 in P-1
REM R1 =  0.1652 for   16314 Fo > 4sig(Fo)  and  0.2867 for all   35025 data
REM   2691 parameters refined using   4693 restraints

END

WGHT      0.1743    124.4652

REM Highest difference peak  1.061,  deepest hole -0.771,  1-sigma level  0.119
Q1    1   0.5949  0.1834  0.7840  11.00000  0.05    1.06
Q2    1   0.4807  0.2345  0.7665  11.00000  0.05    1.05
Q3    1   1.0029  0.7291  0.7495  11.00000  0.05    0.92
Q4    1   0.8963  0.6747  0.7800  11.00000  0.05    0.90
Q5    1   1.0960  0.8404  0.7806  11.00000  0.05    0.90
Q6    1   0.8335  0.0814  0.6035  11.00000  0.05    0.89
Q7    1   0.5399  0.1866  0.7315  11.00000  0.05    0.82
Q8    1   0.7983  0.1299  0.6301  11.00000  0.05    0.82
Q9    1   0.6630  0.1944  0.5520  11.00000  0.05    0.82
Q10   1   0.9585  0.8261  0.7537  11.00000  0.05    0.76
Q11   1   0.7798  0.1196  0.6208  11.00000  0.05    0.75
Q12   1   0.3412  0.3503  0.7408  11.00000  0.05    0.73
```

```
Q13   1   0.3639  0.3699  0.7442  11.00000  0.05    0.73
Q14   1   0.3833  0.3215  0.7008  11.00000  0.05    0.70
Q15   1   0.4992 -0.0967  0.5725  11.00000  0.05    0.66
Q16   1   0.5791  0.2385  0.5224  11.00000  0.05    0.65
Q17   1   0.4222  0.3370  0.7319  11.00000  0.05    0.64
Q18   1   0.4359  0.3380  0.7485  11.00000  0.05    0.64
Q19   1   0.5484  0.2535  0.7669  11.00000  0.05    0.64
Q20   1   0.6199  0.1991  0.5125  11.00000  0.05    0.64
;
_shelx_res_checksum   30904
```

CIF files for the Cu_2CS_3

```
data_monoclinicC

_audit_creation_method            'SHELXL-2014/7'
_shelx_SHELXL_version_number      '2014/7'
_chemical_name_systematic         ?
_chemical_name_common             ?
_chemical_melting_point           ?
_chemical_formula_moiety          ?
_chemical_formula_sum
 'C139 H112 Cu2 N4 S3'
_chemical_formula_weight          2061.58

# start Validation Reply Form
_vrf_PLAT602_monoclinicC
;
PROBLEM: VERY LARGE Solvent Accessible VOID(S) in Structure        ! Info
RESPONSE: PLATON/SQUEEZE were used to treat highly disordered solvent molecules.
;
# end Validation Reply Form

loop_
 _atom_type_symbol
 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'C'  'C'   0.0033   0.0016
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'H'  'H'   0.0000   0.0000
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'N'  'N'   0.0061   0.0033
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'S'  'S'   0.1246   0.1234
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Cu'  'Cu'   0.3201   1.2651
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_space_group_crystal_system       monoclinic
_space_group_IT_number            15
_space_group_name_H-M_alt         'C 2/c'
_space_group_name_Hall            '-C 2yc'
```

```
_shelx_space_group_comment
;
The symmetry employed for this shelxl refinement is uniquely defined
by the following loop, which should always be used as a source of
symmetry information in preference to the above space-group names.
They are only intended as comments.
;

loop_
 _space_group_symop_operation_xyz
 'x, y, z'
 '-x, y, -z+1/2'
 'x+1/2, y+1/2, z'
 '-x+1/2, y+1/2, -z+1/2'
 '-x, -y, -z'
 'x, -y, z-1/2'
 '-x+1/2, -y+1/2, -z'
 'x+1/2, -y+1/2, z-1/2'

_cell_length_a                    26.864(10)
_cell_length_b                    28.131(11)
_cell_length_c                    18.999(7)
_cell_angle_alpha                 90
_cell_angle_beta                  90
_cell_angle_gamma                 90
_cell_volume                      14357(9)
_cell_formula_units_Z             4
_cell_measurement_temperature     293(2)
_cell_measurement_reflns_used     9826
_cell_measurement_theta_min       2.30
_cell_measurement_theta_max       24.79

_exptl_crystal_description        plate
_exptl_crystal_colour             pink
_exptl_crystal_density_meas       ?
_exptl_crystal_density_method     ?
_exptl_crystal_density_diffrn     0.954
_exptl_crystal_F_000              4320
_exptl_transmission_factor_min    0.767
_exptl_transmission_factor_max    0.929
_exptl_crystal_size_max           0.400
_exptl_crystal_size_mid           0.300
_exptl_crystal_size_min           0.100
_exptl_absorpt_coefficient_mu     0.382
_shelx_estimated_absorpt_T_min    0.862
_shelx_estimated_absorpt_T_max    0.963
```

```
_exptl_absorpt_correction_type     multi-scan
_exptl_absorpt_correction_T_min    ?
_exptl_absorpt_correction_T_max    ?
_exptl_absorpt_process_details     ?
_exptl_absorpt_special_details     ?
_diffrn_ambient_temperature        293(2)
_diffrn_radiation_wavelength       0.71073
_diffrn_radiation_type             MoK\a
_diffrn_source                     ?
_diffrn_measurement_device_type    'Bruker APEX-II CCD'
_diffrn_measurement_method         '\f and \w scans'
_diffrn_detector_area_resol_mean   ?
_diffrn_reflns_number              91297
_diffrn_reflns_av_unetI/netI       0.1878
_diffrn_reflns_av_R_equivalents    0.2106
_diffrn_reflns_limit_h_min         -35
_diffrn_reflns_limit_h_max         32
_diffrn_reflns_limit_k_min         -36
_diffrn_reflns_limit_k_max         36
_diffrn_reflns_limit_l_min         -24
_diffrn_reflns_limit_l_max         24
_diffrn_reflns_theta_min           1.801
_diffrn_reflns_theta_max           27.876
_diffrn_reflns_theta_full          25.242
_diffrn_measured_fraction_theta_max    0.997
_diffrn_measured_fraction_theta_full   0.998
_diffrn_reflns_Laue_measured_fraction_max    0.997
_diffrn_reflns_Laue_measured_fraction_full   0.998
_diffrn_reflns_point_group_measured_fraction_max    0.997
_diffrn_reflns_point_group_measured_fraction_full   0.998
_reflns_number_total               17085
_reflns_number_gt                  7281
_reflns_threshold_expression       'I > 2\s(I)'
_reflns_Friedel_coverage           0.000
_reflns_Friedel_fraction_max       .
_reflns_Friedel_fraction_full      .

_reflns_special_details
;
 Reflections were merged by SHELXL according to the crystal
 class for the calculation of statistics and refinement.

 _reflns_Friedel_fraction is defined as the number of unique
 Friedel pairs measured divided by the number that would be
 possible theoretically, ignoring centric projections and
 systematic absences.
```

```
;

_computing_data_collection        'Bruker APEX2'
_computing_cell_refinement        'Bruker SAINT'
_computing_data_reduction         'Bruker SAINT'
_computing_structure_solution     'SHELXS-97 (Sheldrick 2008)'
_computing_structure_refinement 'SHELXL-2014/7 (Sheldrick, 2014)'
_computing_molecular_graphics     'Bruker SHELXTL'
_computing_publication_material   'Bruker SHELXTL'
_refine_special_details           ?
_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
'w=1/[\s^2^(Fo^2^)+(0.1000P)^2^+0.8965P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      ?
_atom_sites_solution_secondary    ?
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     constr
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        .
_refine_ls_number_reflns          17085
_refine_ls_number_parameters      670
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.2165
_refine_ls_R_factor_gt            0.1134
_refine_ls_wR_factor_ref          0.3028
_refine_ls_wR_factor_gt           0.2661
_refine_ls_goodness_of_fit_ref    1.196
_refine_ls_restrained_S_all       1.196
_refine_ls_shift/su_max           0.001
_refine_ls_shift/su_mean          0.000

