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Noninnocent Behavior of Bidentate Amidophosphido $[NP]^{2-}$ Ligands upon Coordination to Copper

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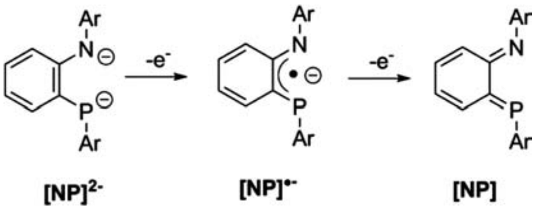
Supporting Information

ABSTRACT: The synthesis and preliminary coordination chemistry of two new redox-active bidentate ligands containing amido and phosphido donors are described. Treatment of the $[^{R}NP]^{2-}$ (R = Ph, 2,4,6-trimethylphenyl) ligands with $CuCl_2$ and PMe_3 results in a dimeric copper(I) P−P coupled product via ligand oxidation. The intermediate of this reaction is proposed to involve a ligand radical generated via oxidation of the $[^{R}NP]^{2-}$ ligand by copper(II), and the existence of such an intermediate is probed using computational methods. Significant radical character on the phosphorus atoms of the alleged $[^{R}NP]^{\bullet -}$/copper(I) intermediate leads to P−P radical coupling.

The study of redox-active ligands has become increasingly widespread in recent years for both catalytic applications[1] and biomimetic studies.[2] The ultimate purpose of these ligands (in both biology and catalysis) is to work in tandem with transition-metal centers to facilitate the multielectron redox transformations required for the activation and functionalization of small-molecule substrates. Redox-active ligands are typically comprised of an aromatic or unsaturated backbone and provide stability for ligand radicals via delocalization throughout the π system. Most redox-active ligands to date are derived from either diimines or 1,2-disubstituted benzene rings and involve combinations of nitrogen, oxygen, and sulfur donors.[1,3−8] Perhaps surprisingly, there have been limited reports of similar arene-based redox-active ligand frameworks containing phosphorus donor atoms. The exploration of phosphorus-containing redox-active ligands has been mostly confined to metallocenes substituted with phosphine donors (i.e., dppf and derivatives thereof)[9,10] and metal clusters appended to phosphine donors.[11]

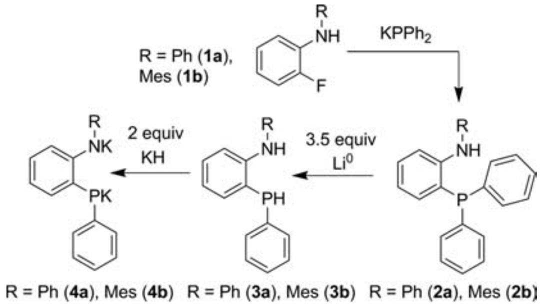
By analogy to reported noninnocent ligands with aryl-linked nitrogen, oxygen, or sulfur donors, it might also be expected that aryl phosphide ligands might be found to display redox activity. Indeed, the bridging phosphido donor of a tridentate pincer ligand in a series of Cu_2P_2 diamond-core complexes was shown to be the center of multielectron redox activity.[12,13] Within our own group, we have investigated pincer ligands with N-heterocyclic phosphido ligands and demonstrated their ability to participate in redox processes via geometrical conformation changes.[14] While tridentate pincer ligands with phosphido donors have shown interesting coordination chemistry with both early and late transition metals[15−23] and bidentate phosphide[24,25] and amidophosphine ligands[26] have been investigated, there are no systematic investigations of the redox activity of bidentate ligands with phosphorus donors. Herein, we turn our attention specifically to the arene-linked mixed-donor amidophosphido ligands $[NP]^{2-}$ (Scheme 1) and examine their noninnocent behavior upon coordination to copper.

Scheme 1



The target ligands were synthesized from commercially available starting materials via a relatively high-yielding (50−67% overall yield) three-step synthetic route (Scheme 2).

Scheme 2



Palladium-catalyzed Buchwald−Hartwig cross-coupling of the corresponding aniline and aryl halide precursors generated the *o*-fluorodiarylamines **1a** and **1b**. Treatment of the aryl fluorides with $KPPh_2$ installed the *o*-diphenylphosphine functionality in **2a** and **2b**. The desired secondary phosphine precursors **3a** and **3b** could then be formed in modest yield via reductive cleavage of one P−C bond using 3.5 equiv of Li^0 metal in tetrahydrofuran (THF), followed by hydrolysis.[27] The ^{31}P NMR spectra of **3a** and **3b** showed singlets at δ −56.9 and −59.6, respectively, and the ^{1}H NMR spectra of these compounds revealed diagnostic doublets at δ 5.19 and 5.33 with large coupling to ^{31}P [$^{1}J_{P-H}$ = 223 (**3a**), 221 Hz (**3b**)] for the phosphorus-bound protons. The doubly deprotonated amidophosphido ligands $[^{R}NP]^{2-}$ [R = Ph

