C10–H10b (15 (2)°) and H9–C9–C10–H10a (11 (3)°). There is no evidence for substantial skeletal twisting as proposed[29] for (*exo*-RC$_7$H$_8$)Mn(CO)$_3$ (vide supra).

Acknowledgment. This work was supported by a grant from the National Science Foundation. (No. CHE-8023964).

Registry No. 1 (L = CO), 95345-58-7; 1 (L = PPh$_3$), 95345-59-8; **2** (L = CO, Nu = PPh$_3$)·BF$_4$, 95345-61-2; **2** (L = CO, Nu = P(4–ClC$_6$H$_4$)$_3$)·BF$_4$, 95405-35-9; **2** (L = CO, Nu = P-(OCH$_2$)$_3$CCH$_3$)·BF$_4$, 95363-22-7; **2** (L = CO, Nu = PBu$_3$)·BF$_4$, 95345-63-4; **2** (L = CO, Nu = P(OPh)$_3$)·BF$_4$, 95345-65-6; **2** (L = CO, Nu = P(2–MeOC$_6$H$_4$)$_3$)·BF$_4$, 95345-67-8; **2** (L = CO, Nu = P(C$_2$H$_4$CN)$_3$)·BF$_4$, 95363-24-9; **2** (L = CO, Nu = pyridine)·BF$_4$, 95345-69-0; **2** (L = Co, Nu = imidazole), 95345-70-3; **2** (L = Co, Nu = C$_6$H$_5$NMe$_2$)·BF$_4$, 95345-72-5; **2** (L = CO, Nu = H$^-$), 32798-86-0; **2** (L = CO, Nu = D$^-$), 95345-87-2; **2** (L = CO, Nu = CN$^-$), 65878-76-4; **2** (L = CO, Nu = OH$^-$), 95345-73-6; **2** (L = CO, Nu = Ph$^-$), 95405-36-0; **2** (L = CO, Nu = P(oBu)$_3$), 95345-86-1; **2** (L = PPh$_3$, Nu = PPh$_3$)·BF, 95345-75-8; **2** (L = PPh$_3$, Nu = P(oBu)$_3$)·BF, 95345-77-0; **2** (L = PPh$_3$, Nu = P(C$_2$H$_4$CN)$_3$)·BF$_4$, 95345-79-2; **2** (L = PPh$_3$, Nu = pyridine)·BF$_4$, 95345-81-6; **2** (L = PPh$_3$, Nu = 3–picoline), 95345-83-8; **2** (L = PPh$_3$, Nu = imidazole), 95345-84-9; **2** (L = PPh$_3$, Nu = H$^-$), 32798-88-2; (C$_7$H$_7$D)Mn(CO)$_3$$^+BF_4$$^-$, 95345-89-4; Mn(CO)$_3$(C$_7H_8$)$^+$, 46238-50-0; Fe(C$_6H_6$)2^{2+}, 51263-22-0; Mn(CO)$_2$(PPh$_3$)(C$_7$H$_8$)$^+$, 95345-90-7; Ru(C$_6$H$_6$)$_2$$^{2+}$, 71825-67-7; Os(C$_6H_6$)$_2$$^{2+}$, 76680-98-3; Fe(Cp)(C$_7H_8$)$^+$, 79105-23-0; Mn(CO)$_3$(C$_6H_6$)$^+$, 41656-02-4; Re(CO)$_3$(C$_6H_6$)$^+$, 68927-89-9; PPh$_3$, 603-35-0; P(4–ClC$_6H_4$)$_3$, 1159-54-2; P(OCH$_2$)$_3CCH_3$, 1449-91-8; PBu$_3$, 998-40-3; P(OPh)$_3$, 101-02-0; P(2-MeOC$_6$H4)$_3$, 4731-65-1; P(C$_2H_4$CN)$_3$, 4023-53-4; C$_6H_5NMe_2$, 121-69-7; P(OBu)$_3$, 102-85-2; pyridine, 110-86-1; imidazole, 288-32-4; 3-picoline, 108-99-6.

Supplementary Material Available: Tables of anisotropic thermal factors and structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

Preparation of Binuclear Copper–Cobalt Compounds. Crystal Structure of (tmed)CuCo(CO)$_4$

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The reaction of L$_2$CuCl with Co(CO)$_4$$^-$ or Co(CO)$_3$PR$_3$$^-$ leads to the formation of binuclear Cu–Co complexes. Solution infrared data indicates that these complexes contain a single Cu–Co bond with no CO–Cu interaction. The solid-state spectra were similar except for that of (tmed)CuCo(CO)$_4$ which exhibits a low-frequency band at 1820 cm^{-1}. A single-crystal structural analysis of this material was undertaken. The molecule [(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)$_2$]CuCo(CO)$_4$ crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.681 (3) Å, b = 8.797 (1) Å, and c = 9.994 (1) Å. Full-matrix least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms and fixed, isotropic thermal parameters for the hydrogens have converged to R = 0.051 and R$_\omega$ = 0.053 for the 862 observed reflections. The Cu and Co are bonded at a distance of 2.38 Å. One of the carbonyl groups asymmetrically bridges the Cu–Co bond; the three remaining carbonyls are terminally bonded to the Co atom. The tmed molecule functions as a bidentate ligand on the Cu, which exhibits nearly planar coordination.

