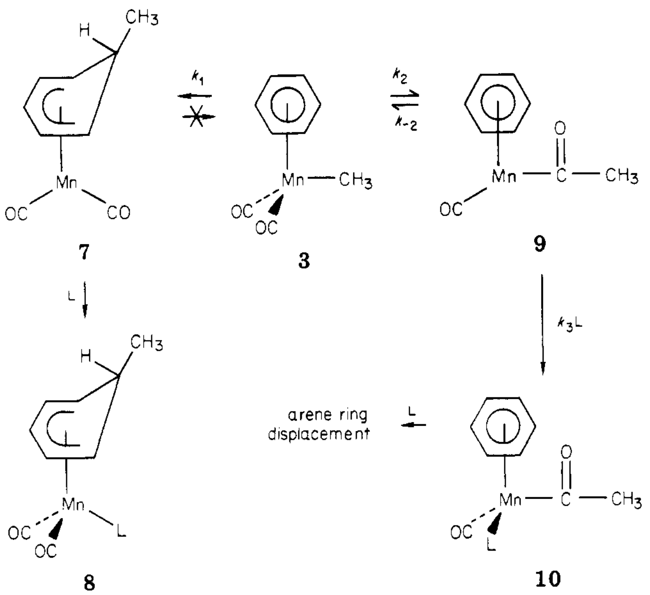
Scheme I



The acyl complex from CO insertion $C_6H_6(CO)(PPh_3)$-Mn–$COCH_3$, **5** (Ph = phenyl), can be observed by treating **3** in more concentrated solutions (0.12 M) with a fivefold excess of PPh_3 in benzene at 55 °C. The approximate half-life for this reaction is 5 h. When the reaction is monitored by ^1H NMR (C_6D_6) the acyl **5** is observed to form by appearance of new proton signals at δ 2.58 (3 H, $COCH_3$) and 4.48 (6 H, d, J_{PH} = 2 Hz, C_6H_6).[9] However, simultaneous with insertion the acyl species **5** decomposes, apparently by loss of the arene ring; thus, **5** cannot be formed quantitatively from **3**. Substantial decomposition is evident in this reaction and the secondary products have not been identified.[10] The details of this insertion reaction are more clearly evident when $(MeO)_3P$ is employed. Treatment of **3** (0.13 M) with $(MeO)_3P$ (2.5 M) in benzene at 55 °C results in initial formation of the acyl complex $C_6H_6(CO)(P(OMe)_3)Mn$–$COCH_3$, **6** ($t_{1/2}$ ca. 5 h).[11] However, competitive with formation of **6** is its clean conversion to *mer*-$(P(OMe)_3)_3(CO)_2Mn$-CH_3 which is isolated as the sole product (76% yield) after 24 h.[12]

The reactions observed here suggest the general mechanism shown in Scheme I.

The formation of the 16-electron endo methyl intermediate **7** is likely to be essentially irreversible,[13] and thus formation of **8** is a first-order process. On the other hand, if formation of the 16-electron acyl **9** is rapid and reversible, then formation of saturated acyl complex **10** is second order. Thus, at low concentrations of external L the second-order formation of **10** is slow and the first-order process predominates, yielding **8**. At high concentrations of external L the second-order reaction is rapid (relative to k_1) and can be driven to yield acyl complex **10**.

There are two general points of interest in regard to these results. First, the observation of a methyl group migration from a metal to a coordinated arene ring is without precedent. The closest analogy is the report by Green[14] of the migration of the molybdenum-bound ethyl group to the C_5H_5 ring in $Cp_2Mo(Cl)(C_2H_5)$ in which the migration product is trapped as a phosphine adduct. In a general way, this migration models an olefin insertion into a metal–carbon bond, a reaction which has seldom been directly observed with isolated alkyl–olefin complexes but which has been frequently inferred in stoichiometric transformations, olefin polymerization, and other catalytic processes.[15,16]

Secondly, the sharp contrast in the mode of reaction between dimethylcuprate and methyllithium with (arene)manganese tricarbonyl cations suggests that alkylcuprates may prove to be useful complementary reagents in reactions with other (polyene)- and polyenylmetal carbonyl complexes. We are currently exploring these reactions and the chemistry of the now easily accessible (arene)$(CO)_2Mn$–COR and (arene)$(CO)_2Mn$–R complexes.

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Registry No. 1, 41656-02-4; 2, 83681-37-2; 3, 65643-62-1; 4, 83681-38-3; 5, 83681-39-4; 6, 83681-40-7; *mer*-$(P(OMe)_3)_3$-$(CO)_2Mn$-CH_3, 25868-36-4; Me_2CuLi, 15681-48-8.

