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A Polar Copper–Boron One-Electron σ-Bond

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Supporting Information

ABSTRACT: Virtually all chemical bonds consist of one or several pairs of electrons shared by two atoms. Examples of σ-bonds made of a single electron delocalized over two neighboring atoms were until recently found only in gas-phase cations such as H_2^+ and Li_2^+ and in highly unstable species generated in solid matrices. Only in the past decade was bona fide one-electron bonding observed for molecules in fluid solution. Here we report the isolation and structural characterization of a thermally stable compound featuring a Cu–B one-electron bond, as well as its oxidized (nonbonded) and reduced (two-electrons-bonded) congeners. This triad provides an excellent opportunity to study the degree of σ-bonding in a metalloboratrane as a function of electron count.

Linus Pauling proposed in 1931 the possibility of one-electron σ-bonding.[1] While such a bond is expected to be much weaker than a prototypical two-electron σ-bond, the gas-phase characterization of the diatomic cations H_2^+ and Li_2^+,[2] in addition to the matrix identification of anionic $\{(MeO)_3B{\cdot}B(OMe)_3\}^-$ and larger radical cations of the type $\{Me_3E{\cdot}EMe_3\}^+$ (E = C, Si, Ge),[3−5] helped place this supposition on firm experimental ground after the middle of the 20th century. Nonetheless, it was only more recently that bona fide one-electron σ-bonding was observed for molecules in fluid solution. The two most definitive systems of this type are depicted in Figure 1 (top) and exhibit nonpolar one-electron σ-bonding between a pair of P or B atoms, respectively.[6−8] Generation of these one-electron σ-bonded systems was aided by the use of covalent tethers, helping to hold the P·P and B·B subunits together. While these systems were not structurally characterized, solution electron paramagnetic resonance (EPR) spectroscopy supported their respective one-electron σ-bonding descriptions.

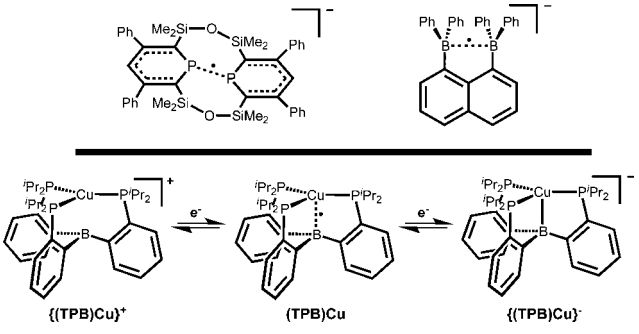

Figure 1. (Top) Symmetrical one-electron-bonded species previously characterized by EPR spectroscopy in fluid solution. (Bottom) Copper complexes described herein.

In this Communication we describe the structural characterization of a formal Cu(0) adduct of a tris(phosphine)borane ligand,[9] (TPB)Cu (TPB = tris[2-(diisopropylphosphino)-phenyl]borane). Because Cu(0) would be exceptional among monomeric copper coordination complexes, we sought to develop a detailed picture of the electronic structure of this complex, with an alternative limiting description being that of Cu(II) wherein the borane ligand accepts a pair of electrons from the Cu center.[10] In valence terminology, zerovalent copper would imply no bonding between the Cu and B centers in (TPB)Cu, whereas divalent copper would imply a Z-type borane ligand accepting a pair of electrons via σ-back-donation from the copper center (Cu→B).[11] As discussed below, neither of these formulations proves most apt. We instead prefer a description of (TPB)Cu that invokes a polarized one-electron σ-bond between the Cu and B centers (i.e., Cu·B). Spectroscopic and theoretical data for (TPB)Cu, in addition to related data for its structurally characterized one-electron oxidized and reduced partners, $\{(TPB)Cu\}^+$ and $\{(TPB)Cu\}^-$ (Figure 1, bottom), in sum support this view. While there are a few known families of metallaboratranes related by formal redox processes,[12] the existence of the (TPB)Cu scaffold in three isolable oxidation states with the same ligand set allows for a uniquely detailed characterization of the electronic structure of metal–boron bonds.

