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Synthesis and Characterization of a Monocyanide-Bridged Bimetallic Iron(II) and Copper(I) Complex

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Introduction

The protonation, alkylation, and silylation of cyano metal complexes have been studied for many years.[1] A variety of [M]-CNH species have been seen, ranging from gas-phase studies[2] to deposition on metal surface.[3] In addition, numerous cyanide-bridged complexes have been reported.[4−18] All of these studies illustrate that the cyanide ligands of cyano metal complexes, in particular, those in anionic metal derivatives, are nucleophiles. We have previously shown that novel cyanide-bridged metal derivatives containing the diamond-shaped heterometallic motif of iron(II) and copper(I) can be isolated from the reaction of $CpFe(CO)(CN)_2^-$ and $Cu(CH_3CN)_4^+$ in the presence of phosphine ligands.[19,20] Namely, $[\eta^5\text{-}C_5H_5Fe(CO)(\mu\text{-}CN)_2Cu(PR_3)_n]_2$ derivatives, where $n = 1$ or 2 and the coordination geometry about the copper(I) centers can be altered between trigonal ($n = 1$) and tetrahedral ($n = 2$), have been characterized via X-ray crystallography. Herein, we extend our investigations of cyanide-bridged heterometallic derivatives of iron(II) and copper(I) utilizing the neutral $CpFe(CO)_2CN$ complex as a source of cyanide ligand. As anticipated, we observe the cyanide ligand in $CpFe(CO)_2(CN)$ to be a weaker nucleophile than those of $[K][CpFe(CO)(CN)_2]$. For example, an equilibrium was observed in the reaction of $CpFe(CO)_2(CN)$ and $[Cu(CH_3CN)_4][BF_4]$ in acetonitrile (Scheme 1), as compared with the aforementioned stable heterometallic complexes afforded from $[K][CpFe(CO)(CN)_2]$. At this time, we report the X-ray structures of $CpFe(CO)_2CN$ (**1**), $Cp^*Fe(CO)_2CN$ (**2**), and $[CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2][BF_4]$ (**4**), along with solution studies of **4** in acetonitrile.

Experimental Section

Methods and Materials. All manipulations were performed under argon using standard Schlenk and glovebox techniques. Dichloromethane was dried and distilled over P_2O_5. Acetonitrile was distilled once from CaH_2 and from P_2O_5, and freshly distilled before use from CaH_2. Diethyl ether was dried in sodium benzophenone stills prior to use. Tricyclohexylphosphine purchased from Strem was used without further purification. $[Cu(CH_3CN)_4][BF_4]$ was prepared according to the published literature procedure.[21] Infrared spectra were measured on a Mattson Galaxy 6021 instrument using a 0.1 mm CaF_2 sealed cell for organic solutions. Elemental analyses were carried out by Canadian Microanalytical Service, Ltd., Canada.

Synthesis of $CpFe(CO)_2(CN)$, 1. The $CpFe(CO)_2(CN)$ compound was synthesized and isolated typically on a 0.1 scale following the published procedure.[22] Bromine was employed for the oxidative cleavage of $[CpFe(CO)_2]_2$ in methanol; 4 equiv of KCN were added in the same flask, and the mixture solution was refluxed for 24 h. The pure product of $CpFe(CO)_2(CN)$ was isolated by acetonitrile extraction. Orange−brown crystals were obtain upon slow diffusion of hexane into a THF solution of $CpFe(CO)_2(CN)$. Anal. Calcd for $C_8H_5O_2NFe$: C, 47.3; H, 2.5; N, 6.9. Found: C, 46.9; H, 2.8; N, 6.5.

Synthesis of $Cp^*Fe(CO)_2(CN)$, 2. According to the published procedure for the isolation of $CpFe(CO)_2(CN)$,[22] addition of Br_2 to $[Cp^*Fe(CO)_2]_2$ in methanol was followed by stirring for 2 h at ambient temperature to produce $Cp^*Fe(CO)_2Br$. In the same flask, 4 equiv of KCN was added followed by heating at 50 °C for 2 h. The resulting solution was evaporated to yield an orange powder in 43% yield. Anal. Calcd for $C_{13}H_{15}O_2NFe$: C, 57.2; H, 5.5; N, 5.1. Found: C, 57.0; H, 5.5; N, 5.0.

