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Synthesis and Structural Characterization of Cu(I) and Ni(II) Complexes that Contain the Bis[2-(diphenylphosphino)phenyl]ether Ligand. Novel Emission Properties for the Cu(I) Species

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The pseudotetrahedral complexes [Cu(NN)(DPEphos)]BF_4, where DPEphos = bis[2-(diphenylphosphino)phenyl]-ether and NN = 1,10-phenanthroline (**1**), 2,9-dimethyl-1,10-phenanthroline (**2**), 2,9-di-*n*-butylphenanthroline (**3**), or two dimethylcyanamides (**4**), and $NiCl_2$(DPEphos) (**5**) have been synthesized and structurally characterized by X-ray crystallography and their solution properties examined by use of a combination of cyclic voltammetry, NMR spectroscopy, and electronic absorption spectroscopy. Complexes **1**–**4** possess a reversible Cu(II)/Cu(I) couple at potentials upward of +1.2 V versus Ag/AgCl. Compounds **1**–**3** exhibit extraordinary photophysical properties. In room-temperature dichloromethane solution, the charge-transfer excited state of the dmp (dbp) derivative exhibits an emission quantum yield of 0.15 (0.16) and an excited-state lifetime of 14.3 μs (16.1 μs). Coordinating solvents quench the charge-transfer emission to a degree, but the photoexcited dmp complex **2** retains a lifetime of over a microsecond in acetone, methanol, and acetonitrile.

Introduction

The relative ease of synthesis and the rich visible absorption spectra of transition metal complexes have continued to foster interest in the use of many of them as platforms on which to examine and develop photochemical applications. Areas of recent interest include their role in solar energy conversion,[1] luminescence-based sensing,[2,3] display devices,[4] probes of biological systems,[5,6] and phototherapy,[7] where, for the sake of brevity, the literature citations focus only on some relatively recent contributions. Because of their ready availability and the prevalence of low-lying charge-transfer (CT) excited states, copper(I) complexes of polypyridine ligands have attracted the attention of several research groups.[8-10] However, these systems have some limitations. One is that the lowest energy CT excitation inevitably stems from a metal−ligand dσ* orbital.[8] An important consequence is that the excited state typically prefers a tetragonally flattened geometry whereas the ground state usually adopts a more tetrahedral-like coordination geometry appropriate for a closed-shell ion.[8,11] Aside from reducing the energy content, the geometric relaxation that occurs in the excited state facilitates relaxation back to the ground state.[12,13] Donor media also tend to quench the lifetime. Blaskie and McMillin[14] first reported this type of exciplex quenching, and by now, many other studies have confirmed the mechanism.[8,9,15,16] Introduction of sterically demanding ligands can impede geometric relaxation as well as solvent attack. For

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example, $[Cu(phen)(PPh_3)_2]^+$, where phen denotes 1,10-phenanthroline, is virtually nonemissive in methanol, while $[Cu(dmp)(PPh_3)_2]^+$, where dmp denotes 2,9-dimethyl-1,10-phenanthroline, has a lifetime of 330 ns in deoxygenated solution.[17] However, even with two bulky triphenylphosphines and a sterically active dmp ligand in the coordination sphere, temperature-dependent emission studies suggest that photoexcited $[Cu(dmp)(PPh_3)_2]^+$ is still subject to exciplex quenching in methanol.[18]

Our interest in exploring the photochemistry of mixed-ligand copper(I) complexes that incorporated *bidentate phosphines* in the coordination sphere has evolved from our recent studies[19] that were focused on the ability of the ligand bis[2-(diphenylphosphino)phenyl]ether (abbreviated DPEphos), and other closely related tridentate ligands containing P,O,P or P,N,P donor sets, to stabilize novel unsymmetrical multiply bonded dirhenium(IV,II) and dirhenium(III,II) complexes, in which these donors were bound in a tridentate fashion. Interestingly, although DPEphos has previously been used as a component of several catalytic palladium(0) and palladium(II) systems for amination and cross coupling reactions,[20] few fully characterized transition metal complexes of this ligand have been isolated. While mononuclear compounds of nickel(0) and (II),[21] palladium(0) and (II),[20d,20g,22] platinum(II),[20d] and rhodium(I)[23] have been described, only one of these, namely the palladium(0) complex Pd(DPEphos)(TCNE) (TCNE = tetracyanoethylene), has been structurally characterized.[21] We set out to address this dearth of structural information by isolating and fully characterizing a series of mixed-ligand copper(I) complexes, that contain this ligand in combination with dimethylcyanamide and various 1,10-phenanthroline ligands, along with the simple pseudotetrahedral nickel(II) complex $NiCl_2$(DPEphos). During the course of this work, we discovered some novel photochemical properties of the copper(I) species, an examination of which became the major focus of this study.

While the conformational requirements imposed by the ether linkage present in DPEphos do not prevent the ligand from acting as a bidentate phosphine, the ligand has a wide bite angle[24] which is likely to influence both ground- and the excited-state properties of resulting copper(I) complexes. In fact, results described in this work show that $[Cu(dmp)(DPEphos)]^+$ and related systems exhibit unusually long-lived CT excited states that are relatively resistant to solvent-induced exciplex quenching. Some of these results have been the subject of a preliminary communication.[25] Note that in this earlier report[25] we abbreviated bis[2-(diphenylphosphino)phenyl]ether as POP, we but now use the alternative of DPEphos.[24]

Experimental Section

A. Starting Materials. The DPEphos ligand was prepared by the literature procedure,[23] as were the phenanthroline ligands 2,9-di-*n*-butyl-1,10-phenthroline (dbp) and 2,9-diphenyl-1,10-phenanthroline (dpp).[26] Samples of dimethylcyanamide, 2,9-dimethyl-1,10-phenanthroline monohydrate ($dmp{\cdot}H_2O$), and triphenylphosphine were purchased from Aldrich Chemical Co., while 1,10-phenanthroline monohydrate ($phen{\cdot}H_2O$) was obtained from Fisher Scientific Co. The copper(I) complex $[Cu(NCCH_3)_4]BF_4$ was prepared by the reaction of $Cu(BF_4)_2$ with Cu metal in refluxing acetonitrile,[27] while $NiCl_2{\cdot}3H_2O$ was supplied by J. T. Baker Chemical Co. and ferrocene was obtained from Aldrich Chemical Co. The emission standard $[Ru(bpy)_3]Cl_2{\cdot}6H_2O$ was acquired from the G. F. S. Smith Chemical Co. Potassium ferrioxalate[28] and $[Cu(dmp)(dppe)]PF_6$,[29] where dppe is 1,2-bis(diphenylphosphino)ethane, were available from previous studies, as were $[Cu(phen)(PPh_3)_2]BF_4$[18] and $[Cu(dmp)(PPh_3)_2]BF_4$.[18] Spectral grade solvents came from standard supply houses.

B. Synthesis of Complexes of the Type [Cu(NN)(DPEphos)]BF_4, Where NN = 1,10-Phenanthroline or a Substituted Phenanthroline Ligand, or Two Dimethylcyanamide Ligands. (i) [Cu(phen)(DPEphos)]BF_4 (1). A typical procedure is as follows. A mixture of $[Cu(NCCH_3)_4]BF_4$ (31 mg, 0.10 mmol) and bis[2-(diphenylphosphino)phenyl]ether (54 mg, 0.10 mmol) in 20 mL of dichloromethane was stirred at 25 °C for 2 h and then treated with a solution of 1,10-phenanthroline monohydrate (20 mg, 0.10 mmol) in 5 mL of dichloromethane. This reaction mixture was stirred for an additional 1 h and filtered and the clear yellow filtrate concentrated to ca. 5 mL. Approximately 5 mL of acetonitrile was added, and the vapor diffusion of diethyl ether into the resulting solution afforded yellow crystals of the complex, [Cu(phen)(DPEphos)]BF_4 (**1**), that were washed with diethyl ether (2 × 5 mL); yield 61 mg (70%). The identity of this product was established by X-ray crystallography. ^1H NMR spectroscopy showed the presence of lattice acetonitrile and diethyl ether, and this was confirmed by the structure determination.

