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

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

R. J. McKinney, R. Hoxmeier, and H. D. Kaesz*

Contribution No. 3400 from the Department of Chemistry,
University of California, Los Angeles, California 90024.

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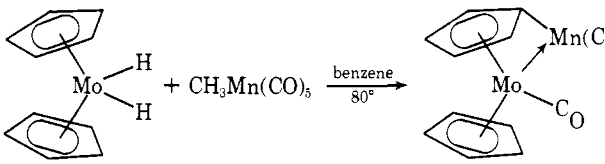
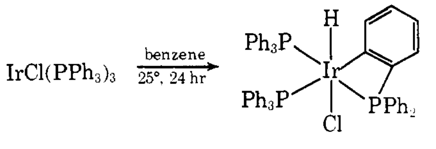
Abstract: The thermolysis of $CH_3Mn(CO)_4P(p\text{-}XC_6H_4)_3$ (X = H, **1a**; F, **1b**; CH_3, **1c**) gives the primary intramolecular aromatic metalation product $(p\text{-}XC_6H_4)_2\overline{P\text{-}\mu\text{-}C_6H_3(X)\text{-}M}n(CO)_4$ (X = H, **2a**; F, **2b**; CH_3, **2c**) along with lesser 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)



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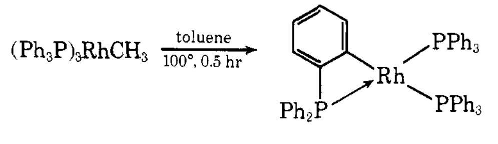


(3)

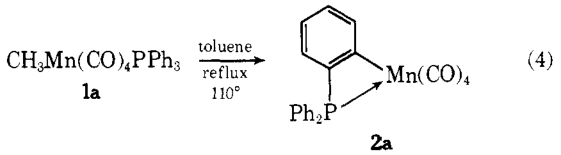
Accordingly, thermolysis of *cis*-$CH_3Mn(CO)_4PPh_3$, **1a**, yielded a product identified as $Ph_2\overline{PC_6H_4M}n(CO)_4$, **2a**, as expected,[1,4] but which was also accompanied by several new substances listed as products **3a** through **7a** under eq 4

Table I. Carbonyl Infrared and ^1H NMR Data for $CH_3Mn(CO)_4L$, 1, and Primary Metalation Products, 2

Compound	L	ν(CO), cm^{-1} [b]	^1H NMR (τ)[c] Phenyl[d]	Methyl[e]
1a	PPh_3 [a]	2055 m, 1983 m, 1968 s, 1939 m	–	10.15
1b	$P(p\text{-}FC_6H_4)_3$	2060 m, 1991 m, 1971 s, 1942 m	2.65	10.45
1c	$P(p\text{-}CH_3C_6H_4)_3$	2056 m, 1980 s, 1968 vs, 1936 s	2.65	10.50
1e	$P(OC_6H_5)_3$	2072 m, 2001 s, 1987 vs, 1962 s	2.8	10.12
2a		2067 m (1987 sh), 1983 s, 1951 s	2.5	
2b		2070 m (1991 sh), 1987 s, 1957 s	2.6	
2c		2064 m (1985 sh), 1980 s, 1948 s	2.7[f]	
2d	P(*o*-tolyl)$_3$	2063 m (1984 sh), 1978 s, 1943 s	2.8[g]	
2e		2083 m (2008 sh), 2004 vs, 1975 m, 1969 s	2.8	

[a] Data for **1a** from ref 6. [b] Cyclohexane solution. [c] The spectrum for **1a** was obtained in benzene solution, and those for all other compounds listed were obtained in $CDCl_3$. [d] Resonance of the phenyl protons; in each case an unresolved multiplet is observed. [e] Resonance of the methyl group on Mn; in each case a doublet with J_{HP} = 8 Hz is observed. [f] For **1c**, methyl resonance of the tolyl group is τ 7.65 (singlet) and in **2c**, τ 7.68 (singlet). [g] The methylene resonance is a broad absorption at τ 7.6 and the methyl resonance of the unmetalated *o*-tolyl rings τ 7.9 (singlet), see supplemental Figure E.[10]

below. The isolation and characterization of derivatives **2a, 6a,** and **7a** and analogous products are discussed in this paper. The products **3a, 4a, 5a,** and their homologs involving secondary metalation are discussed in the following paper.[3]