Synthesis of $[CpFe(CO)_2(\mu\text{-}CN)Cu\cdots(CH_2Cl_2)_3][BF_4]$, 3. 10 mL of dichloromethane was added to the mixture of $CpFe(CO)_2(CN)$ (0.2 mmol, 0.041 g) and $[Cu(CH_3CN)_4][BF_4]$ (0.2 mmol, 0.063 g) in a 50 mL Schlenk flask. After 20 min of stirring at ambient temperature, a yellow−orange reaction solution was formed. The dichloromethane solution of **3** was used immediately in the following synthesis of **4**.

Synthesis of $[CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2][BF_4]$, 4. A 10 mL dichloromethane solution of PCy_3 (0.40 mmol, 0.112 g) was added to a solution of **3** prepared as described above. The reaction solution was stirred for 30 min at ambient temperature, this was followed by removal of the dichloromethane solvent under vacuum to afford an orange residue which was washed by diethyl ether. Yellow−orange crystals of **4** were obtained by slow diffusion of diethyl ether into a dichloromethane solution of **4** maintained at 10 °C for several days. Anal. Calcd for $C_{44}H_{71}FeCuNO_2P_2BF_4$: C, 57.81; H, 7.83. Found: C, 57.2; H, 7.46.

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(1) Fehlhammer, W. P.; Fritz, M. *Chem. Rev.* **1993**, *93*, 1243, and references therein.

(2) (a) Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201. (b) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121. (c) Müller, J.; Herberhold, M. *J. Organomet. Chem.* **1968**, *13*, 399. (d)Pignataro, S.; Foffani, A.; Innorta, G.; Distefano, G. *Advances in Mass Spectrometry*; Kendrick, E., Ed.; Elsevier: Amsterdam, 1968; Vol. 4, p 323. (e) Eller, K.; Sülzle, D.; Schwarz, H. *Chem. Phys. Lett.* **1989**, *154*, 443.

(3) Schardt, B. C.; Stickney, J. L.; Stern, D. A.; Frank, D. G.; Katekaru, J. Y.; Rosasco, S. D.; Salaita, G. N.; Soriaga, M. P.; Hubbard, A. T. *Inorg. Chem.* **1985**, *24*, 1419.

(4) Lim, B. S.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 4898, and references therein.

(5) Corsi, D. M.; Murthy, N. N.; Young, V. G. Jr.; Karlin, K. D. *Inorg. Chem.* **1999**, *38*, 848.

(6) Darensbourg, D. J.; Yoder, J. C.; Holtcamp, M. W.; Klausmeyer, K. K.; Reibenspies, J. H. *Inorg. Chem.* **1996**, *35*, 4764.

(7) (a) Richardson, G. N.; Vahrenkamp, H. *J. Organomet. Chem.* **2000**, *593−594*, 44. (b) Vahrenkamp, H.; Geiss, A.; Richardson, G. N. *J. Chem. Soc., Dalton Trans.* **1997**, 3643.

(8) Contakes, S. M.; Klausmeyer, K. K.; Rauchfuss, T. B. *Inorg. Chem.* **2000**, *39*, 2069.

(9) Dunbar, K. R.; Heitz, R. *Prog. Inorg. Chem.* **1997**, *93*, 1243.

(10) Trylus, K.-H.; Kernbach, U.; Brüdgam, I.; Fehlhammer, W. P. *Inorg. Chim. Acta* **1999**, *291*, 266.

(11) (a) Kristoff, J. S.; Shriver, D. F. **1973**, *12*, 1788. (b) Rupp, J. J.; Shriver, D. F. *Inorg. Chem.* **1967**, *6*, 755.

(12) Fu, D. G.; Chen, J.; Tan, X. S.; Jiang, L. J.; Zhang, S. W.; Zheng, P. J.; Tang, W. X. *Inorg. Chem.* **1997**, *36*, 220.

(13) Braunstein, P.; Herberich, G. E.; Neuschütz, M.; Schmidt, M. U. *J. Organomet. Chem.* **1999**, *580*, 66.

