



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 $[\text{TpCu}]_2(\mu\text{-OH})_2$ with triphenylsilane under a dinitrogen atmosphere gives the bridging dinitrogen complex $[\text{TpCu}]_2(\mu\text{-}1,2\text{-N}_2)$ (**3**). X-ray crystallography reveals an only slightly activated N_2 ligand (N-N : 1.111(6) Å) that bridges between two monovalent 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 $\text{Cu-N}_2\text{-Cu}$ interaction. Addition of MeCN, $\text{CNAr}^{2,6\text{-Me}}$, or O_2 to **3** releases N_2 with formation of $[\text{TpCu}(\text{L})]$ ($\text{L} = \text{NCMe}$, $\text{CNAr}^{2,6\text{-Me}}$) or $[\text{TpCu}]_2(\mu\text{-}\eta^2\text{-O}_2)$ (**1**). Addition of triphenylsilane to $[\text{TpCu}]_2(\mu\text{-OH})_2$ in pentane allows isolation of a key intermediate $[\text{TpCu}]_2(\mu\text{-H})$ (**5**). Although **5** thermally decays under N_2 to give **3**, it reduces unsaturated substrates, such as CO and $\text{HC}\equiv\text{CPh}$ to $\text{HC}(\text{O})\text{H}$ and $\text{H}_2\text{C}=\text{CHPh}$, 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 ($\nu_{\text{N}_2} = 2331\text{ cm}^{-1}$) 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

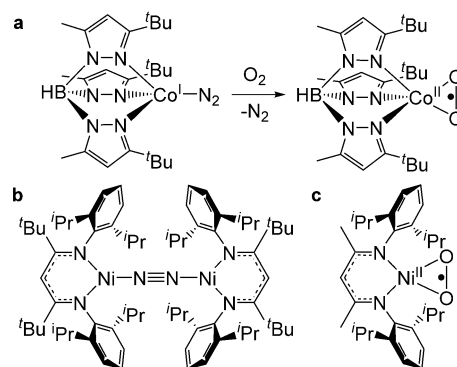


Figure 1. Selected late-transition-metal O_2 and N_2 complexes.

a bridging dinitrogen complex $[\text{Ni}]_2(\mu\text{-}1,2\text{-N}_2)$ ($\nu_{\text{N}_2} = 2164\text{ cm}^{-1}$) and mononuclear superoxo $[\text{Ni}](\eta^2\text{-O}_2)$ species were isolated by Limberg^[6a] and Driess.^[8] (Figure 1b,c). Further reduction with KC_8 gives monoanionic and dianionic species $\text{K}[\text{Ni}](\mu\text{-N}_2)$ and $\text{K}_2[\text{Ni}](\mu\text{-N}_2)$ with lower N_2 stretching frequencies ($\nu_{\text{N}_2} = 1825$ and 1696 cm^{-1} , respectively), mirroring the further reduction of the superoxo complex $[\text{Ni}](\eta^2\text{-O}_2)$ to form the corresponding side-on peroxo species $\{[\text{Ni}](\eta^2\text{-O}_2)\}\text{K}(18\text{-C-6})$.^[11]

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 $[\text{Cu}]\text{-N}_2$ or $[\text{Cu}]_2(\mu\text{-N}_2)$ have been reported. For instance, the tris(pyrazolyl)borate complex $[\text{TpCu}]_2(\mu\text{-}\eta^2\text{-O}_2)$ (**1**; Figure 2a) serves as a model for the reversible binding of O_2 at hemocyanin that occurs at a binuclear $\text{His}_3\text{Cu}^{\text{I}}\cdots\text{CuHis}_3$ site.^[13] Nonetheless, a related $[\text{TpCu}]_2(\mu\text{-N}_2\text{H}_2)$ (**2**; Figure 2c) complex has been isolated ($\nu_{\text{NN}} = 1358\text{ cm}^{-1}$), 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 $[(\text{bpy})\text{Cu-N}_2]^+$ had been detected by electrospray mass spectrometry.^[15] Coordination of N_2 to copper in copper-doped zeolites occurs,^[16] with ν_{N_2} stretching frequencies only slightly depressed from the free value of 2331 cm^{-1} , such as occurs in the copper-exchanged mordenite ($\nu_{\text{N}_2} =$

