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Supplementary Material Available: Tables of calculated hydrogen atom parameters (Table VI), anisotropic thermal parameters (Table VII), and observed and calculated structure factors (Table VIII) (23 pages). Ordering information is given on any current masthead page.

Bimetallic Complexes Containing Copper. The Crystal Structures of (tmed)CuMo$(CO)_3(\eta^5\text{-}C_5H_5)$ and $[(C_6H_5)_3P]_3CuV(CO)_6$

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The reaction of phosphine- or diamine-substituted copper(I) halides with various metal carbonyl anions leads to the formation of heteronuclear bimetallic complexes where one of the metals is copper. These complexes exhibit a wide range of Cu-M and Cu-CO interactions. $(Ph_3P)_3CuV(CO)_6$, prepared from $(Ph_3P)_2CuCl$ and Na(diglyme)$_2$V(CO)$_6$, exists as discrete trigonal planar $(Ph_3P)_3Cu^+$ cations and octahedral $V(CO)_6^-$ anions. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.669$ (1) Å, $b = 12.691$ (2) Å, $c = 19.432$ (2) Å, $\alpha = 102.17$ (2)°, $\beta = 92.03$ (1)°, $\gamma = 108.25$ (1)°, and $Z = 2$. The structure was solved by heavy-atom techniques and refined by full-matrix least squares to $R = 0.050$ and $R_w = 0.054$. The $L_nCuM(CO)_3(\eta^5\text{-}C_5H_5)$ complexes ($L_n = (Ph_3P)_2$ or $(CH_3)_2NCH_2CH_2N(CH_3)_2$; M = Cr, Mo, W) all appear to have a Cu-M bond with a single terminal and two semibridging carbonyl groups. (tmed)CuMo$(CO)_3(\eta^5\text{-}C_5H_5)$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.134$ (1) Å, $b = 14.632$ (2) Å, $c = 13.993$ (2) Å, $\beta = 94.76$ (1)°, and $Z = 4$. The final residuals are $R = 0.027$ and $R_w = 0.032$.

Introduction

A number of heteronuclear bimetallic complexes containing copper with well-defined compositions have been prepared in the past two decades.[1-9] Our recent work with Cu-Co complexes[10] and the work by Carlton and coworkers[8] with some Cu-W complexes have shown some interesting metal carbonyl interactions which were not fully appreciated in the earlier literature. For example, in the case of the Cu-Co complexes a fairly strong interaction between the copper and one of the carbonyl groups was observed in the solid state for (tmed)CuCo$(CO)_4$, but this interaction was apparently not present for similar complexes containing phosphine ligands. These relationships prompted us to expand the scope of our work to include a number of other Cu-metal complexes and metal-ligand combinations.

Results and Discussion

Although the reaction of many metal carbonyl anions with substituted copper halides is often quite straightforward leading to bimetallic species in good yields, there are a number of complications that arise in certain cases. Two of the factors which influence the success of these reactions are the lability of the ligands bound to copper and the reducing properties of the metal carbonyl anions. Di- and triamine-substituted copper(I) halides such as (tmed)CuCl (tmed = *N,N,N′,N′*-tetramethylethylenediamine) are quite easily reduced to copper metal by strong reducing agents. At room temperature in the presence of $V(CO)_6^-$, (tmed)CuCl is quantitatively converted to the metal along with the concurrent formation of $V(CO)_6$. Phosphine-substituted copper(I) halides tend to be much less susceptible to reduction than the amine complexes, and it is often possible to prepare the bimetallic complexes from the phosphine derivative even with relatively strongly reducing anions. The use of phosphine ligands, particularly monodentate phosphines, often introduces another complication in the preparation of the bimetallic complexes. Due to the lability of these ligands, one often finds mixtures of products in which the ligand/copper ratio differs from that of the starting phosphine-substituted copper halide.[10] In the case of the reaction of $[(C_6H_5)_3P]_2CuCl$ with Na(diglyme)$_2$V(CO)$_6$, the tris(phosphine) derivative is the only Cu-V product which can be isolated

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Table I

		elemental analysis									
		% calculated					% found				
compound	ν_{CO},[a] cm^{-1}	C	H	N(P)	Cu	M	C	H	N(P)	Cu	M
(tmed)CuMn$(CO)_5$	2030, 1920, 1860	35.26	4.30	7.48	16.96	14.66	35.06	4.44	6.82	16.94	13.73
$[(C_6H_5)_3P]_3$CuMn$(CO)_5$	2040, 1945, 1885, 1855	67.78	4.34	8.89	6.07	5.26	67.21	4.40	8.97	5.92	5.20
$[(C_6H_5)_3P]_3$CuV$(CO)_6$	~1850	67.39	4.24	8.69	5.94	4.76	67.41	4.44	8.47	5.22	4.01
$[(C_6H_5)_3P]_2$CuCr$(CO)_3(\eta^5$-$C_5H_5)$	1902, 1796, 1753	66.96	4.47	7.85	8.05	6.69	66.52	4.50	7.89	8.33	7.27
(tmed)CuCr$(CO)_3(\eta^5$-$C_5H_5)$	1886, 1795, 1769	44.15	5.56	7.35	16.68	13.65	44.06	5.48	7.22	16.86	14.13
$[(C_6H_5)_3P]_2$CuMo$(CO)_3(\eta^5$-$C_5H_5)$	1896, 1795, 1776	63.43	4.23	7.43	7.63		62.90	4.19	7.50	7.74	
(tmed)CuMo$(CO)_3(\eta^5$-$C_5H_5)$	1891, 1795, 1768	39.58	4.98	6.59	14.69	22.58	39.81	5.19	6.70	14.83	22.32
(tmed)CuW$(CO)_3(\eta^5$-$C_5H_5)$	1894, 1786, 1759	32.76	4.13	5.46	12.39	35.86	32.42	3.97	5.11	12.55	35.35

