Reactions of Metal Carbonyl Anions with Methyl Organometallic Compounds

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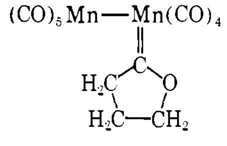
Abstract: The reaction of metal carbonyl anions with methyl metal carbonyl compounds are grouped into three categories: adduct formation, methyl transfer, and no apparent reaction. The formation of acyl anion adducts was observable only in the reactions of $(CO)_5MnCH_3$ with either $Mn(CO)_5^-$ or $Re(CO)_5^-$. The acyl anion adducts could be trapped by alkylation with CH_3OSO_2F which gave *cis*-$(CO)_5MnMn(CO)_4C(OCH_3)CH_3$ and *cis*-$(CO)_5MnRe(CO)_4C(OHC_3)CH_3$, **8.** The latter compound was characterized by X-ray crystallography. The transfer of a methyl group from methyl organometallics to the highly nucleophilic $C_5H_5Fe(CO)_2^-$ was observed in all cases studied.

In 1963 King reported that the reaction of $NaMn(CO)_5$ with either 1,3-dibromopropane or 4-chlorobutyryl chloride gave a compound with the empirical formula $Mn_2(CO)_{10}(CH_2)_3$.[1] This compound has since been shown to be the cyclic metal-carbene complex **1**[2] and not structure **2** as originally proposed by King. One mechanism which we considered for the formation of **1** is shown in Scheme I. The key step in this mechanism is the attack of $Mn(CO)_5^-$ on the alkyl manganese compound **3** which leads to a dinuclear acyl manganese species. This attack at manganese would have to be faster than nucleophilic displacement of bromide from **3.** Since the reaction of $NaMn(CO)_5$ with CH_3I had been reported to give a 90% yield of $(CO)_5MnCH_3$, the possibility of the attack of $Mn(CO)_5^-$ at the manganese atom of **3** appeared questionable. To gain further insight into such reactions, we began a study of the reaction of $Mn(CO)_5^-$ with $(CO)_5MnCH_3$.



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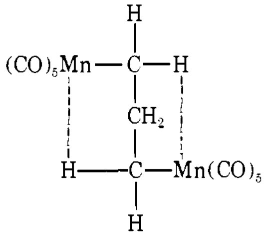

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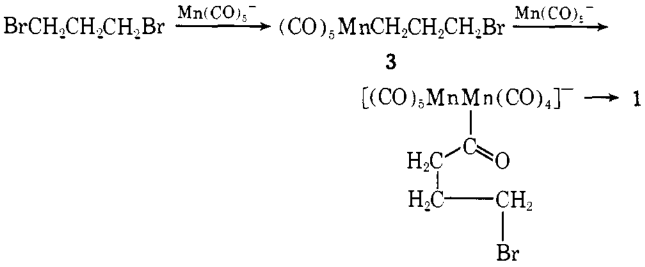
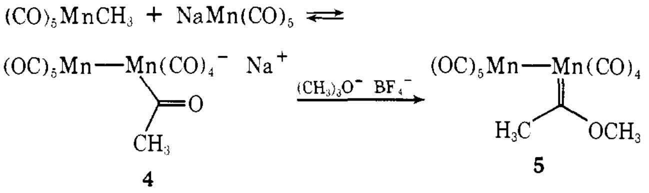
Scheme I



We have found that $Mn(CO)_5^-$ does indeed react with $(CO)_5MnCH_3$ to give a dinuclear acyl manganese anion which can subsequently be alkylated on oxygen to give a dinuclear metal carbene complex (Scheme II).[3]

Since the formation of dinuclear acyl anions provides an interesting possible method for synthesizing mixed dinuclear metal-carbene complexes, we have investigated the scope of this process. The reactions of several metal carbonyl anions with $(CO)_5MnCH_3$, $(CO)_5MnC_6H_5$, and other alkyl metal carbonyl derivatives were investigated.

Scheme II



We report here that this method for synthesizing mixed dinuclear metal-carbene complexes is limited to dinuclear manganese-manganese and rhenium-manganese carbene complexes formed from the reaction of $NaMn(CO)_5$ or $NaRe(CO)_5$ with alkyl- and arylpentacarbonylmanganese(I) compounds.[4] We also report a new methyl transfer process in which one metal carbonyl anion nucleophilically displaces another metal carbonyl anion from a methyl metal carbonyl compound.

Results

Exploratory reactions of metal carbonyl anions with $(CO)_5MnCH_3$ and with other methyl metal carbonyl compounds in tetrahydrofuran were performed in evacuated, sealed NMR tubes and were monitored by NMR for the appearance of a new singlet due to an acyl metal anion in the region between the THF resonances. The result of these initial experiments, which can be grouped into three categories (adduct formation, methyl transfer, and no apparent reaction), are summarized in Table I.

Adduct Formation. The NMR spectrum of a solution prepared from 0.27 mmol each of $NaMn(CO)_5$ and $(CO)_5MnCH_3$ in 0.50 ml of THF consists of a singlet at δ −0.1 due to $CH_3Mn(CO)_5$ and a new singlet at δ 2.51 which we attribute to the dinuclear acetylmanganese anion **4** in addition to the THF resonances. The relative intensities of the two singlets change upon dilution; the ratio of the area of the peak at δ 2.51 due to the adduct **4** to the area of the $(CO)_5MnCH_3$ peak at δ −0.10 changes from 1.71 to 1.08 when the sample volume is increased from 0.50 to 1.20 ml. The equilibrium has thus been shifted to $(CO)_5MnCH_3$ by dilution, as expected from the law of mass action. A marked change in the relative intensities of the two singlets also occurs upon heating: at 40°, the ratio of the intensity of the peak due to **4** to the intensity of the $(CO)_5MnCH_3$ peak is 1.71; at 71°, the ratio decreases to 1.03. These changes are reversible below 90° where irreversible line broadening occurs caused by thermal decomposition.

Formation of a rhenium-manganese acetyl anion was indicated by the appearance of a new singlet at δ 2.44 in the reaction of $NaRe(CO)_5$ with $(CO)_5MnCH_3$. In the initial NMR spectrum an additional acetyl anion resonance at δ

Table I. Reactions of Metal Carbonyl Anions with Methyl Organometallic Compounds[a]

Methyl compounds	$(C_5H_5)Mo(CO)_3^-$	$Mn(CO)_5^-$	$(C_5H_5)W(CO)_3^-$	$Re(CO)_5^-$	$(C_5H_5)Fe(CO)_2^-$
$(CO)_5MnCH_3$	CH_3Mo + Mn–Mn acyl anion 4	Mn–Mn acyl anion 4	NR	Re–Mn acyl anion	CH_3Fe
$(C_5H_5)Mo(CO)_3CH_3$	NR	CH_3Mn + Mn–Mn acyl anion 4	CH_3W	NR	CH_3Fe
$(CO)_5ReCH_3$	. . .	NR	. . .	NR	CH_3Fe
$(C_5H_5)Fe(CO)_2CH_3$	NR	NR	NR	NR	NR
$(C_5H_5)W(CO)_3CH_3$	NR	NR	NR	NR	CH_3Fe

[a] NR = no adduct formation or methyl transfer observed.

