Intramolecular Metalation with Methylmanganese and Methylrhenium Carbonyl Complexes. V. Synthesis and Pathways of Formation of Secondary Metalation Products Derived from Tetracarbonylmethyltriphenylphosphinemanganese and -rhenium Derivatives[1,2]

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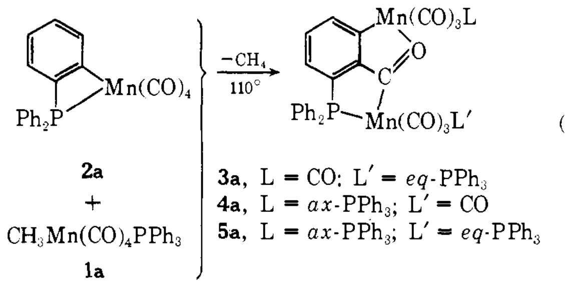
Abstract: The secondary metalation products $(p\text{-XC}_6\text{H}_4)_2\text{P[C}_6\text{H}_2\text{(X)(CO)(Mn(CO)}_3\text{L]Mn(CO)}_3\text{L}'$ (L = CO, L′ = $\text{P}(p\text{-XC}_6\text{H}_4)_3$, **3c**; L = $\text{P}(p\text{-XC}_6\text{H}_4)_3$, L′ = CO, **4**i; L = L′ = $\text{P}(p\text{-XC}_6\text{H}_4)_3$, CO, **5**i, **8**i; and X = H, F, CH_3; i = **a**, **b**, **c**) are formed in the reaction of $\text{CH}_3\text{Mn(CO)}_4\text{L}$ (L = CO, $\text{P}(p\text{-XC}_6\text{H}_4)_3$) and the primary metalation product[2] $(p\text{-XC}_6\text{H}_4)_2\text{P-}\mu\text{-(C}_6\text{H}_3\text{X)-Mn(CO)}_4$ derived from thermolysis of the phosphine substituted alkyl derivative. Structures of secondary metalation products have been determined by single-crystal X-ray diffraction studies reported separately. Formation of both primary and secondary metalation products is accompanied by loss of methane. Formation of secondary metalation products is facilitated by reaction of cyclic acyl derivatives, e.g., $\text{Ph}_2\text{P-}\mu\text{-[C}_6\text{H}_4\text{C(O)]-Mn(CO)}_3\text{L}$ (L = CO, PPh_3), readily obtained from primary metalation product as described previously.[2] Primary and secondary metalation products containing rhenium and combinations of rhenium and manganese have also been obtained from corresponding starting materials. Studies with mixed metal derivatives indicate that the metal in the cyclic acyl ring of the secondary metalation product is derived from the primary metalation product while the metal which becomes substituted on the aromatic ring in position ortho to the acyl group and also coordinated to oxygen of the acyl group is derived from the methyl complex.

In the article immediately preceding,[2] we described isolation and characterization of a primary internal metalation product, $\text{Ph}_2\text{P-}\mu\text{-C}_6\text{H}_4\text{-Mn(CO)}_4$, **2a**, arising from the thermolysis of $\text{CH}_3\text{Mn(CO)}_4\text{PPh}_3$, **1**. In addition to **2a** this reaction yielded two isomers of formula $\text{C}_{44}\text{H}_{28}\text{Mn}_2\text{O}_8\text{P}_2$ (**3a**, **4a**),[2] which are empirical dimers of the primary metalation product and one compound of empirical formula $\text{C}_{61}\text{H}_{43}\text{Mn}_2\text{O}_7\text{P}_3$, **5a**, which is a triphenylphosphine substitution product of the dimers, see reaction 1. The structures



(1)

3a, L = CO; L′ = *eq*-PPh_3
4a, L = *ax*-PPh_3; L′ = CO
5a, L = *ax*-PPh_3; L′ = *eq*-PPh_3

of these derivatives have been determined by X-ray diffraction studies.[3,4]

Although the secondary metalation products were empirical dimers of the primary metalated complexes, attempts to obtain the former simply by heating the latter proved unsuccessful. Furthermore, we also noted that improved yields of these "dimeric" products were obtained when the starting material, **1a**, was thermolyzed in the molten phase, in absence of solvent. Accordingly, we were led to the assumption that the secondary metalation products **3a** and **4a** were obtained from the reaction of 1 mol of the starting methyl complex with 1 mol of the primary metalation product and derivative **5a** would be produced by subsequent reaction of **3a** with PPh_3. These assumptions were subsequently verified by experiment.

The isolation and characterization of these and analogous derivatives containing rhenium and combinations of manganese and rhenium are reported below together with experiments relating to the pathways through which these derivatives are formed.

Results and Discussion

Characterization of the Secondary Metalation Products Derived from the Thermolysis of $\text{CH}_3\text{Mn(CO)}_4\text{PPh}_3$: the Dimers $(\text{C}_6\text{H}_4\text{X})_2\text{P[C}_6\text{H}_2\text{XCO)(Mn(CO)}_4\text{)]Mn(CO)}_3\text{P(C}_6\text{H}_4\text{X)}_3$ (X = H, 3a; F, 3b; CH_3, 3c), $(\text{C}_6\text{H}_4\text{X})_2\text{P[C}_6\text{H}_2\text{X(CO)(Mn(CO)}_3\text{P(C}_6\text{H}_4\text{X)}_3\text{)]Mn(CO)}_4$ (X = H, 4a; F, 4b; CH_3, 4c), and $\text{Ph}_2\text{P[C}_6\text{H}_3\text{(CO)(Mn(CO)}_3\text{PPh}_3\text{)]Mn(CO)}_3\text{PPh}_3$, 5a. It is instructive to examine the spectral features of the above named derivatives in light of their structures. Carbonyl infrared absorptions for these are given in Table I and the spectra of dimer **3a** and its fluorine substituted analog, **3b**, are shown in Figure A.[5] Assignment of these spectra was made possible through the isolation of the analogous unsubstituted compounds and derivatives separately containing the individual metal groupings discussed below. We can see from the carbonyl absorptions, however, that the ring-substituted derivative is analogous to the parent complex.