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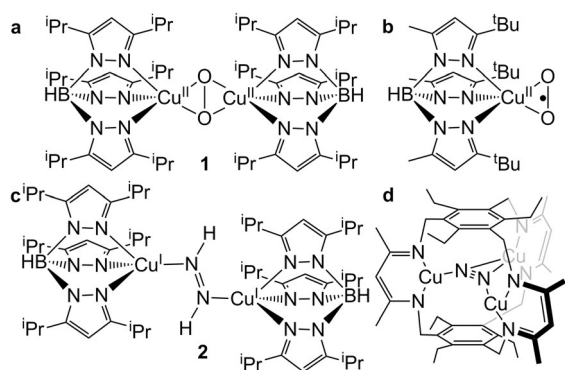


Figure 2. Tris(pyrazolyl)borate copper dioxigen (a and b) and diazene (c) adducts along with a tricopper dinitrogen complex (d).

2299 cm^{-1}).^[16c] Copper coordination polymers contain partially reduced N_2 supporting ligands ($\nu_{\text{N}_2} = 1607 \text{ cm}^{-1}$) 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 ($\nu_{\text{N}_2} = 1952 \text{ cm}^{-1}$) that is kinetically stabilized by the cryptophane binding pocket formed by the linked β -diketiminato ligands.^[7a] Herein, we present the isolation of the first example of an end-on, molecular dicopper dinitrogen complex $[\text{Cu}]_2(\mu\text{-}1,2\text{-N}_2)$ and its formation from a mixed valence, dicopper monohydride $[\text{Cu}]_2(\mu\text{-H})$.

The previously reported, blue $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-OH})_2$ was prepared by mixing a 1M KOH aqueous solution with $\text{iPr}^2\text{TpCu}(\text{NO}_3)$ in toluene under an inert atmosphere.^[17] Reaction of $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-OH})_2$ with two equiv Ph_3SiH 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 $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-}1,2\text{-N}_2)$ (**3**; Figure 3), isolated in 38% yield. The asymmetric unit of **3** consists of two crystallographically independent halves in which each

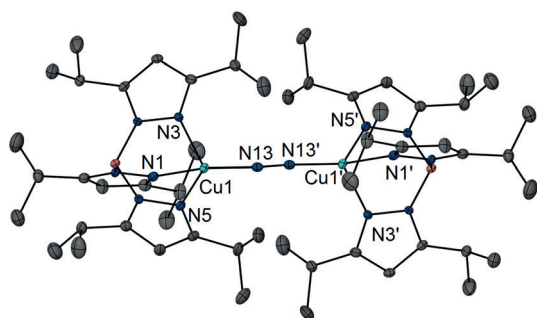


Figure 3. Crystal structure of $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**), selected bond lengths [Å] and angles [$^\circ$] (Molecule A shown). Molecule A: N13–N13' 1.112(5), Cu1–N13 1.829(3), Cu1–N1 2.033(3), Cu1–N3 2.026(3), Cu1–N5 2.046(3), N13'–N13–Cu1 177.0(4); Molecule B: N14–N14' 1.110(6), 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.

$[\text{iPr}^2\text{TpCu}]_2(\mu\text{-N}_2)$ 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_{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 $\text{N}_2 \pi^*$ 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_{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_2Cl_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.

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 $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-}^{15}\text{N}_2)$ (**3**- $^{15}\text{N}_2$) under an $^{15}\text{N}_2$ atmosphere. Raman difference spectra of **3** (Figure S1B in the Supporting Information) clearly identify ν_{N_2} at 2130 cm^{-1} ($^{14}\text{N}_2$) and 2060 cm^{-1} ($^{15}\text{N}_2$), approximately 200 cm^{-1} lower than free $^{14}\text{N}_2$ (2331 cm^{-1}). While the bound N_2 ligand in **3** has a higher ν_{N_2} stretching frequency than in Murray's tricopper dinitrogen complex $\text{Cu}_3\text{N}_2\text{L}$ (1952 cm^{-1}),^[7a] it is significantly lower than more weakly bound N_2 ligands in copper-exchanged zeolites such as Cu-ZSM-5 ($2295, 2207 \text{ cm}^{-1}$).^[16a,e,f]

Simple MO considerations supported by high-level DFT calculations outline the nature of the $[\text{Cu}^{\text{I}}\text{-N}_2\text{-Cu}^{\text{I}}]$ interaction in $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-N}_2)$ (**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 $\text{N}_2 \pi^*$ orbitals. Thus, only modest enhancement in the copper-dinitrogen interaction is anticipated.

