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# T-Shaped Cationic $Cu^I$ Complexes with Hemilabile PNP-Type Ligands

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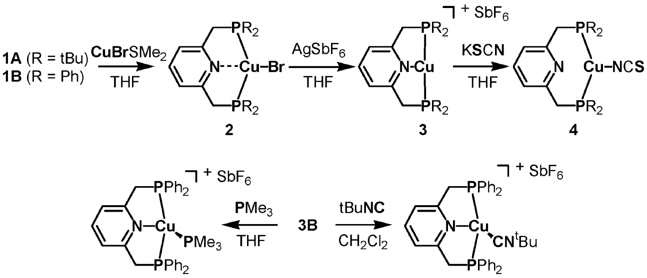
The versatile coordination behavior of the PNP ligands **1A** (2,6-bis[(di-*tert*-butylphosphino)methyl]pyridine) and **1B** (2,6-bis[(diphenylphosphino)methyl]pyridine) to $Cu^I$ is described, whereby a hemilabile interaction of the pyridine N-donor atom to the copper center resulted in a rare T-shaped complex with **1A**, while with **1B** also a tetracoordinated species could be isolated. Theoretical calculations support the weak interaction of the pyridine N donor in **1A** with the Cu center.

The formation of so-called T-shaped (late) transition metal complexes has been reported for a growing number of ligand systems and metal centers, and these inherently electron-deficient complexes often display interesting reactivity.[1] Pincer ligands based on 2,6-bis(methylene-E)benzene (monoanionic upon coordination) or -pyridine (neutral), denoted as ECE and ENE, wherein E is a (hetero)donor atom, have become a common structural motif for the synthesis of a variety of transition metal complexes. It is therefore surprising that complexes with a strict trigonal T-shaped arrangement, wherein no additional ligand is present to stabilize the metal center, are very rare and, to the best of our knowledge, have not been reported for E = phosphorus at all.

Recently, the 2,6-bis(phosphinomethyl)pyridine skeleton has attracted attention within the family of neutral pincer ligands.[2,3] However, to date, no single report on the chemistry of such neutral PNP ligands with copper(I) exists.[4,5] We therefore set out to explore the coordination of the neutral ligands $PNP^{tBu}$ (**1A**)[6] and $PNP^{Ph}$ (**1B**)[2a] with $Cu^I$, anticipating the formation of T-shaped complexes.

**Scheme 1.** Synthesis of Complexes **2**−**4** with Ligands **1A/1B** as Well as Reactivity of **3B** toward Additional Donor Ligands



Reaction of an equimolar amount of **1** with $CuBr(SMe_2)$ in diethyl ether yielded a bright (**A**) or intense yellow (**B**) solid after workup (Scheme 1). Complex **2A** displayed a singlet at $\delta$ 46.2 (acetone-$d_6$) in the $^{31}P$ NMR spectrum ($\delta$ −3.0 for **2B**). Notably, the IR spectrum indicated that the

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(2) For the $PPh_2$-based PNP-ligand, see: (a) Dahlhoff, W. V.; Nelson, S. M. *J. Chem. Soc. A* **1971**, *218*, 4–2190. (b) Sacco, A.; Vasapollo, G.; Nobile, C. F.; Piergiovanni, A.; Pellinghelli, M. A.; Lanfranchi, M. *J. Organomet. Chem.* **1988**, *356*, 397–409. (c) Hahn, C.; Cucciolito, M.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038–9039. (d) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786–2792.

(3) For $PR_2$-based PNP-ligands, see: (a) Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. *Inorg. Chem.* **2006**, *45*, 7252–7260. (b) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 4736–4738. (c) Feller, M.; Ben-Ari, E.; Gupta, T.; Shimon, L. J. W.; Leitus, G.; Diskin-Posner, Y.; Weiner, L.; Milstein, D. *Inorg. Chem.* **2007**, *46*, 10479–10490.

(4) One previous report mentions the intended formation of a $Cu^I$ complex with a PNP ligand, but phosphine and metal oxidation occurred and a $Cu^{II}$−oxide complex was obtained: Lang, H.-F.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2002**, *329*, 9–12.

