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Cu^{I} Complexes with a Noninnocent PNP Ligand: Selective Dearomatization and Electrophilic Addition Reactivity

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The neutral, T-shaped complex Cu^{I}(PN^{-}P^{tBu}) (**2**), featuring a dearomatized 2,6-bis(diphosphino)pyridine (PNP)-pincer ligand, is shown to interact rapidly with electrophiles. This has enabled the synthesis of acetato complex **3**. Furthermore, C−C bond formation onto the deprotonated methylene-bridgehead carbon is observed with MeOTf as the electrophile. This represents the first case of selective modification of the lutidine-based backbone of such noninnocent PNP ligands. Theoretical calculations support the formation of monomeric complex **2** and indicate the high reactivity of the methylene fragment in this Cu^{I} complex.

Traditionally, ligands applied in coordination chemistry and homogeneous catalysis were considered not to partake in the actual chemical reactions ensued by the metal center. Recently, several systems emerged that display noninnocent behavior, mainly acting as a redox-active group[1] or, e.g., as a Lewis base.[2] Fewer examples exist wherein the ligand actually reacts irreversibly.[3] Metal interaction is expected to be facilitating these reactions.

Late-transition-metal complexes incorporating the 2,6-bis(diphosphino)pyridine (PNP) ligand skeleton[4] have been shown to undergo deprotonation of a backbone methylene spacer upon reaction with strong bases rather than nucleophilic substitution at the metal center[5] concomitant with a formal charge switch of the PNP ligand from neutral to monoanionic. Beyond these elegant examples, little fundamental insight into the character and reactivity of the dearomatized PN^{-}P fragment is available.

We recently reported on the chemistry of ligand **PNP^{tBu}** with nickel(II)[6] and copper(I),[7] including the formation of a rare cationic T-shaped complex [Cu^{I}(PNP)]SbF$_6$ (**A**).

Herein we describe the synthesis and reactivity of a neutral Cu^{I} analogue of **A** (Scheme 1). These studies are supported by density functional theory (DFT) calculations. Selective electrophilic C−C bond formation with participation of the ligand scaffold in the addition reaction is observed.

The reaction of equimolar amounts of **1** with the strong base NaN(SiMe$_3$)$_2$ (or KO^{t}Bu) in tetrahydrofuran (THF) led to a rapid color change from yellow to orange. Extraction into diethyl ether yielded complex **2** as an orange solid. This compound proved relatively air-sensitive, especially compared to **1** or the cationic T-shaped complex **A**, [Cu(**PNP^{tBu}**)]SbF$_6$. Alternatively, the latter species can be used as the starting material for the dearomatization reaction.

Solid samples of **2** were relatively stable at −20 °C (up to 1 week). The ^{1}H NMR spectrum indicated the formation of a species of lower symmetry than that observed for complex **1** because three signals were present for the heterocyclic ring

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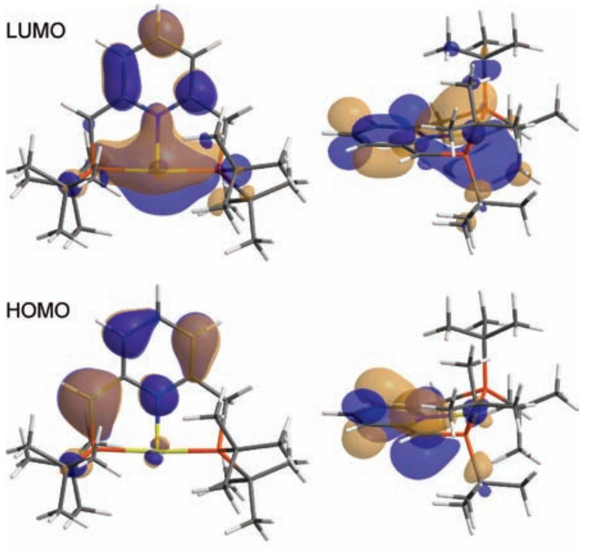
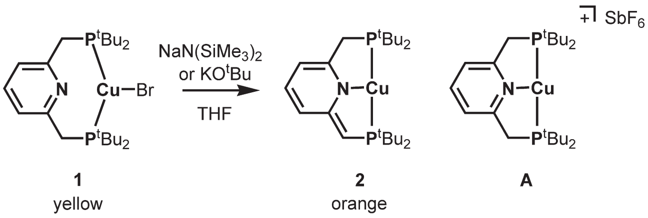


Figure 1. HOMO and LUMO frontier orbital plots for complex **2**.