2.51 was observed. This acetyl anion resonance disappears within an hour with concomitant increase in the resonance at δ 2.44. The nature of the two species observed in solution will be dealt with in detail in the discussion section.

An acetyl anion also appeared at δ 2.51 in the reaction of $NaMn(CO)_5$ with $(C_5H_5)Mo(CO)_3CH_3$; this was demonstrated to be the dimanganese acetyl anion **4** (vide infra). No other dinuclear acetyl anions were detected by NMR. The possibility that acetyl anions complexed to metals other than manganese might have substantially different chemical shifts and thus be obscured by the THF resonances cannot be ruled out. However, the presence of cyclopentadienyl resonances in most of these other cases provides additional means of detecting new species in solution; the formation of an anionic complex would be expected to result in the appearance of a new cyclopentadienyl resonance.[5]

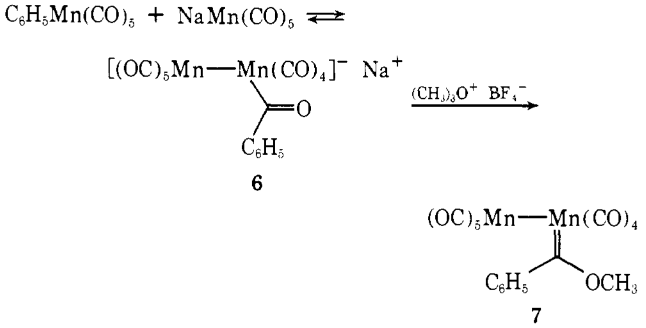
Methyl Transfer. Mixing $NaFe(CO)_2(C_5H_5)$ with $(CO)_5MnCH_3$ resulted in a rapid, exothermic reaction. The NMR spectrum of the mixture indicated that $(CO)_5MnCH_3$ had completely disappeared and that $(C_5H_5)Fe(CO)_2CH_3$ had formed. Analogously, $(C_5H_5)Fe(CO)_2CH_3$ was rapidly formed when $NaFe(CO)_2(C_5H_5)$ was mixed with the other methyl metal carbonyl compounds. This is consistent with the highly nucleophilic character of $NaFe(CO)_2(C_5H_5)$.

Reactions of the other metal carbonyl anions with methyl metal carbonyl compounds were generally more ambiguous. However, from the observations that (1) a small amount of $(CO)_5ReCH_3$ was found in the reaction of $NaRe(CO)_5$ with $(C_5H_5)Mo(CO)_3CH_3$, (2) $(C_5H_5)W(CO)_3CH_3$ was formed in the reaction of $Na(C_5H_5)W(CO)_3$ with $(C_5H_5)Mo(CO)_3CH_3$, and (3) $(C_5H_5)Mo(CO)_3CH_3$ and $(CO)_5MnCH_3$ were both found in the reaction of $Na(C_5H_5)Mo(CO)_3$ with $(CO)_5MnCH_3$ or of $NaMn(CO)_5$ with $(C_5H_5)Mo(CO)_3CH_3$ an approximate order of reactivity, $Na(C_5H_5)Fe(CO)_2 \gg NaRe(CO)_5 \geq Na(C_5H_5)W(CO)_3 > Na(C_5H_5)Mo(CO)_3 \sim NaMn(CO)_5$, can be determined. A similar order of nucleophilicity was obtained by Dessy, Pohl, and King from the relative rates of reactions of metal carbonyl anions with alkyl halides.[6]

No Apparent Reaction. A large number of the metal carbonyl anion-methyl organometallic compound combinations examined exhibited no apparent reaction. For example, $(C_5H_5)Fe(CO)_2CH_3$ did not appear to react with any metal carbonyl anions.

Reactions of Metal Carbonyl Anions with Phenylpentacarbonylmanganese(I). The reactions of several metal carbonyl anions with $(CO)_5MnC_6H_5$ were investigated. NMR results from the reaction of $NaMn(CO)_5$ with $(CO)_5MnC_6H_5$ in THF had indicated the appearance of a new singlet at δ 7.22 which is attributed to the dinuclear benzoylmanganese anion **6**.

This was confirmed by synthesis of the dimanganese phenylmethoxycarbene complex, **7**, from **6**. The reaction of $(CO)_5MnC_6H_5$ with $NaRe(CO)_5$ also resulted in the appearance of a new NMR singlet.



Attempts to Trap the Adducts as Carbene Complexes. Preparative scale reactions were performed in all cases in which dinuclear acyl anions were observed in exploratory NMR reactions and in several cases in which no dinuclear acyl anions had been detected. Typically the methyl metal carbonyl derivative and the metal carbonyl anion (ca. 1 mmol each) were mixed and stirred at room temperature under nitrogen for an appropriate length of time based on the exploratory NMR reaction. After removal of the solvent and methylation of the residue with trimethyloxonium tetrafluoroborate in water or methyl fluorosulfonate,[9] the crude reaction mixture was examined by NMR and TLC for the presence of a metal-carbene complex.

The addition of trimethyloxonium tetrafluoborate to a THF solution of $NaMn(CO)_5$ and $(CO)_5MnCH_3$, which NMR indicated contained an acyl manganese complex, gave a 1:19 mixture of *trans*- and *cis*-(methylmethoxycarbene)nonacarbonyldimanganese (**5**) in 24% yield in addition to a 48% recovery of $(CO)_5MnCH_3$ and a small amount of $Mn_2(CO)_{10}$. When the solution of $NaMn(CO)_5$ and $(CO)_5MnCH_3$ was concentrated and treated with methyl fluorosulfonate, a 65% yield of **5** was obtained. Treatment of the mixture of $NaMn(CO)_5$ and $(CO)_5MnCH_3$ with either methyl iodide or dimethyl sulfate gave only $(CO)_5MnCH_3$. Carbene complex **5** was identical in physical and spectral properties with a sample of **5** prepared from CH_3Li and $Mn_2(CO)_{10}$ according to Fischer's procedure.[7]

The reaction of $NaRe(CO)_5$ with $(CO)_5MnCH_3$ gave, after alkylation with methyl fluorosulfonate, a yellow crystalline solid, **8**, in 29% yield. Elemental analysis demonstrated that the complex contained Re and Mn in a 1:1 ratio. The NMR spectrum (CS_2) of **8** consisted of sharp singlets of equal intensity at δ 2.76 and 4.20 as expected for a methylmethoxycarbene complex. The methoxy resonance of **8** at δ 4.20 is consistent with a cis arrangement of the carbene ligand with respect to the metal-metal bond; the methoxy resonance of *cis*-$Mn_2(CO)_9C(OCH_3)CH_3$ occurs at δ 4.22 while that of *trans*-$Mn_2(CO)_9C(OCH_3)CH_3$ occurs at δ 4.62. The infrared spectrum (heptane) of **8** had eight bands in the metal carbonyl region and confirmed the cis relationship of the carbene ligand and the metal-metal bond. The question of whether the carbene ligand is attached to manganese or to rhenium could not be decided from spectral data. On the basis of (1) the method of synthesis from $(CO)_5MnCH_3$ and $NaRe(CO)_5$ and (2) the failure of $(CO)_5ReCH_3$ and $NaMn(CO)_5$ to react, we assigned the manganese atom as the site of attachment of the carbene.[4] On the basis of an X-ray crystal structure of **8**, we now report that our initial assignment was incorrect and the carbene unit is attached to the rhenium atom. The structure of **8** is shown in Figure 1. The rationalization of the rearrangements involved in the synthesis of **8** will be dealt with in the discussion section.

