Copper(I)–Carbon Monoxide Chemistry: Genesis and Chemical and Structural Properties of Copper(I) Terminal and Bridging Carbonyls[†]

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Abstract: Carbonylation of copper(I) benzoate in methanol carried out in the presence of N,N,N',N'-tetramethylethylenediamine, tmen, or N,N,N',N'-tetramethylpropylenediamine, tmpn, led to the isolation of the only bridging copper(I) carbonyls so far identified, $[Cu_2(tmen)_2(\mu\text{-PhCO}_2)(\mu\text{-CO})](BPh_4)$ (IV), ν_{CO} (Nujol) 1926 cm^{-1}, and $[Cu_2(tmpn)_2(\mu\text{-PhCO}_2)(\mu\text{-CO})](BPh_4)$ (V), ν_{CO} (Nujol) 1925 cm^{-1}. The most relevant structural parameters are the Cu–C bond distances, which range from 1.860 (6) to 1.882 (8) Å, while the C–O bond distances are rather unaffected by the bonding mode of the bridge: 1.143 (11) Å (complex IV) and 1.159 (11) Å (complex V). The Cu–Cu distances are surprisingly short: 2.410 (1) Å (complex IV) and 2.417 (2) Å (complex V). The genesis of IV involves the preliminary formation of a thermally labile precursor such as $[Cu(tmen)(CO)(CH_3OH)](BPh_4)$ (III), whose fate depends on the nature of the ligands present in the reaction medium. In the presence of $PhCO_2^-$ it is converted, at room temperature, to complex IV, whereas upon decomposition in the presence of an excess of tmen, it forms an unprecedented copper(I) tetraamino complex, $[Cu(tmen)_2](BPh_4)$ (VII). In the absence of any ligand, III forms an apparently 14-electron species, $[Cu(tmen)]^+$, which can be used as a convenient source for other copper(I) amino complexes. Crystallographic details for $[Cu_2(tmen)_2(\mu\text{-PhCO}_2)(\mu\text{-CO})](BPh_4)$: space group $I2$ (monoclinic); $a = 31.875$ (3), $b = 9.748$ (1), and $c = 14.344$ (2) Å; $\beta = 95.50$ (2)°; $Z = 4$; $D_{calcd} = 1.239$ g cm^{-3}. The final R factor was 0.043 for 2993 observed reflections. Crystallographic details for $[Cu_2(tmpn)_2(\mu\text{-PhCO}_2)(\mu\text{-CO})](BPh_4)$: space group $P2_1$ (monoclinic); $a = 10.946$ (1), $b = 20.467$ (2), and $c = 10.202$ (1) Å; $\beta = 99.24$ (1)°; $Z = 2$; $D_{calcd} = 1.260$ g cm^{-3}. The final R factor was 0.050 for 3480 observed reflections. Crystallographic details for $[Cu(tmen)_2](BPh_4)$: space group $C2$ (monoclinic); $a = 47.019$ (4), $b = 11.397$ (1), and $c = 10.266$ (1) Å; $\beta = 100.94$ (2)°; $Z = 6$; $D_{cald} = 1.135$ g cm^{-3}. The final R factor was 0.050 for 5466 observed reflections.

The fixation of CO by copper(I) is of interest and importance both in the area of metal-promoted CO reduction[1] and in the simulation of naturally occurring systems containing copper.[2] The chemical environment of copper(I) acting as an active site in binding carbon monoxide and other small molecules (e.g., O$_2$) is hard to define because of its high kinetic lability and its tendency to disproportionate to copper(II) and copper metal. These features of copper(I) chemistry make the solid-state isolation of complexes capable of fixing small molecules a hard task and, in addition, there is no direct relationship between the solid state and solution. A rigid coordination sphere around copper(I) overcomes, at least partially, these difficulties, as elegantly pointed out by Gagné.[3] However, such systems are less flexible in terms of available coordination sites on the metal for promoting the activation as well as the fixation of a small molecule.

We can add that the copper(I) chemistry is largely dominated by the dicopper(I) unit, which has been proposed as the active site in naturally occurring systems.[2,4] Strategies proposed by Lippard, Gagné, and Osborn allowed for the synthesis of model complexes containing such a unit.[5] In only a few cases, however, do the ligands have the requirements for forcing the two copper(II) centers into the appropriate proximity for interacting with the same hydroxo group.[5b] Especially the doubly bridged dicopper(II) complex prepared by Lippard[5b] can be considered a structural model for some dinuclear complexes reported here.

Recently, we reported synthetic procedures allowing the isolation of a rich series of mono- and dinuclear copper(I) carbonyls[6–8] in the solid state. In the case of the dinuclear complexes, however, the two coppers(I) are so far apart that they are independent of each other.[7,8] A modified strategy allows the achievement of the first binuclear copper(I) complex containing a bridging carbonyl. Such a dimetallic unit can be considered as a structural model for the fixation of other small molecules, including O$_2$. The genesis and structural properties of such a unit are the subject of the present report. A brief account of this work appeared recently.[9]

Experimental Section

General. Owing to the air sensitivity of the complexes, all operations were carried out under a dry oxygen-free nitrogen or carbon monoxide atmosphere, using standard Schlenk techniques. Solvents were purified and dried by standard methods, N,N,N',N'-Tetramethylethylenediamine, tmen, and N,N,N',N'-tetramethyl-1,3-propanediamine, tmpn, were dried and distilled before use. Preparation of $[Cu(MeCO_2)]_n$ was carried out

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as reported,[10] and the slightly modified procedure used in the case of [Cu(PhCO$_2$)]$_4$[10] is given below. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer.

Preparation of [Cu(PhCO$_2$)]$_4$. Benzoic acid (30 g, 246 mmol) and copper(I) oxide (2.44 g, 17.06 mmol) were heated in refluxing xylene (300 mL) dried over sodium, until all the oxide had reacted. The green-blue solution crystallized on cooling the excess benzoic acid to form [Cu(PhCO$_2$)]$_4$ and a green copper(II) species. The copper(II) species and the excess benzoic acid were eliminated by washing the solid three times with dry methanol (10 mL); yield 5.2 g (82.6%).

Reaction of [Cu(PhCO$_2$)]$_4$ with Carbon Monoxide. [Cu(PhCO$_2$)]$_4$ suspended in methanol or tetrahydrofuran (THF) absorbed reversibly 1 mol of CO *per* copper atom (ν_{CO} 2080 cm^{-1} in methanol). All attempts to isolate a carbonyl derivative of copper(I) benzoate failed because CO was lost during the filtration.

Preparation of [Cu$_2$(tmen)$_2$(μ-CO)(μ-PhCO$_2$)](BPh$_4$) (IV). Copper(I) benzoate (2.69 g, 14.57 mmol) suspended in methanol (30 mL) absorbed carbon monoxide and gave a white microcrystalline solid that dissolved upon addition of a methanolic (10 mL) solution of tmen (2.17 mL, 14.57 mmol). The solution became slightly green and traces of metallic copper separated out. The IR spectrum showed a strong CO band at 2080 cm^{-1}. The filtered solution was added dropwise, under CO, to a methanolic (15 mL) solution of NaBPh$_4$ (2.49 g, 7.28 mmol). The appearance of a white crystalline solid was followed by its conversion into a yellow solid, and carbon monoxide was lost. All the operations were carried out under a carbon monoxide atmosphere, while the final yellow crystalline solid was filtered under a nitrogen atmosphere and dried in vacuo (5.39 g, 89.5%). Anal. Calcd for [Cu$_2$(tmen)$_2$(μ-CO)(μ-PhCO$_2$)](BPh$_4$) (IV), C$_{44}$H$_{57}$N$_4$O$_3$BCu$_2$: C, 63.86; H, 6.89; N, 6.77. Found: C, 63.81; H, 6.70; N, 6.67. The IR spectrum (Nujol) displays significant bands at 1926 cm^{-1} (ν_{CO}) and at 1400 cm^{-1} (PhCO$_2$).

