and M–Cl vibration band patterns[28] did not show distinct differences between known fac (**4a**) and mer (**5b**) geometries. In fact, the zirconium analogue of **4a**, $ZrCl_3[N(SiMe_2CH_2PMe_2)_2]$ (**5a**), displayed more absorptions in the far-IR region than any of the other mono(ligand) derivatives; it is possible that this zirconium complex crystallizes as a mixture of fac and mer, but this is pure speculation.

Conclusions

It would appear that these tridentate ligands prefer the meridional geometry in solution, but in the solid state other factors, presumably crystal packing, determine the coordination mode. The ligand's preference for the meridional configuration may be due to the planar $M-NSi_2$ unit found in all of these derivatives,[5,6,23,29] which could be less strained when the phosphine arms are trans disposed as compared to the cis orientation in the facial mode. Alternatively, it may be that the meridional geometry is preferred simply on steric grounds since this would minimize intramolecular, nonbonding repulsions between the $-PR_2$ groups of the ligand; while this is tenable for the bulky R = *i*-Pr and *t*-Bu substituents, molecular models of the $-PMe_2$ derivatives and the X-ray crystal structures of **4a** and **4a′** do not show any obvious steric congestion in the facial bonding mode. Certainly the formally d^0 metal centers (Zr(IV), Hf(IV)) would not be expected to exert any stereochemical influence.

These mono(ligand) derivatives are very reactive and can be used to generate group 4[30] alkyl and hydride derivatives; full details of this will be reported in due course.

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Registry No. *fac*-**4a**, 94372-14-2; *mer*-**4a**, 94481-25-1; **4b**, 94372-16-4; **4c**, 94372-18-6; **5a**, 94372-15-3; **5b**, 94372-17-5; **5c**, 94372-19-7; $LiN(SiMe_2CH_2PMe_2)_2$, 94372-10-8; $HN(SiMe_2CH_2Cl)_2$, 14579-91-0; $HN(SiMe_2CH_2PMe_2)_2$, 94372-11-9; $LiN(SiMe_2CH_2P(i\text{-}Pr)_2)_2$, 94372-12-0; $LiN(SiMe_2CH_2P(t\text{-}Bu)_2)_2$, 94372-13-1; $HP(t\text{-}Bu)_2$, 819-19-2; $LiPMe_2$, 21743-25-9; $LiP(i\text{-}Pr)_2$, 21502-53-4.

Supplementary Material Available: Listings of anisotropic thermal parameters (Table VI), calculated hydrogen coordinates and isotropic thermal parameters (Table VII), torsion angles (Table VIII), and observed and calculated structure factor amplitudes (Table IX–XI) (87 pages). Ordering information is given on any current masthead page.

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(30) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, and Istituto di Strutturistica Chimica,
Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy

Reaction of Copper(I)-*N*,*N*′-Ethylenebis(benzaldimine) Complexes with Carbon Monoxide and Isocyanides

ANDRAS TOTH,[†] CARLO FLORIANI,*[†] MARCO PASQUALI,[†] ANGIOLA CHIESI-VILLA,[‡]
AMELIA GAETANI-MANFREDOTTI,[‡] and CARLO GUASTINI[‡]

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Copper(I) halides, CuX (X = Cl, I), react with *N*,*N*′-ethylenebis(benzaldimine), BEN (PhCH=NCH$_2$CH$_2$N=CHPh), in a 1:1 molar ratio to form final products that are probably the dimers $[Cu_2X_2(BEN)_2]$ (II) via the intermediacy of monomeric solvated species, [Cu(X)(BEN)(S)] (I). A monomeric complex is isolated, when S = CO, by reacting CuI with BEN in a carbon monoxide atmosphere ([Cu(BEN)(CO)(I)] (III), ν(C–O) = 2066 cm^{-1}). With *p*-tolyl isocyanide the analogous monomeric complex [Cu(BEN)(*p*-MeC$_6$H$_4$NC)(I)] (IV) (ν(C–N) = 2135 cm^{-1}) is formed. The structures of complexes III and IV were determined by X-ray analyses, showing pseudotetrahedral coordination geometry for Cu(I) in both complexes (C–O = 1.12 (2) Å, *p*-MeC$_6$H$_4$N–C = 1.17 (1) Å). Derivative III represents the first example of a monomeric complex containing the [X–Cu–CO] fragment. When CuI is reacted with an excess of BEN under a carbon monoxide atmosphere and in the presence of NaBPh$_4$, ionization occurs to form $[Cu(BEN)_2](BPh_4)$ (V). The cation $[Cu(BEN)_2]^+$ possesses S_4 symmetry. In complexes II–V the C–N bond distances and stretching vibrations of ligated BEN are only slightly affected by the coordination to copper(I) and vary as follows: 1.267 (5)–1.28 (1) Å; 1625–1635 cm^{-1}. The ligated BEN does not cause a significant disproportionation of copper(I) to copper(II) and copper metal, even in the absence of carbon monoxide, while providing the appropriate electronic properties for binding CO. Such a ligand as BEN seems to affect the electronic balance at the metal by an extent that is intermediate between those of saturated amino ligands and of nitrogen donor heterocycles such as pyridine and 2,2′-bipyridine. Carbonylation of $[Cu(PhCO_2)]_4$, carried out in the presence of BEN, allows the isolation in the solid state of a dicopper(I) complex containing a bridging carbonyl (ν(C–O) = 1958 cm^{-1} (Nujol)), $[Cu_2(PhCO_2)_2(BEN)(\mu\text{-}CO)]$ (X). Crystallographic details for complexes III–V are as follows: complex III, space group $P2_1/n$ (monoclinic), a = 7.113 (2) Å, b = 17.204 (4) Å, c = 14.794 (4) Å, β = 97.87 (3)°, Z = 4, D_{calcd} = 1.68 g cm^{-3}, V = 1793.3 (8) Å^3, final R factor 0.043 for 1698 observed reflections; complex IV, space group $P\bar{1}$ (triclinic), a = 10.139 (7) Å, b = 13.427 (6) Å, c = 9.830 (4) Å, α = 91.56 (5)°, β = 111.31 (5)°, γ = 108.54 (5)°, Z = 2, D_{calcd} = 1.55 g cm^{-3}, V = 1167 (1) Å^3, R factor 0.042 for 2464 observed reflections; complex V, space group $I4_1/a$ (tetragonal), a = 17.167 (2) Å, b = 17.167 (2) Å, c = 15.463 (1) Å, Z = 4, D_{calcd} = 1.24 g cm^{-3}, V = 4557.0 (9) Å^3, final R factor 0.040 for 1049 observed reflections.