The oxygen coordinated acyl carbonyl gives rise to a characteristic absorption in the fingerprint region of the infrared spectrum, as illustrated for **3a** in Figure B.[5] We find a fairly strong band (by comparison to other absorptions in this region) at 1460 cm^{-1}, right between two bands which are assigned to ν(CC) modes of the phenyl rings. We find that there are analogous bands in the spectra of **3b** and **3c** but no comparable bands exist in the spectra of the starting materials $\text{CH}_3\text{Mn(CO)}_4\text{L}$ or $\text{Ph}_2\text{P-}\mu\text{-C}_6\text{H}_4\text{-Mn(CO)}_4$. Several examples of compounds containing acyl groups with oxygen coordinated to a metal have been reported in the literature.[6] In the coordination of ketones (benzophenone, PhCOPh) to TiCl_4[6c] the carbonyl stretching frequencies are lowered by as much as 150 cm^{-1}. The uncoordinated acyl group in the derivative $\text{Ph}_2\text{P-}\mu\text{-C}_6\text{H}_4\text{C(O)-Mn(CO)}_3\text{PPh}_3$,

Table I. Carbonyl Infrared and ^1H NMR Data of Secondary Metalated Products with Manganese

No.	$\nu(CO)$, cm^{-1} [a]	$\nu(>C{=}O \rightarrow M)$ [b]	^1H NMR (τ) [c]
3a	2074 m, 2024 w, 1992 s (1984 sh), 1946 s, 1935 s (1926 sh)	1460	2.4 (m, phenyl)
3b	2082 m, 2027 w, 2000 s (1995 sh), 1957 s, 1950 s, 1938 m	1460	2.7 (m, phenyl)
3c	2071 m, 2023 w, 1989 s (1983 sh), 1944 s, 1931 s (1924 sh)	1465	2.7 (m, phenyl), 7.36 (s, CH_3), 7.70 (s, CH_3); 22:3:15
4a	2073 m, 2011 vs (2006 sh), 1990 m, 1968 s, 1936 s, 1904 m, 1899 m	1470	2.6 (m, phenyl)
4b	2076 m, 2022 vs, 2011 m, 1993 s, 1977 s, 1949 s, 1923 s	1470	2.8 (m, phenyl)
4c	2073 m, 2010 vs (2004 sh), 1988 s, 1966 s, 1934 s, 1901 m, 1895 m	1477	2.8 (m, phenyl), 7.62 (s, CH_3), 7.68 (s, CH_3), 7.75 (s, CH_3); 22:6:3:9
5a	2003 s, 1941 s, 1920 m, 1900 m	1460	2.7 (m, phenyl)

[a] Cyclohexane solution. [b] CCl_4 solution. [c] Key: m = multiplet, s = singlet; 3b, 3c, 4b, and 4c were obtained in $CDCl_3$, 3a in acetone-d_6, and 4a in acetone; relative intensities for the resonances in 3c and 4c are given immediately following the chemical shift data.

7a, gives us a reference point from which to assess the effect of metal coordination in the secondary metalation products. In **7a** the acyl band is observed at 1595 cm^{-1} from which the coordinated acyl group of **3a** at 1460 cm^{-1} is shifted by 135 cm^{-1}. This is comparable to the shifts mentioned above. However, because the uncoordinated acyl stretching frequency is low to begin with, the band at 1460 cm^{-1} is by some 35 cm^{-1} the lowest coordinated acyl stretching frequency thus far observed.[6d]

The secondary metalation products, **4a–c,** isomers of **3a–c,** show more complex but better resolved carbonyl infrared spectra. The spectra of three such derivatives are shown in Figure C.[5] The absorptions can be assigned by comparison with spectra of compounds separately containing the component parts, discussed below. The spectra of **4a** and **4c** differ somewhat from that of **4b**. The shoulders in the former two at 2006 and 2004 cm^{-1}, respectively, are resolved into a peak at 2011 cm^{-1} in **4b**. The former two also show double maxima, i.e., 1904, 1899 and 1901, 1895 cm^{-1}, respectively, where **4b** shows a single maximum, i.e., 1923 cm^{-1}. Since seven carbonyls may not give rise to more than seven principal absorptions, we considered the possibility that the double maxima could be due to positional isomers involving the phosphines. Room temperature ^{31}P NMR spectrum revealed only two signals. Variable temperature ^{31}P NMR spectra between −90 and 90° were obtained to check if these signals were due to some averaging process. The two signals did not vary appreciably. Thus we do not believe that positional isomerism of ligands can be a likely explanation for the double maxima and we suggest that the low energy double maxima in **4a** and **4c** is a result of Fermi resonance of a carbonyl mode with an overtone of some lower energy vibration.

The carbonyl infrared spectrum of **5a** displays four broad absorptions (see Table I). The unsymmetrical nature of several of the bands suggests that these are due to overlapping absorptions. A crystal structure of **5a**[4] has shown that the upper Mn has a facial arrangement of ligands while the lower Mn is meridional with the phosphine trans to the phosphorus atom for which we would expect six absorptions.

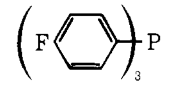
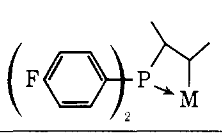
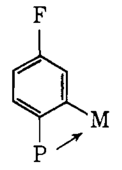
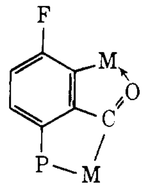
The ^{19}F NMR spectrum at the fluorine substituted derivative, **3b,** with the observed chemical shifts is shown in Figure D.[5] Three resonances are observed with relative areas of 1:2:3, respectively, going to high field. The two high field resonances appear at a chemical shift position and display coupling patterns consistent with fluorine atoms on nonmetalated phenyl rings (see Figure B of previous paper)[2] and are assigned accordingly. The very large downfield shift of the remaining fluorine, which is in position ortho to a manganese on a metalated ring is reminiscent of the large downfield shift of *o*-fluoroiodobenzene with respect to fluorobenzene, i.e., −19.9 ppm. Emsley, Sutcliffe, and Feeney[7] have suggested that this shift is due to intramolecular electric fields arising from van der Waals interaction of bulky substituents with an adjacent fluorine atom; the less electronegative the substituent, the greater the deshielding. Thus, the ortho tetracarbonyl manganese group which would be expected to give rise to greater nonbonding interactions than iodine, might thus be expected to give a larger downfield shift, as indeed is observed, i.e., −28.6 ppm.