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 _atom_site_type_symbol
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 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_site_symmetry_order
 _atom_site_calc_flag
 _atom_site_refinement_flags_posn
 _atom_site_refinement_flags_adp
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_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
Cu1 Cu 0.89703(3) 0.32833(2) 0.76227(3) 0.0572(3) Uani 1 1 d . . . . .
S2 S 1.0000 0.35881(7) 0.7500 0.1119(12) Uani 1 2 d S T P . .
S1 S 0.94767(6) 0.26883(6) 0.77097(13) 0.0934(7) Uani 1 1 d . . . . .
C31 C 0.7745(2) 0.34603(17) 0.9346(2) 0.0438(12) Uani 1 1 d . . . . .
C2 C 0.76443(18) 0.40083(17) 0.7738(2) 0.0433(12) Uani 1 1 d . . . . .
H2 H 0.7424 0.4220 0.7949 0.052 Uiso 1 1 calc R U . . .
C42 C 0.82865(19) 0.32552(16) 0.5900(2) 0.0443(12) Uani 1 1 d . . . . .
C70 C 1.0000 0.2978(3) 0.7500 0.064(2) Uani 1 2 d S T P . .
C24 C 0.83117(18) 0.34636(15) 0.9286(2) 0.0402(11) Uani 1 1 d . . . . .
H24 H 0.8391 0.3256 0.8887 0.048 Uiso 1 1 calc R U . . .
N2 N 0.79834(15) 0.34703(12) 0.70695(16) 0.0368(9) Uani 1 1 d . . . . .
N1 N 0.81326(14) 0.39035(12) 0.79489(17) 0.0374(9) Uani 1 1 d . . . . .
C58 C 0.8125(2) 0.41125(19) 0.5538(2) 0.0491(13) Uani 1 1 d . . . . .
C1 C 0.83558(17) 0.35634(14) 0.7557(2) 0.0349(10) Uani 1 1 d . . . . .
C3 C 0.75634(19) 0.37445(17) 0.7177(2) 0.0443(12) Uani 1 1 d . . . . .
H3 H 0.7276 0.3743 0.6904 0.053 Uiso 1 1 calc R U . . .
C7 C 0.90234(18) 0.46272(15) 0.9391(2) 0.0386(11) Uani 1 1 d . . . . .
C4 C 0.84207(16) 0.41613(15) 0.8469(2) 0.0333(10) Uani 1 1 d . . . . .
C5 C 0.85914(17) 0.46012(15) 0.8284(2) 0.0348(10) Uani 1 1 d . . . . .
C9 C 0.85264(16) 0.39398(14) 0.9106(2) 0.0313(10) Uani 1 1 d . . . . .
C6 C 0.88927(18) 0.48384(16) 0.8759(2) 0.0433(12) Uani 1 1 d . . . . .
H6 H 0.9008 0.5142 0.8653 0.052 Uiso 1 1 calc R U . . .
C8 C 0.88323(17) 0.41847(16) 0.9550(2) 0.0389(11) Uani 1 1 d . . . . .
H8 H 0.8916 0.4047 0.9980 0.047 Uiso 1 1 calc R U . . .
C10 C 0.9389(2) 0.48617(17) 0.9872(2) 0.0487(13) Uani 1 1 d . . . . .
H10A H 0.9297 0.4801 1.0352 0.073 Uiso 1 1 calc R U . . .
H10B H 0.9388 0.5198 0.9788 0.073 Uiso 1 1 calc R U . . .
H10C H 0.9715 0.4737 0.9785 0.073 Uiso 1 1 calc R U . . .
C13 C 0.8992(2) 0.55236(17) 0.7154(2) 0.0526(13) Uani 1 1 d . . . . .
H13 H 0.8753 0.5740 0.7303 0.063 Uiso 1 1 calc R U . . .
C12 C 0.89229(19) 0.50354(16) 0.7241(2) 0.0415(12) Uani 1 1 d . . . . .
C17 C 0.9296(2) 0.47252(17) 0.7028(2) 0.0460(12) Uani 1 1 d . . . . .
H17 H 0.9255 0.4400 0.7097 0.055 Uiso 1 1 calc R U . . .
C11 C 0.84622(18) 0.48370(15) 0.7581(2) 0.0403(11) Uani 1 1 d . . . . .
H11 H 0.8349 0.4580 0.7272 0.048 Uiso 1 1 calc R U . . .
C15 C 0.9785(2) 0.5369(2) 0.6630(2) 0.0566(14) Uani 1 1 d . . . . .
H15 H 1.0076 0.5483 0.6423 0.068 Uiso 1 1 calc R U . . .
C16 C 0.9720(2) 0.48854(19) 0.6723(2) 0.0524(13) Uani 1 1 d . . . . .
H16 H 0.9964 0.4673 0.6578 0.063 Uiso 1 1 calc R U . . .
C14 C 0.9432(2) 0.5675(2) 0.6838(3) 0.0596(15) Uani 1 1 d . . . . .
H14 H 0.9482 0.5998 0.6768 0.072 Uiso 1 1 calc R U . . .
C18 C 0.8027(2) 0.51731(17) 0.7647(2) 0.0499(13) Uani 1 1 d . . . . .
C19 C 0.7894(2) 0.5411(2) 0.8243(3) 0.0633(16) Uani 1 1 d . . . . .

H19 H 0.8076 0.5366 0.8655 0.076 Uiso 1 1 calc R U . . .
C22 C 0.7353(3) 0.5579(3) 0.7063(4) 0.106(3) Uani 1 1 d . . . . .
H22 H 0.7159 0.5629 0.6664 0.127 Uiso 1 1 calc R U . . .
C23 C 0.7755(3) 0.5266(2) 0.7048(3) 0.090(2) Uani 1 1 d . . . . .
H23 H 0.7840 0.5117 0.6627 0.108 Uiso 1 1 calc R U . . .
C20 C 0.7496(3) 0.5718(2) 0.8243(4) 0.084(2) Uani 1 1 d . . . . .
H20 H 0.7398 0.5864 0.8659 0.101 Uiso 1 1 calc R U . . .
C21 C 0.7253(3) 0.5806(3) 0.7656(4) 0.091(2) Uani 1 1 d . . . . .
H21 H 0.7003 0.6034 0.7659 0.109 Uiso 1 1 calc R U . . .
C25 C 0.85568(19) 0.32391(17) 0.9920(2) 0.0421(12) Uani 1 1 d . . . . .
C30 C 0.8921(2) 0.29089(19) 0.9838(3) 0.0533(13) Uani 1 1 d . . . . .
H30 H 0.9020 0.2818 0.9388 0.064 Uiso 1 1 calc R U . . .
C26 C 0.8424(2) 0.33803(18) 1.0607(2) 0.0512(13) Uani 1 1 d . . . . .
H26 H 0.8177 0.3607 1.0673 0.061 Uiso 1 1 calc R U . . .
C27 C 0.8657(2) 0.3185(2) 1.1171(3) 0.0568(15) Uani 1 1 d . . . . .
H27 H 0.8566 0.3277 1.1623 0.068 Uiso 1 1 calc R U . . .
C29 C 0.9147(2) 0.2706(2) 1.0430(3) 0.0764(18) Uani 1 1 d . . . . .
H29 H 0.9384 0.2467 1.0378 0.092 Uiso 1 1 calc R U . . .
C28 C 0.9015(3) 0.2863(3) 1.1082(3) 0.0734(19) Uani 1 1 d . . . . .
H28 H 0.9180 0.2743 1.1475 0.088 Uiso 1 1 calc R U . . .
C32 C 0.7473(2) 0.38623(19) 0.9450(2) 0.0489(13) Uani 1 1 d . . . . .
H32 H 0.7633 0.4154 0.9495 0.059 Uiso 1 1 calc R U . . .
C33 C 0.6965(2) 0.3841(2) 0.9491(2) 0.0560(14) Uani 1 1 d . . . . .
H33 H 0.6781 0.4117 0.9559 0.067 Uiso 1 1 calc R U . . .
C34 C 0.6724(3) 0.3403(3) 0.9430(3) 0.0706(18) Uani 1 1 d . . . . .
H34 H 0.6379 0.3384 0.9453 0.085 Uiso 1 1 calc R U . . .
C36 C 0.7498(2) 0.30372(19) 0.9308(3) 0.0606(15) Uani 1 1 d . . . . .
H36 H 0.7682 0.2759 0.9260 0.073 Uiso 1 1 calc R U . . .
C35 C 0.7003(3) 0.3008(2) 0.9335(3) 0.0783(19) Uani 1 1 d . . . . .
H35 H 0.6849 0.2714 0.9290 0.094 Uiso 1 1 calc R U . . .
C41 C 0.8324(2) 0.29281(18) 0.5373(2) 0.0531(14) Uani 1 1 d . . . . .
H41 H 0.8486 0.3010 0.4958 0.064 Uiso 1 1 calc R U . . .
C37 C 0.80433(18) 0.31259(16) 0.6510(2) 0.0410(12) Uani 1 1 d . . . . .
C46 C 0.6942(2) 0.1902(2) 0.6995(2) 0.0596(15) Uani 1 1 d . . . . .
H46 H 0.7191 0.1673 0.6991 0.072 Uiso 1 1 calc R U . . .
C40 C 0.8126(2) 0.24753(18) 0.5444(2) 0.0566(14) Uani 1 1 d . . . . .
C39 C 0.7891(2) 0.23502(18) 0.6057(2) 0.0584(15) Uani 1 1 d . . . . .
H39 H 0.7764 0.2045 0.6108 0.070 Uiso 1 1 calc R U . . .
C44 C 0.7587(2) 0.25308(17) 0.7299(2) 0.0520(14) Uani 1 1 d . . . . .
H44 H 0.7558 0.2819 0.7586 0.062 Uiso 1 1 calc R U . . .
C38 C 0.7841(2) 0.26783(17) 0.6608(2) 0.0493(13) Uani 1 1 d . . . . .
C45 C 0.7068(2) 0.2367(2) 0.7156(2) 0.0541(14) Uani 1 1 d . . . . .
C47 C 0.6469(3) 0.1770(3) 0.6842(3) 0.0693(17) Uani 1 1 d . . . . .
H47 H 0.6395 0.1455 0.6734 0.083 Uiso 1 1 calc R U . . .
C43 C 0.8170(2) 0.2113(2) 0.4847(3) 0.0712(18) Uani 1 1 d . . . . .
H43A H 0.8270 0.1811 0.5036 0.107 Uiso 1 1 calc R U . . .