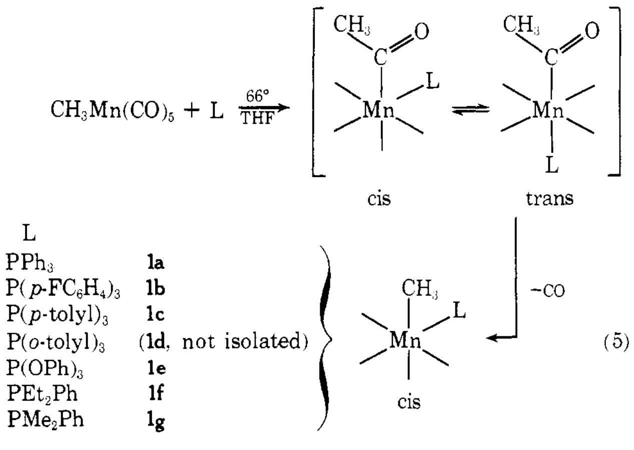


2a

2a	$C_{22}H_{14}MnO_4P$	30%
3a	$C_{44}H_{28}Mn_2O_8P_2$	25%
4a	$C_{44}H_{28}Mn_2O_8P_2$	20%
5a	$C_{61}H_{43}Mn_2O_7P_3$	10%
6a	$C_{23}H_{14}MnO_5P$	4%
7a	$C_{40}H_{29}MnO_4P_2$	4%

Results and Discussion

The tetracarbonylmethyl(phosphine)– or -(phosphite)–manganese complexes were prepared by the reaction of pentacarbonylmethylmanganese with the appropriate phosphine or phosphite in refluxing THF, as summarized below in eq 5. These are strictly analogous to, and include, the known tetracarbonylmethyl(triphenylphosphine)manganese, **1a,** first reported by Kraihanzel and Maples.[6]



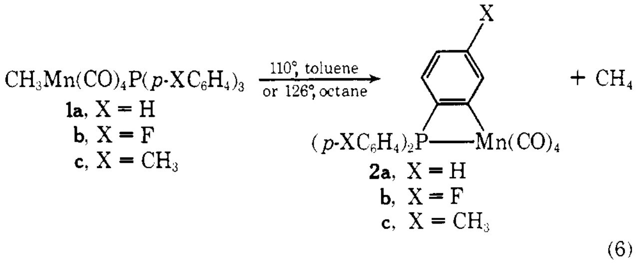
Previous work[6-9] has shown that this type of substitution reaction proceeds through the acyl intermediates shown in the brackets in eq 5. However, these were not isolated in this work. Although an equilibrium between the cis and trans isomers for the acetyl intermediates are usually observed, decarbonylation leads predominantly to a cis product,[6,9] which we have confirmed for our derivatives through carbonyl infrared and NMR spectra summarized in Table I. A representative infrared spectrum, that of the compound, L = $P(p\text{-}F\text{-}C_6H_4)_3$, **1b**, is shown in supplemental Figure A,[10] upper trace.

The presence of some trans isomer is not totally ruled out, however. Calderazzo et al.[8] have separated the two isomers of the corresponding acetyl derivatives, L = PPh_3 (see bracketed species in eq 5) and found that the absorptions for the trans isomer, i.e., 2067(w) and 1957(s) cm^{-1}, overlap bands of the cis isomer, i.e., 2067(w), 1994(m), 1964(s), and 1957(s) cm^{-1}. By analogy, the cis and trans isomers of the alkyl derivatives might be expected to have overlapping absorptions. Examination of the spectrum in supplemental Figure A reveals that the band at 1942 cm^{-1} appears somewhat unsymmetrical and may be overlapping what would be expected to be the strongest absorption of the trans isomer. The fact that the proton NMR spectra display only one methyl doublet in each case (coupling due to phosphorus) might be rationalized in terms of a rapid tautomerism between the isomers, thereby averaging the signals. A crystal structure of tetracarbonylmethyl(triphenylphosphine)manganese,[11] **1a**, suggests there is some trans isomer present in the crystal.

One notable omission in the derivatives of this category is for L = P(*o*-tolyl)$_3$, **1d,** the predominant product under conditions of its preparation being the internally metalated product, **2d**; see below.