The preparation of (TPB)Cu was readily accomplished by stirring a solution of TPB and CuBr in tetrahydrofuran over an excess of sodium/mercury amalgam. Such a procedure yielded an inky purple suspension from which (TPB)Cu could be isolated as black crystals in 50% yield. The cyclic voltammogram of (TPB)Cu exhibits two quasi-reversible waves at −1.60 and −2.76 V vs Fc/Fc^+ (Fc = ferrocene) that correspond to the $\{(TPB)Cu\}^{+/0}$ and $\{(TPB)Cu\}^{0/-}$ redox couples, respectively. We hence sought synthetic access to these redox partners. Stirring a mixture of TPB, CuBr, and $Na\{BAr^F{}_4\}$ in diethyl ether for 2.5 h ($\{BAr^F{}_4\}^-$ = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) followed by removal of the insoluble NaBr by filtration and slow concentration of the filtrate afforded $\{(TPB)Cu\}\{BAr^F{}_4\}$ as yellow blocks (70% yield). Its anionic cousin $\{(TPB)Cu\}^-$ could be generated as an inky blue solution of the salts $\{Na\}\{(TPB)Cu\}$ or $\{K\}\{(TPB)Cu\}$ by stirring a solution of (TPB)Cu in the presence of either metallic sodium or potassium. Crystallization of $\{(TPB)Cu\}^-$ was most readily accomplished as the potassium salt, wherein the potassium countercation is encapsulated by 2 equiv of benzo-15-crown-5, $\{K(benzo\text{-}15\text{-}C\text{-}5)_2\}\{(TPB)Cu\}$. The solid-state

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crystal structures of $\{(TPB)Cu\}\{BAr^F{}_4\}$, (TPB)Cu, and $\{K(benzo\text{-}15\text{-}C\text{-}5)_2\}\{(TPB)Cu\}$ were determined and are shown in Figure 2A. Key NMR, UV−vis, and X-ray diffraction

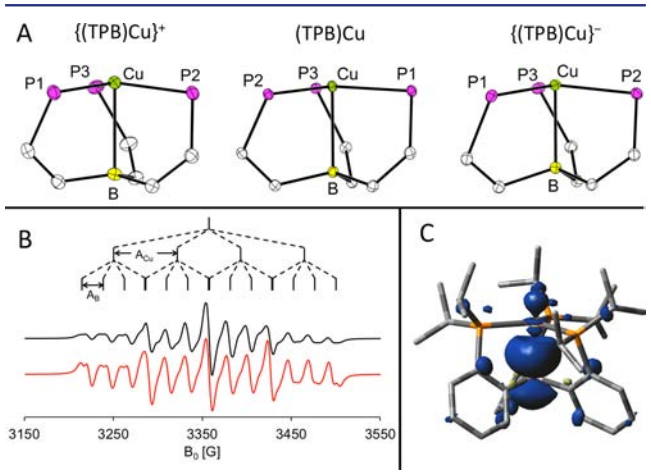

Figure 2. (A) Ellipsoid representation (50% probability) of the XRD crystal structures of $\{(TPB)Cu\}^+$, (TPB)Cu, and $\{(TPB)Cu\}^-$. For clarity only the core atoms are plotted. (B) Experimental (black) and simulated (red) X-band EPR spectrum of (TPB)Cu at room temperature in toluene solution. (C) Spin density of (TPB)Cu calculated by DFT at the B3LYP/6-311+G(d,p)//6-31+G(d) level.

Table 1. NMR, UV−Vis, and Metrical Parameters Relevant to the Description of the Cu−B Interaction

	$\{(TPB)Cu\}^+$	(TPB)Cu	$\{(TPB)Cu\}^-$
$\delta(^{11}B)$ [ppm]	67	paramagnetic	6.7
$\delta(^{31}P)$ [ppm]	19.3	paramagnetic	20.2
λ_{max} [nm] $\{\varepsilon$ [cm^{-1} M^{-1}]$\}$	430 {sh}, 403 {850}, 320 {8000}	665 {2300}, 485 {4200}, 345 {6400}, 310 {sh}	780 {sh}, 615 {4900}, 530 {5100}, 350 {sh}
Cu−B [Å]	2.495	2.289	2.198
⟨Cu−P⟩ [Å]	2.295	2.270	2.244
∑(P−Cu−P) [°]	356.7	359.0	357.5
∑(C−B−C) [°]	355.0	347.1	338.9

(XRD) data are summarized in Table 1. In addition, the geometries of $\{(TPB)Cu\}^+$, (TPB)Cu, and $\{(TPB)Cu\}^-$ were optimized by density functional theory (DFT), and a natural bonding orbitals (NBO) analysis[13] was applied. These data are discussed below.