The appearance of a quartet for the resonance of the fluorine atom on the metalated ring is somewhat surprising (a better resolved resonance of a fluorine in a metalated ring in an analogous secondary metalation product is shown in Figure 6 below; the discussion here pertains to both of these spectra). The quartet is not easily reconciled with the known structure of the unsubstituted derivative for it suggests accidental degeneracy for the coupling of the fluorine atom to the ortho and meta hydrogen atoms as well as to the para phosphorus atom. The observed separation in the multiplet is both the value expected for $J_{H-F(ortho)}$ and double the value expected for $J_{P-F(para)}$ (as observed for the coupling on the nonmetalated rings in this and other derivatives). We believe the most reasonable explanation for the appearance of the resonance as a quartet is that virtual coupling must exist between the two hydrogens and phosphorus leading to the appearance of the quartet whose separation is due to an average of the coupling between all the atoms. If constants typical[7] for each of the pairs of coupled atoms are substituted into the averaging, we obtain a value which reproduces the observed spacing in the quartet, i.e., $(J_{HF(ortho)} = 8) + (J_{HF(meta)} = 5) + (J_{PF(para)} = 2)/3 = 5$ Hz. The presence of virtual coupling may well be due to electron delocalization over the extended ring system in the secondary metalation products.[4]

The ^{19}F NMR spectrum of **4b** obtained under the same conditions as **3b,** is similar to that of the latter except that the degeneracy found in **3b** for the nonmetalated phenyl rings of the diphenylphosphido group has apparently been lifted: 3.75 multiplet, 28.9, 29.0, 31.2 (coupling in all three resonances is the same as that given for **1b** in Figure B of the previous paper)[2] relative areas, 1:1:1:3. The splitting of the resonances from the diphenylphosphido group might be expected from the structure shown above for **4a**. With respect to the plane containing the metalated ring, one of the (FC_6H_4) rings on the diphenylphosphido group is on the same side as $(FC_6H_4)_3P$ axial, while the other is on the side of a CO group on the upper metal.

The chemical shifts of the fluorine resonances of the various fluorinated derivatives discussed above are summarized in Table II, arranged according to the type of ring on which the fluorine resides. The correlation between ring type and chemical shift is quite good and may be diagnostic for the

Table II. ^{19}F NMR Resonances Collected According to the Nature of Their Environment

				
1b	2909^a (30.9)^b			
2b		2822 (30.0)	2585 (27.5)	
3b	2926 (31.2)	2842 (30.2)		663 (7.05)
4b	2923 (31.2)	2731 (29.0) 2717 (28.9)		353 (3.75)

^{a}Hertz from external CF_3CO_2H. ^{b}In ppm from external CF_3CO_2H.

Table III. Carbonyl Infrared Data of $CH_3Re(CO)_4L$, Primary Metalated Derivatives Thereof and Cyclic Acyl Derivatives

No.	ν(CO), cm^{-1a}
1h	2077 m, 1992 s, 1973 vs, 1935 s
1k	2081 m, 1996 s, 1975 vs, 1940 s
2h	2085 m (1990 sh), 1985 s, 1947 s
2k	2088 m (1993 sh), 1989 s, 1954 s
6h^b	2086 m, 2010 ms, 1986 s, 1964 s
6k^b	2089 m, 2014 ms, 1988 s, 1966 s

^{a}Cyclohexane solution. $^b\nu_{acyl}$ = 1600 cm^{-1}.

various environments. Further use of ^{19}F NMR data is made in assignment of the sequence of substitution for the mixed metal derivatives below.

Synthesis of $CH_3Re(CO)_4L$ (L = PPh_3, 1h; $P(p\text{-}FC_6H_4)_3$, 1k), and the Primary Metalation Products Derived Therefrom. The reaction of $CH_3Re(CO)_5$ with L in refluxing THF or benzene, in contrast to the corresponding reaction with manganese complexes described in the previous paper,[2] yields primarily the bis-substituted product $CH_3Re(CO)_3L_2$. It was thus necessary to find another synthetic route to the monosubstituted derivative. This was provided through $ReBr(CO)_5$. The synthesis of *cis*-$ReBr(CO)_4L$, in good yield, has been described by Jolly and Stone,[8] and the corresponding methyl derivative was obtained by reaction with methyllithium, see eq 2.

$$cis\text{-}ReBr(CO)_4L + CH_3Li \xrightarrow[Et_2O]{0^\circ} CH_3Re(CO)_4L \qquad (2)$$

$$L = PPh_3,\ 1h$$
$$L = P(p\text{-}FC_6H_4)_3,\ 1k$$

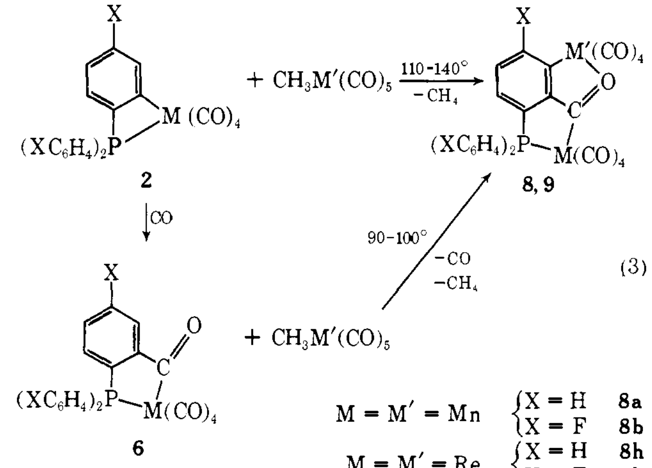
The carbonyl infrared spectra of these derivatives and metalation compounds derived from them are given in Table III. These are entirely analogous to the corresponding manganese derivatives.[2] The absorptions are generally to higher energy except for the lowest energy band in each case which is a few wave numbers lower than its manganese counterpart.

The internal aromatic metalation of $CH_3Re(CO)_4L$ required higher temperatures than for the manganese analogs.[2] The reaction was carried out in refluxing xylene (144°), giving fair yields of the primary metalation product, $(p\text{-}XC_6H_4)_2P\text{-}\mu\text{-}C_6H_3(X)\text{-}Re(CO)_4$ (X = H, **2h**; X = F, **2k**). However, only very small amounts of what appeared from the infrared spectra to be analogs of the secondary manganese metalation products (**3a, b** and **4a, b**) could be isolated from the reaction mixture and correspondingly greater amounts of decomposition were found in the rhenium system compared to the manganese system. An improved method for formation of secondary metalation products was subsequently discovered and is described in the succeeding section. The primary metalation products of rhenium, **2h** and **2k**, are easily converted to the corresponding cyclic acyl derivatives **6h** and **6k** by reaction with CO.

