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Article

Copper(I) Complexes of Bis(2-(diphenylphosphino)phenyl) Ether: Synthesis, Reactivity, and Theoretical Calculations

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The tricoordinated cationic Cu^I complex $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\kappa^1\text{-}P\text{-DPEphos})][BF_4]$ (**1**) (DPEphos = bis(2-(diphenylphosphino)phenyl) ether) containing a dangling phosphorus center was synthesized from the reaction of $[Cu(CH_3CN)_4][BF_4]$ with DPEphos in a 1:2 molar ratio in dichloromethane. When complex **1** is treated with MnO_2, elemental sulfur, or selenium, the uncoordinated phosphorus atom undergoes oxidation to form a P=E bond resulting in the formation of complexes of the type $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\kappa^2\text{-}P,E\text{-DPEphos-E})][BF_4]$ (**2**, E = O; **3**, E = S; **4**, E = Se) containing a Cu–E bond. The zigzag polymeric Cu^I complex $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\mu\text{-}4,4'\text{-bpy})]_n[BF_4]_n$ (**5**) was prepared by the reaction of $[Cu(CH_3CN)_4][BF_4]$ with DPEphos and 4,4′-bipyridine in an equimolar ratio. The stereochemical influences of DPEphos on its coordination behavior are examined by density functional theory calculations.

Introduction

Mixed-ligand Cu^I complexes are of interest because of their luminescent properties, which find applications in the construction of sensors and organic light emitting diodes.[1−4] In recent years, there have been several reports on mixed-ligand complexes containing both bis(phosphines) and polypyridyls.[5,6] These complexes have been easily synthesized by treating bis(phosphines) with appropriate metal precursors followed by the addition of N-donor ligands. The mixed-ligand systems consisting of both bis(phosphines) and partially functionalized or oxidized ligands are less extensive. However, transition-metal complexes containing a variety of dangling phosphorus ligands have been extensively studied.[7] Selective oxidation of one of the phosphorus centers in a bis(phosphine) using H_2O_2, MnO_2, S, and Se is very difficult, since it always leads to the formation of a mixture of products, which complicates the isolation of the desired product. Often, Staudinger reactions of bis(phosphine)s with organic azides afford partially oxidized monophosphineimine derivatives in moderate yield.[8−11] Furthermore, it is more challenging to synthesize a mixed-ligand complex consisting of a bis(phosphine) and its mono-oxide derivative. In the past decade, there have been several reports on the DPEphos ligand (DPEphos = bis(2-(diphenylphosphino)phenyl) ether)

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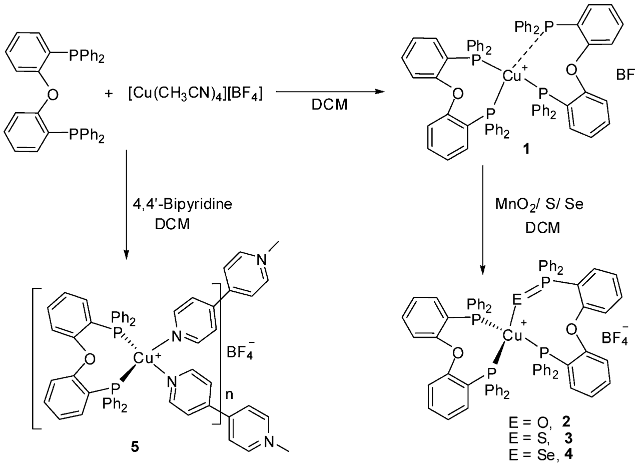
Scheme 1. Synthesis of [Cu(κ^2-*P*,*P*-DPEphos)(κ^1-*P*-DPEphos)][BF$_4$] (**1**) and [Cu(κ^2-*P*,*P*-DPEphos)(μ-4,4′-bpy)]$_n$[BF$_4$]$_n$ (**5**). Reactions of **1** with MnO$_2$, S, and Se



because of its potential applications in various organic transformation reactions.[12−14] Recently, we reported the synthesis of several ruthenium(II) complexes of DPEphos and its iminophosphorane derivative.[10,15] The DPEphos ligand showed several interesting coordination modes with a Ru^{II} center depending upon the bulkiness of other N, S, and P donors. This investigation was aimed at exploring the reactivity of 3d metals such as Cu^{I} toward DPEphos with considerable stereochemical influences, which often produce coordinatively unsaturated yet moderately stable 16-electron complexes with wide catalytic applications. As a part of our research interest,[16] here we describe the reactions of [Cu(CH$_3$CN)$_4$][BF$_4$] with DPEphos, which lead to the formation of interesting tricoordinated Cu^{I} derivatives containing a free P^{III} center that can be readily oxidized with chalcogens. The stereochemical influences of DPEphos on its coordination behavior are substantiated by density functional theory (DFT) calculations.