Introduction

A significant objective in copper(I) chemistry is the synthesis of a complex having a vacant coordination site and electron availability on the metal. These properties are a general prerequisite for the coordination and activation of small molecules like carbon monoxide or dioxygen. Many ligands stabilize the +1 oxidation state for copper, but only a few impart the appropriate properties for reaction with small molecules. Molecules containing S and P donor atoms are ligands par excellence for copper(I),[1]

[†] Università di Pisa.

[‡] Università di Parma.

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preventing any disproportionation to copper(II) and copper metal. Copper(I) complexes with P- and S-containing ligands, however, do not react with CO and dioxygen.[2] A wide range of characteristics was encountered with ligands having nitrogen donor atoms, depending on the denticity of the ligand and on the nature of the nitrogen donor group. Ligands containing unsaturated nitrogen atoms, such as acetonitrile, pyridine, 2,2′-bipyridine, and unsaturated macrocyclic ligands, impart to the metal some of the aforementioned properties for S- and P-containing ligands,[1] though the metal maintains some electronic flexibility.[3] Copper(I) bonded to amino groups is much more reactive, e.g. in reactions with molecular oxygen[4] or carbon monoxide,[5] though it can undergo a competing disproportionation to copper(II) and copper metal. In spite of this, ligands with amino groups in combination with oxygen donor ligands allowed the study of a large number of copper(I) carbonyls as model compounds for the activation of carbon monoxide.[5]

In the present paper we present our studies of the coordination to Cu(I) of the bidentate ligand *N*,*N*′-ethylenebis(benzaldimine), BEN ($PhCH{=}NCH_2CH_2N{=}CHPh$), containing nitrogen donor atoms with characteristics intermediate between those of 2,2′-bipyridine and ethylenediamine. Carbon monoxide and isocyanides coordinate to copper(I) halides in the presence of BEN; the synthesis and structure of such complexes are reported here.

Experimental Section

Syntheses were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by using a standard technique. CuCl,[6] CuI,[6] and *p*-tolyl isocyanide[7] were prepared by published procedures. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Synthesis of *N*,*N*′-Ethylenebis(benzaldimine), BEN. *N*,*N*′-Ethylenebis(benzaldimine) was prepared by refluxing an ethanolic solution (100 mL) of benzaldehyde (16.0 g, 150.9 mmol) and ethylenediamine (4.50 g, 75.0 mmol) for 20 h. By evaporation of the solvent, a yellow oil was obtained, which was crystallized from hot *n*-hexane. Slow cooling of the hexane solution gave yellow crystals of [$PhCH{=}NCH_2CH_2N{=}CHPh$], BEN (ca. 96%), mp 49 °C. Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.35; H, 6.78; N, 11.86. Found: C, 81.1; H, 6.79; N, 11.95. The Schiff base ligand BEN shows a strong large band (Nujol) at 1643 cm^{-1}.

Syntheses of [CuX(BEN)]$_2$ (X = Cl, I) (II). A tetrahydrofuran solution (50 mL) of BEN (1.26 g, 5.34 mmol) was reacted with an equimolar amount of the copper(I) salt CuX (X = Cl, I). A sudden solubilization of the copper salt was followed by the precipitation of the yellow microcrystalline solid (yield ca. 60%) [CuX(BEN)]$_2$. Anal. Calcd for $C_{32}H_{32}N_4Cl_2Cu_2$: C, 57.31; H, 4.78; N, 8.35. Found: C, 56.30; H, 4.65; N, 8.52. ν(C=N) = 1625 cm^{-1} (Nujol). Anal. Calcd for $C_{32}H_{32}N_4I_2Cu_2$: C, 46.77; H, 4.89; N, 6.82. Found: C, 46.83; H, 4.71; N, 6.83. ν(C=N) = 1624 cm^{-1} (Nujol).

