

Synthesis, Structure, and Reactivity of Monomeric Two-Coordinate Copper(I) Complexes

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Abstract: The reaction of $\text{Cu}(\text{CH}_3\text{CN})_4\text{BF}_4$ with a range of imidazoles, pyrazoles, and pyridines yields two-coordinate copper(I) complexes of the form CuL_2BF_4 . Two of those species, ligated by 1-methylpyrazole and 1,3,5-trimethylpyrazole, respectively, have been characterized by X-ray crystallography, and they both show an approximately linear N-Cu-N geometry with Cu-N bond lengths of 1.87 Å. The bis(1-methylpyrazole) complex apparently forms dimeric units in the solid state with intermolecular distances of ca. 3.1 Å. The unhindered pyrazole and pyridine complexes react with carbon monoxide in solution to form presumed three-coordinate adducts, although the binding of CO is quite weak ($P_{1/2} > 1$ atm). The imidazole and the hindered pyrazole and pyridine complexes are all inert toward reaction with carbon monoxide. A likely explanation for this observation is that steric effects prevent the increase in coordination number for the hindered species, and increased orbital overlap between the imidazole-nitrogen and copper(I) ion stabilizes the two-coordinate form for the imidazole-ligated species. Crystal data for $\text{Cu}(\text{MePz})_2\text{BF}_4$: triclinic, $a = 9.352(4)$ Å, $b = 9.805(4)$ Å, $c = 8.164(3)$ Å, $\alpha = 96.97(3)^\circ$, $\beta = 109.15(3)^\circ$, $\gamma = 62.40(3)^\circ$, $V = 626.3(6)$ Å³, space group = $P\bar{1}$, $Z = 2$. Crystal data for $\text{Cu}(1,3,5\text{-trimethylpyrazole})_2\text{BF}_4$: triclinic, $a = 8.561(5)$ Å, $b = 13.065(5)$ Å, $c = 7.886(2)$ Å, $\alpha = 102.40(3)^\circ$, $\beta = 106.08(4)^\circ$, $\gamma = 91.14(4)^\circ$, $V = 824.8(1.3)$ Å³, space group = $P\bar{1}$, $Z = 2$.

The reaction of hemocyanin (Hc)¹ with carbon monoxide is an intriguing one because the binuclear active site binds only one molecule of CO in a nonbridging fashion.^{2,3} Looking beyond the possibility that steric effects from the protein prevent the binding of a second molecule of CO, we recently suggested an explanation for the observed stoichiometry based on the inertness of a bis-(pyrazolyl)copper(I) dimer toward CO.⁴ We have since recognized that the interaction of CO (and perhaps other small ligands) with Cu(I) complexes might provide an indirect way to assess the structure of copper(I) centers in proteins or in solution,⁵ and we, as well as others,⁶⁻⁸ are engaged in a systematic examination of the chemistry of well-defined, coordinatively unsaturated copper(I) complexes. The present paper reports the synthesis, characterization, and reactivity toward carbon monoxide of several mononuclear two-coordinate copper(I) complexes (1-12) ligated by nitrogen heterocycles.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received, unless noted otherwise. 1-Methylpyrazole,⁹ 1,3,5-trimethylpyrazole,¹⁰ and 1-ethyl-3,5-dimethylpyrazole¹¹ were prepared

(1) Abbreviations used in this paper: Hc, deoxyhemocyanin; MeOH, methanol; DMF, dimethylformamide; Melm, methylimidazole; MePz, methylpyrazole; THF, tetrahydrofuran; TMP, 1,3,5-trimethylpyrazole.

(2) Alben, J. O.; Yen, L.; Farrier, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 4475-4476.

(3) This statement is based on a comparison of the stretching frequencies observed for the various carbonyl adducts of HcCO with those for simple coordination compounds. Bridging carbonyl derivatives for copper complexes have $\nu(\text{CO}) < 2000$ cm⁻¹: (a) Pasquali, M.; Floriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092-4099. (b) Doyle, G.; Eriksen, K. A.; Modrick, M.; Ansell, G. *Organometallics* **1982**, *1*, 1613-1618.

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$\text{CuL}_2^+\text{BF}_4^-$
1-12

- 1, L = 1-methylimidazole
- 2, L = 2-methylimidazole
- 3, L = 4-methylimidazole
- 4, L = 1,2-dimethylimidazole
- 5, L = pyrazole
- 6, L = 1-methylpyrazole
- 7, L = 3,5-dimethylpyrazole
- 8, L = 1,3,5-trimethylpyrazole
- 9, L = 1-ethyl-3,5-dimethylpyrazole
- 10, L = 1-benzyl-3,5-dimethylpyrazole
- 11, L = 2-picoline
- 12, L = 2,6-lutidine

by literature methods. Methanol (MeOH) was distilled under N₂ from magnesium methoxide; acetonitrile, dichloromethane, and dimethylformamide (DMF) were distilled from calcium hydride; and tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. "Gold label" nitromethane was purchased from Aldrich and used as received. Microanalyses were performed by Integral Microanalytical Laboratories, Inc., Raleigh, NC, Galbraith Laboratories, Inc., Knoxville, TN, or MicroAnal, Tucson, AR.

¹H NMR spectra were recorded on a Perkin-Elmer R-24B instrument at 60 MHz using CDCl₃ as the solvent. All chemical shifts are relative to an internal standard of Me₄Si. Variable temperature NMR spectra were recorded on a Bruker WM 250 instrument operating at 250.13 MHz. Infrared spectra were obtained by using a matched set of NaCl cells with a path length of 0.1 mm on a Beckman Model 4250 spectrometer. All manipulations involving the cuprous complexes were performed in a Vacuum Atmospheres glovebox operating with less than 1 ppm O₂ and H₂O.

