Metalation of Aromatic Ketones and Anthraquinone with Methylmanganese and Methylrhenium Carbonyl Complexes[1]

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The reaction of $CH_3M(CO)_5$ (M = Mn, Re) with a variety of acetophenones and benzophenones yields the metalated derivatives $RC(O)C_6H_3(X)M(CO)_4$ (R = CH_3 or variously substituted phenyl rings; X = H, CH_3, OCH_3, Cl, F). The products are characterized by mass, infrared and ^1H NMR spectroscopy. The methyl group in *m*-methylacetophenone directs the metal principally to a position para to itself whereas the methoxy group in *m*-methoxyacetophenone directs the metal principally to a position ortho to itself. The reaction of $CH_3Re(CO)_5$ with anthraquinone gives a monometalated product and two bimetalated isomers. Of these, the one containing both rhenium atoms substituted on the same aromatic ring is less favored, in contrast to earlier observations in the ortho-palladation reaction of aromatic diamines.

Introduction

While the ortho-directing effects of oxygen functional groups in the metalation of aromatic rings by complexes of the main group metals such as lithium[2] or thallium[3] are now generally well established, prior to the present work observations of similar effects in the ortho-metalation by complexes of the transition metals were restricted to compounds with functional groups containing nitrogen,[4] phosphorus,[5,6] or sulfur.[7] Indeed, Trofimenko[4] has reported that no cyclo-palladation products could be observed in the reaction of methanolic $NaPdCl_4$ with methyl benzyl ether, acetophenone, or *N,N*-dimethylbenzamide. Our recent observation of "secondary" metalation products such as **1**[6] has led us to attempt the metalation of various aromatic ketones and quinones with $CH_3M(CO)_5$, M = Mn or Re, which proceeds as is described in the present work.[1b] The products thus contain either a manganese or a rhenium tetracarbonyl group coordinated to the oxygen atom of the acyl group as part of a five-membered ring also containing a metal-to-carbon bond. A structure for a representative compound, that of the metalated product of acetophenone, $CH_3C(O)C_6H_4Mn(CO)_4$, has been determined.[8] The new derivatives are thus members of a growing class of compounds containing this type of heteroatom chelating group, prevalent in the group 7 transition metal carbonyl complexes. Previous examples were encountered in a variety of reactions: e.g., **2**, one of the products obtained in the addition of $CH_3Mn(CO)_5$ to *o*-styryl(diphenyl)phosphine;[9] **3**, obtained in the addition of $CH_3Mn(CO)_5$, M = Mn or Re, or $HMn(CO)_5$ to acetylenes;[10] **4**, obtained by treatment of *cis*-(2-oxacyclopentylidene)nonacarbonyldimanganese with butyllithium followed by treatment with acetyl chloride;[11] **5**,
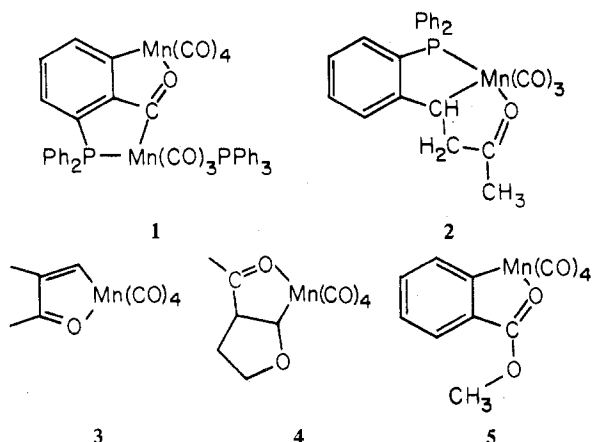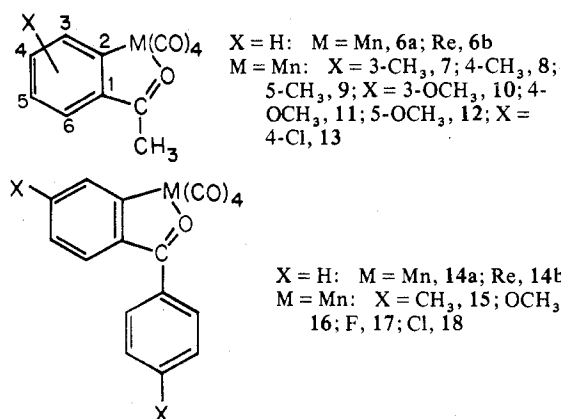

obtained in the bisdicarbonylation of the product resulting from the reaction of $NaMn(CO)_5$ with *o*-carbomethoxybenzoyl chloride.[12]