The reaction of $(CO)_5MnC_6H_5$ with $NaRe(CO)_5$ followed by alkylation with CH_3OSO_2F gave a 24% yield of an analogous phenylmethoxycarbene complex which we now believe is *cis*-$(CO)_5MnReC(OCH_3)(C_6H_5)$ by analogy with **8**.

The reaction of $NaMn(CO)_5$ with $C_5H_5Mo(CO)_3CH_3$ gave a low yield (ca. 26% based on consumed $(C_5H_5)Mo(CO)_3CH_3$) of the dimanganese methylmethoxycarbene complex **5** as a result of methyl transfer from $(C_5H_5)Mo(CO)_3CH_3$ to $NaMn(CO)_5$ to give $(CO)_5MnCH_3$ followed by reaction with additional $NaMn(CO)_5$. Attempts to trap other adducts from reactions of $(CO)_5MnCH_3$ with other metal carbonyl anions as carbene complexes gave only mixtures of the two possible methyl metal carbonyl compounds after methylation. Similar reactions with $(CO)_5MnC_6H_5$ gave only the methyl derivative of the metal carbonyl anion employed, as well as recovered $C_6H_5Mn(CO)_5$.

Discussion

Reaction of $(CO)_5MnCH_3$ with $NaMn(CO)_5$. $(CO)_5MnCH_3$ reacts with $NaMn(CO)_5$ within 4 min at 40° to produce a dinuclear acetylmanganese anion, **4**. The reaction is a rapid equilibrium process. The equilibrium is shifted away from **4** either by dilution or by increased temperature. At 40° in THF, the equilibrium constant for formation of **4** is approximately 9. This reaction is closely analogous to the reaction of $(CO)_5MnCH_3$ with nucleophiles such as phosphine to give substituted acetyltetracarbonylmanganese complexes.[10] These reactions have been demonstrated to proceed by rate determining methyl migration to coordinated CO to produce a coordinately unsaturated $(CO)_4MnCOCH_3$ species which is subsequently trapped by nucleophiles.

The dinuclear acetylmanganese anion can be trapped by O-alkylation to give a metal carbene complex only if very reactive alkylating agents such as $(CH_3)_3O^+\ BF_4^-$ or CH_3OSO_2F are used. The less reactive CH_3I and $CH_3OSO_3CH_3$ react only with the $^-Mn(CO)_5$ in equilibrium with **4** to give $CH_3Mn(CO)_5$.

Mechanism of Formation of *cis*-$(CO)_5MnRe(CO)_4C(OCH_3)CH_3$ (8). The reaction of $NaRe(CO)_5$ with $(CO)_5MnCH_3$ followed by alkylation with CH_3OSO_2F unexpectedly led to the dinuclear carbene complex **8**, in which the carbene was attached to rhenium rather than manganese. The mechanism proposed to explain the formation of the dimanganese acyl anion **4** from $NaMn(CO)_5$ and $(CO)_5MnCH_3$ predicts that the reaction of $NaRe(CO)_5$ with $(CO)_5MnCH_3$ will proceed through a coordinately unsaturated $(CO)_4MnCOCH_3$ intermediate and will lead to a dinuclear complex in which the acyl group is coordinated to manganese. Alkylation of this acyl species would produce a dinuclear carbon complex with the carbene ligand bonded to manganese. A priori, there are three explanations for the observation that the carbene ligand is attached to rhenium in **8**: (1) a methyl exchange reaction between $NaRe(CO)_5$ and $(CO)_5MnCH_3$ precedes the formation of a dinuclear acyl anions; (2) the initially formed acyl manganese intermediate isomerizes to a dinuclear species in which the acyl group is attached to rhenium; (3) an initially formed dinuclear carbene complex in which the carbene complex is attached to manganese isomerizes to **8**.

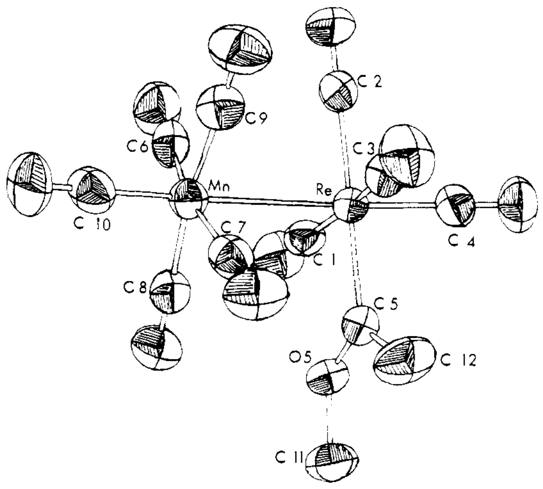
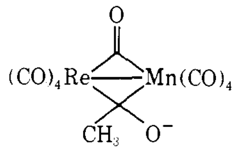


Figure 1. ORTEP diagram of the molecular structure of *cis*-$(CO)_5MnRe(CO)_4C(OCH_3)CH_3$ (**8**).

Explanation (1) can be ruled out on the basis that $NaMn(CO)_5$ does not react with $(CO)_5ReCH_3$ to produce an acyl species which can be observed by NMR or trapped with CH_3OSO_2F.

The possibility of rearrangement of an initial acyl manganese compound to an acyl rhenium compound must be seriously considered. Initially two acyl species were observed at δ 2.44 and 2.51 in the NMR spectrum of a mixture of $(CO)_5MnCH_3$ and $NaRe(CO)_5$; within 1 hr, the signal at δ 2.44 had disappeared and the signal at δ 2.51 had increased. There are four possible dinuclear acyl anions (acyl attached to Mn or Re; acyl cis or trans to the metal-metal bond) which could give rise to these signals and our present data do not allow the rigorous exclusion of any of these species. However, rearranged dinuclear acyl anions with the acyl group attached to rhenium appear unlikely on two grounds. First, intermediate **9** leading to migration of the acyl unit from manganese to rhenium would involve localization of charge on the oxygen atom of the bridging acyl group. Second, *cis*-$(CO)_5MnRe(CO)_4COCH_3^-$ would be expected to be in equilibrium with $(CO)_5ReCH_3$ and $Mn(CO)_5^-$ and no reaction was observed between these two species.