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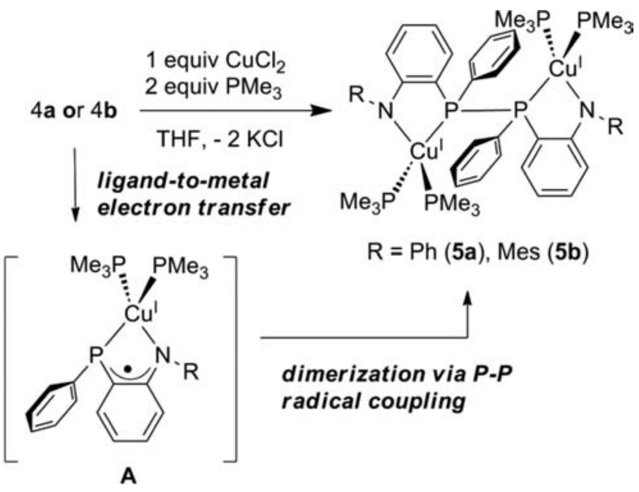
(**4a**), Mes (**4b**)] can be formed quantitatively upon treatment with KH in THF and were isolated as orange solids. The ^{31}P NMR resonance for **4a** was shifted downfield to δ −29.3 upon deprotonation.

The addition of either **4a** or **4b** to $CuCl_2$ in the presence of excess PMe_3 in THF at −78 °C afforded an orange/red solution from which the diamagnetic copper complexes $[(^{R}NP)Cu(PMe_3)_2]_2$ [R = Ph (**5a**), Mes (**5b**)] could be isolated. The ^{31}P NMR spectrum of complex **5a** features two resonances in a 2:1 integral ratio at δ −46.0 and −22.6 (δ −46.6 and −28.2 for **5b**), corresponding to bound PMe_3 and ^{Ph}NP ligands, respectively. Notably, no P−P coupling is observed by ^{31}P NMR, and only one broad signal for the bound PMe_3 ligands is observed in the ^{31}P NMR spectrum of **5a** at all temperatures investigated (228−293 K), but at low temperature (<253 K), the resonances associated with the methyl groups of PMe_3 decoalesce into two separate signals (see Supporting Information, SI). At first, the apparent diamagnetism of complexes **5a** and **5b** suggested a dimeric copper(II) antiferromagnetically coupled product; however, the X-ray structure determination revealed both products to be dimeric copper(I) complexes linked via P−P coupling of the ligated NP ligands (Scheme 3).

Scheme 3



The solid-state structures of complexes **5a** and **5b** reveal that each copper atom adopts a distorted tetrahedral geometry and that the two copper(I) units are oriented in a staggered conformation (Figure 1 and S4 in the SI). The P(1)−P(1′) bond distance of 2.2338(9) Å is similar to that reported for other dimeric complexes linked by $Ar_2P{-}PAr_2$ functionalities (2.15−2.38 Å).[28] The ring linking the amide and phosphine donor atoms maintains its aromatic character, with an average C−C distance of 1.40 Å (see Table S1 in the SI).

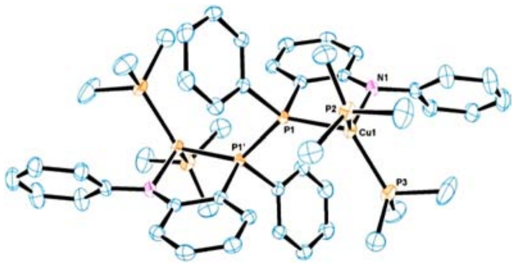


Figure 1. Displacement ellipsoid (50%) representation of complex **5a** with all hydrogen atoms omitted for clarity. Relevant interatomic distances (Å): Cu1−P1, 2.2876(6); Cu1−P2, 2.2584(6); Cu−P3, 2.2773(6); Cu1−N1, 2.0520(16); P1−P1′, 2.2338(9).