Examples of other types of complexes of manganese, rhenium, or iridium containing the chelated keto group may be found in the article by Booth and Hargreaves[10c] to which list we would add the tetracarbonylmanganese hexafluoroacetylacetonates reported by Wojcicki and coworkers.[13]

Results and Discussion

Metalation of Acetophenone, Benzophenone, and Substituted Derivatives. The reaction of $CH_3M(CO)_5$ with the aromatic ketones **6–18** proceeds in hydrocarbon solution at temperatures of 100–125° (M = Mn) or 125–145° (M = Re).

X = H: M = Mn, **6a**; Re, **6b**
M = Mn: X = 3-CH_3, **7**; 4-CH_3, **8**; 5-CH_3, **9**; X = 3-OCH_3, **10**; 4-OCH_3, **11**; 5-OCH_3, **12**; X = 4-Cl, **13**

X = H: M = Mn, **14a**; Re, **14b**
M = Mn: X = CH_3, **15**; OCH_3, **16**; F, **17**; Cl, **18**

Mass spectral data for some representative compounds as well as for three metalated quinones (**20–22** discussed below) are given in Table I. All of the compounds investigated gave satisfactory parent ion peaks followed by fragmentation peaks showing the loss of up to four CO groups; the lower *m/e* regions were not analyzed.

Infrared Data. For the cis tetracarbonyl group on the metal, we expect four ir-active stretching modes;[14] however, only three principal absorptions in this region are observed. The data collected for the compounds studied in this work are presented in Table II while the two representative traces are shown in Figure 1. For most of the compounds, there is a remarkable accidental degeneracy for two of the four expected absorptions. This is confirmed by the presence of a shoulder on the intense central band in a few of these derivatives, see lower trace of Figure 1 and footnotes *c–e* of Table II.

The infrared absorption of the acyl group coordinated through oxygen to metal is expected in the region 1600–1500 cm⁻¹,[10] somewhat weaker in intensity and shifted by about 150 cm⁻¹ to lower energy from that of the carbonyl absorption in the originating ketone. The assignment is complicated in the present compounds due to absorptions of the originating ketones which are also present in this region and whose position and intensity are affected by the absorption of the metal-coordinated acyl group. The data for some representative

Table I. Mass Spectral Data[a]

Compd	Probe T, °C	Parent ion m/e Calcd	Parent ion m/e Obsd	Other[b] m/e
6a	110–116	286	286	258, 230, 202, 174 (x = 1–4)
6b	110	416[c]	416[c]	388, 360, 332, 304 (x = 1–4)
9	126	300	300	244, 216, 188 (x = 2–4)
10	118	316	316	260, 232, 204 (x = 2–4)
11	120	316	316	288, 260, 232, 204 (x = 1–4)
13	110	320	320	264, 236, 208 (x = 2–4)
14a	110–118	348	348	320, 292, 264, 236 (x = 1–4)
14b	125–130	478[c]	478[c]	450, 422, 394, 366 (x = 1–4)
16	120	408	408	324, 296 (x = 3, 4)
17	115	384	384	328, 300, 272 (x = 2–4)
20	200	504[c]	504[c]	476, 448, 420, 392 (x = 1–4)
21	205	780[d]	780[d]	752, 724, 696, 668, 640, 612, 584, 556 (x = 1–8)
22	176	780[d]	780[d]	752, 724, 696, 668, 640, 612, 584, 556 (x = 1–8)

[a] AEI-MS9 mass spectrometer; 70-eV ionizing voltage. [b] Parent ion $-x$(CO). [c] Based on the ^{185}Re peak of the multiplet pattern. [d] Based on the ^{185}Re^{185}Re peak of the multiplet pattern.

