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Reactions of [Cu(X)(BPEP-Ph)] (X = PF₆, SbF₆) with silyl compounds. Cooperative bond activation involving non-coordinating anions†

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Bond activation of silyl compounds, assisted by cooperative action of non-coordinating anions, is achieved using Cu(I) complexes coordinated with a PNP-phosphaalkene ligand, [Cu(X)(BPEP-Ph)] (X = PF₆ (1a), SbF₆ (1b); BPEP-Ph = 2,6-bis[1-phenyl-2-(2,4,6-tri-tert-butylyphenyl)-2-phosphaethenyl]pyridine). Complexes 1a and 1b react with Me₃SiNC to form Me₃SiF and Cu(I) cyanide complexes of the formula [Cu(CN–EF₆)(BPEP-Ph)] (E = P (2a), Sb (2b)), in which the CN ligand is associated with the EF₆ group arising from EF₆. Formation of the intermediary silyl complex [Cu(CNMe₃)(BPEP-Ph)]*SbF₆ (3b) is confirmed by its isolation. Thus, the two-step reaction process involving coordination of Me₃SiCN, followed by nucleophilic attack of SbF₆ on the silicon atom of 3b is established for the conversion of 1b to 2b. Complex 1b cleaves the H–Si bond of PhMeSiH as well. The isolation and structural identification of [Cu(BPEP-Ph)[-BAR₂(1e) (BAR₂ = B(3,5-(CF₃)₂C₆H₃)₄)] as a rare example of a T-shaped, three-coordinated Cu(I) complex is reported as a strong π-acceptor produces a highly electron-deficient Cu(I) center, which has a strong affinity for PF₆⁻ and SbF₆⁻.

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-butylyphenyl)-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 unique redox behavior.⁶ We have also communicated that Cu(I) centers in [Cu(X)(BPEP-Ph)] (X = PF₆ (1a), SbF₆ (1b)) establish strong bonding interactions with PF₆⁻ and SbF₆⁻ as non-coordinating anions in nonpolar solvents as well as in the solid state (Scheme 1).⁷ DFT calculations have revealed that BPEP-Ph

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 electrophilicity of silyl substrates to a considerable extent and facilitate external attack of a nucleophile. Actually, we found that 1a and 1b cause N–Si bond cleavage of Me₃SiNC under mild conditions, where PF₆⁻ and SbF₆⁻ as “non-coordinating anions” act as nucleophiles. We also present the crystal structure of a rare

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⁎Electronic Supplementary Information (ESI) available: Details of crystal structure determination and DFT calculations. CCDC 1417449 and 1417450. See DOI: 10.1039/x0xx00000x
example of a T-shaped, three-coordinated Cu(I) complex, [Cu(BPEP-Ph)3]3–BAr4 (1c) (BAR4 = B{3,5-(CF3)2}C6H4).}

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 X, in CD2Cl2 as a polar solvent. Thus, we considered that both complexes change into the T-shaped species [Cu(BPEP-Ph)]+ in CD2Cl2 by ionic dissociation. However, because a structurally well-defined Cu(I) complex with a T-shaped geometry is very rare, we attempted to isolate [Cu(BPEP-Ph)]+ using bulky BAR4 as a counter anion.

Following the synthetic procedures for 1a and 1b, the complex [Cu(BPEP-Ph)]3–BAr4 (1c) was prepared by anionic exchange of [CuBr(BPEP-Ph)] with NaBAR4 in CH2Cl2. A single crystal suitable for X-ray diffraction analysis was grown from a CH2Cl2 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 BAR4 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).

![Fig. 1 ORTEP drawing of 1c with 50% probability ellipsoids. Hydrogen atoms, BAR4 anion and a crystal solvent (CH2Cl2) are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu–P1 = 2.206(1), Cu–P2 = 2.216(1), Cu–N = 2.074(3), P1–Cu–1 = 1.681(4), P2–C2 = 1.711(4), P1–Cu–N = 84.5(1), P2–Cu–N = 84.5(1), P1–Cu–P2 = 186.9(5).]

The lengths of Cu–P1 (2.206(1) Å), Cu–P2 (2.216(1) Å), and Cu–N (2.074(3) Å) are in a normal range of dative covalent bonds found in PNP-pincer complexes of Cu(I). 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°). Hence, the three-coordinated, T-shaped structure of 1c was confirmed.