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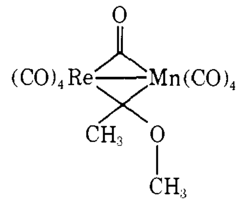

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The possibility that initially $(CO)_5ReMn(CO)_4C(OCH_3)CH_3$ is generated and then rearranges to **8** appears reasonable. Intermediate **10** which would lead to this rearrangement has a bridging carbene ligand. No charge localization is required for the formation of **10**. Bridging carbene ligands have been observed previously.[11]

Nongenerality of Adduct Formation. The fact that dinuclear acyl anions could only be generated from $(CO)_5MnR$ compounds requires explanation. At the outset, it should be pointed out that even in the most favorable case of the reaction of $(CO)_5MnCH_3$ and $NaMn(CO)_5$ to give **4** the equilibrium constant was only about 9. The nongenerality of adduct formation can be explained in terms of the ease with which alkyl metal carbonyl compounds form ligand substituted acyl metal compounds and the nucleophilicity of metal carbonyl anions which leads to a competing methyl transfer side reaction.

The mechanism of formation of dinuclear acyl anions probably requires a prior rearrangement of the alkyl metal carbonyl to a coordinately unsaturated acyl metal compound which is then attacked by the metal carbonyl anion.[10] $(CO)_5MnR$ compounds are the most reactive compounds toward substitution to give $L(CO)_4MnCOCH_3$ that we have studied, and it is therefore not surprising that these are the compounds which yield adducts. The ease of formation of ligand substituted acyl compounds has been found to be $(CO)_5MnCH_3 > (C_5H_5)Mo(CO)_3CH_3 \sim (CO)_5ReCH_3 > (C_5H_5)Fe(CO)_2CH_3 > (C_5H_5)W(CO)_3CH_3$.

Adduct formation was not observed even for $(CO)_5MnR$ compounds when the very nucleophilic $(C_5H_5)Fe(CO)_2^-$ ion was employed. Instead, $(C_5H_5)Fe(CO)_2^-$ attacks the methyl group of $(CO)_5MnCH_3$ to give $(C_5H_5)Fe(CO)_2CH_3$.

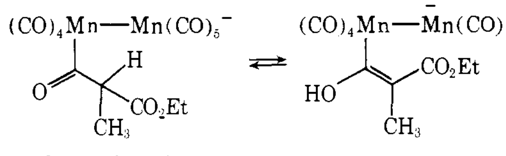
Methyl Transfer Reactions. The methyl transfer reactions reported here are envisioned to arise as a result of an SN2 displacement of a less nucleophilic metal carbonyl anion by a more nucleophilic carbonyl anion.

$$M^- + CH_3M' \rightleftharpoons M{-}CH_3 + M'^-$$

These equilibria should be very similar to the corresponding protonation reactions of the related metal hydrides, and consequently the position of methyl transfer equilibria should reflect the relative basicity and nucleophilicity of the metal carbonyl anions. The relative basicities of the anions employed in this study have previously been measured electrochemically[6] and found to be: $C_5H_5Fe(CO)_2^-$, 1,000,000; $Re(CO)_5^-$, 370; $C_5H_5W(CO)_3^-$, 67; $Mn(CO)_5^-$, 1.1; $C_5H_5Mo(CO)_3^-$, 1. $C_5H_5Fe(CO)_2^-$ is the most basic species and abstracts methyl from all the systems studied. $(C_5H_5)W(CO)_3^-$ abstracts methyl from the less basic $(C_5H_5)Mo(CO)_3CH_3$. $C_5H_5Mo(CO)_3^-$ and $Mn(CO)_5^-$ are bases of comparable strength, and the reaction of either $(CO)_5MnCH_3$ with $C_5H_5Mo(CO)_3^-$ or $(C_5H_5)Mo(CO)_3CH_3$ with $Mn(CO)_5^-$ gave mixtures of $(C_5H_5)Mo(CO)_3CH_3$ and $(CO)_5MnCH_3$.

While reactions of metal carbonyl anions as entering groups in nucleophilic displacement are very common, reactions in which a metal carbonyl anion acts as a leaving group are rare. The reported reaction[12a] of $(C_5H_5)Fe(CO)_2^-$ with $(C_5H_5)Mo(CO)_3CH_2CH_2CH_2Br$ to give $[(C_5H_5)Fe(CO)_2]CH_2CH_2CH_2[(C_5H_5)Fe(CO)_2]$ can be explained by the displacement of a molybdenum anion by the extremely nucleophilic $(C_5H_5)Fe(CO)_2^-$. The racemization of $(CO)_5MnCH(CO_2CH_2CH_3)CH_3$ (**11**) in the presence of $Mn(CO)_5^-$ was explained by Pearson as an SN2 displacement of $Mn(CO)_5^-$ by $Mn(CO)_5^-$.[12b] In view of the facile attack of $Mn(CO)_5^-$ at manganese, the alternate mechanism depicted below should also be considered.

$\mathbf{11} + Mn(CO)_5^- \rightleftharpoons$



Displacement of metal carbonyl anions from tin have previously been observed by Nesmeyanov[13] and by Burlitch.[14]

$$Ph_3SnMn(CO)_5 + C_5H_5Fe(CO)_2^- \longrightarrow Ph_3SnFe(CO)_2C_5H_5 + Mn(CO)_5^-$$

Displacement of cobalt from an alkylcobalt(IV) species has been reported by Johnson.[15]

The results reported here explain why 1,3-dibromopropane reacts with $Mn(CO)_5^-$ to give a cyclic carbene complex, **1**, while reaction with $C_5H_5Fe(CO)_2^-$ leads to a 1,3-diiron compound.[2,16] In the case of the manganese reaction, the intermediate alkyl manganese compound **3** is very subject to attack at manganese to give a dinuclear acyl anion which leads to the cyclic carbene complex.[17] The possible competing reaction involving attack of the relatively weak nucleophile $Mn(CO)_5^-$ on the alkyl halide is not observed. In contrast, the intermediate alkyl iron compound **12** cannot easily form a dinuclear acyl anion. The highly nucleophilic $C_5H_5Fe(CO)_2^-$ anion can readily displace bromide from **12** to give the observed 1,3-diiron compound.

$$\underset{\mathbf{12}}{[(C_5H_5)Fe(CO)_2]CH_2CH_2CH_2Br} \xrightarrow{C_5H_5Fe(CO)_2^-} [(C_5H_5)Fe(CO)_2]CH_2CH_2CH_2[(C_5H_5)Fe(CO)_2]$$

Experimental Section

NMR spectra were determined using Varian A-60A, T-60, and XL-100 spectrometers. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer. Mass spectra were determined using an AEI-902 mass spectrometer.