While many transition-metal (typically multimetallic) diphosphine $R_2P{-}PR_2$ complexes have been reported, they are typically formed directly from $R_2P{-}PR_2$, and in many cases, the P−P bond is cleaved upon addition to transition metals to form phosphido-bridged complexes. Group IV metals have been shown to mediate P−P bond formation via dehydrocoupling,[29−31] and in a few instances, the coupling of two metal-bound phosphido units has been suggested to proceed via a radical mechanism.[32−34]

We speculate that, in the present case, P−P coupling occurs via oxidation of the $[^{R}NP]^{2-}$ ligand by copper(II) upon coordination to form a transient $[^{R}NP]^{\bullet-}$ Cu^{I} complex (**A**) featuring a ligand-based radical (Scheme 3). Intermolecular P−P coupling then leads to complexes **5a** and **5b**. Although no intermediates were observed spectroscopically, computational studies using density functional theory (DFT) were used to better elucidate the electronic structure of the purported ligand radical formed en route to **5a** and **5b**. A geometry optimization was performed on the hypothetical monomer $[^{R}NP]Cu(PMe_3)_2$ (**A**). The geometry about copper in intermediate **A** is pseudotetrahedral, with a relatively planar geometry about the amido nitrogen atom (Σ_N = 358.9°). The geometry about phosphorus, however, is pyramidal (Σ_P = 320.1°) and indicative of stereochemically active electron density. Visualization of the singly occupied molecular orbital (SOMO; Figure 2) reveals significant electron density on the phosphorus atom (Mulliken spin density = 0.40), with very little unpaired spin on the copper center (Mulliken spin density = 0.09). The remainder of the electron density on the SOMO of **A** resides on the amide nitrogen atom (Mulliken spin density = 0.16) and throughout the aromatic π system of the ligand. This delocalization results in a lengthening of the average C−C bond in the *N*-aryl−P ring to 1.43 Å (see Table S1 in the SI). Thus, DFT predicts that, upon treatment with dianionic ligand **4a** or **4b**, copper(II) is reduced by the ligand to form a monomeric $[^{R}NP]^{\bullet-}$/copper(I) intermediate featuring a ligand radical rather than the simple $[^{R}NP]^{2-}$/copper(II) metathesis product. Because the majority of the unpaired electron density resides on the phosphorus atom, intermediate **A** can easily dimerize via P−P coupling to form **5a** or **5b**. Similar phenomena have been observed with catecholate analogues bearing one or two sulfur donors: while phenoxyl radicals are typically delocalized throughout the aromatic π system, phenylthiyl radicals tend to have significantly more radical character on the sulfur atom, and examples of S−S radical dimerization have been reported.[35−38]

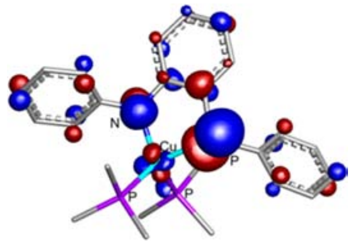


Figure 2. Pictorial representation of the calculated SOMO of intermediate **A**.

Further studies have shown that treatment of **4a** with stoichiometric CuCl in the presence of PMe_3 does not lead to

5a but rather a mixture of Cu^I−PMe_3 adducts and free ligand **3a**; however, the addition of $AgPF_6$ to a mixture of **4a**, CuCl, and PMe_3 produced compound **5a** quantitatively (by ^{31}P NMR spectroscopy). Thus, an outer-sphere oxidant is also capable of oxidizing the $[^RNP]^{2-}$ ligand to eventually form the P−P coupled product. In fact, compound **5a** can also be produced by the addition of 2 equiv of CuCl to **4a** in the presence of PMe_3 (albeit in low yield), presumably via the sacrificial reduction of 1 equiv of copper(I) to copper(0).

Cyclic voltammetry was used to explore the further redox chemistry of **5a** and **5b**. The cyclic voltammograms (CVs) of **5a** and **5b** in THF display irreversible oxidative waves at −0.27 and −0.38 V, respectively (vs $FeCp_2^{0/+}$), presumably assigned to the copper(II)/copper(I) couple. The lower oxidation potential for complex **5b** can be explained by the more electron-releasing nature of the *N*-mesityl rings, and the CV of this complex has a second irreversible feature at −0.11 V, which may be attributed to ligand-based redox activity. Nonetheless, the irreversibility of these oxidative features may imply that oxidation of these complexes to copper(II) involves further ligand-based chemical rearrangement.

In summary, we have reported the syntheses of new bidentate amidophosphido mixed-donor ligands that, based on analogy to similar oxygen-, nitrogen-, and sulfur-donor ligands, have the potential to participate in ligand-based redox activity. Preliminary investigations into their coordination chemistry with $CuCl_2$ result in a reduced dicopper(I) complex in which P−P coupling has occurred. This result suggests that copper(II) is capable of oxidizing the ligand, leading to a ligand-based radical with most of its electron density on phosphorus, allowing radical P−P coupling to occur.

Investigations into the coordination chemistry of this series of ligands with other transition metals are currently underway. Additionally, modified ligands with more sterically encumbering phosphorus-donor substituents are under development to discourage intermolecular coupling processes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental and spectroscopic details for all compounds, CVs of complexes **5a** and **5b**, additional crystallographic data and refinement details for complexes **5a** and **5b**, and computational details. 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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