The carbonyl infrared spectra of the primary metalation products (Table III) closely resemble those of the manganese analogs[2] and show the same behavior with regard to the shift of the bands; i.e., the lower energy band is lower than its manganese counterpart, while the other three are to somewhat higher energy.

^{1}H ^{19}F NMR data obtained for the rhenium complexes are closely analogous to those of the corresponding manganese derivatives. For the following data, obtained for the compounds in $CDCl_3$ solution, these conditions apply: ^{1}H, 60 MHz, chemical shifts in values of τ and for ^{19}F NMR spectra, 94.1 MHz, chemical shifts given in parts per million against external CF_3COOH. $CH_3Re(CO)_4P(p\text{-}FC_6H_4)_3$, **1k**, ^{1}H 2.7 (multiplet, phenyl), 10.49 (d, CH_3, J_{HP} = 7.5 Hz); ^{19}F, 29.7 ($J_{HF(ortho)}$ = 8.5, $J_{HF(meta)}$ = 5.2, J_{PF} = 2.2 HZ); $(p\text{-}FC_6H_4)_2P\text{-}\mu\text{-}C_6H_3(X)\text{-}Re(CO)_4$, **2k**, ^{1}H NMR 2.6 (multiplet, phenyl); ^{19}F NMR, 28.2 ($J_{HF(ortho)} = J_{HF(ortho')}$ = 9.0, $J_{HF(meta)} = J_{PF}$ = 4.5 Hz), 29.0 (multiplet, coupling same as in **1k**), relative areas 1:2.

Formation of Bis(tetracarbonylmetal) Secondary Metalation Products: $(p\text{-}XC_6H_4)_2P[C_6H_2(X)(CO)(M(CO)_4)]M'(CO)_4$. Extension of eq 1 above using simply $CH_3M'(CO)_5$ (M' = Mn or Re) instead of the phosphine substituted methyl complex together with the primary metalation product permitted us to obtain bis(tetracarbonylmetal) secondary metalation products indicated in reaction 3, below. Use of derivatives of rhenium alternatively as the primary metalation product or as the methyl complexes with derivatives of



(3)

M = M' = Mn	X = H	8a
	X = F	8b
M = M' = Re	X = H	8h
	X = F	8k
M = Mn, M' = Re	X = H	9a
	X = F	9b
M = Re, M' = Mn	X = H	9h
	X = F	9k

Table IV. Comparison of Synthesis of Bis(tetracarbonylmetal) Secondary Metalation Products Using $CH_3M(CO)_5$ with Ph_2P-μ-C_6H_4-$M(CO)_4$, **2**, or Ph_2P-μ-$C_6H_4C(O)M(CO)_4$, **6**, and Derivatives

Reactants (g)						
	$CH_3M(CO)_5$, M =	Molar ratio	Solvent[a]	Reaction time (hr)	Product	% yield
2a (0.079)	Mn (0.146)	1:4	A	6	8a	50
6a (0.092)	Mn (0.146)	2:7	B	2.5	8a	80
6b (0.12)	Mn (0.165)	1:3	B	3.5	8b	60
2a (0.075)	Re (0.255)	3:7	A	6	9a	60
6a (0.092)	Re (0.248)	2:7	A	5	9a	65
6b (0.12)	Re (0.276)	1:3	B	7	9b	75
2h (0.10)	Mn (0.20)	1:5	C	2	9h	5
6h (0.100)	Mn (0.248)	1:7	B	2.5	9h	95
6k (0.095)	Mn (0.120)	1:4	B	2.5	9k	85
2h (0.095)	Re (0.300)	1:5	C	6	8h	10
6h (0.184)	Re (0.461)	1:7	A	3	8h	85
6k (0.088)	Re (0.214)	2:9	A	5	8k	80

[a] Solvents: A, toluene, 110°; B, methylcyclohexane, 101°; C, xylene, 140°; 15 ml in each case.

Table V. Carbonyl Infrared and ^1H NMR Data of Bis(tetracarbonylmetal) Secondary Metalation Products

Compound[a]	M	M′	$\nu(CO)$, cm^{-1}[b]	$\nu(>CO \rightarrow M)$[c]	^1H NMR (τ)[d]
8a	Mn	Mn	2085 m, 2071 m, 2014 s, 1998 vs (1992 sh), 1977 s, 1942 s	1473	2.65 (m)
8b	Mn	Mn	2089 m, 2074 m, 2017 ms, 2001 vs, 1979 s, 1960 s	1475	2.6 (m)
8h	Re	Re	2097 m, 2086 m, 2016 ms, 1999 vs, 1983 s, 1976 ms, 1932 s	1452	
8k	Re	Re	2101 m, 2090 m, 2009 ms, 2002 vs, 1989 s, 1979 s, 1948 s	1455	2.6 (m)
9a	Mn	Re	2094 m, 2075 m, 2015 ms, 1995 vs, 1986 s, 1980 s, 1936 s	1460	
9b	Mn	Re	2097 m, 2081 m, 2018 m, 1998 vs, 1991 ms, 1980 ms, 1950 s	1464	2.6 (m)
9h	Re	Mn	2096 m, 2076 m, 2015 s, 2000 vs, 1993 m, 1974 s, 1939 s	1467	
9k	Re	Mn	2097 m, 2081 m, 2017 s, 2002 vs (1998 sh), 1977 s, 1961 s	1468	2.6 (m)

[a] See structural drawing in eq 3. [b] Cyclohexane solution. [c] CCl_4 solution. [d] $CDCl_3$ solution.

manganese serving as complementary reagent permitted us to make mixed metal species. The elucidation of the positions of the different metals in these species, discussed below, provided us with information regarding the reaction path. However, we obtained low yields in reactions involving the primary metalation products of rhenium, **1h**, **1k** (ca. 5–10% of **9h**, **9k**, compared with 50–60% in reactions with the manganese primary metalated derivatives **2a**, **2b**; see above). We subsequently discovered that use of the cyclic acyl complexes, **6** (see previous paper),[2] as starting materials in place of the primary metalations derivatives, **2**, permitted us to lower the necessary reaction temperatures and significantly improve yields (85–95%) of secondary metalation products. This reaction is summarized in the lower path of eq 3 above. A comparison of reaction conditions and yields for the two synthetic routes is summarized in Table IV.

