data reveals that copper decreases the K_m value for Fe^{III}·NTA from 1.5 to 0.5 mM by serving as an electron mediator. Cu(II) is initially reduced by Hb to Cu(I), which subsequently reduces Fe^{III}·NTA. This interaction may be the mechanism by which copper prevents anemia by enhancing the reduction of Fe(III) required for heme synthesis.

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Dicopper(I) Carbonyl Tropocoronands. Preparation, Structural Characteristics, and Reactivity of Neutral Binuclear Cu–CO Macrocyclic Compounds

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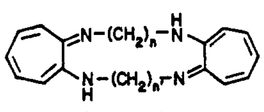
The synthesis, structure, and chemical properties of stable tropocoronand (TC) copper(I) carbonyl compounds are described. These molecules form in the reaction of copper(I) salts with $\mathrm{Li_2}$(TC-*n*,*n'*) (*n*,*n'* = 5,5 and 6,6) under a CO atmosphere in tetrahydrofuran solution. An X-ray diffraction study of $[\mathrm{Cu_2(CO)_2}$(TC-5,5)] (**1**) revealed a binuclear structure with both trigonal-planar metal atoms coordinated to a terminal carbon monoxide ligand (ν_{CO} = 2071 cm^{-1}). The two copper atoms are located at opposite faces of the macrocycle, separated by a distance of 4.132 (1) Å. Infrared, UV-vis, and ^{1}H and ^{13}C NMR spectroscopic data are also reported. The compounds are sensitive to air and temperatures above 35 °C, decomposing to form mononuclear cupric species. Compound **1** is photochemically inert. Both compounds undergo CO substitution reactions in the presence of alkynes and strong nucleophiles. Addition of *n*-butyllithium leads to an intermediate, postulated to be a copper alkyl species, which can serve as an in situ catalyst for the conjugate addition of Grignard reagents to cyclohexenone. Crystal data for $C_{26}H_{30}N_4O_2Cu_2$ (**1**): triclinic, $P\bar{1}$, a = 10.977 (2) Å, b = 11.725 (2) Å, c = 10.216 (1) Å, α = 78.86 (1)°, β = 94.22 (1)°, γ = 106.29 (1)°, V = 1237.9 Å^3, Z = 2. The structure was refined to R_1 = 0.048 on the basis of 2375 data having $F_o > 4\sigma(F_o)$.

Introduction

Tropocoronand macrocycles[1] have proved to be a versatile class of ligands for the complexation of divalent first-row transition metals. For mononuclear copper(II)[2] and nickel(II)[3] complexes, the geometry about the metal center is governed largely by the length of the polymethylene linker chains in $\mathrm{H_2}$(TC-*n*,*n'*). With the tropocoronand ligand $\mathrm{H_2}$(TC-6,6), a binuclear copper(II) complex was obtained in which the metal ions are bridged asymmetrically by acetate and methoxide groups.[4] The present study was initiated to determine whether other binuclear systems could be accessed by using these new macrocyclic ligands, especially for metals in the +1 oxidation state such as copper(I) and rhodium(I). Homobinuclear complexes of these low-valent metals are potentially useful for the binding of small (C_1 or C_2) molecules, for bimetallic activation, or for studies of the conformational preferences of two metals in a macrocyclic host.



(TC-n,n')H$_2$
n,n'= 3,3;4,4;4,5;5,5;6,6

The preparation and characterization of neutral tropocoronand complexes containing the (μ-alkyne)dicopper(I) core have been previously reported.[5] We now describe the molecules $[\mathrm{Cu_2(CO)_2}$(TC-5,5)] (**1**) and $[\mathrm{Cu_2(CO)_2}$(TC-6,6)] (**2**). These compounds, briefly mentioned in a review of metal tropocoronand chemistry,[6] are stable under mild conditions to the loss of carbon monoxide. Following the first X-ray structural characterization[7] of the neutral copper(I) carbonyl complex [Cu(CO){HB(pz)$_3$}], where HB(pz)$_3$ = hydrotris(1-pyrazolyl)borate, several copper carbonyl compounds, mostly ionic species, have been prepared and isolated.[8] A variety of species, including three-coordinate,[9] pseudo-four-coordinate,[10] binuclear,[11] and bridged binuclear (μ-carbonyl)dicopper(I)[12] units, has been structurally characterized. Additional complexes, such as CpCuCO and Cp*CuCO, where Cp and Cp* = cyclopentadienyl and pentamethylcyclopentadienyl anions, respectively, are known but have not yet been fully characterized structurally.[13] Compounds **1** and **2** expand this class of molecules to include neutral, three-coordinate, binuclear copper(I) carbonyl species. The solubility of **1** in most organic solvents has also facilitated exploration of its reaction chemistry.

Experimental Section

General Methods. Grignard and lithium reagents were purchased from Aldrich Chemical Co. and used as received, except for *n*-butyllithium (BuLi), which was titrated[14] periodically to determine the active alkyllithium content. Reagent bottles were flushed with argon, sealed with electrical tape, and stored at 4 °C. Aliquots of reagents were

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withdrawn by syringe and transferred to flame-dried, Ar-flushed, 5-mL round-bottomed flasks. Small quantities of reagent were subsequently withdrawn from these flasks by using gastight microliter syringes. In this manner, the large reagent bottles were subjected to minimal disturbance and, in the case of BuLi, titers remained unchanged for over 1 year.

