H–C–H angle in form B was constrained in the refinement to be 109.5°, while its calculated value after the refinement of form A was 98 (9)°. However, these hydrogen positions are quite poorly determined, since they were refined as half-weight hydrogen atoms in the proximity (approximately 0.8 Å) of the disordered carbonyl oxygen, so no conclusions regarding H–C–H or M–C–H angles should be drawn from the results reported here.

In the few structures in which metal geometry is such that one terminal CO group is clearly trans to μ-CR$_2$ (where R can be H), patterns of M–C bond lengths seem to be emerging which suggest that μ-CR$_2$ may be, in fact, a slightly poorer π acceptor than μ-CO. For example, in three heteronuclear μ-carbene complexes reported by Stone and co-workers, the following M–CO(terminal) bond lengths are seen: in (μ-C(OMe)(C$_6$H$_4$-Me-4))Pt(PMe$_3$)$_2$W(CO)$_4$)(PMe$_3$)[4]—W–CO trans to μ-CR$_2$ = 1.96 (2) Å, trans to PMe$_3$ = 1.95 (1), and trans to CO = 2.02 (2) and 2.03 (2) Å; in (μ-C(OMe)(Ph))Pt(PMe$_3$)$_2$W(CO)$_5$[8]—W–CO trans to CR$_2$ = 1.99 (1) Å and trans to CO = 2.03 (1), 2.04 (1), 2.06 (1), and 2.07 (2) Å; in (μ-C(CO$_2$Me)(Ph))Pt(PMe$_3$)$_2$Cr(CO)$_4$(PMe$_3$)[6]—Cr–CO trans to μ-CR$_2$ = 1.85 (4) Å, trans to PMe$_3$ = 1.75 (5) Å (semibridging), and trans to CO = 1.86 (5) and 1.93 (5) Å. Thus, in these complexes, M–CO trans to μ-CR$_2$ tends to be shorter than M–CO trans to other carbonyls. Two features which complicate the extrapolation to comparison of μ-CR$_2$ and μ-CO are that (1) these complexes do not contain μ-CO for direct comparison and (2) these μ-CR$_2$ bridges all carry aromatic or O-containing substituents and may thus not be strictly comparable to μ-CH$_2$ or μ-CR$_2$ where R = alkyl.

Further, though still not definitive, structural indications along these lines are seen in 1 and in (μ-CH$_2$)(μ-CO)$_2$Fe$_2$(CO)$_6$.[15] In the latter structure, the small but perhaps marginally significant decrease in the Fe-CO(terminal) bond lengths compared to those in Fe(CO)$_9$[30] was viewed as a consequence of strengthening the Fe-CO(terminal) bonding due to the substitution of the slightly poorer π-acceptor μ-CH$_2$ for μ-CO.[15] In similar fashion in 1, the Mn–CO bonds trans to μ-CH$_2$/CO are distinctly shorter (1.823 (3) Å in form A and 1.809 (5) and 1.812 (6) Å in form B, average 1.815 Å) than those trans to terminal CO (1.852 (6) and 1.864 Å in form A and 1.839 (6) and 1.872 (5) Å in form B, average 1.857 Å). These latter values may be compared with, e.g., the values for the seven Mn–CO lengths not trans to Mn–Mn in the nonbridged Mn$_2$(CO)$_9$(CPh(OMe))[31]—average = 1.847 Å and range = 1.832–1.856 Å—in which the Mn–CO length trans to the (terminal) carbene is 1.979 (5) Å. Unfortunately, due to the disorder present in both 1 and in (μ-CH$_2$)(μ-CO)Fe$_2$(CO)$_6$,[15] the terminal CO positions obtained by refinement are the weighted averages of those actually trans to μ-CH$_2$ and those trans to μ-CO, weighted as 1:1 in 1 and as 1:2 in the Fe$_2$ structure. A careful determination of an ordered structure (preferably not involving Cp or phosphines—vide supra) in which one terminal CO is clearly trans to μ-CH$_2$ and one is clearly trans to μ-CO should help to clarify this point.

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Registry No. 1, 83350-15-6.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, anisotropic thermal parameters, and bond lengths and angles involving hydrogens (21 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of Some Carbonyl-Bridged Dinuclear Copper Complexes[†]

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Several complexes of the type (diamine)$_2$Cu$_2$(CO)(O$_2$CR)$^+$X$^-$, which contain both a carbonyl and a carboxylate group bridging two coppers, have been prepared. The preferred method of synthesis involves the reaction of Tl(O$_2$CR) and (diamine)CuI under a CO atmosphere. All the complexes are characterized by a CO absorption in the infrared at approximately 1900–1950 cm^{-1}. A related compound, (tmed)$_2$Cu$_2$(CO)C$_4$O$_4$, which contains a bridging squarate group, was also prepared and the structure of its CH$_2$Cl$_2$ solvate characterized by single-crystal X-ray diffraction. The geometry of the squarate complex is quite similar to that of the benzoate derivative in spite of the charge difference and the much larger "bite" of the squarate ligand compared to the benzoate group.

Introduction

In a recent publication by Floriani's group in Pisa[1] a novel binuclear copper(I) complex was described in which the copper atoms are bridged by a single CO molecule as well as by a benzoate ion. This represents the only known complex of copper with a bridging CO although a few other binuclear copper complexes with terminal CO groups are known[2-7] There is also at least one example of what

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[†] Dedicated to the memory of Rowland G. Pettit.