Table II. Metal–Carbonyl Stretching Absorptions in the Infrared Spectra[a]

Compd	Freq, cm^{-1} [b] m	vs	s
6a	2082	1997	1947
9	2082	1997[c]	1947
8	2082	1996	1945
7	2080	1995	1944
12	2082	1998	1947
11	2082	1997	1944
10	2083	1995	1959
13	2086	2000	1952
6b	2095	1991[d]	1940
14a	2082	1997	1947
15	2082	1996	1945
16	2081	1997	1943
17	2087	2011	1953
18	2087	2003	1955
14b	2096	1993[e]	1939
20	2096	1996	1944
21	2094	1999	1946
22	2092	1999	1947

[a] Cyclohexane solution; Beckman IR4; LiF prism. [b] Absorptions calibrated against the cyclohexane absorption at 2138.5 cm^{-1}. Relative intensities: m, medium; vs, very strong; s, strong. [c] Shoulder 1994 cm^{-1}. [d] Shoulder 1988 cm^{-1}. [e] Shoulder 1990 cm^{-1}.

compounds of both the originating ketones and the principal metalated products derived from them is given in Table III; the spectra in the region 1800–1100 cm^{-1} for the originating ketones and the metalated products derived from these with CH$_3$Mn(CO)$_5$, e.g., **6a**, **9**, **10**, **13**, and **14a**, are given in supplementary Figures A–E,[15] respectively. The metal-coordinated acyl group absorption in the present compounds thus appears in the same range as associated with this group absorption in metal acetylacetonates[16] although in the hexafluoroacetylacetylacetonato complexes of manganese this absorption was observed in the region 1616–1635 cm^{-1}.[13]

^{1}H NMR spectra reveal well-separated resonances for the four aromatic protons on the metalated ring; these are il-
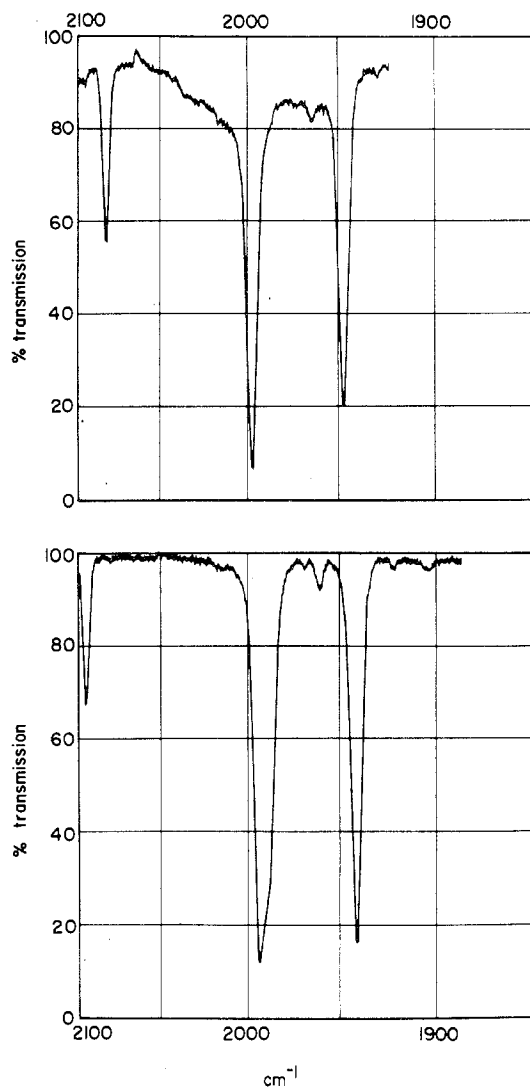

Figure 1. Infrared spectra in the carbonyl stretching region for CH$_3$C(O)C$_6$H$_4$M(CO)$_4$: M = Mn, **6a**, upper trace; M = Re, **6b**, lower trace. A cyclohexane solution, a Beckman IR 4, and an LiF prism were used.

Table III. Acyl Group Infrared Absorptions[a]

Ketone	$\nu_{C=O}$, cm^{-1}	Metalated product	ν(C=O–M), cm^{-1}	Other,[b] cm^{-1}
Acetophenone (A)	1688	6a	1530 m	1580 s
		6b	1525 m	1570 s
(m-CH$_3$)A	1684	9	1523 m	1575 s
(m-OCH$_3$)A	1681	10	1530 m	1570 s
(p-Cl)A	1685	13	1515 s	1560 s
Benzophenone	1659	14a	1519 s	1551 m
		14b	1501 s	1549 m

[a] CCl$_4$ solutions. [b] Other bands in the region 1600–1500 cm^{-1} whose position and intensity are significantly affected upon metalation of the ketone; see text and supplementary Figures A–E.

lustrated for **6a** in Figure 2 and the data for a number of derivatives studied in this work together with three related complexes reported by others, **5**,[12] **19a**, and **19b**,[7] are given in Table IV. The compounds are listed in the order in which they are discussed, following the sequence which led to the assignment of the resonances.