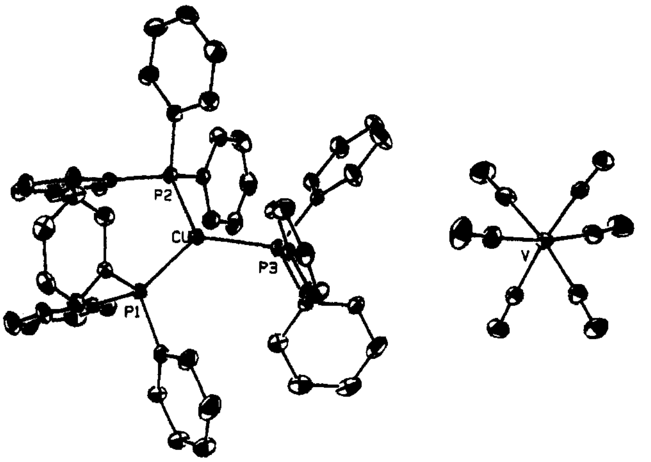

Figure 1. ORTEP drawing of $[(C_6H_5)_3P]_3CuV(CO)_6$. Labeling of carbon atoms has been omitted for clarity.

in pure form. Presumably additional complexes with a lower P/Cu ratio are also formed, but none have been isolated thus far. Higher yields of the $[(C_6H_5)_3P]_3CuV(CO)_6$ can be obtained by the reaction of Na(diglyme)$_2$V$(CO)_6$ with $[(C_6H_5)_3P]_3$CuCl. The compound, which is a yellow crystalline solid, exhibits an infrared spectrum, as a Nujol mull (Table I) similar to that reported for the $V(CO)_6^-$ ion in solution. The spectrum of $[(C_6H_5)_3P]_3CuV(CO)_6$ is also quite similar to the spectrum of (triars)CuV$(CO)_6$ (triars = bis(*o*-dimethylarsinophenyl)methylarsine reported by Kasselleny and co-workers[2] in which they concluded that the vanadium was seven-coordinate with a Cu–V bond. A crystal structure of the $[(C_6H_5)_3P]_3CuV(CO)_6$ complex was undertaken in order to determine its overall structural features. An ORTEP diagram is shown in Figure 1. As can be clearly seen, the molecule consists of discrete $[(C_6H_5)_3P]_3Cu^+$ cations and $V(CO)_6^-$ anions. There is no bonding interaction between the vanadium and copper with the metals being separated by almost 7 Å. The $V(CO)_6^-$ anion has an almost ideal octahedral geometry. In the $[(C_6H_5)_3P]_3Cu^+$ cation the three phosphorus atoms are arranged in a trigonal plane about the copper. Bond lengths and angles (Table II) appear to be quite normal. Attempts to prepare other copper–vanadium complexes, including those in which the copper is chelated by a single bidentate phosphine or amine ligand, failed. Hackett and Manning previously had prepared bis(phenanthroline) and bis(pyridyl) derivatives whose infrared spectra in chloroform lead those authors to the conclusion that the complexes may contain a Cu–V bond.[7] In light of the present structure and the similarity of the infrared spectra of all the $L_nCuV(CO)_6$ derivatives, the possibility that all these complexes are salts of the $V(CO)_6^-$ anion without Cu–V bonding should be considered.

In some respects, the reaction of $Mn(CO)_5^-$ with substituted copper(I) halides parallels that of $V(CO)_6^-$. Diamine complexes such as (tmed)CuMn$(CO)_5$ are stable only at low temperatures. $[(C_6H_5)_3P]_3CuMn(CO)_5$ has been isolated from the reaction of $[(C_6H_5)_3P]_2$CuCl and NaMn$(CO)_5$ as was observed in the case of the $V(CO)_6^-$ derivatives. Although crystals of the $[(C_6H_5)_3P]_3CuMn(CO)_5$ suitable for X-ray diffraction have not been obtained, it seems most likely that this complex is structurally similar to (triars)CuMn$(CO)_5$ whose structure was determined by Kilbourn and co-workers.[11] The triars complex was found to have a Cu–Mn bond with apparently little or no interaction between the CO ligands and copper. The infrared spectra of $[(C_6H_5)_3P]_3CuMn(CO)_5$, (tmed)CuMn$(CO)_5$, and the triars complex are all very similar, but quite different from simple $Mn(CO)_5^-$ salts. This indicates that all these complexes have similar structures, and the absence of low-frequency CO stretches in the solid-state spectra suggests that there probably is no significant interaction between the CO groups and the copper in these complexes.

Table II. Bond Distances and Angles for $[(C_6H_5)_3P]_3CuV(CO)_6$

	Bond Distances, Å		
Cu–P1	2.293 (1)	C1–O1	1.158 (6)
Cu–P2	2.297 (1)	C2–O2	1.138 (7)
Cu–P3	2.296 (1)	C3–O3	1.157 (7)
		C4–O4	1.158 (6)
V–C1	1.938 (7)	C5–O5	1.143 (6)
V–C2	1.938 (7)	C6–O6	1.133 (7)
V–C3	1.946 (7)		
V–C4	1.933 (7)		
V–C5	1.943 (7)		
V–C6	1.963 (7)		
	Bond Angles, deg		
C1–V–C2	173.0 (2)	V–C1–O1	177.7 (5)
C1–V–C3	87.3 (2)	V–C2–O2	176.8 (6)
C1–V–C4	97.4 (2)	V–C3–O3	174.6 (6)
C1–V–C5	90.3 (2)	V–C4–O4	177.1 (6)
C1–V–C6	88.3 (3)	V–C5–O5	176.1 (6)
C2–V–C3	92.1 (3)	V–C6–O6	177.9 (7)
C2–V–C4	89.6 (3)		
C2–V–C5	82.8 (3)		
C2–V–C6	93.0 (3)	P1–Cu–P2	117.47 (5)
C3–V–C4	86.5 (3)	P1–Cu–P3	119.94 (5)
C3–V–C5	95.1 (3)	P2–Cu–P3	122.59 (5)
C3–V–C6	172.0 (3)	nC4–V–C5	172.5 (3)
C4–V–C6	87.4 (3)		
C5–V–C6	91.7 (3)		