Synthesis of [Cu(BEN)(CO)(I)] (III). To a tetrahydrofuran (30 mL) solution of BEN (1.30 g, 5.51 mmol) was added CuI (1.0 g, 5.25 mmol) under a carbon monoxide atmosphere. Copper(I) iodide dissolved, giving suddenly a yellow solution, from which a yellow solid precipitated. The suspension was kept stirring for 2 h (ν(C—O) = 2063 cm^{-1}). The solid was filtered out and dried in a carbon monoxide stream. (ν(C—O) = 2066 cm^{-1}, ν(C=N) = 1635 cm^{-1} (Nujol)) (yield ca. 57%). Yellow crystals suitable for an X-ray analysis were obtained by keeping the mother solution standing for 12 h. Anal. Calcd for [Cu(BEN)(CO)(I)] (III), $C_{17}H_{16}N_2OICu$: C, 44.89; H, 3.52; N, 6.16. Found: C, 44.94; H, 3.69; N, 5.95.

Synthesis of [Cu(BEN)(*p*-MeC$_6$H$_4$NC)(I)] (IV). A tetrahydrofuran solution (25 mL) of BEN (1.30 g, 5.51 mmol) was reacted with solid CuI (1.0 g, 5.25 mmol). *p*-Tolyl isocyanide (0.67 g, 5.49 mmol) was added to the resulting suspension (see above). A quick dissolution of the yellow precipitate occurred, forming a brownish yellow solution. After the solution was gently heated and kept reacting for 10 h, a yellow crystalline solid formed (ca. 37%) (ν(C≡N) = 2135 cm^{-} ν(C=N) = 1630 cm^{-1} (Nujol)). Yellow crystals of IV, suitable for the X-ray analysis, were obtained from the filtrate kept standing for days. Anal. Calcd for $C_{24}H_{23}N_3Cu$: C, 53.00; H, 4.26; N, 7.73. Found: C, 52.95; H, 4.23; N, 7.57.

Synthesis of [Cu(BEN)$_2$](BPh$_4$) (V). Copper(I) iodide (0.50 g, 2.63 mmol) was added to a THF solution (30 mL) of BEN (1.24 g, 5.25 mmol) under a carbon monoxide atmosphere. To the resulting orange solution was added NaBPh$_4$ (0.90 g, 2.63 mmol). Carbon monoxide was lost, and a yellow microcrystalline solid formed (ca. 43%). Yellow needlelike crystals of V, suitable for an X-ray analysis, were obtained from the mother solution after concentration by gentle heating. Anal. Calcd for $C_{56}H_{52}N_4BCu$: C, 78.64; H, 6.08; N, 6.55. Found: C, 78.70; H, 6.16; N, 6.47. ν(C=N) = 1625 cm^{-1} (Nujol).

Synthesis of [Cu$_2$(PhCO$_2$)$_2$(BEN)(μ-CO)] (X). A THF solution of cuprous benzoate (1.20 g, 5.83 mmol) was reacted with carbon monoxide. The absorption of CO was observed (ν(C—O) = 2080 cm^{-1}). Then a THF solution (30 mL) of BEN (1.53 g, 5.83 mmol) was added. Carbon monoxide was partially lost, and a yellow microcrystalline solid was formed. The solid was filtered out and dried under a carbon monoxide stream (ν(C—O) = 1958 cm^{-1}, ν(C=N) = 1633 cm^{-1} (Nujol)). Anal. Calcd for [Cu$_2$(PhCO$_2$)$_2$(BEN)(μ-CO)], $C_{31}H_{26}N_2O_5Cu_2$: C, 58.76; H, 4.11; N, 4.42. Found: C, 58.74; H, 4.35; N, 4.24. If complex X is dissolved in THF under a carbon monoxide atmosphere, the CO band falls at 2069 cm^{-1}, while under a nitrogen atmosphere no CO band was present.

Collection and Reduction of X-ray Data. The crystals selected for study were wedged into thin-walled glass capillaries and sealed under nitrogen. They were mounted on the diffractometer in a random orientation. A summary of crystal data and intensity data collection is given in Table I. The quoted reduced cells were obtained with use of TRACER.[8] Diffraction data were collected at 22 °C with analysis of individual reflection profiles[9] for complex (III). For complexes IV and V the "three-point" technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization reduction.[10] No correction for absorption was carried out for complex III. The data of complexes IV and V were corrected for absorption by following a semiempirical method[11] with maximum and minimum corrections of 1.230 and 1.015, respectively, for complex IV, and 1.426 and 1.007 for complex V.

