**COMMUNICATION**

# Synthesis and coordination behavior of Cu[I] bis(phosphaethenyl)pyridine complexes

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**Cu[I] complexes bearing BPEP as a PNP-pincer type phosphaalkene ligand undergo effective bonding interactions with $SbF_6^-$ and $PF_6^-$ as non-coordinating anions to give $[Cu(SbF_6)(BPEP)]$ and $[Cu_2(BPEP)_2(\mu\text{-}PF_6)]^+$, respectively**
10 **[BPEP = 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine]. NMR and theoretical studies indicate a reduced anionic charge of the $\mu\text{-}PF_6$ ligand, which is induced by the strong π-accepting ability of BPEP.**

Phosphaalkenes with P=C bond(s) are low-coordinate 15 phosphorus compounds that possess extremely low-lying π* orbitals around the phosphorus atom, and thus exhibit strong π-acceptor properties towards transition metals.[1,2] We have demonstrated with bidentate diphosphinidenecyclobutene ligands (DPCB-Y) that this property is useful for catalysis, 20 leading to highly efficient organic transformations.[3] More recently, we have developed 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP) as a tridentate PNP-pincer type phosphaalkene ligand, which successfully stabilizes a coordinatively unsaturated 15-25 electron complex with a high-spin Fe[I] center.[4]

This paper reports the synthesis and structures of BPEP complexes of copper. Although PNP-pincer type ligands are ongoing research topics in coordination chemistry,[5] their copper complexes have been extremely limited.[6–8] In this 30 study, we found that BPEP forms a Cu[I] complex of a highly electron-deficient nature, causing effective bonding interactions with "non-coordinating" anions such as $SbF_6^-$ and $PF_6^-$.

The BPEP ligand was introduced to CuBr in toluene at 90 °C (Scheme 1). The resulting [CuBr(BPEP)] (**1**) was 35 characterized by NMR spectroscopy and elemental analysis. While it has been shown that [CuBr(pnp)] [pnp = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine] as a phosphine analogue adopts a three-coordinate structure without Cu–N bonding,[6] complex **1** has the four-coordinate structure with a distorted 40 tetrahedral configuration as confirmed by X-ray diffraction analysis (see ESI). A similar structure has been found for the complex with a PNP-pincer type phosphinine ligand, and attributed to lower σ-donating ability of low-coordinate phosphorus ligands than phosphine ligands.[7]

45 Complex **1** reacted with silver salts of non-coordinating anions (AgX; X = $SbF_6$ and $PF_6$) to afford complexes of the formula "CuX(BPEP)" [X = $SbF_6$ (**2a**), $PF_6$ (**2b**)]. Since both
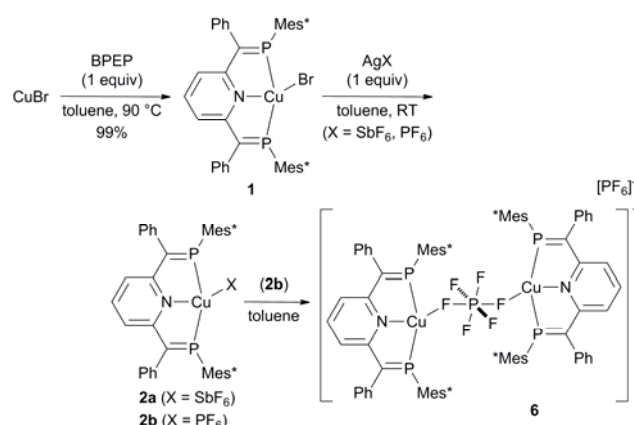


**Scheme 1** Mes* = 2,4,6-tri-*tert*-butylphenyl.

50 complexes exhibited the same ^{31}P NMR chemical shift (δ 213.3) in $CD_2Cl_2$, they should exist in ionic form in a polar solvent without direct interaction between $[Cu(BPEP)]^+$ and $X^-$.

Complex **2a** readily coordinated with MeCN, CO, and 55 [t]BuNC in $CD_2Cl_2$ to form $[Cu(L)(BPEP)]^+SbF_6^-$ [L = MeCN (**3**), CO (**4**), [t]BuNC (**5**)], respectively. The ν(CO) band of **3** appeared at 2132 cm^{−1} in the IR spectrum; the value is close to that of free CO (2143 cm^{−1}). Complex **5** exhibited the ν(NC) band at 2198 cm^{−1}. This value is higher than that of the 60 phosphine analogue $[Cu(^tBuNC)(pnp)]^+SbF_6^-$ (2177 cm^{−1}).[6] These data illustrate the highly electron-deficient nature of the copper center.

