Dalton Transactions

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5dt03166d

Reactions of [Cu(X)(BPEP-Ph)] (X = PF_6, SbF_6) with silyl compounds. Cooperative bond activation involving non-coordinating anions†

Yumiko Nakajima,*[a] Takahiro Tsuchimoto,[b] Yung-Hung Chang,[b] Katsuhiko Takeuchi[b] and Fumiyuki Ozawa*[b]

Received 17th August 2015,
Accepted 25th September 2015

DOI: 10.1039/c5dt03166d

www.rsc.org/dalton

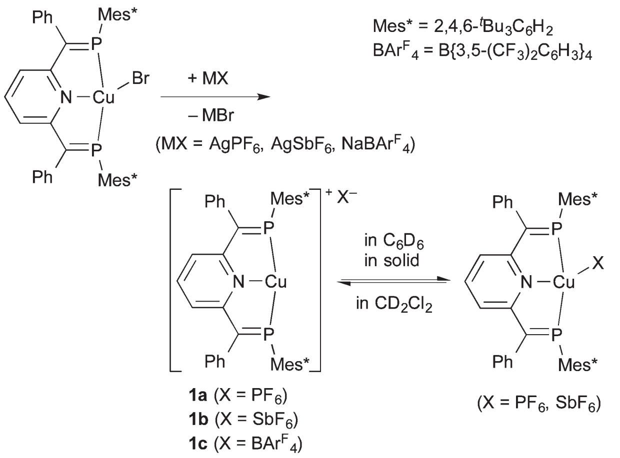
Bond activation of silyl compounds, assisted by the cooperative action of non-coordinating anions, is achieved using Cu(I) complexes coordinated with a PNP-pincer type phosphaalkene ligand, [Cu(X)-(BPEP-Ph)] (X = PF_6 (**1a**), SbF_6 (**1b**); BPEP-Ph = 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine). Complexes **1a** and **1b** react with Me_3SiCN to form Me_3SiF and Cu(I) cyanide complexes of the formula [Cu(CN-EF_5)(BPEP-Ph)] (E = P (**2a**), Sb (**2b**)), in which the CN ligand is associated with the EF_5 group arising from EF_6^-. Formation of the intermediary isonitrile complex $[Cu(CNSiMe_3)(BPEP\text{-}Ph)]^+SbF_6^-$ (**3b**) is confirmed by its isolation. Thus, a two-step reaction process involving coordination of Me_3SiCN, followed by nucleophilic attack of SbF_6^- on the silicon atom of **3b** is established for the conversion of **1b** to **2b**. Complex **1b** cleaves the H–Si bond of $PhMe_2SiH$ as well. The isolation and structural identification of $[Cu(BPEP\text{-}Ph)]^+BAr^F{}_4^-$ (**1c**) ($BAr^F{}_4$ = B{3,5-$(CF_3)_2C_6H_3$}$_4$) as a rare example of a T-shaped, three-coordinated Cu(I) complex is reported.

Introduction

Phosphaalkenes with a P=C bond possess an extremely low-lying π* orbital and exhibit strong π-acceptor properties towards transition metals.[1] We have documented that this particular ligand property often provides interesting structures and reactivities in late transition metal complexes.[2–4]

Our current interest is focused on PNP-pincer complexes supported by 2,6-bis[1-phenyl-2-(2,4,6-tri-*tert*-butylphenyl)-2-phosphaethenyl]pyridine (BPEP-Ph), in which two P=C bonds are linked to 2,6-positions of pyridine. We have demonstrated that this novel tridentate ligand with a highly delocalized π-electron system successfully stabilizes 3d metal complexes in low oxidation states. Representative examples include Fe(I) complexes with a 15-electron configuration,[5] which exhibit a unique redox behavior.[6] We have also communicated that Cu(I) centers in [Cu(X)(BPEP-Ph)] (X = PF_6 (**1a**), SbF_6 (**1b**)) establish strong bonding interactions with PF_6^- and SbF_6^- as non-coordinating anions in nonpolar solvents as well as in the solid state (Scheme 1).[7] DFT calculations have revealed that BPEP-Ph as a strong π-acceptor produces a highly electron-deficient Cu(I) center, which has a strong affinity for PF_6^- and SbF_6^-.

This paper describes bond activation of silyl compounds induced by **1a** and **1b**. We anticipated that the highly electron-deficient Cu(I) center in these complexes could enhance the



Scheme 1 Preparation and solution behavior of Cu(I) BPEP-Ph complexes.

---

[a] *Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan. E-mail: yumiko-nakajima@aist.go.jp*

[b] *International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan. E-mail: ozawa@scl.kyoto-u.ac.jp*

† Electronic supplementary information (ESI) available: Details of crystal structure determination and DFT calculations. CCDC 1417449 and 1417450. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt03166d

electrophilicity of silyl substrates to a considerable extent and facilitate the external attack of a nucleophile. Actually, we found that **1a** and **1b** cause N–Si bond cleavage of Me_3SiNC under mild conditions, where PF_6^- and SbF_6^- as "non-coordinating anions" act as nucleophiles. We also present the crystal structure of a rare example of a T-shaped, three-coordinated Cu(I) complex, $[Cu(BPEP\text{-}Ph)]^+BAr^F{}_4{}^-$ (**1c**) ($BAr^F{}_4 = B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$).