Results and Discussion

The treatment of [Cu(CH$_3$CN)$_4$][BF$_4$] with DPEphos in dichloromethane in a 1:2 molar ratio affords the mononuclear complex [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)][BF$_4$] (**1**) in good yield. The mass spectrum of the complex **1** shows the molecular ion peak at *m*/*z* 1139.21. The ^{31}P{^{1}H} NMR spectrum of **1** shows a single resonance at −15.5 ppm indicating all four phosphorus centers are equivalent. In contrast to this observation, the solid-state structure of complex **1** revealed that the Cu^{I} center is tricoordinated and one of the phosphorus centers is left uncoordinated (Scheme 1). The ^{31}P NMR spectrum suggests the presence of fluxional behavior in the solution state, since the signal broadens at −50 °C. The analogous reaction of [Cu(CH$_3$CN)$_4$][BF$_4$] with 1,2-bis(diphenylphosphino)ethane (dppe) yielded [Cu(dppe)$_2$][BF$_4$], in which Cu^{I} is tetracoordinated with tetrahedral geometry.[17] This difference in the reactivity may be due to the large-bite diphenyl ether backbone and the overall bulkiness of the DPEphos ligand, which probably prevents the fourth P^{III} center from establishing a Cu−P bond.

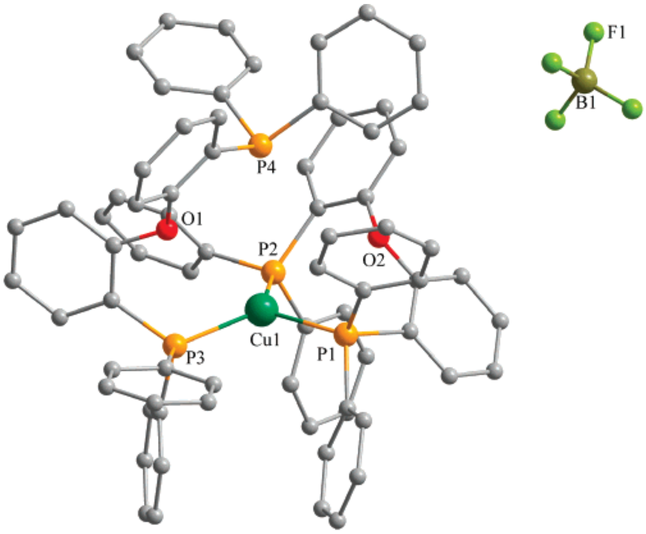


Figure 1. Molecular structure of complex **1**. Hydrogen atoms have been omitted for clarity.

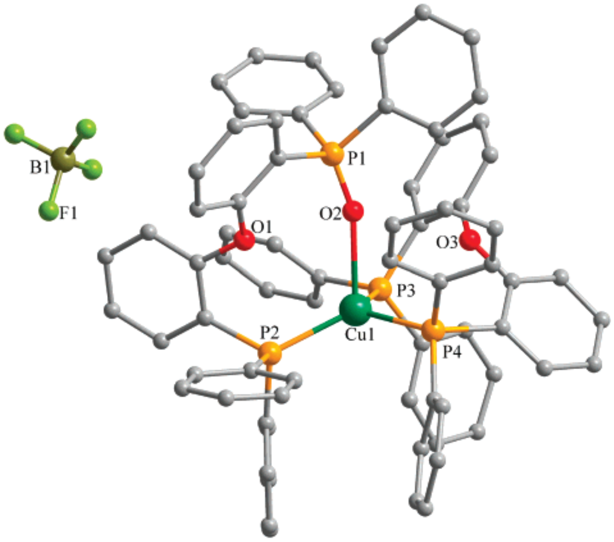


Figure 2. Molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity.

Interestingly, the uncoordinated phosphorus center in complex **1** on treatment with MnO$_2$, S, or Se undergoes oxidation to form the corresponding complexes **2**−**4**, which are identified from the mass spectra, where the molecular ion peaks appear at *m*/*z* 1155.34, 1171.04, and 1219.25, respectively. The ^{31}P NMR spectrum of complex **2** shows

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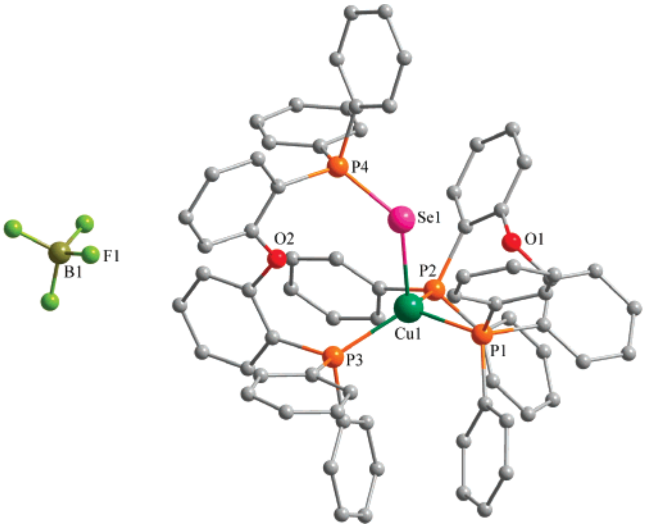

Figure 3. Molecular structure of complex **4**. Hydrogen atoms and uncoordinated solvent molecules have been omitted for clarity.

three sets of unresolved multiplets in the regions of 30.2, −12.1, and −15.1 ppm, respectively, for P(═O), two P atoms of the chelating ligand, and the copper-bound phosphorus center of the mono-oxidized DPEphos. The ^{31}P NMR spectra of complexes **3** and **4** are similar to that of complex **2**. The structures of the complexes **2** and **4** are confirmed by X-ray diffraction studies. Interestingly, the addition of an excess of oxidizing agents did not cleave any of the Cu−P bonds.