Preparation of Metal Carbonyl Anions. $NaMn(CO)_5$, $NaRe(CO)_5$, and $Na(C_5H_5)Fe(CO)_2$ were prepared by reduction of the corresponding dimer with dilute sodium amalgam in THF using procedures similar to those described by King.[18] $Na(C_5H_5)Mo(CO)_3$ in THF and $Na(C_5H_5)W(CO)_3$ in dimethoxyethane were prepared from NaC_5H_5 and $Mo(CO)_6$ or $W(CO)_6$ by procedures similar to those described by King.[18]

Preparation of Alkyl and Aryl Organometallics. $(CO)_5MnCH_3$, mp 94–95° (lit.[19] 95°), and $(CO)_5ReCH_3$, mp 117–118° (lit.[20] 120°), were prepared by the method of Hieber.[19] $(C_5H_5)Fe(CO)_2CH_3$, mp 76–78° (lit.[18] 78–82°), $(C_5H_5)Mo(CO)_3CH_3$, mp 120–121° dec (lit.[18] 124° dec), and $(C_5H_5)W(CO)_3CH_3$, mp 141–143° (lit.[21] 144–145°), were prepared according to the procedure of King.[18] $(CO)_5MnC_6H_5$, mp 51–52° (lit.[22] 52°), was prepared by decarbonylation of $(CO)_5MnCOC_6H_5$. The NMR, ir, and mass spectra of the above compounds confirmed their identity.

NMR Experiments—General Procedure. The metal carbonyl derivative (freshly sublimed or recrystallized; 1 equiv) and metal carbonyl anion (1 equiv) in tetrahydrofuran were placed in a nitrogen-flushed NMR tube. The mixture was degassed by three freeze–thaw cycles. The NMR tube was sealed under vacuum (ca. 0.05 mm). An NMR spectrum was recorded immediately after the mixture had warmed to room temperature. The tubes were maintained at room temperature or at various temperatures up to 100° in the dark, and the reaction mixtures were monitored by NMR.

$(CO)_5MnCH_3$ and $NaMn(CO)_5$. A THF solution of $NaMn(CO)_5$ (0.38 ml, 0.71 *M*, 0.27 mmol) was injected into an NMR tube at probe temperature (~40°) containing a THF solution of $(CO)_5MnCH_3$ (0.50 ml, 0.54 *M*, 0.27 mmol). The tube was shaken and the NMR spectrum recorded 30 sec after mixing. In addition to solvent resonances, the spectrum contained two singlets at δ 2.51 due to *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$ and at δ 0.10 due to $(CO)_5MnCH_3$ in a ratio of 0.3:1. After approximately 4 min the ratio of peaks had reached an equilibrium value of 1.4:1.

In a THF solution initially 0.54 *M* in $(CO)_5MnCH_3$ and 0.54 *M* in $NaMn(CO)_5$, the ratio of the NMR signals at δ 2.51 due to *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$ and at δ −0.10 due to $(CO)_5MnCH_3$ was 1.45:1 at 40°. Upon warming to 71°, the ratio of signals changed to 1.03:1; cooling to 40° reestablished the initial ratio.

The ratio of peaks at δ 2.51 and −0.10 was also affected by dilution. At 40°, a solution initially 0.62 *M* in $(CO)_5MnCH_3$ and 0.62 *M* in $NaMn(CO)_5$ gave signals due to *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$ and $(CO)_5MnCH_3$ in a ratio of 1.84:1. Dilution to 0.21 *M* gave a new ratio of 1.08:1.

The infrared spectrum of a THF solution initially 0.60 *M* in $(CO)_5MnCH_3$ and 0.50 *M* in $NaMn(CO)_5$ was offscale in the metal carbonyl region but exhibited an intense band at 1560 cm^{-1} assigned to the acetyl group of *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$. Dilution to 0.005 *M* resolved the metal carbonyl region but shifted the equilibrium so that only bands for $(CO)_5MnCH_3$ and $NaMn(CO)_5$ were observed.

$(CO)_5MnCH_3$ and $NaRe(CO)_5$. A THF solution initially 0.15 *M* in $(CO)_5MnCH_3$ and 0.15 *M* in $NaRe(CO)_5$ was monitored by NMR. The initial NMR spectrum of the reaction mixture was taken 10 min after mixing the reagents and showed, in addition to the $(CO)_5MnCH_3$ resonance at δ −0.10, two new singlets of approximately equal intensity at δ 2.44 and 2.51 due to acetyl organometallics. The signal at δ 2.51 disappeared within an hour as the signal at δ 2.44 increased. After 10 hr, the $(CO)_5MnCH_3$ resonance had gradually decreased to one-fifth the intensity of the δ 2.44 resonance.

$(CO)_5ReCH_3$ and $NaMn(CO)_5$. A THF solution initially 0.32 *M* in $(CO)_5ReCH_3$ and 0.37 *M* in $NaMn(CO)_5$ did not exhibit any resonances due to acetyl organometallics either upon sitting at room temperature or after heating to 60° for 30 hr. Only the resonance of $(CO)_5ReCH_3$ was observed.

$(CO)_5ReCH_3$ and $NaRe(CO)_5$. The NMR spectrum of a THF solution 0.15 *M* in $(CO)_5ReCH_3$ and 0.15 *M* in $NaRe(CO)_5$ exhibited no acetyl resonances.

$(C_5H_5)Mo(CO)_3CH_3$ and $NaMn(CO)_5$. A THF solution initially 0.62 *M* in $(C_5H_5)Mo(CO)_3CH_3$ and 0.62 *M* in $NaMn(CO)_5$ was monitored by NMR. After 45 hr at ambient temperature, the intensity of the signals at δ 5.43 due to $(C_5H_5)Mo(CO)_3CH_3$ and at δ 5.03 due to $(C_5H_5)Mo(CO)_3^-$ were about equal and the intensity of the signal at δ 0.38 due to $(C_5H_5)Mo(CO)_3CH_3$ was about twice as large as the signals at δ −0.10 due to $(CO)_5MnCH_3$ and at δ 2.53 due to *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$. After 21 days, no further changes in the spectrum were observed. The mixture contained $(C_5H_5)Mo(CO)_3CH_3$, $C_5H_5Mo(CO)_3^-$, $(CO)_5MnCH_3$, and *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$ in a ratio of 1:7:6:1.5.

Similarly, the THF solution initially 0.42 *M* in $(CO)_5MnCH_3$ and 0.42 *M* in $(C_5H_5)Mo(CO)_3^-$ upon standing at ambient temperature for 21 days was found by NMR to contain $(C_5H_5)Mo(CO)_3CH_3$, $(C_5H_5)Mo(CO)_3^-$, $(CO)_5MnCH_3$, and *cis*-$(CO)_5MnMn(CO)_4COCH_3^-$ in a ratio of 1:5:3.5:0.5.

$(CO)_5MnCH_3$ and $C_5H_5Fe(CO)_2^-$. A THF solution containing 0.35 *M* $(CO)_5MnCH_3$ and 0.35 *M* $(C_5H_5)Fe(CO)_2^-$ was prepared at low temperature and its reaction upon warming in an NMR probe at 40° was followed. The peak at δ −0.10 due to $(CO)_5MnCH_3$ disappeared within several minutes and a new peak appeared at δ 0.16 due to $(C_5H_5)Fe(CO)_2CH_3$. No new resonances in the δ 1.8–3.1 range due to acyl species were observed.