The preparation of substituted copper derivatives of the $(\eta^5$-$C_5H_5)M(CO)_3$ anions (M = Cr, Mo, W) proved to be much simpler and straightforward. (tmed)Cu complexes were obtained as stable yellow solids in high yields, either by the reaction of the sodium salt of the $(\eta^5$-$C_5H_5)M(CO)_3^-$ anion with (tmed)CuCl (reaction 1) or by the reaction of the corresponding hydride with copper(I) oxide followed by tmed (reaction 2). Bis(triarylphosphine) complexes

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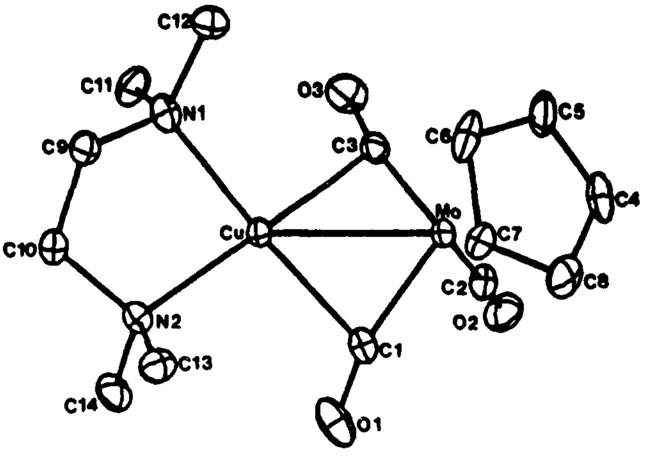

Figure 2. ORTEP drawing of (tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$).

$$(\text{tmed})\text{CuCl} + \text{Na}(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3 \rightarrow (\text{tmed})\text{CuM}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5) + \text{NaCl} \quad (1)$$

$$2(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H} + \text{Cu}_2\text{O} + 2\text{tmed} \rightarrow 2(\text{tmed})\text{CuM}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5) + \text{H}_2\text{O} \quad (2)$$

may also easily be prepared and without complications due to ligand lability and redistribution. These complexes are therefore analogous to the [(C$_6$H$_5$)$_3$P]$_2$CuM(CO)$_3$(η^5-C$_5$H$_5$) (M = Mo, W) complexes reported by Carlton and coworkers.[8] The infrared spectra in the CO stretching region for the three (tmed)CuM(CO)$_3$(η^5-C$_5$H$_5$) complexes are remarkably similar and are also very similar to the bis(triphenylphosphine) derivates. This implies that the structures of all these complexes would have the same type of metal carbonyl bridging, presumably like that observed for one of the forms of [(C$_6$H$_5$)$_3$P]$_2$CuW(CO)$_3$(η^5-C$_5$H$_5$). Because different metals were involved and the ligands on the copper were quite dissimilar both sterically and electronically, we felt it would be interesting to compare the (tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$) structure to those of the [(C$_6$H$_5$)$_3$P]$_2$CuW(CO)$_3$(η^5-C$_5$H$_5$) complexes. A single-crystal X-ray diffraction study was undertaken, and an ORTEP view of the molecule is shown in Figure 2. The overall geometry of this molecule is surprisingly similar to that of one of the [(C$_6$H$_5$)$_3$P]$_2$CuW(CO)$_3$(η^5-C$_5$H$_5$) isomers. Both complexes have a "four-legged piano stool" configuration about the W or Mo atoms as expected, but the similar arrangement of the CO groups seems unusual. In both cases, there is one simple terminal CO group and two semibridging CO's, one of which is located somewhat closer to the copper atom than the other (2.31 and 2.41 Å for the W complex and 2.19 nd 2.43 Å for the Mo complex). The metal–metal bond distance in the Cu–Mo complex is considerably shorter (2.592 Å vs. 2.721 Å) than in the Cu–W compound, but most other significant bond lengths and angles are similar (Table III).

There are also striking similarities between the structures of (tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$) and the (4-CH$_3$C$_5$H$_4$N)Cu(CH$_3$CO$_2$)$_2$Mo(CO)$_2$(η^5-C$_5$H$_5$) complex reported by Werner and co-workers.[9] This latter complex, although containing only two carbonyls and metals in different oxidation states, has a Mo–Cu bond and Cu–CO bonds and angles very similar to the tmed complex.

Compared to complexes of the (η^5-C$_5$H$_5$)M(CO)$_3$ moieties with main-group elements such as tin,[12] the complexes with the L$_2$Cu groups exhibit much lower CO stretching frequencies, a phenomena also observed with the Cu–Mn complexes. Although a number of factors are probably involved, the semibridging nature of some of the carbonyl groups and, most importantly, the relatively higher electron density on the metals bound to copper as compared to tin are influential. It does not appear that the carbonyl stretching frequencies are at all sensitive to the particular group 6 metal or other ligands bound to the copper atom.