An unambiguous assignment is possible in the compounds **8** and **11**, derived from p-methyl- and p-methoxyacetophenone, respectively. In these we observe a doublet of doublets at highest field (assigned as Hb) followed by two doublets of which the one with the larger of the two separations must be

Table IV. ¹H NMR Data for Metalated Aceto- and Benzophenones and Related Compounds[a]

Compd	Chem shift, δ, ppm[b]				Other resonances	Coupling, constants, Hz
	H_a	H_b	H_c	H_d		
8	7.73 d	6.94 dd		7.9 d	R = CH₃, 2.44 s 4-CH₃, 2.54 s	$J_{ab} = 7.7; J_{bd} = 1.5$
11	7.75 d	6.62 dd		7.56 d	R = CH₃, 2.48 s 4-OCH₃, 3.90 s	$J_{ab} = 8.5; J_{bd} = 2.0$
19a[d]	7.56 d	6.90 dd		7.65 d		$J_{ab} = 10; J_{bd} = 1.5$
19b[d]	7.54 d	6.86 dd		7.63 d		$J_{ab} = 9; J_{bd} = 2$
6a	7.83 dd	9.17 td	7.41 td	8.09 dd	R = CH₃, 2.58 s	$J_{ab} = 7.5; J_{ac} = J_{bd} = 1.5;$ $J_{ad} = 0.7; J_{bc} = J_{cd} = 7.0$
6b	7.87 dd	7.13 td	7.38 td	8.04 dd	R = CH₃, 2.60 s	$J_{ab} = J_{bc} = J_{cd} = 7.3;$ $J_{ac} = J_{bd} = 1.5$
5[c]	7.75 ddd	7.19 td	7.50 td	7.94 ddd	R = OCH₃, 4.08 s	$J_{ab} = 7.6; J_{ac} = 1.5; J_{ad} = 0.6;$ $J_{bc} = 7.5; J_{bd} = 1.2; J_{cd} = 7.3$
14a	7.92 dd	7.16 td	7.42 td	8.19 dd	R = C₆H₅, 7.6 m	$J_{ab} = 7.6; J_{ac} = J_{bd} = 1.5;$ $J_{ad} = 0.7; J_{bc} = J_{cd} = 7.0$
14b	8.03 dd	7.26 td	7.50 td	8.12 dd	R = C₆H₅, 7.8 m	$J_{ab} = J_{bc} = J_{cd} = 7.5;$ $J_{ac} = 1.5; J_{ad} = 1.0; J_{bd} = 1.3$
9	7.7 d		7.3 dd	8.00 d	R = CH₃, 2.38 s 5-CH₃, 2.60 s	$J_{cd} = 8.0; J_{ac} = 1.5$
10	7.55 dd	7.20 t	6.94 dd		R = CH₃, 2.60 s, 3-OCH₃, 4.05 s	$J_{ab} = J_{bc} = 7.0; J_{ac} = 1.5$

[a] For proton assignments, see structures shown in Figure 2 and 19 in the text; all spectra were recorded in CDCl₃ solution except for 5 and 6b which were obtained in acetone-d_6. [b] Multiplicity: s, singlet; d, doublet; t, triplet; m, complex multiplet. [c] See ref 12. [d] See ref 7.
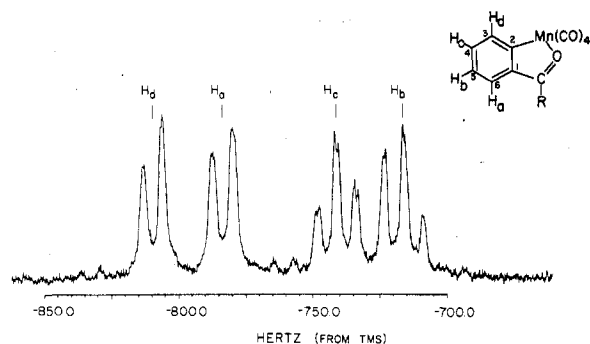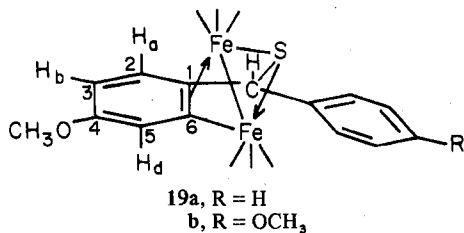

Figure 2. ¹H NMR spectrum, phenyl region, for CH₃C(O)C₆H₄Mn(CO)₄, **6a**, at 100 MHz using a CDCl₃ solution.