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(8) Spectral properties of **4**: ^1H NMR (C_6D_6) δ 1.46 (d, CH_3, $J_{Me,6x}$ = 6 Hz), 1.98 (d, H_1, $J_{1,2}$ = 4 Hz), 2.30 (quint, H_{6x}, $J_{6x,P} = J_{6x,Me}$ = 6 Hz), 4.20 (m, H_2, $J_{2,P} = J_{2,3}$ = 6 Hz), $J_{1,2}$ = 4 Hz), 5.36 (t, H_3, $J_{3,2}$ = 6 Hz), 7–8 (m, PPh_3); (coupling constants established via decoupling experiments); IR (ν_{CO}, isopentane) 1942 (s), 1886 (s) cm^{-1}; ^{13}C NMR (C_6D_6) 21.03 (Me), 29.67 (C_6), 51.83 (C_1), 81.98 (C_3), 96.35 (C_2), 135 (Ph) ppm. high-resolution mass spectrum, calculated 466.0895, found 466.0891.

(9) These parameters are completely consistent with those expected for **5** based on the spectrum of **2** and also on Fp–$COCH_3$.[7]

(10) A triplet observed at δ –0.29 may be due to $(PPh_3)_2Mn(CO)_3CH_3$.

(11) Spectral properties of acyl **6**: ^1H NMR (C_6D_6) δ 2.83 (3 H, s), 3.4–3.6 (9 H, m), 4.63 (6 H, d, J = 3 Hz); IR (ν_{CO}, diethyl ether) 1909 (s), 1560 (m) cm^{-1} (pure samples of **6** cannot be isolated due to contamination with $(P(OCH_3)_3)_3(CO)_2Mn$–CH_3 to which **6** decomposes with a rate competitive with its formation).

(12) Spectral properties: ^1H NMR (C_6D_6) δ 0.08 (3 H, q, J = 9 Hz, CH_3), 3.56 (27 H, m, $P(OMe)_3$); IR (ν_{CO}, CH_2Cl_2) 1942 (s), 1860 (s) cm^{-1}; high resolution mass spectrum, calculated 498.0383, found 498.0388. Anal. Calcd for $C_{12}H_{30}MnO_{11}P_3$: C, 28.93; H, 6.07; Mn, 11.03. Found: C, 29.10; H, 6.09; Mn, 11.11.

(13) The methyl migration is probably not completely irreversible; however, the conversion of **7** to **3** via insertion of manganese into an unstrained, saturated carbon–carbon bond is likely to be slow. All that is required for the applicability of Scheme I is that this reverse reaction (**7** → **3**) be slower than trapping by PPh_3. We are currently investigating the possible **7** → **3** conversion by attempting to generate **7** in the absence of ligand traps.

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Synthesis and Molecular Structure of [Dicyclopentadienyl(tetrahydrofuran)titanium](μ-η^2-carbonyl)cyclopentadienyldicarbonylmolybdenum[†]

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Summary: Reaction of $Cp_2Ti(CO)_2$ with $[CpMo(CO)_2]_2$ in THF yields the novel complex $Cp_2Ti(THF)OCMo(CO)_2Cp$, **1**, containing a μ-η^2 metal carbonyl bridge between the Ti and Mo. The structure of **1** has been determined from

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[†] Dedicated to the memory of Rowland Pettit.

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single-crystal X-ray diffraction data. The compound was found to crystallize in the monoclinic space group $P2_1/a$ with unit cell dimensions of a = 14.333 (2) Å, b = 10.783 (3) Å, c = 14.051 (3) Å, β = 109.19 (2)°, Z = 4, d(calcd) = 1.601 g cm^{-3}, and V = 2050.9 (1.4) Å^3.

As part of a program in the study of complexes of the earlier transition metals directed toward the understanding of syn gas reduction chemistry, we were interested in synthesizing organotitanium complexes with titanium bound to other transition-metal complexes with metal-metal bonds. Although such metal–metal bonded complexes have been reported for the heavier elements Zr and Hf,[1-3] to our knowledge there are no reports of the corresponding titanium compounds. We believed that such metal–metal bonded complexes could be obtained by the reaction between a low-valent titanium complex and a metal dimer possessing a metal–metal multiple bond. In essence, we envisioned the metal–metal multiple bond to react with the titanium as an "inorganic acetylene" to yield a polymetallic complex incorporating Ti–M bonds. In our attempt at using $Cp_2Ti(CO)_2$[4] as the titanium complex and $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$[5] as the metal multiply bonded dimer, the reaction did not proceed as originally envisioned. Nonetheless, an interesting bimetallic complex was obtained on whose structure we now report.