(1) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *J. Am. Chem. Soc.* **1981**, *103*, 186.

apparently is a mononuclear copper carbonyl carboxylate, $Cu(CO)(CF_3CO_2)$, which has been prepared;[8] however, it has not been structurally characterized. As pointed out by the authors,[1] the bridging bonding mode for carbon monoxide may facilitate its metal-promoted reduction. In view of the role played by copper(I) species in the present generation of heterogeneous methanol synthesis catalysts,[9] this discovery has important implications in the understanding of the mechanism of CO reduction and in the development of new, more efficient catalysts for this process.

Because of the potential importance of these carbonyl-bridged copper complexes, we initiated a study of the preparation, characterization, and reactions of these and some similar types of compounds.

Results and Discussion

The method of synthesis employed for the $(tmed)_2Cu_2(\mu\text{-}CO)(\mu\text{-}O_2CC_6H_5)^+$ species involved the reaction of copper(I) benzoate with *N,N,N′,N′*-tetramethylethylenediamine (tmed) in methanol under a CO atmosphere and the subsequent precipitation of the cation as the tetraphenylborate salt (eq 1). Although this method

$$2Cu(O_2CR) + 2\text{diamine} + CO \rightarrow Cu_2(CO)(O_2CR)(\text{diamine})_2^+ + O_2CR^-$$

$$Cu_2(CO)(O_2CR)(\text{diamine})_2^+ + BPh_4^- \rightarrow Cu_2(CO)(O_2CR)(\text{diamine})_2BPh_4 \quad (1)$$

of synthesis works quite well for this particular compound, it is not a particularly useful general synthetic route mainly due to the nonavailability of the copper(I) carboxylates. In contrast to the benzoate and some substituted benzoates, other simple copper(I) carboxylates are much more difficult to obtain in useful quantities and are not very stable or easily handled.[10] Two alternate methods of synthesis were developed which did not require the preparation of the intermediate carboxylates. The first and most general of the methods employs the thallium(I) carboxylates, which are stable and readily prepared from the free acid. The reaction of these Tl salts with (diamine)copper(I) halide complexes under a CO atmosphere results in the formation of the dinuclear CO-bridged cations as the carboxylate salts.

$$2Tl(O_2CR) + 2(\text{diamine})CuX + CO \rightarrow 2TlX + Cu_2(CO)(\text{diamine})(O_2CR)^+ + RCO_2^- \quad (2)$$

The carboxylate salts can either be isolated as such or can be converted to other less soluble salts such as the tetraphenylborate by simple metathetical reactions. Since most thallium carboxylate salts can easily be prepared from the carboxylic acids by the reaction with thallium(I) ethoxide, and the (diamine)copper(I) halide complexes are formed by the simple addition of the diamine to the copper halide, there are few limitations as to the availability of the reactants in this method.

The third synthetic route employs the direct reaction of the carboxylic acid with copper(I) oxide in the presence of the diamine and CO.

$$Cu_2O + 2RCO_2H + 2\text{diamine} + CO \rightarrow Cu_2(CO)(\text{diamine})_2(O_2CR)^+(O_2CR)^- + H_2O \quad (3)$$

Although the simplest procedure, this method of synthesis was not very useful in that it worked well only for formic acid. None of the three methods of synthesis will work in all cases, and the preferred method is best determined by trial and error. The success of a particular synthesis is often affected by a number of different reaction parameters, including the choice of solvent, which often plays a crucial role.

A considerable number of different dinuclear copper complexes with a bridging CO group have now been prepared containing a variety of diamine and carboxylate groups, indicating that these complexes represent a fairly large class. Although the synthesis of several complexes has been successful, not all possible combinations of ligands have been tried nor has every combination tried been successful.

A variety of chelating diamines have been used including ethylenediamine (en), symmetrical and unsymmetrical *N,N*-dimethylethylenediamine (sden and uden), *N,N,-N′,N′*-tetramethylethylenediamine (tmed), *N,N,N′,N′*-tetramethylmethylenediamine (tmmd), *N,N,N′,N′*-tetramethyl 1,3-propylenediamine (tmpd), *N,N,N′,N′*-tetraethylethylenediamine (teed), 2,2-bipyridyl, and 1,10-phenanthroline. With the exception of tmmd, which did not yield any isolable carbonyl complexes, we could find no apparent restrictions as to the structure of the aliphatic diamines with respect to their ability to form the bridging carbonyl complexes, although we tried no diamines with very long bridging groups or with large or bulky substituents on the nitrogen. Aromatic diamines such as 2,2-bipyridyl or 1,10-phenanthroline form only mononuclear complexes with a terminal CO, such as $Cu(bpy)CO^+RCO_2^-$. As might be expected, preparations with monodentate aliphatic amines were not successful, but pyridine appears to form unstable complexes with bridging carbonyls which contain both 1 and 2 equiv of pyridine per copper. It is also interesting to note that the phosphorus analogue of tmed, bis(dimethylphosphino)ethane (dmpe), did not form a complex with a bridging CO or in fact with any CO at all, but rather compounds of the type $Cu(dmpe)RCO_2$ were isolated.

The carboxylic acids which form these bridging carbonyl complexes cover a fairly wide range of acidities (pK_a's from 3.42 to 5.05) and steric characteristics; they include acetic, phenylacetic, trimethylacetic, *p*-nitrobenzoic, *p*-toluic, and formic acids. Very strong acids, especially the halogen-substituted acetic acids, tended to give mononuclear complexes with a terminal CO group of the type $Cu(L_2)(CO)^+RCO_2^-$. These complexes could usually be prepared either from Cu_2O and the free acid or from a copper halide and the sodium or thallium carboxylate. In several cases, disproportionation reactions occur resulting in the deposition of copper metal and the formation of copper(II) species. It is not certain if the complexes are formed but decompose due to their inherent instability or if the disproportionation occurs before the complex is formed.