The reaction of $[Cu(CH_3CN)_4][BF_4]$ with DPEphos and 4,4′-bipyridine in an equimolar ratio afforded a coordination polymer $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\mu\text{-}4,4'\text{-bpy})]_n[BF_4]_n$ (**5**) as a yellow crystalline solid in good yield. The $^{31}P\{^1H\}$ NMR spectrum of complex **5** shows a single peak at −18.7 ppm, which indicates that both phosphorus atoms are equivalent. The presence of the 4,4′-bipyridine ligand in complex **5** is confirmed by the aromatic proton resonances at 7.65 and 8.80 ppm as broad singlets with appropriate intensities in the ^{1}H NMR spectrum. The polymeric structure of complex **5** in the solid state is revealed by the X-ray structural results discussed below and presented in Figure 4.

Molecular Structures. The complexes **1**, **2**, **4**, and **5** are recrystallized from the CH_2Cl_2/Et_2O solvent mixture. All these complexes are obtained as colorless crystalline solids except the complex **5**, which is yellow in color. The Cu^I center in complex **1** (Figure 1) adopts a distorted trigonal-planar geometry, which is evident from the sum of the three P−Cu−P bond angles of 357.05° (Table 1). The uncoordinated dangling phosphorus center is oriented toward the Cu^I center at a distance of 3.958 Å, which is considerably longer than the sum of the van der Waals radii of Cu^I and P (3.20 Å),[18] thus indicating the absence of any bonding interactions. The Cu1−P1, Cu1−P2, and Cu1−P3 bond distances are 2.2686(8), 2.2719(8), and 2.2782(9) Å, respectively, and are comparable with those of $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\mu\text{-NN})][BF_4]$ (2.2614(9) and 2.2712(7) Å) (NN = 2,9-dimethyl-1,10-phenanthroline or 2,9-di-*n*-butyl-1,10-phenanthroline).[5]

The geometry around copper in complex **2** (Figure 2) is pseudotetrahedral. The Cu1−P4, Cu1−P3, and Cu1−P2 bond distances are 2.2855(2), 2.2860(16), and 2.2953(15) Å, respectively, which are slightly longer than those in complex **1**. The Cu−O bond distance is 2.356(5) Å, which is slightly longer than those observed in complexes $[Cu(dppeO)_2][OTf]$ (2.117(6) Å) and $[Cu(BozPHOS)_2][OTf]$ (2.127(19) and 2.122(19) Å) (BozPHOS = 1,2-bis(2,5-dimethylphospholano)benzene mono-oxide).[19,20] In complex **4** (Figure 3), the Cu^I atom exists in distorted-tetrahedral geometry. The Cu1−P1 (2.363(1) Å), Cu1−P2 (2.334(1) Å) and Cu1−P3 (2.330(1) Å) bond distances are ca. 0.06−0.09 Å longer than those found in complex **1**. The P2−Cu1−P3 and P3−Cu1−P1 bond angles of 112.80(3)° and 119.55(3)° are similar to those of complex **2**, whereas the P2−Cu1−P1 bond angle of 108.21(3)° is ca. 11.6° less than that in complex **2**. The Cu1−Se1 bond distance of 2.5877(6) Å is comparable with the same distances (2.675(5) and 2.475(4) Å) observed in $[Cu(dppfSe)_2][BF_4]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene).[21]

The X-ray structural determination shows that complex **5** (Figure 4 and Table 2) exists as a zigzag polymer in which the copper centers are present in a distorted-tetrahedral environment. The structure shows a couple of nonidentical copper centers, which are arranged in pairs alternate to each other. The 4,4′-bipyridine acts as the bridging unit between the two Cu^I centers to construct a polymeric chain in which the alternate 4,4′-bipyridine rings are distorted with a dihedral angle of 31.42° between the planes of two pyridyl rings, whereas the adjacent units are coplanar. Generally, the presence of extended conjugation between metal centers and 4,4′-bipyridine units indicates conducting properties.[22,23] In complex **5**, the extended conjugation is absent due to the twisting of aromatic groups in the 4,4′-bipyridine ligands, which makes them non-coplanar. This may be due to the packing strain in the solid state, which leads to the disorder in the planarity of the 4,4′-bipyridine. The bond angles N2−Cu1−N1, P2−Cu1−P1, N4−Cu2−N3, and P4−Cu2−P3 are 104.46(19)°, 113.28(6)°, 98.81(18)°, and 113.71(6)°, respectively.