H43B H 0.8414 0.2220 0.4514 0.107 Uiso 1 1 calc R U . . .
H43C H 0.7854 0.2081 0.4617 0.107 Uiso 1 1 calc R U . . .
C48 C 0.6107(3) 0.2104(3) 0.6851(3) 0.0791(19) Uani 1 1 d . . . . .
H48 H 0.5783 0.2012 0.6743 0.095 Uiso 1 1 calc R U . . .
C50 C 0.6676(3) 0.2690(2) 0.7177(3) 0.078(2) Uani 1 1 d . . . . .
H50 H 0.6739 0.3003 0.7309 0.094 Uiso 1 1 calc R U . . .
C49 C 0.6193(3) 0.2560(3) 0.7006(4) 0.0831(19) Uani 1 1 d . . . . .
H49 H 0.5937 0.2782 0.7000 0.100 Uiso 1 1 calc R U . . .
C53 C 0.7939(3) 0.1702(2) 0.8766(3) 0.076(2) Uani 1 1 d . . . . .
H53 H 0.7789 0.1574 0.9165 0.091 Uiso 1 1 calc R U . . .
C56 C 0.8369(2) 0.2076(2) 0.7579(3) 0.0638(16) Uani 1 1 d . . . . .
H56 H 0.8514 0.2203 0.7176 0.077 Uiso 1 1 calc R U . . .
C52 C 0.7677(2) 0.19888(19) 0.8326(3) 0.0552(14) Uani 1 1 d . . . . .
H52 H 0.7347 0.2059 0.8430 0.066 Uiso 1 1 calc R U . . .
C51 C 0.7892(2) 0.21786(18) 0.7726(2) 0.0505(14) Uani 1 1 d . . . . .
C54 C 0.8417(3) 0.1606(3) 0.8617(3) 0.089(2) Uani 1 1 d . . . . .
H54 H 0.8597 0.1415 0.8925 0.107 Uiso 1 1 calc R U . . .
C55 C 0.8654(3) 0.1784(2) 0.8015(3) 0.0733(18) Uani 1 1 d . . . . .
H55 H 0.8983 0.1711 0.7912 0.088 Uiso 1 1 calc R U . . .
C57 C 0.85000(19) 0.37589(16) 0.5814(2) 0.0454(12) Uani 1 1 d . . . . .
H57 H 0.8588 0.3866 0.6289 0.054 Uiso 1 1 calc R U . . .
C63 C 0.8261(2) 0.45922(19) 0.5499(3) 0.0581(14) Uani 1 1 d . . . . .
H63 H 0.8579 0.4684 0.5637 0.070 Uiso 1 1 calc R U . . .
C61 C 0.7473(3) 0.4800(3) 0.5077(3) 0.0793(19) Uani 1 1 d . . . . .
H61 H 0.7254 0.5032 0.4916 0.095 Uiso 1 1 calc R U . . .
C59 C 0.7653(2) 0.3998(2) 0.5347(3) 0.0695(17) Uani 1 1 d . . . . .
H59 H 0.7551 0.3683 0.5369 0.083 Uiso 1 1 calc R U . . .
C62 C 0.7935(3) 0.4926(2) 0.5262(3) 0.0683(16) Uani 1 1 d . . . . .
H62 H 0.8034 0.5242 0.5229 0.082 Uiso 1 1 calc R U . . .
C60 C 0.7316(3) 0.4346(3) 0.5117(4) 0.093(2) Uani 1 1 d . . . . .
H60 H 0.6992 0.4265 0.4995 0.111 Uiso 1 1 calc R U . . .
C64 C 0.8977(2) 0.37468(16) 0.5407(2) 0.0447(12) Uani 1 1 d . . . . .
C69 C 0.9422(2) 0.36582(18) 0.5757(2) 0.0504(13) Uani 1 1 d . . . . .
H69 H 0.9420 0.3616 0.6243 0.060 Uiso 1 1 calc R U . . .
C65 C 0.9003(2) 0.38110(17) 0.4671(2) 0.0513(13) Uani 1 1 d . . . . .
H65 H 0.8714 0.3878 0.4418 0.062 Uiso 1 1 calc R U . . .
C67 C 0.9879(2) 0.36832(19) 0.4678(3) 0.0618(15) Uani 1 1 d . . . . .
H67 H 1.0178 0.3656 0.4434 0.074 Uiso 1 1 calc R U . . .
C66 C 0.9441(2) 0.37760(17) 0.4331(3) 0.0538(14) Uani 1 1 d . . . . .
H66 H 0.9448 0.3816 0.3845 0.065 Uiso 1 1 calc R U . . .
C68 C 0.9861(2) 0.36320(19) 0.5400(3) 0.0584(14) Uani 1 1 d . . . . .
H68 H 1.0155 0.3579 0.5647 0.070 Uiso 1 1 calc R U . . .

