be used in the synthesis of related amidate-bridged complexes. This chemistry provides a foundation for understanding the more complex chemistry that leads to the platinum pyrimidine blues and further illustrates the diverse nature of the reactions that occur between *cis*-diammineplatinum and cyclic amidate ligands.

Acknowledgment. This work was supported by National Institutes of Health Research Grant CA 15826. We also thank Thomas V. O'Halloran for experimental assistance with the ^{195}Pt NMR spectral measurements and Engelhard Industries for a loan of $K_2[PtCl_4]$ used to make all platinum complexes described.

Registry No. 1, 85336-85-2; **2**, 76761-63-2; **3**, 85336-86-3; **3A**, 85336-88-5; **11**, 52241-26-2; *cis*-$[Pt(NH_3)_2(NO_3)_2]$, 41575-87-5; $[Pt_2(NH_3)_4(OH)_2](NO_3)_2$, 62048-58-2; *cis*-$[Pt(NH_3)_2Cl_2]$, 15663-27-1; ^{195}Pt, 14191-88-9.

Supplementary Material Available: Atomic positional and thermal parameters, hydrogen bond distances, and observed and calculated structure factors for **1** and **2** (22 pages). Ordering information is given on any current masthead page.

Concerning the Structure and Stability of a Copper(I) Alkoxy Carbonyl

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Abstract: The product of carbonylation (Saegusa, 1974) of planar $(CuO\text{-}t\text{-}Bu)_4$ is shown to retain its state of aggregation: the product is $[CuCO(O\text{-}t\text{-}Bu)]_4$, which is shown by X-ray crystallography to have a Cu_4O_4 core of cubane form. Copper is four-coordinate and coordinatively saturated, exhibiting a trigonally distorted tetrahedral geometry. Evidence from spectroscopic measurements and reactivity studies indicates that the cubane tetramer dissolves unchanged in benzene. The ^{13}C resonance of the coordinated carbonyl, 173 ppm, is upfield of free CO and exhibits coupling to the quadrupolar copper nucleus. The ^{63}Cu NMR spectrum of $[Cu(^{13}CO)O\text{-}t\text{-}Bu]_4$ shows a doublet, indicating that the tetramer dissolves to give a single species and that the CO ligand undergoes neither dissociation nor intramolecular scrambling. An argument is presented to account for the high resistance of $[CuCO(O\text{-}t\text{-}Bu)]_4$ toward decarbonylation. The argument naturally accounts for the comparable stability observed for two other Cu(I) carbonyls. X-ray crystallographic parameters: $a = b = 10.431$ (3) Å, $c = 32.024$ (12) Å, and $\gamma = 120°$ with $Z = 4$ in space group $P\bar{3}c1$ (No. 165).

The carbonyl chemistry of Cu(I) is unusual in having achieved perhaps more commercial than fundamental importance. Cuprous carbonyls are responsible for scavenging CO from gas streams,[1,2] and they are probably implicated in the low-pressure conversion of synthesis gas to methanol.[3-5] Cuprous carbonyls are characterized by two properties;[6] their instability toward decarbonylation and their relatively high C≡O stretching frequency. In recent years, Floriani's group has been influential in establishing the stoichiometry and the spectroscopic and structural features of cuprous carbonyls.[7] His results, employing halo and, mainly, amine ligands, have generally reaffirmed the characteristics of Cu(I) carbonyls stated above. Employing benzoate as a bridging ligand, he has produced a remarkable μ-bridging carbonyl.[7]

We have been attempting to establish, for soluble copper hydrides[8] and copper carbonyls, reaction patterns of possible relevance to the heterogeneous low-pressure methanol synthesis. In this regard, the earlier report of Saegusa et al.[9] that $(CuO\text{-}t\text{-}Bu)_4$ is carbonylated to the first thermally stable (i.e., sublimes in vacuum at 66 °C) copper carbonyl, "CuCO(O-*t*-Bu)," was intriguing. The degree of aggregation of this species is unknown, as is its structure. We were also interested in a possible structural basis for the thermal stability[10] of this carbonyl, particularly since this is the only known carbonyl with an exclusively oxygen-based coligand environment. Finally, such structural information may be revealing with respect to the heterogeneous methanol catalyst, since it originates from the oxides of copper and zinc.