In addition to monocarboxylic acids, a number of other compounds which could potentially act as anionic bridging ligands were investigated. Among these compounds were

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several dicarboxylic acids such as malonic acid, oxalic acid, terephthalic acid, and fumaric acid. The dicarboxylic acids could potentially react in a number of different ways; however, with the exception of oxalic acid, none of the dicarboxylic acids gave any signs of forming any kind of dinuclear copper complexes with a bridging CO group.

If copper carbonyl oxalate $Cu_2(CO)_2(C_2O_4)$ is contacted with an excess of tmed, an insoluble compound with the composition $Cu_2(tmed)(CO)_2C_2O_4$ is obtained. In contrast to $Cu_2(CO)_2C_2O_4$ which has CO stretching bands at 2122 and 2110 cm^{-1}, the tmed adduct has two bands of equal intensity at 2080 and 1930 cm^{-1}. The latter is characteristic of a CO group bridging two coppers, whereas the 2080-cm^{-1} band is typical of polyamine copper complexes with terminal CO's.[11] Because of the insolubility of this material, very little can be said concerning its structure if it is indeed a single pure compound.

An attempt to prepare a complex with a CO and thiocarboxylate as bridging groups failed. Although thallium thiobenzoate reacts smoothly with (tmed)CuI to give TlI and the resulting solution shows a strong IR absorption at ~2080 cm^{-1}, no carbonyl-containing species could be isolated. Upon crystallization from the reaction mixture, only an uncharacterized orange solid was obtained.

In order to determine how unique the carboxylate group is at forming dinuclear copper complexes with bridging carbonyls, we attempted the synthesis (using procedures similar to those employed in preparing the carboxylate derivatives) of complexes derived from β-diketones, catechols, tropolone, and squaric acid (1,2-dihydroxycyclobutenedione). In contrast to the five-membered ring formed by the two coppers and the chelating carboxylate group, the β-diketones would be expected to form seven-membered rings and tropolone and catechol and squaric acid to form six-membered rings. With the exception of the squarate group, none of the above-mentioned potentially bridging ligands proved suitable for the formation of dinuclear copper complexes. Even catechol and its mono- and dichlorinated derivatives proved to be unsuitable.

The reaction of copper(I) squarate with tmed under CO did lead to an interesting binuclear copper complex. When copper(I) squarate, which is formed as an insoluble tan solid by the reaction of squaric acid with Cu_2O under CO, is treated with tmed under a CO atmosphere in methylene chloride, the solids rapidly dissolve, giving a clear yellow solution with infrared bands at 2070 and 1910 cm^{-1}. On evaporation of a portion of the solvent and cooling, pale yellow brown crystals are formed which have the composition $Cu_2(tmed)_2(CO)C_4O_4{\cdot}CH_2Cl_2$. The solid complex which has a single CO stretching band at 1908 cm^{-1} appeared to be electrically neutral, in contrast to the cationic carboxylate derivatives. This plus the fact that additional bands were observed in the infrared at 1640, 1530, and 1450 cm^{-1} indicated that the squarate moiety was not symmetrically coordinated through all four oxygen atoms as is generally observed. In order to confirm this possibility and to compare the overall structure to that of the $Cu_2(tmed)_2(CO)O_2CC_6H_5^+$ cation, a single-crystal X-ray analysis was undertaken.

Figure 1 shows an ORTEP view of the molecule, and Tables I and II give a list of the bond lengths and selected bond angles. The presence of the bridging CO group is confirmed as is the chelating squarate moiety. In many respects, the overall geometry is quite similar to the benzoate derivative. Especially interesting is the similarity of the Cu–Cu bond length (2.422 vs. 2.410 Å) and the bond distances and angles associated with the bridging carbonyl group. This is particularly surprising in lieu of the difference in charge and the "bite" of the chelating squarate as compared to the benzoate. The O–O distance of the oxygen atoms on the chelating groups is 2.19 Å for the benzoate vs. 3.21 Å for the squarate in these complexes.

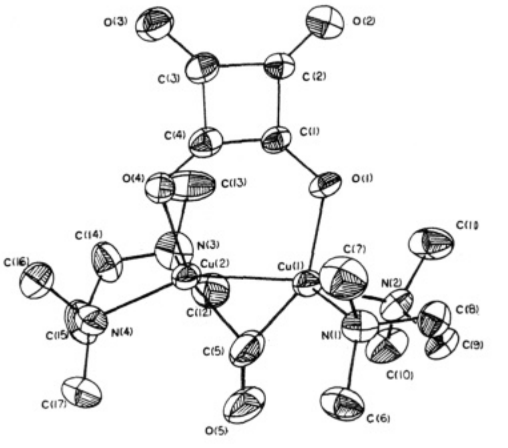

Figure 1. ORTEP view of $(tmed)_2Cu_2(CO)C_4O_4$ showing the coordination about the copper atoms.