1-Benzyl-3,5-dimethylpyrazole. Under a dinitrogen atmosphere, 9.6 g (0.1 mol) of 3,5-dimethylpyrazole was slowly added to a suspension of 2.6 g (0.11 mol) of NaH in 130 mL of dry DMF. The solution was allowed to stir at 60 °C for 2 h and then treated dropwise with 12.7 g (0.1 mol) of benzyl chloride. After stirring at 60 °C for 48 h, the solution was evaporated to an oil at reduced pressure. The residue was treated with 100 mL of water and extracted with three 75-mL portions of benzene. The combined organic portion was washed with 50 mL of water and 50 mL of saturated aqueous NaCl and then dried over Na₂SO₄. The filtered solution was evaporated to give a yellow oil, which was purified by column chromatography on 60-200 mesh silica gel with methylene

(10) Auwers, K. V.; Broche, H. *Chem. Ber.* **1922**, *55*, 3880-3911. A more convenient method of preparation is to treat 2,4-pentanedione with *N*-methylhydrazine slowly and then to distill the product.

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Table I. Crystal Data for Cu(MePz)₂BF₄ (6) and Cu(TMP)₂BF₄ (8)

complex	6	8
formula	C ₈ H ₁₂ BCuF ₄ N ₄	C ₁₁ H ₂₀ BCuF ₄ N ₄
space group	<i>P</i> 1̄	<i>P</i> 1̄
<i>a</i> , Å	9.352 (4)	8.561 (5)
<i>b</i> , Å	9.805 (4)	13.065 (5)
<i>c</i> , Å	8.164 (3)	7.886 (2)
α , deg	96.97 (3)	102.40 (3)
β , deg	109.15 (3)	106.08 (4)
γ , deg	62.40 (3)	91.14 (4)
<i>V</i> , Å ³	626.3 (6)	824.8 (13)
<i>Z</i>	2	2
ρ , g/cm ³	1.67	1.49
cryst size, mm	0.35 × 0.32 × 0.22	0.30 × 0.30 × 0.27
collection range	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
	$2^\circ \leq 2\theta \leq 55^\circ$	$2^\circ \leq 2\theta \leq 55^\circ$
transmission factors,		
min	0.76	0.88
max	1.00	1.00
av	0.90	0.95
no. of data	2872	3784
no. of data	1693	1796
[<i>I</i> ≥ 3 σ (<i>I</i>)]		
<i>R</i>	6.9	7.4
<i>R</i> _w	7.2	7.0

chloride as the eluent: ¹H NMR δ 2.01 (3 H, s), 2.12 (3 H, s), 5.00 (2 H, s), 5.61 (1 H, s), 6.8–7.3 (5 H, m).

Synthesis of [CuL₂]BF₄. In an inert-atmosphere box, 30 mmol of ligand in 100 mL of dry methanol was treated with 4.71 g (15 mmol) of solid Cu(CH₃CN)₄BF₄.⁴ For the cases where L = 2,6-lutidine and 1,2-dimethylimidazole, the solid did not dissolve readily, and a minimum of nitromethane was added. The solvent was then completely removed under vacuum.¹² The residue was dissolved in methanol,¹³ and the solution was filtered and treated with THF to induce crystallization. Slow evaporation of the solution over several days gave, in all cases, colorless, crystalline compounds in yields between 60% and 70%. Most of the solids are stable toward dioxygen for up to several hours; however, in moist air they rapidly turn blue owing to oxidation. Complexes 8–10 and 12 are stable indefinitely in air. Satisfactory C, H, and N analyses were obtained for all compounds.

Reactions with CO. In the inert-atmosphere box each complex (30–50 mg) was dissolved in ~1 mL of nitromethane or CH₂Cl₂ and the flask was removed from the inert-atmosphere box. Some of the solution was transferred under N₂ into a sealed IR cell that had been flushed with N₂, and the spectrum was recorded. The remaining solution was then exposed to CO for 5 min, that solution was transferred to an IR cell, and the spectrum was again recorded. The solution was finally treated with excess ligand under CO, and that spectrum was measured.

Quantitative CO uptake measurements were done as previously reported.⁵

X-ray Data Collection. Crystal data for Cu(MePz)₂BF₄ (6) and Cu(TMP)₂BF₄ (8) are listed in Table I. Data for each structure were collected in the same way: the crystal was coated with epoxy resin on the tip of a glass fiber and subjected to a preliminary diffractometer search that revealed triclinic symmetry. Diffraction data were collected at 293 K on an Enraf-Nonius CAD-4 computer-controlled diffractometer using Mo K α radiation (0.7107 Å) from a graphite-crystal monochromator. The unit cell constants were derived from a least-squares refinement of the setting angles of 25 reflections. The ω -2 θ scan technique was used to record the intensities for a unique set of reflections. Peak counts were corrected for background counts by extending the final scan by 25% at each end to yield net intensities, *I*, which were assigned standard deviations with a conventional ρ factor selected as 0.01. Intensities were corrected for Lorentz and polarization effects and, for 6, were also corrected for decay. The maximum correction was 1.25 (20% decay), and the average correction was 1.08. The data for 6 and 8 were further corrected for absorption effects by using an empirical correction based on ψ scans.

Structure Determination and Refinement. Each structure was solved in a similar manner: a three-dimensional Patterson synthesis was used to locate the copper atom position, and a series of difference Fourier maps

(12) If all of the solvent is not evaporated, one will isolate Cu(CH₃CN)₄BF₄ in some cases rather than the desired two-coordinate complex.

(13) For the case of Cu(1,2-Me₂Im)₂BF₄, a small amount of acetonitrile was added. Complexes 2 and 7 were crystallized from acetone-methanol, and complex 5 crystallized upon concentrating a THF solution of the complex.