Experimental Section

All operations were performed under an N_2 atmosphere by using standard Schlenk techniques for air- and moisture-sensitive materials. Hexanes and tetrahydrofuran were distilled under N_2 prior to use from solutions of the sodium benzophenone ketyl. $(CuO\text{-}t\text{-}Bu)_4$ was prepared as previously described.[9] IR spectra were recorded either in a standard solution cell (0.1-mm path length, room temperature) or in a locally fabricated low-temperature (−78 °C) cell.[12] NMR spectra were recorded either at 220 MHz (^{1}H) or at 90.8 MHz (^{13}C) in benzene-d_6 and referenced to internal Me_4Si. Enriched ^{13}CO was purchased from Mound Laboratory.

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(1) Walker, D. G. *Chemtech.* **1975**, *5*, 308.

(2) "Kirk-Othmer Encyclopedia of Chemical Technology"; Wiley: New York, 1978; p 788.

(3) Natta, G. *Catalysis* **1955**, *3*, 349. P. H. Emmett, ed.

(4) Kung, H. L. *Catal. Rev.* **1980**, *22*, 235.

(5) Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J. B.; Kobylinski, T. P. *J. Catal.* **1979**, *56*, 407.

(6) Bruce, M. I. *J. Organomet. Chem.* **1972**, *44*, 209.

(7) Pasquali, M.; Fluoriani, C.; Venturi, G.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1982**, *104*, 4092 and references therein.

(8) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(9) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930.

(10) We define several operational tests of "stability". At the lower level, many copper carbonyls suffer decarbonylation when N_2 is passed through a solution of the compound. A more stable set of complexes are decarbonylated only when their solution is heated under an inert atmosphere; the COSORB system[1,2] relies on this level of stability. The most stable copper carbonyl survives vacuum sublimation; only CuCO(O-*t*-Bu) passes this test. Such stability is quite possibly kinetic in origin, since one five-coordinate copper carbonyl[11] has a CO binding constant of over 10^4, but it decarbonylates in solution under an N_2 purge.

(11) Gagne, R. R.; Alleson, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170.

(12) Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 1840.

0002-7863/83/1505-3503$01.50/0

Table I. Crystal Data for $[CuCO(OCMe_3)]_4 \cdot 1.5THF$

empirical formula	$C_{20}H_{36}O_8Cu_4 \cdot 1.5C_4H_8O$
color	colorless
cryst dimens, mm	0.15 × 0.18 × 0.22
space group	$P\bar{3}c1$
cell dimens (at −162 °C; 30 reflections)	
a, Å	10.431 (3)
b, Å	10.431 (3)
c, Å	32.024 (12)
γ, deg	120.00 (1)
molecules per cell	4
vol, Å^3	3017.16
D(calcd), g/cm^3	1.50 g/cm^3
wavelength	0.71069
mol wt	658.65
linear abs coeff	28.3 cm^{-1}
total no. of reflctns collected	4103
no. of unique intensities	1791
no. with $F > 0.0$	1638
no. with $F > \sigma(F)$	1531
no. with $F > 2.33\sigma(F)$	1396
final residuals	
$R(F)$	0.0497
$R_w(F)$	0.0341
goodness of fit for the last cycle	2.739
maximum Δ/σ for last cycle	0.05

^{63}Cu NMR measurements were made at 95.76 MHz on a Nicolet NT-360 spectrometer. Data were recorded in the Fourier transform mode in 5-mm tubes with a digital resolution of 30–60 Hz. The pulse interval was ca. 0.03 s. All spectra were recorded without a field lock; measurements on an external standard before and after each spectrum verified that drift was negligible. $[Cu(NCMe)_4]PF_6$ in CH_3CN was employed as the external chemical shift standard (resonances downfield of this signal are given positive chemical shift values); this reference compound showed a line width at 25 °C of 400 Hz. All complexes were studied as nearly saturated solutions. Molecular weight determination was by freezing point depression, using a thermistor, in benzene.