Table I. Interatomic Bond Lengths (Å)

Cu(1)-Cu(2)	2.422 (1)	O(1)-C(1)	1.282 (5)
Cu(1)-O(1)	1.964 (3)	O(2)-C(2)	1.224 (5)
Cu(1)-N(1)	2.147 (4)	O(3)-C(3)	1.244 (5)
Cu(1)-N(2)	2.129 (4)	O(4)-C(4)	1.277 (5)
Cu(1)-C(5)	1.836 (6)	O(5)-C(5)	1.164 (6)
Cu(2)-O(4)	1.974 (3)	N(1)-C(6)	1.484 (6)
Cu(2)-N(3)	2.189 (4)	N(1)-C(7)	1.518 (6)
Cu(2)-N(4)	2.104 (4)	N(1)-C(8)	1.479 (6)
Cu(2)-C(5)	1.860 (5)		
N(2)-C(9)	1.489 (6)	C(1)-C(2)	1.467 (6)
N(2)-C(10)	1.512 (6)	C(1)-C(4)	1.401 (6)
N(2)-C(11)	1.486 (6)	C(2)-C(3)	1.466 (6)
N(3)-C(12)	1.474 (7)	C(3)-C(4)	1.462 (6)
N(3)-C(13)	1 493 (7)	C(8)-C(9)	1.507 (7)
N(3)-C(14)	1.472 (7)	C(14)-C(15)	1.504 (8)
N(4)-C(15)	1.507 (7)		
N(4)-C(16)	1.485 (6)		
N(4)-C(17)	1.495 (7)		

The geometric arrangement of the five groups bound to each copper is very irregular and does not fit a simple description. If one neglects the Cu–Cu interaction, the light atoms form an approximately tetrahedral configuration about the copper. This lack of symmetry might be expected when the coordinating groups are all quite different and a d^{10} species with an essentially spherical electron distribution and nondirected orbitals is involved. There can be little doubt that a copper–copper bond is present in this complex: the Cu–Cu bond distance (2.422 Å) is considerably shorter than in copper metal (2.55 Å)[12] or in $Cu_2(CH_3CO_2)_4{\cdot}2H_2O$ (2.65 Å).[13]

There are a few minor but distinct differences in the structures of the benzoate cation and the neutral squarate complex that can be predicted due to the difference in charge and steric requirements of the bridging ligands. As would be expected, the C–O distance of the CO ligand is noticeably longer and the Cu–C distances are shorter in the neutral squarate complex as compared to those of the cationic benzoate. The tmed ligands also appear to be bent

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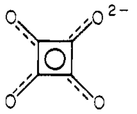
Table II. Interatomic Bond Angles (deg)

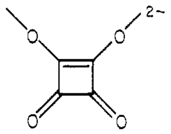
Cu(2)-Cu(1)-O(1)	98.93 (10)	Cu(1)-Cu(2)-N(3)	111.22 (13)	C(9)-N(2)-C(11)	110.69 (43)
Cu(2)-Cu(1)-N(1)	126.67 (11)	Cu(1)-Cu(2)-N(4)	150.00 (12)	N(1)-C(8)-C(9)	109.91 (39)
Cu(2)-Cu(1)-N(2)	141.04 (11)	Cu(1)-Cu(2)-C(5)	48.64 (17)	N(2)-C(9)-C(8)	110.75 (37)
Cu(2)-Cu(1)-C(5)	49.50 (16)	O(4)-Cu(2)-N(3)	99.52 (16)	Cu(2)-N(3)-C(12)	112.51 (36)
O(1)-Cu(1)-N(1)	97.66 (15)	O(4)-Cu(2)-N(4)	99.73 (15)	Cu(2)-N(3)-C(13)	111.32 (34)
O(1)-Cu(1)-N(2)	96.28 (14)	O(4)-Cu(2)-C(5)	146.25 (20)	Cu(2)-N(3)-C(14)	101.31 (33)
O(1)-Cu(1)-C(5)	148.16 (19)	N(3)-Cu(2)-N(4)	85.84 (17)	C(12)-N(3)-C(13)	108.24 (46)
N(1)-Cu(1)-N(2)	86.07 (15)	N(3)-Cu(2)-C(5)	105.75 (23)	C(12)-N(3)-C(14)	112.44 (47)
N(1)-Cu(1)-C(5)	105.18 (22)	N(4)-Cu(2)-C(5)	104.02 (21)	C(13)-N(3)-C(14)	110.97 (48)
N(2)-Cu(1)-C(5)	107.01 (21)	Cu(1)-O(1)-C(1)	123.55 (30)	Cu(2)-N(4)-C(15)	104.55 (32)
O(4)-Cu(2)-Cu(1)	101.37 (9)	Cu(2)-O(4)-C(4)	120.63 (29)	Cu(2)-N(4)-C(16)	109.79 (31)
Cu(1)-N(1)-C(6)	115.52 (33)	C(15)-N(4)-C(16)	112.98 (49)	Cu(2)-N(4)-C(17)	117.25 (34)
Cu(1)-N(1)-C(7)	110.45 (32)	C(15)-N(4)-C(17)	106.10 (43)	O(3)-C(3)-C(2)	136.09 (44)
Cu(1)-N(1)-C(8)	100.92 (28)	C(16)-N(4)-C(17)	106.31 (45)	O(3)-C(3)-C(4)	134.64 (46)
C(6)-N(1)-C(7)	108.43 (40)	N(3)-C(14)-C(15)	112.46 (48)	C(2)-C(3)-C(4)	89.26 (36)
C(6)-N(1)-C(8)	111.00 (40)	N(4)-C(15)-C(14)	109.32 (46)	O(4)-C(4)-C(1)	134.68 (42)
C(7)-N(1)-C(8)	110.34 (39)	O(1)-C(1)-C(2)	133.39 (43)	O(4)-C(4)-C(3)	134.42 (43)
Cu(1)-N(2)-C(9)	103.53 (28)	O(1)-C(1)-C(4)	134.96 (43)	C(1)-C(4)-C(3)	90.90 (37)
Cu(1)-N(2)-C(10)	115.66 (33)	C(2)-C(1)-C(4)	91.64 (36)	Cu(1)-C(5)-Cu(2)	81.86 (23)
Cu(1)-N(2)-C(11)	110.09 (31)	O(2)-C(2)-C(1)	136.41 (44)	Cu(1)-C(5)-O(5)	140.70 (45)
C(9)-N(2)-C(10)	107.59 (38)	O(2)-C(2)-C(3)	135.39 (43)	Cu(2)-C(5)-O(5)	137.43 (46)
C(10)-N(2)-C(11)	109.11 (44)	C(1)-C(2)-C(3)	88.19 (36)		