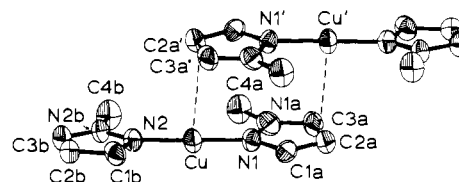


Figure 1. Structure of the Cu(MePz)₂⁺ cation showing 40% probability thermal ellipsoids. Bond distances and angles are compiled in Table IV.

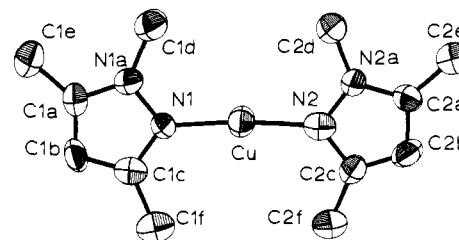


Figure 2. Structure of the Cu(TMP)₂⁺ cation showing 40% probability thermal ellipsoids. Bond distances and angles are compiled in Table V.

revealed the remaining non-hydrogen atoms. The refinement was effected by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight, *w*, is $4F_o^2/\sigma^2(F_o)^2$. Calculated hydrogen atom positions were included during the later stages of refinement in the structure-factor calculations, but they were not refined. Programs used for the structure solution and refinement for 6 and 8 were supplied as a package by Enraf-Nonius. Atomic scattering factors for the non-hydrogen atoms were taken from ref 14 and those for hydrogen atoms from Stewart et al.¹⁵ Although the final *R* factors are high by modern standards, they arise from the most part from high thermal motion in the BF₄ groups. This phenomenon has been observed previously.^{5,16} A final difference Fourier for 6 and 8 showed some residual electron density in the vicinity of the BF₄ groups (<0.44 e Å⁻³), but it could not be fit to a reasonable model for a disordered BF₄ group. Hydrogen atom positions, thermal parameters, and structure factors are included as supplementary material.

Results and Discussion

Synthesis. Two-coordinate Cu(I) complexes are scarcely represented in the chemical literature, and structurally characterized ones are even rarer. Lewin et al.¹⁷ prepared several substituted bis(pyridine) and bis(quinoline)copper(I) species, but those compounds formed only with sterically encumbered donors, precipitating from a solution containing a large excess of the ligand. Reedijk and co-workers also prepared a number of complexes using sterically hindered imidazoles,^{6a} and they reported the synthesis of the bis(pyrazole)copper(I) cation several years ago.^{6b} We have shown here that the reaction to form two-coordinate Cu(I) complexes is not limited by the nature of the heterocycle or by its substitution pattern. Presumably any nitrogen heterocycle¹⁸ will react in a 2:1 stoichiometry with Cu(CH₃CN)₄(BF₄) to form two-coordinate Cu(I) complexes. All of the compounds isolated are soluble in polar solvents such as methanol, acetone, acetonitrile, dimethylformamide, and nitromethane, and several are even soluble to a limited extent in dichloromethane (<0.05 M). In protic solvents, all of the complexes react rapidly and irreversibly with dioxygen to form blue solutions from which we have not yet been able to isolate any well-defined species. In aprotic solvents, the oxidation process is much slower, and those compounds that have sterically hindered pyrazole ligands are stable toward O₂ for

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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(17) Lewin, A. H.; Cohen, I. A.; Michl, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1951–1957.

(18) We also attempted to isolate the bis(pyridine) and bis(imidazole)-copper(I) species, but we obtained oils in each case. Presumably by choosing the correct solvent combination one could also isolate those and other complexes.

Table II. Final Positional Parameters for Cu(MePz)₂BF₄ (6)

atom	x	y	z
Cu	-0.0063 (1)	0.0720 (1)	0.3112 (1)
F1	0.6569 (5)	0.1760 (6)	0.1939 (8)
F2	0.4656 (9)	0.3929 (8)	0.2232 (14)
F3	0.4069 (9)	0.2680 (12)	0.0050 (8)
F4	0.4285 (8)	0.2162 (8)	0.2530 (10)
N1	0.0192 (6)	-0.0952 (5)	0.1656 (6)
N2	-0.0242 (6)	0.2377 (5)	0.4593 (6)
N1a	0.1655 (6)	-0.2033 (6)	0.1446 (7)
N2b	0.1054 (6)	0.2534 (6)	0.5798 (7)
C1a	-0.1013 (7)	-0.1240 (7)	0.0520 (9)
C2a	-0.0307 (8)	-0.2501 (7)	-0.0434 (9)
C3a	0.1374 (8)	-0.2967 (8)	0.0185 (9)
C4a	0.3247 (9)	-0.2108 (8)	0.2519 (10)
C1b	-0.1665 (8)	0.3543 (7)	0.4800 (9)
C2b	-0.1257 (9)	0.4440 (7)	0.6119 (9)
C3b	0.0457 (8)	0.3768 (7)	0.6705 (9)
C4b	0.2789 (9)	0.1454 (9)	0.5933 (10)
B	0.487 (1)	0.264 (1)	0.142 (2)