Complex (IV) (0.573 g, 0.69 mmol) reacted with a toluene solution of P(OEt)$_3$ and gave 0.67 mmol of CO: CO/Cu molar ratio = 0.485. The yellow crystals are air stable in the solid state. The solid is only slightly soluble in toluene, in which the CO band at 1945 cm^{-1} suggests the same structure with a bridging CO found in the solid state. Complex IV (0.42 g) dissolved in THF (10 mL) gave a slightly green-yellow solution, the IR spectrum of which shows two CO bands at 1930 and 2060 cm^{-1}, due to one bridging and one terminal carbon monoxide.

Preparation of [Cu$_2$(tmpn)$_2$(μ-CO)(μ-PhCO$_2$)](BPh$_4$) (V). The preparation of the title complex was carried out as described for the corresponding tmen derivative. It was obtained as a yellow, slightly green crystalline solid (68.7% yield). Anal. Calcd for [Cu$_2$(tmpn)$_2$(μ-CO)-(μ-PhCO$_2$)](BPh$_4$) (V), C$_{46}$H$_{61}$N$_4$O$_3$BCu$_2$: C, 64.57; H, 7.13; N, 6.55. Found: C, 64.27; H, 7.29; N, 6.65. After the reaction of the solid (0.609 g, 0.71 mmol) with a toluene solution of P(OEt)$_3$ at 15.5 °C, 0.661 mmol of carbon monoxide was measured: CO/Cu molar ratio = 0.464. The IR spectrum (Nujol) displays a CO band at 1925 cm^{-1}, while the symmetric C–O stretching of the PhCO$_2$ group falls at 1400 cm^{-1}. Complex V is slightly soluble in toluene (ν_{CO} 1942 cm^{-1}), while it is much more soluble in THF (ν_{CO} 1925 and 2065 cm^{-1}). A decrease of the band at 1925 cm^{-1} coupled with an increase of the band at 2065 cm^{-1} occurs in a few hours.

Conversion of Complex III into Complex IV by the Action of Sodium Benzoate. Complex III (1.53 g, 2.73 mmol) was added to a methanolic solution (25 mL) of anhydrous PhCO$_2$Na (1.45 g, 10.07 mmol) kept in a carbon monoxide atmosphere at room temperature. Formation of a solid suspended in a light green solution and carbon monoxide evolution were observed. The suspension, stirred for 2 h, gave a yellow solid that was shown to be complex IV.

Preparation of [Cu(tmen)(CO)(MeOH)](BPh$_4$) (III). A carbonylated suspension of copper(I) benzoate (1.02 g, 1.38 mmol) in methanol (30 mL) was cooled to −40 °C and then reacted with a methanolic solution (10 mL) of tmen (0.82 g, 5.5 mmol). The resulting solution showed a CO band at 2080 cm^{-1}. The addition of NaBPh$_4$ (1.88 g, 5.5 mmol) dissolved in methanol (10 mL) was carried out at −30 °C. A white crystalline solid rapidly formed; this was filtered and dried at −30 °C in a stream of carbon monoxide (1.10 g, 35%). Anal. Calcd for [Cu-(tmen)(CO)(MeOH)](BPh$_4$), C$_{32}$H$_{40}$N$_2$O$_2$BCu: C, 68.76; H, 7.17; N, 5.02. Found: C, 67.77; H, 7.32; N, 5.15. The IR spectrum (Nujol) shows strong and sharp bands at 3520 and 2480 cm^{-1} (MeOH) and at 2080 cm^{-1} (ν_{CO}). The complex is thermally unstable, losing CO and MeOH at room temperature, both in the solid state and in methanolic solution, even in a carbon monoxide atmosphere (see next paragraph). The thermal lability of III significantly affects the elemental analytical determinations. Complex III suspended in toluene at room temperature decomposes giving methanol (GLC determined) in the range of 0.95–1.05

molecule *per* copper atom. In a few cases, the higher contents of methanol found depended on the incomplete drying (see above) of the solid.

Conversion of Complex III to Complexes VI and VII. [Cu(tmen)-(CO)(MeOH)](BPh$_4$) (1.67 g, 3.00 mmol) was suspended in a methanolic solution (30 mL) of tmen (2.00 mL, 12.80 mmol) at room temperature. The suspension, stirred for a few hours, gave a white crystalline solid that did not contain carbon monoxide (1.04 g, 56.4%). Anal. Calcd for [Cu(tmen)$_2$](BPh$_4$), C$_{36}$H$_{52}$N$_4$BCu: C, 70.32; H, 8.46; N, 9.12. Found: C, 69.91; H, 8.83; N, 9.06.

A suspension of complex III in methanol in the absence of an excess of tmen resulted in the formation of a white solid that was analyzed to be [Cu(tmen)(BPh$_4$)] (VI). Anal. Calcd for C$_{30}$H$_{36}$N$_2$BCu: C, 72.21; H, 7.22; N, 5.62. Found: C, 72.25; H, 7.36; N, 5.79.

Complex [Cu(tmen)(BPh$_4$)] (0.53 g, 1.06 mmol), when reacted with a methanolic solution (10 mL) of tmen (0.2 mL, 1.33 mmol), dissolved giving a solution from which [Cu(tmen)$_2$](BPh$_4$) (VII) crystallized out (0.42 g, 63%).

Carbonylation of [Cu(MeCO$_2$)]$_n$ in the Presence of tmen. Carbon monoxide was slowly absorbed by [Cu(MeCO$_2$)]$_n$ (0.55 g, 4.49 mmol) in methanol (30 mL). On addition of a methanolic solution (10 mL) of tmen (0.67 mL, 4.48 mmol), a light green solution (ν_{CO} 2063 cm^{-1}) was obtained. NaBPh$_4$ (1.69 g, 4.48 mmol) caused the precipitation of a white crystalline solid, which was washed and dried in a stream of CO. It was shown to be [Cu(tmen)(BPh$_4$)] (VI), containing no carbon monoxide (0.93 g, 42.1%). The filtered solution gave upon standing at 0 °C for a few days crystals of [Cu(tmen)$_2$](BPh$_4$) (VII), suitable for X-ray analysis.

Preparation and Properties of [Cu$_2$(tmen)$_2$(CO)$_2$(μ-MeCO$_2$)](BPh$_4$) (VIII). Complex III, [Cu(tmen)(CO)(MeOH)](BPh$_4$) (1.15 g, 2.05 mmol), added to a methanolic solution (30 mL) of dry MeCOONa (0.86 g, 10.50 mmol), lost carbon monoxide giving a light blue suspension, which was stirred for 12 h. The resulting light blue solution (ν_{CO} 2070 cm^{-1}) was concentrated in a stream of carbon monoxide and cooled to −80 °C for 12 h. A white solid crystallized (0.35 g, 44.5%). Anal. Calcd for [Cu$_2$(tmen)$_2$(CO)$_2$(μ-MeCO$_2$)](BPh$_4$), (VIII), C$_{40}$H$_{55}$N$_4$O$_2$BCu$_2$: C, 60.53; H, 6.94; N, 7.06. Found: C, 60.90; H, 7.00; N, 7.05. The IR spectrum (Nujol) shows a strong band at 2060 cm^{-1} for carbon monoxide and at 1430 cm^{-1} for the symmetric C–O stretching of the acetato group. Complex VIII, heated in the solid state for 3 h at 60 °C, turned yellow and the corresponding IR spectrum showed two CO bands of comparable intensity at 2060 and 1920 cm^{-1}. Further heating caused loss of CO rather than higher conversion of the terminal CO into a bridging CO. Complex VIII lost CO when heated in methanol and nonbridging carbonyl was observed.

