Dinitrogen Complexes Hot Paper

International Edition: DOI: 10.1002/anie.201603970
German Edition: DOI: 10.1002/ange.201603970

A Dinitrogen Dicopper(I) Complex via a Mixed-Valence Dicopper Hydride

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Abstract: *Low-temperature reaction of the tris(pyrazolyl)borate copper(II) hydroxide* $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ *with triphenylsilane under a dinitrogen atmosphere gives the bridging dinitrogen complex* $[^{iPr2}TpCu]_2(\mu\text{-}1,2\text{-}N_2)$ *(**3**). X-ray crystallography reveals an only slightly activated* N_2 *ligand (N-N: 1.111(6) Å) that bridges between two monovalent* $^{iPr2}TpCu$ *fragments. While DFT studies of mono- and dinuclear copper dinitrogen complexes suggest weak π-backbonding between the* d^{10} Cu^I *centers and the* N_2 *ligand, they reveal a degree of cooperativity in the dinuclear Cu-*N_2*-Cu interaction. Addition of MeCN,* $CNAr^{2,6\text{-}Me}$*, or* O_2 *to **3** releases* N_2 *with formation of* $^{iPr2}TpCu(L)$ *(L = NCMe,* $CNAr^{2,6\text{-}Me2}$*) or* $[^{iPr2}TpCu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ *(**1**). Addition of triphenylsilane to* $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ *in pentane allows isolation of a key intermediate* $[^{iPr2}TpCu]_2(\mu\text{-}H)$ *(**5**). Although **5** thermally decays under* N_2 *to give **3**, it reduces unsaturated substrates, such as CO and HC≡CPh to HC(O)H and* $H_2C{=}CHPh$*, respectively.*

Coordination of N_2 and O_2 to transition metals represents a crucial step that precedes the multi-electron reduction of these ligands involved in ammonia formation and the oxidation of organic substrates.[1] While binding of O_2 to transition metals has a long history,[2] coordination of N_2 to transition metals was not observed until 1965, likely due to the weak σ-donating and poor π-accepting nature of N_2.[3] In particular, backbonding interactions from transition-metal d orbitals to the degenerate dinitrogen π* antibonding orbitals represents a key interaction that leads to elongation and activation of the N−N bond.[4]

Dinitrogen complexes for Co,[5] Ni,[6] and especially Cu[7] are less common than for the early to middle transition metals a result of the weaker π-backbonding to N_2 at Co, Ni, and Cu centers. Much more easily reduced, dioxygen often binds at metal fragments capable of stabilizing dinitrogen complexes despite the specific electronic differences in M−O_2 and M−N_2 bonding.[2,5e,8,9] For instance, binding of both N_2 ($\nu_{N2} = 2331\ cm^{-1}$) and O_2 have been observed at a sterically demanding tris(pyrazolyl)borate Co complex (Figure 1a).[5e,10] Using β-diketiminate supporting ligands, both a bridging dinitrogen complex $[Ni]_2(\mu\text{-}1,2\text{-}N_2)$ ($\nu_{N2} = 2164\ cm^{-1}$) and mononuclear superoxo $[Ni](\eta^2\text{-}O_2)$ species were isolated by Limberg[6a] and Driess.[8] (Figure 1b,c). Further reduction with KC_8 gives monoanionic and dianionic species $K\{[Ni]_2(\mu\text{-}N_2)\}$ and $K_2\{[Ni]_2(\mu\text{-}N_2)\}$ with lower N_2 stretching frequencies ($\nu_{N2} = 1825$ and $1696\ cm^{-1}$, respectively), mirroring the further reduction of the superoxo complex $[Ni](\eta^2\text{-}O_2)$ to form the corresponding side-on peroxo species $\{[Ni](\eta^2\text{-}O_2)\}K(18\text{-}C\text{-}6)$.[11]

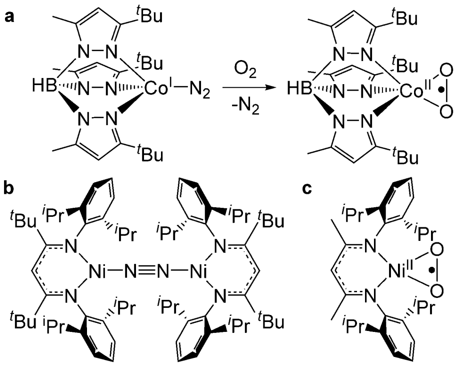

Figure 1. Selected late-transition-metal O_2 and N_2 complexes.