up and away from the squarate group and in addition the plane consisting of the eight atoms of the squarate group is twisted at a considerable angle with respect to the Cu–Cu–CO plane.

The squarate dianion, although almost rigidly planar, deviates from the symmetrical delocalized



structure in a direction approaching



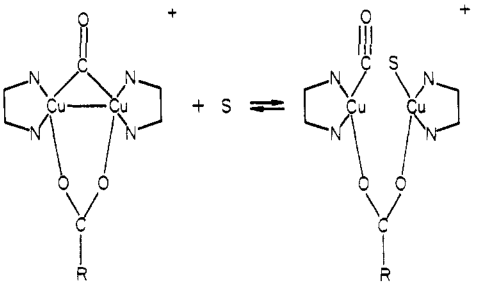
a *diketocyclobutenediolate dianion*.

We have attempted, without success, the preparation of other complexes which would resemble the squarate derivative. Likely candidates were thought to be catecholates with a like charge and similar geometry to the squarate and tropolonates which are uninegative but have a similar chelating bite. In neither case were any well-defined products obtained from the reactions.

In the preparation of the benzoate complex, the intermediate formation of a complex with a terminal CO group was observed and an intermediate with the composition $[Cu(tmed)(CO)CH_3OH]^+BPh_4^-$ was isolated.[1] Although the mechanism of formation of the dinuclear derivatives are not known, it is clear that there are mononuclear copper complexes and free carboxylate groups in solution. We have also found evidence of complexes with terminal carbonyls in solution during the preparation of several other dinuclear carboxylate complexes. Indeed, solutions from which the dinuclear complexes with a bridging CO are crystallized generally contain only low concentrations of the bridging CO complexes, as evidenced by the infrared spectra. In most cases the absorption of these solutions in the terminal CO region (approximately 2080 cm^{-1}) is several times that of the bridging CO region.

Once isolated, the complexes are only fairly stable as solids, although the stability is very dependent on the exact composition of the complex. Most of the complexes slowly decompose on standing and are rapidly oxidized in air. In general, it appears that the neutral squarate complex is more stable than the cationic carboxylate derivatives. The tetraphenylborate salts of the cations tend to be more stable than the carboxylate salts which are often the initial product isolated. Diamines in which the nitrogens are fully substituted, such as tmed, tend to form more stable derivatives than those derived from partially or unsubstituted diamines. The nature of the bridging carboxylate groups also has a large effect on the ease of formation and stability of the complexes. Those derived from formic acid and trimethylacetic acid are less stable than the acetates which are in turn less stable than the benzoate or substituted benzoates.

Except for the neutral squarate derivatives, these complexes are almost totally insoluble in nonpolar solvents. In polar solvents, the complexes are converted slowly to species with no bridging carbonyls as evidenced by the disappearance of the CO stretching band at ~1900–1950 cm^{-1} and the appearance of a new band in the 2060–2080-cm^{-1} region. It is not certain at this time whether the process involves the complete dissociation of the complex into mononuclear species or if it just involves a solvent interaction which breaks the Cu–Cu bond as shown in eq 4. This process appears to be only partially reversible in



(4)

that only a portion of the bridging CO complex can be recovered after conversion to the terminal species. This is most likely due to a gradual loss of CO from the solution after prolonged periods resulting in species containing no carbonyl groups at all.

Experimental Section

Reagents. All reagents obtained from commercial sources were high purity materials and were used without further purification. Tetrahydrofuran and diethyl ether were distilled from lithium aluminum hydride, methylene chloride was distilled from P_2O_5, and pentane was distilled from sodium. The thallium(I) carboxylate salts were prepared by the reaction of equivalent amounts of thallium(I) ethoxide and the carboxylic acid in benzene.

Analysis. Elemental analyses were carried out by either Galbraith Analytical Laboratories or by the Analytical and Information Division, Exxon Research and Engineering Co. The data are summarized in Table III.

Infrared spectra were recorded in solution or as Nujol mulls and were calibrated by comparison with the spectrum of polystyrene film. A Perkin-Elmer Model 283 spectrophotometer was used.