Table III. Bond Distances and Angles for (tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$)

	Bond Distances, Å		
Cu–Mo	2.592 (0)	C(4)–C(5)	1.372 (5)
Cu–C(2)	2.185 (3)	C(5)–C(6)	1.40 (1)
Cu–C(3)	2.415 (6)	C(6)–C(7)	1.397 (5)
Cu–N(1)	2.130 (2)	C(7)–C(8)	1.384 (8)
Cu–N(2)	2.139 (6)		
Mo–C(1)	1.928 (3)	N(1)–C(9)	1.470 (8)
Mo–C(2)	1.956 (7)	N(1)–C(11)	1.475 (5)
Mo–C(3)	1.941 (2)	N(1)–C(12)	1.46 (1)
Mo–C(X)	2.041 (4)	N(2)–C(10)	1.491 (5)
C(1)–O(1)	1.168 (5)	N(2)–C(13)	1.473 (4)
C(2)–O(2)	1.17 (1)	N(2)–C(14)	1.46 (1)
C(3)–O(3)	1.166 (3)	C(9)–C(10)	1.50 (1)
	Bond Angles, deg		
Cu–Mo–C(1)	112.5 (2)	Mo–C(3)–Cu	72.1 (1)
Cu–Mo–C(2)	55.3 (1)	Mo–C(3)–O(3)	171.1 (7)
Cu–Mo–C(3)	62.5 (2)	Cu–C(3)–O(3)	116.6 (7)
Cu–Mo–C(X)	121.2 (1)	Cu–N(1)–C(9)	103.7 (2)
C(1)–Mo–C(2)	80.1 (2)	Cu–N(1)–C(11)	110.1 (2)
C(1)–Mo–C(3)	84.3 (1)	Cu–N(1)–C(12)	114.8 (4)
C(1)–Mo–C(X)	126.0 (3)	C(9)–N(1)–C(11)	110.2 (6)
C(2)–Mo–C(3)	101.5 (3)	C(9)–N(1)–C(12)	108.3 (4)
C(2)–Mo–C(X)	126.1 (1)	C(11)–N(1)–C(12)	109.6 (4)
C(3)–Mo–C(X)	124.7 (2)	Cu–N(2)–C(10)	105.6 (4)
Mo–Cu–C(2)	47.4 (2)	Cu–N(2)–C(13)	105.4 (5)
Mo–Cu–C(3)	45.5 (1)	Cu–N(2)–C(14)	117.6 (4)
Mo–Cu–N(1)	127.5 (2)	C(10)–N(2)–C(13)	111.7 (3)
Mo–Cu–N(2)	142.6 (1)	C(10)–N(2)–C(14)	108.3 (6)
C(2)–Cu–C(3)	81.9 (2)	C(13)–N(2)–C(14)	108.3 (4)
C(2)–Cu–N(1)	174.5 (3)	C(5)–C(4)–C(8)	108.4 (8)
C(2)–Cu–N(2)	99.3 (2)	C(4)–C(5)–C(6)	108.5 (7)
C(3)–Cu–N(1)	95.1 (1)	C(5)–C(6)–C(7)	106.5 (5)
C(3)–Cu–N(2)	165.8 (2)	C(6)–C(7)–C(8)	108.1 (6)
N(1)–Cu–N(2)	84.8 (2)	C(7)–C(8)–C(4)	108.4 (4)
Mo–C(1)–O(1)	177.6 (8)	N(1)–C(9)–C(10)	111.2 (3)
Mo–C(2)–Cu	77.3 (1)	N(2)–C(10)–C(9)	110.9 (7)
Mo–C(2)–O(2)	165.1 (5)		
Cu–C(2)–O(2)	117.6 (6)		

Table IV. Summary of Cu–M and Cu–CO Bonding (Å) in Binuclear Copper Complexes

complex	Cu–M dist	Cu–CO dist	ref
(Ph$_3$P)$_3$CuV(CO)$_6$	6.92		this work
(tmed)CuMo(CO)$_3$(C$_5$H$_5$)	2.59	2.19, 2.41	this work
(Me-py)CuMo(CO)$_3$(OAc)$_2$-(C$_5$H$_5$)	2.56	2.14, 2.45	9
(Ph$_3$P)$_2$CuW(CO)$_3$(C$_5$H$_5$) A	2.72	2.31, 2.41	8
(Ph$_3$P)$_2$CuW(CO)$_3$(C$_5$H$_5$) B	2.71	2.20, 2.26	8
(triars)CuMn(CO)$_5$	2.56		11
(tmed)CuCo(CO)$_4$	2.36	2.03	10
(tmed)$_2$Cu$_2$(CO)(C$_4$O$_4$)	2.42	1.84, 1.86	13

It is interesting to compare the structures of the heteronuclear bimetallic complexes containing copper for which data are available (see Table IV). These compounds display a wide range of Cu–M and Cu–CO interactions. At one end of the scale, [(C$_6$H$_5$)$_3$P]$_3$CuV(CO)$_6$, there is no metal–metal bonding or any interaction between the Cu atom and carbonyl ligands. At the other end, the (tmed)CuCo(CO)$_4$ complex possesses a very short Cu–Co bond and a semibridging carbonyl with a fairly short Cu–C distance (2.03 Å). Intermediate are the (triars)CuMn(CO)$_5$ compounds with a "normal" Cu–Mn bond and no apparent

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Table V. Crystal Data and Data Collection Parameters

	(tmed)CuMo(CO)$_3$(C$_5$H$_5$)	[(C$_6$H$_5$)$_3$P]$_3$CuV(CO)$_6$
formula	CuMoC$_{14}$H$_{21}$O$_3$	CuVC$_{60}$H$_{45}$O$_6$P$_3$
fw, g	424.8	1069.4
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	8.134 (1)	11.669 (1)
b, Å	14.632 (2)	12.691 (2)
c, Å	13.993 (2)	19.432 (2)
α, deg		102.17 (2)
β, deg	94.76 (1)	92.03 (1)
γ, deg		108.25 (1)
V, Å^3	1660 (1)	2655 (1)
ρ(calcd), g cm^{-3}	1.70	1.34
Z	4	2
$\mu_{\mathrm{MoK}\alpha}$, cm^{-1}	20.32	7.08
cryst color	light yellow	dark yellow
cryst size, mm	0.20 × 0.22 × 0.18	0.22 × 0.28 × 0.30
$2\theta_{\max}$, deg	50	50
scan type	$\omega-2\theta$	$\omega-2\theta$
scan rates (2θ), deg min^{-1}	2–13	2–13
scan width, deg	1.00 + 0.35 tan θ	1.00 + 0.35 tan θ
collectn range	$\pm h,+k,+l$	$\pm h,\pm k,+l$
unique data	3182	8997
obs data ($\lvert F_o\rvert^2 \geq 2\sigma(F_o^2)$)	2410	4632
variables	274	640
P factor	0.05	0.05
R	0.027	0.057
R_w	0.032	0.054
esd	1.03	1.32
largest shift/error of final cycle	0.20	0.25
largest peak in final diff Fourier, e Å^3	0.50	0.31