X-ray Crystallography.[11] The crystals examined were wedged into thin-walled glass capillaries and sealed under nitrogen. Preliminary X-ray investigations (from rotation and Weissenberg photographs) and accurate examinations of the cell constants[12] showed the compounds to be monoclinic, and the crystal of VII to be mounted along the [$\bar{1}$01] axis of a monoclinic unit cell. A summary of crystal data and intensity data collection is given in Table I. Lattice constants were determined by least-squares refinement of the 2θ values for 20 reflections having θ > 33°, θ > 37°, and θ > 40° for complexes IV, V, VII, respectively. Data were collected at room temperature by using a single-crystal Siemens AED automated diffractometer. The pulse height discriminator was set to accept 90% of the Cu Kα peak. One reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of the standard reflection for any of the three compounds was observed during data collections. For intensity and background the "five-point technique"[13] was used. For complex VII a total of 8063 nonunique data were measured. After a sort-and-merge procedure 6083 reflections, (hkl), ($h\bar{k}l$), ($\bar{h}kl$), and ($\bar{h}\bar{k}l$), were obtained, representing a unique set in the space group $C2$ or two equivalent sets in the space group $C2/m$. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[14] No absorption corrections were made.

The function minimized during the least-squares refinement was $\sum \omega |\Delta F|^2$. The weighting scheme used was $\omega = k/[\sigma^2(F_o) + |g|(F_o^2)]$; k is redetermined after each structure factor calculation and refined by

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Table I. Summary of Crystal Data and Intensity Data Collection

	complex IV	complex V	complex VII
formula	$C_{44}H_{57}BCu_2N_4O_3$	$C_{46}H_{61}BCu_2N_4O_3$	$C_{36}H_{52}BCuN_4$
a, Å	31.875 (3)	10.946 (1)	47.019 (4)
b, Å	9.748 (1)	20.467 (2)	11.397 (1)
c, Å	14.344 (2)	10.202 (1)	10.266 (1)
β, deg	95.50 (2)	99.24 (1)	100.94 (2)
Z	4	2	6
M	827.9	855.9	615.2
calcd density, g cm^{-3}	1.239	1.260	1.135
space group	$I2^a$	$P2_1$	$C2$
μ, mm^{-1}	1.46	1.45	1.02
μr	0.2	0.4	0.3
2θ limits	6–120	6–130	6–130
unique obsd data	2993	3480	5466
unique total data	3440	4412	6083
cryst dimens, mm^3	0.19 × 0.29 × 0.71	0.40 × 0.76 × 0.61	0.50 × 0.52 × 0.56
radiation		Ni-filtered Cu Kα (λ = 1.54178 Å)	
criterion for obsn		$I > 2\sigma(I)$	
scan type		θ–2θ	
scan speed		2.5–10° θ/min	
scan range		±0.5° from peak center	
bkgd		stationary cryst at ±0.5°	

^{a} The unit cell parameters reduced to the standard setting C_2 (No. 5) are a = 33.677 (3), b = 9.748 (1), and c = 14.344 (2) Å; β = 109.59 (2)°. The transformation matrix from the $I2$ to $C2$ orientation is (–1,0,–1//0,–1,0//0,0,1). Coordinates of equivalent positions for the nonstandard $I2$ setting are (0, 0, 0; $^1/_2$, $^1/_2$, $^1/_2$); x, y, z; $-x$, y, $-z$.

Table II. Fractional Atomic Coordinates × 10^4 for [Cu$_2$(tmen)$_2$(CO)(PhCO$_2$)](BPh$_4$) (IV)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu(1)	1004 (0)	0	3071 (1)	C(53)	2848 (2)	–1493 (10)	6643 (5)
Cu(2)	1413 (0)	1186 (1)	4322 (1)	C(54)	2620 (2)	–813 (10)	7259 (6)
O(1)	1489 (1)	–1255 (5)	3063 (3)	C(55)	2757 (2)	407 (9)	7613 (6)
O(2)	1874 (1)	–168 (8)	4177 (3)	C(56)	3123 (2)	1026 (8)	7321 (5)
O(3)	677 (2)	2574 (9)	3605 (5)	C(61)	4159 (2)	463 (7)	7193 (4)
N(1)	767 (2)	–69 (7)	1651 (3)	C(62)	4228 (2)	1029 (9)	8075 (4)
N(2)	528 (2)	–1478 (8)	3312 (4)	C(63)	4506 (2)	491 (9)	8779 (5)
N(3)	1324 (2)	892 (8)	5765 (3)	C(64)	4735 (2)	–677 (10)	8630 (5)
N(4)	1740 (3)	2980 (9)	4745 (6)	C(65)	4669 (2)	–1284 (9)	7781 (5)
C(1)	374 (2)	–846 (12)	1654 (5)	C(66)	4385 (2)	–744 (8)	7077 (5)
C(2)	395 (2)	–1950 (10)	2351 (5)	H(1a)	300	–1297	970
C(3)	1065 (2)	–879 (12)	1128 (4)	H(1b)	125	–145	1798
C(4)	676 (4)	1273 (14)	1206 (6)	H(2a)	86	–2408	2346
C(5)	147 (3)	–827 (14)	3713 (7)	H(2b)	617	–2712	2158
C(6)	683 (4)	–2614 (13)	3905 (8)	H(7a)	1888	1442	6410
C(7)	1576 (5)	1868 (16)	6249 (8)	H(7b)	1441	2110	6891
C(8)	1618 (8)	2998 (21)	5767 (11)	H(8a)	1314	3490	5730
C(9)	1488 (2)	–477 (13)	6112 (6)	H(8b)	1848	3627	6171
C(10)	866 (3)	929 (19)	5933 (5)	H(22)	1844	–3076	2321
C(11)	1583 (5)	4306 (13)	4327 (10)	H(23)	2435	–4640	2076
C(12)	2175 (4)	2770 (17)	4728 (15)	H(24)	3075	–4585	3182
C(13)	916 (2)	1698 (9)	3623 (4)	H(25)	3143	–2899	4435
C(20)	1821 (2)	–1096 (7)	3596 (4)	H(26)	2566	–1284	4647
C(21)	2170 (2)	–2087 (7)	3503 (4)	H(32)	4436	3030	6836
C(22)	2132 (2)	–3027 (10)	2782 (6)	H(33)	4426	5553	6662
C(23)	2461 (3)	–3923 (13)	2652 (8)	H(34)	3759	6738	6173
C(24)	2821 (3)	–3874 (13)	3262 (7)	H(35)	3114	5393	5807
C(25)	2858 (2)	–2940 (10)	3965 (5)	H(36)	3138	2887	5891
C(26)	2533 (2)	–2032 (8)	4089 (4)	H(42)	3265	431	4716
B	3804 (2)	1037 (8)	6390 (5)	H(43)	3447	–292	3160
C(31)	3790 (2)	2747 (6)	6369 (4)	H(44)	4177	–382	2785
C(32)	4144 (2)	3535 (8)	6591 (4)	H(45)	4741	187	4025
C(33)	4139 (2)	4972 (8)	6507 (4)	H(46)	4581	806	5582
C(34)	3767 (2)	5633 (9)	6228 (5)	H(52)	3388	–1426	5878
C(35)	3409 (2)	4882 (9)	6018 (5)	H(53)	2748	–2488	6376
C(36)	3423 (2)	3462 (8)	6079 (4)	H(54)	2331	–1252	7462
C(41)	3900 (2)	623 (7)	5330 (4)	H(55)	2585	916	8126
C(42)	3593 (2)	348 (8)	4595 (4)	H(56)	3223	2011	7607
C(43)	3697 (2)	–38 (10)	3693 (4)	H(62)	4055	1942	8224
C(44)	4103 (3)	–98 (10)	3478 (5)	H(63)	4545	989	9454
C(45)	4416 (2)	216 (10)	4177 (5)	H(64)	4958	–1092	9171
C(46)	4324 (2)	565 (8)	5062 (5)	H(65)	4841	–2206	7645
C(51)	3355 (2)	402 (6)	6680 (4)	H(66)	4338	–1280	6417
C(52)	3210 (2)	–879 (8)	6364 (5)				

fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o^2)]/k$. The value for g was that giving the smallest variation of the mean value of $\omega(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. In the final stage of refinement, the

values for k and g were 1.000 and 0.002, respectively, for all the structures. The effects of anomalous dispersion were included in all structure factor calculations. Scattering factors were taken from ref 15 for Cu,

from ref 16 for O, N, C, and B, and from ref 17 for H.