Preparation of the Complexes. The method of synthesis of the individual complexes is given in Table III. These three methods are illustrated by the following examples:

Method A. Preparation of $(tmed)_2Cu_2(CO)C_4O_4{\cdot}CH_2Cl_2$. A steady stream of CO was bubbled through a suspension of 2.0 g (8.35 mmol) of $Cu_2C_4O_4$ in 75 mL of CH_2Cl_2 for 10 min. Tetramethylethylenediamine (1.94 g, 16.7 mmol) was then added, and after a 2-h period the solids were almost completely dissolved, giving an almost clear brown solution. The solution was filtered to remove a small amount of residual solid, and the filtrate was reduced to a third its volume on a rotary evaporator, yielding a tan solid. This was recrystallized from a methylene chloride–pentane mixture, giving 3.0 g (61%) of tan crystals.

Method B. Preparation of $(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$ and $(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+(C_6H_5)_4^-$. A suspension of 1.75 g (9.2 mmol) of CuI in 75 mL of methylene chloride was stirred for 30 min under CO, and then tmed (1.07 g, 9.2 mmol) was added and the mixture stirred for an additional 20 min. To the resulting clear solution was added 3.0 g (9.2 mmol) of $TlO_2CC_6H_5$, and the resulting mixture was stirred under CO for 30 more min. The mixture was filtered through a fine glass frit, yielding 3.03 g of TlI (100% recovery). The filtrate could then be reduced to one-third its volume, and upon addition of 100 mL of pentane crude $(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+(O_2CC_6H_5)^-$ could be precipitated. Alternatively, if $NaB(C_6H_5)_4$ (1.57 g, 4.6 mmol) was added in small portions to the filtrate over a 10-min period, a precipitate of $NaO_2CC_6H_5$ gradually forms. This can be filtered off after 30 min and the clear filtrate evaporated to dryness on a rotary evaporator, yielding a pale green residue. Washing the residue several times with pentane resulted in the recovery of 3.7 g (97%) of a pale green product.

Method C. Preparation of $(tmed)_2Cu_2(CO)(O_2CH)^+B(C_6H_5)_4^-$. A suspension of Cu_2O (2.0 g, 14 mmol) in 100 mL of THF solution containing 3.25 g (28 mmol) of tmed was stirred under CO for 20 min followed by the dropwise addition of a solution containing 1.29 g (28 mmol) of formic acid in 25 mL of THF. $NaB(C_6H_5)_4$ (4.78 g, 14 mmol) was slowly added to the suspension, and the resulting mixture was stirred an additional 30 min under CO. The mixture was then filtered removing 1.25 g of white solids consisting mainly of NaO_2CH. The filtrate was evaporated, and the resulting pale green residue was washed with several portions of pentane yielding 9.9 g (94%) of dry product.

Preparation of $Cu_2(CO)_2(C_2O_4)$. A suspension of 2.52 g (0.02 mol) of oxalic acid in 50 mL of THF was added to a suspension of 2.86 g (0.02 mol) of copper(I) oxide in 75 mL of THF while a stream of CO was passed through the mixture. After several hours the red color of the oxide disappeared and a gray solid was formed which after 16 h had turned white. The reaction was allowed to continue for an additional 2 h, and then the suspended solids were collected on a glass frit, washed with several 25-mL portions of ether, and dried. The yield was quantitative. Anal. Calcd for $C_4Cu_2O_6$: C, 17.71; H, 0.00. Found: C, 17.60; H, 0.29.

Reaction of $Cu_2(CO)_2(C_2O_4)$ with tmed. A mixture of 1.17 g (0.043 mol) of $Cu_2(CO)_2(C_2O_4)$ and 1.00 g (0.0086 mol) of tmed in 50 mL of THF was stirred for 16 h at room temperature while a steady stream of CO was passed through the solution. The solid was filtered off, washed with five 25-mL portions of pentane, and vacuum dried. The yield of gray solid was 1.25 g (75%). Anal. Calcd for $C_{10}H_{16}Cu_2N_2O_6$: C, 30.98; H, 4.13; N, 7.23; Cu, 32.81. Found: C, 30.55; H, 4.14; N, 7.99; Cu, 32.31.

Attempted Preparation of $Cu_2(CO)(dmpe)_2C_4O_4$. A suspension of 1.0 g (4.18 mmol) of $Cu_2C_4O_4$ in 50 mL of methylene chloride was stirred under a CO atmosphere while 1.25 g (8.34 mmol) of dmpe was slowly added. After approximately 2 h the solid material had almost completely dissolved. The solution was filtered, but the clear filtrate showed no evidence of any carbonyl