Results and discussion

Solution structures of [Cu(X)(BPEP-Ph)]

While **1a** and **1b** are isolated as crystalline compounds with tight bonding interactions between Cu and X, they show the same NMR spectra, except for X, in CD_2Cl_2 as a polar solvent.[7] Thus, we considered that both complexes change into the T-shaped species $[Cu(BPEP\text{-}Ph)]^+$ in CD_2Cl_2 by ionic dissociation. However, because a structually well-defined Cu(I) complex with a T-shaped geometry is very rare,[8] we attempted to isolate $[Cu(BPEP\text{-}Ph)]^+$ using bulky $BAr^F{}_4{}^-$ as a counter anion.

Following the synthetic procedures for **1a** and **1b**, the complex $[Cu(BPEP\text{-}Ph)]^+BAr^F{}_4{}^-$ (**1c**) was prepared by anionic exchange of [CuBr(BPEP-Ph)] with $NaBAr^F{}_4$ in CH_2Cl_2. A single crystal suitable for X-ray diffraction analysis was grown from a CH_2Cl_2 solution layered with hexane. Fig. 1 presents the X-ray structure of **1c**, adopting a three-coordinated, T-shaped configuration around Cu. The Cu atom is coordinated only with BPEP-Ph. The interatomic distance between Cu and the nearest F atom of $BAr^F{}_4$ was 4.46 Å; this value is much larger than the sum of the van der Waals radii of Cu and F (2.52 Å).[9]

The lengths of Cu–P1 (2.206(1) Å), Cu–P2 (2.216(1) Å), and Cu–N (2.074(3) Å) are in the normal range of dative covalent bonds found in PNP-pincer complexes of Cu(I).[7,8,10] The P1–Cu–P2 angle is 167.11(5)°, whereas the P1–Cu–N and P2–Cu–N angles are 84.5(1) and 84.5(1)°, respectively. The sum of the three angles around Cu is 361.9°, the value of which is almost the same as that previously reported for a T-shaped Cu(I) complex (362.3°).[8] Hence, the three-coordinated, T-shaped structure of **1c** was confirmed.

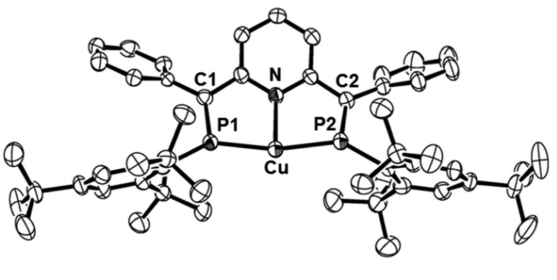
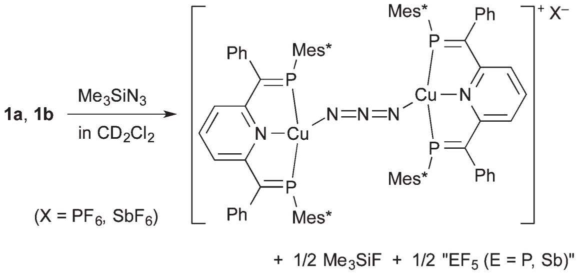


Fig. 1 ORTEP drawing of **1c** with 50% probability ellipsoids. Hydrogen atoms, $BAr^F{}_4$ anions and a crystal solvent (CH_2Cl_2) are omitted for clarity. Selected bond distances (Å) and angles (°): Cu–P1 = 2.206(1), Cu–P2 = 2.216(1), Cu–N = 2.074(3), P1–C1 = 1.691(4), P2–C2 = 1.711(4), P1–Cu–N = 84.5(1), P2–Cu–N = 84.5(1), P1–Cu–P2 = 167.09(5).

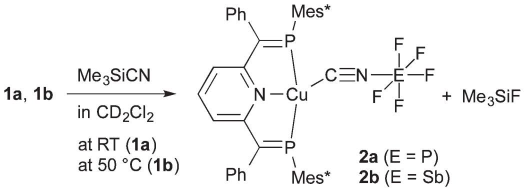
Complex **1c** exhibited a singlet signal assignable to free $BAr^F{}_4{}^-$ (δ −62.9) in the ^{19}F NMR spectrum. The $^{31}P\{^1H\}$ NMR signal was observed at δ 214.4 in CD_2Cl_2, and this value was very close to that of **1a** and **1b** (δ 213.3). Moreover, the ^1H NMR spectrum of the $[Cu(BPEP\text{-}Ph)]^+$ moiety was almost identical to that of **1a** and **1b**. Thus, the ionic dissociation of **1a** and **1b** to form the T-shaped species in CD_2Cl_2 was evidenced.