In similar experiments, $(C_5H_5)Fe(CO)_2^-$ reacted with $(C_5H_5)Mo(CO)_3CH_3$ and with $(C_5H_5)W(CO)_3CH_3$ within an hour to give $(C_5H_5)Fe(CO)_2CH_3$ in both cases. $(C_5H_5)W(CO)_3^-$ reacted with $(C_5H_5)Mo(CO)_3CH_3$ within 22 hr at 75° to give $(C_5H_5)W(CO)_3CH_3$ and $(C_5H_5)Mo(CO)_3^-$.

***cis*-$(CO)_5MnMn(CO)_4C(OCH_3)CH_3$ (5). Method A.** A THF solution of $NaMn(CO)_5$ (0.90 ml, 1.3 *M*, 1.17 mmol) was added by syringe to $(CO)_5MnCH_3$ (210 mg, 1 mmol) in 1 ml of THF at ambient temperature and the reaction mixture was stirred for 5 min. THF was removed on a rotary evaporator and the residue was stirred with methyl fluorosulfonate (1.1 ml, 13.6 mmol) for 5 min. Water was added and the mixture was extracted three times with pentane. The pentane solution was dried (Na_2SO_4), concentrated, and column chromatographed (silica gel–pentane) to give **5** (180 mg, 43%): mp 79–80° (reported[7] 81°); NMR (CS_2) 2.92 δ (s, 3 H), 4.24 (s, 3 H); ir (pentane) 2095(w), 2027(s), 2012(m), 2001(s), 1992(s), 1976(w), 1954(2), and 1949(w). The material was identical with an authentic sample prepared by a modification of the method of Fischer[7] as detailed below.

Method B. Methyllithium in ether (28.6 ml, 1.35 *M*, 38.5 mmol) was added to $Mn_2(CO)_{10}$ (15.0 g, 38.5 mmol) in 600 ml of ether at 0° and the solution was stirred for 1.5 hr at 0°. Solvent was removed under vacuum and the residue was treated with methyl fluorosulfonate (8 ml, 650 mmol) at 0° for 5 min. Workup as above gave *cis*-$(CO)_5MnMn(CO)_4C(OCH_3)CH_3$ (10.4 g, 65%), mp 79–81° (reported[7] 81°).

Reaction of $(CO)_5MnCH_3$ and $NaMn(CO)_5$ with Dimethyl Sulfate. The NMR spectrum of a solution containing $NaMn(CO)_5$ (0.27 mmol), $(CO)_5MnCH_3$ (0.27 mmol), and *p*-di-*tert*-butylbenzene (8.9 mg) in 0.5 ml of THF exhibited an acyl methyl peak ratio of 1.45:1.00. Addition of dimethyl sulfate (0.54 mmol) caused the acyl peak at δ 2.51 to disappear and the methyl peak at δ −0.10 to intensify. The yield of $(CO)_5MnCH_3$, determined by integration using *p*-di-*tert*-butylbenzene as an internal standard, was 105%. The spectrum was scanned 15 sec after addition of dimethyl sulfate and some of the acyl anion was still present. After 30 sec, none remained.

***cis*-$(CO)_5MnRe(CO)_4C(OCH_3)CH_3$ (8).** $(CO)_5MnCH_3$ (0.24 g, 1.15 mmol) and freshly prepared $NaRe(CO)_5$ (1.0 mmol) in 20 ml of tetrahydrofuran were stirred for 12 hr at 25°. Solvent was removed under aspirator vacuum and methyl fluorosulfonate (0.142 g, 1.25 mmol) was added to the resulting red-orange oil. Oxygen-free water was added and the mixture was extracted with three 100-ml portions of pentane. The pentane solution was dried (Na_2SO_4), concentrated under vacuum, and thin layer chromatographed (silica gel, pentane) to give **8.** Further purification by recrystallization from pentane gave 0.16 g (29%): mp 107–108°; $\nu_{max}{}^{heptane}$ 2093(w), 2038(m), 2017(w), 2002(s), 1994(s), 1979(s), 1960(m), and 1950(m) cm^{-1}; $\delta_{TMS}{}^{CS_2}$ 2.76 (s, 3 H, $C(OCH_3)C\mathit{H}_3$) and 4.20 (s, 3 H, $C(OC\mathit{H}_3)CH_3$). Anal. Calcd for $C_{12}H_6O_{10}MnRe$: C, 26.14; H, 1.10; Mn, 9.97. Found: C, 26.34; H, 1.07; Mn, 10.03.

***cis*-$(CO)_5MnRe(CO)_4C(OCH_3)C_6H_5$.** $(CO)_5MnC_6H_5$ (0.44 g, 1.61 mmol) and freshly prepared $NaRe(CO)_5$ (1.46 mmol) in 15 ml of tetrahydrofuran were stirred at 25° for 20 hr. Removal of solvent under aspirator vacuum and addition of methyl fluorosulfonate (1.83 g, 1.61 mmol), followed by similar isolation procedures as above, gave *cis*-$(CO)_5MnRe(CO)_4C(OCH_3)C_6H_5$ (0.216 g, 24%): mp 93–94°; $\nu_{max}{}^{heptane}$ 2093(w), 2040(m), 2000(s), 1993(s), 1964(w), and 1951(m) cm^{-1}; $\delta_{TMS}{}^{acetone\text{-}d_6}$ 4.24 (s, 3 H, $C(OC\mathit{H}_3)C_6H_5$) and 7.1–7.7 (m, 5 H, $C(OCH_3)C_6\mathit{H}_5$). Anal. Calcd for $C_{17}H_8O_{10}MnRe$: C, 33.29; H, 1.31; Mn, 8.96. Found: C, 33.07; H, 1.39; Mn, 8.69.

Preparative Reactions. Following a general procedure analogous to the procedure for the preparation of **8**, A number of preparative reactions of methyl metal carbonyl derivatives with metal carbonyl anions were examined. The reaction mixtures were alkylated with trimethyloxonium tetrafluoroborate and/or methyl fluorosulfonate and then examined by NMR and TLC for the presence of carbene complexes. No carbene complexes were observed in these reactions (see Results).

Crystallographic and X-Ray Data. Crystals of *cis*-$(CO)_5MnRe(CO)_4C(OCH_3)CH_3$ (mp 107–108°) were obtained by slow crystallization from pentane. A crystal centrosymmetrically bonded by the 100, 110, 110, 101, and 001 faces (dimensions 0.2 × 0.1 × 0.1 mm) was mounted in a Lindemann glass capillary under argon and placed on a Syntex P1 autodiffractomer equipped with a graphite-monochromated Mo Kα radiation source. The preliminary Syntex routines[23] indicated a triclinic cell with the following dimensions: a = 8.999 (5), b = 13.093 (2), c = 8.202 (2) Å; α = 111.24 (2), β = 112.22 (3), γ = 84.41 (3)°; V = 833.0 (5) Å^3. The triclinic Laue symmetry and the associated lattice constants are verified in the Syntex procedure by partial rotation photographic projections along each of the three unit cell axes. The calculated density for Z = 2 of 2.20 g/cm^3 agrees within experimental error with the observed value of 2.17 g/cm^3 (determined by flotation in aqueous silver nitrate solutions).