$[CuCO(O\text{-}t\text{-}Bu)]_4$. To an evacuated septum-stoppered 100-mL Schlenk flask containing 0.25 g of $(CuO\text{-}t\text{-}Bu)_4$ (4.57×10^{-4} mol), and 10 mL of THF was added 1 atm of CO. The solution was shaken until the initially undissolved $(CuO\text{-}t\text{-}Bu)_4$ dissolved and a white powder began to appear. The excess CO was then removed by evacuation, the flask was refilled with 1 atm of N_2, and 5 mL of hexanes was added. The flask was cooled to ~−35 °C overnight whereupon colorless cubic crystals appeared. The cold flask was removed from the freezer and cooled to −78 °C and the supernatant removed by means of a cannula. The crystals were washed with 2 × 5 mL portions of cold (−78 °C) hexanes and dried in vacuo: ^1H NMR (in C_6D_6) δ 1.43, along with variable amounts of THF; IR ν_{CO} (in toluene) 2063 cm^{-1}; $^{13}C\{^1H\}$ NMR (on 99% ^{13}CO-enriched material, in C_6D_6, with 0.05 M $Cr(acac)_3$) 173 (±2) ppm (CO), 70.7 ($OC(CH_3)_3$), 33.4 ($OC(CH_3)_3$). The latter two values are the same in the absence of $Cr(acac)_3$. For comparison, *t*-BuOH in C_6D_6 has chemical shifts of 68.5 and 31.3 ppm. Molecular weight, on material recrystallized from toluene: 697 ± 50 (theoretical 659). A separate carbonylation carried out in an NMR tube reveals this reaction to be quantitative.

Crystallography. Crystals grown from toluene displayed one unit cell dimension in excess of 50 Å, making them undesirable for data collection. Crystals from THF (above) displayed a different unit cell, for reasons which became apparent as the structure determination progressed. These colorless crystals were slightly air-sensitive, darkening after approximately 10-min exposure. Several hours of exposure to air gives a wholly green solid. A suitable sample was obtained by cleaving, in a nitrogen atmosphere, a larger crystal to obtain a nearly equidimensional fragment which was mounted and cooled to −162 °C on the goniostat. A systematic search of a limited hemisphere of reciprocal space revealed a trigonal lattice which was subsequently indexed as $P\bar{3}c1$. Data (Table I) were collected (6° ≤ 2θ ≤ 50°, −162 °C)[13] for $+h,+k,+l$ and reduced in the usual manner. The two independent copper atoms were located by direct methods (MULTAN 78), with subsequent atoms located by different Fourier syntheses. A difference map phased on the non-hydrogen atoms revealed the location of all hydrogens as well as several peaks of density 1.5–2.4 e/Å^3 in an apparent void in the lattice. These were assigned and refined as a disordered tetrahydrofuran. Since the assignment of the oxygen was not possible, all were given carbon scattering factors. In the final model the THF was generated by the effect of symmetry operations on three refined atoms, C(15), C(16), and C(17). Once included, the residuals dropped by 0.02 and all hydrogen atoms on the *tert*-butyl group refined properly. A final difference Fourier showed four peaks of density

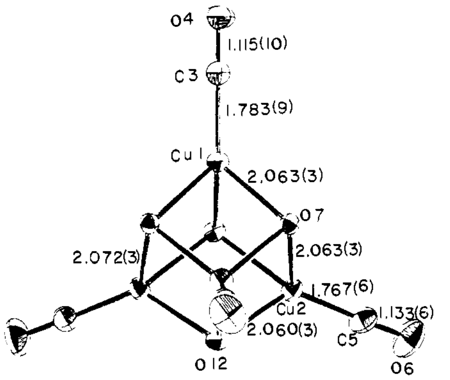

Figure 1. Atom labeling and important bond lengths (Å) in the $Cu_4(CO)_4O_4$ core of $[CuCO(O\text{-}t\text{-}Bu)]_4$. The crystallographic C_3 axis is vertical in this view.