Solvents, except for pentane, were distilled from sodium benzophenone ketyl and were flushed with argon for at least 15 min prior to use. Tropocoronands H_2(TC-5,5) and H_2(TC-6,6) were prepared according to a published method.[15] Tetrakis(acetonitrile)copper(I) tetrafluoroborate was prepared[16] and stored in a nitrogen-filled glovebox. Carbon monoxide gas (CP) was used as received from Matheson. Infrared spectra were recorded from KBr pellets on a Beckman Acculab 10 instrument. Nuclear magnetic resonance spectra were recorded on a Bruker 270 NMR spectrometer using benzene-d_6 solutions, and chemical shifts are referenced to tetramethylsilane.

Gas chromatographic analyses were performed with a Hewlett-Packard (HP) Model 5890 gas chromatograph, equipped with a flame-ionization detector (FID) and an HP-3393A integrator. An HP-1 methylsilicone gum 0.53 mm × 10 m fused-silica column was used for separations. Conditions included a column head pressure of 10 psig and a temperature gradient program, which held the initial oven temperature at 80 °C for 2 min, followed by gradual heating at a rate of 20°/min to a final oven temperature of 200 °C. Products were identified by coinjection with authentic samples.

Synthesis of $[Cu_2(CO)_2(TC\text{-}5,5)]$ (1). A THF (5 mL) solution of Li_2(TC-5,5) was prepared by treating 53.0 mg (0.141 mmol) of H_2(TC-5,5) with 177 μL of a 1.6 M solution of *n*-BuLi (2.0 equiv) in hexane at 0 °C under an inert atmosphere. The yellow solution was stirred for an additional 15 min, taken up in a syringe, and added dropwise to a suspension of $[Cu(NCCH_3)_4](BF_4)$ (solid $CuBr{\cdot}Me_2S$ may also be used) (97.8 mg, 0.311 mmol) in THF (6 mL) that had been stirred under a CO atmosphere for at least 10 min at −78 °C. The resulting turbid yellow-green mixture was stirred at −78 °C for 15 min, allowed to warm up to room temperature, and then filtered under a positive pressure of CO. The reaction vessel was flushed with inert gas until the volatile components evaporated. The resulting yellow-brown solid was transferred to the drybox, where toluene (3 mL) was used to dissolve most of the mixture. After filtration, the filtrate was placed in a recrystallization vial and pentane was carefully layered on top. After it stood for 3 days at −20 °F in the drybox freezer, the solution deposited orange to light brown crystals of $[Cu_2(CO)_2(TC\text{-}5,5)]$, which were collected and washed with fresh pentane (28.6 mg, 36.4% yield). Crystalline samples exposed to air turned slightly darker but were otherwise unchanged. Anal. Calcd for $C_{26}H_{30}N_4O_2Cu_2$: C, 55.98; H, 5.42; N, 10.04. Found: C, 55.74; H, 5.75; N, 10.33. Spectroscopic data: IR (KBr pellet, cm^{-1}) 2924 (m), 2071 (s), 1600 (s), 1516 (s), 1480 (m), 1459 sh (m), 1443 sh (s), 1433 (s), 1403 (m), 1369 (w), 1348 (w), 1284 (s), 1246 (s), 1049 (w), 948 (w), 904 (w), 737 (s); ^{1}H NMR (270 MHz, 296 K, C_6D_6) δ 6.99 (4 H, t, J = 9 Hz), 6.64 (4 H, d, J = 11 Hz), 6.35 (2 H, t, J = 9 Hz), 3.23–3.51 (8 H, complex m), 1.99 (4 H, quintet, J = 8 Hz), and a broad signal centered at 1.62 (8 H); $^{13}C\{^1H\}$ NMR (67.9 MHz, 296 K, C_6D_6) δ 111.24, 133.62, 116.93, 50.20, 31.55, and 27.32 for carbons C12, C13, C14, C31, C32, and C33 (see Figure 1), respectively. Resonances for the carbonyl and C11 carbons were not observed.

Synthesis of $[Cu_2(CO)_2(TC\text{-}6,6)]$ (2). A THF (6 mL) solution of Li_2(TC-6,6), prepared from 29.9 mg (0.074 mmol) of H_2(TC-6,6) and *n*-BuLi (2.0 equiv), was added dropwise to a stirred THF (7 mL) suspension of $[Cu(NCCH_3)_4](BF_4)$ (46.6 mg, 0.148 mmol) under a CO atmosphere at −78 °C. The yellow-green mixture was stirred at low temperature for 15–20 min, during which time a yellow precipitate formed. The mixture was allowed to warm up to room temperature, and the solid was filtered. The yellow powder was washed several times with fresh THF and dried under vacuum (yield 30.0 mg, 69.2%). The product $[Cu_2(CO)_2(TC\text{-}6,6)]$ was stable in air and insoluble in ether, THF, benzene, toluene, acetonitrile, chlorinated solvents, acetone, and acidic methanol. A similar large disparity in solubility was also observed for the complexes "$[Cu_2(NCCH_3)_2(TC\text{-}5,5)]$" (soluble) and "$[Cu_2(NCCH_3)_2(TC\text{-}6,6)]$" (insoluble), the structures of which, we believe, resemble those of the carbonyl adducts described herein and that of the binuclear Cu(I)–acetonitrile complex $[Cu_2(MeCN)_2L]Y_2$, where L is a bis(furanyl) tetraaza macrocycle and Y is ClO_4^- or BPh_4^-.[17] Anal. Calcd for $C_{28}H_{34}N_4O_2Cu_2$: C, 57.42; H, 5.85; N, 9.57. Found: C, 57.18; H, 6.12; N, 9.30. IR (KBr, cm^{-1}): 2932 (s), 2072 (s), 1602 (s), 1513 (s), 1482 (m), 1458 sh (m), 1432 (s), 1404 (s), 1361 (m), 1284 (s), 1246 (s), 1235 (w), 1048 (w), 998 (m), 905 (w), 786 (m), 739 (s).