Solution and Refinement of the Structures. The three structures were solved by conventional Patterson and Fourier methods. Only one-fourth of complex III is symmetry independent, having a 4-fold inversion axis passing through the Cu and B atoms. The full-matrix least-squares

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Table I. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes III–V

	III	IV	V
	$C_{56}H_{52}BCuN_4$	$C_{24}H_{23}CuIN_3$	$C_{17}H_{16}CuIN_2O$
cryst syst	tetragonal	triclinic	monoclinic
space group	$I4_1/a$ [C_{4h}^6; No. 88]	$P\bar{1}$ [C_i^1; No. 2]	$P2_1/n$[a]
cell parameters[b]			
a, Å	17.167 (2)	10.139 (7)	7.113 (2)
b, Å	17.167 (2)	13.427 (6)	17.204 (4)
c, Å	15.463 (1)	9.830 (4)	14.794 (4)
α, deg	90	91.56 (5)	90
β, deg	90	111.31 (5)	97.87 (3)
γ, deg	90	108.54 (5)	90
V, Å^3	4557.0 (9)	1167 (1)	1793.3 (8)
Z	4	2	4
D_{calcd}, g cm^{-3}	1.25	1.55	1.68
mol wt	855.4	543.9	454.8
cryst dimens, mm	0.26 × 0.22 × 0.46	0.32 × 0.32 × 0.51	0.42 × 0.13 × 0.54
linear abs coeff, cm^{-1}	9.55	22.6	29.3
diffractometer	Siemens AED	Philips PW 1100	
scan type	$\theta/2\theta$	$\omega/2\theta$	ω
scan speed	3–12°/min	0.075°/s	0.075°/s
scan width, deg	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $(\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda \tan\theta)$	1.50	1.20
radiation	Ni-filtered Cu Kα (λ = 1.5418 Å)	graphite-monochromated Mo Kα (λ = 0.7107 Å)	
2θ range, deg	6–20	6–48	6–53
reflcns measd	h,k,l	$\pm h,\pm k,l$	$\pm h,k,l$
unique total data	1684	3564	3706
criterion for obsn	$I > 2\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
unique obsd data	1049	2464	1698
no. of variables	192	262	199
overdetermination ratio	5.5	9.4	8.5
max shift/error on last cycle	<0.3	<0.3	<0.3

[a] A nonstandard setting of C_{2h} [No. 14]. Coordinates of equivalent positions are as follows: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$. [b] Unit cell parameters were obtained by least-squares analysis of the setting angles of 20 carefully centered reflections chosen from diverse regions of reciprocal space.

Table II. Fractional Atomic Coordinates ×10^4 for Complex III

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Cu	0 (0)	2500 (0)	6250 (0)	C15	1623 (3)	2049 (4)	3001 (3)
N1	133 (2)	1698 (2)	5234 (2)	C16	1080 (2)	2417 (2)	2459 (3)
C1	−130 (3)	2082 (2)	4430 (2)	H11	−716 (25)	2070 (24)	4380 (26)
C3	479 (2)	1051 (3)	5144 (3)	H12	69 (23)	1797 (23)	3908 (27)
C4	755 (2)	571 (2)	5859 (3)	H3	600 (27)	844 (27)	4514 (33)
C5	1364 (3)	54 (3)	5738 (3)	H5	1522 (30)	18 (30)	5173 (33)
C6	1631 (3)	−400 (3)	6406 (4)	H6	1998 (37)	−825 (39)	6286 (43)
C7	1302 (4)	−357 (3)	7194 (4)	H7	1555 (36)	−722 (36)	7705 (44)
C8	685 (4)	142 (3)	7326 (3)	H8	404 (35)	138 (35)	7910 (41)
C9	416 (3)	606 (3)	6668 (3)	H9	−88 (31)	964 (31)	6730 (33)
B	0 (0)	2500 (0)	1250 (0)	H12	355 (25)	871 (25)	1530 (28)
C11	604 (2)	2019 (2)	1882 (2)	H13	1132 (35)	259 (37)	2463 (40)
C12	691 (2)	1218 (2)	1900 (3)	H14	2088 (33)	1038 (33)	3345 (36)
C13	1218 (3)	842 (3)	2445 (3)	H15	2046 (32)	2357 (32)	3314 (36)
C14	1686 (3)	1262 (4)	2985 (3)	H16	997 (28)	2991 (29)	2540 (32)

Table III. Fractional Atomic Coordinates ×10^4 for Complex IV

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
I	5449 (0)	2684 (0)	3450 (1)	C11	866 (7)	2209 (5)	4363 (7)
Cu	2572 (1)	1706 (1)	1814 (1)	C12	2165 (7)	3040 (6)	4549 (8)
N2	1282 (6)	858 (1)	3070 (6)	C13	2400 (8)	4057 (6)	5142 (8)
N1	2534 (5)	207 (4)	1201 (6)	C14	1302 (10)	4248 (7)	5519 (8)
N	441 (7)	2869 (5)	466 (7)	C15	−28 (9)	3418 (7)	5317 (8)
C2	858 (8)	−275 (5)	2515 (8)	C16	−231 (7)	2411 (6)	4761 (7)
C1	2192 (8)	−427 (5)	2300 (7)	C17	1333 (9)	2455 (6)	875 (8)
C3	2848 (7)	−223 (5)	232 (7)	C18	−676 (8)	3341 (5)	21 (8)
C4	3244 (7)	289 (5)	−937 (7)	C19	−1421 (9)	3449 (6)	916 (8)
C5	3392 (9)	1341 (6)	−1106 (8)	C20	−2513 (10)	3912 (8)	417 (12)
C6	3736 (10)	1752 (7)	−2242 (9)	C21	−2859 (9)	4275 (7)	−891 (13)
C7	3975 (8)	1143 (7)	−3221 (9)	C22	−2129 (12)	4144 (8)	−1787 (11)
C8	3844 (8)	92 (7)	−3054 (8)	C23	−1015 (11)	3682 (7)	−1327 (9)
C9	3475 (7)	−326 (6)	−1918 (7)	C24	−4028 (12)	4810 (10)	−1439 (18)
C10	571 (7)	1100 (5)	3758 (7)				

refinement minimized the function $\sum w(\Delta|F|)^2$. Unit weights were used for complexes III and IV, while for complex V weights were applied according to the scheme $w^{-1} = [\sigma^2(F_o) + 0.002\, F_o^2]$. At convergence R[14] was 0.040, 0.042, and 0.043 for complexes I–III, respectively, and R_w[14]