Despite the prevalence of O_2 binding to copper(I) centers in biology and related coordination complexes,[12] no molecular mononuclear or dinuclear dinitrogen adducts $[Cu]\text{-}N_2$ or $[Cu]_2(\mu\text{-}N_2)$ have been reported. For instance, the tris(pyrazolyl)borate complex $[^{iPr2}TpCu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**1**; Figure 2a) serves as a model for the reversible binding of O_2 at hemocyanin that occurs at a binuclear $His_3Cu^I\cdots{}^ICuHis_3$ site.[13] Nonetheless, a related $[^{iPr2}TpCu]_2(\mu\text{-}N_2H_2)$ (**2**; Figure 2c) complex has been isolated ($\nu_{NN} = 1358\ cm^{-1}$), illustrating the ability of this fragment to support reduced species related to dinitrogen.[14]

Until very recently, no copper coordination compound featuring a bound N_2 ligand had been isolated,[7a] though $[(bpy)Cu\text{-}N_2]^+$ had been detected by electrospray mass spectrometry.[15] Coordination of N_2 to copper in copper-doped zeolites occurs,[16] with ν_{N2} stretching frequencies only slightly depressed from the free value of $2331\ cm^{-1}$, such as occurs the in the copper-exchanged mordenite ($\nu_{N2} =$

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Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201603970.

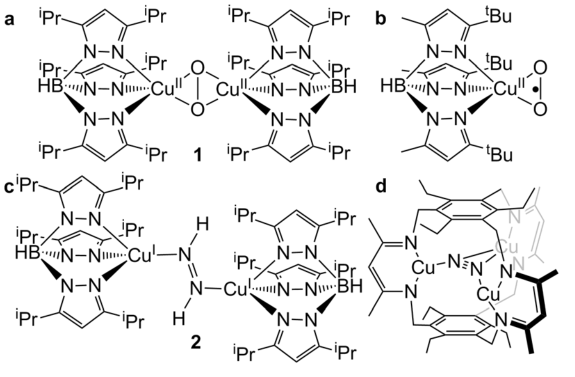


Figure 2. Tris(pyrazolyl)borate copper dioxygen (a and b) and diazene (c) adducts along with a tricopper dinitrogen complex (d).

2299 cm^{-1}).[16c] Copper coordination polymers contain partially reduced N_2 supporting ligands ($\nu_{N2} = 1607$ cm^{-1}) have been prepared recently.[7b] Murray reported a seminal copper coordination complex featuring N_2 as a ligand in 2014 (Figure 2d). It takes advantage of a strongly donating tris(β-diketiminato) ligand which upon incorporation of three Cu^{I} ions, binds N_2 in an unusual trimetallic manner with a reasonably activated N_2 ligand ($\nu_{N2} = 1952$ cm^{-1}) that is kinetically stabilized by the cryptophane binding pocket formed by the linked β-diketiminate ligands.[7a] Herein, we present the isolation of the first example of an end-on, molecular dicopper dinitrogen complex [Cu]$_2$(μ-1,2-N_2) and its formation from a mixed valence, dicopper monohydride [Cu]$_2$(μ-H).