Complex 1c exhibited a singlet signal assignable to free BAR4 (δ = 62.9) in the 19F NMR spectrum. The 31P[19]H) NMR signal was observed at δ 214.4 in CD2Cl2, and this value was very close to that of 1a and 1b (δ 213.3). Moreover, the 1H NMR spectrum of the [Cu(BPEP-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 CD2Cl2 was evidenced.

Bond activation of silyl compounds by 1a and 1b

We previously reported that the Si–N bond of Me3SiN3 is activated by 1a and 1b to form [Cu3(BPEP-Ph)(μ3-N3)]X–(X– = PF6– and SbF6–), respectively (Eq. 1). These reactions very probably involve by-production of Me3SiF and EF5 (E = P and Sb). However, while the formation of Me3SiF was confirmed by NMR spectroscopy, EF5 could not be detected in the reaction systems. On the other hand, we noticed that the reactions with Me3SiCN present all product components including EF5, which is found in an associated form with a cyanido ligand arising from the activation of Me3Si–CN bond (Eq. 2).

- **1a, 1b** Me3SiCN in CD2Cl2

![Complex 1a rapidly reacted with Me3SiCN in CD2Cl2 at ambient temperature to give 2a quantitatively, as confirmed by NMR spectroscopy. The by-production of Me3SiF (δH 0.23, δF = 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 Me3SiCN proceeded at 50 °C for 1 h, and cyanide complex 2b was obtained in 43% yield, along with Me3SiF. 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), reflecting the association with PF5 and SbF5 as strong Lewis acids.

The 31P[19]H) 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 a typical region of phosphahalke ligands. On the other hand, the latter signal assignable to the PF5 group associated with the CN ligand was split into a doublet of quintets, due to the coupling with fluorine nuclei (JPF = 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 19F NMR spectrum of 2a displayed two sets of signals at δ −83.6 (d, JPF = 774 Hz, JFP = 62Hz) and 53.1 (dd, JPF = 745 Hz, JFP = 62 Hz) in the 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 ($\delta$ 262.3) was observed in a normal range of phosphaalkene complexes as well. Although the $^{19}$F NMR signals at $\delta$ ~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 therefore unavailable for structural assignment, the structure associated with an SbF$_6$ 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$_2$SiH at 40 °C formed a bis(phosphaethenyl)pyridinium (87%) and PhMe$_2$SiF (78%), along with insoluble materials (Eq. 3). It is likely that the pyridinium salt is eliminated from a Cu(I) hydride of the formula [CuH(BPEP-Ph)]$^+$SbF$_6^-$, generated by Si–H bond cleavage. It was also confirmed that the reaction of 1b with PhMe$_2$SiD produces the pyridinium salt deuterated at the nitrogen atom selectively.

\[
\text{1b} \rightarrow \text{PhMe}_2\text{SiH (or D) in CDCl}_3 \text{ at 40 °C} \rightarrow \begin{array}{c}
\text{Ph} \\
\text{Mes}^* \\
\text{Sb} \\
\text{F} \\
\text{Me} \\
\text{P} \\
\text{H} \\
\text{(or D)} \\
\text{Ph} \\
\text{Mes}^* \\
\text{SbF}_6^- \\
\text{+ Me}_3\text{SiF} \end{array} \quad (3)
\]

X-ray crystal structure of 2b

Fig. 2 shows the X-ray structure of [Cu(CN-SbF$_5$)(BPEP-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.$^{7,8,10}$ The Cu–N2 length (2.021(5) Å) is in a typical range of 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, but the Cu–C1–N1 bond (178.5(6)$^\circ$) retains the linearity. On the other hand, the N1–Sb bond (2.043(6) Å) is clearly shorter than that of C:N–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 a typical range of nitrogen-coordinated SbF$_5$ groups.$^{14}$

Bond activation process of Me$_3$SiCN

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$_3$SiCN to 1a and 1b. Since Me$_3$SiCN are known to undergo 1,2-silyl group migration on transition metals,$^{15}$ the formation of isostructural intermediates 3a and 3b, instead of nitride homologues, are presumed. Actually, complex 3b could be prepared by the treatment of 1b with Me$_3$SiCN at room temperature, and isolated as a light orange compound in 83% yield. The IR spectrum exhibited the v(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 ESI†).