Table III. Final Positional Parameters for Cu(TMP)₂BF₄ (8)

atom	x	y	z
Cu	0.0010 (1)	0.21370 (8)	0.4595 (1)
F1	0.7432 (6)	0.2527 (5)	0.1067 (10)
F2	0.5234 (8)	0.1948 (6)	-0.1260 (10)
F3	0.5056 (9)	0.2188 (7)	0.1249 (9)
F4	0.5537 (10)	0.3455 (5)	0.0430 (14)
N1	0.0472 (6)	0.0837 (4)	0.3351 (7)
N2	-0.0209 (7)	0.3448 (5)	0.5969 (8)
N1a	-0.0649 (6)	0.0009 (4)	0.2435 (7)
N2a	-0.1609 (6)	0.3728 (4)	0.6343 (7)
C1a	0.0105 (9)	-0.0805 (5)	0.1730 (9)
C1b	0.1710 (9)	-0.0500 (6)	0.2222 (10)
C1c	0.1911 (8)	0.0514 (6)	0.3226 (9)
C1d	-0.2346 (9)	0.0115 (6)	0.2268 (11)
C1e	-0.0837 (11)	-0.1805 (6)	0.0626 (11)
C1f	0.3434 (10)	0.1238 (7)	0.4081 (11)
C2a	-0.1391 (8)	0.4728 (6)	0.7374 (9)
C2b	0.0188 (9)	0.5070 (6)	0.7607 (10)
C2c	0.0889 (9)	0.4260 (5)	0.6760 (9)
C2d	-0.3072 (9)	0.3028 (6)	0.5694 (11)
C2e	-0.2728 (10)	0.5234 (7)	0.7957 (12)
C2f	0.2573 (9)	0.4223 (6)	0.6640 (11)
B	0.591 (1)	0.2566 (8)	0.031 (2)

up to several hours. In no case did we ever observe disproportionation.

In solution, the complexes evidently remain two-coordinate rather than undergoing ligand dissociation or equilibration to form CuL⁺ and CuL₃⁺. This has been established by NMR spectroscopy for **6**, which shows only a single set of peaks in CD₂Cl₂ over the temperature range 213–293 °K. If either of the processes mentioned above were occurring, we should be able to observe the exchange process unless the activation barrier is extremely low. There is no hint of line broadening in any of the spectra to suggest an equilibrium process.

Solid-State Structures.¹⁹ Both structurally characterized compounds **6** and **8** crystallize as colorless platelets in the triclinic space group P $\bar{1}$. The final positional parameters for each are listed in Tables II and III and the structures are presented in Figures 1 and 2, respectively.

The structure of compound **8** serves as a prototype for most of the compounds reported herein. The extremely short Cu–N

(19) We initiated the crystal structure determination of the bis(1,2-dimethylimidazole)copper(I) tetrafluoroborate complex but were forced to abandon this when the cation proved to be disordered. The direct-methods program MULTAN was used to find of the atom positions for the cation, and a difference Fourier map revealed the position of the BF₄ group, which was not disordered. The overall structure was essentially the same as found for the bis(pyrazolyl)copper species described herein, with a linear geometry and Cu–N bond distances <2 Å. Crystal data for **4**: *a* = 9.192 (4) Å, *b* = 10.751 (7) Å, *c* = 7.762 (5) Å, α = 93.47 (6)°, β = 101.65 (6)°, γ = 81.74 (5)°, *V* = 743.1 (14) Å³, space group = P $\bar{1}$, *Z* = 2.

bond distances are evidently characteristic for two-coordinate Cu(I) complexes and compare well with the average distance of 1.87 (1) Å found in several previously reported structures.^{4,6} The N–Cu–N angle in **8** is 174°, which is close to the linear arrangement of donors expected for two-coordination.

Complex **8** is unique in being the first unconstrained two-coordinate Cu(I) that has been structurally characterized. In most of the previously reported structures,^{6c} the complex comprised a chelating ligand that had other potential coordinating atoms in the ligand framework. Thus, the stability of those complexes may have been a result of weak, long-range interactions or of the chelate effect. In **8**, the distances from Cu to atoms in neighboring molecules are >3.7 Å, so long-range interactions are unlikely.

The structure of **6** (Figure 1) is in slight contrast with that found for **8**. The Cu–N distances and N–Cu–N angle in **6** are nearly identical with those in **8**, but the intermolecular distances are shortened notably, and Cu–C2a' and Cu–C3a are 3.150 (4) and 3.221 (4) Å, respectively. Although these distances are too long to be considered as formal bonds, they may qualify as weak intermolecular interactions that produce dimeric aggregates in the solid state. Several pieces of evidence augment this hypothesis. Firstly, pyrazole ring **a** tilts slightly toward the neighboring copper atom, which itself lies almost directly over the middle of the C2a'–C3a' bond, reminiscent of a metal– π (olefin) interaction observed for many transition-metal complexes.²⁰ Secondly, neighboring cations are >5 Å away, ruling out simple crystal-packing phenomena that lead to an infinite stacked array of molecules. Finally, η^2 -arene coordination has been observed previously for Cu(I) in the complex (ethylenediamine)-carbonylcopper(I) tetraphenylborate, wherein one of the phenyl rings of the anion coordinates to copper.²¹ In that case, the bond distances between copper and the two carbons are 2.919 (5) and 2.706 (4) Å, and a formal bond to the π system is probable. The intermolecular attraction in **6** is much weaker, however, and most likely does not persist in solution as demonstrated by the NMR spectrum that shows only the four signals (ignoring spin–spin splitting) associated with the protons on 1-methylpyrazole.

One geometric feature common to **6** and **8** is the nearly coplanar orientation of the two pyrazole rings within each cation. The dihedral angle between the pyrazole planes for **6** is 4.7° and for **8** is 8.7°. Intramolecular contacts between methyl groups (e.g., C1d–C2d or C1f–C2f for **8**) are apparently negligible (>4.1 Å) and thus do not prevent the pyrazoles from being coplanar. This orientation of the ligands, which probably results from crystal packing forces, means that the short bond distances between Cu and N(pyrazole) do not result from back-bonding from Cu(I) to pyrazole– π^* but rather from strong σ -overlap between copper and ligand. A significant back-bonding interaction would dictate that the pyrazole rings be mutually perpendicular in order to maximize delocalization of the d electrons on copper.