The previously reported, blue [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-OH)$_2$ was prepared by mixing a 1 M KOH aqueous solution with $^{\mathrm{iPr2}}$TpCu(NO$_3$) in toluene under an inert atmosphere.[17] Reaction of [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-OH)$_2$ with two equiv Ph$_3$SiH at −20 °C in dichloromethane led to several color changes, starting from a blue solution that transitioned through purple and green before becoming colorless with precipitation of colorless crystals. X-ray crystallography reveals that this colorless product is [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-1,2-N_2) (**3**; Figure 3), isolated in 38 % yield. The asymmetric unit of **3** consists of two crystallographically independent halves in which each [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-N_2) unit is completed by an inversion center through the center of the N−N bond. A single N_2 molecule is captured in between two Cu^{I} centers to give an end-on binding mode (Molecule A: Cu−N 1.829(3); Molecule B: 1.822(3) Å) with a just slightly lengthened N−N bond distance (Molecule A: 1.112(5); Molecule B: 1.110(6) Å) compared to free dinitrogen (1.0975 Å). Each unique copper center of **3** adopts a pseudo-tetrahedral environment ($\tau = 0.774$ and 0.770; idealized tetrahedral geometry $\tau = 1$)[18] with three very similar Cu-N$_{\mathrm{Tp}}$ bond lengths (Molecule A: 2.026(3), 2.033(3), 2.046(3); Molecule B: 2.016(3), 2.025(3), 2.050(3) Å). This pseudo C_3 coordination environment at Cu renders the highest energy Cu d orbitals essentially degenerate to maximize their interaction with the degenerate N_2 π* orbitals (Figure 4). This idealized C_3 structure is in marked contrast to many tris(pyrazolyl)borate copper(II) complexes that often feature two short and one long Cu−N$_{\mathrm{Tp}}$ bonds.[19] Although this dicopper dinitrogen complex **3** is stable in the solid state at −40 °C for an extended period, it decays in solution (CH$_2$Cl$_2$ or toluene) over minutes at room temperature, converting to several untraceable products. Colorless crystals of **3** slowly crack with gas evolution upon standing at room temperature.

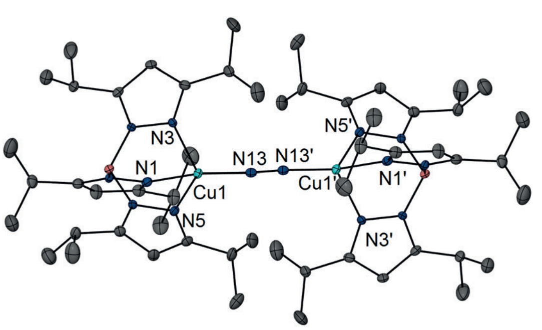


Figure 3. Crystal structure of [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-N_2) (**3**), selected bond lengths [Å] and angles [°] (Molecule A shown). Molecule A: N13-N13′ 1.112(5), Cu1-N13 1.829(3), Cu1-N1 2.033(3), Cu1-N3 2.026 (3), Cu1-N5 2.046(3); N13′-N13-Cu1 177.0(4); Molecule B: N14-N14′ 1.110(6), Cu2-N14 1.822(3), Cu2-N7 2.050(3), Cu2-N9 2.025(3), Cu2-N11 2.016(3); N14′-N14-Cu2 174.7(4). Pink B, dark blue N, light blue Cu.

To unequivocally establish the identity of the trapped diatomic molecule between the two copper centers in **3**, a solid state sample of **3** was subjected to Raman spectroscopy. The assignment of the bound dinitrogen stretching frequency was confirmed through the preparation of ^{15}N labelled [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-$^{15}N_2$) (**3**-$^{15}N_2$) under an $^{15}N_2$ atmosphere. Raman difference spectra of **3** (Figure S1B in the Supporting Information) clearly identify ν_{N2} at 2130 cm^{-1} ($^{14}N_2$) and 2060 cm^{-1} ($^{15}N_2$), approximately 200 cm^{-1} lower than free $^{14}N_2$ (2331 cm^{-1}). While the bound N_2 ligand in **3** has a higher ν_{N2} stretching frequency than in Murray's tricopper dinitrogen complex Cu$_3$N$_2$L (1952 cm^{-1}),[7a] it is significantly lower than more weakly bound N_2 ligands in copper-exchanged zeolites such as Cu-ZSM-5 (2295, 2207 cm^{-1}).[16a,e,f]