Structure Solution and Refinement for Complex IV (Table II). The analysis of a three-dimensional Patterson map indicated that the vector distribution could be interpreted in the noncentrosymmetric space group *I*2. This choice was confirmed by successful refinement of the structure. Approximate coordinates for the two independent copper atoms were obtained from the Patterson synthesis. Two successive Fourier maps established the positions of the remaining nonhydrogen atoms. Refinement was by "blocked" (two blocks) full-matrix least squares, first isotropically to R = 0.11, and then anisotropically to R = 0.048. All hydrogen atoms but those of the methyl groups were introduced in structure factor calculations in idealized positions, riding with free isotropic thermal parameters on their parent atoms. The final R value was 0.043 (R_w = 0.045 and R_g = 0.057) for 2993 observed data. Since the crystal is chiral, we inverted all coordinates ($x, y, z \rightarrow -x, -y, -z$) and refined to convergence again. The resulting residuals R = 0.044, R_w = 0.046, and R_g = 0.059 allow one to conclude that the original assignment of crystal chirality is correct.

In the final cycle no shift-over-error ratio, Δ/σ, was greater than 0.5. The overdetermination ratio NO/NV was 2993:520 $\simeq$ 5.8:1 and GOF = 1.05. A final difference Fourier map revealed no unusual features.

Structure Solution and Refinement for Complex V (Table III). The structure was solved by the heavy-atom method. The initial assumption of space group $P2_1$, based on E statistics calculated as a function of sin θ, resulted in a satisfactory solution and refinement of the structure. ($\langle|E^2 - 1|\rangle$ is equal to 0.74, the theoretical value accepted for noncentrosymmetric structures.) Approximate coordinates for the two independent copper atoms were deduced from the Patterson synthesis. A series of structure factor and difference Fourier calculations revealed the remaining nonhydrogen atoms. Some trouble in this stage of the analysis arose from the presence of a pseudomirror plane passing through the copper atoms, which gave two images for the bridging ligands. The complete structure was achieved by successive cycles of blocked (two blocks) full-matrix least-squares refinement of the different images. The atoms associated with the cation were refined first isotropically, then anisotropically to R = 0.079 (up to this stage the BPh$_4^-$ anion was refined isotropically with "rigid-body" constraints). The anisotropic refinement of C(9) and C(10) resulted in unacceptable values for the distances involving these atoms and in abnormally high thermal parameters. A difference Fourier synthesis computed without the contribution of C(9) and C(10) showed the presence of some diffuse peaks around these atoms, which were then considered disordered. Only the model in which C(9) was statistically distributed in two positions (C(9) and C(9A)) converged in successive refinement. The two "partial" atoms were refined isotropically with site occupation factors of 0.6 and 0.4 for C(9) and C(9A) respectively. The remaining atoms were refined anisotropically and all contraints were removed in the final cycles. Only hydrogen atoms associated with the phenyl rings were introduced in calculated positions as fixed-atom contributions (U_{iso} = 0.08 Å^2). Convergence was reached with R = 0.060 (R_w = 0.060 and R_g = 0.079) for 3480 observed reflections (none rejected). Since the space group is *polar*, the chirality of the crystal was tested by inverting all coordinates ($x, y, z \rightarrow -x, -y, -z$) and refining to convergence once again. The resulting values (R = 0.059, R_w = 0.059, and R_g = 0.077) indicate that the "inverted" structure should be accepted. The previous data were then discarded.

In the final cycle of refinement no parameter was shifted by more than 0.3% of its standard deviation. The overdetermination ratio was 3480:504 $\simeq$ 6.9:1 and GOF = 1.80. In the final difference map there were no peaks greater than 0.4 e Å^{-3}.

Structure Solution and Refinement for Complex VII (Table IV). The systematic absences were consistent with the space groups $C2/m$ or $C2$, or Cm. E statistics calculated as a function of sin θ favor the acentric cases, ($\langle|E^2 - 1|\rangle$ equal to 0.76. The structure was solved by the usual heavy-atom method. From the three-dimensional Patterson map approximate coordinates were obtained for the two independent copper atoms, with one of them lying on the twofold axis of the noncentrosymmetric space group $C2$ according to the number of molecules in the unit cell (Z = 6). The choice of the space group was confirmed by successful solution and refinement of the structure. The successive Fourier maps revealed the atoms of the two independent BPh$_4^-$ anions, one of them showing a crystallographic C_2 symmetry. The atoms of the three independent tmen ligands were found in successive difference maps. The structure was refined by blocked (three blocks) full-matrix least squares,

Table III. Fractional Atomic Coordinates $\times$ 10^4 for $[Cu_2(tmpn)_2(CO)(PhCO_2)]$ (BPh_4) (V)

atom	x/a	y/b	z/c
Cu(1)	−155 (1)	−2500	−1896 (1)
Cu(2)	−1887 (1)	−2602 (1)	−709 (1)
O(1)	705 (5)	−3189 (3)	−677 (6)
O(2)	−887 (4)	−3284 (2)	392 (5)
O(3)	−2198 (7)	−1663 (4)	−2813 (8)
N(1)	1288 (6)	−1800 (3)	−1621 (7)
N(2)	66 (7)	−2913 (4)	−3728 (7)
N(3)	−2243 (8)	−2013 (5)	867 (8)
N(4)	−3563 (6)	−3079 (3)	−1228 (7)
C(1)	2344 (8)	−2093 (6)	−2048 (11)
C(2)	2087 (10)	−2322 (7)	−3510 (10)
C(3)	1373 (11)	−2961 (6)	−3779 (12)
C(4)	1697 (12)	−1688 (6)	−154 (11)
C(5)	947 (10)	−1182 (5)	−2295 (14)
C(6)	−544 (12)	−2552 (9)	−4902 (10)
C(7)	−408 (16)	−3604 (7)	−3779 (14)
C(8)	−2998 (15)	−2377 (14)	1639 (15)
C(10)	−4100 (14)	−3193 (12)	−16 (16)
C(11)	−1058 (12)	−1889 (7)	1800 (12)
C(12)	−2604 (20)	−1350 (9)	398 (17)
C(13)	−4471 (8)	−2751 (5)	−2237 (12)
C(14)	−3245 (12)	−3732 (6)	−1800 (23)
C(20)	176 (6)	−3421 (3)	225 (7)
C(21)	901 (6)	−3899 (3)	1142 (7)
C(22)	2112 (8)	−4054 (4)	1012 (10)
C(23)	2770 (10)	−4510 (6)	1877 (14)
C(24)	2213 (12)	−4791 (6)	2834 (13)
C(25)	1010 (12)	−4621 (5)	3033 (11)
C(26)	355 (9)	−4178 (4)	2145 (9)
C(30)	−1686 (7)	−2062 (4)	−2129 (8)
B	−6428 (8)	−621 (4)	−5923 (8)
C(31)	−7799 (6)	−417 (3)	−6745 (7)
C(32)	−8879 (7)	−483 (4)	−6155 (8)
C(33)	−10058 (7)	−330 (5)	−6855 (11)
C(34)	−10183 (8)	−109 (5)	−8166 (10)
C(35)	−9141 (8)	−48 (4)	−8746 (8)
C(36)	−7973 (7)	−193 (3)	−8055 (7)
C(41)	−6366 (6)	−412 (3)	−4356 (7)
C(42)	−5746 (6)	−763 (3)	−3287 (7)
C(43)	−5656 (8)	−550 (4)	−1965 (8)
C(44)	−6220 (8)	25 (4)	−1662 (10)
C(45)	−6826 (9)	390 (4)	−2701 (9)
C(46)	−6895 (7)	166 (4)	−3977 (8)
C(51)	−5318 (6)	−222 (3)	−6484 (6)
C(52)	−4997 (7)	−363 (3)	−7708 (8)
C(53)	−4071 (8)	−31 (4)	−8233 (9)
C(54)	−3423 (7)	464 (4)	−7508 (10)
C(55)	−3699 (8)	609 (5)	−6266 (10)
C(56)	−4634 (7)	285 (4)	−5773 (8)
C(61)	−6211 (7)	−1402 (4)	−6094 (6)
C(62)	−7129 (8)	−1835 (4)	−6627 (8)
C(63)	−6895 (11)	−2521 (5)	−6728 (10)
C(64)	−5796 (13)	−2762 (5)	−6278 (10)
C(65)	−4869 (11)	−2373 (5)	−5780 (9)
C(66)	−5063 (8)	−1693 (4)	−5688 (8)
C(9)	−4330 (22)	−2339 (13)	579 (24)
C(9a)	−4131 (36)	−2848 (21)	973 (40)