While the ^{31}P NMR signal of **2a** appeared at δ 213.3 in $CD_2Cl_2$, the signal was shifted downfield (δ 234.2) in $C_6D_6$. 65 This tendency was quite different from that observed for **1**, which showed the same chemical shift in $CD_2Cl_2$ and $C_6D_6$ (δ 251.5). As we have documented for DPCB-Y complexes,[9] the ^{31}P NMR chemical shift of the phosphaalkene ligand is rather sensitive to the M–P bond length, and tends to increase as the 70 M–P bond is elongated. Although there is the possibility that the Cu–P distance of **2a** varies with coordinating solvents, it seems more likely that the $SbF_6^-$ anion is associated with the cationic $[Cu(BPEP)]^+$ moiety to form a neutral complex in nonpolar $C_6D_6$. To examine this point, single crystals of **2a** 75 were grown from a toluene solution (87%), and examined by X-ray diffraction analysis.
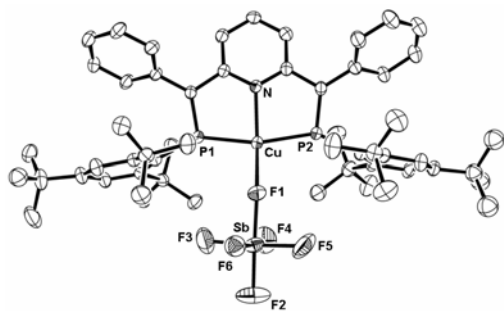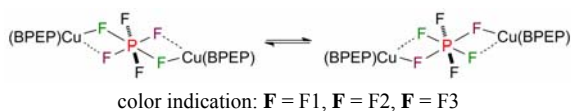
**Fig. 1** ORTEP drawing of **2a** with 50% probability ellipsoids. Hydrogen atoms, disordered *tert*-butyl groups and disordered F6 atom were omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–N 2.107(3), Cu–P1 2.2526(11), Cu–P2 2.2612(11), Cu–F1 2.190(3), Sb–F1 1.916(3), Sb–F2 1.843(4), Sb–F3 1.859(5), Sb–F4 1.846(4), Sb–F5 1.850(5), N–Cu–F1 146.05(15), P1–Cu–P2 156.25(5), Cu–F1–Sb 143.9(2).

Figure 1 shows the structure of **2a**. The copper center has a distorted tetrahedral configuration with the N–Cu–F1 angle of 146.04(15)° and the P1–Cu–P2 angle of 156.25(5)°. The Cu–F1–Sb bond angle is 143.9(2)°, and the Sb atom adopts a typical octahedral configuration. The Cu–N and Cu–P lengths are in the range of PNP-pincer complexes (2.06–2.16 and 2.22–2.32 Å, respectively).[6–8]

The most striking feature of **2a** is the significantly short Cu–F1 bond [2.190(3) Å], which is comparable to that of $Cu^I$ fluorides (~2.1 Å).[10] Reflecting the occurrence of an effective bonding interaction between the Cu and F1 atoms, the Sb–F1 bond is elongated by 0.057–0.073 Å, compared with the other Sb–F bonds. To the best of our knowledge, this is the first example of a $Cu^I$ complex with a coordinated $SbF_6^-$ anion.

Next, we attempted to crystallize $PF_6$ complex **2b** from a toluene solution. However, the crystalline product obtained was not **2b**, but a cationic $PF_6$-bridged dimer of Cu(BPEP) units, having a $PF_6^-$ counter anion (**6**). Figure 2 shows the X-ray structure of the cationic portion, which adopts $C_i$ symmetry with the P3 atom at the point of symmetry. Two Cu(BPEP) units are connected by a $\mu$-$PF_6$ group in a zigzag conformation. The length of the Cu–F1 bond is 2.241(2) Å, which is somewhat longer than that of **2a,** but still in the range of an effective bonding interaction between the Cu and F atoms.[11] Moreover, the P3–F1 bond [1.637(2) Å] is clearly longer than the other P–F bonds [1.586(2) and 1.588(2) Å].