Simple MO considerations supported by high-level DFT calculations outline the nature of the [Cu^{I}]-N_2-[Cu^{I}] interaction in [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-N_2) (**3**). The effective C_3 coordination of the tris(pyrazolyl)borate ligand renders the d_{yz} and d_{xz} orbitals on the d^{10} TpCu^{I} fragment degenerate (Figure S22). This leads to degenerate π-backbonding interactions between the filled Cu d_{yz} and d_{xz} orbitals and the empty π* levels of the N_2 ligand in the mononuclear TpCu-N_2 complex (Figure 4 and S22). Due to the low energies of the Cu d orbitals, weak π-backbonding is expected. Interaction with an additional TpCu^{I} fragment allows for π-backbonding from two trigonal d^{10} Cu^{I} centers, presumably enhancing the overall copper-dinitrogen interaction.[4c,5a,6a,20] This simple MO analysis, however, illustrates that the set of filled d_{yz}/d_{xz} orbitals brought in by the additional TpCu^{I} fragment is non-bonding with respect to the N_2 π* orbitals. Thus, only modest enhancement in the copper-dinitrogen interaction is anticipated.

DFT [BP86 + GD3BJ/6-311 + + G(d,p)/SMD-CH$_2$Cl$_2$/BP86/6-31 + G(d)/gas] calculations on the mono- and dicopper adducts $^{\mathrm{iPr2}}$TpCu-N_2 (**4**) and [$^{\mathrm{iPr2}}$TpCu]$_2$(μ-N_2) (**3**) support these simple MO considerations. The calculated N−N dis-

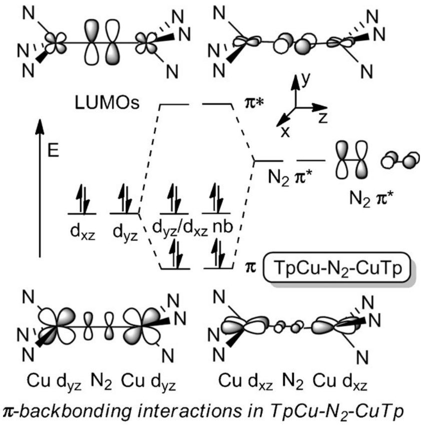
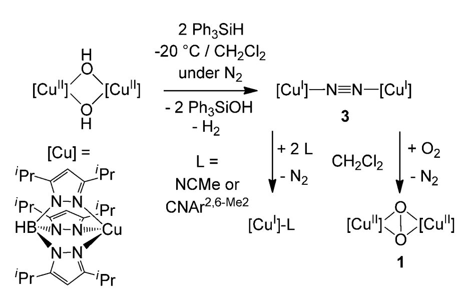


Figure 4. π-backbonding and non-bonding orbital interactions in $[TpCu]_2(\mu\text{-}N_2)$.

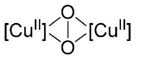
tance marginally increases from $^{iPr2}TpCu\text{-}N_2$ (**4**) (N–N: 1.134 Å) to $[^{iPr2}TpCu]_2(\mu\text{-}N_2)$ (**3**) (N–N: 1.149 Å) with a modest decrease in ν_{N2} (2309 to 2224 cm^{-1}); free N_2 values are 1.117 A and 2349 cm^{-1} at this level of theory. For each mono- and dicopper dinitrogen adduct **4** and **3**, the degenerate sets of LUMOs for both mononuclear and dinuclear dinitrogen complexes are largely N_2 π* in character, with only minor contributions from the corresponding Cu d orbitals (Figures 4, S21, and S22).