Data were collected at $2° \leq 2\theta \leq 45°$ in the variable scan speed mode. Two standard peaks monitored every 50 reflections indicated a 10% decrease in intensity. The data were reduced[24] in the usual fashion and corrected for linear decay to yield 1932 independent reflections for which $I > 2\sigma(I)$. Later the data were corrected for effects of crystal absorption; the calculated transmission factors varied from 0.836 to 0.906 (linear absorption coefficient μ = 85.67 cm^{-1}). The centrosymmetric choice of space groups was later confirmed by the successful refinement of the structure.

The structure was determined by classical heavy atom methods. From the coordinates of the rhenium atom and the manganese atom determined from a Patterson synthesis,[25] an electron density map was calculated (R_1 = 19.9%),[26] which allowed the approximate location of all nonhydrogen atoms.

Isotropic least-squares[27] refinement converged at R_1 = 7.38. At this stage a difference Fourier map revealed the positions of the hydrogen atoms. Further least-squares refinement on all coordinates, anisotropic temperature factors for all nonhydrogen atoms, and isotropic temperature factors for hydrogen atoms resulted in final R_1 = 2.47% and R_2 = 3.10%. Comparison of the observed and calculated structure factor amplitudes is made in Table II.[28] The final positional and thermal parameters with errors estimated

Table III. Positional Parameters (×10^4) for All Atoms and Isotropic Temperature Factors for Hydrogen Atoms (×10^4)[a]

Atom	x	y	z	B, Å^2
Re	2645.4 (3)	3328.1 (2)	330.1 (4)	
C(1)	1485 (2)	4264 (6)	1963 (10)	
C(2)	4770 (9)	3794 (6)	2467 (10)	
C(3)	3743 (10)	2295 (7)	−1229 (11)	
C(4)	2861 (9)	4476 (6)	−511 (10)	
C(5)	401 (9)	2832 (6)	−1865 (10)	
O(1)	838 (7)	4792 (5)	2894 (8)	
O(2)	5948 (7)	4053 (5)	3677 (8)	
O(3)	4404 (9)	1700 (6)	−2111 (10)	
O(4)	3017 (8)	5173 (5)	−977 (9)	
Mn	2440.0 (13)	1566.9 (8)	1740.4 (15)	
C(6)	3152 (10)	2683 (6)	4047 (11)	
C(7)	1718 (10)	726 (6)	−808 (12)	
C(8)	341 (10)	1962 (7)	1475 (11)	
C(9)	4524 (10)	1350 (6)	1908 (11)	
C(10)	2417 (10)	498 (7)	2626 (13)	
O(6)	3599 (8)	3343 (5)	5500 (7)	
O(7)	1263 (8)	171 (5)	−2363 (9)	
O(8)	−931 (7)	2179 (5)	1345 (9)	
O(9)	5829 (8)	1208 (6)	2015 (10)	
O(10)	2419 (9)	−183 (5)	3211 (11)	
O(5)	−886 (6)	3114 (4)	−1472 (6)	
C(11)	−2519 (11)	2854 (8)	−2841 (14)	
C(12)	94 (14)	2215 (11)	−3902 (13)	
H(1)	−3155 (88)	3239 (56)	−1957 (96)	4.6 (1.8)
H(2)	−2715 (106)	3253 (71)	−3488 (120)	6.7 (3.5)
H(3)	−2710 (96)	2066 (71)	−3679 (108)	5.9 (2.0)
H(4)	−727 (164)	1427 (113)	−4585 (182)	12.7 (4.1)
H(5)	−462 (116)	2672 (72)	−4519 (128)	7.3 (2.8)
H(6)	1029 (160)	2013 (103)	−4054 (169)	11.7 (4.2)

Anisotropic Temperature Factors for Nonhydrogen Atoms (×10)[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Re	114	62	159	−7	36	39
C(1)	130	63	214	−17	2	48
C(2)	146	77	222	−21	34	62
C(3)	183	101	226	−3	67	68
C(4)	158	87	220	−7	76	52
C(5)	140	74	202	2	52	58
O(1)	200	98	263	23	97	37
O(2)	158	137	259	−47	−23	83
O(3)	301	137	429	49	255	74
O(4)	266	114	382	9	146	126
Mn	142	56	217	1	58	45
C(6)	191	73	247	11	102	67
C(7)	158	75	334	12	97	65
C(8)	174	90	233	−12	55	64
C(9)	182	76	269	12	71	44
C(10)	173	79	368	2	89	72
O(6)	264	101	218	−22	74	37
O(7)	258	110	263	−5	58	−13
O(8)	160	139	399	16	101	112
O(9)	177	134	492	39	115	88
O(10)	351	103	551	9	157	164
O(5)	124	88	189	−1	16	53
C(11)	144	92	318	−3	1	75
C(12)	235	155	171	8	30	20

[a] Standard deviations in least significant digits in parentheses.

from the full variance-covariance matrix, are given in Table III. Bond lengths and angles are shown in Tables IV and V.

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Table IV. Bond Lengths (Å)[a]

Re–Mn	2.972 (1)	Mn–C(8)	1.857 (8)
Re–C(5)	2.094 (7)	Mn–C(9)	1.826 (8)
C(5)–C(12)	1.493 (11)	Mn–C(10)	1.796 (7)
C(5)–O(5)	1.299 (8)	C(6)–O(6)	1.132 (8)
C(11)–O(5)	1.449 (10)	C(7)–O(7)	1.144 (9)
Re–C(1)	1.997 (8)	C(8)–O(8)	1.125 (8)
Re–C(2)	2.000 (7)	C(9)–O(9)	1.444 (8)
Re–C(3)	1.966 (8)	C(10)–O(10)	1.153 (7)
Re–C(4)	1.915 (7)	C(11)–H(1)	1.05 (6)
C(1)–O(1)	1.127 (8)	C(11)–H(2)	0.83 (8)
C(2)–O(2)	1.118 (8)	C(11)–H(3)	1.00 (8)
C(3)–O(3)	1.143 (9)	C(12)–H(4)	1.16 (14)
C(4)–O(4)	1.144 (8)	C(12)–H(5)	0.91 (9)
Mn–C(6)	1.836 (8)	C(12)–H(6)	0.90 (12)
Mn–C(7)	1.853 (9)		

[a] Standard deviations in least significant digits in parentheses.