Table VI. Positional Parameters and Their Estimated Standard Deviations for (tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$)[a]

atom	x	y	z	B, Å^2
Cu	0.40430 (5)	0.10463 (3)	0.14388 (3)	2.810 (7)
Mo	0.33907 (3)	0.02404 (2)	0.30128 (2)	2.527 (5)
C1	0.4040 (5)	−0.1027 (2)	0.3046 (3)	3.99 (7)
C2	0.2522 (5)	−0.0137 (3)	0.1728 (3)	3.90 (7)
C3	0.5692 (4)	0.04633 (3)	0.2821 (2)	3.78 (7)
N1	0.5498 (3)	0.2241 (2)	0.1294 (2)	3.55 (6)
N2	0.3005 (3)	0.1371 (2)	0.0025 (2)	3.42 (6)
O1	0.4438 (4)	−0.1794 (2)	0.3030 (2)	6.67 (8)
O2	0.1850 (4)	−0.0517 (2)	0.1067 (2)	6.46 (7)
O3	0.7114 (3)	0.0572 (2)	0.2831 (2)	6.13 (7)
C4	0.2346 (6)	0.0273 (3)	0.4530 (3)	5.26 (9)
C5	0.3340 (5)	0.1025 (3)	0.4475 (3)	5.62 (9)
C6	0.2631 (5)	0.1607 (3)	0.3759 (3)	5.16 (8)
C7	0.1178 (5)	0.1184 (3)	0.3385 (3)	4.63 (8)
C8	0.1019 (4)	0.0367 (3)	0.3865 (3)	4.46 (8)
C9	0.4573 (5)	0.2758 (3)	0.0526 (3)	4.30 (8)
C10	0.4009 (5)	0.2146 (3)	−0.0301 (3)	4.38 (8)
C11	0.7138 (5)	0.1988 (3)	0.1000 (3)	5.02 (9)
C12	0.5691 (6)	0.2818 (3)	0.2148 (3)	5.6 (1)
C13	0.1293 (5)	0.1650 (3)	0.0140 (3)	4.81 (9)
C14	0.2977 (5)	0.0650 (3)	−0.0701 (3)	4.97 (9)

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

Cu–CO bonding and the Cu–Mo and Cu–W complexes which also have a Cu–M single bond but which have two semibridging carbonyls with significantly longer Cu–C distances than that found in the Cu–Co complex.

Experimental Section

All syntheses and manipulations were carried out under nitrogen atmosphere unless otherwise specificed. Solvents were dried prior to use by standard procedures. Reagents were obtained from commercial sources or synthesized by well-known standard procedures. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Elemental analyses and infrared data are given in Table I.

(tmed)CuMn(CO)$_5$. To a suspension of 1.31 g of CuI (6.9 mmol) in 70 mL of CH$_2$Cl$_2$ was added 0.8 g of tmed (6.9 mmol) under a CO atmosphere. After the mixture was stirred for 15 min, 2.0 g of NaMn(CO)$_5$ (9.2 mmol) was added and the mixture stirred at room temperature for 15 min. The suspension was filtered giving a pale yellow filtrate which was reduced to approximately 10 mL in volume on a rotary evaporator. The yellow solids (2.42 g) which were obtained were collected on a precooled glass frit and then stored at −20 °C. The cold crystals slowly decomposed to copper metal and Mn$_2$(CO)$_{10}$. Decomposition at room temperature was complete in several hours.

[(C$_6$H$_5$)$_3$P]$_3$CuMn(CO)$_5$. Solid [(C$_6$H$_5$)$_3$P]$_2$CuCl, prepared from 0.34 g (3.5 mmol) of CuCl and 1.80 g (6.9 mmol) of (C$_6$H$_5$)$_3$P, was added to a suspension of 1.00 g (4.6 mmol) of NaMn(CO)$_5$ in 75 mL of CH$_2$Cl$_2$ under nitrogen. The mixture was stirred for 16 h and then filtered. The clear orange filtrate was evaporated to dryness. The residue was recrystallized from a hexane/methylene chloride mixture, yielding 0.90 g of an orange solid which was washed with pentane and dried.

[(C$_6$H$_5$)$_3$P]$_3$CuV(CO)$_6$. A solution of [(C$_6$H$_5$)$_3$P]$_2$CuCl was prepared from 0.58 g (5.9 mmol) of CuCl, 3.08 g (11.7 mmol) of (C$_6$H$_5$)$_3$P, and 75 mL of CH$_2$Cl$_2$, 3.0 g (5.9 mmol) of NaV(CO)$_6$-(diglyme)$_2$ was then added, and the mixture was stirred for 16 h under CO. The suspension was filtered and the filtrate evaporated to dryness. The residue was recrystallized from toluene yielding 1.24 g of bright yellow crystals.

(tmed)CuCr(CO)$_3$(η^5-C$_5$H$_5$). A solution of (tmed)CuCl was prepared by the addition of 0.66 g (6.7 mmol) of CuCl and 0.77 g (6.6 mmol) of tmed to 75 mL of CH$_2$Cl$_2$. A 1.5-g (6.7-mmol) sample of NaCr(CO)$_3$(η^5-C$_5$H$_5$) was then added, and the resulting mixture was stirred under CO for 1 h and then filtered. The filtrate was evaporated to dryness and the residue washed with three 25-mL portions of pentane and then dried, yielding 2.27 g of pale yellow crystals.