DFT [BP86 + GD3BJ/6-311 + G(d,p)/SMD- CH_2Cl_2 /BP86/6-31 + G(d)/gas] calculations on the mono- and dicopper adducts $\text{iPr}^2\text{TpCu-N}_2$ (**4**) and $[\text{iPr}^2\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**) support these simple MO considerations. The calculated N–N dis-

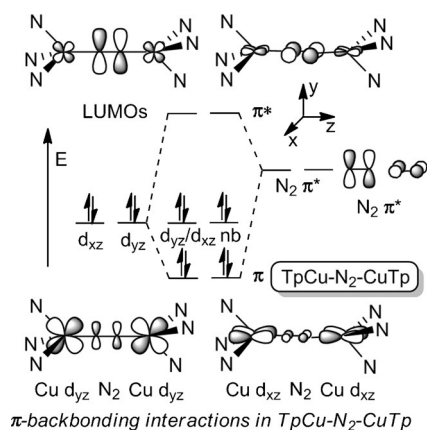
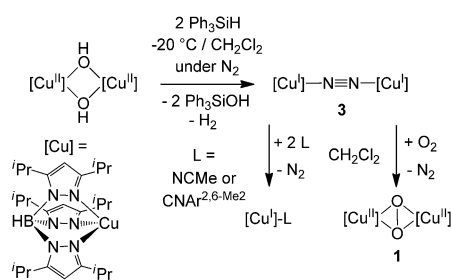


Figure 4. π -backbonding and non-bonding orbital interactions in $[\text{TpCu}]_2(\mu\text{-N}_2)$.

tance marginally increases from ${}^{\text{iPr}_2}\text{TpCu-N}_2$ (**4**) (N–N: 1.134 Å) to $[\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**) (N–N: 1.149 Å) with a modest decrease in ν_{N_2} (2309 to 2224 cm^{-1}); free N_2 values are 1.117 Å 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 $\text{N}_2 \pi^*$ 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 $[\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**) as monitored by ^1H and ^{15}N NMR spectroscopy indicated that the bound N_2 is quite labile. For instance, addition of $^{15}\text{N}_2$ to $[\text{TpCu}]_2(\mu\text{-}^{14}\text{N}_2)$ in $[\text{D}_2]$ dichloromethane at -20°C gives a broad ^{15}N NMR signal ($\delta = 309.0$ ppm vs. NH_3), suggesting dynamic exchange between free $^{15}\text{N}_2$ ($\delta = 309.7$ ppm vs. NH_3) and **3**- $^{15}\text{N}_2$. Addition of either excess MeCN or $\text{CNAr}^{2,6\text{-Me}}$ to a solution of **3** in dichloromethane releases N_2 with clean formation of the corresponding Cu^{I} adducts ${}^{\text{iPr}_2}\text{TpCu}(\text{L})$ ($\text{L} = \text{MeCN}$ or $\text{CNAr}^{2,6\text{-Me}}$) complexes in essentially quantitative yield (Scheme 1). In addition, **3** reacts readily with O_2 at low temperature to form $[\text{TpCu}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-O}_2)$ (**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. $[\text{TpCu}]_2$ 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



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

binding at the ${}^{\text{iPr}_2}\text{TpCu}$ 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 ${}^{\text{iPr}_2}\text{TpCu-NCMe}$ to form ${}^{\text{iPr}_2}\text{TpCu-N}_2$ (**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 ${}^{\text{iPr}_2}\text{TpCu}$ fragment to ${}^{\text{iPr}_2}\text{TpCu-N}_2$. While binding of N_2 to the naked, tripodal ${}^{\text{iPr}_2}\text{TpCu}$ fragment is quite favorable ($\Delta H = -22.2$ kcal mol $^{-1}$, $\Delta G = -11.6$ kcal mol $^{-1}$), addition of a second ${}^{\text{iPr}_2}\text{TpCu}$ fragment to ${}^{\text{iPr}_2}\text{TpCu-N}_2$ 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 ${}^{\text{iPr}_2}\text{TpCu-NCMe}$ with ${}^{\text{iPr}_2}\text{TpCu-N}_2$ predicted to give $[\text{TpCu}]_2(\mu\text{-N}_2)$ 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 $[\text{TpCu}]_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-O}_2)$ (**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 .