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Cu1 0.0702(5) 0.0665(5) 0.0349(3) 0.0066(3) 0.0086(3) 0.0180(4)
S2 0.217(3) 0.0414(11) 0.0776(16) 0.000 -0.090(2) 0.000
S1 0.0563(10) 0.0560(9) 0.168(2) -0.0124(11) -0.0005(12) 0.0041(8)
C31 0.057(3) 0.052(3) 0.023(2) 0.000(2) 0.001(2) -0.006(3)
C2 0.044(3) 0.052(3) 0.034(2) 0.006(2) -0.004(2) 0.005(2)
C42 0.062(3) 0.042(3) 0.029(2) -0.003(2) 0.003(2) -0.014(2)
C70 0.065(5) 0.048(4) 0.080(6) 0.000 -0.027(4) 0.000
C24 0.056(3) 0.041(3) 0.024(2) -0.0009(18) 0.000(2) -0.002(2)
N2 0.052(3) 0.041(2) 0.0171(16) 0.0027(15) -0.0012(16) -0.0106(19)
N1 0.049(2) 0.038(2) 0.0254(17) 0.0004(15) -0.0019(17) -0.0058(18)
C58 0.053(3) 0.069(4) 0.025(2) 0.004(2) 0.004(2) -0.025(3)
C1 0.048(3) 0.033(2) 0.024(2) 0.0004(18) 0.002(2) -0.009(2)
C3 0.051(3) 0.053(3) 0.029(2) 0.007(2) -0.002(2) -0.003(3)
C7 0.054(3) 0.043(3) 0.0189(19) -0.0030(18) -0.001(2) -0.011(2)
C4 0.033(3) 0.040(2) 0.027(2) -0.0089(18) 0.0028(19) -0.006(2)
C5 0.045(3) 0.039(2) 0.0209(19) -0.0054(18) -0.0026(19) -0.003(2)
C9 0.037(3) 0.035(2) 0.0225(19) -0.0018(17) 0.0008(18) -0.004(2)
C6 0.054(3) 0.039(3) 0.037(2) -0.005(2) 0.006(2) -0.006(2)
C8 0.046(3) 0.044(3) 0.026(2) 0.0069(19) 0.003(2) -0.002(2)
C10 0.062(3) 0.049(3) 0.036(2) -0.002(2) -0.008(2) -0.008(3)
C13 0.075(4) 0.046(3) 0.036(3) 0.006(2) 0.003(3) -0.002(3)
C12 0.056(3) 0.046(3) 0.022(2) 0.0049(19) -0.004(2) -0.005(3)
C17 0.059(3) 0.042(3) 0.037(3) 0.011(2) -0.009(2) -0.003(3)
C11 0.052(3) 0.035(2) 0.034(2) 0.0000(19) -0.005(2) -0.009(2)
C15 0.064(4) 0.075(4) 0.031(2) 0.014(3) 0.005(3) -0.010(3)
C16 0.063(4) 0.057(3) 0.037(3) 0.011(2) -0.002(3) -0.001(3)
C14 0.091(5) 0.055(3) 0.033(3) 0.013(2) 0.002(3) -0.012(3)
C18 0.067(4) 0.045(3) 0.037(3) 0.002(2) -0.016(2) -0.001(3)
C19 0.075(4) 0.071(4) 0.044(3) 0.011(3) 0.006(3) 0.020(3)
C22 0.133(7) 0.089(5) 0.098(6) -0.025(4) -0.065(5) 0.049(5)
C23 0.130(6) 0.084(4) 0.057(4) -0.023(3) -0.038(4) 0.039(5)
C20 0.105(6) 0.078(4) 0.069(4) 0.007(3) 0.003(4) 0.027(4)
C21 0.089(5) 0.085(5) 0.099(6) -0.009(4) -0.025(5) 0.022(4)
C25 0.052(3) 0.047(3) 0.027(2) 0.006(2) -0.001(2) -0.012(3)
C30 0.057(3) 0.060(3) 0.043(3) 0.009(2) 0.002(3) -0.011(3)
C26 0.060(3) 0.065(3) 0.028(2) 0.003(2) 0.002(2) -0.013(3)
C27 0.061(4) 0.075(4) 0.034(3) 0.017(3) -0.010(3) -0.029(3)
C29 0.066(4) 0.086(4) 0.076(4) 0.033(4) -0.002(3) -0.001(4)
C28 0.080(5) 0.100(5) 0.041(3) 0.028(3) -0.021(3) -0.036(4)
C32 0.058(4) 0.053(3) 0.035(2) 0.004(2) 0.001(2) -0.010(3)
C33 0.062(4) 0.065(4) 0.042(3) 0.008(2) 0.007(3) -0.001(3)

C34 0.068(4) 0.098(5) 0.046(3) 0.015(3) -0.012(3) -0.028(4)
C36 0.075(4) 0.054(3) 0.053(3) 0.003(3) -0.011(3) -0.019(3)
C35 0.079(5) 0.072(4) 0.084(5) 0.000(4) -0.020(4) -0.031(4)
C41 0.070(4) 0.059(3) 0.030(2) 0.001(2) 0.006(2) -0.033(3)
C37 0.057(3) 0.052(3) 0.0147(19) -0.0023(18) 0.000(2) -0.012(2)
C46 0.081(4) 0.070(4) 0.028(2) 0.001(2) -0.008(3) -0.025(3)
C40 0.081(4) 0.055(3) 0.034(3) -0.015(2) 0.012(3) -0.016(3)
C39 0.089(4) 0.051(3) 0.035(3) -0.006(2) 0.015(3) -0.029(3)
C44 0.076(4) 0.046(3) 0.034(2) -0.009(2) 0.008(3) -0.020(3)
C38 0.073(4) 0.050(3) 0.025(2) -0.001(2) 0.006(2) -0.023(3)
C45 0.073(4) 0.060(3) 0.029(2) 0.000(2) 0.007(3) -0.020(3)
C47 0.090(5) 0.089(5) 0.029(3) -0.005(3) -0.003(3) -0.012(4)
C43 0.098(5) 0.070(4) 0.046(3) -0.023(3) 0.021(3) -0.049(4)
C48 0.094(6) 0.095(5) 0.048(3) -0.003(3) 0.000(3) -0.027(5)
C50 0.114(6) 0.070(4) 0.051(3) -0.004(3) 0.016(4) -0.027(4)
C49 0.078(5) 0.093(5) 0.078(5) 0.003(4) -0.002(4) -0.003(4)
C53 0.082(5) 0.109(5) 0.037(3) 0.016(3) -0.003(3) -0.043(4)
C56 0.067(4) 0.082(4) 0.043(3) 0.015(3) -0.002(3) -0.030(3)
C52 0.056(3) 0.070(4) 0.039(3) 0.002(3) -0.001(3) -0.014(3)
C51 0.066(4) 0.054(3) 0.031(2) 0.001(2) -0.007(2) -0.032(3)
C54 0.081(5) 0.133(6) 0.054(4) 0.025(4) -0.019(4) -0.030(5)
C55 0.069(4) 0.088(5) 0.063(4) -0.001(3) -0.009(3) -0.029(4)
C57 0.066(3) 0.050(3) 0.020(2) -0.0062(19) 0.001(2) -0.019(3)
C63 0.063(4) 0.056(3) 0.056(3) -0.005(3) 0.007(3) -0.014(3)
C61 0.090(5) 0.086(5) 0.062(4) 0.028(3) 0.005(4) 0.012(4)
C59 0.089(5) 0.057(3) 0.063(4) 0.022(3) -0.002(3) -0.017(4)
C62 0.082(5) 0.069(4) 0.054(3) 0.011(3) 0.003(3) -0.003(4)
C60 0.079(5) 0.094(5) 0.105(6) 0.032(4) -0.034(4) -0.019(4)
C64 0.064(3) 0.045(3) 0.025(2) 0.0063(19) 0.002(2) -0.027(3)
C69 0.056(4) 0.063(3) 0.032(2) 0.000(2) 0.002(3) -0.003(3)
C65 0.066(4) 0.055(3) 0.032(2) -0.003(2) 0.004(3) -0.012(3)
C67 0.069(4) 0.060(3) 0.056(3) -0.007(3) 0.019(3) -0.010(3)
C66 0.073(4) 0.054(3) 0.034(3) 0.003(2) 0.006(3) -0.021(3)
C68 0.051(3) 0.069(4) 0.055(3) 0.000(3) -0.009(3) -0.004(3)

_geom_special_details
;
All esds (except the esd in the dihedral angle between two l.s. planes)
are estimated using the full covariance matrix. The cell esds are taken
into account individually in the estimation of esds in distances, angles
and torsion angles; correlations between esds in cell parameters are only
used when they are defined by crystal symmetry. An approximate (isotropic)
treatment of cell esds is used for estimating esds involving l.s. planes.
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loop_

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S1 C70 1.673(4) . ?
C31 C32 1.362(7) . ?
C31 C36 1.364(7) . ?
C31 C24 1.527(7) . ?
C2 C3 1.316(6) . ?
C2 N1 1.403(6) . ?
C2 H2 0.9300 . ?
C42 C41 1.363(6) . ?
C42 C37 1.379(6) . ?
C42 C57 1.537(6) . ?
C70 S1 1.673(4) 2_756 ?
C24 C9 1.498(6) . ?
C24 C25 1.511(6) . ?
C24 H24 0.9800 . ?
N2 C3 1.382(6) . ?
N2 C1 1.388(5) . ?
N2 C37 1.448(5) . ?
N1 C1 1.353(5) . ?
N1 C4 1.449(5) . ?
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C58 C63 1.400(7) . ?
C58 C57 1.509(7) . ?
C3 H3 0.9300 . ?
C7 C8 1.380(6) . ?
C7 C6 1.384(6) . ?
C7 C10 1.494(6) . ?
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C5 C11 1.532(6) . ?
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C8 H8 0.9300 . ?
C10 H10A 0.9600 . ?
C10 H10B 0.9600 . ?
C10 H10C 0.9600 . ?
C13 C14 1.391(8) . ?
C13 C12 1.396(6) . ?
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S1 C70 S2 119.1(2) 2_756 . ?
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C31 C24 H24 105.8 . . ?
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C3 N2 C37 125.0(4) . . ?
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C1 N1 C2 113.9(4) . . ?
C1 N1 C4 119.5(4) . . ?
C2 N1 C4 126.1(4) . . ?
C59 C58 C63 117.3(5) . . ?
C59 C58 C57 124.1(5) . . ?
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N2 C3 H3 126.3 . . ?
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    monoclinicC.res created by SHELXL-2014/7