Table I. Experimental Details of the X-ray Diffraction Study of $[Cu_2(CO)_2(TC\text{-}5,5)]$ (1)

Crystal Parameters[a]

a, *b*, *c*: 10.977 (2), 11.725 (2), 10.216 (1) Å
α, β, γ: 78.86 (1), 94.22 (1), 106.29 (1)°
V: 1237.9 Å^3
Z: 2
ρ_{calcd}, ρ_{obsd}:[b] 1.496, 1.484 (3) g cm^{-3}
fw: 557.65
space group: $P\bar{1}$

Measurement and Treatment of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα (λ_α = 0.7107 Å) graphite monochromatized
temperature: 22 °C
stds:[c] $(\bar{2}\bar{1}6)$, $(1\bar{1}7)$, $(2\bar{1}\bar{6})$
no. of reflns collected: 5279, $3° \le 2\theta \le 52°$ $(+h,\pm k,\pm l)$

Treatment of Intensity Data[d]

linear abs coeff: 16.8 cm^{-1}[e]
no. of reflns after averaging: 4864
obsd unique data: 2375
criterion: $F_o > 4\sigma(F_o)$
R_1, R_2:[f] 0.048, 0.054
residual density: 0.54 e Å^{-3}

[a] From a least-squares fit to the setting angles of 25 reflections having $2\theta > 24°$. [b] By neutral buoyancy in aqueous KI. [c] Monitored every 3600 s of exposure time for intensity and after 250 reflections for orientation control. [d] See ref 18. [e] An empirical absorption correction using ψ scans was applied. [f] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$.

Collection and Reduction of X-ray Data for 1. Multifaceted orange-brown crystals of $[Cu_2(CO)_2(TC\text{-}5,5)]$ were obtained by liquid–liquid diffusion of pentane into a toluene solution of the complex stored in the drybox freezer (−20 °F) over 3–4 days. A cylindrically shaped crystal about 0.2 mm in base diameter and 0.2 mm in height was mounted in a capillary and examined by diffractometer. Open-counter ω scans of several strong, low-angle reflections showed somewhat broad but structureless peaks. Determination of the unit cell by diffractometer revealed a triclinic system. Details for the subsequent data collection are summarized in Table I.[18]

Solution and Refinement of the Structure. The structure was solved by standard heavy-atom methods in space group $P\bar{1}$. Difference Fourier maps were used to locate all non-hydrogen atoms of the molecule. The final model was refined by least-squares methods, with SHELX-76.[19] Hydrogen atoms were fixed in calculated positions (C–H = 0.95 Å) and allowed to "ride" on the carbon atoms to which they were attached. Common isotropic temperature factors, assigned to each group of hydrogen atoms, converged at U = 0.129 (11) Å^2 for the ring hydrogen atoms and U = 0.088 (6) Å^2 for the linker-chain protons. Non-hydrogen atoms were refined anisotropically. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.4470/[\sigma^2(F_o) + 0.000625(F_o)^2]$. Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from ref 20; scattering factors for hydrogen atoms were obtained from ref 21. The total number of variable parameters was 309. Further details are given in Table I. Final non-hydrogen positional parameters are reported in Table II, and interatomic distances and angles are given in Table III. Tables for non-hydrogen thermal parameters, hydrogen positional and thermal parameters, and observed and calculated structure factors are available as supplementary material (Tables S1–S3, respectively).

Reaction of 2 with Dimethyl Acetylenedicarboxylate (DMAD). A solution of Li_2(TC-6,6) in THF (7 mL), prepared from 40.7 mg (0.101 mmol) of H_2(TC-6,6) and *n*-BuLi (2.0 equiv), was added dropwise to a CO-saturated THF (8 mL) suspension of $[Cu(NCCH_3)_4](BF_4)$ (63.4 mg, 0.202 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 0.5 h, producing a yellow precipitate. Neat DMAD (15 μL, 1.2

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Table II. Final Positional Parameters for $[Cu_2(CO)_2(TC\text{-}5,5)]$ (**1**)[a]