The derivatives for L = PEt_2Ph, **1f,** and PMe_2Ph, **1g,** were prepared only in small quantities needed for infrared spectral monitoring of their subsequent attempted metalation reactions. These did not participate in the metalation reaction and thus their characterization is limited to their carbonyl infrared spectra: (cm^{-1}) **1f,** 2061 m, 1988 s, 1961 vs, 1950 w, 1935 s; **1g,** 2061 m, 1988 s, 1961 vs, 1950 m, 1936 s. In both of these derivatives, a weak band at 1950 cm^{-1} is resolved accompanied by a narrowing of the lowest energy band. The band at 1950 cm^{-1} is most likely due to the presence of a small amount of trans isomer.

Metalation products, $(p\text{-}XC_6H_4)_2P(C_6H_3X)Mn(CO)_4$, X = H, 2a; F, 2b; CH_3, 2c, were prepared by the thermolysis of



the tetracarbonylmethyl(phosphine)manganese compounds, **1a**, **1b**, and **1c**. In this reaction, methane is eliminated. The compound, X = H (**2a**), has been described previously.[1a]

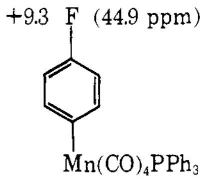
The carbonyl infrared spectra are an important characteristic feature of these derivatives. All consist of four bands in agreement with that expected for an octahedral *cis*-$M(CO)_4$ arrangement. These are generally to somewhat higher energy than those of the starting materials, **1a–c**, and are not as well separated; there is a near degeneracy in the middle two modes. A representative spectrum, that of the compound, X = F (**2b**), is shown in the lower trace of supplemental Figure A.

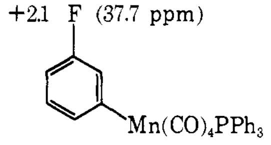
The substituted phenyl phosphine derivatives, **2b** and **2c**, are analogous to **2a**, as confirmed through the carbonyl infrared as well as mass spectral data and elemental analyses (see Table I above, and Tables III and IV in experimental section below). The slight shifts to higher energy for each band in **2b**, relative to those in **2a**, are consistent with the electron withdrawing effect that fluorine would be expected to have on metal carbonyl bonding.[13] A shift to lower energy is observed for the bands of **2c**, as expected from the electron donating capacity of a methyl substituent.

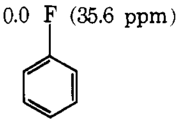
^1H NMR spectra (60 or 100 MHz) have in general not proved useful for resolution of the phenyl resonances in these metalated species. In most cases, no distinguishing features could be observed other than a somewhat greater complexity when compared with the corresponding absorptions of the starting materials. A significant downfield shift for protons ortho to a metal has been noted for internal metalation derivatives involving palladium or platinum and aryl phosphites,[14] azobenzenes with Mn, Re, Fe, Ni, Mo,[15] and aryl thioketones with Fe,[16] which in each case contain five-membered metalation rings. However, the absence of such a downfield shift has been reported in the case of internal metalation products involving four-membered rings, i.e., with Pt and P-*t*-Bu(*p*-tolyl)$_2$ or P-*t*-Bu$_2$(*p*-tolyl).[17] In our compounds, also containing four-membered rings, we do not see the ortho shift. The ^1H NMR spectrum of the metalated species, X = CH_3 (**2c**), displayed only a somewhat broadened, unsymmetrical methyl resonance, indicating that the methyl hydrogens on the metalated ring have substantially the same chemical shift as those of the nonmetalated phenyl rings.

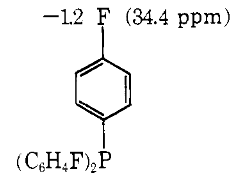
Good spectroscopic characterization was provided by the ^{19}F NMR spectrum of the fluorinated derivative, **2b**, shown in supplemental Figure B.[10] It reveals two well-resolved resonances with relative areas of 1:2; the splitting pattern of the resonance at 30.0 ppm is consistent with the fluorine coupling to the four protons and phosphorus of an unmetalated phenyl ring (the constants are given in the caption to Figure B and are consistent with literature findings).[18] The other resonance at 27.5 ppm shows a splitting pattern due to three nonequivalent protons and a phosphorus. The two protons ortho to the fluorine give different coupling constants (7.75 vs. 10.0 Hz) but we have no way at present of distinguishing between them.