TITL monoclinicC in C2/c
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ZERR    4.00   0.01000   0.01070   0.00690   0.0000   0.0000   0.0000
LATT 7
SYMM -X, Y, 0.5-Z
SFAC C  H  N  S  Cu
UNIT 556  448  16  12  8
L.S. 11
BOND $H
ACTA
FMAP 2
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PLAN 20
SIZE 0.100 0.300 0.400
WGHT    0.100000    0.896500
FVAR       0.36326
MOLE 1
CU1   5    0.897035    0.328330    0.762272    11.00000    0.07022    0.06649 =
      0.03492    0.00659    0.00862    0.01800
S2    4    1.000000    0.358808    0.750000    10.50000    0.21666    0.04139 =
      0.07757    0.00000   -0.08981    0.00000
S1    4    0.947672    0.268830    0.770968    11.00000    0.05626    0.05604 =
      0.16776   -0.01235   -0.00050    0.00412
C31   1    0.774503    0.346031    0.934597    11.00000    0.05667    0.05191 =
      0.02271    0.00046    0.00056   -0.00606
C2    1    0.764425    0.400835    0.773776    11.00000    0.04417    0.05190 =
      0.03367    0.00599   -0.00353    0.00487
AFIX  43
H2    2    0.742412    0.421973    0.794935    11.00000   -1.20000
AFIX   0
C42   1    0.828651    0.325522    0.589972    11.00000    0.06231    0.04179 =
      0.02871   -0.00322    0.00270   -0.01426
C70   1    1.000000    0.297794    0.750000    10.50000    0.06544    0.04824 =
      0.07955    0.00000   -0.02697    0.00000
C24   1    0.831166    0.346360    0.928572    11.00000    0.05632    0.04062 =
      0.02355   -0.00089   -0.00022   -0.00187
AFIX  13
H24   2    0.839138    0.325622    0.888687    11.00000   -1.20000
AFIX   0
N2    3    0.798336    0.347032    0.706954    11.00000    0.05243    0.04088 =
      0.01711    0.00268   -0.00116   -0.01060
N1    3    0.813255    0.390347    0.794890    11.00000    0.04925    0.03753 =
      0.02545    0.00035   -0.00192   -0.00581
C58   1    0.812519    0.411246    0.553840    11.00000    0.05308    0.06908 =
      0.02523    0.00365    0.00421   -0.02503
C1    1    0.835581    0.356344    0.755657    11.00000    0.04836    0.03263 =
      0.02368    0.00042    0.00175   -0.00912
C3    1    0.756336    0.374447    0.717705    11.00000    0.05083    0.05327 =
      0.02866    0.00660   -0.00189   -0.00333
AFIX  43
H3    2    0.727627    0.374287    0.690352    11.00000   -1.20000
AFIX   0
C7    1    0.902337    0.462723    0.939086    11.00000    0.05407    0.04292 =
      0.01887   -0.00303   -0.00060   -0.01081
C4    1    0.842071    0.416125    0.846871    11.00000    0.03280    0.04047 =
      0.02653   -0.00893    0.00275   -0.00610
C5    1    0.859137    0.460121    0.828419    11.00000    0.04450    0.03891 =
      0.02086   -0.00545   -0.00259   -0.00283
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C9    1    0.852643    0.393980    0.910632    11.00000    0.03653    0.03471 =
      0.02252   -0.00183    0.00076   -0.00413
C6    1    0.889273    0.483838    0.875918    11.00000    0.05415    0.03873 =
      0.03692   -0.00489    0.00637   -0.00631
AFIX  43
H6    2    0.900830    0.514170    0.865330    11.00000   -1.20000
AFIX   0
C8    1    0.883226    0.418465    0.955029    11.00000    0.04636    0.04411 =
      0.02621    0.00686    0.00296   -0.00249
AFIX  43
H8    2    0.891574    0.404724    0.997959    11.00000   -1.20000
AFIX   0
C10   1    0.938854    0.486168    0.987203    11.00000    0.06161    0.04850 =
      0.03610   -0.00201   -0.00837   -0.00839
AFIX 137
H10A  2    0.929654    0.480087    1.035192    11.00000   -1.50000
H10B  2    0.938838    0.519821    0.978811    11.00000   -1.50000
H10C  2    0.971530    0.473659    0.978516    11.00000   -1.50000
AFIX   0
C13   1    0.899245    0.552360    0.715419    11.00000    0.07507    0.04639 =
      0.03646    0.00638    0.00325   -0.00182
AFIX  43
H13   2    0.875336    0.574049    0.730317    11.00000   -1.20000
AFIX   0
C12   1    0.892290    0.503541    0.724050    11.00000    0.05649    0.04620 =
      0.02173    0.00494   -0.00361   -0.00537
C17   1    0.929641    0.472515    0.702839    11.00000    0.05888    0.04231 =
      0.03684    0.01118   -0.00911   -0.00267
AFIX  43
H17   2    0.925458    0.440030    0.709741    11.00000   -1.20000
AFIX   0
C11   1    0.846218    0.483697    0.758082    11.00000    0.05227    0.03477 =
      0.03371   -0.00001   -0.00490   -0.00916
AFIX  13
H11   2    0.834908    0.457956    0.727223    11.00000   -1.20000
AFIX   0
C15   1    0.978542    0.536917    0.662999    11.00000    0.06402    0.07473 =
      0.03095    0.01392    0.00451   -0.01045
AFIX  43
H15   2    1.007559    0.548269    0.642258    11.00000   -1.20000
AFIX   0
C16   1    0.971988    0.488538    0.672346    11.00000    0.06286    0.05708 =
      0.03731    0.01091   -0.00164   -0.00110
AFIX  43
H16   2    0.996411    0.467256    0.657836    11.00000   -1.20000
AFIX   0
```

```
C14   1    0.943181    0.567453    0.683759    11.00000    0.09055    0.05521 =
      0.03306    0.01344    0.00249   -0.01220
AFIX  43
H14   2    0.948182    0.599823    0.676765    11.00000   -1.20000
AFIX   0
C18   1    0.802660    0.517309    0.764694    11.00000    0.06720    0.04547 =
      0.03703    0.00230   -0.01619   -0.00062
C19   1    0.789446    0.541119    0.824305    11.00000    0.07484    0.07086 =
      0.04423    0.01111    0.00646    0.01985
AFIX  43
H19   2    0.807584    0.536585    0.865456    11.00000   -1.20000
AFIX   0
C22   1    0.735276    0.557942    0.706269    11.00000    0.13251    0.08869 =
      0.09753   -0.02489   -0.06502    0.04924
AFIX  43
H22   2    0.715907    0.562851    0.666353    11.00000   -1.20000
AFIX   0
C23   1    0.775461    0.526561    0.704757    11.00000    0.12960    0.08426 =
      0.05727   -0.02300   -0.03810    0.03938
AFIX  43
H23   2    0.784008    0.511688    0.662742    11.00000   -1.20000
AFIX   0
C20   1    0.749589    0.571769    0.824252    11.00000    0.10547    0.07764 =
      0.06932    0.00737    0.00269    0.02702
AFIX  43
H20   2    0.739764    0.586358    0.865924    11.00000   -1.20000
AFIX   0
C21   1    0.725280    0.580572    0.765619    11.00000    0.08947    0.08471 =
      0.09888   -0.00938   -0.02486    0.02248
AFIX  43
H21   2    0.700271    0.603432    0.765892    11.00000   -1.20000
AFIX   0
C25   1    0.855679    0.323912    0.991962    11.00000    0.05233    0.04726 =
      0.02683    0.00630   -0.00113   -0.01206
C30   1    0.892112    0.290891    0.983756    11.00000    0.05684    0.05989 =
      0.04310    0.00902    0.00168   -0.01104
AFIX  43
H30   2    0.902026    0.281776    0.938838    11.00000   -1.20000
AFIX   0
C26   1    0.842390    0.338029    1.060681    11.00000    0.06010    0.06541 =
      0.02806    0.00263    0.00222   -0.01292
AFIX  43
H26   2    0.817660    0.360723    1.067343    11.00000   -1.20000
AFIX   0
C27   1    0.865689    0.318497    1.117066    11.00000    0.06149    0.07512 =
      0.03394    0.01684   -0.01011   -0.02919
```