Introduction

Motivated by the use of copper oxide in the commercial low-pressure methanol synthesis catalysts,[1] there has been a renewed interest in the chemistry of copper(I) carbonyl species. Although the function of the copper in the Cu/Zn methanol catalysts is not known for certain, it has been postulated that CO is activated by forming a Cu(I) complex.[2] This type of activation by Cu(I) complexes has yet to be demonstrated in homogeneous systems although a variety of different types of copper(I) carbonyl complexes are known.

One of the more interesting classes of compounds in the binuclear copper complexes with a bridging carbonyl group first discovered by Floriani and his co-workers.[3,4] It has been suggested that these complexes with bridging carbonyls contain CO in an environment with facilitates its metal-promoted reduction, but this has not been substantiated. In addition to our work on homobinuclear copper complexes,[5] we wished to also investigate some heterobinuclear complexes containing copper and another transition metal. A small number of these complexes had previously been prepared and characterized[6] but little was known of their catalytic properties. The structure of one complex, (*o*-triars)CuMn(CO)$_5$, has been determined and was found to have a Cu–Mn bond but little interaction between the copper atom and the carbonyl groups.[7] It

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[1] The production of methanol under relatively mild conditions is described in a number of patents. Among the most pertinent are the following assigned to either BASF or ICI, Ltd.: Ger. Apt. 2 056 612, Ger. Pat. 2 302 658, Fr. Pat. 1 489 682, Fr. Pat. 2 037 567, Ger. Pat. 2 116 949, and U.S. Pat. 3 326 956.

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Table I. Infrared Spectral Data for Some Cu-Co Complexes

complex	solv	frequencies[a]			
(tmed)CuCo(CO)$_4$	CH$_2$Cl$_2$	2028 (m)	1946 (s)	1926 (s)	1860 (s)
	mull	2020 (m)	1930 (vs)	1820 (m)	
(o-triars)CuCo(CO)$_4$[b]	CHCl$_3$	2033	1945	1919	
[(phen)CuCo(CO)$_4$]$_n$[c]	mull	2017	1936	1900	1842
[(bpy)CuCo(CO)$_4$]$_n$[c]	mull	2020	1938	1926	1857
(Ph$_3$P)CuCo(CO)$_4$	mull	2042 (m)	1930 (vs, bd)		
(Ph$_3$P)$_2$CuCo(CO)$_4$	mull	2023 (m)	1945 (s)	1905 (s)	1868 (s)
(Ph$_3$P)$_3$CuCo(CO)$_4$	mull	2028 (m)	1948 (s)	1910 (s)	1871 (s)
[(CH$_3$)$_2$P(CH$_2$)$_2$P(CH$_3$)$_2$]CuCo(CO)$_4$	mull	2025 (m)	1935 (vs, bd)	1890 (s)	
(Ph$_2$P(CH$_2$)$_2$PPh$_2$)CuCo(CO)$_4$	mull	2028 (m)	1940 (vs)	1912 (vs)	1880 (sh)
(Ph$_2$P(CH$_2$)$_4$PPh$_2$)CuCo(CO)$_4$	mull	2030 (m)	1933 (s)	1907 (s)	1874 (vs, bd)
(Ph$_2$PCH$_2$PPh$_2$)CuCo(CO)$_4$	mull	2032 (m)	1972 (m)	1935 (vs)	1890 (sh)
(Ph$_2$P(CH$_2$)$_4$PPh$_2$)Cu$_2$[Co(CO)$_4$]$_2$	mull	2040 (s)	1966 (s)	1941 (s)	1911 (vs)
[Ph$_2$(CH$_3$)P]$_2$CuCo(CO)$_4$	mull	2020 (m)	1930 (s)	1905 (s)	1873 (s)
[(n-C$_4$H$_9$)$_3$P]$_2$CuCo(CO)$_4$	CH$_2$Cl$_2$	2020 (m)	1940 (s)	1908 (s)	1880 (s)
(Ph$_3$P)$_2$CuCo(CO)$_3$PPh$_3$	mull	2022 (vw)	1958 (m)	1895 (s)	1827 (s)
[Ph$_2$(CH$_3$)P]$_2$CuCo(CO)$_3$[P(CH$_3$)Ph$_2$]	CH$_2$Cl$_2$	2028 (m)	1948 (s)	1875 (vs)	
[(n-C$_4$H$_9$)$_3$P]$_2$CuCo(CO)$_3$P(n-C$_4$H$_9$)$_3$	neat	2020 (m)	1935 (s)	1875 (vs, bd)	