Bond activation of silyl compounds by 1a and 1b

We previously reported that the Si–N bond of Me_3SiN_3 is activated by **1a** and **1b** to form $[Cu_2(BPEP\text{-}Ph)_2(\mu\text{-}N_3)]^+X^-$ ($X^- = PF_6^-$ and SbF_6^-), respectively (eqn (1)).[7] These reactions very probably involve the by-production of Me_3SiF and EF_5 (E = P and Sb). However, while the formation of Me_3SiF was confirmed by NMR spectroscopy, EF_5 could not be detected in the reaction systems. On the other hand, we noticed that the reactions with Me_3SiCN present all product components including EF_5, which is found in an associated form with a cyanido ligand arising from the activation of the Me_3Si–CN bond (eqn (2)).



(1)



(2)

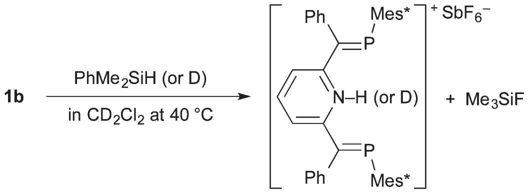
Complex **1a** rapidly reacted with Me_3SiCN in CD_2Cl_2 at ambient temperature to give **2a** quantitatively, as confirmed by NMR spectroscopy. The by-production of Me_3SiF (δ_H 0.23, δ_F −157.9) was observed as well. Complex **2a** was isolated as a light yellow solid in 68% yield. Complex **1b** was less reactive than **1a**; however, the reaction with Me_3SiCN proceeded at 50 °C for 1 h, and the cyanide complex **2b** was obtained in 43% yield, along with Me_3SiF. Although complexes **2a** and **2b** did not give a satisfactory elemental analysis, they were unequivocally characterized by IR and NMR spectroscopy. The ν(CN) absorption bands of **2a** and **2b** were observed at 2196 and 2158 cm^{-1}, respectively. These wavenumbers are clearly higher than those of common Cu(I) cyanides (*ca.* 2100 cm^{-1}),[11] reflecting the association with PF_5 and SbF_5 as strong Lewis acids.[12]

The $^{31}P\{^1H\}$ NMR spectrum of **2a** exhibited two sets of signals at δ 264.1 and −151.6. The former signal due to BPEP-Ph appeared in the typical region for phosphaalkene ligands. On the other hand, the latter signal assignable to the

PF_5 group associated with the CN ligand was split into a doublet of quintets, due to the coupling with fluorine nuclei ($^1J_{PF}$ = 774 and 745 Hz). This coupling pattern was consistent with the octahedral configuration around phosphorus, linked to one fluorine atom at the apical position and four fluorine atoms at the equatorial positions. Indeed, the ^{19}F NMR spectrum of **2a** displayed two sets of signals at δ −83.6 (dq, $^1J_{PF}$ = 774 Hz, $^2J_{FF}$ = 62 Hz) and −53.1 (dd, $^1J_{PF}$ = 745 Hz, $^2J_{FF}$ = 62 Hz) in an intensity ratio of 1 : 4, which are assigned to the apical and equatorial fluorine atoms, respectively.

The ^{31}P{^{1}H} NMR signal of **2b** (δ 262.3) was observed in the normal range of phosphaalkene complexes as well. Although the ^{19}F NMR signals at δ −131.0 and −108.0 were significantly broadened due to the quadrupole moment of antimony (^{121}Sb, I = 5/2, ^{123}Sb, I = 7/2) and were therefore unavailable for structural assignment, the structure associated with the SbF_5 group could be confirmed by X-ray diffraction analysis (*vide infra*).

Complex **1b** cleaved the Si–H bond of hydrosilanes. For instance, the reaction with $PhMe_2SiH$ at 40 °C formed bis(phosphaethenyl)pyridinium (87%) and $PhMe_2SiF$ (78%), along with insoluble materials (eqn (3)). It is likely that the pyridinium salt is eliminated from the Cu(I) hydride of the formula $[CuH(BPEP\text{-}Ph)]^+SbF_6^-$, generated by Si–H bond cleavage. It was also confirmed that the reaction of **1b** with $PhMe_2SiD$ produces a pyridinium salt deuterated at the nitrogen atom selectively.