theory	$[\text{Cu}] = {}^{\text{iPr}_2}\text{TpCu}$	ΔH	ΔG
$[\text{Cu}^{\text{I}}]\text{-NCMe} + \text{N}_2 \rightarrow [\text{Cu}^{\text{I}}]\text{-N}_2 + \text{NCMe}$		+0.3	+0.6
$[\text{Cu}^{\text{I}}]\text{-N}_2 + [\text{Cu}^{\text{I}}]\text{-NCMe} \rightarrow [\text{Cu}^{\text{I}}]\text{-N}_2\text{-}[\text{Cu}^{\text{I}}] + \text{NCMe}$		-7.3	-3.1
$[\text{Cu}^{\text{I}}] + \text{N}_2 \rightarrow [\text{Cu}^{\text{I}}]\text{-N}_2$ (4)		-22.2	-11.6
$[\text{Cu}^{\text{I}}]\text{-N}_2 + [\text{Cu}^{\text{I}}] \rightarrow [\text{Cu}^{\text{I}}]\text{-N}_2\text{-}[\text{Cu}^{\text{I}}]$		-29.8	-15.3
$[\text{Cu}^{\text{I}}]\text{-N}_2\text{-}[\text{Cu}^{\text{I}}] + \text{O}_2 \rightarrow [\text{Cu}^{\text{I}}]\text{-O-O-}[\text{Cu}^{\text{I}}] + \text{N}_2$		-43.2	-38.9

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

Intrigued by the numerous color changes observed upon mixing of Ph_3SiH and $[\text{TpCu}]_2(\mu\text{-OH})_2$ that ultimately leads to $[\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**), we set out to investigate possible intermediates en route to N_2 capture. Reaction between $[\text{TpCu}]_2(\mu\text{-OH})_2$ 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 $[\text{TpCu}]_2(\mu\text{-OH})_2$ 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 $[\text{TpCu}]_2(\mu\text{-H})$ (**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 $\{[\text{Cu}_3\text{H}]\}^+$ core (Cu–Cu = 2.5331(15); Cu–H 1.45(2) Å) supported by N-heterocyclic car-

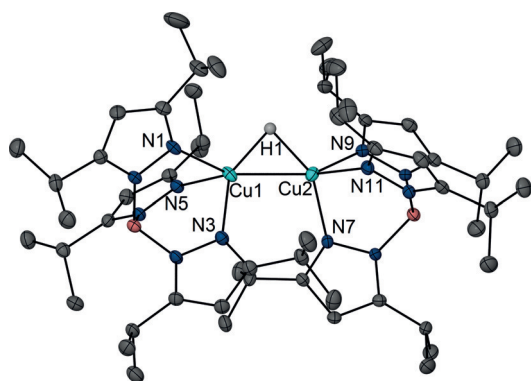


Figure 5. Crystal structure of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**), selected bond lengths [Å] and angles [°]: Cu1–Cu2 2.5117(4), Cu1–H1 1.78(3), Cu2–H1 1.79(3), Cu1–N1 2.114(2), Cu1–N3 1.9997(19), Cu1–N5 2.116(2), Cu2–N7 2.024(2), Cu2–N9 2.061(2), Cu2–N11 2.109(2); Cu1–H–Cu2 89(1).

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

Hyperfine coupling from two $^{63/65}\text{Cu}$ nuclei observed in the frozen glass EPR spectra of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**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 ($A_{\parallel}(\text{2 Cu}) = 260$ MHz, $A_{\perp}(\text{2 Cu}) = 35$ MHz; Figure 6). IR spectra of **5/5-D**

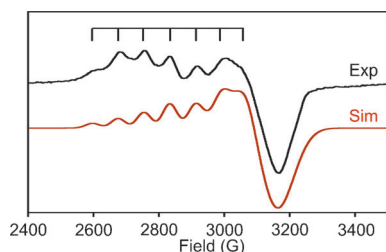
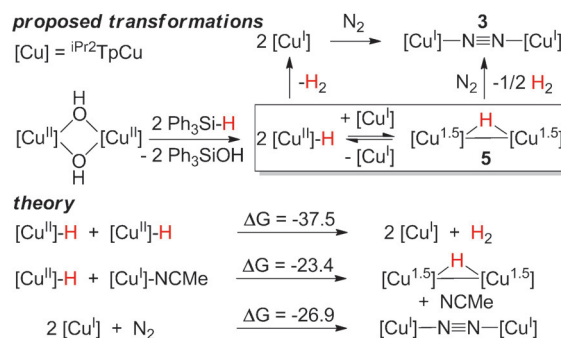


Figure 6. X-band EPR spectrum of **5** in frozen toluene at 80 K.