ATOM	X	Y	Z
Cu1	0.16789(7)	0.30855(7)	0.36753(7)
Cu2	-0.64650(8)	1.24500(8)	0.05103(7)
O1	-0.7429(6)	1.0315(5)	0.3800(5)
O2	-0.6691(7)	1.5160(6)	-0.0046(6)
N1	0.2513(4)	0.4317(4)	0.4092(4)
N2	0.0188(4)	0.4613(4)	0.3210(4)
N3	-0.5151(5)	1.0980(6)	0.1323(4)
N4	-0.7475(5)	1.1201(5)	0.0492(4)
C1	0.2192(7)	0.1397(7)	0.3715(6)
C2	-0.6617(8)	1.4106(9)	0.0164(7)
C11	0.1690(5)	0.5507(6)	0.4024(5)
C12	-0.7955(6)	1.6496(6)	0.4424(6)
C13	0.1425(7)	0.7751(7)	0.4423(6)
C14	-0.9884(7)	1.8516(6)	0.4007(6)
C15	-1.0782(7)	1.8064(7)	0.3511(6)
C16	-1.0710(6)	1.6878(6)	0.3300(5)
C17	0.0342(5)	0.5668(6)	0.3494(5)
C21	0.4522(6)	-0.0129(7)	0.1466(5)
C22	0.5385(7)	-0.1318(7)	0.1976(6)
C23	0.5261(8)	-0.2559(8)	0.2158(6)
C24	0.4237(9)	-0.3043(8)	0.1954(6)
C25	0.2972(8)	-0.2303(7)	0.1529(6)
C26	0.2520(7)	-0.1006(7)	0.1148(5)
C27	0.3119(6)	0.0019(7)	0.1003(5)
C31	0.3885(5)	0.4028(6)	0.4573(6)
C32	0.4737(6)	0.2691(6)	0.4449(5)
C33	0.5121(6)	0.2547(6)	0.3197(6)
C34	0.5997(6)	0.1225(6)	0.3027(6)
C35	0.6150(6)	0.1031(7)	0.1775(6)
C41	-1.1091(6)	1.4663(6)	0.2674(6)
C42	-1.1039(6)	1.3400(6)	0.2332(5)
C43	-0.0012(6)	0.3114(6)	0.1260(5)
C44	0.0034(6)	0.1847(6)	0.0912(6)
C45	0.1145(6)	0.1503(6)	-0.0001(5)

[a] Numbers in parentheses are errors in the last significant digit(s). See Figure 1 for atom-labeling scheme.

Table III. Interatomic Distances (Å) and Angles (deg) for $[Cu_2(CO)_2(TC\text{-}5,5)]$ (**1**)[a]

Cu1 —— Cu2	4.132(1)		
Cu1 - C1	1.771(7)	Cu2 - C2	1.749(9)
Cu1 - N1	1.938(6)	Cu2 - N3	1.922(5)
Cu1 - N2	1.940(4)	Cu2 - N4	1.937(6)
N1 - C11	1.332(7)	N3 - C21	1.33(1)
N1 - C31	1.478(7)	N3 - C35	1.487(9)
N2 - C17	1.318(9)	N4 - C27	1.313(7)
N2 - C41	1.473(8)	N4 - C45	1.488(8)
C1 - O1	1.128(9)	C2 - O2	1.12(1)
C11 - C17	1.503(8)	C21 - C27	1.524(9)
C11 - C12	1.40(1)	C21 - C22	1.403(9)
C12 - C13	1.345(9)	C22 - C23	1.38(1)
C13 - C14	1.428(9)	C23 - C24	1.35(1)
C14 - C15	1.37(1)	C24 - C25	1.39(1)
C15 - C16	1.35(1)	C25 - C26	1.36(1)
C16 - C17	1.445(7)	C26 - C27	1.40(1)
C31 - C32	1.509(8)	C41 - C42	1.50(1)
C32 - C33	1.518(9)	C42 - C43	1.598(8)
C33 - C34	1.518(9)	C43 - C44	1.51(1)
C34 - C35	1.51(1)	C44 - C45	1.521(8)
O1 - C1 - Cu1	175.5(7)	O2 - C2 - Cu2	178.6(8)
C1 - Cu1 - N1	134.9(3)	C2 - Cu2 - N3	134.7(3)
C1 - Cu1 - N2	142.0(3)	C2 - Cu2 - N4	141.7(3)
N1 - Cu1 - N2	83.1(2)	N3 - Cu2 - N4	83.3(2)
C11 - N1 - C31	118.7(5)	C21 - N3 - C35	120.6(5)
C11 - N1 - Cu1	114.5(4)	C21 - N3 - Cu2	115.2(4)
C31 - N1 - Cu1	126.4(4)	C35 - N3 - Cu2	124.3(5)
C31 - N1 - C17	154.6(4)	C35 - N3 - C27	156.5(4)
C17 - N2 - C41	119.3(4)	C27 - N4 - C45	119.7(6)
C17 - N2 - Cu1	114.0(4)	C27 - N4 - Cu2	115.2(4)
C41 - N2 - Cu1	126.5(4)	C45 - N4 - Cu2	125.1(4)
C41 - N2 - C11	154.3(4)	C45 - N4 - C21	155.9(5)
N1 - C11 - C12	123.2(5)	N3 - C21 - C22	123.5(6)
N1 - C11 - C17	112.9(6)	N3 - C21 - C27	113.0(5)
C12 - C11 - C17	123.9(5)	C22 - C21 - C27	123.4(7)
C13 - C12 - C11	134.2(6)	C23 - C22 - C21	132.3(7)
C12 - C13 - C14	129.8(8)	C24 - C23 - C22	132.2(7)
C15 - C14 - C13	124.5(7)	C23 - C24 - C25	124.6(8)
C16 - C15 - C14	131.7(6)	C26 - C25 - C24	129.7(9)
C15 - C16 - C17	132.5(7)	C25 - C26 - C27	134.4(7)
N2 - C17 - C16	121.9(5)	N4 - C27 - C26	124.0(6)
N2 - C17 - C11	114.7(4)	N4 - C27 - C21	113.3(6)
C16 - C17 - C11	123.4(6)	C26 - C27 - C21	122.7(5)
N1 - C31 - C32	111.5(6)	N2 - C41 - C42	111.6(4)
C31 - C32 - C33	113.4(5)	C41 - C42 - C43	112.2(5)
C32 - C33 - C34	115.4(5)	C44 - C43 - C42	112.2(5)
C35 - C34 - C33	114.3(5)	C43 - C44 - C45	111.6(6)
N3 - C35 - C34	111.7(5)	N4 - C45 - C44	111.1(5)