The procedures for the synthesis of **2**−**5** were essentially identical to that described in (i). Only the quantities of ligand that were used, the product yields, and the elemental microanalyses are given.

(ii) Synthesis of [Cu(dmp)(DPEphos)]BF_4 (2). 2,9-Dimethyl-1,10-phenanthroline (21 mg, 0.10 mmol). Yield: 57 mg (63%).

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Table 1. Crystallographic Data for the Complexes of Composition $[Cu(phen)(DPEphos)]BF_4{\cdot}1.5Et_2O{\cdot}CH_3CN$ (**1**), $[Cu(dmp)(DPEphos)]BF_4{\cdot}CH_2Cl_2$ (**2**), $[Cu(dbp)(DPEphos)]BF_4{\cdot}CH_3CN$ (**3**), $[Cu(NCNMe_2)_2(DPEphos)]BF_4{\cdot}0.5CH_2Cl_2{\cdot}0.5H_2O$ (**4**), and $NiCl_2(DPEphos)$ (**5**)

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{56}H_{54}BCuF_4N_3O_{2.50}P_2$	$C_{51}H_{42}BCl_2CuF_4N_2OP_2$	$C_{58}H_{55}BCuF_4N_3OP_2$	$C_{42.50}H_{42}BClCuF_4N_4O_{1.50}P_2$	$C_{36}H_{28}Cl_2NiOP_2$
fw	1021.37	982.11	1022.40	880.58	668.19
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.9326(3)	10.7133(2)	11.6779(2)	14.9521(3)	9.9627(2)
b, Å	14.3210(3)	14.7971(2)	14.0495(2)	16.9940(3)	11.2002(3)
c, Å	15.1443(4)	28.8529(5)	17.6505(3)	18.2098(4)	17.6107(4)
α, deg	105.8830(13)	90	77.3452(6)	69.2158(8)	79.8739(13)
β, deg	99.3086(13)	98.1590(7)	71.4646(7)	82.2185(8)	76.6783(13)
γ, deg	106.9454(12)	90	66.7766(6)	77.5514(16)	76.7340(9)
V, Å^3	2490.1(2)	4527.6(2)	2508.57(10)	4215.4(2)	1845.43(11)
Z	2	4	2	4	2
ρ_{calcd}, g/cm^{-3}	1.362	1.441	1.353	1.387	1.202
μ, mm^{-1}	0.561	0.727	0.555	0.712	0.782
$R\ (F_o)^a$	0.061	0.062	0.049	0.060	0.044
$R_w\ (F_o^2)^b$	0.154	0.161	0.125	0.145	0.122
GOF	1.030	1.050	1.037	1.048	0.930

$^a\ R = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $^b\ R_w = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$.

Anal. Calcd for $C_{50.5}H_{41}BClCuF_4N_2OP_2$ (i.e., **2**$\cdot 0.5CH_2Cl_2$): C, 64.32; H, 4.43. Found: C, 64.32; H, 4.42.

(iii) Synthesis of [Cu(dbp)(DPEphos)]BF$_4$ (3). 2,9-Di-*n*-butyl-1,10-phenanthroline (29 mg, 0.10 mmol). Yield: 70 mg (71%). Anal. Calcd for $C_{58}H_{55}BCuF_4N_3OP_2$ (i.e., **3**$\cdot CH_3CN$): C, 68.14; H, 5.42. Found: C, 68.36; H, 5.29.

(iv) Synthesis of [Cu(NCNMe$_2$)$_2$(DPEphos)]BF$_4$ (4). Dimethylcyanamide (0.5 mL). Yield: 37 mg (45%). Anal. Calcd for $C_{42.5}H_{42}BClCuF_4N_4O_{1.5}P_2$ (i.e., **4**$\cdot 0.5CH_2Cl_2\cdot 0.5H_2O$): C, 60.84; H, 4.86. Found: C, 60.23; H, 4.76.

C. Synthesis of NiCl$_2$(DPEphos) (5). A mixture of $NiCl_2\cdot 3H_2O$ (236 mg, 1.0 mmol) and DPEphos (540 mg, 1.0 mmol) in 50 mL of *n*-butanol was refluxed for 3 h to obtain a purple solid, that was filtered off and washed with ethanol (2 × 10 mL) and diethyl ether (2 × 10 mL). This product was recrystallized from CH_2Cl_2/Et_2O; yield, 580 mg (87%). Anal. Calcd for $C_{36}H_{28}Cl_2NiOP_2$: C, 64.71; H, 4.22. Found: C, 64.19; H, 4.43.

D. Synthesis of [Cu(dpp)$_2$]BF$_4$ (6). A solution of 2,9-diphenyl-1,10-phenanthroline monohydrate (33 mg, 0.10 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $[Cu(NCCH_3)_4]BF_4$ (15.5 mg, 0.05 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 30 min to produce a clear red solution that was filtered and the filtrate concentrated to about 5 mL. Vapor diffusion of diethyl ether into the resulting solution gave red crystals that were filtered off and washed with diethyl ether (2 × 5 mL); yield, 31 mg (76%). This complex was identified on the basis of its known spectroscopic properties.[30]

All attempts to prepare $[Cu(dpp)(DPEphos)]BF_4$, with the use of the procedure described in section B(i), afforded complex **6**.

E. X-ray Crystallography. Single crystals of complexes **1**−**4** were obtained by vapor diffusion of diethyl ether into solutions of the complexes in mixtures of dichloromethane and acetonitrile (ca. 1:1). Crystals of **5** were obtained through the slow evaporation of a solution of this complex in a 1:1 mixture of 1,2-dichloroethane and benzene that had been exposed to di-isopropyl ether vapor. Data collections were carried out at 150(±)K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. Lorentz and polarization corrections were applied to the data sets. The key crystallographic data are given in Table 1.

The structures **1**, **4**, and **5** were solved by direct methods using SIR97[31] while the structures of **2** and **3** were solved with the use of the structure solution program PATTY in DIRDIF 92.[32] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were placed in calculated positions according to idealized geometries with C−H = 0.95 Å and U(H) = $1.3U_{eq}$(C). They were included in the refinement but constrained to ride on the atom to which they are bonded. An empirical absorption correction using SCALEPACK[33] was applied. The final refinements were performed by the use of the program SHELXL-97.[34]

In all structures except that of **5**, the crystals were found to contain identifiable solvent molecules (see Table 1), the atoms of which refined satisfactorily with anisotropic thermal parameters with the exception of the diethyl ether molecules present in the crystal of **1**. In this case, only the O atom of a well behaved $(C_2H_5)_2O$ molecule was refined anisotropically, the C atoms isotropically; isotropic thermal parameters were used for the O and C atoms of a second (disordered) $(C_2H_5)_2O$ molecule that was located about a center of inversion. During the structure refinement of **5**, an unidentifiable and badly disordered solvent molecule (probably CH_2Cl_2) was removed with the squeeze option in PLATON.[35]

The largest peaks remaining in the final difference maps of **1**−**5** were 1.33, 0.73, 1.33, 1.10, and 0.68 e/Å^3, respectively.

F. Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 2000 FT-IR spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained with the use of a Varian INOVA 300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent. The $^{31}P\{^1H\}$ spectra were recorded at 121.6 MHz, with 85% H_3PO_4 as an external standard. Electrochemical measurements were carried out with use of a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. E_0 values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and were

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uncorrected for junction potentials. Under our experimental conditions, $E_0 = +0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple.

Electronic absorption spectra were obtained with use of a Varian Cary 100 Bio instrument, while the fluorometer was a SLM Aminco SPF 500C unit, and the cryostat was an Oxford Instruments DN 1704 with a ITC4 temperature controller. The pulsed laser used for the lifetime studies was a Laser Science VSL-337ND-S unit with a DLMS-220 pumped dye attachment. The digitizing oscilloscope was a Tektronix 520.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

G. Methods Used in Studies of the Electronic Absorption Spectra and Emission Properties of the Copper(I) Complexes. Absorbance versus concentration plots yielded estimated molar extinction coefficients for the copper complexes. For the luminescence studies, repeated freeze−pump−thaw cycles removed dissolved dioxygen from solution. A user-written program TAURES provided satisfactory fits of the emission decay on the assumption of a single-exponential process. A long-necked cell facilitated temperature-dependent, steady-state emission measurements in the cryostat. With $[\mathrm{Ru(bpy)_3}]^{2+}$ in water as the standard ($\Phi = 0.042$),[36] the method of Parker and Rees[37] yielded the emission quantum yields. The origin of the instrumental correction factors has been described.[12] For quenching studies with Lewis bases, Stern−Volmer analyses of emission intensities versus quencher concentration yielded quenching rate constants.[38] The fluorometer lamp was the source for the photostability measurements, and the actinometer was ferrioxalate.[39]

Results

(a) Synthesis and Structural Characterization of Copper(I) and Nickel(II) Complexes. The pale yellow, diamagnetic, mixed-ligand complexes of the type [Cu(NN)(DPEphos)]$\mathrm{BF_4}$, where DPEphos = bis[2-(diphenylphosphino)phenyl]ether and NN = 1,10-phenanthroline (phen) (**1**), 2,9-dimethyl-1,10-phenanthroline (dmp) (**2**), 2,9-di-*n*-butyl-1,10-phenanthroline (dbp) (**3**), or two dimethylcyanamides (**4**), were prepared by the reaction of $[\mathrm{Cu(NCCH_3)_4}]\mathrm{BF_4}$ with stoichiometric quantities of the ligands DPEphos and NN in dichloromethane at 25 °C. For the synthesis of paramagnetic $\mathrm{NiCl_2}$(DPEphos) (**5**), a mixture of $\mathrm{NiCl_2{\cdot}3H_2O}$ and DPEphos was refluxed in *n*-butanol. Yields of these products ranged from 45% to 87%. Attempts to prepare the complex [Cu(dpp)(DPEphos)]$\mathrm{BF_4}$, where dpp = 2,9-diphenyl-1,10-phenanthroline, gave only red crystalline $[\mathrm{Cu(dpp)_2}]\mathrm{BF_4}$.[30] In all instances, single-crystal X-ray structure determinations of **1**−**5** showed the presence of pseudotetrahedral metal-containing species in which the DPEphos ligand was bound only through its pair of P donor atoms.

The ORTEP[40] representations of these structures are shown in Figures 1−5 while important bond length and bond angles are given in Table 2. In addition to the data summarized in Table 2, we note that the dihedral angles between the NCuN and PCuP planes of complexes **1**−**4** are 91.6°, 97.7°, 101.2°, and 88.3°, respectively, while for nickel(II) complex **5** the dihedral angle between the ClNiCl and PNiP planes is 91.9°. As shown in Table 2, the ether O atom of DPEphos is at a nonbonding distance (>3.1 Å) to the metal center in all cases. The resulting eight-membered $\overline{\mathrm{C{-}C{-}P{-}M{-}P{-}C{-}C{-}O}}$ rings assume a tublike conformation in the solid state, with a dihedral angle between the phenyl rings of the $[\mathrm{C_6H_4{-}O{-}C_6H_4}]$ unit having values of 77.9°, 72.6°, 74.4°, 93.9°, and 89.3° for **1**−**5**, respectively. In the structure of **4**, the Cu−N bond lengths involving the $\mathrm{Me_2NC{\equiv}N}$ ligands (for molecule 1) are 1.999(4) and 2.023(4) Å, and the N≡C distances are 1.143(6) and 1.146(5) Å, while the Cu−N≡C angles are 151.1(4)° and 167.3(4)°. The Cu−N and N≡C distances for molecule 2 in the asymmetric unit are essentially the same as for molecule 1 (vide supra), but the Cu−N≡C angles again show a significant variation from one another (165.8(4)° and 173.8(4)°) and from those of

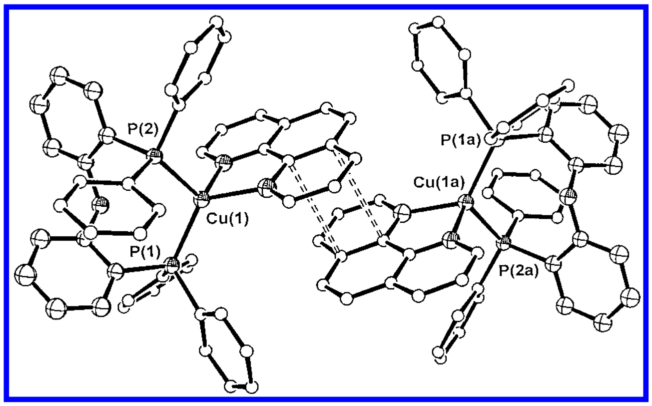

Figure 1. ORTEP[40] representation of the structure of the cation [Cu(phen)(DPEphos)]$^+$ present in **1** showing the pairwise stacking of phen ligands between neighboring cations. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the $\mathrm{Ph_2P}$ groups which are circles of arbitrary radius.

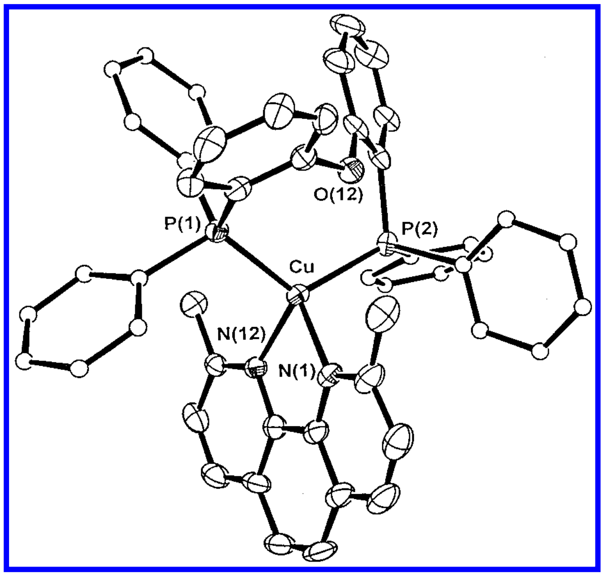

Figure 2. ORTEP[40] representation of the structure of the cation [Cu(dmp)(DPEphos)]$^+$ present in **2**. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the $\mathrm{Ph_2P}$ groups which are circles of arbitrary radius.