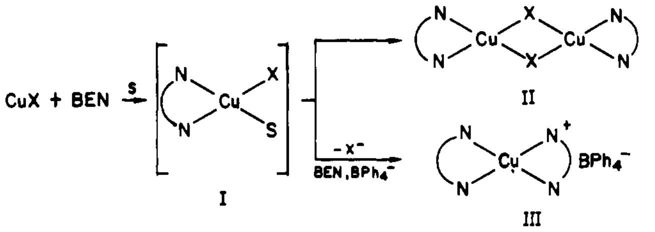
Table IV. Fractional Atomic Coordinates $\times 10^4$ for Complex V

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
I	1909 (1)	982 (0)	1928 (1)	C6	5807 (18)	1838 (7)	5265 (9)
Cu	5628 (2)	1014 (1)	2261 (1)	C7	6907 (19)	1692 (8)	6110 (8)
O	6996 (17)	2609 (6)	2453 (9)	C8	7854 (17)	1006 (10)	6258 (8)
N1	6282 (11)	99 (5)	3144 (5)	C9	7784 (16)	453 (7)	5560 (9)
N2	6689 (11)	299 (5)	1319 (6)	C10	7119 (14)	387 (6)	519 (7)
C	6558 (16)	1987 (7)	2384 (8)	C11	6808 (14)	1087 (7)	−29 (6)
C1	6228 (16)	−590 (6)	2563 (8)	C12	7885 (17)	1206 (8)	−735 (8)
C2	7320 (15)	−431 (6)	1785 (8)	C13	7710 (21)	1872 (10)	−1261 (8)
C3	6727 (14)	−10 (6)	3996 (7)	C14	6417 (21)	2415 (9)	−1117 (9)
C4	6771 (14)	605 (6)	4708 (7)	C15	5250 (19)	2305 (8)	−445 (9)
C5	5742 (16)	1296 (7)	4557 (8)	C16	5470 (16)	1655 (7)	107 (8)

(complex III) was 0.047 with an error in an observation of unit weight[15] of 0.95. Atomic scattering factors were taken from ref 12 (and included anomalous scattering contributions) for non-hydrogen atoms and from ref 13 for H. Hydrogen atoms located from difference Fourier syntheses were included in fixed positions (B_{iso} = 6.3 Å^2) for complexes IV and V while for complex III their positional and isotropic thermal parameters were allowed to refine. The maximum electron density on the final difference Fourier syntheses of complexes IV and V was <0.9 e/Å^3 and was in the vicinity of the iodine atom position. No significant peak above the general background was present in the final difference map of complex III.

Results and Discussion

Reaction of copper(I) halides, CuX (X = Cl, I), with *N*,*N*′-ethylenebis(benzaldimine), BEN, in a 1:1 molar ratio in THF led to the isolation of complexes I containing the intact [Cu–X] unit. The proposed structure for complexes I is based on the analytical data, on the structure of $[(\text{tmen})_2\text{Cu}_2\text{I}_2]$[16] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) obtained by the same reaction, and on the structure of closely related complexes described later. Complexes II supposedly are formed via the mononuclear solvated species I, which was isolated when S was replaced by CO or *p*-tolyl isocyanide (vide infra). When reaction 1 was carried out in the presence of an excess of BEN ligand and $NaBPh_4$, the ionization of the Cu–X bond occurs and complex III is formed. The best way to perform this reaction is to carry it out under a carbon monoxide atmosphere, so that the reaction of BEN in excess is probably occurring on the preformed [Cu(BEN)(CO)(I)] (vide infra). III was isolated as a yellow crystalline solid, whose X-ray structure is reported (vide infra). The C═N stretching frequency of the ligand BEN is only slightly affected upon coordination to the metal, since it is shifted down by ca. 20 cm^{-1} in complexes II and III. Reaction 1 occurred without significant disproportionation of copper(I) to copper(II) and copper metal. The tendency to disproportionate is related to the nature of the nitrogen donor atoms. Saturated amino groups promote a facile disproportionation of copper(I), while nitrogen donor atoms in aromatic molecules such as pyridine and 2,2′-bipyridine stabilize the +1 oxidation state. The BEN ligand seems to have, as expected, properties intermediate between those of the two classes of nitrogen donor ligands.