Table V. Bond Angles (deg)[a]

C(1)–Re–C(2)	91.2 (3)	C(6)–Mn–C(7)	165.5 (3)
C(1)–Re–C(3)	174.9 (2)	C(6)–Mn–C(8)	89.0 (4)
C(1)–Re–C(4)	93.1 (3)	C(6)–Mn–C(9)	89.3 (4)
C(1)–Re–C(5)	87.9 (3)	C(6)–Mn–C(10)	96.2 (4)
C(1)–Re–Mn	87.3 (2)	C(7)–Mn–C(8)	89.3 (3)
C(2)–Re–C(3)	89.4 (3)	C(7)–Mn–C(9)	90.3 (4)
C(2)–Re–C(4)	91.0 (3)	C(7)–Mn–C(10)	98.3 (4)
C(2)–Re–C(5)	178.6 (2)	C(8)–Mn–C(9)	171.7 (3)
C(2)–Re–Mn	86.9 (2)	C(8)–Mn–C(10)	95.4 (3)
C(3)–Re–C(4)	92.0 (3)	C(9)–Mn–C(10)	92.9 (3)
C(3)–Re–C(5)	91.4 (3)	Mn–C(6)–O(6)	177.5 (6)
C(3)–Re–Mn	87.7 (2)	Mn–C(7)–O(7)	177.2 (7)
C(4)–Re–C(5)	90.1 (3)	Mn–C(8)–O(8)	177.8 (6)
C(4)–Re–Mn	177.8 (2)	Mn–C(9)–O(9)	179.5 (7)
C(5)–Re–Mn	92.0 (2)	Mn–C(10)–O(10)	179.2 (9)
Re–C(1)–O(1)	179.5 (6)	C(5)–O(5)–C(11)	124.8 (7)
Re–C(2)–O(2)	179.1 (6)	O(5)–C(11)–H(1)	99.7 (41)
Re–C(3)–O(3)	178.9 (8)	O(5)–C(11)–H(2)	108.5 (63)
Re–C(4)–O(4)	178.5 (7)	O(5)–C(11)–H(3)	113.0 (47)
Re–C(5)–O(5)	118.3 (5)	H(1)–C(11)–H(2)	100.9 (65)
Re–C(5)–C(12)	126.9 (6)	H(1)–C(11)–H(3)	123.4 (59)
O(5)–C(5)–C(12)	114.7 (7)	H(2)–C(11)–H(3)	109.8 (72)
Re–Mn–C(6)	83.2 (2)	C(5)–C(12)–H(4)	115.5 (65)
Re–Mn–C(7)	82.3 (2)	C(5)–C(12)–H(5)	105.6 (58)
Re–Mn–C(8)	87.2 (2)	C(5)–C(12)–H(6)	109.7 (83)
Re–Mn–C(9)	84.5 (2)	H(4)–C(12)–H(5)	104.9 (79)
Re–Mn–C(10)	177.3 (3)	H(4)–C(12)–H(6)	106.9 (93)
		H(5)–C(12)–H(6)	114.4 (88)

[a] Standard deviations in least significant figures in parentheses.

Supplementary Material Available. Table II, a comparison of observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3053.

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(24) The integrated intensity (I) was calculated according to the expression

$$I = [S - (B_1 + B_2)/B_R]T_R$$

where S is the scan counts, B_1 and B_2 are the background counts, B_R is the ratio of background time to scan time ($B_R = 0.67$ for this data set) and T_R is the 2θ scan rate in degrees per minute. The standard deviation of I was calculated as

$$\sigma(I) = T_R[S + (B_1 + B_2)/B_R^2 + q(I)^2]^{1/2}$$

where q in this case was set equal to 0.003.

(25) All crystallographic programs used in structural determination and least-squares refinement were written by J. C. Calabrese. The absorption correction program DEAR (J. F. Blount) uses the Gaussian integration method of Busing and Levy. Plots were made using ORTEP (C. K. Johnson).

(26) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100\%$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2} \times 100\%$.

(27) All least-squares refinements were based on the minimization of $\Sigma w_i||F_o| - |F_c||^2$ with the individual weights $w_i = 1/\sigma(F_o)^2$. Atomic scattering factors used for all nonhydrogen atoms are from H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964); those for the hydrogen atoms are from R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(28) See paragraph at end of paper regarding supplementary material.

Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. IV.[1] Primary Metalation Products Derived from the Thermolysis of Tetracarbonylmethyltriphenylphosphinemanganese and Related Derivatives[2]

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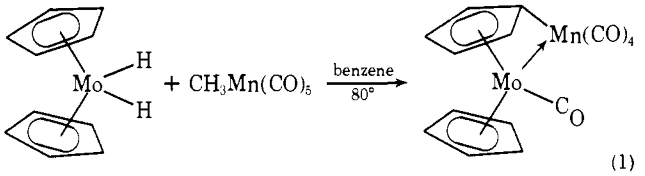
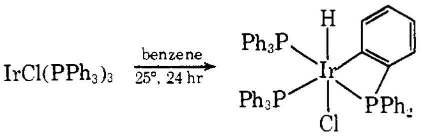
Abstract: The thermolysis of $CH_3Mn(CO)_4P(p\text{-}XC_6H_4)_3$ (X = H, **1a**; F, **1b**; CH_3, **1c**) gives the primary intramolecular aromatic metalation product $(p\text{-}XC_6H_4)_2\overline{P\text{-}\mu\text{-}C_6H_3(X)\text{-}M}n(CO)_4$ (X = H, **2a**; F, **2b**; CH_3, **2c**) along with lesser amounts of secondary metalation products derived from the reaction of **1** with **2** (discussed in the paper immediately following).[3] Minor amounts of cyclic acyl products $(C_6H_5)_2\overline{P\text{-}\mu\text{-}[C_6H_3C(O)]\text{-}M}n(CO)_3L$, L = CO, **6a**, and L = PPh_3, **7a**, separately shown to be derived from the reaction of **2a** with CO and **PPh**$_3$, respectively, were also isolated. Relative rates of the thermolysis reaction are in the order X = CH_3 > H > F. The reaction of $CH_3Mn(CO)_5$ with either $P(o\text{-tolyl})_3$ or $P(OPh)_3$ leads also to primary metalation derivatives, i.e., $(o\text{-tolyl})_2\overline{P\text{-}\mu\text{-}C_6H_4CH_2\text{-}M}n(CO)_4$, **2d**, and $(PhO)_2\overline{P\text{-}\mu\text{-}OC_6H_4\text{-}M}n(CO)_4$, **2e**, respectively. Comparison of reaction conditions suggests that steric considerations are the major factor in the ability of a methylmanganese carbonyl complex to give primary metalation derivatives.

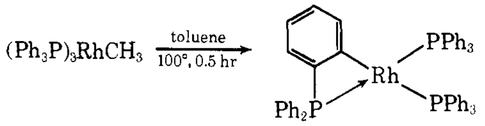
In 1971, Hoxmeier, Deubzer, and Kaesz reported[1a] the synthesis and crystal structure of a novel aromatic metalation product derived from the reaction of methylmanganese pentacarbonyl with di(η^5-cyclopentadienyl)dihydridomolybdenum, as shown in eq 1. This led them to attempt metalation with alkylmanganese complexes of other aromatic rings, in particular the phenyl rings in coordinated triphenylphosphine (**PPh**$_3$). The ortho metalation of PPh_3 had been earlier demonstrated by Bennett[4a] in iridium complexes (see eq 2) and also for an alkylrhodium derivative by Keim[4b] (see eq 3). These and related reactions have been recently reviewed.[5]



(1)



(2)



(3)

Accordingly, thermolysis of *cis*-$CH_3Mn(CO)_4PPh_3$, **1a**, yielded a product identified as $Ph_2\overline{PC_6H_4M}n(CO)_4$, **2a**, as expected,[1,4] but which was also accompanied by several new substances listed as products **3a** through **7a** under eq 4