(3)

X-ray crystal structure of 2b

Fig. 2 shows the X-ray structure of $[Cu(CN\text{-}SbF_5)(BPEP\text{-}Ph)]$ (**2b**), which adopts a distorted tetrahedral configuration around Cu. A similar structure has been observed for four-coordinated Cu(I) complexes with a pincer ligand.[10] The Cu–N2 length (2.021(5) Å) is in the typical range for Cu(I) complexes. The Cu–P1 and Cu–P2 bonds (2.321(2) and 2.310(2) Å) are slightly longer than those in PNP-pincer analogues so far reported.[7,8,10] The Cu–C1 and C1–N1 bond lengths (1.886(7) and 1.180(8) Å) are ordinary for Cu(I) complexes,[13] and the Cu–C1–N1 bond (178.5(6)°) retains its linearity. On the other hand, the N1–Sb bond (2.043(6) Å) is clearly shorter than that of C_2N_2–SbF_5 (2.213(5) Å) and pyrazine–SbF_5 (2.172(5) Å).[14] The Sb atom adopts a distorted octahedral configuration, and the Sb–F bond lengths (1.843(4)–1.861(5) Å) are in the typical range for nitrogen-coordinated SbF_5 groups.[14]

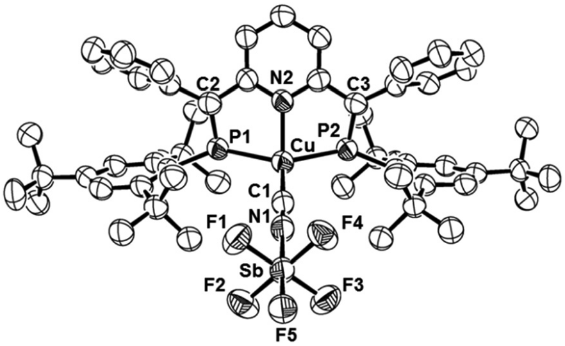
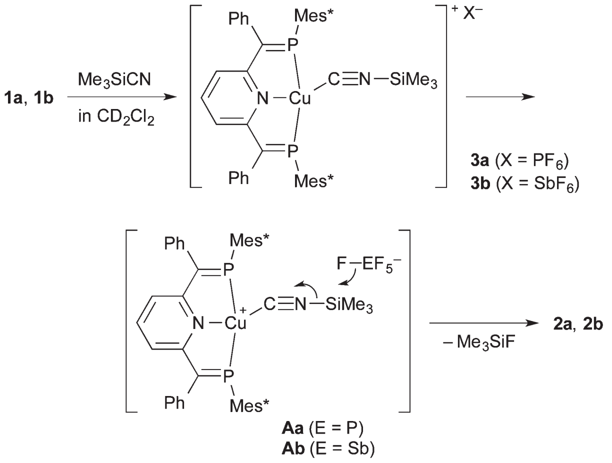


Fig. 2 ORTEP drawing of **2b** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Cu–C1 = 1.886(7), Cu–P1 = 2.321(2), Cu–P2 = 2.310(2), Cu–N2 = 2.021(5), C1–N1 = 1.180(8), N1–Sb = 2.043(6), Sb–F1 = 1.843(4), Sb–F2 = 1.858(4), Sb–F3 = 1.849(4), Sb–F4 = 1.847(4), Sb–F5 = 1.861(5), P1–C2 = 1.690(6), P2–C3 = 1.705(6), N–Cu–C1 = 126.2(2), P1–Cu–P2 = 135.95(7), Cu–C1–N1 = 178.5(6), C1–N1–Sb = 174.5(6), N1–Sb–F1 = 88.3(2), N1–Sb–F2 = 90.2(2), N1–Sb–F3 = 89.1(2), N1–Sb–F4 = 87.4(2), N1–Sb–F5 = 178.6(2).



Scheme 2 Bond activation of Me_3SiCN promoted by **1a** and **1b**.

Bond activation process of Me_3SiCN

Scheme 2 illustrates a plausible process for the formation of **2a** and **2b** from **1a** and **1b**, respectively. The first step is the coordination of Me_3SiCN to **1a** and **1b**. Since Me_3SiCN is known to undergo 1,2-silyl group migration on transition metals,[15] the formation of isonitrile intermediates **3a** and **3b**, instead of nitrile homologues, is presumed. Actually, complex **3b** could be prepared by the treatment of **1b** with Me_3SiCN at room temperature, and isolated as a light orange compound in 83% yield. The IR spectrum exhibited the ν(CN) absorption band at 2156 cm^{-1}, and this value is consistent with the isonitrile coordination. Complex **3b** was also examined by X-ray diffraction analysis. While the data quality was low (R_1 = 0.1713), the core structure of **3b** could be confirmed (see the ESI†).

Isonitrile complexes **3a** and **3b** then undergo nucleophilic attack of PF_6^- and SbF_6^- ions, respectively, on the silicon atom (**Aa** and **Ab**), leading to N–Si bond cleavage of the Me_3SiNC ligand. Finally, $[Cu(CN)(BPEP\text{-}Ph)]$ thus generated combines with PF_5 and SbF_5 to form **2a** and **2b**, respectively.