Suggested by its modest thermal stability, the solution behavior of $[^{iPr2}TpCu^I]_2(\mu\text{-}N_2)$ (**3**) as monitored by ^1H and ^{15}N NMR spectroscopy indicated that the bound N_2 is quite labile. For instance, addition of $^{15}N_2$ to $[^{iPr2}TpCu^I]_2(\mu\text{-}^{14}N_2)$ in [D$_2$]dichloromethane at −20 °C gives a broad ^{15}N NMR signal (δ = 309.0 ppm vs. NH_3), suggesting dynamic exchange between free $^{15}N_2$ (δ = 309.7 ppm vs. NH_3) and **3**-$^{15}N_2$. Addition of either excess MeCN or $CNAr^{2,6\text{-}Me}$ to a solution of **3** in dichloromethane releases N_2 with clean formation of the corresponding Cu^I adducts $^{iPr2}TpCu(L)$ (L = MeCN or $CNAr^{2,6\text{-}Me}$) complexes in essentially quantitative yield (Scheme 1). In addition, **3** reacts readily with O_2 at low temperature to form $[^{iPr2}TpCu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**1**; 98 % UV/Vis yield; Scheme 1, X-ray structure in Figure S15). In the absence of such added ligands, loss of N_2 from **3** in dichloromethane leads to a mixture of products. $[TpCu]_2$ dimers with bridging pyrazole arms have been crystallographically identified for other Tp ligands.[21]

Given the lability of N_2 under experimental conditions, we employed DFT calculations to outline the strength of N_2 binding at the $^{iPr2}TpCu$ fragment. At equal concentrations, binding of N_2 is comparable to that of MeCN, a commonly employed ligand that often provides labile copper(I) complexes. For instance, exchange of N_2 at $^{iPr2}TpCu\text{-}NCMe$ to form $^{iPr2}TpCu\text{-}N_2$ (**4**) with release of MeCN is predicted to be essentially thermoneutral ($\Delta H = 0.3$ kcal mol^{-1}; $\Delta G = 0.6$ kcal mol^{-1}). DFT calculations reveal modest cooperativity that exists in the binding of a second $^{iPr2}TpCu$ fragment to $^{iPr2}TpCu\text{-}N_2$. While binding of N_2 to the naked, tripodal $^{iPr2}TpCu$ fragment is quite favorable ($\Delta H = -22.2$ kcal mol^{-1}, $\Delta G = -11.6$ kcal mol^{-1}), addition of a second $^{iPr2}TpCu$ fragment to $^{iPr2}TpCu\text{-}N_2$ is even more favorable ($\Delta H = -29.8$ kcal mol^{-1}, $\Delta G = -15.3$ kcal mol^{-1}). This positive cooperativity is reflected in the reaction of $^{iPr2}TpCu\text{-}NCMe$ with $^{iPr2}TpCu\text{-}N_2$ predicted to give $[^{iPr2}TpCu]_2(\mu\text{-}N_2)$ and MeCN with $\Delta H = -7.3$ kcal mol^{-1} and $\Delta G = -3.1$ kcal mol^{-1}. Under experimental conditions, however, we do not see the displacement of MeCN by N_2, perhaps due to the low solubility of N_2 in CH_2Cl_2 solution.[22] On the other hand, binding of O_2 in the experimentally observed $[^{iPr2}TpCu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**1**) is predicted to be considerably more favorable than N_2 binding in **3** ($\Delta H = -43.2$ kcal mol^{-1} and $\Delta G = -38.9$ kcal mol^{-1}; Scheme 1 and Scheme 2). Thus, such dicopper sites are highly selective for O_2 over N_2.



Scheme 1. Synthesis and reactivity of $[^{iPr2}TpCu^I]_2(\mu\text{-}N_2)$ (**3**).

theory		[Cu] = ^{iPr2}TpCu	ΔH	ΔG
$[Cu^I]$-NCMe + N_2	⟶	$[Cu^I]$-N_2 + NCMe	+0.3	+0.6
$[Cu^I]$-N_2 + $[Cu^I]$-NCMe	⟶	$[Cu^I]$-N_2-$[Cu^I]$ + NCMe	-7.3	-3.1
$[Cu^I]$ + N_2	⟶	$[Cu^I]$-N_2 (**4**)	-22.2	-11.6
$[Cu^I]$-N_2 + $[Cu^I]$	⟶	$[Cu^I]$-N_2-$[Cu^I]$	-29.8	-15.3
$[Cu^I]$-N_2-$[Cu^I]$ + O_2	⟶	 + N_2	-43.2	-38.9

Scheme 2. Calculated thermodynamic parameters for the formation of $[^{iPr2}TpCu]_2(\mu\text{-}N_2)$ (**3**) and $[^{iPr2}TpCu]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}O_2)$ (**1**). Values in kcal mol^{-1} at 298 K.