The infrared spectra in the carbonyl stretching region for the bis(tetracarbonylmetal) secondary metalation products are summarized in Table V and a representative spectrum, that of **8a**, is shown in the central trace of Figure E.[5] These derivatives show somewhat sharper bands than the spectra of the secondary metalation products described above, possibly due to the lower degree of phosphine substitution on the metals. An assignment of the absorptions may be proposed by comparisons with the spectra of separate species each containing one of the two different metal groups found in the bis(tetracarbonylmetal) secondary metalation products. These are shown in the upper and lower traces of Figure E. For the upper trace, the compound is obtained from the metalation of acetophenone by $CH_3Mn(CO)_5$,[9] while in the lower trace the compound was obtained as discussed in the previous paper;[2] the maxima of the two comparison spectra are given in the caption to the figure. For two cis tetracarbonylmetal groups in these derivatives, we could have expected up to eight maxima. It is clear from the correlations shown in Figure E that the central and most intense band must contain three accidentally or near-accidentally degenerate modes giving a satisfactory account of the absorptions.

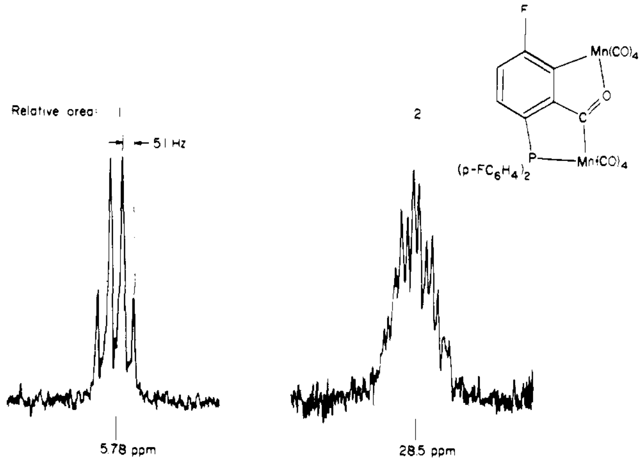


Figure 1. ^{19}F NMR spectrum of **8b**, $CDCl_3$ solution. 94.1 MHz. Chemical shifts are in parts per million from external CF_3COOH.

^1H NMR spectra of the bis(tetracarbonylmetal) secondary metalation products were of little diagnostic use; however, ^{19}F NMR spectra of the fluorinated derivatives, **8b**, **8k** and **9b**, **9k**, showed significant differences among these complexes. The ^{19}F resonances of a representative compound, **8b**, are shown in Figure 1 and the data obtained for the mixed metal compounds (**9b**, **9k**) and comparison compounds containing one type of metal (**8b**, **8k**) are summarized in Figure 2. Chemical shift and coupling constant data for these derivatives are found in the caption to Figure 2. In Figure 1, the low field quartet shows better resolution than obtained for the analogous resonance in the secondary metalation product, **3b** (see Figure D). The same discussion advanced above regarding the apparent coupling pattern in this multiplet would apply to the splitting observed here and for all the secondary metalation products thus far exam-

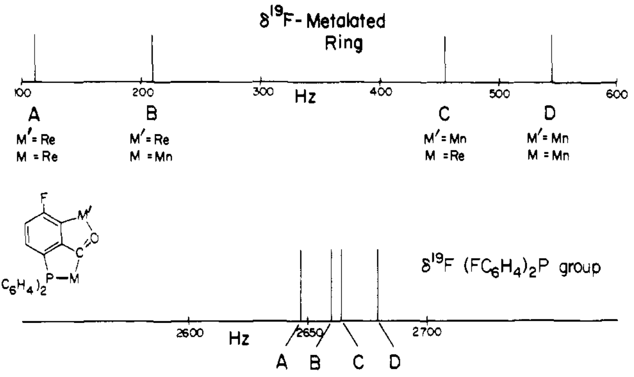


Figure 2. Schematic representation of fluorine resonances at 94.1 MHz of **8b** (D), **8k** (A), **9b** (B), and **9k** (C). The resonance positions shown on the upper bar graph are for the fluorines on the metalated rings. Each is a quartet with a coupling constant of 5 Hz, while those of the lower bar graph are for fluorines on unmetalated rings and show coupling the same as in **1k** (see text). Chemical shifts from external CF_3COOH in hertz and (parts per million): **8b**, 545 (5.78), 2692 (28.5); **8k**, 111 (1.18), 2647 (28.1); **9b**, 210 (2.23), 2660 (28.3); **9k**, 455 (4.84), 2664 (28.3).

ined. Turning to Figure 2, the characteristic resonances are summarized on the two bar graphs. On the lower are the resonances of the fluorines on the unmetalated rings while the upper are the resonances of the fluorine on the metalated rings; these assignments proceed first by relative intensity and coupling patterns and second by their correspondence to resonances in related derivatives discussed above (see Table II). At the opposite edges of the upper graph are the resonances due to the ReRe and MnMn derivatives (**8k** and **8b**, respectively). Close to the ReRe signal we find a signal for the product (**9b**) due to the reaction of $CH_3Re(CO)_5$ with the cyclic acyl derivative of manganese, **6b**, while the product, **9k**, from the reaction of the cyclic acyl derivative of rhenium, **6k**, with $CH_3Mn(CO)_5$ displays a resonance close to that of the MnMn derivative. This indicates that the metal in the alkyl complex, $CH_3M'(CO)_5$, is the one which is found coordinated to the acyl oxygen and metalating the ring in the position ortho to the fluorine, as indicated in reaction 3 above. The positions of the resonances of the fluorines on the unmetalated rings fall in the same relative order of descending frequency as the resonances shown above. This suggests that the effect on the fluorine atoms in the unmetalated rings of the metal atom M' is opposite to and slightly greater than that of metal atom M, an interesting result. A recent structure determination of a mixed metal derivative[10] confirms the sequence of metalation as suggested by the interpretation of the ^{19}F NMR results above.