[a] w = weak, m = medium, s = strong, v = very, bd = broad, and sh = shoulder. [b] Reference 5. [c] Reference 9.

was assumed that the complexes with other metal carbonyl anions such as Co(CO)$_4^-$, V(CO)$_6^-$, and (η^5-C$_5$H$_5$)W(CO)$_3^-$ would have structures of the same type since this type of structure has been found for some similar Au(I) derivatives.[8]

A recent communication[9] reported the synthesis and structure of the complexes [(C$_6$H$_5$)$_3$P]$_2$CuM(CO)$_3$(C$_5$H$_5$) (M = Mo or W). These complexes contain a rather long M–Cu bond, but two of the carbonyl groups are bent toward the Cu atom showing a definite Cu–CO interaction.

Results and Discussion

In the synthesis of the binuclear copper complexes with the bridging CO groups we found that these complexes could be prepared only if the Cu atoms were bound to chelating groups such as aliphatic diamines.[5] Other chelating ligands such as diphosphines or compounds with oxygen or sulfur donor atoms proved unsuitable. Our initial efforts to synthesize heterobinuclear complexes therefore concentrated on preparing complexes with diamines chelating the copper since there seemed to be a greater probability of observing Cu–CO interactions with the diamine ligands than with phosphines and the like.

The reaction of (tmed)CuCl (tmed = N,N,N',N'-tetramethylethylenediamine) with either TlCo(CO)$_4$ or NaCo(CO)$_4$ gives excellent yields of a pale yellow crystalline compound with the composition (tmed)CuCo(CO)$_4$. The infrared spectrum of this complex was considerably different than that reported for (o-triars)CuCo(CO)$_4$[6] but was quite similar to the mull spectra of the complex [Co(CO)$_4$Cu(bpy)]$_n$ reported by Hackett and Manning[10] as shown in Table I. As a mull, the spectrum of the tmed complex is quite different from the solution spectrum in that the lowest frequency band is at 1820 cm^{-1} compared to 1860 cm^{-1} in solution. The number and the frequencies of the infrared bands made it quite clear that the structure of the (tmed)CuCo(CO)$_4$ complex, at least in the solid state, must be fundamentally different than the o-triars analogue.

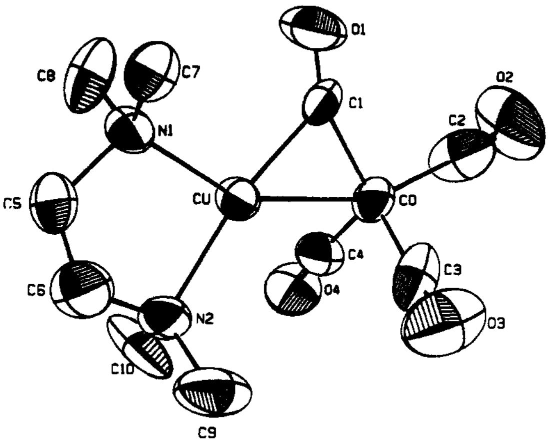

Figure 1. ORTEP view of (tmed)CuCo(CO)$_4$.

Table II. Selected Bond Lengths for (tmed)CuCo(CO)$_4$

atom 1	atom 2	dist, Å	atom 1	atom 2	dist, Å
Cu	Co	2.379 (1)	C3	O3	1.05 (3)
Cu	C1	2.032 (9)	C4	O4	1.20 (3)
Cu	N1	2.085 (6)	N1	C5	1.538 (14)
Cu	N2	2.102 (7)	N1	C7	1.46 (3)
Co	C1	1.798 (9)	N1	C8	1.44 (4)
Co	C2	1.749 (10)	N2	C6	1.464 (13)
Co	C3	1.74 (3)	N2	C9	1.47 (3)
Co	C4	1.79 (3)	N2	C10	1.44 (4)
C1	O1	1.156 (12)	C5	C6	1.32 (2)
C2	O2	1.143 (12)			

The solution spectra of the tmed complex is very similar to that of the bipyridyl derivative and the species present in solution is probably similar for both complexes. On the basis of the low frequency of the CO vibrations, it was suggested that the spectrum of the [Co(CO)$_4$Cu(bpy)]$_n$ complex was due to an anionic species[10] although no supporting evidence was given. There was no speculation as to the nature of the anionic species, but it could not be simply a Co(CO)$_4^-$ salt since Co(CO)$_4^-$ salts are generally characterized by a single intense broad band at approximately 1900 cm^{-1}.