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).

Although we have been unable to observe any intermediate in the formation of **5**, we propose that it forms via $\text{iPr}_2\text{TpCu}^{\text{I}}$ capture of $\text{iPr}_2\text{TpCu}^{\text{II}}\text{-H}$ produced by hydride exchange between HSiPh_3 and $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-OH})_2$ (Scheme 3). DFT studies reveal that bimolecular coupling of the putative copper(II) hydride $\text{iPr}_2\text{TpCu}^{\text{II}}\text{-H}$ to generate H_2 along with 2 equiv iPr_2TpCu is quite thermodynamically downhill ($\Delta H = -29.0\text{ kcal mol}^{-1}$, $\Delta G = -37.5\text{ kcal mol}^{-1}$). Similarly, capture of $\text{iPr}_2\text{TpCu}^{\text{II}}\text{-H}$ by $\text{iPr}_2\text{TpCu}^{\text{I}}\text{-NCMe}$ to stabilize the copper hydride as $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**) with formation of MeCN is also favorable ($\Delta H = -30.7\text{ kcal mol}^{-1}$, $\Delta G = -23.4\text{ kcal mol}^{-1}$).

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



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

strates. Given the challenges in the isolation of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**), for reactivity studies we prepared **5** in situ via the reaction of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-OH})_2$ and two equiv HSiPh_3 , monitoring the formation and loss of **5** via its low energy optical signature at $\lambda = 810\text{ nm}$ ($\epsilon = 1060\text{ M}^{-1}\text{ cm}^{-1}$). $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**) reacts readily with both CO and phenylacetylene at -15°C in CH_2Cl_2 to produce formaldehyde (63%) and styrene (96%) within 30 min. Reaction of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**) with $\text{DC}\equiv\text{CPh}$ 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 $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ slowly deposit colorless crystals of $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-N}_2)$.

In light of Kitajima's seminal finding that TpCu complexes such as $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-O}_2)$ (**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 $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-N}_2)$ (**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 $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-H})$ (**5**), a unique dicopper hydride capable of reducing triply bound substrates such as CO and $\text{HC}\equiv\text{CPh}$. This $[\text{Cu}]_2(\mu\text{-H})$ bonding mode that “protects” a highly reactive terminal $[\text{Cu}^{\text{II}}]\text{-H}$ species via a coordinatively unsaturated $[\text{Cu}^{\text{I}}]$ species is reminiscent of dicopper carbenes $[\text{Cu}]_2(\mu\text{-CPh}_2)$ ^[24] and nitrenes $[\text{Cu}]_2(\mu\text{-NR})$ ^[25] that dissociate a copper(I) fragment $[\text{Cu}^{\text{I}}]$ to reveal reactive $[\text{Cu}]\text{=CPh}_2$ and $[\text{Cu}]\text{=NR}$ species.

Despite the modest backbonding ability exhibited by many Cu^{I} complexes, alongside Murray's report of a $[\text{Cu}]_3(\mu\text{-N}_2)$ 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 iPr_2TpCu fragment supports both the N_2 and $\text{HN}=\text{NH}$ ligands in $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-N}_2)$ (**3**) and $[\text{iPr}_2\text{TpCu}]_2(\mu\text{-N}_2\text{H}_2)$ (**2**) complexes (Figure 2c).^[14] Moreover, closely related tris(pyrazolyl)borate and tris(pyrazolyl)methane copper complexes support reduced nitrogen species, such as isolable copper(I) hydrazine adducts $[\text{Cu}^{\text{I}}]\text{-NH}_2\text{NH}_2$ and $\{[\text{Cu}^{\text{I}}]_2(\mu\text{-NH}_2\text{NH}_2)\}^{2+}$, respectively.^[26]

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