[a] See footnote *a* of Table II.

equiv) was added, the CO line was replaced by N_2, and the mixture was allowed to warm up to ambient temperature gradually over a period of 45 min. The resulting burgundy mixture was filtered and concentrated in vacuo. The residual red solid was transferred to the drybox and recrystallized from toluene/pentane (−20 °F, 3 days) to yield 38.3 mg (56.6%) of $[Cu_2(\mu\text{-DMAD})(TC\text{-}6,6)]$.[5]

The more soluble compound **1** also undergoes CO substitution with DMAD, but the reaction proceeds much more rapidly. Addition of the disubstituted acetylene led immediately to the dark burgundy color indicative of the formation of the (μ-alkyne)dicopper(I) tropocoronand complex.

Irradiation of 1 in 2-Methyltetrahydrofuran (2-MeTHF). A 10^{-2}–10^{-3} M solution of **1** was prepared in the drybox with use of 2-MeTHF freshly distilled from sodium and degassed with N_2. The emerald green solution was sealed in a 1 mm path length calcium fluoride cell and irradiated for 5 min at −160 °C, by using a high-pressure mercury lamp with quartz and H_2O filters. The cell was then placed in a Nicolet FTIR instrument and the IR spectrum recorded quickly at −160 °C.[22] No changes in the intensity of the CO absorption band at 2071 cm^{-1} were observed, as monitored by difference FTIR spectra of irradiated and freshly prepared samples. Moreover, additional experiments conducted at increasingly higher temperatures ($-160\ °C < T \leq 20\ °C$) and irradiation times of up to 20 min reveal no photoejection of CO to form, possibly, a species containing the $Cu_2(\mu\text{-CO})$ core.[12]

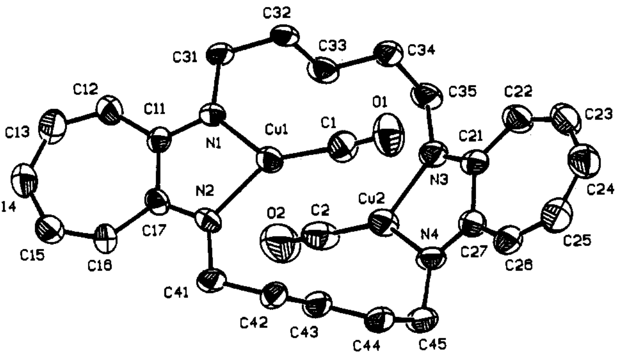


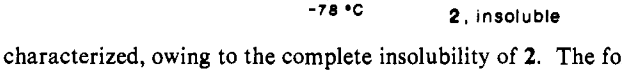
Figure 1. Structure of $[Cu_2(CO)_2(TC\text{-}5,5)]$ (**1**) showing the 50% probability thermal ellipsoids and atom-labeling scheme.

Disproportionation of 1 To Form Mononuclear Cupric Species. Toluene or THF solutions of **1**, when exposed to air or heated above room temperature, produce dark turbid mixtures, from which was isolated a black soluble product identified by its spectroscopic properties as the known mononuclear cupric compound $[Cu(TC\text{-}5,5)]$.[2] Solutions of **1** in benzene-d_6, sealed in NMR tubes, deposit a mirror of copper metal after a few weeks at room temperature. An unidentified insoluble olive green precipitate also forms during thermal decomposition or air oxidation of **1**.

Compound 1 as Catalyst for Michael Addition Reaction. Compound **1** was prepared by the method described above, with 20.6 mg (0.055 mmol) of $H_2(TC\text{-}5,5)$, *n*-BuLi (0.110 mmol), and 34.5 mg (0.110 mmol) of $[Cu(NCCH_3)_4](BF_4)$. Excess CO was flushed out with argon, and the light brown solution containing **1** was filtered and cooled to −78 °C. Upon addition of *n*-BuLi (0.110 mmol), a clear red solution was obtained. Two THF solutions, each containing 5.48 mmol in 10 mL of *n*-BuMgCl and 2-cyclohexen-1-one, were next added dropwise and simultaneously to the cooled red solution. The resulting product mixture was stirred an additional 10 min at low temperature and then quenched with 5 mL of a saturated aqueous ammonium chloride solution. The organic layer was separated, dried ($MgSO_4$), and analyzed by GLC. Three principal components were detected. These compounds were identified as unreacted 2-cyclohexen-1-one (1.7 relative area), 1-butyl-2-cyclohexen-1-ol (1.0), and 3-butylcyclohexan-1-one (4.0), respectively, by comparison of their retention times with those of standard solutions containing authentic materials. The results indicate that, under the above conditions, the reaction does not go to completion and that the regioselectivity (4:1, 1,4-vs 1,2-addition) is modest.