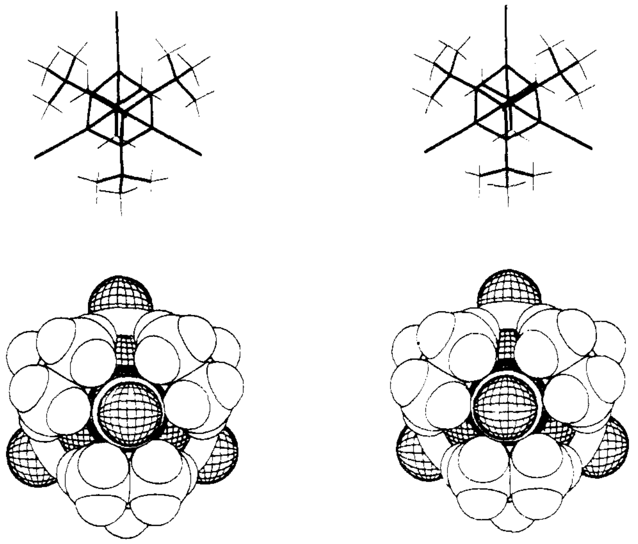

Figure 2. Stick-figure and space-filling drawings of $[CuCO(O\text{-}t\text{-}Bu)]_4$, viewed down the C_3 axis. Hatched atoms are oxygen (peripheral) and copper.

Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $[CuCO(O\text{-}t\text{-}Bu)]_4 \cdot 1.5THF$

	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Cu(1)	6667*	3333*	4414.3 (3)	16
Cu(2)	6113 (1)	1446 (1)	3637.6 (2)	17
C(3)	6667*	3333*	4971 (3)	20
O(4)	6667*	3333*	5319 (2)	32
C(5)	5578 (6)	−365 (6)	3467 (2)	24
O(6)	5229 (5)	−1535 (5)	3366 (1)	39
O(7)	7886 (3)	2819 (3)	4011 (1)	15
C(8)	8924 (6)	2394 (6)	4152 (2)	21
C(9)	10141 (7)	3661 (7)	4405 (2)	27
C(10)	8107 (7)	1017 (7)	4423 (2)	27
C(11)	9601 (7)	2054 (7)	3780 (2)	24
O(12)	6667*	3333*	3300 (2)	18
C(13)	6667*	3333*	2850 (3)	22
C(14)	5124 (8)	2214 (8)	2698 (2)	33
C(15)	655 (41)	947 (29)	2719 (8)	132
C(16)	1546 (55)	1546*	2500*	115
C(17)	1280 (53)	0*	2500*	110

[a] Parameters marked by an asterisk are fixed by symmetry. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

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(13) Data collection and processing techniques are described in: Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Table III. Bond Distances (Å) and Angles (deg) for the $[CuCO(O\text{-}t\text{-}Bu)]_4$ Unit[a]