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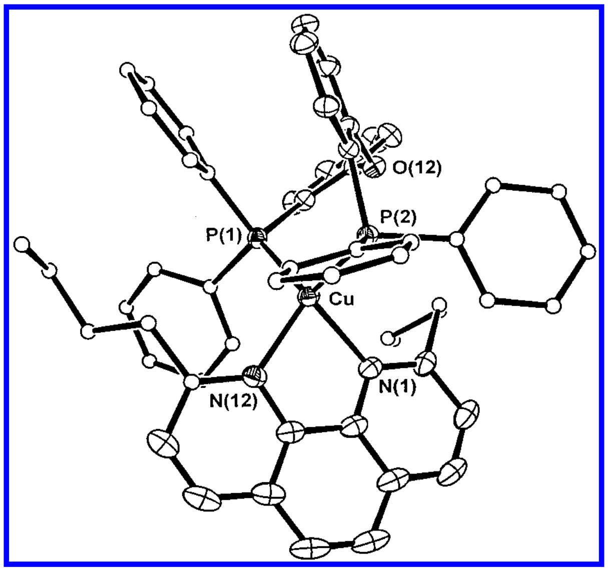

Figure 3. ORTEP[40] representation of the structure of the cation [Cu(dbp)(DPEphos)]$^+$ present in **3**. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the Ph_2P groups which are circles of arbitrary radius.

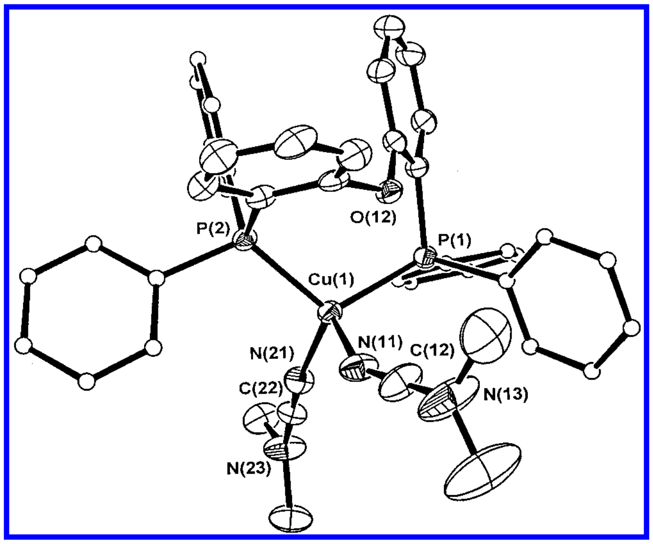

Figure 4. ORTEP[40] representation of the structure of the cation [Cu(NCNMe$_2$)$_2$(DPEphos)]$^+$ present in **4**. Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the Ph_2P groups which are circles of arbitrary radius.

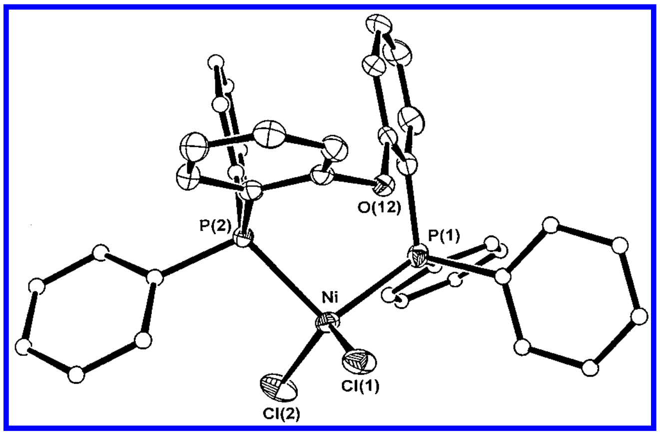

Figure 5. ORTEP[40] representation of the structure of the complex NiCl$_2$(DPEphos) (**5**). Thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms of the Ph_2P groups which are circles of arbitrary radius.

molecule 1. This large spread in the $Cu-N\equiv C$ angles (range 151.1(4)° to 173.8(4)°) presumably reflects a shallow energy minimum for the Cu−nitrile bond and the sensitivity of these angles to crystal packing forces. By way of comparison, the structure of the homoleptic nitrile complex $[Cu(NCCH_3)_4]BF_4$ has $Cu-N\equiv C$ angles that range from 169.9(5)° to 179.0(7)°.[41] The solution properties of **4** show the presence of a single copper(I) species. The only complex for which a significant intermolecular interaction was present in the solid state was compound **1**, wherein the phen ligands of the pairs of symmetry related cations partially overlay one another. The components of this pair are related to one another through a center of inversion that is located between the phen rings; the closest intermolecular C···C and C···N contacts are in the range 3.59−3.64 Å.

Pseudotetrahedral nickel(II) complex **5** is of a type encountered previously, of which NiCl$_2$(PP), where PP = 4,6-bis(diphenylphosphino)-2,8-dimethylphenoxathiine (which is a more rigid variant of DPEphos)[42] or bis(diphenylphosphinoethyl)ether,[43] are close structural analogues. The complex of $(Ph_2PCH_2CH_2)_2O$ has Cl−Ni−Cl and P−Ni−P angles of 127.1(2)° and 107.1(1)°, which are similar to the corresponding angles in **5** of 123.10(3)° and 101.22(2)°, respectively.

(b) Spectroscopic, Electrochemical, and Magnetic Properties of Copper(I) and Nickel(II) Complexes. Diamagnetic copper(I) complexes **1**−**4** display very similar spectroscopic and electrochemical properties in accord with their close structural similarity. ^1H NMR spectroscopy (in $CDCl_3$) confirmed the presence of lattice solvent molecules as established by X-ray crystallography. The aromatic DPEphos and phenanthroline ligand protons of **1**−**3** appear as complex sets of multiplets (some overlapping) in the region $\delta = +8.9$ to $+6.8$, with the 2,9 protons of the phen ligand of **1** assigned to a multiplet centered at $\delta = +8.90$. For complex **2**, the methyl resonances of the dmp ligand are at $\delta = +2.47$, while the *n*-butyl resonances of the dbp ligand in **3** consist of multiplets at $\delta = +2.86$, $+1.28$, $+0.78$, and $+0.65$. The ^1H NMR spectrum of **4** (in $CDCl_3$) shows resonances for the DPEphos ligand as overlapping multiplets at $\delta = \sim+7.4$, $\sim+7.0$, and $+6.78$, while the methyl groups of the Me$_2$NCN ligands are characterized by a singlet at $\delta = +2.72$. The $^{31}P\{^1H\}$ NMR spectra of solutions of **1**−**4** in $CDCl_3$ show singlets at $\delta = -9.3$, -11.9, -12.4, and -13.6, respectively, for the coordinated phosphine ligand DPEphos; for the free ligand, $\delta = -18.4$ in $CDCl_3$. The presence of the $[BF_4]^-$ anion was seen in the IR spectra of **1**−**4** (recorded as KBr pellets) with the $\nu(B-F)$ mode at 1058 (±5) (vs) cm^{-1}. In addition, the IR spectrum of **4** showed a split band at 2216(s) cm^{-1} assigned to $\nu(C\equiv N)$ of the Me$_2$NCN ligands.