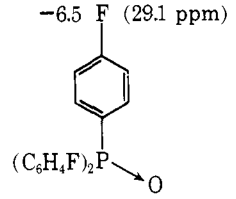
The ^{19}F chemical shifts of some substituted fluorobenzenes which are related to the derivative discussed above, **2b**, are displayed below.[18,19] Numbers to the left of fluorine are the shifts in parts per million from fluorobenzene and those in parentheses from CF_3CO_2H. Note that the observed shift for **2b** is −8.1 ppm, which is a greater shift to lower field than we might expect from the addition of the shifts of (m-FC_6H_4)$Mn(CO)_4PPh_3$ and **1b** (i.e., 2.1–4.7 = −2.6 ppm, downfield from fluorobenzene).

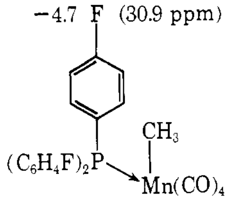


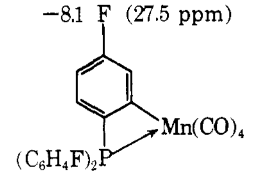












Ir Fingerprint Band. Internal metalation gives rise to a characteristic band in the region of the infrared between 1500 and 1400 cm^{-1}. A portion (1800–800 cm^{-1}) of the spectrum of a representative derivative, **2a**, is shown in supplemental Figure C[10] together with the same region in the spectrum of the methylmanganese compound, **1a**, from which it was synthesized. In the spectrum of **1a**, upper trace, we find two bands at 1435 and 1480 cm^{-1} which are assigned to ν(CC) modes of the phenyl rings.[3a] However, the spectrum of **2a**, lower trace, displays three absorptions in the same area. The third band may be assigned to the metalated phenyl ring.[3a]

Pathways of Formation of the Primary Metalation Products. When the thermolysis reaction of the methylmanganese complex, **1**, is carried out in more dilute solutions and in a less polar solvent (i.e., approximately 0.3 g in 100 ml of octane at 126°), the formation of the primary metalation product, **2**, is maximized at about 70% yield in each case. Under these conditions the time necessary for disappearance of starting material was observed to be as follows: **1c**, 2 hr; **1a**, 3 hr; and **1b**, 6 hr. This ordering of substituent effect on relative rate i.e., $CH_3 > H > F$, is the same as that observed by Bennett and Milner for that internal metalation of $IrCl[P(C_6H_4X)_3]_3$ (i.e., oxidative addition of an ortho carbon–hydrogen bond to iridium). Since the sequence of substituent effect is similar to that of electrophilic aromatic substitution, this mechanism has been suggested for the metalation reaction.

On the other hand, a radical abstraction pathway for metalation by the alkylmetal carbonyl complexes must also be considered. In a recent study by Stille and Regan,[20a] evidence is presented to indicate that aryl migration in some rhodium complexes proceeds through a radical process. Since alkyl migration is no doubt involved in reactions of the methylmanganese complexes, we believe the metalation reaction in this work could also proceed via attack by migrating methyl group upon the hydrogen in the ortho position of one of the phenyl rings. This hydrogen is particularly accessible to such a migrating radical[20b,c] and would thus be scavenged from the ring. Further comments relating to steric effects of coordinated phosphines are presented below.

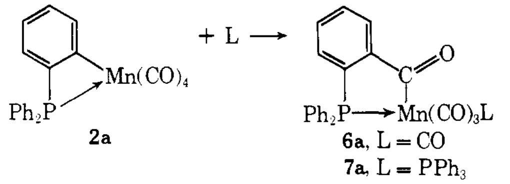
Reactions of the Primary Metalation Product 2a with Carbon Monoxide and with Triphenylphosphine. Formation of Cyclic Acyl Derivatives. Two of the compounds isolated

Table II. Carbonyl Infrared and ^1H NMR Data of Cyclic Acyl Derivatives

	ν(CO), cm^{-1}	ν(>CO)	^1H NMR (τ)^c
6a	2068 m, 2005 m, 1976 s, 1963 s^a	1618^b	2.3 (mult)
7a^e	2021 vw, 2012 s (1946 sh), 1936 s, 1915 s (1911 sh)^b	1592 m, 1560 m^d	
7a^f	2021 vw, 1936 s, 1911 m^b	1595 ms, 1565 w^d	2.5 (mult)

^{a}Cyclohexane solution. ^{b}CCl$_4$ solution. ^{c}CDCl$_3$ solution. ^{d}KBr pellet. ^{e}Product obtained at room temperature. ^{f}Product after heating.

in low yield in the thermolysis of $CH_3Mn(CO)_4PPh_3$ were identified as products resulting from the reaction of the primary metalated product, **2a**, either with carbon monoxide to give **6a** or triphenylphosphine to give **7a**.