first isotropically to R = 0.114 and then anisotropically for all nonhydrogen atoms to R = 0.058. The hydrogen atoms associated with the phenyl rings were introduced in idealized positions with fixed isotropic temperature factors (U_{iso} = 0.08 Å^2) and not refined. At convergence the residual R was 0.053 (R_w = 0.056, and R_g = 0.076) for 5466 observed data (none rejected). To test the correct chirality of the crystal, we inverted all coordinates ($x, y, z \rightarrow -x, -y, -z$) and refined to convergence again. The resulting residuals (R = 0.050, R_w = 0.053, and R_g = 0.072) provide evidence that the correct crystal chirality is defined by the inverted coordinates.

In the final cycle of refinement, no parameter was shifted by more than 0.3% of its standard deviation. The overdetermination ratio was 5466:570 $\simeq$ 9.6:1 and GOF = 1.67. In the final difference map there were no peaks greater than 0.4 e Å^{-3}.

Results and Discussion

The absorption of carbon monoxide by copper(I) compounds [Cu^{I}X] is a general phenomenon observed either in aqueous acid

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Table IV. Fractional Atomic Coordinates × 10^4 for [Cu(tmen)$_2$](BPh$_4$) (VII)

| atom	x/a	y/b	z/c
Cu(1)	-1712 (1)	0 (0)	-7692 (1)
Cu(2)	-5000 (0)	-862 (1)	0 (0)
N(1)	-1288 (1)	-352 (4)	-8059 (4)
N(2)	-1588 (1)	1802 (4)	-7514 (4)
N(3)	-2117 (1)	-470 (4)	-9053 (4)
N(4)	-1889 (1)	-941 (4)	-6270 (4)
N(5)	-4718 (1)	-15 (5)	1577 (3)
N(6)	-4622 (1)	-1782 (5)	-374 (5)
C(1)	-1178 (2)	830 (9)	-8267 (9)
C(2)	-1269 (2)	1710 (8)	-7286 (9)
C(3)	-1115 (1)	-955 (9)	-6863 (6)
C(4)	-1284 (1)	-1108 (9)	-9228 (6)
C(5)	-1679 (2)	2452 (6)	-6399 (7)
C(6)	-1689 (2)	2431 (5)	-8788 (6)
C(7)	-2261 (1)	-1260 (9)	-8260 (6)
C(8)	-2200 (2)	-1029 (11)	-6874 (8)
C(9)	-2297 (1)	565 (8)	-9528 (7)
C(10)	-2062 (1)	-1138 (9)	-10225 (6)
C(11)	-1754 (2)	-2072 (7)	-5912 (7)
C(12)	-1867 (2)	-296 (8)	-5016 (7)
C(13)	-4430 (1)	-344 (9)	1331 (9)
C(14)	-4412 (2)	-1493 (12)	824 (11)
C(15)	-4756 (2)	-380 (9)	2891 (6)
C(16)	-4741 (1)	1277 (6)	1576 (7)
C(17)	-4653 (2)	-3090 (9)	-523 (14)
C(18)	-4535 (2)	-1398 (11)	-1601 (9)
B(1)	-3346 (1)	100 (5)	-7692 (4)
C(21)	-3379 (1)	351 (3)	-9289 (4)
C(22)	-3649 (1)	421 (5)	-10151 (4)
C(23)	-3681 (1)	523 (5)	-11489 (4)
C(24)	-3444 (1)	580 (4)	-12064 (4)
C(25)	-3170 (1)	511 (5)	-11293 (4)
C(26)	-3142 (1)	375 (4)	-9922 (4)
C(31)	-3608 (1)	731 (5)	-7085 (4)
C(32)	-3713 (1)	1832 (6)	-7503 (5)
C(33)	-3917 (1)	2441 (7)	-6953 (7)
C(34)	-4020 (1)	1976 (9)	-5940 (7)
C(35)	-3924 (1)	893 (9)	-5446 (5)
C(36)	-3718 (1)	274 (6)	-6028 (4)
C(41)	-3047 (1)	627 (4)	-6805 (4)
C(42)	-2920 (1)	1648 (5)	-7168 (4)
C(43)	-2670 (1)	2158 (6)	-6398 (5)
C(44)	-2545 (1)	1635 (6)	-5222 (5)
C(45)	-2669 (1)	654 (6)	-4801 (5)
C(46)	-2916 (1)	154 (5)	-5592 (4)
C(51)	-3353 (1)	-1342 (4)	-7615 (3)
C(52)	-3108 (1)	-2026 (4)	-7520 (4)
C(53)	-3117 (1)	-3246 (5)	-7586 (4)
C(54)	-3379 (1)	-3828 (1)	-7770 (4)
C(55)	-3623 (1)	-3171 (6)	-7854 (5)
C(56)	-3613 (1)	-1977 (5)	-7781 (5)
B(2)	0 (0)	-601 (7)	-5000 (0)
C(61)	-257 (1)	207 (5)	-4566 (4)
C(62)	-344 (1)	1275 (5)	-5199 (5)
C(63)	-577 (1)	1941 (6)	-4940 (5)
C(64)	-730 (1)	1555 (6)	-4010 (6)
C(65)	-657 (1)	511 (7)	-3394 (7)
C(66)	-427 (1)	-165 (5)	-3676 (5)
C(71)	174 (1)	-1389 (5)	-3785 (5)
C(72)	230 (1)	-1045 (6)	-2475 (5)
C(73)	415 (1)	-1664 (8)	-1434 (6)
C(74)	539 (1)	-2671 (8)	-1743 (8)
C(75)	487 (1)	-3088 (7)	-3022 (8)
C(76)	311 (1)	-2438 (6)	-4004 (6)

solutions or, to a lesser extent, in organic solvents.[18] Its dependence on the nature of the anion [X],[8,18] although known for a limited number of examples, is important.

The main purpose of the present investigation was to provide synthetic routes leading to dinuclear copper(I) complexes capable of reacting with small molecules, primarily with carbon monoxide.