![Image](https://example.com/image.png)

**Scheme 2** Bond activation of Me$_3$SiCN promoted by 1a and 1b.

Isonitrile complexes 3a and 3b then undergo nucleophilic attack of PF$_6^-$ and SbF$_6^-$ ions, respectively, on the silicon atom (4a and 4b), leading to N–Si bond cleavage of the Me$_3$SiNC...
ligand. Finally, [Cu(CN)(BPEP-Ph)] thus generated combines with PF₆ and SbF₅ to form 2a and 2b, respectively.

The differences in relative stability between 3a and [2a + Me₃SiF] and 3b and [2b + Me₃SiF] were evaluated by DFT calculations. The conversion of 3a to [2a + Me₃SiF] was an exothermic process by 4.6 kcal/mol, whereas that of 3b to [2b + Me₃SiF] was exothermic by 9.2 kcal/mol. Principally, the exothermicity observed for both systems must be due to the formation of Me₃SiF with an extremely strong Si–F bond (158 kcal/mol). On the other hand, the additional stability energy for the conversion of 3b would be derived from higher association energy of SbF₅ than PF₆ to the CN ligand in [Cu(CN)(BPEP-Ph)], which is caused by higher Lewis acidity of SbF₅.

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 Me₃SiCN is caused by a kinetic reason. A plausible explanation may be found in a large difference in the fluoride ion affinity between PF₆ (pF₂ = 9.49) and SbF₅ (pF₂ = 12.03). Namely, SbF₅ is reluctant to eliminate F⁻, compared with PF₆, and therefore 1b with SbF₅ is much less reactive than 1a with PF₆.

Conclusions

We have demonstrated that [Cu(X)(BPEP-Ph)] (X = PF₆ (1a), SbF₅ (1b)) bind a PNP-pincer type phosphalkene ligand (BPEP-Ph) to bond activation of Me₃SiCN in CD₂Cl₂, to give Cu(1) cyanides of the formula [Cu(CN-2E)(BPEP-Ph)] (E = P (2a), Sb (2b)), along with by-production of Me₃SiF. The reactions proceed via coordination of Me₃SiCN to give the isocyano complexes [Cu(CNMe)(BPEP-Ph)](X = PF₆ (3a), SbF₅ (3b)), followed by Si–N bond cleavage caused by nucleophilic attack of PF₆⁻ and SbF₅⁻ on the silicon atom. Although PF₆⁻ and SbF₅⁻ as non-coordinating anions are known to be poorly nucleophilic, complexes 1a and 1b smoothly react with Me₃SiCN under mild conditions. This is probably because the strong n-accepting ability of BPEP-Ph reduces electron density of the Cu–CN–SiMe₃ 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, C₆D₆) or CaH₂ (hexane, CH₂Cl₂, CD₂Cl₂) and distilled. CuBr, NaBARF₄, AgPF₆, Me₃SiCN, PhMe₃SiH and trimethoxybenzene were obtained from commercial sources and used without purification. BPEP-Ph and [CuBr(BPEP-Ph)] were prepared as previously reported. ³¹H NMR spectra were recorded at 25 °C on a Bruker AVANCE 400 spectrometer (³¹H NMR, 400.13 MHz; ¹³C NMR, 100.62 MHz; ¹⁹F NMR, 376.46 MHz; ³¹P NMR, 161.98 MHz). Chemical shifts are reported in δ (ppm), referenced to ³¹H (of residual solvent signals) and ¹³C signals of deuterated solvents as internal standards or to the ¹⁹F signal of CF₃C=O (δ 163.0) and to the ¹⁹F signal of 85% H₂PO₄ (δ 0.0) as external standards. IR spectra were recorded on a JASCO FTIR-4100 spectrometer. Elemental analysis was performed by the ICR Analytical Laboratory, Kyoto University.

Preparation of 1c. A suspension of NaBARF₄ (28.0 mg, 0.032 mmol) in CH₂Cl₂ (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 CH₂Cl₂/hexane, and stored at −35 °C to give brown crystals of 1c (52.0 mg, 0.030 mmol, 94%).