2a

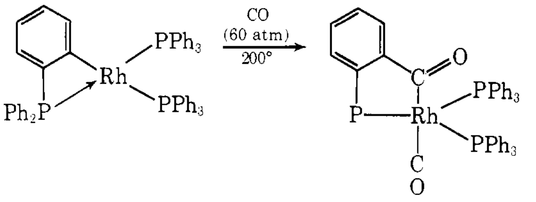
6a, L = CO

7a, L = PPh$_3$

(7)

Carbonylation of the primary metalation product, **2a**, will occur though very slowly at room temperature and under an atmospheric pressure of CO, to give the yellow crystalline product, $Ph_2\overline{PC_6H_4C(O)Mn}(CO)_4$, **6a** (see eq 7, above). The insertion of carbon monoxide to form an acyl derivative is verified by the presence of an acyl carbonyl stretching mode at 1618 cm^{-1} in the infrared spectrum. The carbonyl region of the infrared spectrum is better resolved than that of the metalated derivative from which it is formed, **2a**, but maintains a pattern characteristic for *cis*-$M(CO)_4$ derivatives, see Table II.

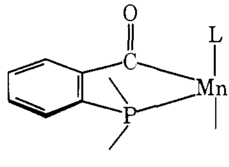
"Carbonyl insertion" into a metal-carbon bond of an internally metalated derivative has been verified in only one other case, i.e., the acyl derivative formed in the reaction of CO with a rhodium metalated triphenylphosphine derivative;[21] see eq 8. However, carbonyl insertion products have been postulated as intermediates in the formation of indazolone.[22]



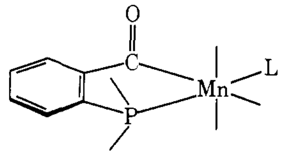
(8)

The attempted decarbonylation of the acyl derivative, **6a**, at 126° in octane solution, led only to 10% of **2a** with recovery of 85% of **6a**, after 1.5 hr. The acyl derivative, with its five-membered ring, must be regarded as relatively more stable than the metalated derivative, **2a**, containing a four-membered ring.

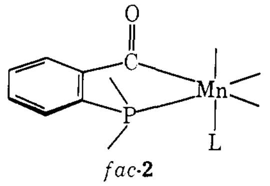
The reaction of PPh_3 with **2a** at room temperature yields an orange powder, **7a**, which is insoluble in most organic solvents. The substance is not sufficiently volatile for mass spectral analysis, but carbon and hydrogen analysis (see Table IV) is consistent with a simple addition of PPh_3 to **2a**, forming an acyl derivative, $\overline{Ph_2PC_6H_4C(O)Mn}(CO)_3PPh_3$, **7a** (see eq 7, L = PPh_3). The fact that no gas is evolved during the reaction lends support to this formulation. The carbonyl infrared spectrum reveals at least four bands consistent with the presence of more than one isomer. Indeed four isomers are possible (see below), two *facial* species which are optical isomers of each other and would have identical infrared spectra and two meridional isomers, each of which would be expected to give three carbonyl absorptions.



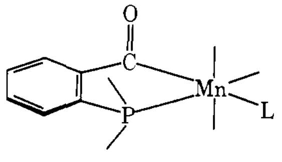
fac-1



mer-1



fac-2



mer-2

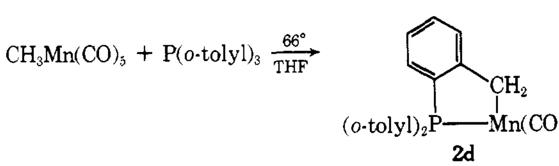
The infrared spectrum in the fingerprint region, supplemental Figure D,[10] upper trace, shows two somewhat broadened maxima at 1592 and 1560 cm^{-1} which can be assigned to acyl carbonyl stretches. We might expect three absorptions in this region if all of the isomers are present, i.e., one for the *facial* isomers and one each for the *meridional* isomers. However, the position of this band for the isomers which have a carbonyl group trans to the acyl carbonyl, i.e., fac$_{1,2}$ and mer$_1$, might be nearly the same, and would be expected to be of higher energy than the corresponding stretch in the isomer with the phosphine trans to the acyl group, i.e., mer$_2$. We therefore suggest that the band at 1592 cm^{-1} is due to the three isomers, fac$_{1,2}$ and mer$_1$, while the band at 1560 cm^{-1} is due to the mer$_2$ isomer.