(5) Tetrahedral coordination of $Cu^I$ to a supermesityl substituted bis(phosphaethenyl)pyridine ligand was recently reported, see: Hayashi, A.; Okazaki, M.; Ozawa, F.; Tanaka, R. *Organometallics* **2007**, *26*, 5246–5249.

(6) (a) Kawatsura, M.; Hartwig, J. F. *Organometallics* **2001**, *20*, 1960–1964. (b) Hermann, D.; Gandelman, M.; Rozenberg, H.; Shimon, L. J. W.; Milstein, D. *Organometallics* **2002**, *21*, 812–818.

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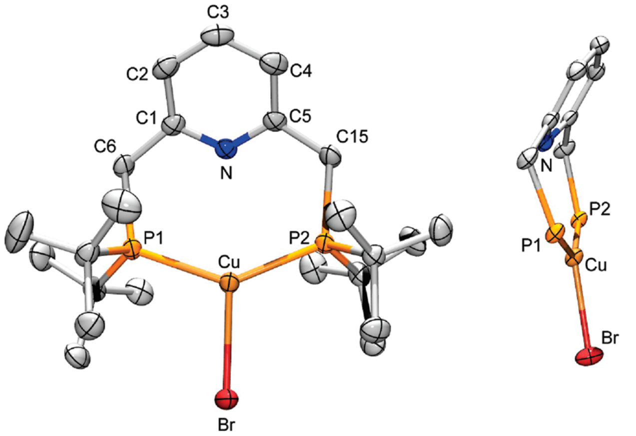

**Figure 1.** Displacement ellipsoid plots (50% probability level) of complex **2A**, Cu(**1A**)Br. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Cu−$P_1$, 2.3150(5); Cu−$P_2$, 2.3104(5); Cu···N, 2.8938(17); Cu−Br, 2.4376(3); $P_1$−Cu−$P_2$, 140.75(2); $P_1$−Cu−Br, 106.555(16); $P_2$−Cu−Br, 112.658(16); $P_1$−Cu···N, 70.43(5); $P_2$−Cu···N, 70.37(5); Br−Cu···N, 174.03(4); Cu−$P_1$−$C_6$, 114.56(7); Cu−$P_2$−$C_{15}$, 115.42(7); Cu···N···$C_3$, 133.34(8).

pyridine nitrogen showed variable coordination behavior toward $Cu^I$, depending on the ligand environment. For **2A**, bands were observed at $\nu$ 1584 (shoulder) and 1576 $cm^{-1}$ that are assigned to an uncoordinated pyridine fragment,[7] similar as seen for ligand **1**, while for **2B**, the well-separated bands at $\nu$ 1587 and 1567 $cm^{-1}$ are indicative of a true Cu−N bonding interaction (see the Supporting Information for the molecular structure of **2B**, with an intramolecular Cu−N distance of 2.160(3) Å, confirming this statement).

Recrystallization from $Et_2O$ at −20 °C yielded yellow block-shaped single crystals suitable for X-ray diffraction (Figure 1) for complex **2A**, which crystallized in the monoclinic space group $P2_1/c$, and with Cu−P atom distances of 2.3104(5) and 2.3150(5) Å. The $P_1$−Cu−$P_2$ angle was found to be 140.75(2)°, leading to a distorted equilateral triangular geometry for the copper ion. The nitrogen atom of the pyridine ring is well outside the bonding distance at ~2.89 Å. Furthermore, the pyridine ring is tilted out of the P−Cu−P plane, as deduced from the angle Cu···$N_1$···$C_3$ of 133.34(8)°.

We wondered whether the pyridine ring might be included in the coordination environment of the $Cu^I$ ion in the absence of the strongly $\sigma$-donating halide coligand. This would open up a new coordination mode if additional exogenous ligation could be repressed. The reaction of $AgSbF_6$ with complex **2** in THF yielded complex **3** as a bright green (**3A**) or light-yellow solid (**3B**) after solvent removal. Surprisingly, these compounds are not very susceptible to decomposition by air.[8] The $^{31}P$ NMR spectrum showed signals at $\delta$ 42.6 (**3A**) and $\delta$ 0.5 (**3B**) in acetone-$d_6$, while IR spectroscopy revealed that the pyridine ring is coordinated to the $Cu^I$ ion, with bands at 1591 and 1566 $cm^{-1}$ (**3A**) or 1596 and 1567 $cm^{-1}$ (**3B**). The $^1H$ NMR spectrum did not indicate ligation of any additional solvent molecule. Recrystallization of complex **3A** from THF/pentane furnished suitable single crystals that were analyzed by X-ray diffraction (Figure 2). Complex **3A** was shown to crystallize in the triclinic space group $P\bar{1}$.