NMR spectroscopy revealed that the dimeric structure of **6** was preserved in $CD_2Cl_2$, even in the presence of excess MeCN or CO. Furthermore, dynamic behavior on the NMR time-scale was observed within the molecule (Scheme 2).



color indication: **F** = F1, **F** = F2, **F** = F3

**Scheme 2**

Figure 3(a) shows the $^{19}F$ NMR spectrum measured at room temperature, showing two sets of doublets at δ –73.7 ($^1J_{PF}$ = 711 Hz) and –77.8 ($^1J_{PF}$ = 978 Hz). Since the chemical shift and $^1J_{PF}$ constant for the former signal were identical to those of $Bu_4NPF_6$, this signal is assigned to $PF_6^-$ as the counter anion. Accordingly, the latter arises from the $\mu$-$PF_6$ group. A
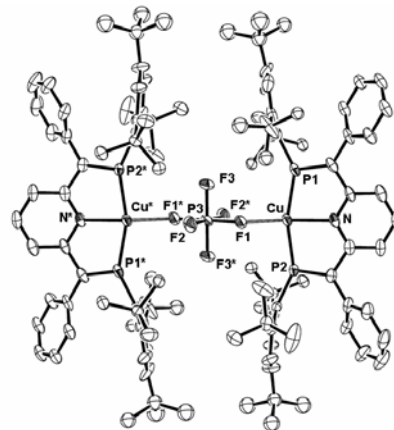


**Fig. 2** ORTEP drawing of **6** with 50% probability ellipsoids. Hydrogen atoms and counter anion ($PF_6^-$) are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–N 2.097(3), Cu–P1 2.2613(10), Cu–P2 2.2638(9), Cu–F1 2.241(2), P3–F1 1.637(2), P3–F2 1.586(2), P3–F3 1.588(2), N–Cu–F1 144.32(9), P1–Cu–P2 157.34(4), N–Cu–F1 144.32(9), Cu–F1–P3 128.95(13).
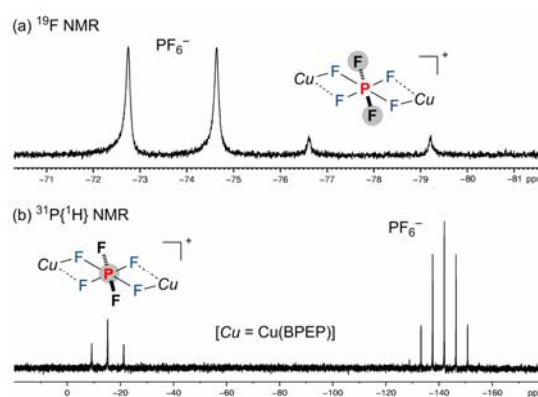


**Fig. 3** (a) $^{19}F$ and (b) $^{31}P\{^1H\}$ NMR spectra of **6** in $CD_2Cl_2$ at 20 °C.

remarkable feature of the spectrum is the significantly weak intensity of the latter signal at δ –77.8. The $^1J_{PF}$ value (978 Hz) is clearly larger than that of the $PF_6^-$ anion (711 Hz), and comparable to that of neutral $PF_5$ (938 Hz).[12]

The $^{31}P\{^1H\}$ NMR spectrum shown in Fig. 3(b) consists of two sets of signals at δ –17.3 ($^1J_{PF}$ = 978 Hz) and –143.0 ($^1J_{PF}$ = 711 Hz), arising from $\mu$-$PF_6$ and $PF_6^-$, respectively. The former signal appears as a triplet, while the latter shows septet coupling as expected for $PF_6^-$; namely, the P–F couplings for four out of the six fluorine atoms are missing from the signal of the $\mu$-$PF_6$ group. This phenomenon is rationalized by assuming effective interactions of the four fluorine atoms with copper centers having a quadrupole moment ($I$ = 3/2) *via* the rapid motion illustrated in Scheme 2. This behavior was not frozen at –80 °C.

To gain further insight into the bonding interaction between copper and the $\mu$-$PF_6$ group, DFT calculations were carried out. Initially, we attempted geometry optimization for a model compound of the cationic part of **6**, [(bpep)Cu-($\mu$-$PF_6$)-Cu-(bpep)]$^+$ (**6'**), in which the 2,4,6-tri-*tert*-butylphenyl (Mes*) and phenyl groups on the BPEP ligands were replaced by hydrogen atoms. However, although the dimeric structure of **6** was reproduced, distances between the Cu and F atoms were unreasonably shortened (Cu–F1 = 2.16 Å; Cu–F2 = 2.48 Å).

This is probably due to the absence of the bulky Mes* groups. Therefore, the geometry of the Cu-($\mu$-PF$_6$)-Cu core was fixed to the X-ray structure, and the remaining portion was optimized assuming $C_2$ symmetry around the F3–Cu–F3* axis.

Figure 4 shows the optimized geometry of **6'** under the above structural constraints. The Mayer's bond orders ($B$) for Cu–F and P–F bonds are also presented. There is evidence for a bonding interaction between Cu and F1 ($B = 0.32$) and a weakening of the P3–F1 bond ($B = 0.66$). It is also observed that the F2 atom interacts with the Cu atom with a bond order of 0.13, despite the long distance between those atoms (3.054 Å). Bonding interactions of F atoms with Cu centers are also observed in several molecular orbitals (see ESI).