19a, R = H
b, R = OCH₃

Ha while the other must be Hd. In **8**, Ha appears at higher field than Hb as it does in all the other derivatives listed in Table IV except for **9**, in which the reverse is anomalously observed. A similar pattern and assignment proceeds from derivatives **19a** and **19b**, obtained in the metalation of p-methoxy- and p,p'-dimethoxybenzophenone with Fe₂(CO)₉.[7] Proceeding next to the unsubstituted derivative, **6a**, a series of double-resonance experiments permitted us to associate the highest field triplet, labeled Hb (see Figure 2) with the doublet labeled Ha and the lower field triplet He with the doublet Hd. A self-consistent pattern of chemical shifts is thus established for this and the other unsubstituted derivatives **6b**, **5**, **14a**, and **14b**, which may be contrasted to the resonances reported for a series of metalated azobenzene derivatives.[17] In these the proton nearest the metal, H¹, is assigned to the lowest field resonance as is the corresponding proton in this work, Hd. The assignments of the two protons meta to the metal, H² and H⁴, however, are reversed from the assignment of the corresponding protons in this work, Hc and Ha; for

C₆H₅N=NC₆H₄Mn(CO)₄, δ (ppm) is as follows: H¹, 8.18 dd; H², 7.98 dd; H³, 7.20 dd. No resonance for H³ equivalent to Hb in this work is given for this compound but its position is noted in the rhenium analog, whose resonances δ (ppm) are as follows: H¹, 8.15 dd; H², 7.92 dd; H³, 7.55 m; H⁴, 7.13 t. No coupling constants were reported in this work.

Directing Effects of the CH₃ and OCH₃ Groups on the Aromatic Ring. In the metalation of m-methyl- and m-methoxyacetophenone, two isomers are possible, namely, one with the metal in position ortho and one in position para to the substituent, i.e., 3-CH₃ (**7**) and 5-CH₃ (**9**) or 3-OCH₃ (**10**) and 5-OCH₃ (**12**) derivatives (see general structural formula above). The principal isomers obtained in these reactions were **9** and **10**, respectively. Assignment of these proceeded unambiguously from the ¹H NMR data, Table IV; for the substituent in position 5, we expect for the ring protons a doublet of doublets identifying Hc and two additional doublets, one with the larger separation for Hd and one with the smaller separation for Ha. This is observed for the principal isomer isolated in the metalation of m-methylacetophenone (**9**) in which the metal atom has understandably been directed para to the methyl group. However, for the principal isomer (**10**) derived from the metalation of m-methoxyacetophenone, we observe a triplet (Hb) with two doublets of doublets (assigned on the basis of the chemical shifts as Hc and Ha, respectively). This pattern indicates metalation ortho to the methoxy group and the existence of some polar interaction to account for this directing tendency not observed between the methyl and the metal tetracarbonyl group. The two other isomers of these compounds, namely, the 3-methyl (**7**) and the 5-methoxy (**12**) derivatives are obtained in very small quantities permitting at the present only a recording of their carbonyl absorptions (see Table II).

The metalation of quinones was also attempted. When anthraquinone was treated with CH₃Mn(CO)₅, a bright green, very air-sensitive product was formed in small amounts accompanied by larger amounts of Mn₂(CO)₁₀. The reaction of duroquinone and anthrone with either CH₃Mn(CO)₅ or CH₃Re(CO)₅ similarly yielded no tangible amounts of new products. However, the reaction of anthraquinone with CH₃Re(CO)₅, in equimolar amounts, leads to a red derivative, **20**, accompanied by smaller amounts of bimetalation products, a second red compound, **21**, and a green derivative, **22**. The bimetalated derivatives are obtained in larger quantities by

separate treatment of **20** with $CH_3Re(CO)_5$.