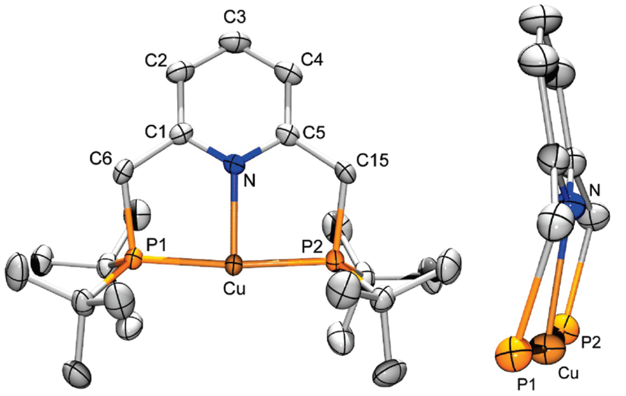

**Figure 2.** Displacement ellipsoid plots (50% probability level) of the cationic part of complex **3A**, [Cu(**1A**)]$SbF_6$. The noncoordinated $SbF_6$ counterion and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): $Cu_1$−$P_1$, 2.2211(8); $Cu_1$−$P_2$, 2.2215(8); $Cu_1$−$N_1$, 2.091(2); $P_1$−$C_6$, 1.858(3); $P_2$−$C_{15}$, 1.865(3); $Cu_1$···$Sb_1$, 5.4520(5); $Cu_1$···$F_3$, 4.400(3); $P_1$−$Cu_1$−$P_2$, 172.44(3); $N_1$−$Cu_1$−$P_1$, 87.22(7); $N_1$−$Cu_1$−$P_2$, 87.49(7); $Cu_1$−$P_1$−$C_6$, 98.47(10); $Cu_1$−$P_2$−$C_{15}$, 98.69(10); $Cu_1$···$N_1$···$C_3$, 161.13(15).

Coordination of the pyridine N atom is evident from the Cu−N bond length of 2.091(2) Å, which results in a large $P_1$−Cu−$P_2$ angle of 172.44(3)° and N−Cu−P angles of 87.22(7) and 87.49(2)°. The closest Cu contact to the $SbF_6$ counterion is with fluorine-atom $F_3$, but the distance of 4.400(3) Å is clearly outside of the bonding range. The $Cu^I$ environment in complex **3A** has approximate local $C_{2v}$ symmetry with a T-shaped geometry around copper, somewhat related to the $Cu^I$ complex reported by Halcrow et al. featuring a bis(pyrazolyl)pyridine ligand.[9] To the best of our knowledge, this kind of trigonal, T-shaped arrangement is unprecedented for copper(I) complexes with a P−N−P donor set, judging from a search of the Cambridge Crystal Structure Database.[10]

From the side view of complex **3A**, shown in Figure 2, the nonplanar arrangement of the pyridine ring with the $Cu^I$ center is evident, which leads to an out-of-plane distortion of ~19°. Arguably, this conformation may lead to unusual reactivity, due to weaker (i.e., hemilabile) binding of the pyridine N atom with the Cu ion, as the $\pi$ orbital of the nitrogen donor does not overlap perfectly with the $d_{xz}$ orbital of the copper center. Niecke et al. reported a diphosphine macrocycle incorporating two pyridine rings that showed a distorted tetrahedral or "seesaw" geometry upon coordination to $Cu^I$.[11] Ligand **1A** appears to be unable to enforce a similar stable tetracoordinate geometry; the addition of $^t$BuNC to a solution of **3A** in THF did not induce stable coordination of the neutral coligand in the solid state.[11] This most likely relates to the steric hindrance induced by the phosphine groups and the resulting unfavorable crystal packing,

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(7) (a) Hahn, C.; Vitagliano, A.; Giordano, F.; Taube, R. *Organometallics* **1998**, *17*, 2060–2066. (b) Müller, G.; Klinga, M.; Leskelä, M.; Rieger, B. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2839–2846, and references therein.