Table III. Preparation and Analyses of the Dinuclear Copper Complexes

complex	method of preparan	ν_{CO}, cm^{-1}	elemental anal. found (calcd)			
			C	H	N	Cu
$(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+B(C_6H_5)_4^-$	B	1917	60.72 (63.83)	7.41 (6.94)	7.71 (6.77)	15.78 (15.35)
$(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1922				23.62 (20.18)
$(en)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1915	41.08 (44.09)	5.51 (5.06)	10.26 (10.82)	
$(tmed)_2Cu_2(CO)(O_2CH)^+B(C_6H_5)_4^-$	C	1922	62.45 (60.71)	7.61 (7.11)	8.20 (7.45)	15.35 (16.90)
$(tmed)Cu_2(CO)(O_2CCH_3)^+O_2CCH_3^-$	B	1920	31.34 (33.92)	5.56 (5.70)	7.80 (7.20)	30.78 (32.63)
$(tmed)_2Cu_2(CO)C_4O_4{\cdot}CH_2Cl_2$	A	1905	38.99 (36.98)	5.93 (5.86)	9.90 (9.59)	22.73 (21.74)
$(tmed)_2Cu_2(CO)O_2CC(CH_3)_3{}^+B(C_6H_5)_4^-$	B	1937	59.51 (62.43)	7.36 (7.61)	7.68 (6.94)	15.08 (15.73)
$(tmed)_2Cu_2(CO)(O_2CCH_3)^+O_2CCH_3^-$	B	1923	38.61 (40.38)	5.72 (5.86)	8.39 (9.59)	22.46 (21.74)
$(tmed)_2Cu_2(CO)(O_2CCH_2C_6H_5)^+O_2CCH_2C_6H_5^-$	B	1930	49.97 (52.94)	6.41 (7.05)	8.81 (8.52)	
$(tmed)_2Cu_2(CO)(O_2CC_6H_4CH_3)^+O_2CC_6H_4CH_3^-$	B	1923				19.25 (19.32)
$(tmed)_2Cu_2(CO)(O_2CC_6H_4NO_2)^+B(C_6H_5)_4^-$	B	1920	58.33 (60.54)	6.47 (6.00)	8.10 (8.02)	13.86 (14.56)
$(py)_4Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1943	59.61 (58.89)	3.99 (4.24)	6.98 (7.85)	17.99 (17.80)
$(py)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1945	51.09 (54.05)	3.76 (3.63)	5.15 (5.04)	22.29 (22.87)
$(teed)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1925	55.22 (56.65)	7.52 (7.88)	7.45 (7.55)	
$(sden)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1906	49.18 (48.15)	4.82 (5.97)	9.86 (9.77)	
$(uden)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5^-$	B	1900	46.26 (48.15)	5.32 (5.97)	10.78 (9.77)	
$(tmpd)_2Cu_2(CO)C_4O_4$	A	1900	40.53 (53.25)	6.87 (6.88)	10.00 (10.62)	23.48 (24.09)
$(teed)_2Cu_2(CO)C_4O_4$	A	1903	49.22 (49.08)	8.07 (7.91)	9.10 (9.16)	19.81 (20.77)

Table IV. Atomic Coordinates for $(tmed)_2Cu_2(CO)C_4O_4 \cdot CH_2Cl_2$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu(1)	0.61598 (5)	0.2473 (1)	0.16365 (8)	C(3)	0.3915 (4)	0.1592 (8)	0.1802 (6)
Cu(2)	0.60439 (5)	0.1457 (1)	0.33553 (8)	C(4)	0.4649 (3)	0.1711 (7)	0.2232 (6)
				C(5)	0.6798 (4)	0.2117 (9)	0.2947 (7)
Cl(1)	0.3981 (3)	0.4548 (4)	0.5109 (3)	C(6)	0.6841 (5)	0.5088 (9)	0.2147 (8)
Cl(2)	0.3975 (3)	0.5043 (4)	0.2816 (3)	C(7)	0.5612 (4)	0.5147 (9)	0.1454 (8)
				C(8)	0.6327 (4)	0.4477 (8)	0.0198 (7)
O(1)	0.5225 (2)	0.2269 (6)	0.0728 (4)	C(9)	0.6851 (4)	0.3525 (8)	0.0061 (7)
O(2)	0.3604 (3)	0.1998 (7)	−0.0269 (5)	C(10)	0.7275 (4)	0.1402 (9)	0.0538 (9)
O(3)	0.3435 (3)	0.1349 (7)	0.2236 (5)	C(11)	0.6144 (5)	0.1716 (10)	−0.0724 (8)
O(4)	0.5057 (2)	0.1595 (6)	0.3203 (4)	C(12)	0.6731 (5)	−0.0982 (10)	0.2844 (9)
O(5)	0.7374 (3)	0.2238 (9)	0.3355 (6)	C(13)	0.5517 (5)	−0.1156 (10)	0.2476 (10)
				C(14)	0.6186 (6)	−0.0972 (10)	0.4425 (8)
N(1)	0.6254 (3)	0.4462 (6)	0.1374 (5)	C(15)	0.6648 (5)	−0.0119 (10)	0.5256 (8)
N(2)	0.6638 (3)	0.2224 (6)	0.0282 (5)	C(16)	0.5798 (4)	0.1408 (13)	0.5645 (7)
N(3)	0.6133 (4)	−0.0596 (7)	0.3246 (6)	C(17)	0.6936 (5)	0.2040 (11)	0.5735 (8)
N(4)	0.6374 (3)	0.1208 (7)	0.5114 (5)	C(18)	0.4082 (6)	0.3896 (11)	0.3844 (9)
C(1)	0.4723 (4)	0.2003 (7)	0.1149 (6)				
C(2)	0.3990 (4)	0.1891 (7)	0.0668 (6)				

absorption in the infrared. An air sensitive white solid was obtained upon partial evaporation of the solution and cooling to −20 °C.

Attempted Preparation of $Cu_2(CO)(OSCC_6H_5(tmed)_2{}^+ \cdot OSCC_6H_5{}^-$. A solution of (tmed)CuI was prepared by the addition of 1.12 g (5.88 mmol) of CuI and 0.68 g (5.85 mmol) of tmed to 75 mL of methylene chloride under a CO atmosphere. To this stirred solution was added 2.0g (5.86 mmol) of $Tl(OSCC_6H_5)$, and the mixture was stirred under CO for 15 min and filtered. A 1.96-g sample of TlI was recovered and the orange filtrate showed a moderately strong infrared band at 2070 cm^{-1}. Upon evaporation of the solvent 1.70 g of orange solid was obtained which no longer showed any infrared absorption in the CO stretching region.