Reaction with Carbon Monoxide. The reaction of Cu(I) complexes with CO is readily monitored by infrared spectroscopy, and except for one type of complex that has a bridging carbonyl (ν (CO) < 2000 cm⁻¹),³ all known copper carbonyls have terminal M–CO coordination with stretching frequencies between 2000 and 2200 cm⁻¹.²²

Many of the complexes **1–12** are inert toward carbon monoxide,

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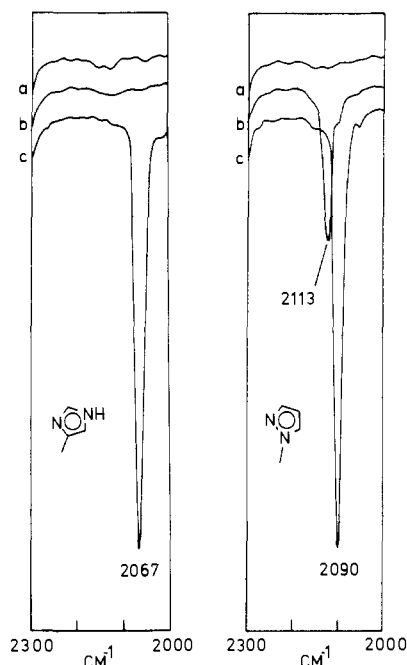


Figure 3. Infrared spectra for $\text{Cu}(\text{MeIm})_2\text{BF}_4$ (left) and $\text{Cu}(\text{MePz})_2\text{BF}_4$ (right) in dichloromethane solution under (a) N_2 , (b) CO , and (c) CO after addition of excess ligand.

and those that do react do so only slightly. This general lack of reactivity appears to be a result of several factors, of which steric effects exert the greatest influence.

Bis(imidazole)copper(I) complexes **1–4** are all inert toward CO , as illustrated in Figure 3b specifically for $\text{Cu}(\text{4-MeIm})_2^+$. In these instances, additional donors are able to bind to CuL_2^+ , yet *carbon monoxide in the absence of other ligands does not*.²³ The case for this can be made as follows. Lewin showed that unhindered pyridines form complexes of the type CuL_4^+ and that pyridine derivatives having a single substituent α to the ligating nitrogen can form complexes of the type CuL_3^+ .¹⁷ Thus, with the unhindered 1-methylimidazole and the α -substituted 2- and 4-methylimidazoles, higher coordination numbers should be attainable. When $\text{Cu}(\text{4-MeIm})_2^+$ (**3**) is treated with CO by itself, no reaction is observed (Figure 3b). Excess 4-methylimidazole added to the solution, however, promotes formation of a carbonyl derivative (Figure 3c) and substantiates the contention that the copper is sterically accessible to additional ligands. This is important because it shows that steric effects of the ligands are not preventing the coordination of CO ; therefore electronic effects must be responsible for the inertness of these species.

The bis(pyrazole) and bis(pyridine)copper(I) complexes **5–12** differ from their imidazole analogues. Two-coordinate copper(I) complexes prepared with the unhindered ligand pyrazole and the mono(α -substituted) ligands 1-methylpyrazole, 2-picoline, and 3,5-dimethylpyrazole react with CO as shown in the right half of Figure 3b to form what we presume are three-coordinate carbonyl derivatives since their stretching frequencies are higher than those observed for four-coordinate complexes in which ν_{CO} is at ca. 2080 cm^{-1} .^{5,22} However, addition of excess ligand promotes formation of a different carbonyl adduct (Figure 3c), probably of the form $\text{CuL}_3(\text{CO})^+$ based on ν_{CO} (Table VI). In contrast, the bis(α -substituted) heterocycles form complexes **8**, **9**, **10**, and **12**, which are inert toward CO , even in the presence of additional ligand, most likely because steric effects prevent an

(23) In the infrared spectra that we recorded, we would occasionally observe an absorption when we exposed the two-coordinate bis(imidazole) complexes to carbon monoxide. However, the peak's intensity varied greatly depending on the history of the sample, and its position was the same as that observed for the tris(imidazole)carbonyl adducts. We conclude that this absorption was promoted by impurities in the sample since highly crystalline preparations showed no absorption (<5%) of CO either by infrared spectroscopy or by manometric uptake experiments.

Table IV. Bond Distances and Angles for $\text{Cu}(\text{MePz})_2\text{BF}_4$

Distances, Å					
Cu–N1	1.873 (3)	Cu–N2	1.879 (3)	N1–N1a	1.338 (4)
N1–C1a	1.325 (4)	N2–N2b	1.347 (4)	N2–C1b	1.340 (4)
N1a–C3a	1.336 (5)	N1a–C4a	1.431 (5)	N2b–C3b	1.323 (5)
N2b–C4b	1.444 (5)	C1a–C2a	1.385 (5)	C2a–C3a	1.343 (5)
C1b–C2b	1.375 (5)	C2b–C3b	1.352 (6)	B–F1	1.353 (8)
B–F2	1.316 (7)	B–F3	1.117 (9)	B–F4	1.411 (9)
Cu–C2a'	3.150 (4)	Cu–C3a'	3.221 (4)	C4a–C4b	4.145 (6)
Angles, deg					
N1–Cu–N2	178.2 (2)	Cu–N1–N1a	125.9 (3)		
Cu–N1–C1a	128.1 (3)	N1a–N1–C1a	105.8 (3)		
Cu–N2–N2b	126.1 (3)	Cu–N2–C1b	127.4 (3)		
N2b–N2–C1b	106.1 (3)	N1–N1a–C3a	110.7 (3)		
N1–N1a–C4a	121.1 (3)	C3a–N1a–C4a	128.2 (4)		
N2–N2b–C3b	109.8 (4)	N2–N2b–C4b	120.6 (3)		
C3b–N2b–C4b	129.6 (4)	N1–C1a–C2a	110.2 (3)		
C1a–C2a–C3a	105.4 (4)	N1a–C3a–C2a	107.9 (5)		
N2–C1b–C2b	109.7 (4)	C1b–C2b–C3b	105.4 (4)		
N2b–C3b–C2b	109.0 (4)	F1–B–F2	103.8 (6)		
F1–B–F3	121.9 (7)	F1–B–F4	104.9 (8)		
F2–B–F3	119.5 (11)	F2–B–F4	92.7 (6)		
F3–B–F4	109.4 (6)				