Summary and Conclusions

A representative summary of the reactions reported here is presented in Figure 3. The secondary metalation products, shown at the right of the figure, are derived from the reaction of a methyl-metal complex with one of two complementary reagents, either a primary metalation product in reaction B, or a cyclic acyl derivative in reactions A or C. The reactions with the cyclic acyl derivatives occur at lower temperatures (ca. 90°) than those with the primary metalation products (ca. 110°). In reaction B, two isomeric secondary metalation products, **3a** and **4a**, are produced. These can be separately obtained through reactions A or C in yields of 57 and 91%, respectively. At the lower temperature of ca. 90° required for reaction of the methyl complex $CH_3Mn(CO)PPh_3$, **1a**, with acyl complex **6a**, the self-metalation of **1a** which would produce **2a** and then also **3a** (together with **4a**) is essentially quenched. The cyclic acyl derivatives are obtained from primary metalation product by its reaction either with CO or with PPh_3, also as shown in Figure 3 (discussed for the manganese derivatives in the previous paper).[2]

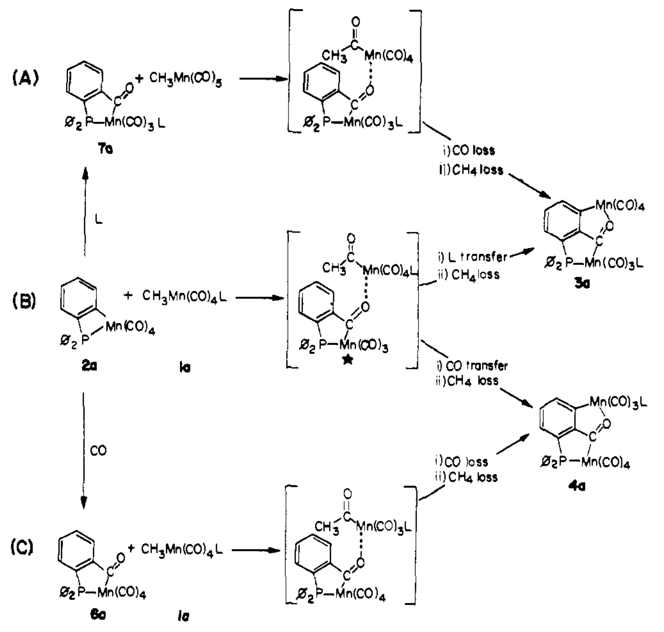


Figure 3. A representative summary of reactions with suggested intermediates.

Mixed metal derivatives can also be produced through such routes. However, in working with PPh_3 substituted derivatives, products arising from ligand dissociation must also be expected. In the reaction of $CH_3Re(CO)_5$ with $Ph_2\overline{P[C_6H_4C(O)]M}n(CO)_4PPh_3$, **7a**, for instance, only the products $CH_3Re(CO)_4PPh_3$ and $Ph_2\overline{PC_6H_4Mn}(CO)_4$, **2a**, were obtained, each in 80% yield. Product **2a** is derived from **7a** by loss of PPh_3, which ligand appears in the substituted methyl-rhenium complex.

In a separate work[9] we have shown that aromatic ketones and quinones can be ortho metalated by pentacarbonylmethylmanganese or -rhenium. This observation and the lower temperatures required for metalation of the cyclic acyl derivatives discussed above strongly suggests that, in the metalation sequence (B), some cyclic acyl derivative must be present as an intermediate or transition state. This would be formed by migration of aryl group to carbonyl in the primary metalation product possibly imposing temporary coordinative unsaturation on the metal. The driving force for this transformation would derive from the conversion of a four-membered ring in the starting material to a five-membered ring in the intermediate or transition state. The acyl group thus formed would direct entering metal alkyl complex toward metalation in the ortho position, very likely through an intermediate adduct shown in the center of sequence B, Figure 3. Products **3a** and **4a** would be produced by transfer respectively either of PPh_3 or CO from entering metal to the metal in the cyclic acyl ring, each accompanied or followed by loss of methane. In principle, this reaction should proceed with a number of alkyl complexes other than those specifically discussed here, and work in this direction as well as attempts to refine the mechanistic scheme suggested here is in progress.

Experimental Section

Comments relating to general reaction conditions and reagents given in the previous paper,[2] apply here as well. In addition, the following work required CH_3Li (in diethyl ether, 2.2 *M*) and

Table VI. Elemental Analyses

	Empirical formula	Calculated % C	Calculated % H	Found % C	Found % H
2k	$C_{22}H_{11}F_3O_4PRe$	43.07	1.79	42.72	2.02
3a	$C_{44}H_{28}Mn_2O_8P_2$	61.68	3.29	62.23	3.44
3b	$C_{44}H_{22}F_6Mn_2O_8P_2$	54.77	2.28	54.81	2.66
4a	$C_{44}H_{28}Mn_2O_8P_2$	61.68	3.29	62.08	3.43
4b	$C_{44}H_{22}F_6Mn_2O_8P_2$	54.77	2.28	54.15	2.31
6h	$C_{23}H_{14}O_5PRe$	47.02	2.39	47.22	2.47
8a	$C_{27}H_{13}Mn_2O_9P$	52.12	2.11	52.13	2.28
8b	$C_{27}H_{10}F_3Mn_2O_9P$	47.93	1.48	48.02	1.68
9a	$C_{27}H_{13}MnO_9PRe{\cdot}CH_2Cl_2$	40.09	1.79	40.00	1.69
9h	$C_{27}H_{13}MnO_9PRe$	43.0	1.73	43.05	2.08
8h	$C_{27}H_{13}O_9PRe_2$	36.65	1.47	36.68	1.40
		% F	% P	% F	% P
	3b	11.83	6.43	12.43	6.49
	4b	11.83	6.43	12.97	6.49
	8b	8.49	4.61	8.92	4.56

$Re_2(CO)_{10}$ (Strem Chemicals). $P(p\text{-}FC_6H_4)_3$ was prepared as described in the companion paper and $CH_3Re(CO)_5$ was synthesized by the method of Hieber and Braun.[11]

Elemental analyses and/or mass spectra were obtained only for derivatives for which no well-characterized analogs existed. These are displayed in Tables VI and VII, respectively. It should be noted that, for **4a**, the mass spectrum revealed a highest mass fragment 84 *m/e* units below that expected for a dimer. It is interesting that the corresponding parent − 3CO peak in the spectrum of **3a** is more intense than the parent ion. The intervening (P − CO) and (P − 2CO) peaks are nonexistent.

Infrared and NMR data for all new derivatives have been presented in Tables I, II, and III, above. Yields quoted below are based on molecular formulas as determined from mass spectra and elemental analyses.

Attempted Dimerization of 2a. A quantity of **2a** (0.10 g) was refluxed in 10 ml of toluene for 52 hr. The reaction was monitored periodically through infrared spectra. Besides a small amount of intractable decomposition, only **2a** and a small amount of **7a** were recovered. Molten reaction of **2a** at 145° for 20 min yielded the same results.