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Table 2. Comparison of the Important Bond Lengths (Å) and Bond Angles (deg) for Complexes **1**−**5**[a]

1		**2**		**3**		**4**[b]		**5**	
Cu−N(1)	2.071(3)	Cu−N(1)	2.104(3)	Cu−N(1)	2.097(2)	Cu(1)−N(11)	2.023(4)	Ni−Cl(1)	2.2080(7)
Cu−N(10)	2.064(3)	Cu−N(12)	2.084(3)	Cu−N(12)	2.109(2)	Cu(1)−N(21)	1.999(4)	Ni−Cl(2)	2.2177(7)
Cu−P(1)	2.2314(8)	Cu−P(1)	2.2691(11)	Cu−P(1)	2.2712(7)	Cu(1)−P(1)	2.2767(13)	Ni−P(1)	2.3308(7)
Cu−P(2)	2.2614(9)	Cu−P(2)	2.2728(11)	Cu−P(2)	2.2793(6)	Cu(1)−P(2)	2.2718(13)	Ni−P(2)	2.3053(7)
Cu···O(12)	3.205	Cu···O(12)	3.151	Cu···O(12)	3.205	Cu(1)···O(12)	3.128	Ni···O(12)	3.206
N(1)−Cu−N(10)	80.83(11)	N(1)−Cu−N(12)	80.88(13)	N(1)−Cu−N(12)	80.51(8)	N(11)−Cu(1)−N(21)	105.79(15)	Cl(1)−Ni−Cl(2)	123.10(3)
P(1)−Cu−P(2)	110.81(3)	P(1)−Cu−P(2)	116.44(4)	P(1)−Cu−P(2)	112.91(2)	P(1)−Cu(1)−P(2)	111.51(5)	P(1)−Ni−P(2)	101.22(2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Data are given for one of the two molecules present in the asymmetric unit (molecule 1); both molecules are essentially identical.

Table 3. Physical Data for Solutions of Copper(I) Complexes in Dichloromethane at Room Temperature

		absorbance	corrected emission		
complex	E_0,[a] V vs Ag/AgCl	λ_{max},[b] nm	λ_{max}, nm	Φ[c]	τ,[d] μs
[Cu(phen)(DPEphos)]BF_4	+1.22 (90)	391 (3000)	700	0.0018	0.19
[Cu(dmp)(DPEphos)]BF_4	+1.35 (130)	383 (3100)	565	0.15	14.3
[Cu(dbp)(DPEphos)]BF_4	+1.40 (90)	378 (2900)	560	0.16	16.1
[Cu($NCNMe_2$)(DPEphos)]BF_4	+1.29 (120)	*e*	*e*	*e*	*e*
[Cu(phen)$(PPh_3)_2$]BF_4[f]	+1.34[g]	370 (3900)	680	0.0007	0.22
[Cu(dmp)$(PPh_3)_2$]BF_4[h]	*e*	365 (2500)	560	0.0014	0.33
[Cu(dmp)(dppe)]PF_6	+1.17 (80)	400 (3200)	630	0.010	1.33

[a] Anodic−cathodic peak separation (in mV) given in parentheses. [b] Molar absorptivity (M^{-1} cm^{-1}) given in parentheses. [c] Error ±10%. [d] Error ±5%. [e] Not recorded. [f] Spectroscopic data taken from ref 18. [g] Anodic maximum ($E_{p,a}$ value) corresponds to a multielectron process. [h] Spectroscopic data recorded in methanol and taken from ref 17.

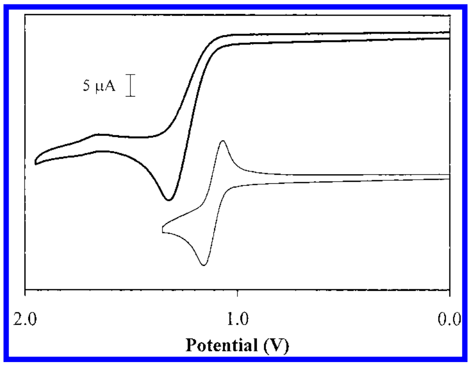

Figure 6. Single scan cyclic voltammograms of [Cu(phen)$(PPh_3)_2$]BF_4 (top) and [Cu(dmp)(dppe)]PF_6 (bottom) in dichloromethane at room temperature. Scan rate 50 mV s^{-1} in 0.1 M TBAH.

The cyclic voltammetric properties of solutions of **1**−**4** in 0.1 M TBAH−CH_2Cl_2 are similar, each showing a reversible process ($i_{p,a} = i_{p,c}$) that corresponds to a net one-electron oxidation of the bulk complex. These data are given in Table 3, along with related information for salts of the [Cu(phen)$(PPh_3)_2$]$^+$ and [Cu(dmp)(dppe)]$^+$ cations. The CV of [Cu(dmp)(dppe)]PF_6 resembles those of **1**−**4**; its E_o value is the most accessible of this group of five complexes. However, in the case of [Cu(phen)$(PPh_3)_2$]BF_4, the oxidation is irreversible and appears to be a multielectron process as a consequence of the rapid decomposition of the Cu(II) species. A comparison of the single scan CVs of [Cu(dmp)(dppe)]PF_6 and [Cu(phen)$(PPh_3)_2$]BF_4 is shown in Figure 6.

The electronic absorption spectral data for the copper(I) complexes **1**−**4** are presented in Table 3, and the spectral traces for solutions of compounds **1** and **2** in dichloromethane (DCM) are compared in Figure 7. By analogy with previous work,[17,44−46] the absorption band that occurs in the vicinity of 360 nm ($\epsilon = 3{-}4000$ M^{-1} cm^{-1}) corresponds to a metal-to-ligand charge-transfer transition. More intense intraligand transitions appear at shorter wavelengths. The MLCT absorption maxima occur at longer wavelengths for the [Cu(NN)(DPEphos)]$^+$ species as opposed to the analogous [Cu(NN)$(PPh_3)_2$]$^+$ series, and in each series, the phen complex exhibits the longest wavelength CT absorption. Within the series of DPEphos complexes, the absorption maximum shifts to longer wavelength as the average Cu−P bond distance decreases.

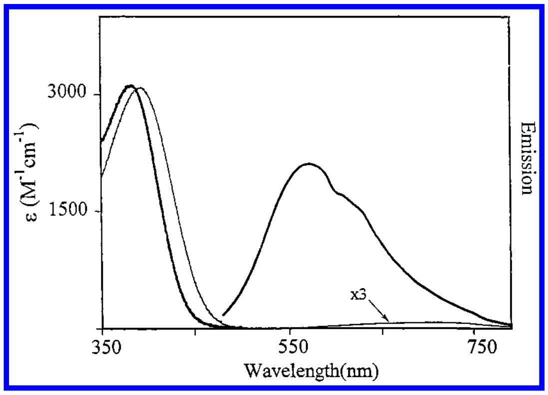

Figure 7. Absorption and emission spectra in dichloromethane at room temperature: absorbance of [Cu(dmp)(DPEphos)]$^+$ (thick) and [Cu(phen)(DPEphos)]$^+$ (thin) (left axis); corrected emission spectra with same conventions (right axis). Areas reflect the relative quantum yields.