[(C$_6$H$_5$)$_3$P]$_2$CuCr(CO)$_3$(η^5-C$_5$H$_5$). This complex was prepared from 0.88 g (8.9 mmol) of CuCl, 4.66 g (17.8 mmol) of (C$_6$H$_5$)$_3$P, and 2.00 g (8.9 mmol) of NaCr(CO)$_3$(η^5-C$_5$H$_5$) in the same manner as the tmed analogue, yielding 6.59 g of yellow crystalline product.

[(C$_6$H$_5$)$_3$P]$_2$CuMo(CO)$_3$(η^5-C$_5$H$_5$). This complex was prepared from 0.60 g (6.1 mmol) of CuCl, 3.18 g (12.1 mmol) of (C$_6$H$_5$)$_3$P, and 1.64 g (6.1 mmol) of NaMo(CO)$_3$(η^5-C$_5$H$_5$) in the same manner as the Cr derivative, yielding 4.77 g of yellow solid.

(tmed)CuMo(CO)$_3$(η^5-C$_5$H$_5$). A solution of (tmed)CuI was prepared by the addition of 1.42 g (7.5 mmol) of CuI and 0.87 g (7.5 mmol) of tmed to 75 mL of CH$_2$Cl$_2$. A 2.0-g (7.5-mmol) sample of $NaMo(CO)_3(\eta^5\text{-}C_5H_5)$ was then added under a CO atmosphere. The mixture was stirred for 30 min at room temperature and then filtered. The filtrate was evaporated to dryness and the residue washed several times with 25-mL portions of pentane, yielding 2.86 g of pale yellow product.

Table VII. Positional Parameters and Their Estimated Standard Deivations for $[(C_6H_5)_3P]_3CuV(CO)_6$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Cu	0.32998 (6)	0.24458 (5)	0.75239 (3)	3.16 (1)
V	0.14443 (9)	0.25581 (8)	0.26740 (5)	4.29 (2)
P1	0.4095 (1)	0.1312 (1)	0.80280 (7)	3.40 (3)
P2	0.2506 (1)	0.3650 (1)	0.82546 (7)	3.37 (3)
P3	0.3304 (1)	0.2338 (1)	0.63298 (7)	3.22 (3)
C1	0.2489 (5)	0.3865 (4)	0.2378 (3)	4.2 (1)
O1	0.3117 (4)	0.4621 (3)	0.2180 (2)	6.0 (1)
C2	0.0452 (6)	0.1137 (5)	0.2871 (3)	5.1 (2)
O2	−0.0103 (5)	0.0277 (4)	0.2966 (2)	7.9 (2)
C3	0.0157 (6)	0.2568 (5)	0.2014 (4)	5.6 (2)
O3	−0.0586 (4)	0.2665 (4)	0.1645 (3)	8.4 (2)
C4	0.0753 (6)	0.3386 (5)	0.3401 (3)	5.4 (2)
O4	0.0309 (4)	0.3839 (4)	0.3841 (3)	8.1 (1)
C5	0.2031 (6)	0.1546 (5)	0.1991 (3)	5.2 (2)
O5	0.2330 (5)	0.0899 (4)	0.1601 (3)	8.2 (1)
C6	0.2760 (6)	0.2768 (5)	0.3401 (3)	6.1 (2)
O6	0.3527 (4)	0.2925 (5)	0.3824 (3)	9.8 (2)
C7	0.3242 (5)	0.0784 (4)	0.8717 (3)	3.5 (1)
C8	0.1992 (5)	0.0527 (5)	0.8636 (3)	4.6 (2)
C9	0.1289 (5)	0.0106 (5)	0.9135 (4)	5.6 (2)
C10	0.1831 (6)	−0.0040 (5)	0.9732 (3)	6.0 (2)
C11	0.3062 (6)	0.0209 (5)	0.9817 (3)	6.2 (2)
C12	0.3762 (5)	0.0623 (5)	0.9320 (3)	4.9 (2)
C13	0.5644 (5)	0.2014 (4)	0.8449 (3)	3.3 (1)
C14	0.6063 (5)	0.3196 (5)	0.8646 (3)	4.5 (1)
C15	0.7185 (5)	0.3772 (5)	0.9025 (3)	5.1 (2)
C16	0.7906 (5)	0.3165 (6)	0.9203 (3)	5.6 (2)
C17	0.7527 (5)	0.1983 (5)	0.8987 (3)	4.8 (2)
C18	0.6398 (5)	0.1432 (4)	0.8616 (3)	4.4 (1)
C19	0.4167 (5)	0.0027 (4)	0.7430 (3)	4.0 (1)
C20	0.3303 (6)	−0.1037 (5)	0.7381 (3)	5.2 (2)
C21	0.3327 (7)	−0.1976 (5)	0.6877 (4)	6.7 (2)
C22	0.4195 (7)	−0.1868 (5)	0.6429 (4)	7.6 (2)
C23	0.5051 (6)	−0.0838 (6)	0.6463 (4)	7.6 (2)
C24	0.5018 (5)	0.0112 (5)	0.6960 (3)	5.4 (2)
C25	0.3313 (5)	0.5163 (4)	0.8389 (3)	3.8 (1)
C26	0.3178 (6)	0.5967 (5)	0.8965 (3)	5.7 (2)
C27	0.3741 (7)	0.7107 (5)	0.9022 (4)	7.0 (2)
C28	0.4481 (6)	0.7478 (5)	0.8541 (4)	6.5 (2)
C29	0.4630 (6)	0.6708 (6)	0.7971 (4)	6.2 (2)
C30	0.4037 (5)	0.5562 (5)	0.7891 (3)	4.9 (2)
C31	0.0963 (4)	0.3459 (4)	0.7919 (3)	3.5 (1)
C32	0.0512 (5)	0.4325 (5)	0.7910 (3)	4.6 (2)
C33	−0.0687 (5)	0.4086 (5)	0.7643 (4)	6.2 (2)
C34	−0.1430 (5)	0.3000 (6)	0.7397 (3)	6.1 (2)
C35	−0.0975 (6)	0.2110 (6)	0.7392 (3)	5.8 (2)
C36	0.0204 (5)	0.2343 (5)	0.7658 (3)	4.8 (2)
C37	0.2343 (5)	0.3451 (4)	0.9155 (3)	3.7 (1)
C38	0.1220 (6)	0.3133 (5)	0.9403 (3)	5.1 (2)
C39	0.1112 (7)	0.2924 (6)	1.0076 (3)	6.7 (2)
C40	0.2135 (7)	0.3011 (5)	1.0471 (3)	6.7 (2)
C41	0.3250 (6)	0.3336 (5)	1.0256 (3)	6.7 (2)
C42	0.3365 (5)	0.3566 (5)	0.9585 (3)	5.8 (2)
C43	0.4820 (4)	0.2518 (4)	0.6058 (2)	3.2 (1)
C44	0.5101 (5)	0.1681 (5)	0.5589 (3)	4.7 (2)
C45	0.6273 (5)	0.1868 (5)	0.5419 (3)	5.4 (2)
C46	0.7164 (5)	0.2887 (5)	0.5684 (3)	4.9 (2)
C47	0.6889 (5)	0.3714 (5)	0.6161 (3)	5.3 (2)
C48	0.5744 (5)	0.3528 (5)	0.6351 (3)	5.0 (2)
C49	0.2373 (4)	0.1013 (4)	0.5736 (3)	3.3 (1)
C50	0.2032 (6)	0.0955 (5)	0.5036 (3)	5.0 (2)
C51	0.1362 (6)	−0.0060 (6)	0.4592 (3)	6.9 (2)
C52	0.1009 (5)	−0.1041 (5)	0.4838 (4)	6.3 (2)
C53	0.1336 (6)	−0.1007 (5)	0.5520 (4)	6.0 (2)
C54	0.2022 (5)	0.0022 (5)	0.5979 (3)	4.6 (2)
C55	0.2856 (5)	0.3415 (4)	0.6017 (3)	3.5 (1)
C56	0.1801 (5)	0.3599 (5)	0.6277 (3)	4.5 (1)
C57	0.1374 (5)	0.4371 (5)	0.5999 (3)	5.6 (2)
C58	0.1996 (6)	0.4993 (5)	0.5558 (3)	6.0 (2)
C59	0.3029 (6)	0.4829 (5)	0.5349 (3)	6.9 (2)
C60	0.3480 (6)	0.4053 (5)	0.5568 (3)	5.7 (2)