Results and Discussion

Syntheses. The preparation of binuclear copper(I) carbonyl tropocoronand complexes **1** and **2** was accomplished by allowing suspensions of tetrakis(acetonitrile)copper(I) tetrafluoroborate to react with either $Li_2(TC\text{-}5,5)$ or $Li_2(TC\text{-}6,6)$, respectively, under an atmosphere of CO (eq 1). Compound **1** was more fully



(1)

characterized, owing to the complete insolubility of **2**. The formulation of **2** is supported by elemental analyses and the fact that its solid-state infrared spectrum is virtually identical with that of **1**. The striking difference in solubility between binuclear

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(22) Typical procedures and instrumentation are described in: Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 6005.

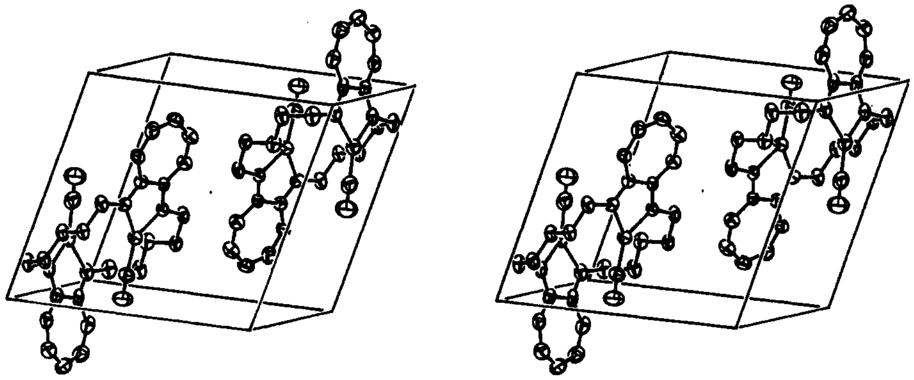

Figure 2. Stereoview of the unit cell of **1**.

Table IV. Structural and Infrared Data for the Cu–CO Unit in Selected Copper(I) Carbonyl Complexes[a]

compd[b]	Cu–(CO), Å	C–O, Å	ν_{CO} (Nujol), cm^{-1}	ref
$[Cu(CO)\{HB(pz)_3\}]$	1.765 (14)	1.120 (6)	2083	7
$[Cu(CO)(LBF_2)]$	1.780 (3)	1.112 (4)	2068	24
$[Cu(CO)(dien)](BPh_4)$	1.776 (5)	1.123 (6)	2080	25
$[Cu(CO)(en)](BPh_4)$	1.806 (6)	1.110 (7)	2117	10a
$[Cu(CO)\{NH(py)_2\}](ClO_4)$	1.808 (2)		2110	10b
$[Cu(CO)(OEs)]_n$	1.784 (8)	1.116 (8)	2117	26
$[Cu_2(CO)_2(en)_3](BPh_4)_2$	1.73 (1); 1.75 (1)	1.17 (2); 1.16 (2)	2078	11b
$[Cu_2(CO)_2(hm)_3](BPh_4)_2$	1.80 (2); 1.79 (2)	1.12 (3); 1.13 (3)	2055; 2066	11c
$[Cu_2(CO)_2(tmen)_2Cl](BPh_4)$	1.786 (5); 1.757 (5)	1.134 (7); 1.148 (7)	2065	27
$[Cu_2(CO)_2(tmen)_2Br](BPh_4)$	1.814 (13); 1.748 (16)	1.094 (17); 1.155 (20)	2070	27
$[Cu_2(CO)_2(tmen)_2I](BPh_4)$	1.795 (15); 1.820 (16)	1.124 (19); 1.102 (22)	2063; 2073	27
$[Cu_2(CO)_2(TC\text{-}5,5)]$	1.771 (7); 1.749 (9)	1.128 (9); 1.12 (1)	2071[c]	*d*
$[Cu_2(\mu\text{-}CO)(tmen)_2(\mu\text{-}PhCO_2)](BPh_4)$	1.868 (8); 1.860 (6)	1.143 (11)	1926	12
$[Cu_2(\mu\text{-}CO)(tmp)_2(\mu\text{-}PhCO_2)](BPh_4)$	1.882 (8); 1.863 (9)	1.159 (11)	1925	28

[a] Table adapted from ref 8. [b] Abbreviations used: $^-HB(pz)_3$ = hydrotris(1-pyrazolyl)borate; LBF_2 = difluoro(3,3′-(trimethylenedinitrilo)bis(2-butane oximato))borate; dien = diethylenetriamine; en = ethylenediamine; $NH(py)_2$ = bis(2-pyridyl)amine; OEs = ethanesulfonate; hm = histamine; tmen = *N,N,N′,N′*-tetramethylethylenediamine; TC-5,5 = 6,7,8,9,10,11,18,19,20,21,22,23-dodecahydrodicyclohepta[*b,k*][1,4,11,14]tetraazacyclooctadecine; tmp = *N,N,N′,N′*-tetramethylpropylenediamine. [c] KBr pellet. [d] This work.