At least two types of solvent effects are evident in the absorption data. First, studies of dmp-containing complex **2** reveal that the MLCT maximum shifts slightly toward shorter wavelengths in more polar solvents. More specifically, the maximum shifts from 383 nm in DCM to 377 nm in methanol and to 375 nm in acetone or acetonitrile. On simple polarity grounds, the observed negative solvatochromism implies that the complex has a smaller dipole moment in the excited state than the ground state. As previously observed for [Cu(dmp)$(PPh_3)_2$]$^+$,[45,47] the other effect is that [Cu(dmp)(DPEphos)]$^+$ undergoes solvent-dependent, ligand redistribution reactions. Figure 8 shows how addition of excess DPEphos alters the absorbance of **2** in acetonitrile. At a copper concentration of 0.1 mM, addition of 0.5−1.0

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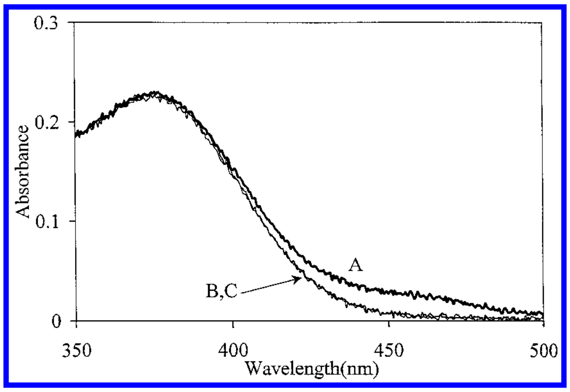

Figure 8. Absorbance of $[Cu(dmp)(DPEphos)]^+$ in acetonitrile: trace of a 0.1 mM solution (A); traces with 0.1 and 0.5 mole excess of DPEphos ligand added (B and C, respectively).

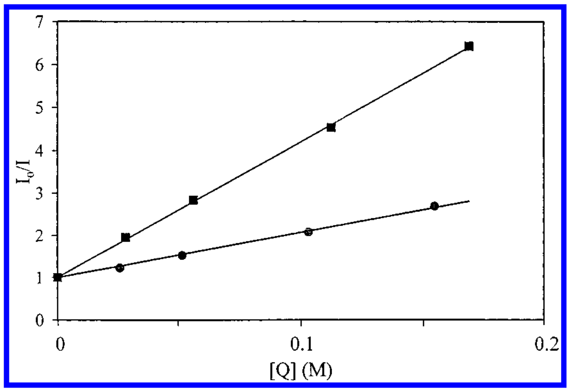

Figure 9. Stern−Volmer quenching of photoexcited $[Cu(dmp)(DPEphos)]^+$ in dichloromethane at room temperature; quenching by DMF (■) and DMSO (●).

mol DPEphos/mol Cu suppresses the growth of an absorption band at ca. 450 nm that arises from the formation of $[Cu(dmp)_2]^+$ in solution. Similar equilibria occur in DMF solution. The redistribution equilibrium in eq 1 could account for the influence that excess DPEphos has on the appearance of $[Cu(dmp)_2]^+$ in solution:

$$2[Cu(dmp)(DPEphos)]^+ = [Cu(dmp)_2]^+ + [Cu(DPEphos)]^+ + DPEphos \quad (1)$$

where $[Cu(DPEphos)]^+$ represents a copper(I) species understood to have solvent molecules completing its coordination sphere. A quantitative analysis would be very difficult because multiple species absorb in the vicinity of 375 nm, including $[Cu(dmp)]^+$ and $[Cu(dmp)_2]^+$.[48] Fortunately, DPEphos dissociation is not significant in DCM, and a small excess of the phosphine effectively suppresses formation of other dmp-containing complexes in alternative solvents.

Some of the most dramatic findings of this work are the exceptionally high emission yields the $[Cu(dmp)(DPEphos)]^+$ and $[Cu(dbp)(DPEphos)]^+$ systems exhibit in DCM solution compared to previously studied systems (Table 3). In addition, data in the same table reveal that the complexes also exhibit extremely long excited-state lifetimes. In contrast, the emission yield and the lifetime of photoexcited $[Cu(phen)(DPEphos)]^+$ are very similar to those of the $[Cu(phen)(PPh_3)_2]^+$ analogue. Both phen complexes are also alike in exhibiting a comparatively large shift between the absorption and emission maxima.

Solvent effects on the emission from $[Cu(dmp)(DPEphos)]^+$ vary. Because of the relatively small dipole moment of the excited state, the corrected emission maximum is relatively constant. Thus, in DCM, the emission maximizes at ca. 565 nm, whereas in three more basic solvents (acetone, MeCN, and MeOH) the emission maximum falls at ca. 560 nm. However, the excited-state lifetime is shorter in basic media, that is, 3.8 μs in acetone, 1.1 μs in MeCN, and 2.4 μs in MeOH. Quenching of the emission is complete in the more strongly donating solvents DMF and DMSO, almost certainly because of associative (exciplex) quenching, vide infra. Stern−Volmer studies, carried out in MeOH, reveal quenching rate constants of 4.5×10^6 M^{-1} s^{-1} for DMF and 1.4×10^7 M^{-1} s^{-1} for DMSO. The quenching data are presented in Figure 9.

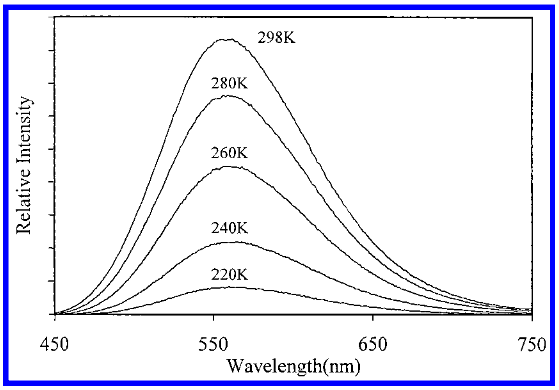

Figure 10. Increase in emission from $[Cu(dmp)(DPEphos)]^+$ in methanol with an increase in temperature.

In MeOH and DCM, the emission from $[Cu(dmp)(DPEphos)]^+$ shows the distinctive temperature dependence often found for copper(I) complexes containing phenanthroline ligands, at least in DCM solution.[18,49] In particular, Figure 10 shows that the emission intensity *increases* at higher temperatures in MeOH. At higher temperatures, the emission maximum also shifts to shorter wavelengths.

The complexes have good photostability in solution. Irradiation of deoxygenated solutions of $[Cu(dmp)(DPEphos)]BF_4$ at 380 nm (6.1×10^{14} photons/sec) in dichloromethane at room temperature produced a negligible absorbance change after 2 h. The estimated quantum yield for photoinduced decomposition is $\phi \lesssim 0.001$.

The spectroscopic and magnetic properties of nickel(II) complex **5** are in accord with its pseudotetrahedral structure as established by X-ray crystallography.[50,51] The magnetic moment of **5** is 3.22 μ_β at 300 K, similar to the value of 3.26 μ_β reported for $NiCl_2[(Ph_2PCH_2CH_2)_2O]$.[52] The electronic absorption spectrum of a solution in dichloromethane

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shows the characteristic $^3T_1(P) \leftarrow {}^3T_1$ transition (ν_3) at 18150 cm^{-1} ($\epsilon = 150$), with a weak broad shoulder at ~15600. A rising absorption at the limit of our measurements (~12000 cm^{-1}) signals the appearance of the expected $^3A_2 \leftarrow {}^3T_1$ transition (ν_2).[50] The corresponding spectrum of $NiCl_2[(Ph_2PCH_2CH_2)_2O]$ shows these transitions at 18700 and 11700 cm^{-1}, respectively.[52]

Discussion

The present study has provided copper(I) and nickel(II) complexes that establish the propensity of the DPEphos ligand to coordinate in a bidentate P,P fashion to afford mononuclear pseudotetrahedral structures. These compounds (**1**−**5**) provide a useful structural benchmark for the η^2-bonding mode of this ligand. This behavior contrasts with the η^3-P,O,P bonding mode encountered in the multiply bonded dirhenium species we isolated previously.[19] Of special significance are the unusually long-lived, high quantum yield emissions that several of the copper(I) complexes exhibit in fluid solution. This behavior was not observed in the case of dimethylcyanamide complex **4**. The following discussion relates to the unusual spectroscopic properties of compounds **1**−**3**.