```
AFIX  43
H27   2    0.856556    0.327654    1.162294    11.00000   -1.20000
AFIX   0
C29   1    0.914737    0.270581    1.042951    11.00000    0.06650    0.08639 =
      0.07634    0.03293   -0.00249   -0.00126
AFIX  43
H29   2    0.938415    0.246713    1.037822    11.00000   -1.20000
AFIX   0
C28   1    0.901550    0.286303    1.108202    11.00000    0.07984    0.09959 =
      0.04092    0.02788   -0.02137   -0.03584
AFIX  43
H28   2    0.917958    0.274285    1.147460    11.00000   -1.20000
AFIX   0
C32   1    0.747256    0.386226    0.945049    11.00000    0.05819    0.05321 =
      0.03520    0.00441    0.00066   -0.01049
AFIX  43
H32   2    0.763309    0.415364    0.949471    11.00000   -1.20000
AFIX   0
C33   1    0.696481    0.384108    0.949101    11.00000    0.06157    0.06477 =
      0.04154    0.00805    0.00682   -0.00112
AFIX  43
H33   2    0.678058    0.411717    0.955914    11.00000   -1.20000
AFIX   0
C34   1    0.672446    0.340345    0.942968    11.00000    0.06813    0.09781 =
      0.04588    0.01487   -0.01225   -0.02805
AFIX  43
H34   2    0.637927    0.338400    0.945312    11.00000   -1.20000
AFIX   0
C36   1    0.749816    0.303719    0.930760    11.00000    0.07530    0.05376 =
      0.05284    0.00271   -0.01066   -0.01884
AFIX  43
H36   2    0.768206    0.275892    0.926027    11.00000   -1.20000
AFIX   0
C35   1    0.700314    0.300769    0.933543    11.00000    0.07905    0.07161 =
      0.08411    0.00033   -0.01961   -0.03070
AFIX  43
H35   2    0.684851    0.271351    0.928981    11.00000   -1.20000
AFIX   0
C41   1    0.832409    0.292812    0.537326    11.00000    0.07035    0.05901 =
      0.02990    0.00068    0.00635   -0.03328
AFIX  43
H41   2    0.848592    0.301034    0.495800    11.00000   -1.20000
AFIX   0
C37   1    0.804328    0.312592    0.650979    11.00000    0.05678    0.05157 =
      0.01472   -0.00230    0.00006   -0.01155
C46   1    0.694197    0.190235    0.699483    11.00000    0.08121    0.07007 =
```

```
      0.02751    0.00141   -0.00750   -0.02486
AFIX  43
H46   2    0.719087    0.167259    0.699142    11.00000   -1.20000
AFIX   0
C40   1    0.812621    0.247534    0.544351    11.00000    0.08120    0.05463 =
      0.03400   -0.01471    0.01188   -0.01583
C39   1    0.789109    0.235020    0.605726    11.00000    0.08923    0.05119 =
      0.03468   -0.00610    0.01509   -0.02926
AFIX  43
H39   2    0.776382    0.204469    0.610837    11.00000   -1.20000
AFIX   0
C44   1    0.758660    0.253078    0.729935    11.00000    0.07636    0.04592 =
      0.03363   -0.00873    0.00756   -0.01958
AFIX  13
H44   2    0.755850    0.281923    0.758585    11.00000   -1.20000
AFIX   0
C38   1    0.784081    0.267826    0.660798    11.00000    0.07257    0.05024 =
      0.02511   -0.00114    0.00606   -0.02315
C45   1    0.706831    0.236709    0.715571    11.00000    0.07285    0.06045 =
      0.02891    0.00003    0.00678   -0.01951
C47   1    0.646908    0.176993    0.684215    11.00000    0.09041    0.08902 =
      0.02851   -0.00541   -0.00312   -0.01203
AFIX  43
H47   2    0.639489    0.145544    0.673358    11.00000   -1.20000
AFIX   0
C43   1    0.817005    0.211326    0.484700    11.00000    0.09754    0.07030 =
      0.04568   -0.02304    0.02118   -0.04897
AFIX 137
H43A  2    0.826974    0.181146    0.503613    11.00000   -1.50000
H43B  2    0.841412    0.222010    0.451354    11.00000   -1.50000
H43C  2    0.785382    0.208078    0.461662    11.00000   -1.50000
AFIX   0
C48   1    0.610701    0.210423    0.685079    11.00000    0.09438    0.09483 =
      0.04796   -0.00334   -0.00047   -0.02732
AFIX  43
H48   2    0.578326    0.201232    0.674337    11.00000   -1.20000
AFIX   0
C50   1    0.667577    0.269025    0.717692    11.00000    0.11440    0.07000 =
      0.05098   -0.00365    0.01616   -0.02723
AFIX  43
H50   2    0.673942    0.300266    0.730939    11.00000   -1.20000
AFIX   0
C49   1    0.619256    0.255972    0.700620    11.00000    0.07786    0.09326 =
      0.07829    0.00260   -0.00196   -0.00283
AFIX  43
H49   2    0.593663    0.278230    0.700024    11.00000   -1.20000
```

```
AFIX   0
C53   1    0.793894    0.170180    0.876642    11.00000    0.08219    0.10864 =
      0.03716    0.01624   -0.00252   -0.04326
AFIX  43
H53   2    0.778932    0.157360    0.916495    11.00000   -1.20000
AFIX   0
C56   1    0.836936    0.207583    0.757873    11.00000    0.06651    0.08215 =
      0.04275    0.01526   -0.00245   -0.03049
AFIX  43
H56   2    0.851395    0.220274    0.717561    11.00000   -1.20000
AFIX   0
C52   1    0.767695    0.198876    0.832610    11.00000    0.05623    0.07044 =
      0.03895    0.00175   -0.00078   -0.01439
AFIX  43
H52   2    0.734678    0.205913    0.843000    11.00000   -1.20000
AFIX   0
C51   1    0.789161    0.217862    0.772565    11.00000    0.06633    0.05420 =
      0.03093    0.00149   -0.00697   -0.03151
C54   1    0.841662    0.160633    0.861736    11.00000    0.08069    0.13266 =
      0.05390    0.02489   -0.01852   -0.02983
AFIX  43
H54   2    0.859708    0.141536    0.892486    11.00000   -1.20000
AFIX   0
C55   1    0.865367    0.178382    0.801525    11.00000    0.06858    0.08815 =
      0.06311   -0.00083   -0.00913   -0.02899
AFIX  43
H55   2    0.898331    0.171076    0.791204    11.00000   -1.20000
AFIX   0
C57   1    0.850004    0.375895    0.581416    11.00000    0.06574    0.04999 =
      0.02038   -0.00623    0.00095   -0.01922
AFIX  13
H57   2    0.858783    0.386641    0.628887    11.00000   -1.20000
AFIX   0
C63   1    0.826147    0.459224    0.549926    11.00000    0.06260    0.05571 =
      0.05601   -0.00533    0.00653   -0.01357
AFIX  43
H63   2    0.857941    0.468409    0.563715    11.00000   -1.20000
AFIX   0
C61   1    0.747304    0.480032    0.507683    11.00000    0.08955    0.08622 =
      0.06206    0.02830    0.00490    0.01189
AFIX  43
H61   2    0.725437    0.503244    0.491597    11.00000   -1.20000
AFIX   0
C59   1    0.765268    0.399818    0.534707    11.00000    0.08863    0.05651 =
      0.06343    0.02167   -0.00156   -0.01664
AFIX  43
```