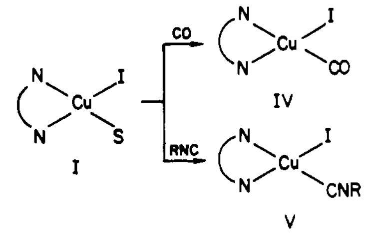


(1)

X = Cl, I; S = THF

N‿N = BEN = *N*,*N*′- ethylenebis(benzaldimine) $(PhCH{=}NCH_2CH_2N{=}CHPh)$

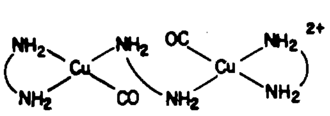
When reaction 1 was carried out under a carbon monoxide atmosphere or in the presence of *p*-tolyl isocyanide, the solvent molecule, S, in the proposed intermediate species I is replaced by either CO or $p\text{-MeC}_6\text{H}_4\text{NC}$:



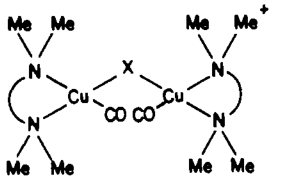
(2)

R = $p\text{-MeC}_6\text{H}_4\text{NC}$

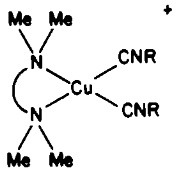
Both complexes IV and V have been structurally characterized (vide infra). It should be emphasized that complex IV does contain the [I–Cu–CO] fragment, which has been supposed to be present when carbon monoxide is absorbed by copper(I) halides.[17] Neutral copper(I)–carbonyl complexes containing the [Cu–X] unit have never been identified.[17,18] Utilization of amino ligands leads to the ionization of the Cu–X bond in the presence of either CO or isocyanides. As a proof of this, complexes VI–VIII have been isolated.[19,20] On the other hand, it seems that ligands containing unsaturated nitrogen donor atoms (py, MeCN) are competitive with carbon monoxide in binding copper(I), except for those cases in which they belong to a polydentate ligand.[21]



VI



VII



VIII

H₂N‿NH₂ = $NH_2CH_2CH_2NH_2$; Me₂N‿NMe₂ = $Me_2NCH_2CH_2NMe_2$

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(14) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$.

(15) Defined as $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variable parameters.

(16) Toth, A.; Floriani, C., unpublished results.

(17) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209–226 and references therein.

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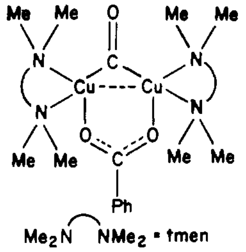
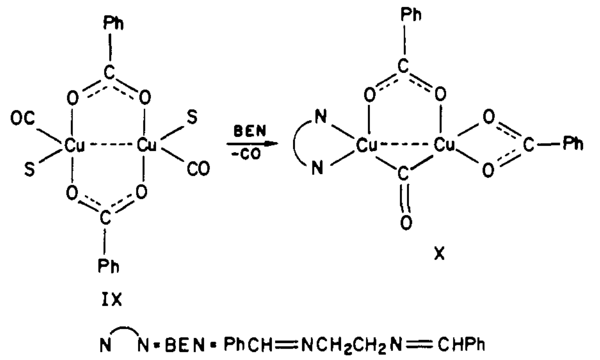
(20) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *Inorg. Chem.* **1979**, *18*, 3535–3542.

The absorption of carbon monoxide by dimeric complexes [Cu(bpy)X]$_2$ (bpy = 2,2′-bipyridine, X = Cl, I) has recently been described.[22] The structure of the copper(I) complexes in solution is attributed to the solvent used: the halogen-bridged dimer is supposed to be the dominant form in acetone, while ethanol is suggested to cleave the halogen bridge to give a solvated form. In both solvents absorption of carbon monoxide is observed, forming different complexes. A single CO is absorbed by the dimer in acetone to form, as proposed, a five-coordinated copper(I) binding CO, while the second copper(I) does not bind CO. In ethanol, formation of the monomeric carbonyl complex [Cu(bpy)(CO)X] from the corresponding solvated form was proposed to occur. No X-ray diffraction evidence is available, however, for these proposed structures for the bipyridine–copper(I) complexes. Our results for the related BEN complexes in THF show that, while the dimeric structure of complexes I occurs in the solid state, they probably form a solvated species in solution that is the common precursor of complexes III–V.

Carbonylation of copper(I) benzoate in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, tmen, gave the first bridging carbonyl in copper(I) chemistry:[23]



A related reaction was carried out with use of BEN, instead of tmen, as ancillary ligand. Copper(I) benozate gives a labile carbonyl compound, IX,[23b] in THF, which partially loses carbon monoxide in the reaction with BEN. A microcrystalline solid formed, having a CO stretching band at 1958 cm^{-1}. This is diagnostic for the presence of a bridging carbon monoxide in copper(I) complexes.[23] The structure of X is suggested on the basis of the presence of a bridging CO, on the analytical data, and on the structure of similar dicopper(I) complexes containing bridging CO.[23] Complex X contains a labile CO, which is lost on dissolving the solid in THF under a nitrogen atmosphere. Under a carbon monoxide atmosphere and in solution, X displays a CO band at 2070 cm^{-1}, for a terminal CO. The splitting of the bridging carbon monoxide by a coordinating solvent has already been observed for other dicopper(I)–bridging carbonyl complexes.[23]