Theoretical Calculations. To ascertain that the overall bulkiness of the DPEphos ligand is the single factor determining the product of the reaction of $[Cu(CH_3CN)_4][BF_4]$ with DPEphos, DFT calculations were performed for the cationic systems in question. The geometry-optimized structure for the three-coordinated $[Cu(\kappa^2\text{-}P,P'\text{-DPEphos})(\kappa^1\text{-}P\text{-DPEphos})]^+$ (see Figure 5a) is in good agreement with the X-ray crystal structure determined for **1**: the calculated values of some key parameters are Cu1−P1 = 2.326 Å, Cu1−P2 = 2.338 Å, Cu1−P3 = 2.318 Å, ∠P1−Cu1−P2 = 113.8°, ∠P2−Cu1−P3 = 120.7°, ∠P1−Cu1−P3 = 124.3°, and $\sum\angle PCuP = 358.8°$. The average error in the

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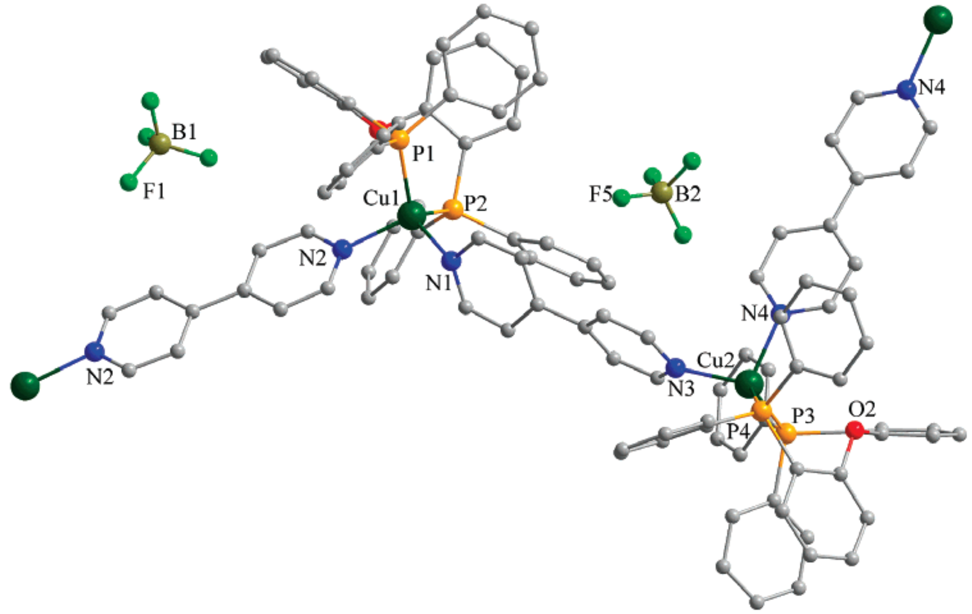

Figure 4. Molecular structure of complex **5**. Hydrogen atoms and uncoordinated solvent molecules have been omitted for clarity.

Table 1. Selected Bond Distances and Bond Angles for Complexes **1** and **2**

complex 1				complex 2			
bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
Cu1−P1	2.2686(8)	P1−Cu1−P3	121.85(3)	Cu1−P4	2.2855(15)	P4−Cu1−P3	112.52(6)
Cu1−P2	2.2719(8)	P1−Cu1−P2	113.87(3)	Cu1−P3	2.2860(16)	P4−Cu1−P2	119.20(6)
Cu1−P3	2.2782(9)	P3−Cu1−P2	121.33(3)	Cu1−P2	2.2953(15)	P3−Cu1−P2	119.85(6)
B1−F1	1.366(4)	C54−O1−C55	120.5(2)	Cu1−O2	2.356(5)	P4−Cu1−O2	96.41(12)
B1−F2	1.336(4)	C18−O2−C19	117.9(2)	P1−O2	1.463(5)	P3−Cu1−O2	89.39(13)
Cu1···P4	3.958			B1−F1	1.317(7)	P2−Cu1−O2	112.20(12)
				B1−F2	1.318(6)	P1−O2−Cu1	161.6(3)

Table 2. Selected Bond Distances and Bond Angles for Complexes **4** and **5**

complex 4				complex 5			
bond distances (Å)		bond angles (deg)		bond distances (Å)		bond angles (deg)	
Cu1−P3	2.3303(10)	P2−Cu1−P3	112.80(3)	Cu1−N2	2.072(5)	N2−Cu1−N1	104.46(19)
Cu1−P2	2.3344(9)	P3−Cu1−P1	119.55(3)	Cu1−N1	2.109(5)	N2−Cu1−P2	112.62(15)
Cu1−P1	2.3634(9)	P2−Cu1−P1	108.21(3)	Cu1−P2	2.2762(18)	N1−Cu1−P2	111.34(13)
Cu1−Se1	2.5877(6)	P3−Cu1−Se1	113.60(3)	Cu1−P1	2.2983(17)	N2−Cu1−P1	107.23(14)
P4−Se1	2.1513(9)	P2−Cu1−Se1	106.35(3)	Cu2−N4	2.078(4)	N1−Cu1−P1	107.37(14)
B1−F1	1.373(6)	P1−Cu1−Se1	94.28(3)	Cu2−N3	2.081(5)	P2−Cu1−P1	113.28(6)
B1−F2	1.387(6)	P4−Se1−Cu1	126.09(3)	Cu2−P4	2.2552(17)	N4−Cu2−N3	98.81(18)
				Cu2−P3	2.2846(17)	N4−Cu2−P4	112.13(14)
				B1−F1	1.400(12)	N3−Cu2−P4	116.49(14)
				B1−F2	1.385(12)	N4−Cu2−P3	103.67(14)
						N3−Cu2−P3	110.34(14)
						P4−Cu2−P3	113.71(6)