Intrigued by the numerous color changes observed upon mixing of Ph_3SiH and $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ that ultimately leads to $[^{iPr2}TpCu]_2(\mu\text{-}N_2)$ (**3**), we set out to investigate possible intermediates en route to N_2 capture. Reaction between $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ and two equiv $HSiPh_3$ in dichloromethane at −20 °C affords a purple complex over an hour. Although the purple intermediate is reasonably stable at −20 °C at low concentrations (e.g. 1 mM), crystallization attempts are often frustrated by the formation of colorless crystals of the dicopper dinitrogen species **3**. Fortunately, reaction between $[^{iPr2}TpCu]_2(\mu\text{-}OH)_2$ and $HSiPh_3$ in 1 mM pentane solution at −20 °C, followed by crystallization at −40 °C affords purple crystals suitable for X-ray crystallographic analysis. X-ray diffraction reveals that the purple intermediate is the dicopper hydride $[^{iPr2}TpCu]_2(\mu\text{-}H)$ (**5**; Figure 5). Two Cu centers with nearly identical coordination environments are bridged by a single hydride ligand found in the Fourier difference map (Cu1-H1 1.78(3), Cu2-H1 1.79(3) Å) to give a short Cu–Cu distance (2.5117(4) Å). These Cu–H bonds are somewhat longer than a previously reported triangular copper $\{[Cu^I{}_2H]\}^+$ core (Cu-Cu = 2.5331-(15); Cu-H 1.45(2) Å) supported by N-heterocyclic car-

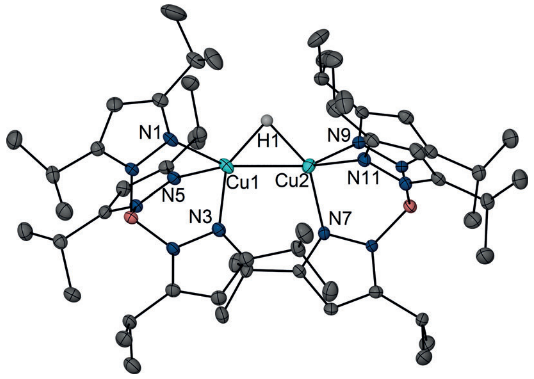


Figure 5. Crystal structure of [^{iPr2}TpCu]$_2$(μ-H) (**5**), selected bond lengths [Å] and angles [°]: Cu1-Cu2 2.5117(4), Cu1-H1 1.78(3), Cu2-H11.79(3), Cu1-N1 2.114(2), Cu1-N3 1.9997(19), Cu1-N5 2.116(2), Cu2-N7 2.024(2), Cu2-N9 2.061(2), Cu2-N11 2.109(2); Cu1-H-Cu2 89(1).

benes.[23] To our knowledge, **5** represents the first example of a mixed-valence dicopper hydride.

Hyperfine coupling from two $^{63/65}$Cu nuclei observed in the frozen glass EPR spectra of [^{iPr2}TpCu]$_2$(μ-H) (**5**) at 80 K suggests a single unpaired electron shared equally among the two copper centers. The axial spectrum of **5** ($g_{\parallel} = 2.250$, $g_{\perp} = 2.060$) possesses strong, axial hyperfine coupling ($A_{\parallel}(2\,\mathrm{Cu}) = 260$ MHz, $A_{\perp}(2\,\mathrm{Cu}) = 35$ MHz; Figure 6). IR spectra of **5**/**5**-D show an isotope-sensitive Cu-H-Cu vibration at 1573 cm^{-1} (**5**) and 1265 cm^{-1} (**5**-D). Nonetheless, no difference is observed between EPR spectra of **5** and **5**-D. DFT calculations predict little unpaired electron density at the bridging H and indicate that the Cu centers carry an overwhelming majority of the spin density (Figure S29).