20

21

22
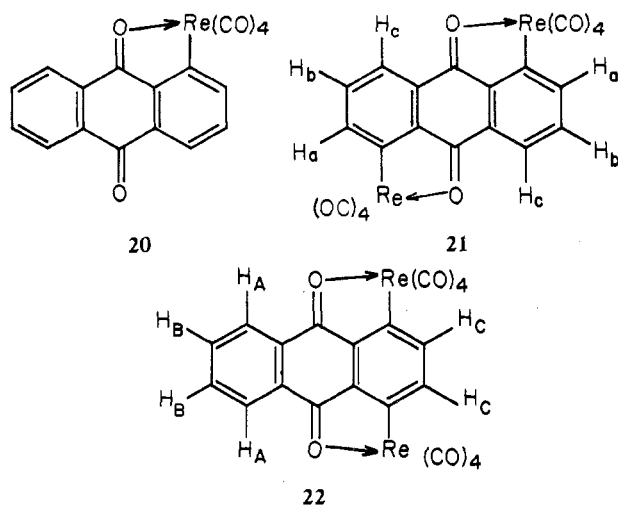
The expected parent and CO fragmentation peaks were observed in the mass spectra; see Table I. The infrared spectra of all three derivatives display three maxima which are nearly superimposable as indicated in Table II. While in the first two, **20** and **21**, group theory predicts four carbonyl stretching modes on the basis of either local or overall molecular symmetry, seven carbonyl bands are predicted on the basis of the molecular symmetry of **22** (C_{2v}). The fact that only four are observed for this derivative as well indicates that the carbonyl groups are not coupled strongly across the aromatic ring and that local interactions prevail, for which four bands are predicted as observed.

The ^1H NMR spectrum of the monometalated product, **20**, is quite complex as would be expected for an A_2B_2CDE system, and no assignment was attempted. Of the two bimetalated species, the green derivative, **22**, is the more soluble; in dichloromethane this gives an A_2B_2 pattern (similar to that of pure anthraquinone) together with a singlet as expected for the isomer where both metals are on the same ring. δ (ppm): H_A, 8.26; H_B, 7.84. $J_{AB} = 6$ Hz; $J_{A'B} = J_{AB'} = 3$ Hz.

Because of the lower solubility of **21**, it was necessary to accumulate several scans to see its ^1H NMR. This indicated a pair of doublets and a triplet as expected for the structure shown above. The assignments are as follows. δ (ppm): H_a, 8.35 d; H_c, 7.90 d; H_b, 7.54 t. $J_{ab} = J_{bc} = 7.5$ Hz; $J_{ac} < 1.5$ Hz.

The ratio of bimetalated derivatives **21:22** is approximately 3:2. There is thus a preference for the isomer in which metalation occurs on different rings. This observation as well as the tendency for the metalation to be sequential (i.e., a substantially large portion of anthraquinone is monometalated prior to the appearance of any bimetalated derivatives) contrasts markedly with the palladation of N,N,N',N'-tetraethyl-p-xylylenediamine reported by Trofimenko.[4] When the diamine is treated with equimolar amounts of $PdCl_2$, half of the organic starting material appears as bimetalated product while the remainder is recovered unchanged. This has been taken as further evidence for electrophilic behavior in the palladation reaction with $PdCl_2$. The metalation of ketones with methylrhenium pentacarbonyl must thus be governed by other factors as earlier noted in the reaction of substituted azobenzenes with $CH_3Mn(CO)_5$.[18]

Attempts to extend the metalation to aliphatic ketones, e.g., 4-heptanone and methyl *tert*-butyl ketone, proved unsuccessful.

Experimental Section

All reactions were carried out in Schlenk glassware under nitrogen which was passed over BTS catalyst (Badische Anilin-Soda-Fabrik A.G.) to remove trace amounts of oxygen and subsequently dried over

Table V. Elemental Analyses

Compd	Empirical formula	% calcd		% obsd	
		C	H	C	H
6a	$C_{12}H_7O_5Mn$	50.4	2.45	50.54	2.69
6b	$C_{12}H_7O_5Re$	34.5	1.68	34.77	1.70
14a	$C_{17}H_9O_5Mn$	58.6	2.59	58.94	2.90
14b	$C_{17}H_9O_5Re$	42.68	1.88	42.42	1.86
20	$C_{18}H_7O_6Re$	42.77	1.38	42.82	1.40
21	$C_{22}H_6O_{10}Re_2$	32.92	1.25	32.98	1.14

molecular sieves (Linde 5A). Solvents employed were those available from commerical vendors. Tetrahydrofuran (THF) was freshly distilled from calcium hydride under nitrogen before use. Hydrocarbon and chlorinated hydrocarbon solvents were dried over either molecular sieves or $MgSO_4$ and deoxygenated with bubbling nitrogen. Anhydrous diethyl ether (Mallinkrodt) was used as received.