(14) Matsumoto, N.; Sunatsuki, Y.; Miyasaka, H.; Hashimoto, Y.; Luneau, D.; Tuchagues, J.-P. *Angew. Chem., Int. Ed.* **1999**, *38*, 171.

(15) Bowmaker, G. A.; Hartl, H.; Urban, V. *Inorg. Chem.* **2000**, *39*, 4548.

(16) Falvello, L. R,; Tomás, M. *Chem. Commun.* **1999**, 273.

(17) Connelly, N. G.; Hicks, O. M.; Lewis, G. R.; Orpen, A. G.; Wood, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3643.

(18) Christofide, A.; Connelly, N. G.; Lawson, H. J.; Loyns, A. C.; Orpen, A. G.; Simmonds, M. O.; Worth, G. H. *J. Chem. Soc., Dalton Trans.* **1991**, 1595.

(19) Darensbourg, D. J.; Lee, W.-Z.; Adams, M. J.; Larkins, D. L.; Reibenspies, J. H. *Inorg. Chem.* **1999**, *38*, 1378.

(20) Darensbourg, D. J.; Lee, W.-Z.; Adams, M. J.; Yarbrough. J. C. *Eur. J. Inorg. Chem.* **2001**, 2811.

(21) Kubas, G. J. *Inorg. Synth.*; Shriver, D. F., Ed.; John Wiley and Sons: New York, 1979; Vol. 19, p 90.

(22) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165.

10.1021/ic010683z CCC: $20.00

Scheme 1

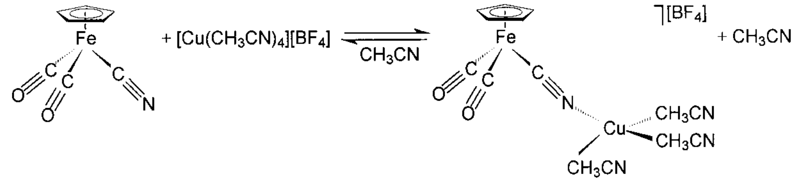

Table 1. X-ray Crystallographic Data for Complexes **1**, **2**, and **4**

	1	**2**	**4**
formula	$C_8H_5FeNO_2$	$C_{13}H_{15}FeNO_2$	$C_{44}H_{71}FeCuN-O_2P_2BF_4$
formula wt	202.98	273.11	914.16
space group	$P2_12_12_1$	$P2_1/n$	P-1
Z	4	4	2
volume, Å^3	792.7(3)	1260.56(17)	2297.3(6)
cryst syst	orthorhombic	monoclinic	triclinic
a, Å	5.8658(11)	11.8561(9)	10.0793(16)
b, Å	10.519(2)	7.8275(6)	12.0241(18)
c, Å	12.847(2)	14.1601(11)	19.503(3)
α, deg	90	90	93.483(5)
β, deg	90	106.4120(10)	93.217(2)
γ, deg	90	90	102.516(3)
$d_{calcd.}$, g/cm^3	1.701	1.439	1.322
temp, K	110(2)	110(2)	110(2)
wavelength, Å	0.71073	0.71073	0.71073
abs coeff, mm^{-1}	1.852	1.185	0.900
GOF on F^2	1.051	1.010	0.741
R,[a] %	4.31	5.74	7.58
R_w,[b] %	10.86	13.67	19.46

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

X-ray Crystallography. Yellow−orange crystals of **1**, **2**, or **4** were coated with mineral oil and mounted on a glass fiber with apezeon grease at room temperature. The mounted crystal was then placed in a cold nitrogen stream (Oxford) maintained at 110 K on a Bruker SMART 1000 three-circle goniometer. X-ray data of **1**, **2**, and **4** was obtained on a Bruker CCD diffractometer and covered more than a hemisphere of reciprocal space by a combination of three sets of exposures.

Crystal data and details of data collection for complexes **1**, **2**, and **4** are provided in Table 1. The structures were solved by direct methods. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded R(F) and wR(F^2) values, as indicated in Table 1, at convergence. Hydrogen atoms were place in idealized positions, with isotropic thermal parameters fixed at 1.2 or 1.5 times the value of the attached atom. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-ray Crystallography, Volume C.