(8) Solid samples of complexes **2** and **3** appear to be stable in air. A full investigation of the electrochemical properties of these and related compounds will be reported elsewhere.

(9) Foster, C. L.; Kilner, C. A.; Thornton-Pett, M.; Halcrow, M. A. *Polyhedron* **2002**, *21*, 1031–1041.

(10) Cambridge Crystallographic Database, February 2008.

(11) Ekici, S.; Nieger, M.; Glaum, R.; Niecke, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 435–438.

(12) Coordination of $^t$BuNC was indicated by NMR and IR spectroscopy, but recrystallization of the green solid led to reorganization, as indicated by NMR spectroscopy (see the Supporting Information).

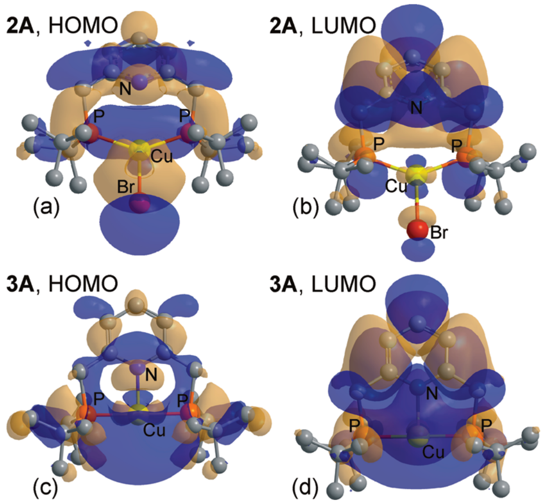

**Figure 3.** Frontier orbital plots for the (a) HOMO and (b) LUMO of complex **2A** and the (c) HOMO and (d) LUMO for complex **3A**, based on DFT calculations.

as indicated also by the results of DFT B3LYP/6-31G(d) calculations.[13]

The observed out-of-plane tilting of the pyridine ring is reproduced in the calculations. There is significant $\sigma$-bonding character of the Cu−Br bond in **2A**, and the Cu−N $\sigma$ interaction is nonbonding. The highest occupied molecular orbital (HOMO) for both complex **2A** and **3A** (Figure 3) shows strongly bonding Cu−P interactions, whereas antibonding character for the Cu−N interaction is observed for the cationic fragment in **3A**. The LUMO for **3A** indicates a strongly bonding interaction between Cu and N. This indicates the hemilabile character of the Cu−N bond.

With strongly donating anionic ligands, the above T-shaped geometry is not retained. Thus, the addition of 1 equiv of KSCN to a light-green solution of **3A** in THF resulted in the rapid formation of a deep-green solution. Characterization of the corresponding green solid showed that the hemilabile Cu−N$_{Py}$ bond is disrupted, indicated by the diagnostic IR band for the free pyridine fragment ($\nu$ 1574 cm$^{-1}$) and a bound thiocyanate ligand ($\nu$ 2067 cm$^{-1}$) in the solid state. The product was formulated as Cu($\kappa^2$-*P*,*P*-**1**)(NCS), complex **4**.[14]

As we were unable to crystallographically characterize a tetracoordinated Cu$^{I}$ complex supported by ligand **1A**, we turned our attention to the diphenylphosphino analogue **1B**. Instantaneous fading of the yellow color to leave a colorless solution was evident upon the addition of 1 equiv of $PMe_3$ (**5**) or $^t$BuNC (**6**) to a solution of **3B** in THF (Scheme 1), as deduced from the respective $^1$H NMR spectra. Complex **6** showed an IR band at $\nu$ 2177 cm$^{-1}$. Furthermore, the coordination around the Cu$^{I}$ center in complex **5** (Figure 4) was elucidated by an X-ray crystal structure determination. Complex **5** crystallized in the monoclinic space group $P2_1/n$ with four formula units per unit cell.