predicted bond lengths is 0.035 Å with the single largest deviations observed for the Cu−P interactions (ca. 0.06 Å longer). The calculated bond angles are also fairly accurate and generally show errors less than 2° for bonds involving C, P, and Cu atoms. On the other hand, the calculated torsional angles show larger deviations from the experimental values. In particular, the torsional angles involving the backbone atoms of the κ^1-*P*-coordinated DPEphos ligand are as much as 10° in error. This results in a significantly elongated distance from the uncoordinated phosphorus atom P4 to the Cu$^{\mathrm{I}}$ center in the calculated structure, 4.541 Å (cf. 3.958 Å found in the X-ray crystal structure of **1**). The above discrepancies result mainly from the flat potential energy surface along the Cu1···P4 bond at distances greater than the sum of the van der Waals radii for these atoms.

The crystallographic data[24] reported for the cation $[\mathrm{Cu}(\mathrm{PPh}_3)_4]^+$ was used to build an analogous structure $[\mathrm{Cu}(\kappa^2\text{-}P,P'\text{-DPEphos})_2]^+$ in which the Cu$^{\mathrm{I}}$ center is four-coordinated by two DPEphos ligands. The structure of this hypothetical system was optimized with DFT and compared to the structure determined for $[\mathrm{Cu}(\kappa^2\text{-}P,P'\text{-DPEphos})(\kappa^1\text{-}P\text{-DPEphos})]^+$ (see Figure 5b). As expected, the coordination of the Cu$^{\mathrm{I}}$ center to four phosphorus atoms instead of three increases the Cu−P bond lengths significantly: the average bond

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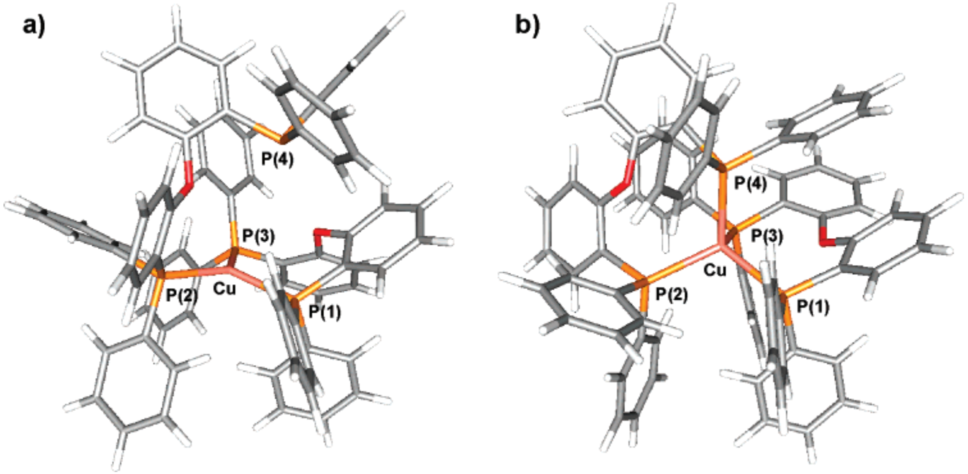

Figure 5. Optimized structure of (a) [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ and (b) [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$.

Table 3. Crystallographic Information for Complexes **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
formula	$C_{72}H_{56}CuO_2P_4BF_4$	$C_{72}H_{56}CuO_3P_4BF_4$	$C_{73}H_{58}BC_{l2}CuF_4O_{2.5}P_4Se$	$C_{97}H_{78}B_2C_{l7.5}Cu_2F_8N_4O_2P_4$
fw	1227.41	1243.41	1399.28	2022.09
cryst syst	orthorhombic	orthorhombic	triclinic	triclinic
space group	*Pbcn*	*Pbcn*	$P\bar{1}$	$P\bar{1}$
a (Å)	20.1286(16)	20.187(5)	12.898(2)	13.803(2)
b (Å)	24.5174(17)	24.542(5)	13.6337(6)	19.089(4)
c (Å)	24.833(3)	24.756(4)	19.150(2)	20.051(5)
α (deg)	90	90	104.166(6)	69.255(19)
β (deg)	90	90	94.444(12)	77.065(16)
γ (deg)	90	90	94.259(7)	72.710(15)
V (Å^3)	12255(2)	12265(4)	3240.0(7)	4675.5(15)
Z	8	8	2	2
ρ_{calc} (g cm^{-3})	1.331	1.347	1.434	1.436
μ(Mo Ka) (mm^{-1})	0.520	0.521	1.139	0.805
F(000)	5072	5136	1428	2063
cryst size (mm)	0.22 × 0.26 × 0.33	0.21 × 0.31 × 0.33	0.35 × 0.30 × 0.28	0.17 × 0.21 × 0.33
T (K)	150	293	150	150
2θ range (deg)	3.0 − 25.0	3.1 − 25.0	3.0 − 25.0	3.0 − 25.0
total no. reflns	10 745	10 546	11 256	16 433
no. of indep reflns	758 [$R_{int} = 0.041$]	767 [$R_{int} = 0.141$]	802 [$R_{int} = 0.034$]	1141 [$R_{int} = 0.072$]
GOF (F^2)	1.089	0.776	1.104	1.030
R_1[a]	0.0489	0.0580	0.0388	0.0736
R_2[b]	0.1502	0.1508	0.1197	0.2066