For complexes **1**, **2**, and **4**, the following program(s) were used to solve the structures: SHELXS-86 (Sheldrick);[23] program(s) used to refine the structure, SHELXL-97 (Sheldrick);[24] program(s) used for molecular graphics, SHELXTL Version 5.0 (Bruker);[25] and software used to prepare material for publication, SHELXTL Version 5.0 (Bruker).[25]

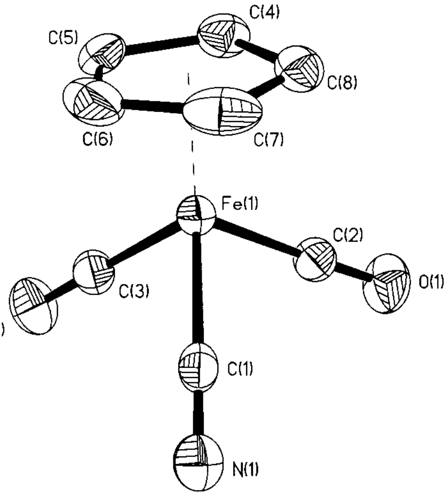

Figure 1. Thermal ellipsoid drawing of complex **1**, $CpFe(CO)_2CN$.

Table 2. Infrared Spectroscopic Data in the ν_{CO} and ν_{CN} Regions

compound	solvent	ν_{CN} (cm^{-1})	ν_{CO} (cm^{-1})
$CpFe(CO)_2(CN)$ **1**	CH_3CN	2121	2056, 2009
	CH_2Cl_2	2121	2059, 2014
$Cp^*Fe(CO)_2(CN)$ **2**	CH_3CN	2112	2032, 1983
$[CpFe(CO)_2(\mu\text{-}CN)Cu(CH_3CN)_3][BF_4]$	CH_3CN	2143	2062, 2016
$[CpFe(CO)_2(\mu\text{-}CN)Cu(CH_2Cl_2)_3][BF_4]$ **3**	CH_2Cl_2	2160	2070, 2029
$[CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2][BF_4]$ **4**	CH_2Cl_2	2137	2065, 2022

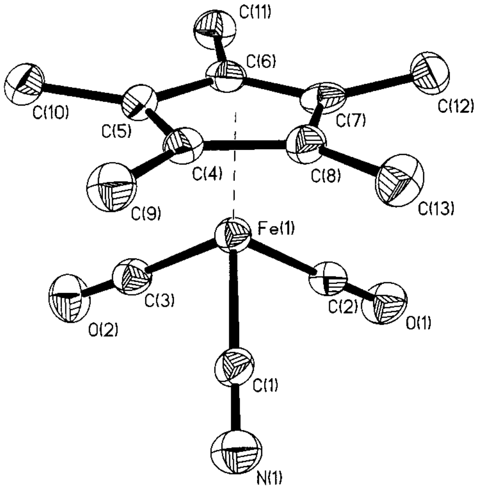

Figure 2. Thermal ellipsoid drawing of complex **2**, $^*CpFe(CO)_2CN$.

Results and Discussion

$CpFe(CO)_2(CN)$ (**1**) was synthesized following the published procedure, and the $^*CpFe(CO)_2(CN)$ (**2**) analogue was prepared originally herein in a similar manner.[22] The enhanced π-electron density donated to the iron(II) center by the *Cp ligand is seen in the lower ν_{CN} and ν_{CO} values in complex **2**. The ν_{CO} vibrations are shifted to lower frequency by 25 cm^{-1}, whereas the ν_{CN} vibration decreases by 9 cm^{-1} (see Table 2). These observations reflect the fact that CO is a better π-acceptor than CN^-, and concomitantly, is more sensitive to electronic

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(23) Sheldrick, G. *SHELXS-86 Program for Crystal Structure Solution*, 1986, Institüt für Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Gottingen, Germany.

(24) Sheldrick, G. *SHELXL-97 Program for Crystal Structure Refinement*, 1997, Institüt für Anorganische Chemie der Universitat, Tammanstrasse 4, D-3400 Gottingen, Germany.