Demonstration of the Source of Dimers 3a and 4a. Reaction of the Primary Metalation Product, $Ph_2P\text{-}\mu\text{-}C_6H_4\text{-}Mn(CO)_4$, 2a, with $CH_3Mn(CO)_4PPh_3$, 1a. When it was observed that improved yields of secondary metalation products **3a** and **4a** were achieved by carrying out the metalation reaction in the absence of solvent in the molten phase of **1a** (maintained under nitrogen at 145° for 15-20 min) while none were produced simply by heating **2a** (see above), it was surmised that these products might arise from the reaction of the primary metalation products with starting material. Accordingly, a quantity of **2a** (0.10 g, 0.23 mmol) was refluxed in 15 ml of toluene for 3 hr at which time the infrared spectrum was checked and showed no reaction (there was slight darkening of the solution due to decomposition). At this time 0.20 g of **1a** was added to the reaction. Separation of the products by column chromatography revealed an improvement in yield of **3a** (20%) and **4a** (30%) based on the amount of **1a** reacted.

Synthesis of Secondary Metalation Products. $Ph_2P[C_6H_3(CO)(Mn(CO)_3L)]Mn(CO)_3L'$ (L = CO, L′ = PPh_3, 3a; L = PPh_3, L′ = CO, 4a; L= L′ = PPh_3, 5a) and the Fluorine Substituted Derivatives 3b and 4b. The title products were obtained in thermolysis of the corresponding methyl complexes $CH_3Mn(CO)_4P(p\text{-}XC_6H_4)_3$ (X = H, **1a**; X = F, **1b**). These reactions were described in the previous paper[2] and the present products were obtained in the chromatographed separation of the thermolysis reaction mixtures.

As explained above, the possibility of ligand tautomerism was investigated in compound **4a**. Variable temperature ^{31}P NMR spectra were obtained on a 251-MHz instrument (superconducting magnet) at 100.5 MHz from −90 to 40° in acetone and from 40 to 90° in toluene. The only observable change was an apparent sharpening of a singlet at 66.2 ppm as the temperature was lowered. The other resonance at 84.5 ppm remained unchanged throughout. The resonance positions are given relative to $P(OC_2H_5)_3$.

The Reaction of 3a with PPh_3. Compound **3a** (0.10 g, 0.12 mmol) and PPh_3 (0.03 g, 0.12 mmol) were refluxed in benzene (25 ml) for 3 hr. Subsequent column chromatography using a 25% benzene-hexane solution as eluent gave 0.12 g of **5a** (93% yield).

Synthesis of $CH_3Re(CO)_4L$ (L = PPh_3, 1h; L = $P(p\text{-}FC_6H_4)_3$, 1k). $CH_3Re(CO)_5$ (1.05 g, 3.1 mmol) and $P(p\text{-}FC_6H_4)_3$ (1.10 g, 3.5 mmol) were refluxed in 75 ml of THF. Following the reaction by the infrared spectrum, the monosubstituted product was apparent after 1 day and continued to increase through the second day. At this time, peaks assignable to the bis-substituted isomer began to appear and the monosubstituted product remained fairly constant thereafter. The reaction was stopped after 8 days and the product mixture chromatographed with hexane. All major products are colorless on the column. The desired monosubstituted product, **1h**, was obtained in approximately 10% yield.

Synthesis of $CH_3Re(CO)_4L$ by Way of $BrRe(CO)_4L$. $BrRe(CO)_4L$ was obtained by the method reported by Jolly and Stone,[8] and further reacted with CH_3Li to give the desired products, **1h** and **k**. $Re_2(CO)_{10}$ (2.31 g, 3.5 mmol) was suspended in 40 ml of carbon tetrachloride and cooled to 0°. Br_2 (0.30 ml, 5.5 mmol) was dissolved in 40 ml of CCl_4 and added dropwise with stirring. After addition, the mixture was allowed to warm to room temperature and stirred for 4 hr more. The solvent and excess bromine were stripped off, and the off-white product dried shortly under vacuum (ca. 0.5 hr). This product ($BrRe(CO)_5$) was placed in a 300-ml Schlenk flask with PPh_3 (1.80 g, 7 mmol) and refluxed in 150 ml of $CHCl_3$ for 12 hr. The solvent was removed and the residue chromatographed on silica gel first with hexane and then with a 2:3 ether-hexane mixture. The product, $BrRe(CO)_4PPh_3$, is colorless on the column and was recrystallized from ether-hexane.

The $BrRe(CO)_4PPh_3$ was dissolved in 100 ml of anhydrous diethyl ether in a dry 250-ml Schlenk flask under nitrogen and cooled to 0°. Five milliliters of 3.0 *M* CH_3Li in ether was added and the solution stirred for 0.5 hr. Excess CH_3Li was destroyed by adding distilled water slowly to the solution while stirring. At this point, inert atmosphere is no longer needed. The ether portion was

Table VII. Mass Spectral Data[a]

Compound	Probe temp, °C	Parent ion Calcd	Parent ion Obsd	(Parent ion) − *x*CO's
3a	122–215	856	856	772, 744, 716, 688, 660, 632 (x = 3–8)
3b	175	964		880, 852, 824, 796, 768, 740 (x = 3–8)
4a	165–220	856		772, 744, 716, 688, 660, 632 (x = 3–8)
4b	190	964		880, 852, 824, 796, 768, 740 (x = 3–8)
1k	120	628[b]	628[b]	613 ($P\text{-}CH_3$), 585, 557, 529 (x = 1–3)
2k	165–160	612[b]	612[b]	584, 556, 528, 500 (x = 1–4)
6h	118	586[b]	586[b]	558, 530, 502, 474, 446 (x = 1–5)
8a	135–140	622	622	538, 510, 482, 454, 426, 398, 370 (x = 3–9)
8h	160–170	882[c]	882[c]	854, 826, 798, 770, 742, 714, 686, 658, 630 (x = 1–9)
8k	168	936[c]	936[c]	908, 880, 852, 824, 796, 768, 740, 712, 684 (x = 1–9)
9a	160	752[b]	752[b]	724, 696, 668, 640, 612, 584, 556, 528, 500 (x = 1–9)
9b	160	806[b]	806[b]	778. 750. 722, 694, 666, 638, 610, 582, 554 (x = 1–9)
9h	160–166	752[b]	752[b]	668 (x = 3), complex thereafter
9k	148	806[b]	806[b]	722, 694, 666, 638 (x = 3–6) complex thereafter

[a] Obtained at 70 eV. [b] Based on ^{185}Re peak. [c] Based on $^{185}Re^{185}Re$ peak of multiplet.

washed several times with water, separated, and then the ether stripped off. The yellowish residue was chromatographed with a 10% benzene-hexane eluent on silica gel. The product **1h**, is colorless and comes off the column first followed closely by an unidentified yellow band. The product was crystallized yielding 3.5 g (55%). The same procedure was used when L = $P(p\text{-}FC_6H_4)_3$ to give **1k**.