Scheme 1. Synthesis of Cu^{I} Complex **2** Featuring a Dearomatized PN^{-}P Ligand and Its Structural Resemblance to the Cationic Derivative **A**

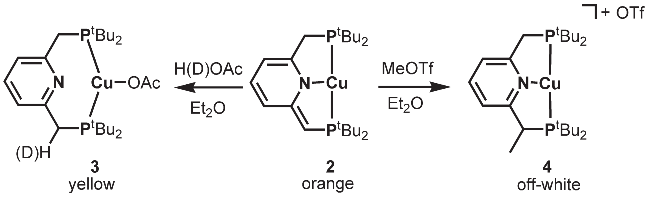


protons, together with distinct signals for the PyC*H*P and PyC*H*$_2$P spacer units as well as two well-separated doublets for the *tert*-butyl groups on the inequivalent P atoms. The ^{31}P NMR spectrum featured two doublets at δ 41 and 32, with a coupling constant J_{P-P} of 80 Hz. Dearomatization of the pyridine ring was evidenced by the IR spectrum, which showed only one band for the resulting coordinated amido unit at ν 1593 cm^{-1}. This species, therefore, appears to exist as a three-coordinate Cu^{I} center with a diphosphineamido ligand.

The high solubility of the complex precluded the isolation of suitable crystalline material for an X-ray crystallographic investigation; we therefore resorted to DFT calculations at the B3LYP/6-31G(d) level for a more insightful picture of this unusual species.[8] Our hypothesis on the structure of complex **2** as a T-shaped complex bearing a dearomatized PNP ligand was corroborated by these computations (Figure 1).

A pronounced difference is noticeable for the electronic structural plot of **2** compared to that previously calculated for complex **1**.[7] Extensive delocalization of the π system of the dearomatized heterocycle toward the deprotonated =CH(P) group is observed [highest occupied molecular orbital (HOMO); Figure 1].[8] The lowest unoccupied molecular orbital (LUMO) shows a major contribution of the Cu−N$_{Py}$ bond, supporting the amide character of the N atom. According to natural bond order charge analysis, the =CH(P) C atom bears the largest relative negative charge, −0.795.

Scheme 2. Reactivity of **2** toward Electrophiles



The dearomatized heterocyclic framework within complex **2** is quickly reprotonated to regenerate the initial pyridine fragment: the addition of 1 mol equiv of acetic acid in THF yielded complex **3** (Scheme 2), as was verified by an independent synthesis of this brown-yellow species by the reaction of **PNP^{tBu}** with Cu(OAc) in toluene. This provides further evidence for the mononuclear character of intermediate species **2**. Preliminary experiments have indicated that phenylacetylene and benzylmercaptan also readily reprotonate **2**. With stoichiometric amounts of methanol, water, or 2,2,2-trifluoroethanol, no reprotonation was apparent, even at elevated temperatures.[9] Reprotonation is assumed to take place directly at the =CH(P) fragment, but the intermediacy of the amido group in the reprotonation process cannot be ruled out.

The band for the dangling pyridine fragment was obscured by one of the strong bands attributed to the acetate ligand (ν 1572 and 1388 cm^{-1}). The ^{31}P NMR spectrum displayed a singlet at δ 42.7, and the acetate fragment led to a singlet at δ 2.30 in the ^{1}H NMR spectrum. The analogous acetic acid-d_1 gave clean formation of complex **3^{D}** with full incorporation of the deuteron in the methylene bridgehead of the ligand backbone, as deduced from the integration ratio of the respective methylene and acetate protons in the ^{1}H NMR spectrum.