(25) *SHELXTL Version 5.0*, Bruker Analytical X-ray Systems: Madison, WI, 1999.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $CpFe(CO)_2(CN)$ (**1**) and $*CpFe(CO)_2(CN)$ (**2**)

interatomic parameter	complex **1**	complex **2**
Fe−C(1)	1.933(4)	1.909(3)
Fe−C(2)	1.779(4)	1.769(3)
Fe−C(3)	1.779(3)	1.779(3)
Fe−C_p(ave)	2.089[4]	2.105[3]
Fe−C(2)−O(1)	177.9(3)	179.0(3)
Fe−C(3)−O(2)	179.5(4)	177.2(3)
Fe−C(1)−N(1)	179.4(3)	178.1(3)
C(3)−Fe-C(2)	94.59(16)	94.56(14)
C(3)−Fe-C(1)	91.50(15)	92.49(14)
C(2)−Fe-C(1)	92.06(15)	92.23(13)

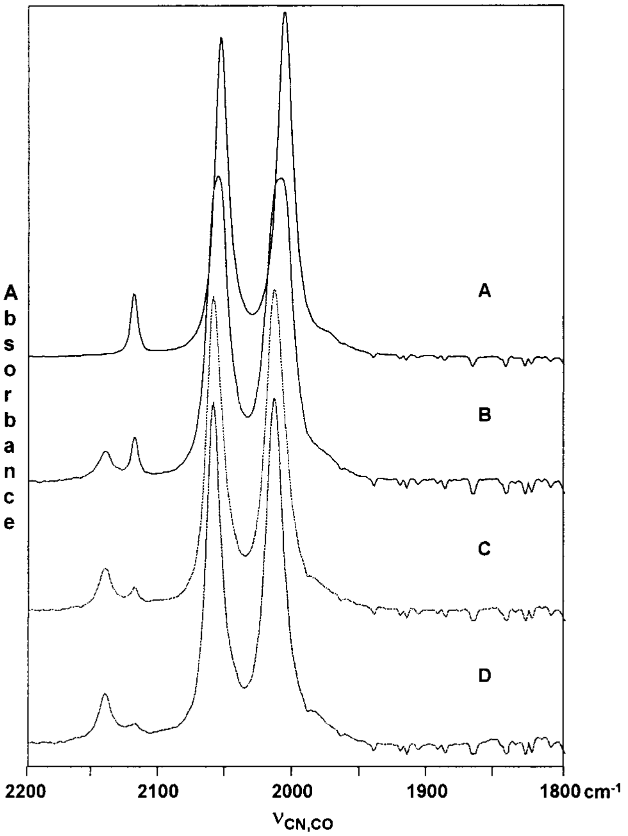

Figure 3. Infrared spectra of the equilibrium reaction of $CpFe(CO)_2CN$ with $[Cu(CH_3CN)_4][BF_4]$ in acetonitrile. Ratio of $CpFe(CO)_2CN$ to $[Cu(CH_3CN)_4][BF_4]$: **A**. 1:0; **B**. 1:1; **C**. 1:4; and **D**. 1:8.

environment changes occurring at the metal center. The X-ray structures of these two closely related derivatives were determined, and their thermal ellipsoid representations are provided in Figures 1 and 2. Selected bond distances and angles are tabulated in Table 3. In both instances the average Fe−CO bond distance in **1** and **2** is shorter than the Fe−CN bond distance by 0.158 and 0.135 Å, respectively. Upon addition of $CpFe(CO)_2CN$ to 1 equiv of $[Cu(CH_3CN)_4][BF_4]$ in acetonitrile at ambient temperature, infrared spectroscopy in the ν_{CO} and ν_{CN} regions revealed the presence of two iron species in solution, these were assigned as complex **1** and a copper(I) adduct of complex **1**. As expected, the ν_{CO}/ν_{CN} modes of complex **1** are shifted to higher frequencies upon complex formation with copper(I), with the ν_{CN} experiencing the greater shift. Under these conditions the ratio of **1** to its copper(I) adduct was 0.8, as determined by intensity measurements. Figure 3 illustrates the titration of $CpFe(CO)_2CN$ with varying quantities of $[Cu(CH_3CN)_4][BF_4]$ in acetonitrile, as monitored by infrared spectroscopy. An equilibrium constant (K_{eq}) at 25 °C of 4.3×10^3 was determined for the process described in Scheme 1. Hence, at high concentration, acetonitrile is competitive with the cyanide ligand in **1** for binding to the copper(I) center.