Cu(1)	Cu(2)		3.043 (2)
Cu(2)	Cu(2)′		3.036 (2)
O(7)	O(12)		2.787 (6)
O(7)	O(7)′		2.791 (6)
O(7)	C(8)		1.432 (6)
O(12)	C(13)		1.440 (9)
C(8)	C(9)		1.528 (8)
C(8)	C(10)		1.522 (8)
C(8)	C(11)		1.515 (7)
C(13)	C(14)		1.520 (7)
Cu(2)	C(5)	O(6)	178.7 (5)
O(7)	Cu(1)	O(7)′	85.0 (1)
O(7)	Cu(2)	O(7)′	84.8 (2)
O(7)	Cu(2)	O(12)	85.2 (1)
O(7)	Cu(1)	C(3)	128.7 (1)
O(7)	Cu(2)	C(5)	127.9 (2)
O(12)	Cu(2)	C(5)	130.3 (2)
Cu(1)	O(7)	Cu(2)	94.8 (1)
Cu(2)	O(7)	Cu(2)′	94.5 (1)
Cu(2)	O(12)	Cu(2)′	94.9 (2)
Cu(1)	O(7)	C(8)	123.0 (3)
Cu(2)	O(7)	C(8)	121.5 (3)
Cu(2)	O(12)	C(13)	121.7 (1)
O(7)	C(8)	C(9)	109.2 (4)
O(7)	C(8)	C(10)	108.5 (4)
O(7)	C(8)	C(11)	109.7 (4)
C(9)	C(8)	C(10)	110.2 (5)
C(9)	C(8)	C(11)	109.7 (5)
C(10)	C(8)	C(11)	109.5 (5)
O(12)	C(13)	C(14)	108.6 (4)
C(14)	C(13)	C(14)′	110.3 (4)

[a] The *t*-Bu group bound to O(7) is labeled C(8)–C(11). The corresponding group on O(12) contains C(13), C(14), and the two C_3-related C(14)'s.

0.5–0.85 e/Å^3 in the vicinity of the THF; all other peaks were less than 0.5 e/Å^3.

Views of the molecule and important bond lengths appear in Figures 1 and 2. The results of the X-ray study are presented in Tables II and III. Anisotropic U's, F_o, F_c, and hydrogen atom parameters are available as supplementary material. Refined C–H distances range from 0.86 (8) to 1.01 (6) Å, C–C–H angles range from 105 (3) to 113 (4)°, while H–C–H angles range from 100 (4) to 116 (4)°.

Results

CuCO(O-*t*-Bu) exists as a cubane tetramer which produces an 18-electron configuration at each copper without the need of any metal–metal bonds (Figure 1). In the crystals studied, the tetramer has a crystallographic C_3 axis passing through Cu1 and O12 so that the Cu(1)–C(3)–CO(4) unit is linear by symmetry. The tetramer is regular both with respect to the Cu···Cu separations (3.04 Å) and the alkoxide O···O separations (2.79 Å). Chemically equivalent Cu–C and Cu–O bond lengths are all equal within 3σ (difference) yielding overall (noncrystallographic) T_d symmetry. The O–Cu–O angles are all acute (~84°) resulting in O–Cu–C(carbonyl) angles which are remarkably large (~130°). The space-filling drawing (Figure 2) reveals the carbonyl carbon (but *not* the butoxide oxygen) to be sterically accessible. It also shows the manner in which the *tert*-butoxide methyl groups interleave the three adjacent carbonyl groups; these two threefold rotors exist in a staggered conformation.