A well-proven synthetic procedure for the isolation of a variety of copper(I) carbonyls[6-8] was applied to the carbonylation of (carboxylato)copper(I) derivatives [Cu(RCO$_2$)]$_n$, R = Me or Ph.[10] These materials were chosen because the copper(I) centers in these compounds are in very close proximity.[19]

Compound I takes up reversibly 1 mol of carbon monoxide *per* copper in either methanol or tetrahydrofuran (THF) solutions at room temperature. The IR spectrum (ν_{CO} 2080 cm^{-1}, R = Ph; ν_{CO} 2063 cm^{-1}, R = Me) shows the presence of terminal carbon monoxide only, in spite of the fact that the final carbonyl is very probably not a simple mononuclear species:

$$\frac{1}{2}[Cu(PhCO_2)]_4 + 2CO \xrightarrow{S = MeOH} \quad (1)$$
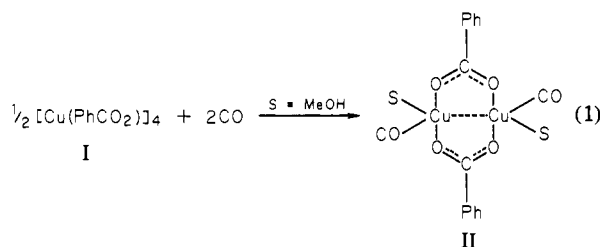
The structure proposed for II receives support from some indirect evidence from the solid-state of other Cu(I) benzoato species with coordinating unsaturated ligands, where the binuclear unit shown is always maintained.[20,21]

The absorption of carbon monoxide by copper(I) benzoate led to a significantly different result when carried out into the presence of N,N,N',N'-tetramethylethylenediamine, tmen. The resulting (see Experimental Section) light green solution (ν_{CO} 2080 cm^{-1}) gave, on addition of NaBPh$_4$ at room temperature, a thermally labile carbonyl complex (ν_{CO} 2080 cm^{-1}) (III), losing carbon monoxide to form a thermally stable yellow crystalline solid, [Cu$_2$(tmen)$_2$(μ-PhCO$_2$)(μ-CO)](BPh$_4$) (IV), as summarized schematically in eq 2. The isolation of III was achieved by

NN = tmen; S = MeOH

$$(2)$$
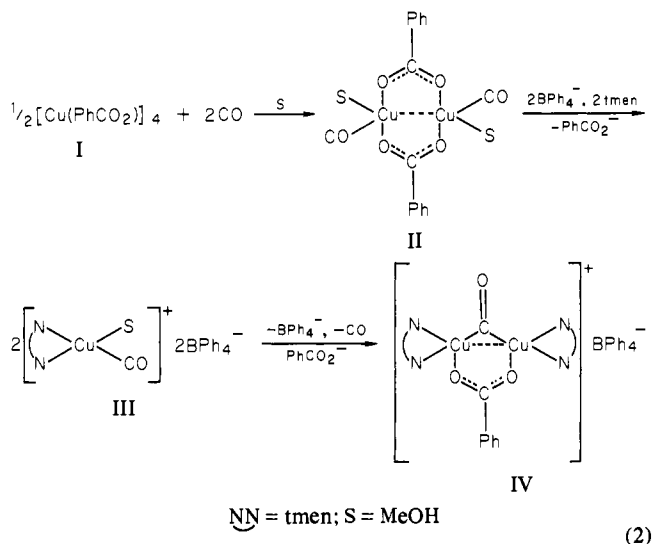
carrying out the addition of NaBPh$_4$ at 0 °C, since the transformation (III) → (IV) is prevented at low temperature. The last step of the proposed scheme is supported by the observed transformation of III to IV in the presence of sodium benzoate.

Before considering the influence of the factors leading to the successful isolation of the first dicopper(I) bridging carbonyl, we present the details of the structures of IV and [Cu$_2$(tmpn)$_2$(μ-PhCO$_2$)(μ-CO)](BPh$_4$) (V), obtained by replacing tmen by N,N,N',N'-tetramethylpropylenediamine (tmpn).

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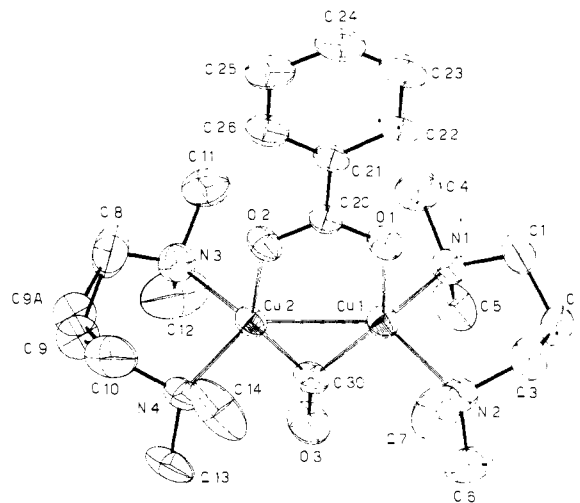(20) Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1975**, 637-43.

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Table V. Selected Interatomic Distances (Å) and Angles, (deg)

Complex IV

Cu(1)–C(13)	1.868 (8)	N(1)–Cu(1)–N(2)	86.6 (3)	C(1)–Cu(2)–C(13)	49.9 (2)
Cu(1)–O(1)	1.972 (4)	N(1)–Cu(1)–O(1)	100.6 (2)	Cu(1)–C(13)–Cu(2)	80.6 (3)
Cu(1)–N(1)	2.105 (5)	N(1)–Cu(1)–C(13)	112.6 (3)	Cu(1)–C(13)–O(3)	141.2 (6)
Cu(1)–N(2)	2.144 (7)	N(2)–Cu(1)–O(1)	98.7 (2)	Cu(2)–C(13)–O(3)	138.1 (6)
Cu(1)–Cu(2)	2.410 (2)	N(2)–Cu(1)–C(13)	112.9 (3)	O(1)–C(20)–O(2)	123.8 (6)
Cu(2)–C(13)	1.860 (6)	O(1)–Cu(1)–C(13)	134.6 (2)	O(1)–C(20)–C(21)	117.3 (5)
Cu(2)–O(2)	2.001 (4)	Cu(2)–Cu(1)–C(13)	49.6 (2)	O(2)–C(20)–C(21)	118.8 (5)
Cu(2)–N(3)	2.135 (5)	N(3)–Cu(2)–N(4)	86.6 (3)	C(20)–C(21)–C(22)	119.1 (6)
Cu(2)–N(4)	2.096 (9)	N(3)–Cu(2)–O(2)	100.3 (2)	C(20)–C(21)–C(26)	121.1 (6)
C(13)–O(3)	1.143 (11)	N(3)–Cu(2)–C(13)	111.9 (3)	C(26)–C(21)–C(22)	119.8 (6)
O(1)–C(20)	1.254 (7)	N(4)–Cu(2)–O(2)	103.3 (3)	Cu(1)–O(1)–C(20)	122.4 (4)
O(2)–C(20)	1.231 (4)	N(4)–Cu(2)–C(13)	107.9 (4)	Cu(2)–O(2)–C(20)	120.1 (4)
C(20)–C(21)	1.489 (9)	O(2)–Cu(2)–C(13)	135.8 (2)		