In order to determine the exact nature of the (tmed)CuCo(CO)$_4$ complex in the solid state, a single-crystal X-ray diffraction study was undertaken. An ORTEP view of the molecule is shown in Figure 1, and Tables II and III give a list of selected bond lengths and bond angles.

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Table III. Selected Bond Angles for (tmed)CuCo(CO)$_4$

atom 1	atom 2	atom 3	angle, deg	atom 1	atom 2	atom 3	angle, deg
Co	Cu	C1	47.3 (2)	Co	C1	O1	159 (1)
Co	Cu	N1	151.2 (2)	Co	C2	O2	170 (3)
Co	Cu	N2	121.9 (2)	Co	C3	O3	175 (3)
C1	Cu	N1	103.9 (3)	Co	C4	O4	174 (2)
C1	Cu	N2	169.1 (4)	Cu	N1	C5	102.9 (5)
N1	Cu	N2	86.9 (2)	Cu	N1	C7	114 (2)
Cu	Co	C1	56.2 (3)	Cu	N1	C8	110 (2)
Cu	Co	C2	155.8 (3)	C5	N1	C7	122 (2)
Cu	Co	C3	90.1 (7)	C5	N1	C8	96 (2)
Cu	Co	C4	86.1 (7)	C7	N1	C8	110.2 (9)
C1	Co	C2	99.6 (4)	Cu	N2	C6	103.2 (6)
C1	Co	C3	120 (1)	Cu	N2	C9	113 (2)
C1	Co	C4	115 (1)	Cu	N2	C10	110 (2)
C2	Co	C3	103 (1)	C6	N2	C9	111 (3)
C2	Co	C4	108 (1)	C6	N2	C10	109 (3)
C3	Co	C4	109.2 (6)	C9	N2	C10	111 (1)
Cu	C1	Co	76.5 (3)	N1	C5	C6	115 (2)
Cu	C1	O1	123.5 (7)	N2	C6	C5	121 (2)

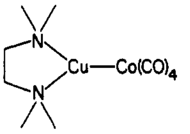
The molecule is not ionic but does possess a number of interesting features.

The metal atoms are separated by a distance of 2.378 (1) Å which is clearly within bonding distance and is considerably shorter than would be expected based on Cu–Cu and Co–Co bond length observed in the metals[11] (2.55 and 2.51 Å, respectively). The Co–Co single bond length observed in $Co_2(CO)_8$ was 2.51 Å[12] while a Cu–Cu distance of 2.41–2.42 Å was observed in complexes containing a bridging CO group.[4,5] The latter complexes also contained other bridging groups which would be expected to result in a shortening of the Cu–Cu bond. Although bond lengths are poor indicators of bond order, the short Cu–Co bond might suggest some multiplebond character. Because complexes with Cu–Cu or Cu–M multiple bonds suitable for comparison are unknown, this cannot be proven. In the (*o*-triars)CuMn(CO)$_5$ complex the Cu–Mn distance of 2.56 Å is in fairly good agreement with the average of the Cu–Cu and Mn–Mn distances found in the metals (2.54 Å) which lends some support for a higher bond order in the Cu–Co complex.

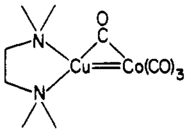
Another interesting feature is the bonding of the carbonyl group C(1)–O(1). This carbonyl can best be described as an asymmetrically or semibridging carbonyl and is similar to the Cu–C interaction reported for $[(C_6H_5)_3P]_2CuW(CO)_3(C_5H_5)$.[9] The Co–C(1) distance is 1.81 Å while the Cu–C(1) distance is 2.04 Å which is considerably longer than the distances of 1.84–1.87 Å found in complexes with a CO symmetrically bridging two copper atoms. The carbonyl group is bent toward the Cu atom with a Co–C(1)–O(1) angle of 159° and a Cu–C(1)–O(1) angle of 124°. The Cu–O(1) distance of 2.84 Å is too long for the carbonyl group to be considered an η^2-four-electron donor. The remaining three carbonyl groups are terminally bound to the Co atom at an average distance of 1.76 Å with no interaction with the Cu atom.

The coordination about the Cu atom is very nearly planar with the Cu, Co, C(1), N(1), and N(2) atoms defining the plane. This type of coordination geometry is somewhat unusual for Cu since most four-coordinate Cu(I) complexes are nearly tetrahedral although planar three-coordinate Cu(I) complexes are more common.

A consideration of the structural data and the spectroscopic data does not give one a clear understanding of the bonding of the (tmed)CuCo(CO)$_4$ complex in the solid state. Each of the two extreme representations shown in A and B contain features which partially explain the observed data, and perhaps the "true" representation lies somewhere between.