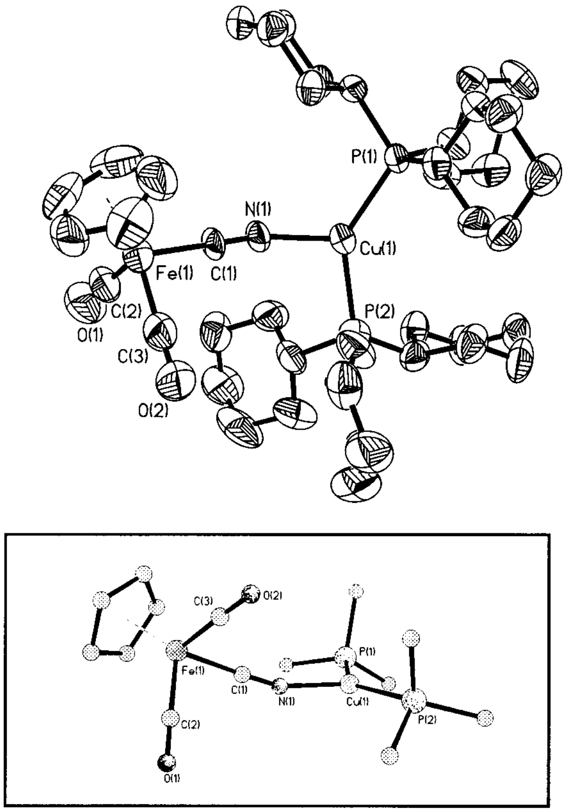

Figure 4. Thermal ellipsoid drawing of the cation of complex **4**, $CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2^+$. The insert illustrates the nonlinear bonding in the C−N−Cu unit.

$$K_{eq} = \{[CpFe(CO)_2(\mu\text{-}CN)Cu(CH_3CN)_3][BF_4]\}\{CH_3CN\}/\{CpFe(CO)_2(CN)\}\{[Cu(CH_3CN)_4][BF_4]\} \quad (1)$$

In contrast, when the reaction between complex **1** and $Cu(CH_3CN)_4^+$ was performed in methylene chloride, infrared spectroscopy showed the presence of only one iron species, where the ν_{CN} and ν_{CO} vibrations were shifted to higher frequencies, at 2160w (ν_{CN}) and 2070s, 2029s cm^{-1} (ν_{CO}), than the corresponding values in **1**. Because these ν_{CN} and ν_{CO} vibrations are considerably higher than those of $[CpFe(CO)_2(\mu\text{-}CN)Cu(CH_3CN)_3][BF_4]$, we proposed this solution species to be $[CpFe(CO)_2(\mu\text{-}CN)Cu\cdots(CH_2Cl_2)_n][BF]$ (**3**) with weak Cu···Cl interactions. The ν_{CN} vibrational mode in complex **3** is shifted by 39 cm^{-1} to higher frequency than that seen in **1**, whereas the ν_{CO} modes are only shifted an average of 13 cm^{-1}. On the other hand, when the CN ligand on iron(II) is made more basic by replacing the CO groups with dppe(1,2-bis(diphenylphosphino)ethane), the corresponding process to that in Scheme 1 proceeds completely to the right. That is, the ν_{CN} band of CpFe(dppe)CN in acetonitrile at 2064 cm^{-1} is wholly displaced to 2081 cm^{-1} upon addition of 1 equiv of $[Cu(CH_3CN)_4][BF_4]$.[26]

Complex **3** was derivatized upon addition of 2 equiv of PCy_3 to a dichloromethane solution of **3**. As anticipated, based on the good donor ability of the PCy_3 ($pK_a = 9.70$)[27] ligands, both ν_{CN} and ν_{CO} stretches in this new adduct, **4**, were shifted to lower frequencies from those of complex **3** (Table 2). X-ray quality crystals of **4** were obtained upon the slow diffusion of

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(26) Phelps, A. L.; Adams, M. J.; Darensbourg, D. J., unpublished observations.