In view of the high lability of copper complexes, it is important to establish whether a precipitated solid is representative of the species present in solution or whether it is merely the least soluble participant in a mobile equilibrium. A cryoscopic molecular weight determination (in benzene) yielded a value of 697, which is within experimental error of the theoretical value (659) for a tetramer. The ^{1}H NMR of a solution of $[CuCO(O\text{-}t\text{-}Bu)]_4$ in C_6D_6 shows only a single signal; as does the infrared spectrum (2063 cm^{-1} in toluene). The infrared spectrum is unchanged under 1 atm of CO even at −78 °C (toluene), indicating that additional CO cannot substitute for the alkoxide bridges. We have sought evidence for the production of species with an average CO/Cu ratio of less than unity; such species might be intermediates in the carbonylation of $(CuO\text{-}t\text{-}Bu)_4$. The ^{1}H NMR spectrum (16 °C) of equimolar $(CuO\text{-}t\text{-}Bu)_4$ and $[CuCO(O\text{-}t\text{-}Bu)]_4$ in C_6D_6 exhibits only the two individual resonances of the dissolved compounds. No conproportionation, and no rapid CO exchange, occurs. As a final test of possible equilibria yielding trimers, dimers, etc., we examined the influence of added *t*-BuOH on the ^{1}H NMR spectrum of a C_6D_6 solution of $[CuCO(O\text{-}t\text{-}Bu)]_4$. We anticipated that the four-coordinate oxygen of the tetramer has no unused basicity, while the μ-O-*t*-Bu group in a dimer or trimer could exchange with *t*-BuOH by proton transfer to an alkoxide lone pair. This latter contention is supported by the observation that a 1:4 mixture of $[Cu(\mu\text{-}O\text{-}t\text{-}Bu)]_4$ (δ 1.30) and *t*-BuOH (CH_3 at δ 1.07) shows only one methyl proton resonance at δ 1.16 (220 MHz at 16 °C in C_6D_6). When 4 mol of *t*-BuOH are added to 1 mol of $[CuCO(O\text{-}t\text{-}Bu)]_4$ in C_6D_6, the δ 1.43 ^{1}H NMR signal of the latter appears unchanged.

The $^{13}C\{^1H\}$ NMR spectrum of 99% enriched $[Cu(^{13}CO)O\text{-}t\text{-}Bu]_4$ at 25 °C shows (in addition to two sharp singlets for the O-*t*-Bu group) an exceptionally broad resonance ($\Delta\nu_{1/2} = 2 \times 10^3$ Hz) centered at about 173 ppm. This resonance has a flat-topped appearance which develops a barely discernible four-line structure at 60 °C. The spacing between these lines (6×10^2 Hz) is assigned as $J(Cu\text{–}^{13}C)$. This establishes the integrity of the Cu–CO bond against rapid dissociation/rearrangement. The appearance of such coupling is indicative of pseudotetrahedral symmetry at copper, which is inconsistent with reorganization of $[CuCO(O\text{-}t\text{-}Bu)]_4$ to a dimer or trimer upon dissolution.

The ^{63}Cu NMR spectrum of a C_6D_6 solution of 99% enriched $[Cu(^{13}CO)O\text{-}t\text{-}Bu]_4$ is a broad and essentially unstructured single line (δ 49) at 25 °C. However, by 60 °C, the relaxation rate of this quadrupolar nucleus has slowed to the point where a clearly defined doublet ($J(^{63}Cu\text{–}^{13}C) = 8 \times 10^2$ Hz) is observed at δ 40.2. This is, to our knowledge, the first ^{63}Cu resonance observed for a copper complex lacking rigorous T_d symmetry. This result independently establishes the dissociative stability of the Cu–CO bond (at 60 °C) and also rules out facile intramolecular scrambling of carbonyl ligands among the four metals in $[CuCO(O\text{-}t\text{-}Bu)]_4$. The observation of a single chemical shift also establishes that $[CuCO(O\text{-}t\text{-}Bu)]_4$ dissolves to give a single species.

Discussion

The tetrameric aggregation of the unit CuCO(O-*t*-Bu) contrasts to the linear monomeric form adopted by Au(CO)Cl[14] but is consistent with the tendency of Cu(I) to approach coordinative saturation (i.e., to utilize all nine valence orbitals[15]) when this is sterically possible. The cubane structure adopted is also that found in isoelectronic $[ZnCH_3(OMe)]_4$.[16] The structure found here for sterically unhindered $[CuCO(O\text{-}t\text{-}Bu)]_4$ (Figure 2) confirms that the alternative step tetramer[17] is adopted primarily to reduce ligand–ligand repulsions.