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

$(tmed)CuW(CO)_3(\eta^5\text{-}C_5H_5)$. A solution of 0.5 g (3.5 mmol) of Cu_2O in 75 mL of CH_2Cl_2 was stirred with 0.81 g (7.0 mmol) of tmed for 1 h under a CO atmosphere. A solution of 2.34 g (7.0 mmol) $(\eta^5\text{-}C_5H_5)W(CO)_3H$ in 10 mL of CH_2Cl_2 was then added dropwise and the resulting mixture stirred an additional 3 h. The mixture was filtered and the pale yellow filtrate evaporated to dryness on a rotary evaporator yielding 3.20 g of pale yellow product.

X-ray Data for $(tmed)CuMo(CO)_3(C_5H_5)$. A pale yellow crystal was selected for the experiment and mounted in a thin-walled glass capillary. The unit cell dimensions were determined by a least-squares fit of 25 diffractometer measured 2θ values. Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and parameters listed in Table V. The background was counted on either side of the measured peak for half the time of the total scan. The data were corrected for Lorentz, polarization, and background effects. Three check reflections showed no loss in intensity with time. Absorption corrections were not applied since psi scan data revealed the effect to be minimal (maximum variation ±4%).

The structure was solved by conventional heavy-atom techniques. Approximate positional parameters for the Cu and Mo atoms were determined by interpretation of the three-dimensional Patterson synthesis. After initial refinement of the metal atoim parameters, the remaining non-hydrogen atoms were located by successive least-squares refinement and difference Fourier maps. A difference map calculated after full-matrix least-squares refinement with anisotropic temperature factors revealed the location of all hydrogen atoms. Final cycles of refinement with anisotropic temeprature factors for all non-hydrogen atoms, isotropic temperature factors for hydrogen atoms, and anomalous dispersion corrections for Cu and Mo converged to $R = 0.027$ and $R_w = 0.032$. The quantity minimized in least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma(F_o)$. All calculations were performed on a PDP 11/60 computer using the Enraf-Nonius structure determination package programs. Selected bond distances and angles are given in Table III, and positional parameters are given in Table VI. Anisotropic temperature parameters, complete tables of bond distances and angles, and calculated and observed structure factors are given as supplementary material.

X-ray Data for $[(C_6H_5)_3P]_3CuV(CO)_6$. A dark yellow crystal was mounted in a thin-walled glass capillary. The procedure used for crystal structure determination and refinement was the same as for $(tmed)CuMo(CO)_3(C_5H_5)$. A summary of the crystallographic data is given in Table V. Psi scan data indicated absorption effects to be negligible (maximum variation ±2%). Most of the hydrogen atoms were located on a difference map; the remainder were entered at theoretically calculated positions. The hydrogens were assigned isotropic temperature factors of 5.0 Å^2 and were not varied in refinement procedures. Full-matrix least-squares refinement with anisotropic temperature factors for a non-hydrogen atoms, and anomalous dispersion corrections for Cu and V have converged to $R = 0.057$ and $R_w = 0.054$. Selected bond distances and angles are given in Table II, positional parameters are given in Table VII, and anisotropic temperature factors, complete bond lengths and angles, and structure factors are given as supplementary material.

