Inorg. Chem. **2008**, *47*, 4442−4444

Inorganic Chemistry
Communication

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

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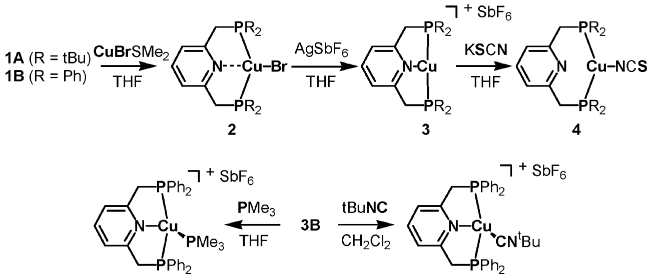
Received February 15, 2008

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 δ 46.2 (acetone-d_6) in the ^{31}P NMR spectrum (δ −3.0 for **2B**). Notably, the IR spectrum indicated that the

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(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.

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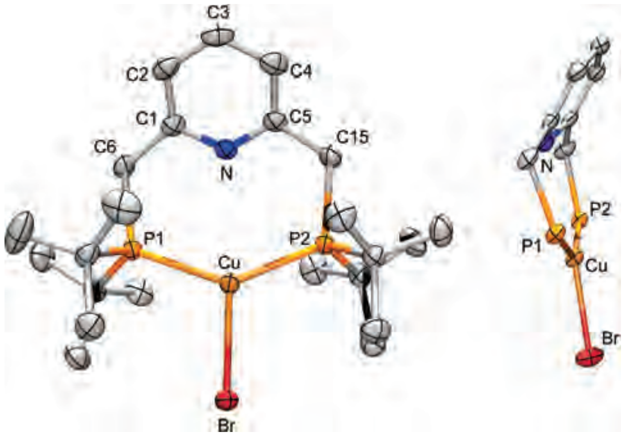

Figure 1. Displacement ellipsoid plots (50% probability level) of complex **2A**, Cu(**1A**)Br. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): Cu−P_1, 2.3150(5); Cu−P_2, 2.3104(5); Cu···N, 2.8938(17); Cu−Br, 2.4376(3); P_1−Cu−P_2, 140.75(2); P_1−Cu−Br, 106.555(16); P_2−Cu−Br, 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).

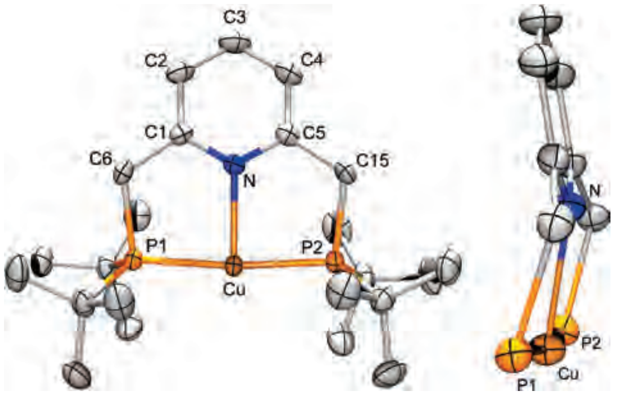

Figure 2. Displacement ellipsoid plots (50% probability level) of the cationic part of complex **3A**, [Cu(**1A**)]SbF_6. The noncoordinated SbF_6 counterion and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): Cu_1−P_1, 2.2211(8); Cu_1−P_2, 2.2215(8); Cu_1−N_1, 2.091(2); 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).

pyridine nitrogen showed variable coordination behavior toward Cu^I, depending on the ligand environment. For **2A**, bands were observed at ν 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 ν 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 σ-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 δ 42.6 (**3A**) and δ 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 $P\bar{1}$.

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 π 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).

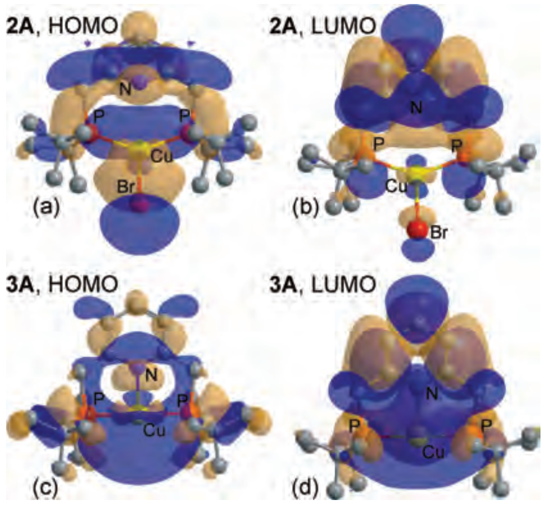

Figure 3. Frontier orbital plots for the (a) HOMO and (b) LUMO of complex **2A** and the (c) HOMO and (d) LUMO for complex **3A**, based on DFT calculations.

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 σ-bonding character of the Cu−Br bond in **2A**, and the Cu−N σ 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 (ν 1574 cm^{-1}) and a bound thiocyanate ligand (ν 2067 cm^{-1}) in the solid state. The product was formulated as Cu(κ^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 ν 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.

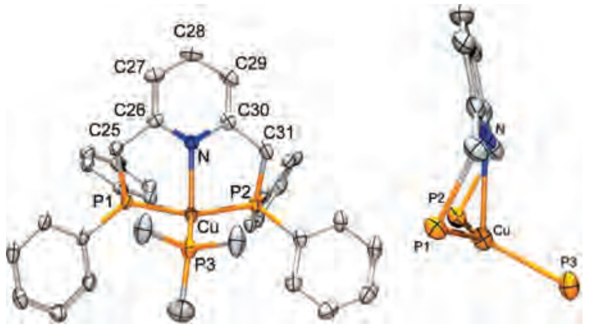

Figure 4. Displacement ellipsoid plots (50% probability level) of the cationic part of complex **5**. The noncoordinated SbF$_6$ counterion and hydrogen atoms are omitted for clarity. Selected atom distances (Å) and angles (deg): Cu−P$_1$, 2.2765(8); Cu−P$_2$, 2.2792(7); Cu−P$_3$, 2.2391(9), Cu−N, 2.157(2); 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).

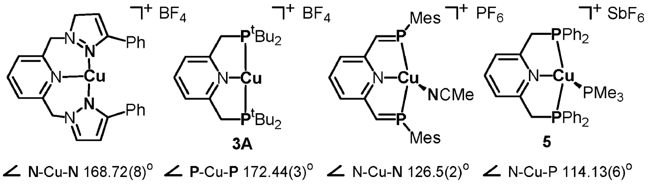

Figure 5. Structural correlation of T-shaped complex **3A** and distorted trigonal-pyramidal species **5** with relevant literature precedents.[5,9]

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]

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.

Acknowledgment. This research has been made possible by an Innovation grant (VENI) from the Dutch Research Council—Chemical Sciences (NWO−CW) to J.I.v.d.V. and support from Eindhoven University of Technology.

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.