The N−Cu−P$_1$ and P$_1$−Cu−P$_2$ angles of 80.99(6)° and 133.64(3)°, respectively, and the observed dihedral angle P$_1$−P$_2$−Cu−P$_3$ of 176.69(6)° give rise to a distorted trigonal-pyramidal Cu$^{I}$ center. The assumed T-shaped geometry present in **3B** clearly shows flexible behavior, but a true “seesaw” arrangement was not observed. Figure 5 summarizes some notable structural comparisons of complexes **3A** and **5** with Cu$^{I}$ species based on bis(carbene)pyridine[5] and bis(phosphaalkenyl)pyridine.[9]

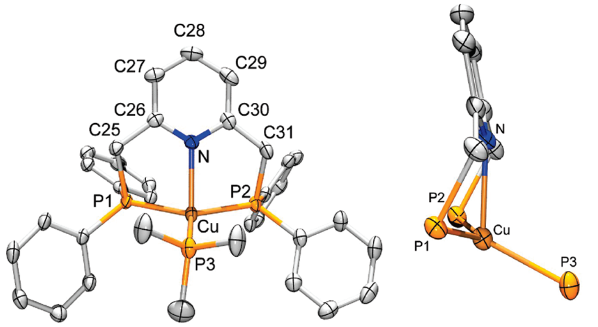

**Figure 4.** Displacement ellipsoid plots (50% probability level) of the cationic part of complex **5**. The noncoordinated SbF$_6$ counterion and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): Cu−P$_1$, 2.2765(8); Cu−P$_2$, 2.2792(7); Cu−P$_3$, 2.2391(9), Cu−N, 2.157(2); P$_1$−C$_{25}$, 1.853(3); P$_2$−C$_{31}$, 1.853(3); P$_1$−Cu−P$_2$, 133.64(3); P$_1$−Cu−P$_3$, 110.46(3); P$_2$−Cu−P$_3$, 115.84(3); N−Cu−P$_1$, 80.99(6); N−Cu−P$_2$, 82.63(6); N−Cu−P$_3$, 114.13(6), Cu−P$_1$−C$_{25}$, 97.35(8); Cu−P$_2$−C$_{31}$, 95.44(8); Cu−N···C$_{28}$, 166.30(12).

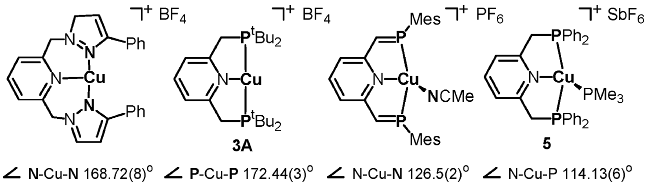

**Figure 5.** Structural correlation of T-shaped complex **3A** and distorted trigonal-pyramidal species **5** with relevant literature precedents.[5,9]

In summary, ligand class **1** exhibits hemilabile coordination of the pyridine nitrogen donor toward Cu$^{I}$. The selective formation of T-shaped complexes **3** is demonstrated. The addition of thiocyanate disrupts the Cu−N$_{Py}$ bond and regenerates a trigonal planar geometry for the Cu$^{I}$ ion. The coordination of neutral donor ligands is governed by steric factors; only in the case of **3B** was stable coordination of $PMe_3$ and $^t$BuNC observed, also in the solid state. The built-in hemilabile coordination—switch of the PNP—ligand will prove useful for catalytic applications of these Cu$^{I}$ complexes, and initial screening studies are ongoing.

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**Supporting Information Available:** Experimental details for complexes **2**−**6**, molecular structures of complexes **2B** and **4**, computational calculations (including full citation of ref 13), crystallographic details and CIF files for compounds **2A**, **2B**, **3A**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Calculations were performed at B3LYP/6-31G(d) level: Frisch, M. J.; et al. *Gaussian 03*, revision B.05; Gaussian, Inc.: Pittsburgh PA, 2003 (see Supporting Information for full details).

(14) We confirmed this by an independent synthesis of **4** starting from **1A** and commercially available Cu(SCN). This complex shows distorted trigonal planar geometry around the Cu$^{I}$, analogous to complex **2**. See Figure S2 in the Supporting Information.