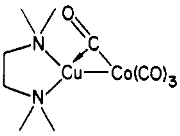


A



B

Structure B with 18-electron configurations about both Co and Cu explains the short Cu–Co bond and the low-frequency infrared bond but requires a fully bridging CO group which is clearly not observed. Structure A with a 16-electron configuration about the Cu is probably a good representation of the species in solution but does not explain the short Cu–Co bond or the observed infrared spectrum. An intermediate case such as structure C, which is consistent with the infrared data and the observed bond lengths and angles, may be a suitable compromise.



C

A number of similar complexes of the type $L_2CuCo(CO)_4$, where L_2 is a bidentate or two monodentate phosphine ligands, have also been prepared. The synthesis of complexes with chelating phosphines was straightforward, but the preparation of compounds with monodentate ligands bound to the copper was more difficult.

If one attempts to prepare complexes of the type $(R_3P)_2CuCo(CO)_4$ by the reaction of the $(R_3P)_2CuCl$ complex with $TlCo(CO)_4$, one initially obtains powdered products with the expected composition and whose infrared spectra are similar to the solution spectrum of the tmed derivative. Any attempt to recrystallize the initial product results in the formation of complex mixtures due to the lability of the phosphine ligands. For instance, in the case of $[(C_6H_5)_3P]_2CuCo(CO)_4$ at least four components including $(C_6H_5)_3PCuCo(CO)_4$, $[(C_6H_5)_3P]_2CuCo(CO)_4$, $[(C_6H_5)_3P]_3CuCo(CO)_4$, and $[(C_6H_5)_3P]_2CuCo(CO)_3P(C_6H_5)_3$ could be identified both in solution and in the solid "recrystallized" product. The triphenylphosphine ligands therefore not only become redistributed among the copper atoms but also can displace a carbonyl group on the cobalt. Each of the observed components have been prepared

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Table IV. Elemental Analyses

compound	analysis									
	calcd					found				
	C	H	N(P)	Cu	Co	C	H	N(P)	Cu	Co
(tmed)$CuCo(CO)_4$	34.25	4.59	7.99	18.12	16.80	33.34	4.78	7.91	18.01	16.06
$(Ph_3P)CuCo(CO)_4$	53.14	3.02	6.24	12.79	11.19	52.31	3.15	6.14	12.32	10.80
$(Ph_3P)_2CuCo(CO)_4$	63.29	3.96	8.17	8.38	7.77	62.70	4.08	7.84	8.91	7.32
$(Ph_3P)_3CuCo(CO)_4$	68.14	4.41	9.11	6.22	5.77	68.21	4.28	8.24	6.38	5.67
$(Ph_3P)_2CuCo(CO)_3PPh_3$	68.92	4.53	9.37	6.40	5.94	69.21	4.45	8.73	6.43	5.59
$(Ph_2P(CH_2)_2PPh_2)CuCo(CO)_4$	56.88	3.79	9.79	10.04	9.31	55.92	3.77	9.38	10.59	8.76
(dmpe)$CuCo(CO)_4$	31.22	4.16	16.12	16.53	15.32	30.51	4.46	16.85	16.31	15.32
$(Ph_2P(CH_2)_4PPh_2)CuCo(CO)_4$	58.15	4.27	9.37	9.61	8.92	57.81	4.58	9.32	9.28	8.13
$(Ph_2P(CH_2)_4PPh_2)Cu_2[Co(CO)_4]_2$	48.28	3.15	6.92	14.19	13.16	47.20	3.21	6.51	14.07	13.19
$(Ph_2PCH_2PPh_2)CuCo(CO)_4$	56.28	3.58	10.00	10.27	9.52	56.75	4.07	9.60	9.83	9.29
$[(Ph_2P(CH_3)]_2CuCo(CO)_4$				10.00	9.28				10.22	9.30
$[(n\text{-}C_4H_9)_3P]_2CuCo(CO)_4$				9.94	9.22				10.52	9.14
$[(n\text{-}C_4H_9)_3P]_2CuCo(CO)_3P(n\text{-}C_4H_9)_3$				7.81	7.24				8.33	7.59
$[Ph_2P(CH_3)]_2CuCo(CO)_3P(CH_3)Ph_2$				7.87	7.30				7.71	7.59

independently from the appropriate (phosphine)copper halide and the cobalt carbonyl anion. This type of redistribution reaction is also observed for the $L_3CuCo(CO)_4$ and $LCuCo(CO)_4$ complexes.