The differences in the relative stability between **3a** and [**2a** + Me_3SiF] and **3b** and [**2b** + Me_3SiF] were evaluated by DFT calculations. The conversion of **3a** to [**2a** + Me_3SiF] was an exothermic process by 4.6 kcal mol^{-1}, whereas that of **3b** to [**2b** + Me_3SiF] was exothermic by 9.2 kcal mol^{-1}. Principally, the exothermicity observed for both systems must be due to the formation of Me_3SiF with an extremely strong Si–F bond (158 kcal mol^{-1}).[16] On the other hand, the additional stability of **2b** would be derived from the higher association energy of SbF_5 than PF_5 to the CN ligand in [Cu(CN)(BPEP-Ph)], which is caused by the higher Lewis acidity of SbF_5.[12]

It should be noted that the thermodynamic features associated with the conversion of isonitrile complexes (**3a** and **3b**) to cyanide complexes (**2a** and **2b**) are inconsistent with the reactivity order of the starting complexes (**1a** and **1b**). Thus, it is reasonable that the much higher reactivity of **1a** than **1b** towards Me_3SiCN is caused due to a kinetic reason. A plausible explanation may be found in the large difference in the fluoride ion affinity between PF_5 ($pF^- = 9.49$) and SbF_5 ($pF^- = 12.03$);[12] namely, SbF_6^- is reluctant to eliminate F^-, compared with PF_6^-, and therefore **1b** with SbF_6^- is much less reactive than **1a** with PF_6^-.

Conclusions

We have demonstrated that [Cu(X)(BPEP-Ph)] (X = PF_6 (**1a**), SbF_6 (**1b**)) bearing a PNP-pincer type phosphaalkene ligand (BPEP-PH) led to the bond activation of Me_3SiCN in CD_2Cl_2, giving Cu(I) cyanides of the formula [Cu(CN-EF_5)(BPEP-Ph)] (E = P (**2a**), Sb (**2b**)), along with the by-production of Me_3SiF. The reactions proceed *via* coordination of Me_3SiCN to give the isocyanide complexes [Cu($CNSiMe_3$)(BPEP-Ph)]X (X = PF_6 (**3a**), SbF_6 (**3b**)), followed by Si–N bond cleavage caused by nucleophilic attack of PF_6^- and SbF_6^- on the silicon atom. Although PF_6^- and SbF_6^- as non-coordinating anions are known to be poorly nucleophilic, complexes **1a** and **1b** smoothly react with Me_3SiCN under mild conditions. This is probably because the strong π-accepting ability of BPEP-Ph reduces the electron density of the Cu–CN–$SiMe_3$ moiety, and thus facilitates the novel bond activation process involving cooperative action of the non-coordinating anions.

Experimental

All manipulations were performed under a dry and oxygen-free dinitrogen atmosphere using Schlenk techniques or a glove box. Solvents were dried over sodium/benzophenone ketyl (toluene, C_6D_6) or CaH_2 (hexane, CH_2Cl_2, CD_2Cl_2) and distilled. CuBr, $NaBAr^F_4$, $AgPF_6$, Me_3SiCN, $PhMe_2SiH$ and trimethoxybenzene were obtained from commercial sources and used without purification. BPEP-Ph and [CuBr(BPEP-Ph)] were prepared as previously reported.[5,7]

^1H NMR spectra were recorded at 25 °C on a Bruker Avance 400 spectrometer (^1H NMR, 400.13 MHz; ^{13}C NMR, 100.62 MHz; ^{19}F NMR, 376.46 MHz; ^{31}P NMR, 161.98 MHz). Chemical shifts are reported in δ (ppm), referenced to ^1H (of residual solvent signals) and ^{13}C signals of deuterated solvents as internal standards or to the ^{19}F signal of C_6F_6 (δ 163.0) and to the ^{31}P signal of 85% H_3PO_4 (δ 0.0) as external standards. IR spectra were recorded on a Jasco FT/IR-4100 spectrometer. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

Preparation of 1c

A suspension of $NaBAr^F_4$ (28.0 mg, 0.032 mmol) in CH_2Cl_2 (3 mL) was added to a solution of [CuBr(BPEP-Ph)] (30.0 mg, 0.032 mmol) at room temperature. The mixture was stirred at room temperature for 1 h, and concentrated to dryness under vacuum. The residue was extracted with toluene (1 mL) and filtered through a Celite pad to remove the precipitate of NaBr formed in the system. The filtrate was concentrated to dryness under reduced pressure, dissolved in CH_2Cl_2/hexane, and stored at −35 °C to give brown crystals of **1c** (52.0 mg, 0.030 mmol, 94%).

1c: ^1H NMR (CD_2Cl_2): δ 1.33 (s, 18H, ^{t}Bu), 1.57 (s, 36H, ^{t}Bu), 6.75 (d, J = 7.4 Hz, 4H, Ar), 7.10 (t, J = 7.4 Hz, 4H, Ar), 7.23–7.21 (m, 2H, Ar), 7.27–7.25 (m, 2H, Ar), 7.39 (s, 4H, Ar), 7.56 (s, BAr^F_4, 4H), 7.66 (t, J = 8.3 Hz, 1H, Ar), 7.73 (s, 8H, BAr^F_4). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.5, 34.6, 35.6, 39.2, 118.0, 122.1, 124.1, 125.2, 125.6, 128.8, 129.0, 129.4, 130.2, 135.4, 137.0, 140.9, 155.5, 157.5, 157.7, 162.3, 181.2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 214.4 (br). ^{19}F NMR (CD_2Cl_2): δ −62.9 (s). Anal. calcd for $C_{87}H_{83}BCuF_{24}NP_2$: C, 60.23; H, 4.82; N, 0.81. Found: C, 60.11; H, 5.11; N, 0.80.