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_2 = \{[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

length for the four Cu−P bonds in [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ is 2.454 Å. The coordination sphere around the central Cu^I atom in [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ is almost ideal tetrahedron as evidenced by the P−Cu−P bond angle range of 104.5−111.2°. The bond parameters in the two DPEphos ligands are not significantly different between [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ and [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ except for the Cu−P−C and C−O−C bond angles, which are opened up by 3−6° in the former species due to the increased steric bulk of the two ligands.

To examine the differences and similarities in the bonding of [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ and [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ more closely, the energetics of the process in which two DPEphos ligands chelate a Cu^I center either unsymmetrically or symmetrically were determined. With the use of the energy decomposition analysis method, the steric and electronic contributions to the chelation energy can be separated by the expression

$$\Delta E_{\mathrm{chelation}} = \Delta E_{\mathrm{prep}} + \Delta E_{\mathrm{int}}$$

in which ΔE_{prep} is the preparation energy required to alter the geometry of two ground states of DPEphos ligands to the geometry they acquire in the overall complex and ΔE_{int} is the interaction energy between the prepared fragments and the Cu^I center. The interaction energy ΔE_{int} can further be decomposed into three physically meaningful terms

$$\Delta E_{\mathrm{int}} = \Delta V_{\mathrm{elec}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orbital}}$$

in which ΔV_{elec} is the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments, $\Delta E_{\mathrm{Pauli}}$ is the exchange repulsion component resulting from the destabilizing interactions between the occupied orbitals on each fragment, and $\Delta E_{\mathrm{orbital}}$ accounts for the stabilizing interactions between the occupied and empty fragment orbitals. The orbital interaction term can additionally be partitioned into contributions from distinct irreducible representations of the interacting system.

As seen from Table 4, the individual P−Cu^I interactions are significantly weaker in [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ than in

Table 4. Energy Decomposition Analysis of [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ and [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ [a]

	$\Delta E_{\mathrm{chelation}}$	ΔE_{prep}	ΔE_{int}	ΔV_{elec}	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\mathrm{orbital}}$
[Cu(κ^2-*P*,*P*-DPEphos)-(κ^1-*P*-DPEphos)]$^+$	−740	19	−759	−765	635	−600
[Cu(κ^2-*P*,*P*-DPEphos)$_2$]$^+$	−677	116	−793	−677	528	−610

[a] Energies are reported in kJ mol^{-1}.

[Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ (170 kJ mol^{-1} per bond vs 250 kJ mol^{-1} per bond), but the total interaction energy term ΔE_{int} is nevertheless more negative for the complex [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$, which contains one more P−Cu$^{\mathrm{I}}$ bond. Hence, if contributions from ΔE_{prep} are neglected, the four-coordinate structure becomes the global energy minimum by approximately 30 kJ mol^{-1}. However, the preparation energy ΔE_{prep} is almost 100 kJ mol^{-1} smaller for the three-coordinate complex than for the four-coordinate cation. This difference in ΔE_{prep} is more than enough to compensate the less favorable bonding interactions in [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$, which alter the energy of the three-coordinate structure with a dangling phosphorus center 60 kJ mol^{-1} lower relative to the energy of the symmetric four-coordinate system. Table 4 also shows the contribution of ΔV_{elec}, $\Delta E_{\mathrm{Pauli}}$, and $\Delta E_{\mathrm{orbital}}$ in ΔE_{int} for both complexes. We note that the $\Delta E_{\mathrm{Pauli}}$ term, which is responsible for the steric repulsion, is smaller for [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ due to its tetrahedral coordination and, hence, elongated P−Cu$^{\mathrm{I}}$ distances and that the attractive electrostatic interaction ΔV_{elec} is more negative for [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ due to its significantly stronger P−Cu$^{\mathrm{I}}$ interactions (see above). The orbital interaction terms are predicted to be comparable between the two systems.