With the possible exception of $(C_6H_5)_3PCuCo(CO)_4$, the infrared data seem to indicate that all the phosphine-containing $L_nCuCo(CO)_4$ complexes have a simple Cu–Co bond with no semibridging carbonyl interaction of the type observed for the tmed complex in the solid state. All the complexes of this type display the typical four-band pattern, and none exhibit a low-frequency CO stretching band which we have attributed to the unique carbonyl group. This correlation is somewhat tenuous since supporting data which might distinguish between structures with all terminal carbonyls and those with semibridging carbonyls has not been obtained. ^{13}C NMR spectra of the carbonyls bound to the Co atom were not observed, presumably due to quadrapole broadening effects of the Co nuclei, and other supporting evidence is lacking.

The infrared spectrum of the $(C_6H_5)_3PCuCo(CO)_4$ complex is quite different from the spectra observed for the other phosphine-containing $L_nCuCo(CO)_4$ complexes in that no bands are observed below 1900 cm^{-1} and only two bands are seen as compared to the usual four-band pattern. Interestingly, the spectra of the $(C_6H_5)_3PCuCo(CO)_4$ complex is quite similar to that of the (*o*-triars)$CuCo(CO)_4$ complex and the $(Ph_2P(CH_2)_4PPh_2)Cu_2[Co(CO)_4)]_2$ complex. The spectrum of the latter complex has three closely spaced intense bands in the 1900–2000 cm^{-1} region whereas the $(C_6H_5)_3PCuCo(CO)_4$ complex has only one very strong band in this region. This single broad band may be formed by the overlap of the three CO vibrations. The $(Ph_2P(CH_2)_4PPh_2)Cu_2[Co(CO)_4]_2$ complex presumably consists of a $CuCo(CO)_4$ group bound to each end of the diphosphine; thus, the compound can be regarded as two independent $LCuCo(CO)_4$ groups. Because of the large separation of the $Co(CO)_4$ groups, no coupling of the CO vibrations would be expected. The $Ph_2P(CH_2)_4PPh_2$ ligand can apparently function as either two monodentate phosphines as discussed above or as a simple chelating diphosphine, since we have also prepared $(Ph_2P(CH_2)_4PPh_2)CuCo(CO)_4$. The properties of this compound are similar to those of other $L_2CuCo(CO)_4$ complexes.

By carrying out the reaction between $(R_3P)_2CuCl$ and $NaCo(CO)_3PR_3$, we have prepared some complexes of the type $(R_3P)_2CuCo(CO)_3PR_3$. We expect that these compounds are similar to the $Co(CO)_4$ derivatives, although the $(Ph_3P)_2CuCo(CO)_3PPh_3$ complex displays a fairly unusual spectrum with an exceptionally low-frequency CO stretching band at 1827 cm^{-1}. The cause of this low-frequency band and the reason for the differences in the spectra of the $(R_3P)_2CuCo(CO)_3PR_3$ complexes is not known at this time.

Table V. Crystal Data and Data Collection Parameters

formula	$CuCoC_{10}H_{16}N_2O_4$
fw	350.7
crystal system	orthorhombic
space group	$Pna2_1$
a, Å	16.681 (3)
b, Å	8.797 (1)
c, Å	9.994 (1)
V, $Å^3$	1466 (1)
ρ(calcd), g cm^{-3}	1.59
Z	4
$\mu_{MoK\alpha}$, cm^{-1}	25.9
cryst color	green
cryst size, mm	0.20 × 0.25 × 0.25
$2\theta_{max}$, deg	50
scan type	$\omega - 2\theta$
scan rates, deg min^{-1}	2-13
scan width, deg	1.00 + 0.35 tan θ
unique data	1367
obsd data ($\lvert F_o \rvert^2 \geq 2\sigma(F_o^2)$)	862
variables	162
p factor	0.05
R	0.051
R_W	0.053
esd	1.65
largest shift/error of final cycle	0.17
largest peak in final diff Fourier, e $Å^{-3}$	0.71

Experimental Section

Reagents. All reagents obtained from commercial sources were high-purity materials and were used without further purification. Tetrahydrofuran was distilled from lithium aluminum hydride, methylene chloride was distilled from P_2O_5, and hexane was dried by storing over sodium. $NaCo(CO)_4$[13] and $NaCo(CO)_3P(C_6H_5)_3$[14] were prepared by sodium amalgam reduction of $Co_2(CO)_8$ and $Co_2(CO)_6[P(C_6H_5)_3]_2$, respectively. $TlCo(CO)_4$ was prepared by the literature method.[15]

Analysis. Elemental analyses were carried out by either the Analytical and Information Division, Exxon Research and Engineering Co., or Galbraith Analytical Laboratories. All new compounds reported gave satisfactory elemental analyses which are given in Table IV.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer either in solution or as Nujol mulls. The spectra were calibrated by comparison with the spectrum of polystyrene film.