A smooth reaction takes place between $Cp_2Ti(CO)_2$ and $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$ in tetrahydrofuran (THF) solution at room temperature.[6] From this reaction mixture a bright green complex, 1, may be isolated. In addition to 1, $[CpMo(CO)_3]_2$ is formed in the above reaction. Complex 1 is highly air and moisture sensitive, yielding $[CpMo(CO)_3]_2$ as the only carbonyl-containing species on exposure to air. Compound 1 is very soluble in THF, slightly soluble in toluene, and insoluble in aliphatic hydrocarbons and reacts with halogenated hydrocarbons. The infrared spectrum of 1 in THF displays ν(CO) = 1920 (s), 1830 (s), and 1650 (s) cm^{-1}. Complex 1 is paramagnetic, so no structural information could be obtained from ^{1}H or ^{13}C NMR spectroscopy. We were particularly interested in discovering what carbonyl bonding mode is responsible for the very low carbonyl stretching frequency at 1650 cm^{-1}, so we undertook a single-crystal X-ray diffraction study of 1.

Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution of 1 in THF. A crystal of dimensions 0.56 mm × 0.44 mm × 0.50 mm was selected for analysis and then sealed in a Lindemann capillary in contact with the mother liquor from which it was grown.[7] Initially, 25 intensities were located and centered on an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation (λ = 0.71073 Å). A least-squares analysis of the positions of these intensities revealed that the complex is monoclinic, with unit cell dimensions of a = 14.333 (2) Å, b = 10.783 (2) Å, c = 14.051 (3) Å, and β = 109.19 (2)°. A unit cell volume of 2050.9 (1.44) Å^3, coupled with a calculated formula weight of 495.29 g mol^{-1} (based on a model of one Mo, one Ti, four O, 22 C, and 23 H), and Z = 4, gives a d(calcd) of 1.601 g cm^{-3}. There were 3597 unique intensities collected in the range of $0° < \theta < 25°$, with 1847 observations meeting the criterion $(F_o)^2 > 2\sigma\ (Fo)^2$. These included rejections for $(\sin\theta)\lambda^{-1} < 0.07$, which were made because the background measurements showed interference from the beam stop on the diffractometer. Examination of the systematic absences $h0l$, h odd; $0k0$, k odd, led to the space group determination of $P2_1/a$.[8]

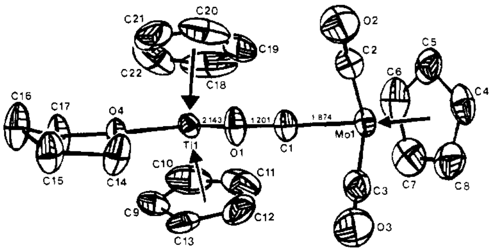

Figure 1. ORTEP diagram showing the labelling scheme of $Cp_2Ti(THF)OCMo(CO)_2Cp$, 1.

Table I. Selected Bond Lengths (Å) and Angles (deg) in $Cp_2Ti(THF)OCMo(CO)_2Cp$ (1)

	Bond Lengths		
Mo-C(1)	1.874 (7)	C(1)-O(1)	1.201 (8)
Mo-C(2)	1.920 (8)	C(2)-O(2)	1.154 (8)
Mo-C(3)	1.930 (8)	C(3)-O(3)	1.162 (9)
Ti-O(1)	2.143 (5)		
Ti-O(4)	2.197 (5)		
	Bond Angles		
Mo-C(1)-O(1)	177.95 (63)	Ti-O(1)-C(1)	135.35 (46)
Mo-C(2)-O(2)	177.04 (72)	O(1)-Ti-O(4)	79.89 (18)
Mo-C(3)-O(3)	177.15 (70)		

The positions of the metal atoms were located through a combination of Patterson and direct methods techniques. The remaining non-hydrogen atoms were identified by subsequent difference Fourier syntheses, which were alternated with cycles of least-squares refinement. A total of twenty-eight non-hydrogen atoms were refined with anisotropic thermal parameters in a full-matrix least-squares calculation which converged to residuals of R_1 = 0.051 and R_2 = 0.050. These residuals were based on 1847 observations and 254 variables, including a scale factor and an extinction correction of the form $|F_c|\ (1 + gIc)^{-1}$, where the parameter g converged to 2.894×10^{-7}. The final difference Fourier synthesis yielded maximum peaks of 0.33 e Å^{-3} in positions near the metal atoms.

The ORTEP diagram of 1 is shown in Figure 1 and shows the complex to be [dicyclopentadienyl(tetrahydrofuran)titanium]μ-η^2-carbonylcyclopentadienyldicarbonylmolybdenum, $Cp_2Ti(THF)OCMo(CO)_2Cp$. The structure consists of a Cp_2Ti unit coordinated by a molecule of THF and by the oxygen atom of one of the carbonyl ligands of a $CpMo(CO)_3$ fragment. Thus, the Ti and Mo atoms are held together, not by a metal–metal bond, but by a μ-η^2 bridging carbonyl. The two terminal carbonyl ligands on the molybdenum have Mo–C and C–O distances averaging

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[6] In a nitrogen-filled glovebox, 1.6 g (6.8 mmol) of $Cp_2Ti(CO)_2$ was added to a solution of 3.0 g (6.9 mmol) of $[CpMo(CO)_2]_2$ in 50 mL of THF, and the resulting solution was stirred at room temperature for 18 h. The THF was removed under reduced pressure to yield a brown solid. The brown solid was washed with several portions of toluene to remove $[CpMo(CO)_3]_2$. This left behind 2.1 g of 1 as a bright green solid. When this reaction is carried out in toluene, a toluene-insoluble microcrystalline powder analyzing for $(Cp_2Ti{\cdot}CpMo(CO)_3)_x$ is isolated. Work is continuing on the characterization of this material.