Reaction of 1a with Me_3SiCN

The compounds [CuBr(BPEP)] (15.0 mg, 0.016 mmol) and AgPF6 (4.7 mg, 0.019 mmol) were mixed in toluene (1 mL) at room temperature.[7] The solution was filtered through a Celite pad to remove AgBr and unreacted $AgPF_6$. Me_3SiCN (4 μL, 0.032 mmol) was added to the filtrate. The solution turned light orange immediately. The solution was concentrated to dryness, and the residue was washed with hexane, extracted with toluene, and filtered through a Celite pad. The filtrate was concentrated to dryness under vacuum to give **2a** as a light yellow solid (11.0 mg, 0.011 mmol, 68%).

2a: ^1H NMR (CD_2Cl_2): δ 1.34 (s, 18H, ^{t}Bu), 1.48 (s, 36H, ^{t}Bu), 6.66 (brs, 4H, Ar), 7.08 (br, 4H, Ar), 7.14 (m, 2H, Ar), 7.27 (d, 2H, J = 6.8 Hz, Ar), 7.36 (s, 4H, Ar), 7.63 (t, 1H, J = 7.8 Hz, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.7, 34.5, 35.7, 39.1, 123.2, 128.3, 129.0, 129.7, 129.9, 137.9, 138.3, 153.9, 157.2, 157.6, 158.6, 174.9. The ^{13}C NMR signal of CN was obscure due to low signal intensity. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −151.6 (dq, $^1J_{PF}$ = 745, 774 Hz, PF_5), 264.1 (brs, P=C). ^{19}F NMR (CD_2Cl_2): δ −53.1 (dd, 4F, $^1J_{PF}$ = 745 Hz, $^2J_{FF}$ = 62 Hz), −83.6 (dq, 1F, $^1J_{PF}$ = 774 Hz, $^2J_{FF}$ = 62 Hz). IR (ATR): 2196 cm^{-1} (ν_{CN}).

Reaction of 1b with Me_3SiCN

To an NMR sample tube were charged a CD_2Cl_2 solution (0.4 mL) of **1b** (7.1 mg, 0.0064 mmol) and then Me_3SiCN (2 μL, 0.016 mmol). The solution was allowed to stand at 50 °C for 1 h, and then examined by NMR spectroscopy. The formation of Me_3SiF (δ_H 0.23, δ_F −157.9) was observed. The solution was concentrated to dryness, and the residue was extracted with toluene (1 mL) and filtered through a Celite pad. The filtrate was concentrated and stored at −35 °C to give a light yellow crystalline solid of **2b** (3.1 mg, 0.0028 mmol, 43%).

2b: ^1H NMR (CD_2Cl_2): δ 1.33 (s, 18H, ^{t}Bu), 1.48 (s, 36H, ^{t}Bu), 6.67 (brs, 4H, Ar), 7.08 (brs, 4H, Ar), 7.15 (m, 2H, Ar), 7.23 (d, 2H, J = 7.6 Hz, Ar), 7.36 (s, 4H, Ar), 7.64 (t, 1H, J = 7.9 Hz, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.6 (s, ^{t}Bu), 34.6 (s, ^{t}Bu), 35.6 (s, ^{t}Bu), 39.2 (s, ^{t}Bu), 123.7 (br, Ar), 125.8 (s, Ar), 128.4 (s, Ar), 128.7 (s, Ar), 129.5 (s, Ar), 129.8 (s, Ar), 138.3 (s, Ar), 138.6 (s, Ar), 154.4 (s, Ar), 157.1 (s, Ar), 157.7 (s, Ar), 175.7 (brs, P═C). The ^{13}C NMR signal of CN was obscure due to low signal intensity. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 263.5 (brs). ^{19}F NMR (CD_2Cl_2): δ −108.0 (br, 4F), −131.0 (br, 1F). IR (ATR): 2158 cm^{-1} (ν_{CN}).