(TPB)Cu is a stable radical, and its room-temperature EPR spectrum is shown in Figure 2B. The spectrum shown displays a 13-line pattern whose faithful simulation requires the inclusion of hyperfine coupling to both ^{63}Cu (I = 3/2, $A_{iso}(^{63}Cu)$ = 191 MHz) and ^{11}B (I = 3/2, $A_{iso}(^{11}B)$ = 64 MHz), in addition to the minor isotopes ^{65}Cu (I = 3/2) and ^{10}B (I = 3) at natural abundance. The doubling of the outmost lines—due to the different gyromagnetic ratios of ^{63}Cu and ^{65}Cu—confirms the assignment of the larger coupling constant to Cu. An EPR spectrum of (TPB)Cu recorded at 77 K in frozen toluene displays an axial signal with virtually isotropic g values ($g_{\|}$ = 2.006, $g_{\perp}$ = 2.010) but strongly anisotropic hyperfine tensors ($A_{\|}(^{63}Cu)$ = 335 MHz, $A_{\perp}(^{63}Cu)$ = 93 MHz, $A_{\|}(^{11}B)$ = 110 MHz, $A_{\perp}(^{11}B)$ = 40 MHz), consistent with the unpaired electron being located in an orbital of σ symmetry delocalized over the B and Cu atoms. This interpretation was corroborated by a natural atomic orbital[13] population analysis of the spin density obtained from DFT calculations that reveal a spin population of 0.57 on B (0.06 2s, 0.51 2p) and 0.13 on Cu (0.01 4s, 0.10 4p, 0.02 3d), the remaining spin being delocalized over the phosphine P atoms (2% each) and the phenylene linkers. The fact that the spin population of the 4p orbital of Cu largely exceeds that of the 3d orbital supports the description of the Cu·B bond in (TPB)Cu as a one-electron bond with only marginal participation of internal 3d orbitals of Cu.

The comparative XRD, NMR, and UV−vis data obtained for the redox series $\{(TPB)Cu\}^+$, (TPB)Cu, and $\{(TPB)Cu\}^-$ shed additional light on the nature of the Cu−B interaction. The XRD structure of $\{(TPB)Cu\}\{BAr^F{}_4\}$ exhibits a long Cu−B distance of 2.495 Å and a nearly planar boron center with a sum of the C−B−C angles (∑(C−B−C)) of 355°, indicating a very weak—if any—retrodative B←Cu interaction. This suggestion is additionally corroborated by a ^{11}B chemical shift of 67 ppm, virtually equal to that measured for triphenylborane (67.4 ppm)[14] and that calculated for the metal-free TPB ligand (65.4 ppm).[9] The yellow color of $\{(TPB)Cu\}^+$, constrasting with the generally colorless appearance of tris(phosphine)-copper(I) cations,[15,16] is caused by an additional band (λ_{max} = 403 nm) assigned to a copper-to-boron charge-transfer transition.[17] Bourissou has previously reported[17] the related neutral complex (TPB)CuCl, in which a weak B←Cu interaction was inferred on the basis of the ^{11}B chemical shift at 53.8 ppm and pyramidalization (∑(C−B−C) = 347.0°), despite a long Cu−B distance of 2.508 Å. Evidently, formal abstraction of the Cl^- from (TPB)CuCl decreases the Lewis basicity of the Cu(I) center to the point where electron donation to the unsaturated boron atom becomes close to negligible. Accordingly, an NBO analysis of the DFT-calculated electron density associates an energy of only 3.6 kcal/mol to the $Cu(3d_{z^2})\rightarrow B$ interaction, to be compared with the ca. 8 kcal/mol calculated for (TPB)CuCl.[17]

As electrons are added to yellow $\{(TPB)Cu\}^+$ to generate dark purple (TPB)Cu, and then its dark indigo anion $\{(TPB)Cu\}^-$, intense bands appear in the visible region of the spectrum (Table 1). These new absorptions are tentatively attributed to charge-transfer transitions from the high-lying σ(Cu−B) orbital to π^* orbitals of the phenylene linkers of the TPB ligand. The main geometrical changes (Table 1) that are manifest include a marked shortening of the Cu−B distance from 2.495 Å in $\{(TPB)Cu\}^+$ to 2.289 Å in (TPB)Cu, and then to 2.198 Å in $\{(TPB)Cu\}^-$. Also evident in the series is a gradual pyramidalization of the boron center as the electron count is increased. This is reflected in the sum of the C−B−C angles (∑(C−B−C)), which decreases from 355.0° to 347.1° to 338.9° in the series. Whereas the hybridization at boron changes markedly, the geometry of the P_3Cu subunit in each structure shows negligible variation. Accordingly, the ^{11}B NMR resonance shifts from 67 ppm in $\{(TPB)Cu\}^+$ to 6.7 ppm in $\{(TPB)Cu\}^-$, whereas the ^{31}P chemical shift varies a negligible amount, from 19.3 to 20.2 ppm, respectively. These X-ray and NMR data collectively suggest that the Cu−B interaction increases in the order $\{(TPB)Cu\}^+$ < (TPB)Cu < $\{(TPB)Cu\}^-$. The Cu−B bonding in $\{(TPB)Cu\}^+$ is insignificant but becomes more prevalent in (TPB)Cu with the onset of one-electron σ-bonding, and it becomes that of a prototypical two-electron bond in $\{(TPB)Cu\}^-$.