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Table VI. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Cu	0.24325 (5)	0.3636 (1)	0.2680 (0)	3.89 (2)	H5A	0.107	0.183	0.137	6.00*
Co	0.36346 (6)	0.5090 (1)	0.2700 (5)	4.33 (2)	H5B	0.044	0.138	0.251	6.00*
C1	0.2648 (5)	0.591 (1)	0.265 (3)	5.7 (2)	H6A	0.147	0.059	0.372	6.00*
C2	0.4210 (6)	0.675 (1)	0.272 (3)	7.7 (3)	H6B	0.153	−0.011	0.218	6.00*
C3	0.3952 (6)	0.413 (2)	0.412 (1)	5.4 (3)	H7A	0.095	0.536	0.385	6.00*
C4	0.3917 (7)	0.402 (1)	0.125 (2)	6.3 (3)	H7B	0.018	0.417	0.373	6.00*
N1	0.1185 (4)	0.3484 (7)	0.268 (2)	4.9 (2)	H7C	0.096	0.372	0.469	6.00*
N2	0.2446 (4)	0.1247 (7)	0.265 (2)	5.1 (2)	H8A	0.082	0.527	0.139	6.00*
O1	0.2149 (4)	0.6817 (7)	0.274 (3)	8.6 (2)	H8B	0.104	0.359	0.055	6.00*
O2	0.4547 (5)	0.7868 (9)	0.256 (2)	10.9 (3)	H8C	0.027	0.394	0.170	6.00*
O3	0.4104 (8)	0.359 (1)	0.502 (1)	10.1 (3)	H9A	0.354	0.069	0.332	6.00*
O4	0.4178 (5)	0.336 (1)	0.0296 (8)	6.7 (2)	H9B	0.291	0.142	0.444	6.00*
C5	0.1037 (6)	0.180 (1)	0.234 (1)	6.4 (4)	H9C	0.294	−0.039	0.416	6.00*
C6	0.1596 (7)	0.085 (1)	0.275 (4)	10.3 (4)	H10A	0.271	−0.057	0.166	6.00*
C7	0.0799 (7)	0.423 (2)	0.382 (2)	6.9 (4)	H10B	0.229	0.109	0.082	6.00*
C8	0.0875 (8)	0.408 (2)	0.145 (2)	8.0 (4)	H10C	0.327	0.089	0.091	6.00*
C9	0.290 (1)	0.058 (2)	0.377 (2)	10.0 (4)					
C10	0.275 (1)	0.072 (1)	0.139 (2)	8.6 (4)					

[a] Atoms with an asterisk were refined isotropically. Anisotropically atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Preparation of the Complexes. Unless otherwise stated all operations and manipulations were carried out in a nitrogen-filled glove box.

(tmed)CuCo(CO)$_4$. A solution of (tmed)CuI was prepared by adding 0.62 g (5.3 mmol) of *N,N,N′,N′*-tetramethylethylenediamine and 1.02 g (5.3 mol) of CuI to 125 mL of CH_2Cl_2 and stirring under a CO atmosphere for 30 min. A 2.0-g (5.3-mmol) sample of $TlCo(CO)_4$ was then added to the solution, and the mixture was stirred an additional 2 h. The mixture was then filtered under N_2 to remove the suspended TlI, and the clear yellow filtrate was evaporated to dryness on a rotary evaporator. The resulting solid was recrystallized from a mixture of CH_2Cl_2 and hexane giving 1.58 g (85%) of clear yellow crystals of (tmed)CuCo(CO)$_4$.

(Diphosphine)CuCo(CO)$_4$ Complexes. A solution containing 5 mmol of the (diphosphine)CuCl complex in 75 mL of CH_2Cl_2 was prepared by adding equivalent amounts of the appropriate diphosphine to CuCl in CH_2Cl_2 under a CO atmosphere. A 1.88-g (5-mmol) sample of $TlCo(CO)_4$ was then added and the mixture stirred for 2 h. The TlCl which precipitated quantitatively was then filtered off, and the clear filtrate was reduced in volume to approximately 20 mL. The yellow solids which had formed were then collected on a filter, washed several times with 50-mL portions of hexane, and dried. The (diphosphine)CuCo(CO)$_4$ complexes were routinely obtained in at least 70% yield after recrystallization from CH_2Cl_2/hexane.

$(R_3P)_nCuCo(CO)_4$ Complexes. The $(R_3P)_nCuCl$ complexes were prepared by the addition of the appropriate amount of the phosphine to a suspension of CuCl in methylene chloride in order to arrive at the required stoichiometry. The $(R_3P)_nCuCl$ complexes were isolated by partial evaporation of the solvent and cooling. The $(R_3P)_nCuCl$ compounds (5 mmol) were then redissolved in 75 mL CH_2Cl_2, and an exactly equivalent amount of $NaCo(CO)_4$ was added in increments over a 1-h period. The mixtures were allowed to stir under a CO atmosphere for several hours at room temperature and then filtered to remove the NaCl which had formed. The filtrate was evaporated to near dryness, and the solids were collected on a filter, washed with several portions of hexane, and dried. Yields of the crude products ranged from 70 to 95%. These materials could not be recrystallized without reaction and must be used as is.