compounds of $H_2(TC\text{-}5,5)$ vs those of $H_2(TC\text{-}6,6)$ has also been observed for copper(I) acetonitrile and rhodium(I) carbonyl analogues,[6] but there is no apparent explanation for this phenomenon. This solubility difference accounts, in part, for the large difference in isolated yield between compounds **1** (<40%) and **2** (70%). Like most known copper(I) carbonyl compounds, these complexes are subject to disproportionation and loss of CO. Precipitation of **2** from solution precludes the formation of decomposition products. Also, the TC-6,6 system is less likely to form the mononuclear complex [Cu(TC-6,6)] in which the Cu(II) coordination geometry is unfavorably constrained toward tetrahedral.[4] In contrast, recrystallized samples of **1** were sometimes contaminated with crystals of [Cu(TC-5,5)], and a benzene solution of **1** kept at room temperature in a sealed NMR tube eventually deposited a copper mirror. As demonstrated by its substitution reactions (vide infra), carbon monoxide can be readily displaced in $[Cu_2(CO)_2(TC\text{-}5,5)]$.

Compounds **1** and **2** are rare examples of molecules containing neutral, trigonal-planar copper(I) carbonyl centers characterized both spectroscopically and structurally. They represent the second class of neutral binuclear cuprous compounds obtained by using tropocoronand macrocycles, the first being the (μ-alkyne)dicopper series $[Cu_2(\mu\text{-}RC{\equiv}CR)(TC\text{-}n,n')]$.[5] Although ($\mu$-carbonyl)dicopper(I) species are known,[12] no evidence for such species has yet been obtained with tropocoronand ligands.

Structure. The structure of $[Cu_2(CO)_2(TC\text{-}5,5)]$ is shown in Figure 1, and a stereoview of the unit cell contents is displayed in Figure 2. As can be seen from these illustrations, two nitrogen atoms of the aminotropone iminate ligand and one terminal carbon monoxide molecule are coordinated to each trigonal-planar copper(I) center. Related copper(I) carbonyl complexes, $[Cu(CO)\{NH(py)_2\}](ClO_4)$ and $[Cu(CO)(en)](BPh_4)$ (see Table IV), are trigonal planar with a weakly coordinating anion, either a perchlorate oxygen atom in the former[10b] or a phenyl group of BPh_4^- in the latter.[10a] In $[Cu_2(CO)_2(TC\text{-}5,5)]$, there are no such additional intra- or intermolecular bonding interactions (<3.5 Å), and best-planes calculations through Cu and its three bonded (2 N, 1 C) atoms show maximum deviations of 0.01 and −0.05 Å, for Cu1 and Cu2, respectively.

The metal atoms in **1** are situated on opposite sides of the mean plane passing through the tropocoronand ligand and are separated by a distance of 4.132 (1) Å. As a consequence, the ligand adopts a conformation different from that of the saddle- or U-shaped arrangement found for other binuclear copper tropocoronands, where the metal ions sit on the same side of the ligand.[4,5] The present S-shaped, or "staircase", geometry of **1** resembles the configuration of other transition-metal complexes of binucleating macrocycles previously studied in our laboratory. In this earlier work,[23] three general conformations were identified for binuclear complexes of the macrocyclic ligand 1,4,7,13,16,19-hexaaza-10,22-dioxacyclotetracosane, namely, S-shaped, U-shaped, and planar arrangements. Thus far, both S- and U-shaped conformations have been observed for polymethylene chain linked tropocoronands. The planar arrangement has not been observed for the binuclear tropocoronands but is likely to occur for bimetallic derivatives having polyatomic bridging ligands of appropriate dimensions.

The stereochemistry about the copper(I) centers is trigonal planar, as reflected by the sum of the angles, being 360.0° for Cu1 and 359.6° for Cu2. The average Cu–N bond length of 1.934 (6) Å is similar to that found for the (μ-alkyne)dicopper(I) compounds, 1.911 (5) Å, and the N–Cu–N bite angle of 83.2 (3)° observed for **1** is also nearly the same as for the μ-alkyne compounds, where it is 84.1 (2)°. These values are, however, much smaller than those observed for the $[Cu(CO)\{NH(py)_2\}](ClO_4)$ complex,[10b] which has an N–Cu–N angle of 95.52 (5)°. Examination of the Cu–CO bond lengths listed in Table IV[24–28] reveals

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[23] Coughlin, P. K.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 2328.

the average value for **1**, 1.760 (11) Å, to be at the short end of the range for structurally characterized copper(I) carbonyl compounds. This result is reasonable since the majority of compounds listed in Table IV are four-coordinate.

Spectra. The NMR spectra of **1** are typical of symmetric binuclear tropocoronand complexes and show no evidence for the presence of the syn isomer, in which both Cu–CO units reside on the same face of the macrocycle. Isomerism of this kind occurs for the $[Rh_2(CO)_4(TC\text{-}5,5)]$ analogues.[6,29] Finally, the infrared spectra of **1** and **2** are very similar, nearly superimposable. The CO stretching frequency falls in the range of other terminally coordinated copper(I) carbonyl complexes (Table IV).