One advantage of the DPEphos systems is that ligand redistribution equilibria pose few problems in the case of copper(I). For example, only a small excess of the chelating phosphine is necessary to ensure that the $[Cu(dmp)(DPEphos)]^+$ species is the predominant copper−dmp complex in solution. This is not the case with $[Cu(dmp)(PPh_3)_2]^+$ which is in equilibrium with a number of species in DCM and in MeCN.[17,45,47]

(a) Flexibility within $[Cu(NN)(DPEphos)]^+$ Systems. A variety of observations reveal that the mixed-ligand framework is much more flexible when 1,10-phenanthroline is the coligand with DPEphos. Even solid state measurements reveal the flexibility of the phen derivative because only in the $[Cu(phen)(DPEphos)]^+$ structure does one observe a canting of the DPEphos ligand toward the NN ligand. As a result of the displacement within the P−Cu−P plane, the coordination environment about copper approaches trigonal pyramidal with P(2) apical and P(1) equatorial. This so-called rocking distortion, which has precedent in structures of various $[Cu(NN)_2]^+$ systems,[53−56] results in elongation of the Cu−P(2) bond relative to Cu−P(1). As with other copper(I) systems, the driving force for the distortion probably derives from the fact that exposing a face of the phenanthroline ligand opens the way for intermolecular stacking interactions to occur in the lattice.[53,54] In the structures of $[Cu(dmp)(DPEphos)]^+$ and $[Cu(dbp)(DPEphos)]^+$ (Figures 2 and 3), where there is no sign of intermolecular stacking, the most prominent distortion is a tetragonal flattening about copper, as indicated by the nonorthogonality of the CuNN and CuPP planes. Although the $[Cu(phen)(DPEphos)]^+$ species shows minimal flattening in the solid state, the distortion is undoubtedly possible in solution because the phen ligand has no substituents in the 2,9 positions. That would explain the relative ease of oxidation of $[Cu(phen)(DPEphos)]^+$, ca. 0.15 V less positive than either the dmp or dbp analogue (Table 3), even though the presence of electron-donating alkyl substituents might be expected to stabilize the copper(II) form of the couple. Actually, extensive studies of Cu(II)/Cu(I) couples in related complexes have shown that sterically active alkyl groups raise the potential when they inhibit flattening motions that stabilize the copper(II) oxidation state.[12,57,58] Thus, phen complex **1** is likely to adopt the most flattened structure upon oxidation. Still another indication of the flexibility of the $[Cu(phen)(DPEphos)]^+$ species comes from spectral data. Data in Table 3 reveal that $[Cu(phen)(DPEphos)]^+$ shows by far the largest shift between the emission and the CT absorption maximum in the series. As Riesgo et al.[59] have emphasized, a large Stokes-like shift occurs when the copper system undergoes a substantial structural relaxation in the excited state. In accordance with the electrochemical results, photoexcited phen complex **1** is likely to undergo a flattening distortion because CT excitation entails formal oxidation of the copper center.

(b) Excited-State Energetics. The $[Cu(NN)(DPEphos)]^+$ systems exhibit higher energy CT states and more positive Cu(II)/Cu(I) potentials than the $[Cu(NN)_2]^+$ analogues. In the latter complexes, narrow, ca. 82°, N−Cu−N bite angles help drive down the energy of CT excitation because the highest filled d_{xz} and d_{yz} orbitals of the metal have $d\sigma^*$ character with respect to the phenanthroline lone pairs.[60] Wider P−Cu−P bite angles may ease $d\sigma^*$ interactions in $[Cu(NN)(DPEphos)]^+$ and related systems and in so doing enhance the energy required for CT excitation. At the same time, the larger, more diffuse donor orbitals of phosphine ligands probably stabilize copper(I) versus copper(II) forms. Substituent effects vary. In the case of $[Cu(phen)_2]^+$, introduction of 2,9 methyl substituents induces a shift of the CT absorption to longer wavelength,[61] but $[Cu(phen)(DPEphos)]^+$ has the longest wavelength CT absorption maximum within the DPEphos series. Here, the interligand steric repulsions that are responsible for elongation of the Cu−P bonds in $[Cu(dmp)(DPEphos)]^+$ and $[Cu(dbp)(DPEphos)]^+$ probably also account for destabilization of the CT excited state.

As is the norm for $[Cu(NN)_2]^+$ and related mixed-ligand systems,[49] the temperature dependence of the emission from $[Cu(dmp)(DPEphos)]^+$ as depicted in Figure 10 indicates that there are at least two emitting states, the higher energy of

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which exhibits a distinctly greater emission yield. The effect arises because the energy gap between the singlet (^{1}CT) and triplet (^{3}CT) excited states is small and because the radiative rate constant of a ^{3}CT state is not very favorable for a first-row transition metal ion. At higher temperatures, increased participation of the ^{1}CT excited state also causes the emission to shift to shorter wavelength. However, the overall shift in Figure 10 is small, a possible indication that other excited states also participate.[62]

(c) Photophysics. One of the important factors influencing excited-state dynamics is the energy of the excited state; indeed, the often-invoked energy gap law predicts that the lifetime increases roughly as an exponential function of the energy.[63−65] However, [Cu(phen)(DPEphos)]$^+$ has a high-energy CT absorption but a relatively low energy emission maximum. The reason for this is the geometric relaxation that occurs in the excited state because of a d-orbital vacancy that promotes a tetragonal flattening. In effect, the distortion narrows the gap between the ground and excited states, enhances the coupling between the two states, and shortens the excited-state lifetime. As in [Cu(NN)$_2$]$^+$ systems with relatively bulky ligands,[12,58] the excited states of [Cu(dmp)(DPEphos)]$^+$ and [Cu(dbp)(DPEphos)]$^+$ experience less flattening because of the steric requirements of the dmp and dbp ligands. The upshot is that these systems have relatively small shifts between the absorption and emission maxima and much longer excited-state lifetimes.

As implied by Riesgo et al.,[59] it is also possible to foster nested energy surfaces by building interligand strain into the ground state so as to bias the structure in favor of the excited state. It is interesting that X-ray structural data indicate that both [Cu(dmp)(DPEphos)]$^+$ and [Cu(dbp)(DPEphos)]$^+$ exhibit somewhat flattened structures. The distortion, which is larger in the dbp complex, may well reflect a steric interaction involving the ether linkage of DPEphos and one of the alkyl substituents of the phenanthroline ligand. If so, the flattening distortion is intrinsic and will moderate the structural reorganization that attends formation of the CT excited state in solution. A related effect occurs in some [Cu(NN)$_2$]$^+$ systems containing 2,9 aryl substituents. Like most bis-phenanthroline complexes of copper(I), photoexcited [Cu(dpp)$_2$]$^+$ has a flattened geometry, whereas cooperative intraligand substituent effects enforce a pseudotetrahedral coordination geometry on the dptmp analogue (dptmp = 2,9-diphenyl-3,4,7,8-tetramethyl-1,10-phenanthroline).[56] Nevertheless, the emission energies of the two complexes are surprisingly similar. The explanation is that limited structural relaxation occurs with excitation of the [Cu(dpp)$_2$]$^+$ species because intra- and/or interligand interactions also impose a flattened geometry on the ground state.[56]