Complex V

Cu(1)–C(30)	1.882 (8)	N(1)–Cu(1)–N(2)	101.6 (3)	Cu(1)–Cu(2)–C(30)	50.1 (3)
Cu(1)–O(1)	2.011 (6)	N(1)–Cu(1)–O(1)	97.3 (3)	Cu(1)–C(30)–Cu(2)	80.4 (3)
Cu(1)–N(1)	2.117 (6)	N(1)–Cu(1)–C(30)	108.9 (3)	Cu(1)–C(30)–O(3)	138.3 (7)
Cu(1)–N(2)	2.100 (8)	N(2)–Cu(1)–O(1)	99.1 (3)	Cu(2)–C(30)–O(3)	141.3 (7)
Cu(1)–Cu(2)	2.417 (2)	N(2)–Cu(1)–C(30)	107.9 (3)	O(1)–C(20)–O(2)	124.8 (6)
Cu(2)–C(30)	1.863 (9)	O(1)–Cu(1)–C(30)	137.0 (3)	O(1)–C(20)–C(21)	116.5 (6)
Cu(2)–O(2)	2.003 (5)	Cu(2)–Cu(1)–C(30)	49.5 (2)	O(2)–C(20)–C(21)	118.7 (6)
Cu(2)–N(3)	2.096 (9)	N(3)–Cu(2)–N(4)	101.6 (3)	C(20)–C(21)–C(22)	120.6 (7)
Cu(2)–N(4)	2.071 (7)	N(3)–Cu(2)–O(2)	97.1 (3)	C(20)–C(21)–C(26)	118.9 (7)
C(30)–O(3)	1.159 (11)	N(3)–Cu(2)–C(30)	108.4 (4)	C(26)–C(21)–C(22)	120.4 (7)
O(1)–C(20)	1.256 (10)	N(4)–Cu(2)–O(2)	101.4 (2)	Cu(1)–O(1)–C(20)	119.5 (5)
O(2)–C(20)	1.235 (8)	N(4)–Cu(2)–C(30)	106.9 (3)	Cu(2)–O(2)–C(20)	121.5 (4)
C(20)–C(21)	1.491 (9)	O(2)–Cu(2)–C(30)	136.7 (3)		

Complex VII

Cu(1)–N(1)	2.136 (7)	N(1)–Cu(1)–N(2)	87.0 (2)	N(2)–Cu(1)–N(4)	124.6 (2)
Cu(1)–N(2)	2.133 (5)	N(3)–Cu(1)–N(4)	84.7 (2)	N(5)–Cu(2)–N(6)	86.6 (2)
Cu(1)–N(3)	2.204 (6)	N(1)–Cu(1)–N(3)	124.5 (2)	N(5)–Cu(2)–N(5)[a]	125.8 (2)
Cu(1)–N(4)	2.106 (5)	N(1)–Cu(1)–N(4)	122.1 (2)	N(5)–Cu(2)–N(6)[a]	120.1 (2)
Cu(2)–N(5)	2.120 (4)	N(2)–Cu(1)–N(3)	118.5 (2)	N(6)–Cu(2)–N(6)[a]	121.9 (2)
Cu(2)–N(6)	2.160 (5)				
Cu(1)–N(1)–C(1)	102.7 (5)	Cu(1)–N(3)–C(7)	103.4 (7)	Cu(2)–N(5)–C(13)	102.4 (4)
Cu(1)–N(2)–C(2)	101.4 (4)	Cu(1)–N(4)–C(8)	103.5 (4)	Cu(2)–N(6)–C(14)	100.9 (5)
Cu(1)–N(1)–C(3)	108.7 (3)	Cu(1)–N(3)–C(9)	112.8 (4)	Cu(2)–N(5)–C(15)	114.1 (5)
Cu(1)–N(1)–C(4)	114.1 (3)	Cu(1)–N(3)–C(10)	112.1 (3)	Cu(2)–N(5)–C(16)	114.7 (3)
Cu(1)–N(2)–C(5)	115.5 (4)	Cu(1)–N(4)–C(11)	114.6 (4)	Cu(2)–N(6)–C(17)	115.6 (5)
Cu(1)–N(2)–C(6)	110.6 (3)	Cu(1)–N(4)–C(12)	112.4 (4)	Cu(2)–N(6)–C(18)	112.4 (5)

[a] $\bar{x} - 1, y, \bar{z}$.
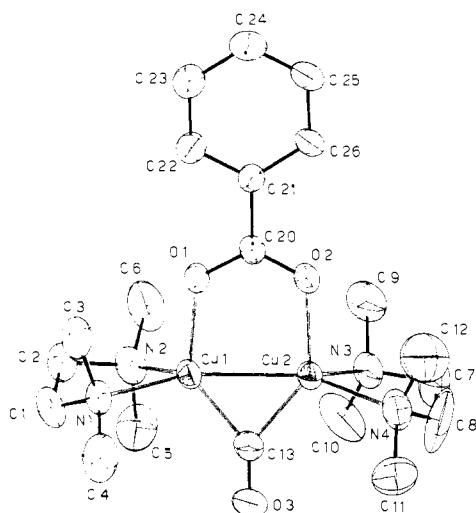
Figure 1. ORTEP diagram of the dinuclear unit $[Cu_2(tmen)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)]^+$, showing 30% probability ellipsoids.

Figure 2. ORTEP diagram of the dinuclear cation $[Cu_2(tmpn)_2(\mu\text{-}PhCO_2)(\mu\text{-}CO)]^+$, showing 30% probability ellipsoids.

Figures 1 and 2 give ORTEP views of the cations present in complexes IV and V, respectively. Related bond distances and angles are given in Table V. The structural data are rather similar in both complexes. The coordination geometry is pseudotetrahedral around each copper(I), with the five-membered rings (Cu–tmen) having λ (Cu(2), N(3), C(7), C(8), N(4)) and δ (Cu(1), N(1), C(2), N(2)) conformations in complex IV and with the six-membered rings (Cu–tmpn) having a chair conformation

around Cu(1) and Cu(2) and a half-chair conformation if C(9A) is considered in complex V. Copper(I)–nitrogen bonds are short, averaging 2.100 Å in complex V.[22] The dinuclear skeleton (Cu(1),

(22) Structural parameters concerning [Cu(tmen)] and [Cu(tmpn)] units are very close to those reported. See ref 8 and: Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *Inorg. Chem.* **1979**, *18*, 3535–42. Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Ibid.* **1979**, *18*, 2296–300.

Cu(2), O(1), O(2), C(20)) and the bridging CO are nearly co-planar in both complexes, the dihedral angles formed between the planes defined by (Cu(1), Cu(2) and >C=O) and by (Cu(1), Cu(2), O(1), O(2), C(20)) being 11.1° (complex IV) and 0.0° (complex V). The most relevant structural parameters concern the Cu(1)–CO–Cu(2) unit, and they include a very short Cu-(1)–Cu(2) proximity, (2.410 (2) Å in complex IV and 2.417 (2) Å in complex V),[23] and the longest Cu–C distance so far observed in copper(I) carbonyl chemistry:[3,6-8,24] Cu(1)–C(13), 1.868 (8) Å; Cu(2)–C(13), 1.860 (6) Å in complex IV; Cu(1)–C(30), 1.882 (8) Å; Cu(2)–C(30), 1.863 (9) Å in complex V. The Cu–C bond distances are significantly shorter than those found in copper-(I)-alkyl complexes.[25] The C–O bond distance is not affected by the bridging bonding mode displayed by carbon monoxide and it is very close to that found in a series of terminal carbonyl complexes: C(13)–O(3) = 1.143 (1) Å in complex IV and C-(30)–O(3) = 1.159 (11) Å in complex V.[3,6-8,24]