(3)

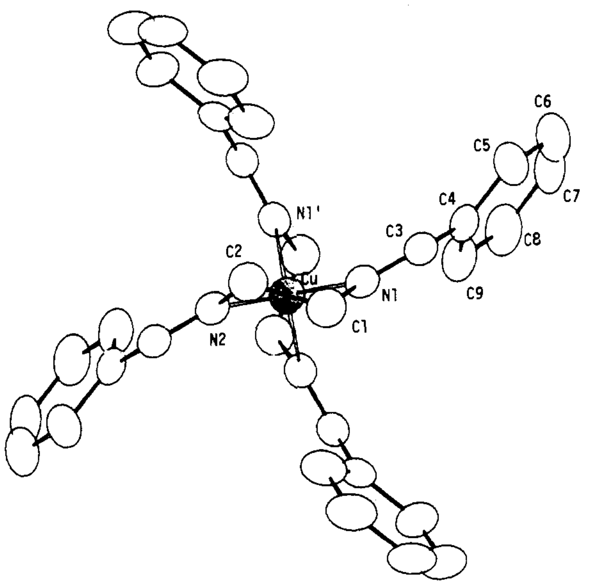


Figure 1. ORTEP projection of the cation of III viewed along the $\bar{4}$ axis (50% probability ellipsoids, hydrogens omitted for clarity). Primes denote the symmetry operation $y - {}^1/_4$, $\bar{x} + {}^1/_4$, $\bar{z} + {}^5/_4$; N2 and C2 are related to N1 and C1, respectively, by the symmetry operation $\bar{x}$, ${}^1/_2 - y$, z.

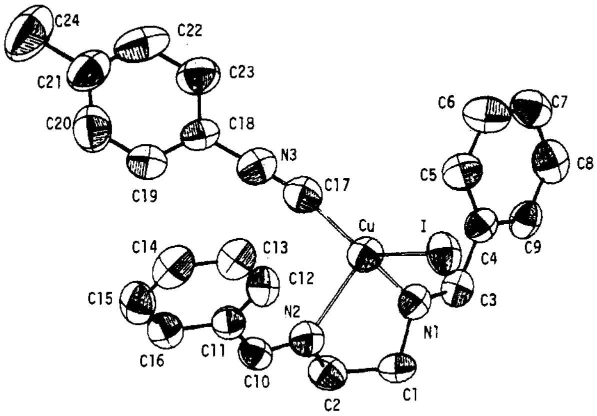


Figure 2. ORTEP diagram of IV (50% probability ellipsoids, hydrogen atoms omitted for clarity).

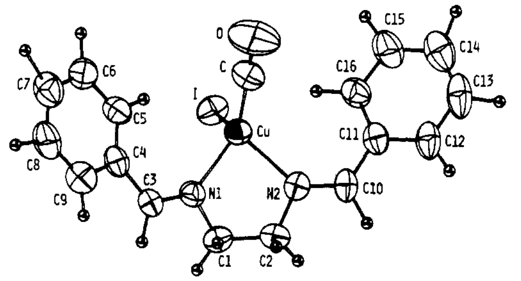


Figure 3. ORTEP diagram of V (50% probability ellipsoids).

Description of the Solid-State Structure of Complexes III–V. The structure of complex III consists of discrete [Cu(PhCH=NCH$_2$CH$_2$N=CHPh)]$^{2+}$ cations and [BPh$_4$]$^-$ anions (Figure 1) having the copper and boron atoms on a 4-fold inversion axis parallel to [001] at a distance of ${}^1/_2c$ to each other. No contacts less than 3.5 Å are present between the two ions. Complexes IV and V contain the Cu(PhCH=NCH$_2$CH$_2$N=CHPh) unit bonded to iodine and *p*-tolyl isocyanide or carbon monoxide (Figures 2 and 3). In all complexes coordination around copper is distorted tetrahedral. The Schiff base is chelating the metal through the nitrogen atoms. Except for the orientation of the phenyl rings, the geometry of Cu(PhCH=NCH$_2$CH$_2$N=CHPh) is practically

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Table V. Selected Bond Distances (Å) and Angles (deg)

Complex III[a]			
Cu-N1	2.101 (3)	N1-C3	1.267 (5)
N1-C1	1.478 (5)	C3-C4	1.458 (6)
C1-C2	1.503 (5)		
N1-Cu-N2	83.2 (1)	Cu-N1-C3	135.0 (3)
N1-Cu-N1'	124.0 (1)	C1-N1-C3	116.2 (3)
Cu-N1-C1	107.7 (2)	N1-C3-C4	124.4 (4)