$CH_3Mn(CO)_5$ was prepared by the method of Closson, Kozikowski, and Coffield,[19] and $CH_3Re(CO)_5$ was prepared by the method of Hieber and Braun.[20]

Elemental Analyses. Satisfactory carbon and hydrogen analyses were obtained for some representative compounds by Heather King of the UCLA Microanalytical Laboratory. The data are presented in Table V.

Infrared spectra in the carbonyl stretching region were obtained on a Beckman IR4 spectrophotometer equipped with LiF prism. Solution spectra were obtained in CaF_2 cells (1.0-mm path length) using cyclohexane absorption at 2138.5 cm^{-1}.

Solution spectra in the range 4000–500 cm^{-1} were recorded on a Perkin-Elmer 421 grating spectrophotometer. NaCl cells of 0.1-mm path length were used. CCl_4 which is transparent in the region of the characteristic bands of interest in this study (namely, acyl and oxygen-coordinated acyl absorptions 1800–1400 cm^{-1}) was used as solvent.

Nuclear magnetic resonance spectra were obtained on a Varian A-60D spectrometer and in a few cases also on a Varian HA-100 instrument.

Metalation of Acetophenone and Substituted Acetophenones. $CH_3Mn(CO)_5$ (0.272 g, 1.30 mmol) and an excess of acetophenone (ca. 1 ml) were refluxed in 25 ml of octane for 0.5 hr. The solution was cooled under nitrogen and applied directly to a silica gel–hexane chromatography column giving three bands. The first was identified as $Mn_2(CO)_{10}$ from its infrared spectrum and was obtained in 10% yield based on $CH_3Mn(CO)_5$. A control reaction in which $CH_3Mn(CO)_5$ was refluxed under similar conditions for the same length of time in the absence of acetophenone also yielded about 10% $Mn_2(CO)_{10}$. The second band gave 0.194 g of a yellow crystalline product, **6a** (68% yield). The third band was obtained in trace amounts and was not fully characterized. A similar minor product was obtained in each of the three reactions described below.

Similarly $CH_3Re(CO)_5$ (0.182 g, 0.53 mmol) and an excess of acetophenone (1 ml) refluxed in 25 ml of octane for 4 hr gave, upon chromatography, 0.090 g of the yellow crystalline product **6b**; yield 41%.

The reactions with substituted acetophenones were each carried out using 0.106 g (0.50 mmol) of $CH_3Mn(CO)_5$ with an equimolar amount of the ketone in 20 ml of methylcyclohexane under reflux (101°); longer reaction times (about 3 hr) were required. Work-up of these mixtures as described above yielded the various substituted derivatives in 50–60% yield for methyl- and methoxy-substituted ketones but only in 35–45% yield for the halogen-substituted ketones.

Metalation of Benzophenone. $CH_3Mn(CO)_5$ (0.819 g, 3.9 mmol) was allowed to react with an excess of benzophenone (ca. 5 g) in 50 ml of refluxing benzene for 5 hr. The solvent was removed and the residue applied to a silica gel–hexane column in hexane. $Mn_2(CO)_{10}$ (0.090 g) was removed first followed by 0.490 g of a yellow-orange crystalline product, **14a** (60% yield).

Similarly $CH_3Re(CO)_5$ (0.660 g, 1.93 mmol) and benzophenone (0.382 g, 2.10 mmol), refluxed in 25 ml of toluene for 12 hr, gave after chromatography 0.45 g of a yellow crystalline product, **14b** (48% yield). The reaction had apparently not gone to completion as some $CH_3Re(CO)_5$ was detected by ir in the eluent preceding the product.