The Cu—CO and C≡O distances found here are well within the range of those found in other copper(I) carbonyls.[7] The Cu–(μ_3-OR) distance, 2.06 Å, is much longer than the average 1.84 Å found in the wholly planar $(CuO\text{-}t\text{-}Bu)_4$.[18] In $(CuO\text{-}t\text{-}Bu)_4$, copper is electron deficient (two-coordinate), and multiple Cu–O bonding is indicated. The Cu–(μ-O-*t*-Bu) distance in $(Cu(PPh_3)O\text{-}t\text{-}Bu)_2$ is 1.98 Å.[19] The dimensions of the Cu_4O_4 core in $[CuCO(O\text{-}t\text{-}Bu)]_4$ are within 0.03 Å of those in $[ZnCH_3(OMe)]_4$.[16]

The trigonal distortion of the copper coordination sphere (∠C–Cu–O ≈ 130°) exceeds that in all $[(R_3E)CuX]_4$[20] (X = halide)

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(14) Jones, R. G. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 823.

(15) Evans, D. G.; Mingos, D. M. P. *J. Organomet. Chem.* **1982**, *232*, 171.

(16) Shearer, H. M. M.; Spencer, C. B. *Acta Crystallogr., Sect. B* **1980**, *B36*, 2046.

(17) Churchill, M. R.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 3267.

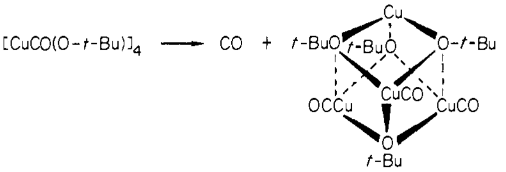
(18) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142.

(19) Unpublished results from this laboratory.

(20) Teo, B. K.; Calabrese, J. C. *Inorg. Chem.* **1976**, *15*, 2467.

cubanes studied to date but is quite comparable to that in $[ZnCH_3(OMe)]_4$.

This structural study reveals no unusual molecular dimensions which would explain the resistance of $[CuCO(O\text{-}t\text{-}Bu)]_4$ toward decarbonylation. For example, there is no evidence that a set of μ_3-OR ligands yields an exceptionally short Cu–CO distance. Consequently, it is perhaps preferable to focus on the character of the initial decarbonylation product (eq 1) to rationalize the observed stability. The product $Cu_4(CO)_3(O\text{-}t\text{-}Bu)_4$ has been drawn with the unsaturated copper center in a pyramidal geometry due to the constraint of the rigid tridentate cubane "ligand". Moreover, if the copper were to be drawn toward the center of the cube, it would experience Cu^I/Cu^I (closed-shell) repulsions. Such pyramidality makes this intermediate unstable,[21-23] and the activation enthalpy of eq 1 is consequently increased over a situation lacking steric constraints. The *tert*-butoxide carbonyl thus achieves *kinetic* stability. This claim is also consistent with the observation that $(CuO\text{-}t\text{-}Bu)_4$ does not react with $[CuCO(O\text{-}t\text{-}Bu)]_4$ to give some $Cu_4(O\text{-}t\text{-}Bu)_4(CO)_n$ ($n < 4$) species. Finally, this argument accommodates the fact that the most stable of the nitrogen-ligated copper carbonyls, $(HBpz_3)CuCO$[24,25] and $[Cu(dien)CO]BPh_4$,[26] also involve ligands which cannot accommodate a trigonal-planar copper coordination geometry following decarbonylation.[27-29] For comparison, $Ni(CO)_4$ is known to decompose promptly to nickel metal at 25 °C when it is not held under a CO atmosphere; decomposition via a low E_a CO-loss path, involving planar $Ni(CO)_3$, is indicated.