The above analysis clearly demonstrates that the coordination of a Cu$^{\mathrm{I}}$ center with four phosphorus atoms is, in principle, the energetically most favorable situation, but the entire energy gain will be lost in distorting the two DPEphos ligands to a geometry that facilitates such coordination. Hence, these results confirm that the observed difference in the reactivity of dppe and DPEphos toward [Cu(CH$_3$CN)$_4$][BF$_4$] is in fact due to the overall bulkiness of the DPEphos ligand, which allows P,P′-chelation to copper via only one of the two ligands. This was conclusively confirmed by running a full geometry optimization for a three-coordinate structure analogous to [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ in which the four phenyl groups in the individual DPEphos ligands were replaced with sterically much less demanding methyl groups. Since the substitution of phenyl to methyl lowers the preparation energy significantly, the interaction energy term now dominates the total chelation energy. Thus, the optimization leads to the immediate coordination of the dangling phosphorus atom to the Cu$^{\mathrm{I}}$ center, giving a four-coordinate structure with identical Cu−P bonds at 2.345 Å (cf. calculated Cu−P bonds in [Cu(κ^2-*P*,*P*′-DPEphos)$_2$]$^+$ and [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)]$^+$ at 2.454 and 2.326 Å, respectively).

Conclusion

The 16-electron complex [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)][BF$_4$] (**1**) containing one uncoordinated phosphorus center readily undergoes oxidation to form an 18-electron complex with Cu−E (E = O, S, or Se) bond. The large bite angle of the diphenyl ether backbone and the overall bulkiness of the ligand play a vital role for this interesting feature of the complex **1**. The complexes **2**−**4** are the first examples of mixed-ligand Cu$^{\mathrm{I}}$ bis-chelating complexes containing both bis(phosphine) and its monochalcogenide (PQP=E) derivative. The Cu−O (**2**) and Cu−Se (**4**) bond distances are ca. 0.2 Å longer than those found in analogous compounds. The coordination polymer [Cu(κ^2-*P*,*P*′-DPEphos)(μ-4,4′-bpy)]$_n$[BF$_4$]$_n$ (**5**) exhibits a one-dimensional zigzag polymeric structure. The distorted-tetrahedral Cu$^{\mathrm{I}}$ centers are connected with 4,4′-bipyridine units, and the aromatic rings of alternating units are tilted by an angle of 31.42°. The DFT calculations clearly indicate the stereochemical influences of the ligand framework and the phosphorus substituents on its coordination behavior. We are currently investigating the catalytic utility of the tricoordinated Cu$^{\mathrm{I}}$ complex in hydroamination and other related organic transformation reactions.

Experimental Section

General Methods. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All solvents were purified by conventional procedures and distilled under nitrogen prior to use.[25] DPEphos[11] and [Cu(CH$_3$CN)$_4$][BF$_4$][26] were prepared according to the published procedures. H$_2$O$_2$ (30% solution in water) (Merck), MnO$_2$ (SD-Fine), sulfur (Merck), selenium (Lancaster), and 4,4′-bipyridine (Aldrich) were purchased from commercial sources and used as received. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded using a Varian 400 Mercury Plus spectrometer operating at the appropriate frequencies, using TMS and 85% H$_3$PO$_4$ as the internal and external references, respectively. Microanalyses were performed on a Carlo Erba Model 1112 elemental analyzer. Electrospray ionization (EI) mass spectrometry experiments were carried out using a Waters Q-Tof micro-YA-105 mass spectrometer. Melting points were recorded using capillary tubes and are uncorrected.

Syntheses. [Cu(κ^2-*P*,*P*′-DPEphos)(κ^1-*P*-DPEphos)][BF$_4$] (1). A solution of [Cu(CH$_3$CN)$_4$][BF$_4$] (0.100 g, 0.318 mmol) in CH$_2$Cl$_2$ (8 mL) was added dropwise to a stirring solution of DPEphos (0.342 g, 0.636 mmol) also in CH$_2$Cl$_2$ (15 mL) at room temperature. After 8 h, the reaction mixture was concentrated to a 5 mL volume, and Et$_2$O (5 mL) was added and allowed to stay at room temperature for 1 day to obtain colorless crystals of **1**. Yield: 93% (0.363 g, 0.295 mmol). Anal. Calcd for C$_{72}$H$_{56}$O$_2$P$_4$CuBF$_4$: C, 70.45; H, 4.60. Found: C, 70.48; H, 4.66. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.44−7.28 (m, *Ph*, 56H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$): δ −15.5 (s). MS (EI): *m*/*z* 1139.21 [M]$^+$.

[Cu(κ^2-*P*,*P*′-DPEphos)(κ^2-*P*,*O*-DPEphos-O)][BF$_4$] (2). A mixture of **1** (0.060 g, 0.049 mmol) and MnO$_2$ (50 mg) in CH$_2$Cl$_2$ (5 mL) was stirred for 2 h at room temperature and filtered to obtain a colorless solution, which was concentrated to a 3 mL volume, and Et$_2$O (5 mL) was added to give colorless crystals of **2**. Yield: 87% (0.053 g, 0.042 mmol). Anal. Calcd for C$_{72}$H$_{56}$O$_3$P$_4$CuBF$_4$: C, 69.55; H, 4.54. Found: C, 69.19; H, 4.38. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.43−7.45 (m, *Ph*, 56H). ^{31}P{^{1}H} NMR (162 MHz,

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$CDCl_3$): δ 30.2 (q, *P*═*O*, $^3J_{PP}$ = 6.6 Hz, 1P), −12.1 (s, br, *Cu*−*P*, 2P), −15.1 (s, br, *Cu*−*P*, 1P). MS (EI): *m*/*z* 1155.34 [M]$^+$.