(27) Rahman, Md. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P *Organometallics* **1989**, *8*, 1, and references therein.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2][BF_4]$, **4**

bond distances		bond angles	
Cu−N(1)	1.990(6)	P(1)−Cu-P(2)	140.11(6)
Cu−P(1)	2.2560(14)	Cu−N(1)−C(1)	161.3(5)
Cu−P(2)	2.3042(16)	Fe−C(1)−N(1)	177.4(5)
Fe−C(1)	1.890(8)	C(2)−Fe−C(3)	91.4(3)
Fe−C(2)	1.785(7)	C(3)−Fe−C(1)	91.6(3)
Fe−C(3)	1.784(8)	C(2)−Fe−C(1)	92.5(3)
Fe−C_{Cp}(ave)	2.066[8]	Fe−C(2)−O(1)	178.8(7)
		Fe−C(3)−O(2)	178.2(8)

diethyl ether into a dichloromethane solution of **4** over several days at 10 °C. The solid-state structure of complex **4** was determined by X-ray crystallographic analysis. The thermal ellipsoid drawing of the cation of complex **4** is presented in Figure 4. Selected bond distances and angles for complex **4** are tabulated in Table 4. The coordination geometry of the copper(I) center is distorted trigonal planar, with a obtuse P(1)−Cu−P(2) angle of 140.11(6)° due to the bulky PCy_3 ligands (cone angle = 170°).[27] The Cu(I) center is only 0.213 Å out of the plane defined by N(1), P(1), and P(2). Consistent with solution infrared spectral observations, the Fe−CN bond distance(1.890(8) Å) is slightly shorter in complex **4** than that in **1** (1.933(4) Å), whereas the Fe−CO bond distance is not significantly perturbed. Although, there are no constraints in the coordination sphere of the iron(II) and copper(I) centers, as the insert in Figure 4 shows, there is nonlinear bonding in the C−N−Cu unit, with a bond angle of 161.3(5)°. This nonlinear bonding is also seen in heme−cyanide−copper model complexes for cyanide-inhibited cytochrome *c* oxidases (CcO).[4,5] Addition of a third equivalent of PCy_3 to a methylene chloride solution of complex **4** led to release of the $CpFe(CO)_2CN$ derivative with concomitant formation of $Cu(PCy_3)_3^+$.

Summary

The experiments reported here describe the interaction of the cyanide ligand in the neutral $CpFe(CO)_2CN$ derivative with copper(I) in both acetonitrile and methylene chloride solutions. In acetonitrile solution, acetonitrile competes with the Fe−CN moiety for binding to copper(I), where an equilibrium is established with $K_{eq} = 4.3 \times 10^3$ @ 25 °C. On the other hand, in methylene chloride, complete adduct formation is observed. Adduct formation in solution is based on shifts of the ν_{CO} and ν_{CN} vibrations to higher frequencies, as compared to the corresponding values in $CpFe(CO)_2CN$, with ν_{CN} being more significantly affected by complex formation. Upon adding 2 equiv of PCy_3 to a methylene chloride solution of $CpFe(CO)_2CN$ and $Cu(CH_3CN)_4^+$, the complex cation $CpFe(CO)_2(\mu\text{-}CN)Cu(PCy_3)_2^+$ is formed and isolated as its BF_4^- salt in crystalline form. X-ray crystallography has shown that the interatomic distances and angles in the parent complex $CpFe(CO)_2CN$ and its copper(I) adduct are quite similar. Further, the Fe−CN−Cu bridge is nonlinear, displaying a C−N−Cu angle of 161.3(5)°.

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Supporting Information Available: Complete details in CIF format of the X-ray diffraction studies of **1**, **2**, and **4**, including an illustration of the disorder noted in the BF_4^- anion and one of the cyclohexyl rings in **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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