```
H59   2    0.755054    0.368266    0.536921    11.00000   -1.20000
AFIX   0
C62   1    0.793512    0.492615    0.526219    11.00000    0.08171    0.06919 =
      0.05404    0.01100    0.00335   -0.00273
AFIX  43
H62   2    0.803357    0.524230    0.522904    11.00000   -1.20000
AFIX   0
C60   1    0.731598    0.434564    0.511711    11.00000    0.07861    0.09447 =
      0.10494    0.03228   -0.03363   -0.01882
AFIX  43
H60   2    0.699165    0.426458    0.499506    11.00000   -1.20000
AFIX   0
C64   1    0.897724    0.374683    0.540653    11.00000    0.06415    0.04485 =
      0.02517    0.00627    0.00236   -0.02691
C69   1    0.942222    0.365815    0.575706    11.00000    0.05576    0.06298 =
      0.03242    0.00010    0.00192   -0.00323
AFIX  43
H69   2    0.942016    0.361609    0.624259    11.00000   -1.20000
AFIX   0
C65   1    0.900270    0.381097    0.467067    11.00000    0.06641    0.05532 =
      0.03208   -0.00334    0.00364   -0.01242
AFIX  43
H65   2    0.871446    0.387789    0.441830    11.00000   -1.20000
AFIX   0
C67   1    0.987924    0.368321    0.467797    11.00000    0.06937    0.06026 =
      0.05584   -0.00677    0.01885   -0.01032
AFIX  43
H67   2    1.017812    0.365580    0.443431    11.00000   -1.20000
AFIX   0
C66   1    0.944131    0.377601    0.433116    11.00000    0.07278    0.05414 =
      0.03448    0.00349    0.00631   -0.02111
AFIX  43
H66   2    0.944784    0.381606    0.384534    11.00000   -1.20000
AFIX   0
C68   1    0.986117    0.363200    0.539955    11.00000    0.05097    0.06907 =
      0.05522    0.00000   -0.00866   -0.00432
AFIX  43
H68   2    1.015451    0.357853    0.564716    11.00000   -1.20000
AFIX   0
HKLF 4

REM  monoclinicC in C2/c
REM R1 =  0.1134 for    7281 Fo > 4sig(Fo)  and  0.2165 for all   17085 data
REM    670 parameters refined using      0 restraints