[Cu(κ^2-*P*,*P*′-DPEphos)(κ^2-*P*,*S*-DPEphos-S)][BF$_4$] (3). A mixture of **1** (0.060 g, 0.049 mmol) and elemental sulfur (0.0016 g, 0.049 mmol) in CH_2Cl_2 (5 mL) was stirred for 24 h at room temperature and filtered. The filtrate was concentrated to 3 mL, and Et_2O (5 mL) was added to give colorless crystals of **3**. Yield: 76% (0.047 g, 0.037 mmol). Anal. Calcd for $C_{72}H_{56}O_2SP_4CuBF_4$: C, 68.66; H, 4.48; S, 2.55. Found: C, 68.98; H, 4.62; S, 2.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.48−7.60 (m, *Ph*, 56H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 35.5 (t, *P*═*S*, $^3J_{PP}$ = 26 Hz, 1P), −6.3 (s, br, *Cu*−*P*, 1P), −9.1 (m, br, *Cu*−*P*, 1P), −14.1 (m, br, *Cu*−*P*, 1P). MS (EI): *m*/*z* 1171.04 [M]$^+$.

[Cu(κ^2-*P*,*P*′-DPEphos)(κ^2-*P*,*Se*-DPEphos-Se)][BF$_4$] (4). This procedure is similar to that of **3**, using selenium (0.004 g, 0.049 mmol). Yield: 82% (0.052 g, 0.040 mmol). Anal. Calcd for $C_{72}H_{56}O_2SeP_4CuBF_4$: C, 66.19; H, 4.32. Found: C, 66.51; H, 4.58. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.46−8.04 (m, *Ph*, 56H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 22.0 (m, br, *P*═*Se*, 1P), −7.8 (m, br, *Cu*−*P*, 2P), −14.2 (s, br, *Cu*−*P*, 1P). MS (EI): *m*/*z* 1219.25 [M]$^+$.

[Cu(κ^2-*P*,*P*′-DPEphos)(μ-4,4′-bpy)]$_n$[BF$_4$]$_n$ (5). A mixture of [Cu(CH_3CN)$_4$]BF$_4$ (0.060 g, 0.191 mmol) and DPEphos (0.103 g, 0.191 mmol) in CH_2Cl_2 (10 mL) was stirred for 4 h at room temperature. 4,4′-Bipyridine (0.030 g, 0.191 mmol) in CH_2Cl_2 solution was added to the reaction mixture dropwise and stirring was continued for 4 h to get a clear yellow solution. The reaction mixture was concentrated to 5 mL, and Et_2O (5 mL) was added to give yellow crystals of **3**. Yield: 94% (0.152 g). Anal. Calcd for $C_{46}H_{36}OP_2N_2CuBF_4$: C, 65.38; H, 4.29; N, 3.31. Found: C, 65.21; H, 4.49; N, 3.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71−7.54 (m, *Ph*, 28H), 7.65 (s, *bpy*, 4H), 8.80 (s, br, *bpy*, 4H). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −18.7 (s).

Computational Details. DFT calculations were performed primarily for cations [Cu(κ^2-*P*,*P*-DPEphos)$_2$]$^+$ and [Cu(κ^2-*P*,*P*-DPEphos)(κ^1-*P*-DPEphos)]$^+$. The molecular structures were fully optimized by using a combination of the GGA PBEPBE exchange-correlation functional (within the resolution of the identity approximation)[27−30] with the Ahlrichs' triple-ζ valence basis set augmented by one set of polarization functions (def-TZVP). All basis sets were used as they are referenced in the *Turbomole 5.9* internal basis set library. Geometry optimizations were performed with *Turbomole 5.9*.[31] The program *ADF 2006.01*[32] was used to calculate the individual components of ΔE_{int} in the energy decomposition analysis (EDA). The analysis followed the Morokuma−Ziegler partition scheme[33] and utilized the PBEPBE functional in combination with a STO-type all-electron basis sets of TZP quality; scalar relativistic ZORA formalism was also applied in all EDA calculations.

Crystal Structure Determination. Single crystals of **1**, **2**, **4**, and **5** suitable for X-ray diffraction were grown by the slow diffusion of diethyl ether into dichloromethane solution and mounted on a glass fiber with epoxy resin. Unit cell determination and data were collected on an Oxford Diffraction XCALIBUR-S CCD system using Mo Kα radiation (λ = 0.71073 Å). The structures were solved and refined by full-matrix least-squares techniques of F^2 using *SHELX-97* (*SHELXL* program package).[34] The absorption corrections were done via a multiscan, and all data were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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