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Cu K-edge X-ray near-edge absorbtion spectroscopy (XANES) data were obtained on single-crystal samples of {(TPB)Cu}{BAr^F_4}, (TPB)Cu, and {K(benzo-15-C-5)$_2$}-{(TPB)Cu} to further explore how the relative state of oxidation of the copper centers changes across the series, if at all (Figure 3, left). Owing to the high oxygen sensitivity of these

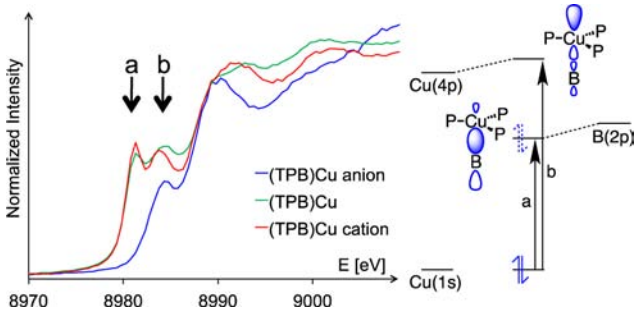

Figure 3. Cu K-edge XAS spectra collected on single-crystal samples of (TPB)Cu, {(TPB)Cu}{BAr^F_4}, and {K(benzo-15-C-5)$_2$}{(TPB)-Cu} (left), and a schematic orbital-interaction diagram illustrating assigned transitions (right).

copper complexes, particularly anion **5**, the single-crystal XAS data were collected under a nitrogen atmosphere at 100 K. Potential photon damage to the complexes during XANES collection was ruled out by comparing the multiple sweeps of XAS scans, as well as comparing the single-crystal XRD data collected at the end of the XANES scans to the XRD data independently collected and already described above. The XANES spectrum of {(TPB)Cu}$^-$ is qualitatively similar to those of other tetracoordinate Cu(I) complexes[18] and exhibits a first peak at ca. 8984 eV that is assigned to the dipole-allowed Cu(1s)→Cu(4p) transition (labeled b, Figure 3). Formal one- and two-electron oxidation of {(TPB)Cu}$^-$ to generate (TPB)Cu and {(TPB)Cu}$^+$, respectively, results in the appearance of an additional band of comparable intensity but at appreciably lower energy, ca. 8981 eV (labeled a, Figure 3). The band at ca. 8984 eV is preserved. The appearance of the new band at 8981 eV is unexpected for a copper center that is being formally oxidized, but such a band is consistent with oxidation of electrons in a B→Cu dative bond that is heavily polarized toward boron. This additional band is therefore tentatively assigned to a transition from Cu(1s) to an orbital of B(2p) parentage, whose large intensity is due to strong mixing with the Cu(4p) orbital (Figure 3 right). In {(TPB)Cu}$^-$ this transition is not observed, presumably because the bonding orbital is filled by two electrons.[19]

To summarize, we have provided the first structural snapshot of one-electron σ-bonding in a complex, whose characterization is complemented by the structures of its one-electron oxidized and reduced relatives. The structural, spectroscopic, and theoretical data in hand collectively suggest that sequential reduction of the cation {(TPB)Cu}$^+$ to (TPB)Cu and then to {(TPB)Cu}$^-$ results in the gradual formation of a polar Cu−B σ-bond to which the ionic resonance structures $R_3B^{\bullet-}$ Cu^+ for (TPB)Cu and $R_3B{:}^{2-}$ Cu^+ for {(TPB)Cu}$^-$ strongly contribute, in agreement with the location of the spin density in (TPB)Cu residing mostly on B (*vide supra*). In additional support of this view, NBO analysis carried out on the anion {(TPB)Cu}$^-$ identifies an occupied lone pair with a large p character (13.3% s, 86.8% p) on the boron atom. Second-order perturbation analysis associates energies of 69.2 and 56.5 kcal/mol with the delocalization of that orbital into Cu 4s and 4p orbitals, respectively, comparable in magnitude to those associated with the P→Cu interactions (72.7 kcal/mol to Cu(4s), 82.5 kcal/mol to Cu(4p)). While boron-centered radical anions had been long known as solution species,[22] and one example had been isolated as a crystalline salt,[23] the few known analogous boron(I) dianions are highly unstable and involve extensive π-delocalization.[24,25]

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) As a cautionary note, the polarization vector $\vec{e}$ was aligned nearly perpendicular to the Cu-B bond for $\{K(benzo\text{-}15\text{-}C\text{-}5)_2\}\{(TPB)Cu\}$. Therefore, an alternative explanation for the absence of transition a in $\{(TPB)Cu\}^-$ could be due to the polarization effect.[20,21] For complexes (TPB)Cu and $\{(TPB)Cu\}^+$, however, $\vec{e}$ was aligned predominantly along the Cu−B bond, and hence enhancement of transition a would be anticipated.
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