[7] Crystals of 1 contain coordinated THF which would be lost over a period of time resulting in decomposition, hence the need to mount crystals in contact with the mother liquor.

[8] Absorption corrections were not made on the data since psi scan measurements showed that corrections to the intensities would average 0.96 (±2), with μ = 10.295 cm^{-1}.

1.925 ± 0.005 and 1.150 ± 0.004 Å, respectively, while the bridging carbonyl has a shortened Mo–C distance of 1.874 Å and a longer C–O bond of 1.201 Å. It is also interesting to note that the Ti–O(carbonyl) distance is significantly shorter than the Ti–O(THF) distance (2.143 (5) Å vs. 2.197 (5) Å). Table I lists some selected bond lengths and bond angles for complex 1.

Various examples of such bridging carbonyl structures have been reported over the years and have been described in terms of Lewis acid adducts of metal carbonyls.[9] Most have involved main-group Lewis acids coordinating to metal carbonyl oxygens, but recently examples of transition metals[10] and lanthanide metal[11] complex adducts have been reported. In the present case, 1 may be considered formally to consist of the Lewis acid Cp_2Ti^+ forming Lewis acid–base adducts both with THF and with $CpMo(CO)_3^-$. The short Mo–C_1 distance is an indication that the metal carbyne structure Mo≡C—O—Ti contributes a significant degree to the overall bonding picture in this complex.[12] The presence of the Cp_2Ti^{III+} center in the molecule accounts for its paramagnetism.[13] The formation of the μ-η^2-carbonyl bridge rather than a metal–metal bond may be explained as a consequence of the high charge/low ionic radius of the titanium making it a relatively "hard" center. Thus, instead of binding to the "softer" molybdenum center, it forms an acid–base pair with the "harder" oxygen site of a carbonyl ligand.[15]

The mechanism of the formation of 1 from $Cp_2Ti(CO)_2$ and $CpMo(CO)_2{\equiv}Mo(CO)_2Cp$ is an intriguing area for speculation since, at first glance, it would appear to require the cleavage of a Mo–Mo triple bond. No reaction takes place between $Cp_2Ti(CO)_2$ and $CpMo(CO)_3$–$Mo(CO)_3Cp$ at room temperature in THF which shows the necessity for having the multiple bond. At present, we favor the hypothesis depicted in Scheme I. Initially, carbon monoxide is lost from the $Cp_2Ti(CO)_2$, saturating the Mo–Mo multiple bond, yielding $[CpMo(CO)_3]_2$ and a "titanocene"-like species. This titanocene-like species may then reduce the metal dimer to the mononuclear anions forming complex 1. There is precedent for the reduction of the dimer $[CpCr(CO)_3]_2$ to the anion using cobaltocene and other electron-rich metallocenes.[17]

Scheme I

$$\mathrm{Cp_2Ti(CO)_2 + CpMo(CO)_2{\equiv}Mo(CO)_2Cp \rightarrow \text{“}Cp_2Ti\text{”} + CpMo(CO)_3{-}Mo(CO)_3Cp}$$

$$\mathrm{2\text{“}Cp_2Ti\text{”} + CpMo(CO)_3{-}Mo(CO)_3Cp \xrightarrow{THF} 2Cp_2Ti(THF)OCMo(CO)_2Cp}$$

In keeping with the view that 1 is an adduct of $CpMo(CO)_3^-$, 1 reacts with CH_3I to yield $CpMo(CO)_3CH_3$ and $(Cp_2TiI)_2$ while the reaction with acetic acid yields $CpMo(CO)_3H$ and $(Cp_2TiOAC)_2$. There appears to be no reaction at room temperature between 1 and carbon monoxide or hydrogen.

It would appear that the reaction between an unsaturated metal dimer and a low-valent metal carbonyl provides a unique method for the preparation of novel bimetallic complexes. We are currently investigating how far the scope of such reactions may be extended and the factors which determine whether metal–metal or metal–oxygen bonding occurs.

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Supplementary Material Available: Crystal and data collection data, all positional and thermal parameters, bond lengths and bond angles, and listings of *h*, *k*, l, F_o, and F_c for compound 1 (14 pages). Ordering information is given on any current masthead page.

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