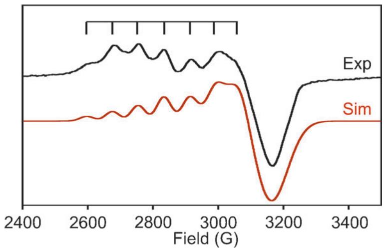
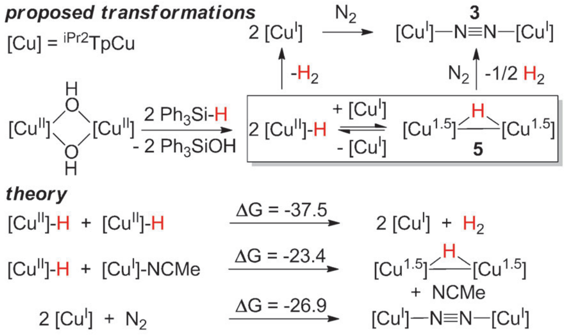


Figure 6. X-band EPR spectrum of **5** in frozen toluene at 80 K.

Although we have been unable to observe any intermediate in the formation of **5**, we propose that it forms via ^{iPr2}TpCu^{I} capture of ^{iPr2}TpCu^{II}-H produced by hydride exchange between HSiPh$_3$ and [^{iPr2}TpCu]$_2$(μ-OH)$_2$ (Scheme 3). DFT studies reveal that bimolecular coupling of the putative copper(II) hydride ^{iPr2}TpCu^{II}-H to generate H$_2$ along with 2 equiv ^{iPr2}TpCu is quite thermodynamically downhill ($\Delta H = -29.0$ kcal mol^{-1}, $\Delta G = -37.5$ kcal mol^{-1}). Similarly, capture of ^{iPr2}TpCu^{II}-H by ^{iPr2}TpCu^{I}-NCMe to stabilize the copper hydride as [^{iPr2}TpCu]$_2$(μ-H) (**5**) with formation of MeCN is also favorable (ΔH =-30.7 kcal mol^{-1}, $\Delta G = -23.4$ kcal mol^{-1}).

To provide further support for a reactive hydride intermediate, we examined reactions with small molecule substrates.



Scheme 3. Proposed mechanism for the formation of [^{iPr2}TpCu]$_2$(μ-H) (**5**) from [^{iPr2}TpCu]$_2$(μ-OH)$_2$. Free energies in kcal mol^{-1} at 298 K.

Given the challenges in the isolation of [^{iPr2}TpCu]$_2$(μ-H) (**5**), for reactivity studies we prepared **5** in situ via the reaction of [^{iPr2}TpCu]$_2$(μ-OH)$_2$ and two equiv HSiPh$_3$, monitoring the formation and loss of **5** via its low energy optical signature at $\lambda = 810$ nm ($\varepsilon = 1060\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$). [^{iPr2}TpCu]$_2$(μ-H) (**5**) reacts readily with both CO and phenylacetylene at −15 °C in CH$_2$Cl$_2$ to produce formaldehyde (63 %) and styrene (96 %) within 30 min. Reaction of [^{iPr2}TpCu]$_2$(μ-H) (**5**) with DC≡CPh gave a mixture of *cis*- and *trans*-styrene-D$_1$ in 37 % and 56 % yield, respectively (Figure S8). Upon standing at −40 °C in dichloromethane, purple solutions of [^{iPr2}TpCu]$_2$(μ-H) slowly deposit colorless crystals of [^{iPr2}TpCu]$_2$(μ-N$_2$).