$(R_3P)_nCuCo(CO)_3(R_3P)$ Complexes. Compounds were prepared in exactly the same manner as described above except that $NaCo(CO)_3(PR_3)$ salts were used in place of $NaCo(CO)_4$.

X-ray Diffraction Analysis. Crystal data and data collection parameters are listed in Table V. A crystal of (tmed)CuCo(CO)$_4$ was mounted in a thin-walled glass capillary. All diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Accurate cell dimensions and the crystal orientation were determined by a least-squares fit of 25 diffractometer measured 2θ values between 13° and 20.5°. Three check reflections monitored after every hour of radiation time showed no loss in intensity with time. Absorption corrections were not applied since inspections of the psi scan data revealed the effect to be minimal.

Systematic extinctions ($0kl$, $k + 1 = 2n + 1$; $h0l$, $h = 2n$) were consistent with space group $Pna2_1$ or the centrosymmetric equivalent *Pnam*. The Cu and Co atomic positions were determined by interpretation of the three-dimensional Patterson map. The coordinates of the remaining non-hydrogen atoms were determined by successive least-squares refinements and difference Fourier maps. A difference map calculated after full-matrix least-squares refinement with anisotropic temperature factors revealed the location of many of the hydrogen atoms. The remaining hydrogens were entered at their theoretically calculated positions. The hydrogens were assigned isotropic temperature factors and fixed in subsequent cycles of refinement which converged to $R = 0.051$ and $R_w = 0.053$. The quantity minimized in the least-squares refinement was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$. Table VI gives a list of the atomic coordinates.

Refinement was also carried out in space group *Pnam* in which the molecule is centered on the mirror planes at $z = \pm 0.25$. The following atoms lie on the mirror plane: Cu, Co, Cl, O1, N1, C5, C6, and N2. Full-matrix least-squares refinement with 97 variables converged at $R = 0.058$ and $R_w = 0.064$, a significantly higher result.[16]

Registry No. (tmed)CuCo(CO)$_4$, 95251-35-7; $(Ph_3P)CuCo(CO)_4$, 95251-36-8; $(Ph_3P)_2CuCo(CO)_4$, 95251-37-9; $(Ph_3P)_3CuCo(CO)_4$, 95251-38-0; $(Ph_3P)_2CuCo(CO)_3PPh_3$, 95251-39-1; $(Ph_2P(CH_2)_2PPh_2)CuCo(CO)_4$, 95251-40-4; (dmpe)CuCo(CO)$_4$, 95251-41-5; $(Ph_2P(CH_2)_4PPh_2)CuCo(CO)_4$, 95251-42-6; $Ph_2P(CH_2)_4PPh_2)Cu_2[Co(CO)_4]_2$, 95251-43-7; $(Ph_2P(CH_2)_4PPh_2)CuCo(CO)_4]_2$, 95251-44-8; $[(Ph_2P(CH_3)]_2CuCo(CO)_4$, 95251-45-9; $[(n\text{-}C_4H_9)_3P]_2CuCo(CO)_4$, 95251-46-0; $[(n\text{-}C_4H_9)_3P]_2CuCo(CO)_3P(n\text{-}C_4H_9)_3$, 95251-47-1; $[Ph_2P(CH_3)]_2CuCo(CO)_3P(CH_3)Ph_2$, 95251-48-2; (tmed)CuI, 95251-49-3; $TlCo(CO)_4$, 38991-21-8; $(Ph_2P(CH_{)2}PPh_2)CuCl$, 15380-26-4; (dmpe)CuCl, 95251-50-6; $(Ph_2P(CH_2)_4PPh_2)CuCl$, 47692-92-2; $(Ph_2PCH_2PPh_2)CuCl$, 12689-16-6; $NaCo(CO)_4$, 14878-28-5; $(Ph_3P)_2CuCl$, 25577-10-0; $(Ph_3P)_3CuCl$, 15709-76-9; $(Ph_2MeP)_2CuCl$, 89725-99-5; $[(n\text{-}C_4H_9)_3P]_2CuCl$, 36423-09-3; $NaCo(CO)_3(PPh_3)$, 33570-17-1; $NaCo(CO)_3[P(n\text{-}C_4H_9)_3]$, 29477-05-2; $NaCo(CO)_3(Ph_2MeP)$, 55888-64-7; Co, 7440-48-4; Cu, 7440-50-8.

Supplementary Material Available: Tables of thermal parameters, complete bond lengths and bond angles, and structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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