Table 1 compares the charge distributions in [(bpep)Cu-($\mu$-PF$_6$)-Cu(bpep)]$^+$ (**6'**) and [Cu(bpep)]$^+$ (**2'**), which were evaluated by natural population analysis. The $\mu$-PF$_6$ group of **6'** is charged to –0.84, meaning that the negative charge of the PF$_6^-$ anion (–1.00) is reduced by bridging coordination with two molecules of **2'**. Since the copper center of **6'** is more positively charged than that of **2'**, it is concluded that the negative charge of the PF$_6^-$ anion is distributed to the bpep ligand upon the formation of **6'**, very probably via $\pi$-back-bonding between copper and bpep.

Complexes **2a** and **2b** undergo ionic dissociation in CD$_2$Cl$_2$ as a polar solvent (*vide supra*). It was found that the complexes cleave the Si–N bond of Me$_3$SiN$_3$ to afford [Cu$_2$(BPEP)$_2$($\mu$-N$_3$)]$^+$X$^-$ [X = SbF$_6$ (**7a**), PF$_6$ (**7b**)] in 96 and 36% yields, respectively, along with Me$_3$SiF (Scheme 3). The reactions probably proceed via cooperative activation of Me$_3$SiN$_3$ by the electrophilic copper center and nucleophilic fluoride ion. Since it is known that it is very difficult to dissociate a fluoride ion from SbF$_6^-$ and PF$_6^-$ as non-coordinating anions,[13] the high reactivity of **2a** and **2b** should be attributed to the high electrophilicity of [Cu(BPEP)]$^+$.

In summary, we have reported novel Cu$^I$ complexes bearing a phosphaalkene-based PNP-pincer ligand (BPEP). Thanks to the strong $\pi$-accepting ability of the P=C bonds, the [Cu(BPEP)]$^+$ species possesses a highly electron-deficient copper center, exhibiting strong affinity towards SbF$_6^-$ and PF$_6^-$ as non-coordinating anions. Thus, SbF$_6^-$ is coordinated with [Cu(BPEP)]$^+$ to form [Cu(SbF$_6$)(BPEP)] (**2a**) as a neutral species. On the other hand, PF$_6^-$ formed [Cu$_2$(BPEP)$_2$($\mu$-PF$_6$)]$^+$PF$_6^-$ (**6**). The dinuclear structure of **6** is stable in solution even in the presence of excess MeCN or CO. This is due to the occurrence of effective bonding interactions between the Cu and F atoms.

## Notes and references

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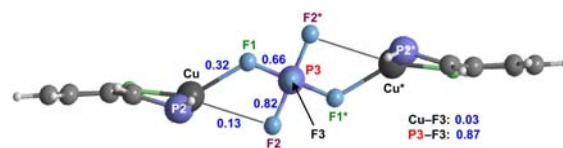
**Table 1** Charge distribution in **6'** and [Cu(bpep)]$^+$ (**2'**)

| Component | Complex | |
| --- | --- | --- |
| | [Cu$_2$(bpep)$_2$($\mu$-PF$_6$)]$^+$ (**6'**) | [Cu(bpep)]$^+$ (**2'**) |
| Cu | +0.78 | +0.67 |
| bpep | +0.14 | +0.33 |
| $\mu$-PF$_6$ | –0.84 | — |

The values were determined by DFT calculations and NBO analysis.



**Fig. 4** The optimized structure and Mayer's bond orders for a model compound of **6**, [(bpep)Cu-($\mu$-PF$_6$)-Cu(bpep)]$^+$ (**6'**).
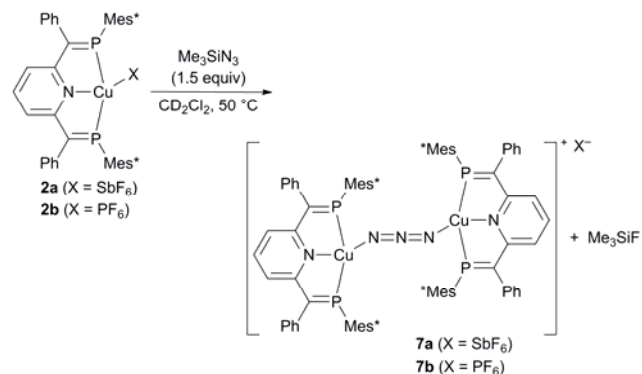


**Scheme 3**

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# COMMUNICATION

**Graphical and textual abstract for the Table of Contents**

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