Reaction of 1b with $PhMe_2SiH$

To an NMR sample tube was charged a CD_2Cl_2 solution (0.4 mL) of **1b** (12.0 mg, 0.011 mmol). $PhMe_2SiH$ (20 μL, 0.013 mmol) was added, and the solution was allowed to stand at 40 °C for 24 h. The formation of $PhMe_2SiF$ (0.0086 mmol, 78%) was confirmed by ^1H NMR analysis using trimethoxybenzene (1.2 mg, 0.0071 mmol) as an external standard. The solution was concentrated to dryness, and the residue was washed with hexane (2 mL × 3), extracted with toluene, and filtered through a Celite pad. The filtrate was concentrated to dryness to give $[H\text{-BPEP-Ph}]^+SbF_6^-$ (10.0 mg, 0.0096 mmol, 87%). ^1H NMR (CD_2Cl_2): δ 1.24 (s, 18H, ^{t}Bu), 1.36 (s, 36H, ^{t}Bu), 6.45 (d, 4H, J = 7.2 Hz, Ar), 6.96 (t, 4H, J = 7.8 H, Ar), 7.07 (t, 2H, J = 7.4 Hz, Ar), 7.21 (s, 4H, Ar), 8.22 (br, 2H, Ar), 8.31 (t, 1H, J = 8.0 Hz, Ar), 10.74 (br, 1H, NH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 31.3, 34.4, 35.4, 38.7, 123.1, 123.2, 129.3, 129.4, 129.6, 130.1, 136.0, 146.3, 153.5, 154.7, 155.9, 166.9. Anal. calcd for $C_{55}H_{72}NP_2SbF_6$: C, 63.22; H, 6.95; N, 1.34. Found: C, 62.80; H, 6.85; N, 1.36.

Reaction of 1b with $PhMe_2SiD$

Complex **1b** (12.7 mg, 0.012 mmol) was similarly treated with $PhMe_2SiD$ (2.4 mg, 0.016 mmol) instead of $PhMe_2SiH$, and $[D\text{-BPEP-Ph}]^+SbF_6^-$ (10.4 mg, 0.0099 mmol, 83%) was isolated. The ^1H NMR spectrum showed the disappearance of the pyridinium proton signal (δ 10.74). Instead, the ^2H NMR spectrum revealed the formation of the deuterated product $[D\text{-BPEP-Ph}]^+SbF_6^-$.

Preparation of 3b

A CD_2Cl_2 solution (0.4 mL) of **1b** (8.5 mg, 0.0076 mmol) was charged into an NMR sample tube, and Me_3SiCN (5.0 μL, 0.040 mmol) was added. The solution turned light orange immediately. The solution was concentrated to dryness to give a solid product of **3b** (7.6 mg, 0.0063 mmol, 83%).

3b: ^1H NMR (CD_2Cl_2): δ 0.48 (s, 9H, Me_3), 1.35 (s, 18H, ^{t}Bu), 1.46 (s, 36H, ^{t}Bu), 6.65 (brs, 4H, Ar), 7.11 (t, 4H, J = 7.0 Hz, Ar), 7.21 (m, 2H, Ar), 7.30 (d, 2H, J = 7.6 Hz, Ar), 7.37 (s, 4H, Ar), 7.68 (t, 1H, J = 7.8 Hz, Ar). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −1.69, 31.4, 34.6, 35.5, 39.0, 123.4, 123.9, 126.4, 128.3, 128.5, 129.7, 137.6, 138.2, 154.3, 156.7, 157.4, 175.5. The ^{13}C NMR signal of CN was obscure due to low signal intensity. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, RT): δ 262.3 (brs). IR (ATR): 2156 cm^{-1} (ν_{CN}).

X-ray crystal structure determination

The intensity data for **1c** and **3b** were collected on a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). For **2b**, synchrotron radiation experiment (λ = 0.71069 Å) was carried out at the BL38B1 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2010B1488). The data sets were corrected for Lorentz and polarization effects and absorption. The structures were solved by direct methods (SHELXS-97)[17] and refined on F^2 for all reflections (SHELXL-97).[18] Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were placed at the calculated positions. The crystallographic data and the summary of solution and refinement are listed in Table S1 (see the ESI†). Further information has been deposited with the Cambridge Crystallographic Data Centre (CCDC reference numbers 1417449 for **1c** and 1417450 for **2b**). The structure of **3b** could not be fully refined due to poor quality of the diffraction data.

DFT calculations

All calculations were carried out with the Gaussian 09 program package.[19] Geometry optimization was performed by the DFT method without any symmetry constraints, where the B3PW91 functional was employed, using the model compounds $[Cu(CNSiMe_3)(BPEP\text{-}Ph')]$, $[Cu(CN\text{-}PF_5)(BPEP\text{-}Ph')]$ and $[Cu(CN\text{-}SbF_5)(BPEP\text{-}Ph')]$ (BPEP-Ph′ = 2,6-bis(2-mesityl-2-phosphaethenyl)pyridine). The Cu and Sb atoms were described with the SDD basis set and the LANL2DZdp basis set, respectively. The 6-311G(d) basis sets were applied to P, N, Si and the C atom of CN. The 6-311G basis sets were applied to other C and H atoms. The core electrons of Cu and Sb were replaced with effective core potentials (ECPs).

Acknowledgements

This work was supported by MEXT Grant-in-Aid for Scientific Research on Innovative Areas “Stimuli-responsive Chemical Species” (no. 15H00967 (Y.N.) and 24109010 (F.O.)) and by KAKENHI (no. 26288050 (F.O.)) from JSPS. We are grateful to Professor Shigeyoshi Sakaki (Kyoto University) for helpful discussions on DFT calculations.