An X-ray crystal structure determination confirmed the proposed constitution for complex **3** (Figure 2). As anticipated, the Cu^{I} core is in a distorted trigonal-planar arrangement with a P$_1$−Cu−P$_2$ angle of 139.762(15)°. There is no true Cu−N$_{Py}$ bond because the Cu$_1\cdots$N$_1$ distance of 2.8791(13) Å is too large and the line Cu$_1\cdots$N$_1$ forms an angle of 41.23(6)° with the least-squares plane of the pyridine ring. The acetate ligand is coordinated in a κ^1-O mode because the intramolecular Cu−O distances are 2.1028(13) Å (Cu$_1$−O$_1$) and 2.6099(13) Å (Cu$_1\cdots$O$_2$). Monodentate coordination of acetates, although uncommon, has been reported before with Cu^{I}.[10]

To explore this ligand-based nucleophilicity of complex **2** further, MeOTf was chosen as a candidate substrate.[11]

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[8] Calculations were performed at B3LYP/6-31G(d) level: Frisch, M. J. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh, PA, **2003** (see the Supporting information, ref S2, for full details).

[9] This is in contrast with observations on analogous Pt[a] and Ru[b] complexes with dearomatized PNP and PNN skeletons:(a) Vuzman, D.; Poverenov, E.; Shimon, L. J. W.; Diskin-Posner, Y.; Milstein, D. *Organometallics* **2008**, *27*, 2627. (b) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. *Science* **2009**, *324*, 74–77. For Rh(SN^{-}N) complexes, reprotonation also proved more cumbersome. See: Schaub, T.; Radius, U.; Diskin-Posner, Y.; Leitus, G.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2008**, *27*, 1892–1901.

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[11] During our investigations, the addition of MeOTf to the amide N atom of a monoanionic, aliphatic PNP scaffold within a Pd complex was reported: Marziale, A. N.; Herdtweck, E.; Eppinger, J.; Schneider, S. *Inorg. Chem.* **2009**, *48*, 3699–3709.

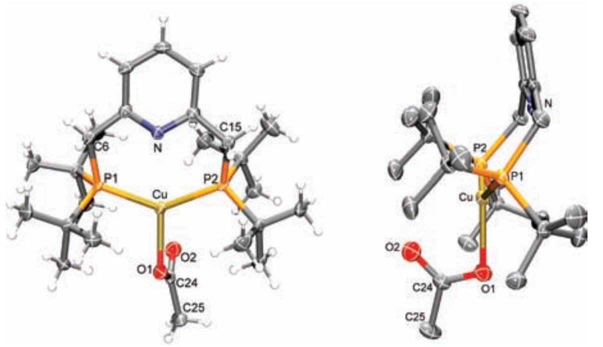

Figure 2. Displacement ellipsoid plot (50% probability) of complex **3**, Cu(OAc)(**PNP^{tBu}**) as well as a side view (excluding H atoms). Selected bond lengths (Å) and angles (deg): Cu_1-P_1 2.3017(4), Cu_1-P_2 2.3098(4), $Cu_1\cdots N_1$ 2.8791(13), Cu_1-O_1 2.1028(13), $Cu_1\cdots O_2$ 2.6099(13); $P_1-Cu_1-P_2$ 139.762(15), $P_1-Cu_1-O_1$ 108.69(4), $P_1-Cu_1\cdots N_1$ 70.09(3), $O_1-Cu_1\cdots N_1$ 147.53(5), $Cu_1-P_1-C_6$ 116.03(5), $Cu_1-O_1-C_{24}$ 102.06(11), $P_1-Cu_1\cdots O_2$ 114.19(3), $P_2-Cu_1\cdots O_2$ 97.88(3).

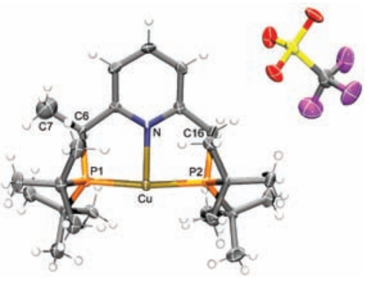

Figure 3. Displacement ellipsoid plot (50% probability) of complex **4**, [Cu(*Me***PNP^{tBu}**)]OTf. Only one of the two independent molecules present in the asymmetric unit is displayed. Selected bond lengths (Å) and angles (deg): Cu_1-P_1 2.212(2), Cu_1-P_2 2.214(2), Cu_1-N_1 2.109(5), C_6-C_7 1.523(8); $P_1-Cu_1-P_2$ 171.82(10), $P_1-Cu_1-N_1$ 87.89(15), $P_2-Cu_1-N_1$ 87.05(15), $Cu_1-P_1-C_6$ 98.2(2), $Cu_1-P_2-C_{16}$ 98.7(2), $P_1-C_6-C_7$ 120.5(5).