In light of Kitajima's seminal finding that TpCu complexes such as [^{iPr2}TpCu]$_2$(μ-O$_2$) (**1**) may be used to model O$_2$ binding and activation in dicopper enzymes hemocyanin and tyrosinase,[13] it is surprising that the corresponding bridging N$_2$ species [^{iPr2}TpCu]$_2$(μ-N$_2$) (**3**) was isolated over 20 years later. DFT studies reveal that N$_2$ binding is competitive with MeCN, a typical weakly bound ligand in isolable copper(I) complexes, but is much weaker than O$_2$ binding. Formation of this dicopper dinitrogen complex involves the intermediacy of [^{iPr2}TpCu]$_2$(μ-H) (**5**), a unique dicopper hydride capable of reducing triply bound substrates such as CO and HC≡CPh. This [Cu]$_2$(μ-H) bonding mode that "protects" a highly reactive terminal [Cu^{II}]-H species via a coordinatively unsaturated [Cu^{I}] species is reminiscent of dicopper carbenes [Cu]$_2$(μ-CPh$_2$)[24] and nitrenes [Cu]$_2$(μ-NR)[25] that dissociate a copper(I) fragment [Cu^{I}] to reveal reactive [Cu]=CPh$_2$ and [Cu]=NR species.

Despite the modest backbonding ability exhibited by many Cu^{I} complexes, alongside Murray's report of a [Cu]$_3$(μ-N$_2$) complex,[7a] our experimental and computational results suggest that there may be a larger family of synthetically accessible Cu-N$_2$ complexes. This may offer new opportunities for N$_2$ reduction chemistry, especially since the ^{iPr2}TpCu fragment supports both the N$_2$ and HN=NH ligands in [^{iPr2}TpCu]$_2$(μ-N$_2$) (**3**) and [^{iPr2}TpCu]$_2$(μ-N$_2$H$_2$) (**2**) complexes (Figure 2 c).[14] Moreover, closely related tris(pyrazolyl)borate and tris(pyrazolyl)methane copper complexes support reduced nitrogen species, such as isolable copper(I) hydrazine adducts [Cu^{I}]-NH$_2$NH$_2$ and {[Cu^{I}]$_2$(μ-NH$_2$NH$_2$)}$^{2+}$, respectively.[26]

Acknowledgements

T.H.W. is grateful for support from the National Science Foundation (CHE-1459090) and the Georgetown Environment Initiative. T.H.W. also acknowledges NSF for funds to purchase an X-ray diffractometer (CHE-1337975). T.R.C. thanks NSF for support of this research through grant CHE-1464943.

Keywords: copper · dinitrogen · hydride · mixed-valent compounds · reduction

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Received: April 24, 2016
Revised: June 14, 2016

Communications

Dinitrogen Complexes

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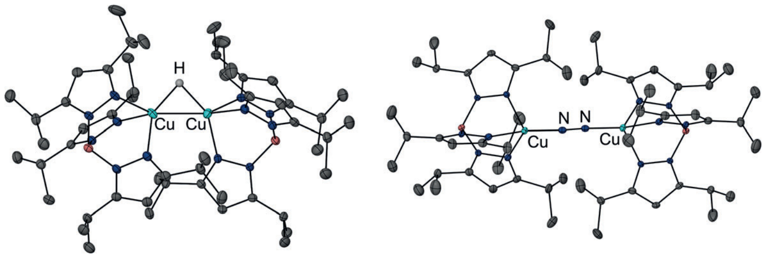
A Dinitrogen Dicopper(I) Complex via a Mixed-Valence Dicopper Hydride



Caught between two coppers: A tris(pyrazolyl)borate (Tp) dicopper N_2 complex $[Cu^I]_2(\mu\text{-}N_2)$ forms through the intermediacy of a mixed-valence dicopper hydride $[Cu^{1.5}]_2(\mu\text{-}H)$. Besides allowing a direct comparison between N_2 and O_2 binding at copper(I), this $[Cu^I]_2(\mu\text{-}N_2)$ complex represents a key member in a family of TpCu complexes $[Cu^I]_2(\mu\text{-}NH{=}NH)$ and $[Cu^I](NH_2NH_2)$ featuring reduced N_2 ligands.