This is confirmed by the IR spectrum (Nujol) displaying CO bands at 1926 and 1925 cm^{-1} (complexes IV and V), which are at unusually high frequencies for a bridging CO. Two aspects of the structure described deserve comment. Whether a very short Cu(I)–Cu(I) distance means the existence of a bond seems to be a philosophical question,[23] so that close proximity of two Cu(I) atoms cannot contribute substantially to the stability of the di-nuclear skeleton. The most attractive feature of the structures of IV and V stems from their strong resemblance to the dinuclear units proposed to be present in many copper proteins.[4] We can say that the existence of such complexes is limited to the solid state or to nonpolar solvents like toluene, where, however, these complexes are poorly soluble. THF solutions show the simulta-neous presence of a terminal and a bridging CO at 2060 and 1930 cm^{-1} (complex IV) and at 2065 and 1925 cm^{-1} (complex V), which can be explained by the equilibrium shown

$$\text{(3)}$$

NN = tmen, tmpn

The special role of the bridging carboxylato RCO$_2^-$ group in bridging two copper(I) atoms close together is quite evident, and we found an unexpectedly large influence of the R substituent. When copper(I) benzoate was replaced by copper(I) acetate, we did not observe the sequence shown in (2). The carbonylation of copper(I) acetate carried out in the presence of tmen followed by the addition of NaBPh$_4$ gave the result summarized in eq 4 (see Experimental Section). The nature of the compounds ap-pearing in (4) will be discussed independent from their genesis.
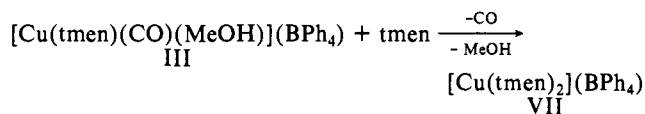

[Cu(tmen)(BPh$_4$)] $\xrightarrow{\text{tmen}}$ [Cu(tmen)$_2$](BPh$_4$) (4)

VI   VII

S = MeOH, NN = tmen

The direct carbonylation of [Cu(MeCO$_2$)]$_n$ does not lead to complexes containing the acetato group as a ligand. Access to

(23) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–9 and references cited therein.

(24) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Salah, O. M. A.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051–9.

(25) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131–44 and references cited therein.

such a complex was achieved by reacting III with an excess of sodium acetate:

2[Cu(tmen)(CO)(MeOH)](BPh$_4$) $\xrightarrow[\text{-BPh}_4^-, \text{-MeOH}]{\text{MeCO}_2^-}$

III

$$\text{(5)}$$

VIII

There is no evidence for a bridging CO group in the IR spectrum of complex VIII (ν_{CO} (Nujol) 2060 cm^{-1}). It lost carbon monoxide upon heating (60 °C) in the solid state to form a light yellow solid that displays two strong CO bands of comparable intensity at 2060 and 1920 cm^{-1}. The appearance of a CO band at 1920 cm^{-1} is diagnostic for the formation of a copper(I) bridging carbonyl coming from the following route:

VIII   IX

$$\text{(6)}$$

The total conversion of VIII into IX has never been observed, the maximum yield achieved being 50%, since extended heating led to decomposition rather than to an improvement of the yield of VIII. The result obtained by using copper(I) acetate confirms the preeminent role that the kinetic lability of copper(I) has in this chemistry and also the influence of solid-state effects. The role of the amino ligand is rather crucial and we found that starting from potentially polynuclear copper(I) compounds, tmen is able to "freeze" and stabilize a dicopper(I) unit [Cu–X–Cu], where X is the original anion in the copper(I) compounds. This is a

A

B

X = Cl, Br, I; N*N* = en, NN = tmen

quite general result, provided we have present fully alkylated chelating diamino ligands like tmen and tmpn.[8]

Less sterically hindered nitrogen atoms, as found in ethylene-diamine, en, allow the diamino ligand to display a bridging bonding mode.[6] Therefore the carbonylation of the same copper(I) halides in the presence of en and tmen gave different results, as shown above. This observation was further supported by the carbony-lation of copper(I) benzoate leading, in the presence of en, to complex A. Species like B have potential as precursors for bridging carbonyls; however the bond angles around the bridging halide ligand are such that they probably prevent the required CO elimination.[8] This prompted us to use the same approach for dicopper complexes having more sterically appropriate bridging

Figure 3. ORTEP drawing of the two independent cations, [Cu(tmen)₂]⁺, present in complex VII, showing 30% probability ellipsoids.

ligands, like the carboxylato group.

The chain length bridging the two dimethylamino residues seems not to be a relevant influence, so the utilization of *N,N,-N',N'*-tetramethylpropylenediamine, tmpn, allowed the isolation of [Cu₂(tmpn)₂(µ-PhCO₂)(µ-CO)](BPh₄) (V), (ν_{CO} 1925 cm⁻¹).

The key species that seems to be the precursor of all copper(I) carbonyl complexes isolated so far is a complex of type III, in which a bidentate amino ligand must be present. Although thermally labile, III can be isolated, as described in the Experimental Section, in the form of a tetraphenylborate derivative. It loses both methanol and CO simultaneously at room temperature, even in the solid state, and this is confirmed by the IR spectrum. When the same decomposition occurs in solution, the highly coordinatively unsaturated moiety [Cu(tmen)]⁺ can be isolated as a crystalline tetraphenylborate derivative, [Cu(tmen)(BPh₄)] (VI), which, very probably, exists in a tight ion-pair form, with the phenyl group of BPh₄⁻ interacting with the metal center, as was found in the X-ray analysis of the related [Cu(en)(CO)(BPh₄)].[6] Therefore, both III and VI can be considered appropriate sources for the [Cu(tmen)]⁺ unit in forming other complexes in the presence of coligands. The conversion of III and VI into VII occurs as a spontaneous reaction due to the presence of an excess of tmen in the reaction medium (see Experimental Section: Carbonylation of [Cu(MeCO₂)]ₙ). Figure 3 shows an ORTEP drawing of the two independent cations contained in

$$[\text{Cu(tmen)(CO)(MeOH)]}(\text{BPh}_4) + \text{tmen} \xrightarrow[-\text{MeOH}]{-\text{CO}}$$

$$\text{III}$$

$$[\text{Cu(tmen)}_2](\text{BPh}_4)$$
$$\text{VII}$$

complex VII. The coordination geometry around each copper is nearly tetrahedral, the dihedral angle between plane Cu(1), N(1), N(2) and plane Cu(1), N(3), N(4) being 86.1°. C–N bond distances fall in the range 2.214 (4)–2.204 (6) Å, found for other copper(I)–tmen complexes,[22] including IV and V. The conformation of both five-membered rings in cation C is λ, while it is δ in cation D. The isolation and structural characterization of a copper(I) complex containing only nitrogens as donor atoms are significant results, because the stability of copper(II) over copper(I) is normally largely enhanced by ethylenediamine-type ligands. Complex VII can be considered a unique structural model for tetrahedral copper(I) surrounded by saturated amino donor groups.[26]

Conclusions

The present contribution to copper(I) coordination chemistry can be summarized as mainly due to (i) the isolation and structural characterization of the first dicopper(I) unit, where both metal atoms interact with the same small molecule (complexes IV and V can be assumed to be structural models for the activation of other small molecules (e.g., O₂) promoted by copper(I); substitution of CO by other small molecules in complexes IV and V can be envisaged), (ii) the very strong resemblance between the dicopper(I) units proposed to be present in copper proteins and the very simple structure of IV and V, (iii) the possible role of a bridging carbonyl in copper-promoted reduction of carbon monoxide (this depends both on the bonding mode displayed by CO in complexes IV and V and on the fact that copper(I) acetate was the first discovered homogeneous hydrogenation catalyst[27]), (iv) the isolation and structural characterization of the first unexpectedly stable bis(ethylenediamine)copper(I) complex (complex VII), and (v) the identification of the labile precursor (complex III) of a large number of copper(I)–amino–carbonyl complexes.

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(27) Calvin, M. *Trans. Faraday Soc.* **1938**, *34*, 1181. *J. Am. Chem. Soc.* **1939**, *61*, 2230–4. James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319–405. James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; Chapter 2.