(d) Exciplex Quenching. In copper complexes with low-lying MLCT states, the formal increase in oxidation state of the metal center that occurs in the excited state paves the way to exciplex quenching via attack by Lewis bases.[12,14,15,58,66] Curves A and B in Figure 11 show schematically how formation of a new metal−ligand bond in the excited state can compress the energy separation between the ground and excited states and thereby promote relaxation. In the case of [Cu(dmp)$_2$]$^+$, quenching is very efficient even in weakly donating solvents such as acetonitrile and methanol. For example, at room-temperature, photoexcited [Cu(dmp)$_2$]$^+$ has a lifetime of 95 ns in deoxygenated DCM as compared with only 2 ns in acetonitrile.[67] For better donors such as DMF and DMSO, the rate constants for quenching the excited state are of the order of 10^8 M^{-1} s^{-1} according to Stern−Volmer quenching studies carried out in DCM.[66] In contrast, quenching of the CT excited state of [Cu(dmp)(DPEphos)]$^+$ occurs with a rate constant approximately 2 orders of magnitude smaller, such that the excited state retains a microsecond lifetime in weakly donating solvents such as acetone and methanol. As with other systems involving bulky ligands,[12,53] steric crowding undoubtedly inhibits an increase in the coordination number of the metal center of the [Cu(dmp)(DPEphos)]$^+$ system.

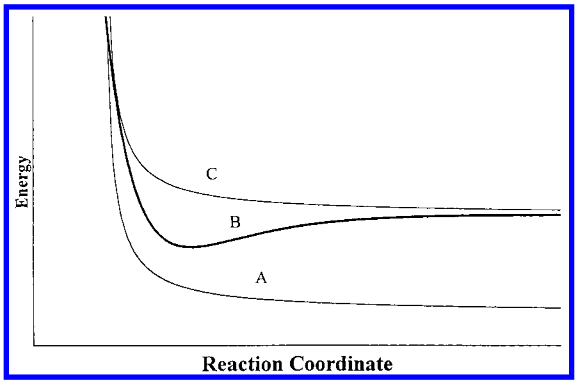

Figure 11. Schematic potential energy surfaces for ligand addition to a copper complex. The copper−ligand distance decreases from right to left: repulsive interaction for the pseudotetrahedral d^{10} ground state (A); exciplex formation with a CT excited state (B); same excited state as in B but with a severely crowded coordination sphere (C).

According to lifetime data with methanol as the solvent, exciplex quenching is also about an order of magnitude slower for [Cu(dmp)(DPEphos)]$^+$ than [Cu(dmp)(PPh$_3$)$_2$]$^+$. This result is surprising because one would expect two PPh$_3$ groups to occupy a larger volume than DPEphos because of interligand repulsions and the absence of the ether linkage. Consistent with this expectation, the Cu−N and Cu−P distances are, in fact, about 0.02 Å shorter in the mixed-ligand DPEphos complex as compared with [Cu(dmp)(PPh$_3$)$_2$]$^+$.[45] The quenching results suggest that, aside from introducing steric bulk, ligands can impose conformational restrictions that hamper expansion of the coordination number. The fact that exciplex quenching is not important for [Cu(dmp)(DPEphos)]$^+$ in methanol also accounts for another important contrast with the [Cu(dmp)(PPh$_3$)$_2$]$^+$ species. Thus, Palmer and McMillin[18] showed that the [Cu(dmp)(PPh$_3$)$_2$]$^+$ species is unusual in that the emission

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intensity increases at lower temperatures in methanol. They concluded that in this case the temperature dependence of solvent-induced exciplex quenching outweighs the effect of thermal equilibration between the emitting ^{1}CT and ^{3}CT excited states, vide supra.

In addition to constraining the ligand arrangement within the coordination sphere of copper, the ether oxygen of DPEphos can influence exciplex quenching in other ways as well. One possibility is via intramolecular exciplex quenching. In principle, nucleophilic attack by oxygen at the copper center is feasible because DPEphos is capable of functioning as a tridentate ligand.[19] There is precedent for intramolecular exciplex quenching in a $[Cu(NN)_2]^+$ system with *N*-(*p*-toluidino)methyl substituents in the 2,9 positions of the phenanthroline ligand.[68] However, formation of η^3-DPEphos is at best a slow process in $[Cu(dmp)(DPEphos)]^+$ and $[Cu(dbp)(DPEphos)]^+$ in view of the lifetimes. Finally, the ether group can influence exciplex quenching by virtue of being a π-donating substituent. Sakaki et al.[69] have argued that electron-rich phosphines suppress exciplex quenching by reducing the effective charge on the metal center. A single substituent would probably not have much impact, but Sakaki et al.[69] find adding *p*-methoxy substituents to the phenyl groups significantly enhances the excited-state lifetime in a series of complexes related to $[Cu(dmp)(PPh_3)_2]^+$. In particular, the lifetime increases from 0.7 μs for the PPh_3 complex to 5.5 μs for the $P(C_6H_4OMe\text{-}p)_3$ derivative in EtOH−water (60:40). A similar effect occurs in substituted terpyridine complexes of platinum(II) where delocalization of the “hole” onto the substituent diminishes platinum(III) character and suppresses exciplex quenching of the CT excited state.[70,71]

Concluding Remarks. Crystallographic analyses of three structures of the type $[Cu(NN)(DPEphos)]BF_4$, where NN denotes a 1,10-phenanthroline ligand, as well as the structures of $[Cu(NCNMe_2)(DPEphos)]BF_4$ and $NiCl_2(DPEphos)$, each reveal a metal complex with a pseudotetrahedral coordination geometry. The copper−phenanthroline complexes exhibit particularly well-behaved properties in solution. For example, by comparison with the $[Cu(dmp)(PPh_3)_2]BF_4$ system, speciation of the DPEphos analogue is easy to control because the addition of a slight excess of phosphine ensures that $[Cu(dmp)(DPEphos)]^+$ is the dominant copper-containing complex in solution. In addition, the Cu(II)/Cu(I) couples of the $[Cu(NN)(DPEphos)]^+$ species are chemically reversible on the cyclic voltammetry time scale. Although photoexcited $[Cu(phen)(DPEphos)]^+$ is comparatively short-lived, the $[Cu(dmp)(DPEphos)]^+$ system exhibits an extremely long lifetime of 14.3 μs in dichloromethane solution and an impressive quantum efficiency of 15%. Donor solvents usually quench charge-transfer emission from copper(I) systems, but $[Cu(dmp)(DPEphos)]^+$ exhibits an excited-state lifetime of 3.8 μs in acetone and 2.4 μs in methanol. However, DMF and DMSO are very effective quenchers. The emission from $[Cu(dmp)(DPEphos)]^+$ occurs at a significantly higher energy than that of $[Cu(phen)(DPEphos)]^+$ in dichloromethane solution because of interligand steric interactions that inhibit an excited-state flattening distortion. Although DPEphos is a flexible ligand capable of chelating to a metal with a P−M−P angle that can range from 101° (this work) to as much as 150° in the η^3-bound form,[19] all evidence suggests that a four-coordinate pseudotetrahedral geometry is remarkably stable for systems such as $[Cu(dmp)(DPEphos)]^+$. The fact that expansion of the coordination number also tends to be slow in the excited state enhances the potential the mixed-ligand DPEphos complexes have for practical, luminescence-based applications because (Lewis) base-induced quenching is usually a severe limitation with copper systems.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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