Table V. Bond Distances and Angles for $\text{Cu}(\text{TMP})_2\text{BF}_4$

Distances, Å					
Cu–N1	1.878 (3)	Cu–N2	1.863 (4)	N1–N1a	1.361 (4)
N1–C1c	1.333 (4)	N2–N2a	1.351 (4)	N2–C2c	1.323 (5)
N1a–C1a	1.353 (5)	N1a–C1d	1.434 (5)	N2a–C2a	1.361 (5)
N2a–C2d	1.437 (5)	C1a–C1b	1.347 (6)	C1a–C1e	1.482 (6)
C1b–C1c	1.369 (6)	C1c–C1f	1.497 (6)	C2a–C2b	1.365 (6)
C2a–C2e	1.467 (6)	C2b–C2c	1.367 (6)	C2c–C2f	1.472 (6)
B–F1	1.281 (8)	B–F2	1.293 (7)	B–F3	1.332 (8)
B–F4	1.202 (7)				
Cu–Cu'	5.755 (1)	C1d–C2d	4.333 (6)	C1f–C2f	4.169 (6)
Angles, deg					
N1–Cu–N2	173.8 (2)	Cu–N1–N1a	125.1 (3)		
Cu–N1–C1c	128.8 (3)	N1a–N1–C1c	106.1 (4)		
Cu–N2–N2a	123.6 (3)	Cu–N2–C2c	129.4 (4)		
N2a–N2–C2c	107.0 (4)	N1–N1a–C1a	109.5 (4)		
N1–N1a–C1d	120.0 (4)	C1a–N1a–C1d	130.4 (4)		
N2–N2a–C2a	110.1 (4)	N2–N2a–C2d	122.2 (4)		
C2a–N2a–C2d	127.7 (4)	N1a–C1a–C1b	107.5 (4)		
N1a–C1a–C1e	120.9 (5)	C1b–C1a–C1e	131.5 (5)		
C1a–C1b–C1c	106.9 (4)	N1–C1c–C1b	109.9 (4)		
N1–C1c–C1f	120.5 (5)	C1b–C1c–C1f	129.5 (5)		
N2a–C2a–C2b	105.8 (4)	N2a–C2a–C2e	121.5 (4)		
C2b–C2a–C2e	132.7 (5)	C2a–C2b–C2c	107.6 (4)		
N2–C2c–C2b	109.5 (4)	N2–C2c–C2f	121.5 (5)		
C2b–C2c–C2f	129.0 (5)	F1–B–F2	119.0 (7)		
F1–B–F3	108.7 (8)	F1–B–F4	112.1 (6)		
F2–B–F3	98.2 (6)	F2–B–F4	114.0 (9)		
F3–B–F4	102.3 (7)				

Table VI. Carbonyl Stretching Frequencies for $\text{CuL}_x(\text{CO})^+$ Species

ligand	$\nu_{\text{CO}},^a\text{ cm}^{-1}$	
	$x = 2$	$x = 3$
1-methylimidazole		2067
2-methylimidazole		2059
4-methylimidazole		2067
1,2-dimethylimidazole		2062
pyrazole	2117 (1.9) ^b	2090
1-methylpyrazole	2113 (2.2) ^b	2090
3,5-dimethylpyrazole	2112 (6.1) ^b	2076
2-picoline	2112 (5.4) ^b	2085

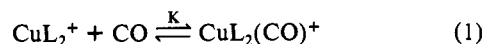
^a CH_2Cl_2 solution. ^b Numbers in parentheses refer to $P_{1/2}$ (atm) for CO binding in nitromethane solution at 25°C .

increase in their coordination number.

In order to assess more quantitatively the binding of CO by the two-coordinate pyrazole and pyridine derivatives, we examined their uptake of CO by a manometric method.²⁴ In all cases, the

binding of carbon monoxide is quite weak, ranging from ca. 2 to 6 atm depending on the ligand (Table VI).

The ligand basicity²⁵ is a useful quantity that correlates roughly within a given series of compounds with the relative reactivities of two-coordinate Cu(I) complexes toward carbon monoxide (eq 1). We can use the series L = 2-methylimidazole ($pK_a = 7.86$),



1-methylpyrazole ($pK_a = 2.04$), and 2-picoline ($pK_a = 5.97$) to discuss this reactivity trend since all three complexes have analogous steric requirements; hence they should have similar solvation energies.²⁶ The equilibrium constant for reaction 1 will increase (or $P_{1/2}$ will decrease) if either the product is stabilized or the reactant is destabilized within the series of complexes under consideration. We expect, on the basis of on ligand basicities, that the stability of the carbonyl adduct, thus the magnitude of K , should increase in the order L = 1-methylpyrazole < 2-picoline < 2-methylimidazole. That is, better σ donation of ligand to metal will favor binding an excellent π -acid like carbon monoxide. This trend is just opposite from that based on the observed $P_{1/2}$ values for CO binding by **2**, **5**, and **10** (Table VI). Therefore, the values of K must be rationalized on the basis of the stability of the two-coordinate reactant, and that stability must increase in the order L = 1-methylpyrazole < 2-picoline < 2-methylimidazole. The stability of the bis(2-methylimidazole)copper(I) cation vs. the bis(1-methylpyrazole)copper(I) cation, for example, probably reflects greater overlap between the bonding orbitals of copper and the ligand in the former case, expected from the basicity or σ -donating ability of the heterocycle. The crystallographic results are consistent with this notion since the observation of very short Cu-N bond distances for two-coordinate species suggests that the copper- σ (ligand) interaction exerts the more important influence on the stability of the complex.

