TITLE:

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CITATION:

Nakajima, Yumiko ...[et al]. Synthesis and coordination behavior of Cu(I) bis(phosphaethenyl)pyridine complexes.. Chemical communications 2011, 47(22): 6332-6334

ISSUE DATE:

2011-06-14

URL:

<http://hdl.handle.net/2433/156702>

RIGHT:

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Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

Synthesis and coordination behavior of Cu^I bis(phosphaethenyl)pyridine complexes

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Cu^I complexes bearing BPEP as a PNP-pincer type phosphalkene ligand undergo effective bonding interactions with SbF₆[−] and PF₆[−] as non-coordinating anions to give [Cu(SbF₆)(BPEP)] and [Cu₂(BPEP)₂(μ-PF₆)]⁺, respectively [BPEP = 2,6-bis(1-phenyl-2-phosphaethenyl)pyridine]. NMR and theoretical studies indicate a reduced anionic charge of the μ-PF₆ ligand, which is induced by the strong π-accepting ability of BPEP.

Phosphaalkenes with P=C bond(s) are low-coordinate 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 diposphenidene-cyclobutene ligands (DPCB-Y) that this property is useful for catalysis, 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 phosphalkene ligand, which successfully stabilizes a coordinatively unsaturated 15-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 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 SbF₆[−] and PF₆[−].

The BPEP ligand was introduced to CuBr in toluene at 90 °C (Scheme 1). The resulting [CuBr(BPEP)] (**1**) was 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 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

Complex **1** reacted with silver salts of non-coordinating anions (AgX; X = SbF₆ and PF₆) to afford complexes of the formula “CuX(BPEP)” [X = SbF₆ (**2a**), PF₆ (**2b**)]. Since both

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

complexes exhibited the same ³¹P NMR chemical shift (δ 213.3) in CD₂Cl₂, 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 ^tBuNC in CD₂Cl₂ to form [Cu(L)(BPEP)]⁺SbF₆[−] [L = MeCN (**3**), CO (**4**), ^tBuNC (**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 phosphine analogue [Cu(^tBuNC)(pnp)]⁺SbF₆[−] (2177 cm^{−1}).⁶ These data illustrate the highly electron-deficient nature of the copper center.

While the ³¹P NMR signal of **2a** appeared at δ 213.3 in CD₂Cl₂, the signal was shifted downfield (δ 234.2) in C₆D₆. This tendency was quite different from that observed for **1**, which showed the same chemical shift in CD₂Cl₂ and C₆D₆ (δ 251.5). As we have documented for DPCB-Y complexes,⁹ the ³¹P NMR chemical shift of the phosphalkene ligand is rather sensitive to the M–P bond length, and tends to increase as the 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 SbF₆[−] anion is associated with the cationic [Cu(BPEP)]⁺ moiety to form a neutral complex in nonpolar C₆D₆. To examine this point, single crystals of **2a** 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).

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) $^{31}\text{P}\{^1\text{H}\}$ 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 $\delta -77.8$. The $^1J_{\text{PF}}$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shown in Fig. 3(b) consists of two sets of signals at $\delta -17.3$ ($^1J_{\text{PF}} = 978$ Hz) and -143.0 ($^1J_{\text{PF}} = 711$ Hz), arising from $\mu\text{-PF}_6$ 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 $\mu\text{-PF}_6$ 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 $\mu\text{-PF}_6$ group, DFT calculations were carried out. Initially, we attempted geometry optimization for a model compound of the cationic part of **6**, [(bpep)Cu($\mu\text{-PF}_6$)] $^+$ (**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).

Scheme 2

Figure 3(a) shows the ^{19}F NMR spectrum measured at room temperature, showing two sets of doublets at $\delta -73.7$ ($^1J_{\text{PF}} = 711$ Hz) and -77.8 ($^1J_{\text{PF}} = 978$ Hz). Since the chemical shift and $^1J_{\text{PF}}$ 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 $\mu\text{-PF}_6$ group. A

This is probably due to the absence of the bulky Mes* groups. Therefore, the geometry of the Cu-(μ-PF₆)-Cu core was fixed to the X-ray structure, and the remaining portion was optimized assuming C₂ 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-(μ-PF₆)-Cu(bpep)]⁺ (**6'**) and [Cu(bpep)]⁺ (**2'**), which were evaluated by natural population analysis. The μ-PF₆ group of **6'** is charged to –0.84, meaning that the negative charge of the PF₆[–] 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 PF₆[–] anion is distributed to the bpep ligand upon the formation of **6'**, very probably via π-back-bonding between copper and bpep.

Complexes **2a** and **2b** undergo ionic dissociation in CD₂Cl₂ as a polar solvent (*vide supra*). It was found that the complexes cleave the Si–N bond of Me₃SiN₃ to afford [Cu₂(BPEP)₂(μ-N₃)]⁺X[–] [X = SbF₆ (**7a**), PF₆ (**7b**)] in 96 and 36% yields, respectively, along with Me₃SiF (Scheme 3). The reactions probably proceed via cooperative activation of Me₃SiN₃ by the electrophilic copper center and nucleophilic fluoride ion. Since it is known that it is very difficult to dissociate a fluoride ion from SbF₆[–] and PF₆[–] 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 π-accepting ability of the P=C bonds, the [Cu(BPEP)]⁺ species possesses a highly electron-deficient copper center, exhibiting strong affinity towards SbF₆[–] and PF₆[–] as non-coordinating anions. Thus, SbF₆[–] is coordinated with [Cu(BPEP)]⁺ to form [Cu(SbF₆)(BPEP)] (**2a**) as a neutral species. On the other hand, PF₆[–] formed [Cu₂(BPEP)₂(μ-PF₆)]⁺PF₆[–] (**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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† Electronic Supplementary Information (ESI) available: experimental procedures and analytical data, additional crystallographic data and computational details. See DOI: 10.1039/b000000x/

‡ This work was supported by a Grant-in-Aid for Scientific Research from MEXT Japan and the JST PRESTO program.

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

Component	Complex	
	[Cu ₂ (bpep) ₂ (μ-PF ₆)] ⁺ (6')	[Cu(bpep)] ⁺ (2')
Cu	+0.78	+0.67
bpep	+0.14	+0.33
μ-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-(μ-PF₆)-Cu(bpep)]⁺ (**6'**).

Scheme 3

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Cite this: DOI: 10.1039/c0xx00000x

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Graphical and textual abstract for the Table of Contents

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