Internal Metalation of $CH_3Re(CO)_4PPh_3$, 1b. The title compound (1.01 g, 1.75 mmol) was refluxed in 60 ml of xylene for 7 hr. The solvent was aspirated over a steam bath and the residue chromatographed on silica gel with 20% benzene–hexane. The first band, **2h**, was colorless and gave an infrared spectrum similar to **2a**.[2] The yield was 0.56 g (58%) and the product was crystallized from ether–hexane as white clusters. The remaining bands were found in less than 5% yields by weight. Infrared spectra showed patterns similar to those found for the dimers **3a** and **4a** among others; these products were not characterized.

Internal Metalation of $CH_3Re(CO)_4P(p\text{-}FC_6H_4)_3$, 1k. The title compound (0.93 g, 1.48 mmol) was refluxed in 20 ml of xylene for 12 hr. The work up procedure was the same as above and yielded snow white cluster crystals, **2k** (44% yield).

The Reaction of $(XC_6H_4)_2\overline{PC_6H_3XM}(CO)_4$ (M = Mn, 2a (X = H), 2b (X= F); M = Re, 2h (X = H), 2k (X = F)) with Carbon Monoxide. The synthesis described in paper IV[2] for the reaction of **2a** with CO utilizing a Hoke cylinder at elevated temperatures was used. (1) The primary metalated derivative, **2a** (0.338 g, 0.77 mmol), was dissolved in 30 ml of benzene and degassed by the freeze–thaw method in a Hoke cylinder. The cylinder was pressurized with 50 psi of CO and closed off and the temperature of the cylinder lowered to −198° with liquid nitrogen. The cylinder was removed from the liquid nitrogen and again pressurized with 50 psi while still cold. This procedure brings the pressure in the cylinder to about 100 psi at room temperature. The cylinder was brought to room temperature and then placed in an oven at 90° for 4 hr. Upon cooling the cylinder was vented and emptied into a round-bottom flask and the solvent stripped off leaving a bright yellow residue which was chromatographed on silica gel using 30% dichloromethane-hexane as eluent. Two pale yellow bands wash off first (small amounts of $Mn_2(CO)_{10}$ and unreacted **2a**) and then a bright yellow band is removed which yields 0.303 g of yellow crystals, **6a** (84% yield). (2) **2b** (0.259 g) was dissolved in 30 ml of benzene, treated, and worked up exactly as with **2a** above (except the cylinder was allowed to stand overnight under pressure after heating). **6b** (0.241 g) was recovered as yellow crystals (89% yield). (3) Compound **2h** (0.40 g) was dissolved in 25 ml of toluene and pressurized in a Hoke cylinder as with **2a** above. The cylinder was placed in an oven at 125° for 24 hr and then worked up as above. Yellow crystals, **6h**, were recovered (0.38 g, 90% yield). (4) Exactly the same procedure was used in treating **2k** with CO to form **6k** in 92% yield.

Synthesis of the Mixed Metal Secondary Metalation Derivatives. Due to their similar nature, the following 12 reactions have been tabulated for simplicity in Table IV above. In each case the reactants were dissolved in a given amount of solvent and refluxed under nitrogen for the length of time shown. Where the solvent was methylcyclohexane, the cooled reaction mixture was applied directly to a silica gel–hexane chromatography column and eluted beginning with 10% benzene–hexane. Where the solvent was toluene or xylene, the solvent was removed by aspiration over a steam bath and the residue redissolved in hexane before application to the column. The yellow products were then recrystallized from ether–hexane or dichloromethane–hexane. Where $CH_3Mn(CO)_5$ was used either with toluene or xylene as solvent, substantial amounts of $Mn_2(CO)_{10}$ were found. In the case of the reaction of **2h** with $CH_3Mn(CO)_5$, where xylene was used as solvent, $Mn_2(CO)_{10}$ was obtained in about 75% yield based on $CH_3Mn(CO)_5$.

The yields of the desired product were based on the first reactant in the table in each case. The $CH_3M(CO)_5$ (M = Mn, Re) was in excess in each case because of the aforementioned tendency for them to decompose under reaction conditions.

Reaction of 7a with $CH_3Mn(CO)_5$. $CH_3Mn(CO)_5$ (0.209 g, 1.0 mmol) and **7a** (0.122 g, 0.18 mmol) were refluxed in 30 ml of toluene for 1.5 hours. Chromatography gave a band containing **1a, 2a,** and **8a** (by ir) (0.072 g) and a second band, **3a** (0.090 g) in 57% yield. **7a** (0.012 g) was also recovered and so the yield of **3a** was actually 69% based on the amount of **7a** reacted.

Reaction of 6a with 1a. Products **6a** (0.116 g, 0.25 mmol) and **1a** (0.197 g, 0.45 mmol) were refluxed in 25 ml of methylcyclohexane for 4 hr. The solution was cooled and applied directly to a chromatography column. Besides the **2a** formed in the internal metalation of **1a**, **4a** was found in 91% yield based on **8a**. Only a trace of **3a** was found.

The Reaction of 7a with $CH_3Re(CO)_5$. Compound **7a** (0.335 g, 0.485 mmol) and $CH_3Re(CO)_5$ (0.220 g, 0.645 mmol) were refluxed in toluene (30 ml) for 3.5 hr. Removal of solvent and column chromatography of the product mixture with silica gel–hexane yielded a yellow band whose ir spectrum revealed approximately equimolar amounts of $CH_3Re(Co)_4PPh_3$, **1h**, and the primary metalated derivative $Ph_2\overline{P\text{-}\mu\text{-}C_6H_4\text{-}Mn}(CO)_4$, **2a**.

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Supplementary Material Available. Various spectral traces presented as Figures A through 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 Street, 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 JACS-75-3066.

References and Notes

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