A solution of **7a** (mixture) shows three maxima, all three of which display shoulders in the carbonyl stretching region, see Table II. Upon heating, the infrared spectrum is observed to change giving a simplified pattern without evolution of gas, see Table II. The infrared spectrum in the fingerprint region, lower trace of supplemental Figure D, shows a narrowing and increase in intensity of the higher energy acyl band, and a slight narrowing and decrease in intensity of the lower energy acyl band. Carbon and hydrogen analysis is consistent with no change in the empirical formula from that observed before heating.

The pattern seen in the carbonyl infrared spectrum is characteristic of *mer*-$M(CO)_3$ derivatives and suggests that the *facial* isomers are no longer present. The fingerprint region infrared spectrum suggests that both the meridional isomers may still be present but in the ratio of approximately 2:1, mer$_1$ to mer$_2$. An attempt to separate these two isomers by fractional crystallization led to small orange crystals whose fingerprint region infrared spectrum was identical with that shown in supplemental Figure D, lower trace.

Several studies[8] have led to the conclusion that substitution of pentacarbonylmethylmanganese occurs by alkyl migration to a cis carbonyl followed by reversible attack of the ligand at the site vacated by the methyl group. This would lead to isomers *fac*-**1** or *fac*-**2** or both (see structural formulas above) as the kinetically determined products, in agreement with our observations. Equilibration of these products leads to a mixture of the meridional isomers *mer*-**1** and *mer*-**2**, which, according to our observations, are thermodynamically preferred.

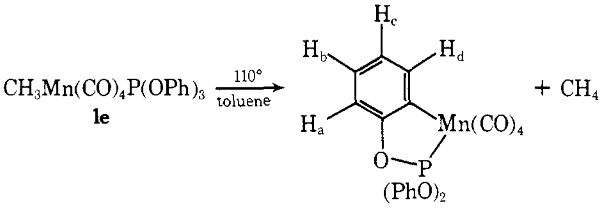
Metalation Products $(o\text{-}CH_3C_6H_4)_2\overline{PC_6H_4CH_2Mn}(CO)_4$, **2d, and** $(C_6H_5O)_2\overline{POC_6H_4Mn}(CO)_4$, **2e.** To compare the metalation reaction leading to products which contain four-membered metallocycles with those leading to products which could contain five-membered metallocycles, we investigated the reactions of tris(*o*-tolyl)phosphine and triphenyl phosphite with $CH_3Mn(CO)_5$. As indicated above, no intermediate ligand substituted alkyl complex could be isolated for the former ligand, the reaction proceeding directly to the metalation product **2d** at temperatures considerably below those required for the metalation of the other compounds. The carbonyl infrared spectrum of **2d** is closely analogous to that observed for the primary metalation product derived when L = P(*p*-tolyl)$_3$, **2c** (see Table I). The mass spectrum and carbon hydrogen analysis (Tables III and IV) confirm that we have a metalation product rather than the parent phosphine substituted methyl manganese carbonyl complex expected. The proton NMR spectrum, supplemental Figure E[10] and Table I, clearly shows that metalation has occurred on the methyl group. The phenyl proton multiplet at τ 2.8 appears unchanged when compared with a spectrum of the uncoordinated phosphine. There are two resonances in the methyl region, i.e., a small broad resonance at τ 7.6 and a sharp singlet at τ 7.9. The relative areas are respectively 12:2:6, indicating that the phenyl protons are untouched while one of the methyl groups has lost a hydrogen, in agreement with the structure shown above. This shows that an alkyl group can compete effectively with an aromatic ring in formation of internal metalation products when geometry leads to the formation of a five-membered ring, as has been observed for platinum and palladium compounds.[17,23-25]



2d

(9)

Compound **2e** is derived from the thermolysis of the methyl manganese complex, **1e**, in refluxing toluene.