	complex V	complex IV
Cu-N1	2.070 (7)	2.058 (8)
Cu-N2	2.199 (6)	2.077 (9)
Cu-I	2.619 (3)	2.624 (2)
Cu-C	1.858 (9)	1.800 (9)
N1-C1	1.47 (1)	1.46 (1)
N2-C2	1.47 (1)	1.47 (1)
C1-C2	1.52 (1)	1.50 (2)
N1-C3	1.28 (1)	1.27 (1)
N2-C10	1.26 (1)	1.27 (1)
C3-C4	1.47 (1)	1.49 (2)
C10-C11	1.48 (1)	1.45 (2)
C-N	1.17 (1)	
C-O		1.12 (2)
N-C18	1.41 (1)	
N1-Cu-N2	83.4 (2)	84.4 (4)
I-Cu-C	121.4 (3)	112.7 (4)
I-Cu-N1	101.4 (2)	103.7 (2)
I-Cu-N2	113.1 (2)	108.1 (3)
N1-Cu-C	131.2 (3)	126.8 (4)
N2-Cu-C	98.7 (4)	117.2 (5)
Cu-N1-C1	105.8 (4)	105.2 (6)
Cu-N1-C3	136.1 (5)	138.3 (8)
C1-N1-C3	117.7 (6)	116.5 (9)
N1-C3-C4	125.7 (7)	125.1 (9)
Cu-N2-C2	104.3 (5)	107.8 (7)
Cu-N2-C10	134.6 (5)	116.1 (9)
C2-N2-C10	117.8 (6)	116.1 (9)
N2-C10-C11	123.6 (7)	125.5 (9)
Cu-C-N	167.9 (7)	
Cu-C-O		174.7 (11)
C-N-C18	176.9 (8)	
N-C18-C19	120.7 (7)	
N-C18-C23	118.4 (8)	

[a] The apex indicates the symmetry operation $y - {}^1/_4, \bar{x} + {}^1/_4, \bar{z} + {}^5/_4$, while the atoms related to N1 and C1 by the symmetry operation $\bar{x}, {}^1/_2 - y, z$ are labeled N2 and C2, respectively, to make the discussion on the three complexes uniform.

the same in the three complexes. The Cu–N distances (2.058 (8)–2.101 (3) Å) fall in the lower part of the range usually observed for this type of bond,[17,20,23a] except the Cu–N2 distance (2.199 (6) Å) for complex IV, which is significantly longer than the others. This lengthening is probably a consequence of steric hindrance between the C11...C16 and C18...C23 phenyl rings. The different sizes of the coordinating ligands are also responsible for some differences observed in the bond angles around copper and nitrogen (Table V) and for the different twists of the phenyl rings around their axes. The N–Cu–N bite angles are, however, not significantly different: 83.2 (1), 83.4 (2), and 84.4 (4)° in complexes III, IV, and V, respectively. In complex III the four Ph rings are twisted by 25.6 (3)° with respect to the C3–C4 bond and assume the configuration imposed by the presence of the crystallographic $\bar{4}$ axis (Figure 1). In complexes IV and V the torsion angles around the C3–C4 and C10–C11 bonds are 2.8 (6) and 16.7 (5)°, respectively, for complex IV and 20.2 (8) and 22.5 (8)°, respectively, for complex V. The conformations of the five-membered chelate rings are λ and δ, respectively, for the two rings in complex III, and it is λ for complexes IV and V (referred to the coordinates quoted in the tables), even if in complex V the C2 atom lies on the CuN_2 plane. All the coordinated nitrogen atoms are slightly but significantly pyramidal, except the N1 atom of complex V, whose geometry is planar (Table SVII). The torsion angles around the C1–C2 bond are −53.5 (4)° in complex III, −61.4 (8)° in complex IV, and −51.1 (11) in complex V. The N–C and C–C bond distances in the chelate rings correspond well to single bonds (Table V). The values of the N–C distances (1.26 (1)–1.28 (1) Å) external to the chelation rings are very close to the value accepted for a double $N_{sp^2}{=}C_{sp^2}$ bond (1.26 Å).

The Cu–I distances (2.619 (3) Å in complex IV, 2.624 (2) Å in complex V) are in good agreement with those observed in the $[Cu_2(tmen)_2(CO)_2(I)]^{2+}$ cation,[17] where iodine is bridging two $Cu(tmen)_2(CO)_2$ units, and the Cu–C distances (1.859 (9) Å in complex IV and 1.800 (9) Å in complex V) agree well with those observed in other Cu–isocyanide[20] and Cu–carbonyl[17] complexes, respectively. The Cu–C–N (167.9 (7)°) and Cu–C–O (174.7 (11)°) systems show significant departure from linearity.

All the other bond distances and angles within the structures fall in the usual range (Table SVI).

Some of the results obtained by using the BEN ligand with copper(I) halides can be summarized as follows. The BEN ligand seems to have properties that are intermediate between those of amino-saturated groups and unsaturated nitrogen belonging to heterocyclics. It (i) provides marginal stabilization of the Cu(I) state and (ii) in the presence of halides permits binding of carbon monoxide without the Cu–X bond cleavage.

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Registry No. II (X = Cl), 94249-94-2; II (X = I), 94249-97-5; III, 94278-60-1; IV, 94249-95-3; V, 94249-96-4; X, 94249-98-6; BEN, 104-71-2; benzaldehyde, 100-52-7; ethylenediamine, 107-15-3.

Supplementary Material Available: Listings of observed and calculated structure factors, unrefined hydrogen coordinates for complexes IV (Table SI) and V (Table SII), thermal parameters (Tables SIII–V), nonessential bond distances and angles (Table SVI), and least-squares planes (Table SVII) (44 pages). Ordering information is given on any current masthead page.