¹³C NMR (CD₂Cl₂): δ 133.1 (s, 18H, C₆H₅), 157.9 (s, 36H, C₆H₅), 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, Ar), 4.99 (s, 18H, C₆H₅) (ppm). ³¹P [¹³H] NMR (CD₂Cl₂): 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. ¹³P [¹³H] NMR (CD₂Cl₂): δ 314.4 (br). ¹⁹F NMR (CD₂Cl₂): δ −62.9 (s). Anal. calc. for C₇₃H₶₃BCuF₂N₂P₂: C, 60.23; H, 4.82; N, 0.81. Found: C, 60.11; H, 5.11; N, 0.80.

Reaction of 1a with Me₃SiCN. A toluene solution of 1a was prepared from [CuBr(BPEP)] (15.0 mg, 0.016 mmol) and AgPF₆ (4.7 mg, 0.019 mmol) at room temperature. The solution was filtered through a Celite pad to remove AgBr and unreacted AgPF₆. Me₃SiCN (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%).

²¹Ne NMR spectra were recorded at 25 °C on a Bruker AVANCE 400 spectrometer (²¹Ne NMR, 400.13 MHz; ¹³C NMR, 100.62 MHz; ¹⁹F NMR, 376.46 MHz; ³¹P NMR, 161.98 MHz).
Reaction of 1b with PhMeSiH. To an NMR sample tube was charged a CD$_2$Cl$_2$ solution (0.4 mL) of 1b (12.0 mg, 0.011 mmol). PhMeSiH (20 μL, 0.013 mmol) was added, and the solution was allowed to stand at 40 °C for 24 h. The formation of PhMeSiS$^+$ (0.0086 mmol, 78%) was confirmed by $^1$H 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-BPEP-Ph]$^{+}$SbF$_6^-$ (10.0 mg, 0.0096 mmol, 87%). $^1$H NMR spectrum (CD$_2$Cl$_2$): $\delta$ 1.24 (s, 18H, $^{19}$Bu), 1.36 (s, 36H, $^{19}$Bu), 6.45 (d, 4H, $J = 7.2$ Hz, Ar), 6.96 (t, 4H, $J = 7.8$ Hz, 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 NMR (CD$_2$Cl$_2$): $\delta$ 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, 157.7, 159.9, 166.9. Anal. calc'd for C$_{50}$H$_{29}$NP$_2$SbF$_{6}$: C, 63.22; H, 6.95; N, 1.34. Found: C, 62.80; H, 6.85; N, 1.36.

Preparation of 3b. A CD$_2$Cl$_2$ solution (0.4 mL) of 1b (8.5 mg, 0.0076 mmol) was charged to an NMR sample tube, and Me$_2$SiCN (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: $^1$H NMR (CD$_2$Cl$_2$): $\delta$ 0.48 (s, 9H, Me$_3$), 1.35 (s, 18H, $^{19}$Bu), 1.46 (s, 36H, $^{19}$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 [${}^1$H] NMR (CD$_2$Cl$_2$): $\delta$ –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. $^{19}$F NMR (CD$_2$Cl$_2$): $\delta$ –108.0 (br, 4F), –131.0 (br, 1F). IR (ATR): 2158 cm$^{-1}$ (υCN).

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 ($\lambda = 0.71070$ Å). For 2b, synchrotron radiation experiment ($\lambda = 0.71069$ 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 method (SHELSXS-97) and refined on $F^2$ for all reflections (SHEXLX-97). Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were placed at calculated positions. The crystallographic data and the summary of solution and refinement are listed in the Table S1 (see 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. Geometries optimization was performed with the DFT method without any symmetry constraints, where the B3PW91 functional was employed, using the model compounds [Cu(CNSiMe)$_3$(BPEP-Ph)$^+$], [Cu(CN-PP$_2$)(BPEP-Ph)$^+$] and [Cu(CN-SbF$_3$)(BPEP-Ph)$^+$] (BPEP-Ph = 2,6-bis(2-mesityl-2-porphaphenyl)pyridine). The Cu and Sb atoms were described with the SDD basis set and the LANL2Dzp 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).

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Notes and references

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