2e

(10)

The product, separated and isolated by column chromatography, would not crystallize in our hands and therefore we had to work with a pale yellow oil. The mass spectrum (Table III) indicated that we had the metalated derivative desired but also showed that some of the nonmetalated methyl complex was still present. Though the carbonyl infrared spectrum revealed a pattern analogous to those of the metalated products described above, no bands could be observed belonging to the parent cis methyl manganese complex, **1e.** It may be, however, that the hitherto unexplained shoulder in the spectrum at 1975 cm^{-1} might belong to the trans isomer of the parent complex which could not be internally metalated and could not be separated from the metalated product.

The proton NMR spectrum is inconclusive with respect to the presence of some trans isomer of the parent complex because all of the solvent (hexane) could not be removed after chromatography. However, the phenyl proton multiplet, supplemental Figure F, reveals greater complexity than the parent complex, and a small pair of doublets appears on the downfield side of the bulk of the multiplet (at τ 2.45 and 2.55). Though the magnitude of the downfield shift for protons ortho to metals is usually considerably greater than this,[14] these compare favorably with those observed in the metalation of azobenzene with manganese carbonyl complexes, and with manganese or rhenium metalated aryl ketones.[1c] On this basis, these two doublets are tentatively assigned to the proton ortho to the metal in the metalated ring.

The thermolysis of the triphenyl phosphite methylmanganese complex, **1e**, also yields a small amount (7.5%) of a product, **7e,** whose carbonyl infrared spectrum is identical with that of $(PhO)_2\overline{POC_6H_4Mn}(CO)_3P(OPh)_3$ as reported by Darensbourg, Darensbourg, and Drew,[26] i.e., 2038 s, 1981 s, 1953 m cm^{-1}. They obtained the derivative from the reaction of $PhCH_2(CO)Mn(CO)_5$ with 2 equiv of $P(OPh)_3$.

Comparison of the Metalation of P(*o*-tolyl)$_3$ and P(OPh)$_3$ and Failure to Observe Metalation in PMe$_2$Ph and PEt$_2$Ph. The metalated *o*-tolylphosphine and phenyl phosphite derivatives **2d** and **2e**, respectively, differ from those discussed above in that **2d** and **2e** involve sterically favored five-membered metalation rings.[17,22] These might be expected to facilitate the metalation reaction. Indeed we find that the *o*-tolyl group is metalated under relatively mild conditions. However, the metalation reaction of the phosphite derivative $CH_3Mn(CO)_4P(OPh)_3$, **1e**, is comparable in temperature and time to that of the triphenylphosphine derivative, $CH_3Mn(CO)_4PPh_3$, **1a**, which forms a metalation product with a four-membered ring. Thus ring size cannot be the major reason for facility in metalation of the *o*-tolyl ring.

In light of the possible mechanisms discussed above, steric crowding or the bulkiness of a ligand, might be expected to play a role. It has been shown for platinum complexes[17] that steric crowding as introduced by *tert*-butyl groups on the ligand is often required to observed internal metalation. Lack of steric crowding would therefore inhibit metalation. Indeed we have found that upon heating the complexes $CH_3Mn(CO)_4L$ where L = $P(CH_3)_2Ph$, **1g**, or $P(C_2H_5)_2Ph$, **1f**, no metalation was observed. Tolman has shown[27] that tris-*o*-tolylphosphine is among the most sterically hindered of the known tertiary phosphines or phosphites, having a cone angle some 35% greater than triphenylphosphine and some 60% greater than triphenyl phosphite. This high degree of steric hindrance and large cone angle would greatly increase the proximity of hydrogen on the metalation site to the migrating methyl radical as the mechanism postulated above suggests. Since triphenyl phosphite is less crowded than triphenylphosphine, it might thus be expected to require higher temperatures or longer reaction times for metalation to occur, as is observed.

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 molecular sieves (Linde 5A). Solvents employed were those available from commercial 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 $MgSO_4$ (anhydrous) and deoxygenated by passing a stream of nitrogen through them. Anhydrous diethyl ether (Mallinkrodt) was used as received.