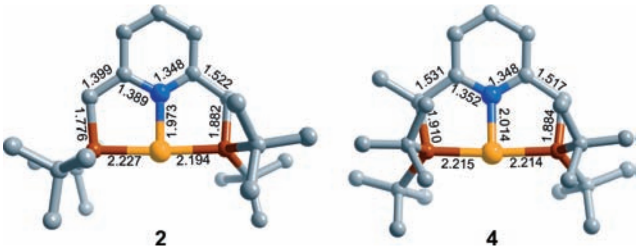

Figure 4. DFT-optimized structures for complexes **2** and **4**, including relevant calculated bond lengths (Å).

The addition of 1 equiv of methyl triflate as an electrophilic reagent to an orange solution of **2** in diethyl ether led to the precipitation of an off-white solid at room temperature. IR and NMR spectroscopy indicated clean formation of complex **4**, [Cu(*Me***PNP^{tBu}**)]OTf, with the methyl group substituted at the formerly deprotonated methylene bridgehead position. Notably, two bands reappeared in the IR spectrum at ν 1588 and 1567 cm^{-1} for the coordinated pyridine ring, and the ^{1}H NMR spectrum showed two multiplets (integral ratio 1:2) at δ 4.19 and 3.88 for the $-CHP$ and $-CH_2P$ groups, respectively, as well as a doublet at δ 2.02 for the methyl substituent in the backbone. Consequently, the inequivalent *tert*-butyl groups of the phosphine were observed as four individual doublets. In the ^{31}P NMR spectrum, two doublets were present at δ 58 and 45, with a coupling constant J_{P-P} of 80 Hz. Use of CD_3OTf aided in the elucidation of the spectral data.

An X-ray crystal structure determination on light-yellow single crystals, obtained by slow diffusion of pentane into a THF solution of **4**, confirmed the proposed constitution of this compound (Figure 3). Formation of a new C−C single bond by the addition of the methyl group of MeOTf to the methylene bridgehead atom is proven by the presence of carbon C_7 in the structure, with the C_6-C_7 bond length of 1.523(8) Å indicative of a C−C single bond. The Cu^I center is coordinated in a T-shaped geometry, with angles P_1-Cu-P_2 and P_1-Cu-N of 171.82(10)° and 87.89(15)°, respectively, which is comparable with the structure of [Cu(**PNP**)]SbF_6 (**A**).[7] No interaction of the Cu center with the triflate counterion is observed; the nearest contact is over 6 Å removed from the Cu^I center.

From DFT calculations,[8] the geometric parameters for the three complexes **1**, **2**, and **4** were computed, and the results for the latter two species are depicted in Figure 4.

Deprotonation of **1** leads to significant shortening of the C−C bond length to 1.399 Å [C_1-C_6 in **1**, calcd 1.505 Å; X-ray crystal structure, 1.502(4) Å],[7] concomitant with shortening of the relevant P−C bond by ~0.14 Å, indicating partial ylide character in the dearomatized state.[12] The Cu−N distance lengthens by ~0.04 Å in **4** compared to intermediate **2**, related to the switch from monoanionic to neutral charge of the N atom. The calculated Mulliken charges are in agreement with this observation, showing a higher negative charge on the amido-like N atom in **2** ($-0.715e^-$) compared to the pyridine-like N atom in species **4** ($-0.640e^-$).

In summary, we have reported the facile, selective, and efficient methylation of a bis(phosphino)pyridine framework. This reaction sequence relies on the dearomatization of the PNP scaffold combined with electrophilic addition using MeOTf. The described C−C coupling methodology is believed to provide a general route to new metal complexes with (chiral) substituted PNP-ligand scaffolds. Furthermore, we explore catalytic applications with Cu^I complexes. Also, other variations on the ligand framework are under investigation.

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Supporting Information Available: Experimental details for complexes **2**−**4**, computational calculations (including the full citation of ref 8), crystallographic details, and CIF files for compounds **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Similar trends were observed for a related dearomatized Ru species and its parent complex (see ref 5c): Zhang, J.; Leitus, G.; Ben-David, Y.; Milstein, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 1113–1115.