Biological Implications. The inertness of bis(methylimidazole)copper(I) species toward carbon monoxide supports our earlier explanation⁴ for the stoichiometry of CO binding by hemocyanin.² To recount that hypothesis, we suggest that the coordination sphere about each copper is essentially two-coordinate (based on EXAFS studies²⁷) but that near one of the copper centers is an additional donor that can coordinate and promote CO binding to that copper. The other center remains two-coordinate, hence unreactive toward CO, leading to the observation that Hc binds only one CO per binuclear active site. This assumes that there is sufficient room to bind two CO molecules; therefore the stoichiometry observed is not merely a result of steric effects. In retrospect we see that the lack of reactivity of the two-coordinate copper(I) complex we reported earlier⁴ was actually due to steric effects imposed by the ligand; but the work reported herein demonstrates that alkylimidazoles, which in biological systems is represented by the amino acid histidine, do form two-coordinate species that are unreactive toward CO because of electronic effects.

Besides providing an explanation for the stoichiometry of CO binding by Hc, these results should be applicable to probing the active-site structure of the reduced form for other copper proteins as well. EXAFS spectroscopy is one of the few methods that can provide information about the ligands in the first coordination

sphere of the "spectroscopically invisible" d^{10} cuprous ion; however, low-Z atoms at longer distances may remain unobservable. The reaction of the copper center with a ligand like CO, on the other hand, provides a spectroscopic probe whose properties vary as a function of the environment about the metal. Thus if a cuprous-containing protein is treated with carbon monoxide and no reaction is observed, one can conclude that the copper site must be either two- or four-coordinate (but not square planar in the latter case²⁸) and those two possibilities should be distinguishable from EXAFS studies. On the other hand, if a carbonyl adduct is formed, then the active site must be three-coordinate or three-coordination must be readily accessible.^{29,30} An example of this type of behavior is apparently exhibited by a two-coordinate copper(I) benzimidazole complex prepared by Reedijk^{6d} which reacts with carbon monoxide in solution, presumably because the "extra" (i.e., noncoordinating in the solid state) nitrogen donors in the ligand framework are able to coordinate in solution, forming three-coordinated copper ions prior to binding CO. This conclusion is based on the reactivity and structure of a similar copper(I) complex prepared by Gagné^{22a} for which the structure of the carbonyl adduct has been determined and in which all of the nitrogen donors in the ligand are bound to copper.

Two copper proteins for which EXAFS results are in hand and for which carbonyl adducts have been examined are hemocyanin and cytochrome oxidase.³¹ Deoxyhemocyanin, as mentioned above, is thought to be two-coordinate²⁷ or three-coordinate³² from EXAFS measurements, and the fact that it forms a carbonyl derivative indicates that a three-coordinate form is readily attainable if not initially present. The active site in reduced cytochrome oxidase is less well-defined, and the EXAFS results have stirred much debate.³³ The formation of a carbonyl adduct for cytochrome oxidase suggests a three-coordinate copper(I) center bound perhaps by two histidyl imidazoles and a cysteinyl thiolate.³⁴ Unfortunately, there is at present no example of a copper carbonyl adduct ligated by a thiolate ion, so there is nothing with which to compare the observed infrared stretching frequency for the enzyme to assess the likelihood of that mode of ligation. Filling this void is the thrust of future work in our laboratory.

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Registry No. 1, 86695-86-5; 2, 86695-87-6; 3, 86695-89-8; 4, 86695-90-1; 5, 86695-91-2; 6, 86695-93-4; 7, 86695-94-5; 8, 86695-96-7; 9, 86695-98-9; 10, 86696-00-6; 11, 86696-02-8; 12, 86696-03-9; Cu(Pz)₂

(28) Cf. ref 22h. In a biological system, it would be difficult to form a square-planar copper(I) center with only protein side chains as ligands.

(29) All of the above arguments about carbon monoxide reactivity with copper-containing proteins presuppose that the active site of the protein is accessible to exogenous ligands like CO.

(30) There is only a fine line of course between the case of a metal center that is three-coordinate, a metal center that is two-coordinate but has a third ligand nearby, and a metal center that is four-coordinate yet has a very weakly bound ligand.

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(CO)⁺, 86696-04-0; Cu(1-MePz)₂(CO)⁺, 86696-05-1; CuL₂(CO)⁺ (L = 3,5-dimethylpyrazole), 86696-06-2; CuL₂(CO)⁺ (L = picoline), 86696-07-3; Cu(1-MeIm)₃(CO)⁺, 86696-08-4; Cu(2-MeIm)₃(CO)⁺, 86696-09-5; Cu(4-MeIm)₃(CO)⁺, 86696-10-8; CuL₃(CO)⁺ (L = 1,2-dimethylimidazole), 86696-11-9; Cu(Pz)₃(CO)⁺, 86696-12-0; Cu(1-MePz)₃(CO)⁺, 86696-13-1; CuL₃(CO)⁺ (L = 3,5-dimethylpyrazole), 86696-14-2; CuL₃(CO)⁺ (L = 2-picoline), 86696-15-3; Cu(CH₃CN)₄B-

F₄, 15418-29-8; CO, 630-08-0; 1-benzyl-3,5-dimethylpyrazole, 1134-81-2; 3,5-dimethylpyrazole, 67-51-6.

Supplementary Material Available: Final hydrogen atom positions, listings of observed and calculated structure factors, and final thermal parameters for **6** and **8** (29 pages). Ordering information is given on any current masthead page.