Reaction of $CH_3Re(CO)_5$ with Anthraquinone. $CH_3Re(CO)_5$ (0.574 g, 1.68 mmol) and anthraquinone (0.174 g, 0.84 mmol) were refluxed in 5 ml of o-xylene for 2.5 hr. The solvent was removed by a vacuum pump and the residue was applied to a silica gel–hexane

column. A deep red band began to pull away but never completely separated ·from a very dark green-black band and so they were collected together giving 0.225 g of a green-black material, **21** and **22** (33% based on anthraquinone). A very minor red band was then collected (3 mg) and then a bright red band was removed with 5% dichloromethane–hexane giving 0.271 g of a red crystalline product, **20** (54% based on anthraquinone). Mass spectral data and ir bands are given in Tables I and II above; absorption of uncoordinated quinone is at 1669 cm⁻¹ (CCl₄ solution).

Reaction of 20 with CH₃Re(CO)₅. CH₃Re(CO)₅ (0.108 g, 0.32 mmol) and **20** (0.153 g, 0.30 mmol) were refluxed in 35 ml of octane for 11 hr. The solution was cooled and applied directly to a silica gel–hexane column. A deep red band not well separated from a green-black band was collected and rechromatographed as described below. A minor red band followed next (unidentified) and finally 0.041 g of unreacted **20** was eluted from the column. The materials collected in the first two bands were rechromatographed giving a long red band consisting of 0.054 g of **21** and 0.038 g of **22**, i.e., yields of 30% and 21%, respectively, based on the amount of **20** consumed. Derivative **21** is recrystallized from a dichloromethane–hexane mixture giving dark microcrystalline material; derivative **22** is recrystallized from a concentrated hexane solution to give green-black crystals. Mass spectral and ir data are given in Tables I and II above.

Miscellaneous other reactions were attempted, namely, of CH₃Mn(CO)₅ with (a) heptanone, (b) methyl *tert*-butyl ketone, (c) anthraquinone, (d) anthrone, and (e) duroquinone, each in octane solutions using 0.50 mol of the metal carbonyl with excess of the ketone. Similarly, the reaction of CH₃Re(CO)₅ was attempted with methyl *tert*-butyl ketone and duroquinone. For reactions of (a) and (b), the CH₃Mn(CO)₅ was largely unreacted except for some decomposition to Mn₂(CO)₁₀ as evidenced by the infrared data. Similar monitoring also revealed no reaction of (b) with CH₃Re(CO)₅. In the cases of the quinones, reaction was observed to take place almost immediately as evidenced by the appearance of a bright green color for the reaction mixture. The infrared spectrum in each case, however, revealed M₂(CO)₁₀ (M = Mn or Re) as the only carbonyl-containing species being formed. The green reaction mixtures were found to be extremely air sensitive at room temperature and not further investigated here.

Registry No. 6a, 50831-23-7; **6b**, 55401-21-3; **7**, 55401-22-4; **8**, 55401-23-5; **9**, 55401-24-6; **10**, 55401-25-7; **11**, 55401-26-8; **12**, 55401-27-9; **13**, 55401-28-0; **14a**, 50726-81-3; **14b**, 50726-82-4; **15**, 55401-29-1; **16**, 55401-30-4; **17**, 55401-31-5; **18**, 55401-32-6; **20**, 50726-83-5; **21**, 55401-33-7; **22**, 55450-64-1; CH₃Mn(CO)₅, 13601-24-6; CH₃Re(CO)₅, 14524-92-6.

Supplementary Material Available. Infrared spectra presented as Figures A–E 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 $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50092V-9-75.

References and Notes

(1) (a) This paper may be considered as part VII in a series on the metalation reaction; for part VI, see S. S. Crawford, G. Firestein, and H. D. Kaesz, *J. Organomet. Chem.*, in press. (b) The present work was submitted as part of a plenary lecture at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., Aug 1973, and communicated in preliminary form by the present authors in *J. Am. Chem. Soc.*, **95**, 7910 (1973).

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(4) Cf. S. Trofimenko, *Inorg. Chem.*, **12**, 1215 (1973), and references cited therein.

(5) Cf. G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970), and references cited therein including especially the work of M. A. Bennett and S. D. Robinson and their coworkers. A more recent collection of references is given in ref 7.

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(7) Cf. H. Alper and A. S. K. Chan, *J. Am. Chem. Soc.*, **95**, 7905 (1973), and references cited therein.

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