Notes and references

1 J. Dugal-Tessier, E. D. Conrad, G. R. Dake and D. P. Gates, in *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis*, ed. P. C. J. Kamer and P. W. N. M. van Leeuwen, Wiley, Chichester, UK, 2012, ch. 10.

2 F. Ozawa and M. Yoshifuji, *Dalton Trans.*, 2006, 4987.

3 For recent examples, see: Y.-H. Chang, Y. Nakajima, H. Tanaka, K. Yoshizawa and F. Ozawa, *J. Am. Chem. Soc.*, 2013, **135**, 11791; Y. Nakajima, Y. Okamoto, Y.-H. Chang and F. Ozawa, *Organometallics*, 2013, **32**, 2918; Y.-H. Chang, Y. Nakajima, M. Tanaka, K. Yoshizawa and F. Ozawa, *Organometallics*, 2014, **33**, 715; K. Takeuchi, A. Minami, Y. Nakajima and F. Ozawa, *Organometallics*, 2014, **33**, 5365.

4 For related studies using phosphaalkene ligands, see: A. Jouaiti, M. Geoffroy and G. Bernardinelli, *Tetrahedron Lett.*, 1992, **33**, 5071; A. S. Ionkin and W. J. Marshall, *Heteroat. Chem.*, 2002, **13**, 662; S. Ito, M. Nanko and K. Mikami, *ChemCatChem*, 2014, **6**, 2292.

5 Y. Nakajima, Y. Nakao, S. Sakaki, Y. Tamada, T. Ono and F. Ozawa, *J. Am. Chem. Soc.*, 2010, **132**, 9934; Y. Nakajima and F. Ozawa, *Organometallics*, 2012, **31**, 2009.

6 Y.-F. Lin, Y. Nakajima and F. Ozawa, *Dalton Trans.*, 2014, **43**, 9032; Y.-F. Lin, N. Ichihara, Y. Nakajima and F. Ozawa, *Organometallics*, 2014, **33**, 6700.

7 Y. Nakajima, Y. Shiraishi, T. Tsuchimoto and F. Ozawa, *Chem. Commun.*, 2011, **47**, 6332.

8 J. I. van der Vlugt, E. A. Pidko, D. Vogt, M. Lutz, A. L. Spek and A. Meetsma, *Inorg. Chem.*, 2008, **47**, 4442.

9 J. Emsley, *The Elements*, Oxford, New York, 3rd edn, 1998.

10 A. Hayashi, M. Okazaki, F. Ozawa and R. Tanaka, *Organometallics*, 2007, **26**, 5246; C. Müller, E. A. Pidko, M. Lutz, A. L. Spek and D. Vogt, *Chem. – Eur. J.*, 2008, **14**, 8803; J. I. van der Vlugt, E. A. Pidko, D. Vogt, M. Lutz and A. L. Spek, *Inorg. Chem.*, 2009, **48**, 7513; J. I. van der Vlugt, E. A. Pidko, R. C. Bauer, Y. Gloaguen, M. K. Rong and M. Lutz, *Chem. – Eur. J.*, 2011, **17**, 3850.

11 Y. L. Xiao, Q.-H. Jin, Y.-H. Deng, Z.-F. Li, W. Yang, M.-H. Wu and C.-L. Zhang, *Inorg. Chem. Commun.*, 2012, **15**, 146; D. Saravanabharathi, Monika, P. Venugopalan and A. G. Samuelson, *Polyhedron*, 2002, **21**, 2433; J. Ellermann, F. A. Knoch, K. J. Meier and M. Moll, *J. Organomet. Chem.*, 1992, **428**, C44.

12 K. O. Christea, D. A. Dixonc, D. McLemorec, W. W. Wilsonb, J. A. Sheehyb and J. A. Boatz, *J. Fluorine Chem.*, 2000, **101**, 151.

13 G. C. Fortman, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2010, **29**, 3966; M. P. Coles and P. B. Hitchcock, *Polyhedron*, 2001, **20**, 3027.

14 I. C. Tornieporth-Oetting, T. M. Klapötke, T. S. Cameron, J. Valkonen, P. Rademacher and K. J. Kowski, *J. Chem. Soc., Dalton Trans.*, 1992, 537; D. Mootz and K. Bartmann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 391.

15 M. Ma, A. Stasch and C. Jones, *Chem. – Eur. J.*, 2012, **18**, 10669; H. Nakazawa, K. Kamata and M. Itazaki, *Chem. Commun.*, 2005, 4004; M. F. C. Guedes da Silva, M. A. N. D. A. Lemos, J. J. R. F. da Silva, A. J. L. Pombeiro, M. A. Pellinghelli and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 2000, 373; J. S. Thayer, *Inorg. Chem.*, 1968, **12**, 2599.

16 R. Walsh, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, Wiley, Chichester, UK, 1989, ch. 5.

17 G. M. Sheldrick, *SHELXS-97*, University of Göttingen, Germany, 1997.

18 G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, 1997.

19 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian, Inc., Wallingford, CT, 2010.