Registry No. $(tmed)CuMn(CO)_5$, 98542-00-8; $[(C_6H_5)_3P]_3CuMn(CO)_5$, 98542-01-9; $[(C_6H_5)_3P]_3CuV(CO)_6$, 98542-02-0; $(tmed)CuCr(CO)_3(\eta^5\text{-}C_5H_5)$, 98542-03-1; $[(C_6H_5)_3P]_2CuCr(CO)_3(\eta^5\text{-}C_5H_5)$, 98542-04-2; $(tmed)CuMo(CO)_3(\eta^5\text{-}C_5H_5)$, 98542-05-3; $[(C_6H_5)_3P]_2CuMo(CO)_3(\eta^5\text{-}C_5H_5)$, 98542-06-4; $(tmed)CuW(CO)_3(\eta^5\text{-}C_5H_5)$, 98542-07-5; CuI, 7681-65-4; $NaMn(CO)_5$, 13859-41-1; Cu, 7440-50-8; $Mn_2(CO)_{10}$, 10170-69-1; $[(C_6H_5)_3P]_2CuCl$, 25577-10-0; $NaV(CO)_6(diglyme)$, 15531-13-2; (tmed)CuCl, 83347-89-1; $NaCr(CO)_3(\eta^5\text{-}C_5H_5)$, 12203-12-2; $NaMo(CO)_3(\eta^5\text{-}C_5H_5)$, 12107-35-6; (tmed)CuI, 95251-49-3; CuCl, 7758-89-6; Cu_2O, 1317-39-1; (η^5-C_5H_5)W(CO)$_3$H, 12128-26-6; [($C_6H_5)_3P]_3$CuCl, 15709-76-9.

Supplementary Material Available: Tables of anisotropic temperature factors, complete bond lengths and angles, and structure factors for (tmed)CuMo(CO)$_3$(C_5H_5) and [($C_6H_5)_3P]_3$CuV(CO)$_6$ (56 pages). Ordering information is given on any current masthead page.

Silenes and Silenoids. 9. The Synthesis of Polyfunctional Bis(group 14)-Substituted Cyclopentadienes via a Novel Cleavage Reaction of Silicon–Carbon Bonds by Chloride Ion[†]

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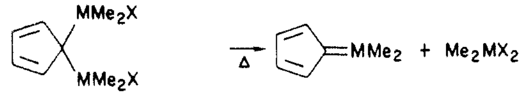
Group 14 substituted cyclopentadienes of the type $C_5H_4(MMe_2X)(M'Me_2Y)$, 1 (M and/or M′ = Si or Ge, X and/or Y = Cl or Me), can be conveniently prepared in good yields by the reaction of *n*-butyllithium with cyclopentadienyltrimethylsilane followed by treatment with Me_2MCl_2 (M = Si or Ge). In hexane the reaction gives 1 (M = Si, M′ = Si or Ge, X = Me, Y = Cl). In THF, with excess Me_2MCl_2, an unprecedented lithium chloride catalyzed cleavage of the trimethylsilyl group occurs to give excellent yields of 1 (M and M′ = Si or Ge, X and Y = Cl). Methanolysis gives the corresponding methoxy compounds 1 (X and Y = OMe). The chloride ion cleavage reaction occurs only in THF and when the substrate bears a chlorodimethylsilyl or -germyl substituent.

Introduction

We recently reported that 1,1-bis(dimethylmethoxysilyl)cyclopentadiene 1 (M = Si, X = OMe) serves as an efficient precursor to dimethylsilafulvene 2 under unusually mild conditions.[1] Such bis(silyl)- or bis(germyl)cyclopentadienes 1 with functionality on both metalloid substituents have not previously been reported. Compounds of this type are of interest because of their potential as precursors to sila- or germafulvenes 2 under relatively mild conditions.[1]



1. M = Si, Ge; X = Cl, OMe

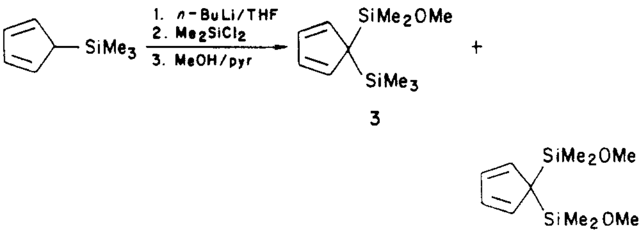
2

In addition, bis(triorganosilyl)cyclopentadienes are found as mixtures of isomers due to nondegenerate metallotropic rearrangements which occur at room temperature.[2] However, when one of the alkyl groups on silicon is replaced with a Lewis base substituent, 1,1-bis(silyl)cyclopentadienes are obtained which are not fluxional at room temperature. For example 1-(dimethylmethoxysilyl)-1-(trimethylsilyl)cyclopentadiene, **3**, does not undergo metallotropic rearrangement at room temperature, a fact which has been attributed to an intramolecular interaction between the methoxy oxygen and the trimethylsilyl group.[3]

In the course of our mechanistic investigation of the silene vs. silenoid problem as related to silafulvenes,[1] we discovered a novel route to bis functional silyl and germyl cyclopentadienes. The details of this discovery are reported in this paper.

Results and Discussion

The synthesis of **3** by the reaction of [(trimethylsilyl)cyclopentadienyl]lithium with dimethyldichlorosilane followed by methanolysis in the presence of pyridine has been reported by Barton and co-workers.[3] When we carried out this reaction using 1.4 equiv of dimethyldichlorosilane and THF as the solvent, in addition to a 30% yield of the expected product **3**, we obtained a 15% yield of 1,1-bis(dimethylmethoxysilyl)cyclopentadiene, **4**. We subsequently discovered that the use of two or more equivalents of dimethyldichlorosilane and longer reaction times gave yields of **4** in excess of 65%.



3

4

The ^1H, ^{13}C, and ^{29}Si NMR spectra of **4** indicate that at room temperature it exists essentially exclusively as the 1,1-isomer and is not fluxional. The ^1H NMR spectrum shows an A_2B_2 pattern for the vinyl protons, a single

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

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