X-ray Diffraction Data. An irregularly shaped yellow crystal of the $(tmed)_2Cu_2(CO)C_4O_4 \cdot CH_2Cl_2$ complex of approximate dimensions 0.5 × 0.5 × 0.5 mm^3 was selected for the x-ray examinations. An Enraf-Nonius CAD4 diffractometer was employed for data collection, using Mo Kα radiation (λ = 0.71073 Å). Initially, 25 reflections were automatically located and centered; when these reflections were indexed at 23 °C, a monoclinic unit cell with dimensions of a = 20.329 (8) Å, b = 10.594 (1) Å, c = 12.213 (5) Å, and β = 104.14 (33)° was obtained.

Data were collected in the range $0° < \theta < 25°$ utilizing the diffractometer in an ω–2θ scan mode with a variable scan rate of 4°–20° min^{-1}. The scan of each intensity was begun 0.6° below the Kα_1 angle and terminated 0.6° above the Kα_2 angle, with a total background counting time equal to half the scan time and evenly divided on each side of the reflection peak. In all, 4985 diffracted intensities were collected −2625 of the total were considered to be observed with $F_o > 2\sigma(I)$. There were three reflections monitored throughout the data collection at periodic intervals to ensure that the crystal was not deteriorating, and no significant intensity changes were observed.

Consideration of the systematic absences $0k0$, k odd, and $h0l$, h odd, led to the space group determination of $P2_1/a$ with equivalent positions $\pm(x, y, z)$ and $\pm(^1/_2 - x, ^1/_2 + y, \bar{z})$. A calculated density of 1.522 g cm^{-3} was obtained by using a unit cell volume of 2551 Å^3, Z = 4, and a formula weight of 584.48 g mol^{-1} for $Cu_2Cl_2O_5N_4C_{18}H_{34}$. Absorption corrections were not made on the data since the inspection of the psi scan data revealed the effect to be minimal (μR = 0.44).

The positions of the two copper atoms in the complex were found through interpretation of a Patterson Fourier synthesis. The remaining non-hydrogen atoms were identified in subsequent difference Fourier analyses—alternated with cycles of least-squares refinement. Anisotropic thermal parameters were applied to all thirty-one atoms, and a full-matrix least-squares refinement with 281 variables, including the scale factor, an extinction coefficient, and 2625 observations, converged to residuals of R_1 = 0.0497 and R_2 = 0.0598.

The quantity minimized in the least-squares refinement was $\omega(|F_o| - |F_c|)$, where $\omega = \sigma(F_o)^{-2}$ and $\sigma(F_o) = \sigma(I)/2|F_o|Lp$, where L and p are the Lorentz and polarization corrections. The form of the extinction correction that was applied is $|F_c|\ (1 + gI_c)^{-1}$, where the parameter g was refined and converged to 8.927×10^{-8}. The final residuals were R_1 = 0.0497 and R_2 = 0.0598, where $R_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega|F_o|^2]^{1/2}$, based on a data-to-parameter ratio of 9.3:1. Unit weights were used in the least-squares refinement, and the error in an observation of unit weight was 2.914, with al the parameter shifts less than their estimated standard deviations. (Sin θ)λ^{-1} rejections were made on reflections where 0.07 > (sin θ)λ^{-1} > 0.99 in order that those reflected with asymmetric backgrounds due to interference with the beam stop on the diffractometer may be eliminated. The final difference Fourier synthesis yielded a uniform background of ~0.25 eÅ^{-3} throughout the unit cell. Table IV gives a list of the atomic coordinates. Tables of the thermal parameters and the structure factor amplitudes are given as supplemental material.

Registry No. $(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+B(C_6H_5)_4{}^-$, 75812-17-8; $(tmed)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83376-24-3; $(en)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83312-00-9; $(tmed)_2Cu_2(CO)(O_2CH)^+B(C_6H_5)_4{}^-$, 83312-02-1; $(tmed)_2Cu_2(CO)(O_2CCH_3)^+O_2CCH_3{}^-$, 83312-10-1; $(tmed)_2Cu_2(CO)C_4O_4 \cdot CH_2Cl_2$, 83312-06-5; $(tmed)_2Cu_2(CO)O_2CC(CH_3)_3{}^+B(C_6H_5)_4{}^-$, 83312-08-7; $(tmed)_2Cu_2(CO)(O_2CCH_2C_6H_5)^+O_2CCH_2C_6H_5{}^-$, 83312-12-3; $(tmed)_2Cu_2(CO)(O_2CC_6H_4CH_3)^+O_2CC_6H_4CH_3{}^-$, 83333-38-4; $(tmed)_2Cu_2(CO)(O_2CC_6H_4NO_2)^+B(C_6H_5)_4{}^-$, 83312-14-5; $(py)_4Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83312-16-7; $(tmed)Cu_2(CO)(O_2CCH_3)^+O_2CCH_3{}^-$, 83312-04-3; $(py)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83312-18-9; $(teed)_2Cu_2(CO)(O_2CC_6H_5)^O{}_2CC_6H_5{}^-$, 83312-20-3; $(sden)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83312-22-5; $(uden)_2Cu_2(CO)(O_2CC_6H_5)^+O_2CC_6H_5{}^-$, 83312-24-7; $(tmpd)_2Cu_2(CO)C_4O_4$, 83312-25-8; $(teed)_2Cu_2(CO)C_4O_4$, 83312-26-9.

Supplementary Material Available: Tables of the thermal parameters and the structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.