(1)

The only previous ^{13}C NMR measurements on copper(I) carbonyls are those reported[30] for solution species (not isolated) claimed to be $Cu(CO)_n^+$ (n = 1–4). In strong acid solvents all of these had essentially the same chemical shift, 169 ppm. In marked contrast to $[CuCO(O\text{-}t\text{-}Bu)]_4$, the $Cu(CO)_n^+$ species had line widths of 8–37 Hz, with the tetracarbonyl not significantly sharper than any other species. The accumulted evidence[30] on the $Cu(CO)_n^+$ species is that they undergo rapid CO exchange. Consequently, their lines widths are determined by viscosity broadening in the viscous solvents employed; quadrupolar broadening is therefore not a factor in the observed spectra, as it is in $[CuCO(O\text{-}t\text{-}Bu)]_4$.

The ^{13}C chemical shifts of CO bound to Cu(I) are upfield (smaller δ values) of free CO (184 ppm[31]). These are among the highest field metal carbonyl chemical shifts observed. This extreme position is apparently diagnostic of minimal back-bonding. For comparison, a series of $Pt(CO)Cl_2(py)$ complexes ($\nu_{CO} \approx 2135$ cm^{-1}) has $\delta(^{13}CO)$ in the range of 150–152 ppm.[32] The chemical shift of $Cu(CO)_n^+$ (ν_{CO} = 2140–2180 cm^{-1}) is negligibly different from that of $[CuCO(O\text{-}t\text{-}Bu)]_4$, whose ν_{CO} value is 100 cm^{-1} lower. The chemical shift of Cu(I) carbonyls is apparently insensitive to environment.

Finally we wish to point out an apparent paradox arising from a comparison of spectroscopic and structural data on cuprous carbonyls. Carbonyl stretching frequencies in such complexes are high (>2050 cm^{-1}), suggesting minimal backbonding. On the other hand, Cu–CO distances are short (1.75–1.80 Å), consistent with a strong bond.[33]

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Registry No. $[CuCO(O\text{-}t\text{-}Bu)]_4\cdot 1.5THF$, 85479-94-3; $(CuO\text{-}t\text{-}Bu)_4$, 60842-00-4; ^{63}Cu, 14191-84-5.

Supplementary Material Available: Listing of anisotropic temperature factors, hydrogen atom positional parameters, and observed and calculated structure factors for $[CuCO(O\text{-}t\text{-}Bu)]_4\cdot 1.5$ THF (13 pages). Ordering information is given on any current masthead page.

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(21) Burdett, J. K. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 1599.

(22) Burdett, J. K. *Inorg. Chem.* **1975**, *14*, 375.

(23) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(24) Bruce, M. I.; Ostazewski, A. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

(25) Churchill, M. R.; DeBoer, B. G.; Ratella, F.; Abu Salah, O. M.; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051.

(26) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684.

(27) When $Cu(HPpz_3)CO$ does decarbonylate it forms a *dimer*, with four-coordinate copper: Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

(28) An argument of this sort has been proposed to explain the reluctance of $OsH(CH_3)(CO)_4$ to reductively eliminate methane: Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139.

(29) In copper(I) carbonyls which are salts, it is of course necessary to avoid a nucleophilic counterion which might replace CO to give a tetrahedral product.

(30) Souma, Y.; Iyoda, J.; Sano, H. *Inorg. Chem.* **1976**, *15*, 968.

(31) Heaton, B. T.; Jonas, J.; Eguchi, T.; Hoffman, G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 331.

(32) Cooper, D. G.; Powell, J. *Inorg. Chem.* **1977**, *16*, 142.

(33) Ni^{II}–alkyl (1.94 Å)[34] and Zn^{II}–Me (1.95 Å)[16] distances lead to a predicted Cu^{II}–alkyl distance of 1.95 Å; this sets a lower limit on the Cu^I–alkyl distance. Subtracting 0.07 Å for the difference between the single-bond radii of sp^3 and sp carbon yields a lower limit on the predicted Cu^I–CO single bond length of 1.88 Å.

(34) Barnett, B. L.; Krüger, C. *J. Organomet. Chem.* **1972**, *42*, 169.