Reactivity. Equations 2–5 summarize reactions attempted with compound **1**. Unlike the very stable (μ-alkyne)dicopper(I) tropocoronands, compound **1** decomposes readily in solution upon exposure to dioxygen or heat (eq 2), producing the mononuclear complex [Cu(TC-5,5)], metallic copper, and an unidentified insoluble olive powder. The compound is, however, stable over long periods in the crystalline state. The thermal instability of solutions of **1** limits its use as a catalyst for slow reactions, such as hydroformylation of alkenes.

$$\mathbf{1} \xrightarrow{O_2 \text{ or heat}} [\mathrm{Cu(TC\text{-}5,5)}] + \mathrm{Cu(0)} \qquad (2)$$

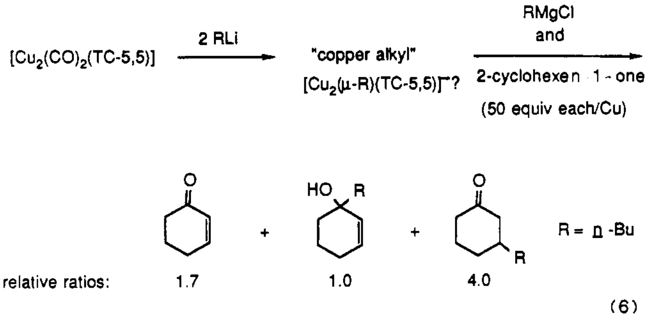
$$\mathbf{1} \xrightarrow{\mathrm{EtO_2CC{\equiv}CCO_2Et\ (DEAD)}} [\mathrm{Cu_2(\mu\text{-}DEAD)(TC\text{-}5,5)}] \qquad (3)$$

$$\mathbf{1} \xrightarrow[-160\ ^\circ\mathrm{C} \leq T \leq 20\ ^\circ\mathrm{C}]{h\nu} \text{no reaction} \qquad (4)$$

$$\mathbf{1} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{RLi}} \text{copper alkyl?} \qquad (5)$$

Both **1** and **2** undergo smooth irreversible reactions with added alkynes to produce the previously reported μ-alkyne complexes. Owing to the heterogeneous nature of this reaction for **2**, it proceeds much slower than that for **1**. The ease of this substitution reaction for $[Cu_2(CO)_2(TC\text{-}n,n')]$ compounds further underscores their chemical similarity to the putative $[Cu_2(NCCH_3)_2(TC\text{-}n,n')]$ complexes, which were postulated as intermediates in the synthesis of (μ-alkyne)dicopper(I) compounds.[5] Compound **1** is quite inert toward the attempted photochemical ejection of CO (eq 4). When a 2-methyltetrahydrofuran solution of **1** was irradiated with a high-pressure mercury lamp over a temperature range of −160 °C $\leqslant T \leqslant$ 20 °C (5–20 min), no product was obtained. Apparently, this irradiation excites only MLCT transitions involving the TC π^* orbitals, and the Cu–CO σ^* orbital, which ordinarily plays a role in metal–carbonyl bond scission,[30] remains unpopulated. We had hoped to isolate a compound with a bridging carbonyl group, analogous to $[Cu_2L_2(\mu\text{-}CO)(\mu\text{-}PhCO_2)](BPh_4)$, where L = tmen or tmp (see Table IV). Such a complex would require both copper atoms to be on the same face of the macrocycle (syn isomer), a situation encountered for $[Rh_2(CO)_4(TC\text{-}5,5)]$ complexes[29] but not yet for dicopper(I) tropocoronands.

When a THF solution of **1** was treated with 2.0 equiv of *n*-butyllithium, a red color was immediately obtained. Subsequent charging of this solution with equimolar amounts of *n*-butylmagnesium chloride and 2-cyclohexen-1-one (each 50 equiv/equiv of copper) at −78 °C, yielded a mixture of products (eq 6). GLC analyses revealed the presence of three major components, unreacted cyclohexenone, 1-butyl-2-cyclohexen-1-ol, and 3-butylcyclohexanone. The presence of greater than stoichiometric amounts of the last component, which arises from 1,4-addition of the *n*-butyl group to cyclohexenone, suggests the intermediacy of a copper alkyl species that serves as a catalyst for the 1,4-addition (Michael reaction). The catalytic reaction is not very regiospecific for it also produces, in significant amounts, tertiary alcohol, the 1,2-addition product obtained in typical reactions of Grignard reagents with α,β-unsaturated ketones. Organocopper reagents, on the other hand, are commonly used in organic synthesis for the β-substitution of unsaturated carbonyl compounds.[31] The nature of the present copper alkyl species is unknown at this time, although we speculate that an anionic, alkyl-bridged dicopper(I) tropocoronand complex may be involved, on the basis of preliminary NMR data.[32] The identity of this intermediate and the factors affecting the selectivity of the catalytic process are currently under investigation.



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Registry No. 1, 110487-72-4; **2**, 110487-73-5; $[Cu(NCCH_3)_4][BF_4]$, 15418-29-8; $[Cu_2(\mu\text{-}DMAD)(TC\text{-}6,6)]$, 98901-06-5; Cu(TC-5,5), 98394-07-1; *n*-BuMgCl, 693-04-9; 2-MeTHF, 96-47-9; 2-cyclohexen-1-one, 930-68-7; 1-butyl-2-cyclohexen-1-ol, 88116-46-5; 3-butylcyclohexan-1-one, 39178-69-3.

Supplementary Material Available: Tables S1 and S2, reporting thermal parameters for non-hydrogen atoms and hydrogen atom positional and thermal parameters, respectively, for $[Cu_2(CO)_2(TC\text{-}5,5)]$ (2 pages); Table S3, reporting observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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