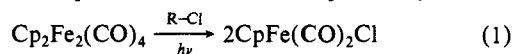
Mechanisms of the Photoreactions of Cp₂Fe₂(CO)₄ with Phosphines and Chlorocarbons

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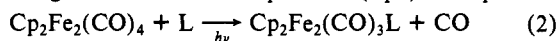
Contribution No. 6241 from the Chemical Laboratories, California Institute of Technology, Pasadena, California 91125. Received August 24, 1982

Abstract: Irradiation ($\lambda > 500$ nm) of Cp₂Fe₂(CO)₄ (Cp = η^5 -C₅H₅) in the presence of PR₃ (R = Ph, O-*i*-Pr) in cyclohexane solution at room temperature yields a single product, Cp₂Fe₂(CO)₃(PR₃). The reaction with PPh₃ (366 nm) is inhibited by excess CO. A reaction intermediate was trapped by irradiating Cp₂Fe₂(CO)₄ in the presence of P(O-*i*-Pr)₃ at -78 °C in ethyl chloride or THF solution. The infrared spectrum of the intermediate has $\nu(\text{C}\equiv\text{O}) = 1720$ cm⁻¹, and its electronic spectrum does not exhibit a $\sigma \rightarrow \sigma^*$ band. The evidence suggests that the intermediate is Cp(CO)₂Fe-CO-Fe(CO)(P(O-*i*-Pr)₃)Cp, a molecule in which a single CO bridges the Fe atoms and in which there is no direct Fe-Fe bond. The mechanism of the photoreaction of PR₃ with Cp₂Fe₂(CO)₄ is proposed to involve formation of the CO-bridged intermediate Cp₂Fe₂(CO)₄(PR₃), followed by loss of CO to give the product Cp₂Fe₂(CO)₃(PR₃). The 366-nm photoreaction of Cp₂Fe₂(CO)₄ with CCl₄ or CHCl₃ to give CpFe(CO)₂Cl occurs mainly by a CpFe(CO)₂ radical pathway, because the chlorine atom abstraction is not inhibited by 6 atm of CO.

Photochemical reactions of Cp₂Fe₂(CO)₄ (Cp = η^5 -C₅H₅), a molecule in which there are two bridging carbonyl ligands,² have been reported in several papers.³⁻⁶ For example, Gianotti has shown³ that Cp₂Fe₂(CO)₄ reacts photochemically with chloro-carbon solvents (eq 1). One reasonable possibility for the



mechanism of this reaction involves homolytic cleavage of the Fe-Fe unit, followed by abstraction of Cl from R-Cl by the CpFe(CO)₂ radical fragment.^{3,4} However, there is some evidence that CpFe(CO)₂ fragments are not formed on irradiation, namely, the observation that the photoreactions of Cp₂Fe₂(CO)₄ with nucleophiles give monosubstituted products (eq 2). Caspar and



Meyer have recently shown that two primary photoproducts result from either UV or visible flash photolysis of Cp₂Fe₂(CO)₄ in cyclohexane or benzene.⁷ They observed CpFe(CO)₂ fragments as well as a long-lived intermediate that decayed by first-order kinetics. The long-lived intermediate reacted with donor ligands to give substituted products of the type Cp₂Fe₂(CO)₃L.

Owing to our interest in metal cluster photochemistry, we decided to investigate further the photoreactions of Cp₂Fe₂(CO)₄ with phosphines and chlorocarbons. The objective of our work was to determine whether 17-electron CpFe(CO)₂ fragments are involved as intermediates in these reactions or whether some other

pathway predominates. A preliminary account of our findings has appeared.⁸

Experimental Section

Cp₂Fe₂(CO)₄ was obtained from ROC/RIC. Phosphine and phosphite derivatives of the type Cp₂Fe₂(CO)₃(PR₃) were prepared by a standard method.⁶ Triphenylphosphine (PPh₃) and trimethyl phosphite (P(OMe)₃) were obtained from MCB. Tri-*n*-butylphosphine (P(*n*-C₄H₉)₃) and triisopropyl phosphite (P(O-*i*-Pr)₃) were obtained from Aldrich. Ethyl chloride was obtained from Eastman.

Electronic absorption spectra were recorded with a Cary 17 spectrophotometer. Infrared spectra were recorded with Perkin-Elmer 225 and Beckman IR-12 instruments. A 1000-W high-pressure Hg-Xe arc lamp was used for the 336-, 450-, and 505-nm and "broad-band" irradiations. The 366-nm Hg line was isolated by using a Corning CS 7-83 filter; the 450- and 505-nm lines were isolated by using dielectric interference filters obtained from Edmund Scientific Co. For the broad-band irradiations, Pyrex ($\lambda > 320$ nm) and Corning CS 3-69 ($\lambda > 500$ nm) filters were used. EPR spectra were recorded with a Varian E-line Century Series spectrometer, equipped with a 12-in. magnet. Temperature regulation was provided by an Air Products Heli-Trans system, and frequencies were determined with a PRD Electronics, Inc., frequency meter.

Ferrioxalate actinometry was used for quantum yield determinations at 366 nm.⁹ The procedure was modified to adopt the precautions suggested by Bowman and Demas.¹⁰ Reineke actinometry was used for quantum yields at 450 and 505 nm.¹¹ In all cases the quantum yields were determined by monitoring the disappearance of the 525-nm band in Cp₂Fe₂(CO)₄. The absorption spectra of the phosphine substitution products Cp₂Fe₂(CO)₃(PR₃) overlap with the spectrum of Cp₂Fe₂(CO)₄ at 525 nm. Thus, to minimize the error in the quantum yield measurement of the substitution reaction, only the first 10% of the reaction was monitored. At such small conversions the absorption by the product is

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