END
```

```
WGHT      0.1864      0.0000

REM Highest difference peak  0.716,  deepest hole -0.880,  1-sigma level  0.094
Q1    1   0.9137  0.3491  0.7438  11.00000  0.05    0.72
Q2    1   1.0197  0.3610  0.7391  11.00000  0.05    0.72
Q3    1   0.9354  0.3846  0.7832  11.00000  0.05    0.50
Q4    1   0.9238  0.3056  0.7528  11.00000  0.05    0.50
Q5    1   1.0100  0.1964  1.0029  11.00000  0.05    0.48
Q6    1   0.8505  0.3775  0.7459  11.00000  0.05    0.46
Q7    1   1.0479  0.3304  0.7826  11.00000  0.05    0.44
Q8    1   0.8577  0.3458  0.7597  11.00000  0.05    0.43
Q9    1   0.8890  0.3806  0.7579  11.00000  0.05    0.42
Q10   1   0.6306  0.3095  0.9951  11.00000  0.05    0.42
Q11   1   0.9697  0.1823  0.6348  11.00000  0.05    0.41
Q12   1   0.8377  0.3316  1.1769  11.00000  0.05    0.40
Q13   1   0.8704  0.3427  0.8832  11.00000  0.05    0.39
Q14   1   0.8373  0.3699  0.7806  11.00000  0.05    0.38
Q15   1   0.9006  0.2724  0.7572  11.00000  0.05    0.37
Q16   1   0.8872  0.3652  0.7181  11.00000  0.05    0.37
Q17   1   0.8410  0.3373  0.7988  11.00000  0.05    0.35
Q18   1   0.9391  0.2293  0.5826  11.00000  0.05    0.35
Q19   1   0.5183  0.3084  0.7576  11.00000  0.05    0.34
Q20   1   0.6864  0.3263  0.7958  11.00000  0.05    0.33
;
_shelx_res_checksum   49448
```

Coordinates for DFT optimized structure of $(MeCu)_2S\text{-}CO_2$

Cu	2.193800	0.332300	-0.196100
S	0.022400	0.170800	-0.381100
C	4.070200	0.312900	-0.021000
C	6.195300	-0.437100	0.313000
H	6.973100	-1.166500	0.518200
C	6.272500	0.905300	0.071100
H	7.129000	1.571100	0.023700
C	4.591700	2.722900	-0.424000
C	4.329300	-2.134600	0.458800
C	0.014200	-1.664000	-0.024300
N	4.969800	1.345100	-0.130400
N	4.851300	-0.780600	0.252800
Cu	-2.543300	-0.841600	0.063000
C	-4.049000	0.258300	0.085000
C	-6.197600	1.013900	-0.060400
H	-7.268300	0.948000	-0.227500
C	-5.407900	2.080300	0.263500
H	-5.659500	3.121600	0.440000
C	-2.944000	2.419500	0.699700
C	-5.790500	-1.436000	-0.509800
N	-4.106000	1.604500	0.346700
N	-5.355800	-0.086000	-0.164000
H	-2.992500	2.714600	1.758400
H	-2.913100	3.318500	0.067600
H	-6.553000	-1.786500	0.201100

H	4.794000	-2.825400	-0.259700
H	4.549600	-2.469000	1.483300
H	5.080200	3.068200	-1.347200
H	-6.199100	-1.460900	-1.530800
H	-2.036800	1.823100	0.527600
H	-4.913400	-2.093300	-0.455400
H	3.240500	-2.129900	0.304600
H	4.868700	3.386400	0.408900
H	3.503100	2.747000	-0.559900
O	1.074900	-2.288700	0.062300
O	-1.180800	-2.156300	0.107700

Coordinates for DFT optimized structure of $(MeCu)_2S\text{-}CS_2$

Cu	-2.549800	0.694700	0.007300
S	-1.520700	2.706600	0.049000
S	0.000100	0.136600	0.001000
C	-3.872100	-0.650600	-0.146000
C	-5.708400	-1.970800	0.181800
H	-6.626400	-2.300900	0.658500
C	-5.013900	-2.490600	-0.873600
H	-5.217600	-3.353300	-1.500700
C	-2.895400	-1.856400	-2.100600
C	-5.385900	-0.000600	1.729800
C	-0.000100	1.885400	-0.000100
N	-3.900000	-1.680300	-1.055100
N	-5.002400	-0.852300	0.609100
S	1.520400	2.706800	-0.050400
Cu	2.549600	0.694900	-0.006900
C	3.872300	-0.650100	0.146100
C	5.707900	-1.970900	-0.182700
H	6.625300	-2.301600	-0.660400
C	5.014700	-2.489700	0.873900
H	5.218900	-3.351900	1.501500
C	2.897800	-1.853900	2.103100
C	5.383800	-0.002000	-1.732200
N	3.901100	-1.679000	1.056100
N	5.001600	-0.852600	-0.610200
H	3.275200	-1.485700	3.069000
H	2.634200	-2.917400	2.193000

H	6.430100	0.320200	-1.626700
H	-6.431900	0.321900	1.622600
H	-5.261000	-0.531900	2.685400
H	-3.271700	-1.489700	-3.067500
H	5.257300	-0.534000	-2.687100
H	2.005100	-1.279400	1.820200
H	4.727900	0.878100	-1.719800
H	-4.729600	0.879200	1.717800
H	-2.631300	-2.919800	-2.188700
H	-2.003200	-1.281200	-1.817500

Coordinates for DFT optimized structure of $(MeCu)_2S\text{-}N_2O$

Cu	-0.000100	0.009500	0.002400
C	1.601700	-0.000100	-1.031300
C	3.096900	-0.138500	-2.727800
H	3.432200	-0.279100	-3.742300
C	3.791000	0.120600	-1.592200
H	4.847900	0.252000	-1.427900
C	3.201300	0.485200	0.826900
C	0.672000	-0.483500	-3.295600
N	2.864200	0.200800	-0.567300
N	1.761600	-0.208500	-2.367000
H	0.651300	0.266500	-4.088500
H	0.788600	-1.475500	-3.736400
H	3.580400	1.504600	0.921200
H	-0.265000	-0.446400	-2.744200
H	3.958900	-0.219000	1.174600
H	2.307300	0.377900	1.439600
N	-1.594200	0.042600	0.993500
N	-1.575100	0.050800	2.207100
O	-2.603500	0.103500	2.993600
S	0.007500	-0.005800	3.257700
Cu	-1.398400	0.122300	4.982700
C	-2.483600	0.170000	6.564000
C	-4.291400	0.112600	7.931200
H	-5.334000	0.017800	8.188000
C	-3.204300	0.331700	8.710900
H	-3.116900	0.466300	9.776700

C	-0.737800	0.583100	8.293500
C	-4.700000	-0.225300	5.473100
N	-2.110600	0.363000	7.861100
N	-3.835600	0.017600	6.627300
H	-0.440800	-0.177400	9.019000
H	-0.631700	1.573300	8.742300
H	-5.166900	-1.209000	5.557800
H	-5.476600	0.540600	5.426000
H	-0.096800	0.515200	7.416800
H	-4.101600	-0.185900	4.565700

Coordinates for DFT optimized structure of $(MeCu)_2SO$

Cu	-1.773000	-1.054000	-0.362400
S	-0.158800	-1.823600	-1.567600
C	-3.025000	0.165900	0.335300
C	-4.132000	2.149900	0.509700
H	-4.375000	3.180600	0.269000
C	-4.671500	1.300600	1.434700
H	-5.469100	1.449800	2.156500
C	-4.235100	-1.093900	2.116500
C	-2.327600	1.968800	-1.259100
N	-3.985100	0.097200	1.313800
N	-3.132500	1.446800	-0.148800
H	-2.958400	2.096900	-2.151600
H	-1.894300	2.938900	-0.974800
H	-5.266900	-1.448000	1.973400
H	-1.512800	1.258700	-1.491200
H	-4.064200	-0.885800	3.183500
H	-3.536400	-1.871100	1.782600
Cu	1.584700	0.108400	-0.896700
C	3.020100	0.229300	0.274500
C	4.863500	0.909000	1.439300
H	5.666700	1.578300	1.732500
C	4.540100	-0.343800	1.877600
H	5.008200	-0.975000	2.626900
C	2.746800	-2.033000	1.314000
C	3.909600	2.498000	-0.276200
N	3.419000	-0.742700	1.161800
N	3.930100	1.242400	0.465500

H	2.356000	-2.139200	2.336900
H	3.448900	-2.852600	1.101100
H	3.778100	3.349500	0.408500
H	4.841800	2.625500	-0.846300
H	1.910400	-2.076700	0.599400
H	3.061700	2.454300	-0.972300
O	0.156700	-0.111700	-2.035200

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Author: Nicholas A. Piro, Michael F. Lichterman, W. Hill Harman, et al

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Publisher: American Chemical Society

Date: Feb 1, 2011

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Author: Amy C. Rosenzweig
Publication: Nature Structural and Molecular Biology
Publisher: Nature Publishing Group
Date: Mar 1, 2000

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Author: Esther M. Johnston, Cíntia Carreira, Simone Dell'Acqua, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Mar 1, 2017

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Author: Charlène Esmieu,Maylis Orio,Stéphane Torelli,Laurent Le Pape,Jacques Pécaut,Colette Lebrun,Stéphane Ménage

Publication: Chemical Science

Publisher: Royal Society of Chemistry

Date: Aug 4, 2014

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Title: Reduction of Nitrous Oxide to Dinitrogen by a Mixed Valent Tricopper-Disulfido Cluster

Author: Itsik Bar-Nahum, Aalo K. Gupta, Stefan M. Huber, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Mar 1, 2009

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Author: Brittany J. Johnson, William E. Antholine, Sergey V. Lindeman, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Oct 1, 2016

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Title: Enzymatic conversion of carbon dioxide

Author: Jiafu Shi,Yanjun Jiang,Zhongyi Jiang,Xueyan Wang,Xiaoli Wang,Shaohua Zhang,Pingping Han,Chen Yang

Publication: Chemical Society Reviews

Publisher: Royal Society of Chemistry

Date: Jun 9, 2015

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Title: Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO2 Fixation

Author: Aaron M. Appel, John E. Bercaw, Andrew B. Bocarsly, et al

Publication: Chemical Reviews

Publisher: American Chemical Society

Date: Aug 1, 2013

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Title: Activation of CO2 by a Heterobimetallic Zr/Co Complex

Author: Jeremy P. Krogman, Bruce M. Foxman, Christine M. Thomas

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Sep 1, 2011

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Title: Interrogating heterobimetallic co-catalytic responses for the electrocatalytic reduction of CO2 using supramolecular assembly

Author: Charles W. Machan,Clifford P. Kubiak

Publication: Dalton Transactions

Publisher: Royal Society of Chemistry

Date: Jul 4, 2016

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Title: Mechanism of N2O Reduction by the μ4-S Tetranuclear CuZ Cluster of Nitrous Oxide Reductase

Author: Serge I. Gorelsky, Somdatta Ghosh, Edward I. Solomon

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Jan 1, 2006

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Title: Catalyst Control of Selectivity in CO2 Reduction Using a Tunable Heterobimetallic Effect

Author: Sharareh Bagherzadeh, Neal P. Mankad

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: Sep 1, 2015

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Title: Multimetallic Cooperativity in Uranium-Mediated CO2 Activation

Author: Oliver Cooper, Clément Camp, Jacques Pécaut, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

Date: May 1, 2014

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Author: Charles W. Machan, Steven A. Chabolla, Jian Yin, et al

Publication: Journal of the American Chemical Society

Publisher: American Chemical Society

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Ph.D., Inorganic Chemistry, University of Illinois at Chicago, 2017.

MS., Organic Chemistry, University of Tehran, 2010.

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Teaching Assistant, Department of Chemistry, University of Illinois at Chicago, Chicago, IL, 2013-2017.

PROFESSIONAL MEMEBERSHIPS:

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PUBLICATIONS:

1. **Bagherzadeh, S**.; Mankad, N. P., Extremely efficient hydroboration of ketones and aldehydes by copper carbene catalysis. *Chem Commun* **2016,** *52* (19), 3844-3846.
2. **Bagherzadeh, S**.; Mankad, N. P., Catalyst Control of Selectivity in CO_2 Reduction Using a Tunable Heterobimetallic Effect. *J Am Chem Soc* **2015**, *137* (34), 10898-10901.
3. Banerjee, S.; Karunananda, M. K.; **Bagherzadeh, S**.; Jayarathne, U.; Parmelee, S. R.; Waldhart, G. W.; Mankad, N. P., Synthesis and Characterization of Heterobimetallic Complexes with Direct Cu-M Bonds (M = Cr, Mn, Co, Mo, Ru, W) Supported by N-Heterocyclic Carbene Ligands: A Toolkit for Catalytic Reaction Discovery. *Inorg Chem* **2014,** *53* (20), 11307-11315.
4. Jayarathne, U.; Mazzacano, T. J.; **Bagherzadeh, S**.; Mankad, N. P., Heterobimetallic Complexes with Polar, Unsupported Cu-Fe and Zn-Fe Bonds Stabilized by N-Heterocyclic Carbenes. *Organometallics* **2013,** *32* (14), 3986-3992.
5. Adib, M.; Mahdavi, M.; **Bagherzadeh, S**.; Zhu, L. G.; Rahimi-Nasrabadi, M., Reaction between anthranilic acids, salicylaldehydes and isocyanides in water: an efficient

synthesis of 2-{[2-(alkylimino)-1-benzofuran-3-yliden] amino}benzoic acids. *Tetrahedron Lett* **2010,** *51* (1), 27-29.

6. Adib, M.; **Bagherzadeh, S**.; Mahdavi, M.; Bijanzadeh, H. R., An efficient one-pot synthesis of 3-aryl-1,2,4-oxadiazol-5-amines under solvent-free conditions. *Mendeleev Commun* **2010,** *20* (1), 50-51.
7. Adib, M.; Mahdavi, M.; **Bagherzadeh, S**.; Bijanzadeh, H. R., An Efficient and Direct Solvent-Free Synthesis of Naphtho[1,2-b] furans, Naphtho[2,1-b]furans, and Furo[3,2-c]chromenes. *Synlett* **2009,** (15), 2542-2544.