Commercial reagents were used as received from suppliers: $Mn_2(CO)_{10}$, Pressure Chemical Co.; CH_3I and PPh_3, Matheson Coleman and Bell; tris-*p*- and -*o*-tolylphosphine, Strem Chemicals, Inc.; PCl_3, Mallinkrodt; 4-bromofluorobenzene, Aldrich; triphenyl phosphite, Matheson Coleman and Bell. $CH_3Mn(CO)_5$ was prepared according to the literature.[28]

Mass spectra were obtained on an AEI-MS9 mass spectrometer. Satisfactory spectra were obtained for most compounds at an ionizing voltage of 70 meV and probe temperatures varying between 100 and 200°. The pertinent data are given in Table III, in the pre-

Table III. Mass Spectral Data[a]

Compd	Probe temp (°C)	Parent ion Calcd	Parent ion Obsd	Other peaks (parent ion − xCO)
1e	100–110	492	492	477,[b] 449, 421, 493, 465 (x = 1–4)
2a	132	428	428	400, 372, 344, 316, (x = 1–4)
2b	150	482	482	454, 426, 398, 370 (x = 1–4)
2c	160	470	470	442, 414, 386, 358 (x = 1–4)
2d	140–150	470	470	442, 386, 358 (x = 1, 3, 4)
2e	88–105	476	476	420, 392, 364 (x = 2–4)

[a] Ionizing voltage 70 eV. [b] Parent ion less CH_3.

Table IV. Elemental Analyses[a]

Empirical formula	Calculated % C	Calculated % H	Found % C	Found % H
2a, $C_{22}H_{14}MnO_4P$	61.68	3.29	61.65	3.46
2b, $C_{22}H_{11}F_3MnO_4P$	54.77	2.28	54.18	2.41
2d, $C_{25}H_{20}MnO_4P$	63.62	4.25	63.73	4.10
6a, $C_{23}H_{14}MnO_5P$	60.52	3.07	60.26	3.13
7a, $C_{40}H_{29}MnO_4P_2$	69.57	4.20	69.22	4.33

[a] Ms. Heather King, UCLA.

vious section. It should be noted that several of the compounds did not give parent ion peaks but gave a fragment corresponding to the loss of several carbonyl groups as the highest observable mass unit.

Elemental analyses of selected compounds are shown in Table IV. Other new compounds were characterized through analogous spectroscopic data.

Infrared spectra in the carbonyl stretching region were obtained on a Beckman IR4 instrument equipped with a LiF prism. Solution spectra were obtained in CaF_2 cells (1.0-mm pathlength) using cyclohexane as solvent. The absorption frequencies were calibrated against a cyclohexane absorption at 2138.5 cm^{-1}.

Where solubility permitted, solution infrared spectra in the range 4000-500 cm^{-1} were also obtained, on a Perkin-Elmer 421 grating spectrometer. NaCl cells of 0.1-mm pathlength were used. CCl_4 which is transparent in the region of the characteristic bands of interest in this study (namely metal carbonyl, 2200-1800 cm^{-1}, metal acyl, 1800-1600 cm^{-1}, and oxygen coordinated metal acyl, 1600-1400 cm^{-1}) was used primarily as solvent. Where possible, spectra were also obtained in CS_2 solution to investigate the region opaque to CCl_4 (ca. 800-700 cm^{-1}). However, no bands of particular interest were found here.

Nuclear Magnetic Resonance (NMR) Spectra. Proton NMR spectra were obtained on a Varian A-60D spectrometer, and in a few cases on a Varian HA-100 instrument. ^{19}F NMR spectra were obtained on a Varian HA-100 at 94.1 MHz, using CF_3COOH as the external standard.

Proton NMR spectra of compounds **2a–7a** consist of unresolvable multiplets in the phenyl region and have not proved satisfactory for structure elucidation. However, the phenyl multiplets for the fluorinated analogs, **1b–2b**, are more clearly defined, though not further investigated here because all the necessary information for structure elucidation can be obtained from the ^{19}F NMR spectra.

Preparation of $P(p\text{-}FC_6H_4)_3$. The procedure used was an adaptation of general Grignard methods described by Kosolapoff.[29] *p*-Bromofluorobenzene (25.0 g, 16.7 ml; 200 mmol), in 30 ml of anhydrous diethyl ether was added dropwise to 3.42 g (140 mmol) of Mg turnings in a dry 300-ml Schlenk flask. As soon as the reaction began to cloud up, the flask was cooled in an ice bath and the rate of addition adjusted to maintain the reaction. (Additional ether may be needed because it boils off during the reaction.) After all the Mg dissolved, PCl_3 (6.52 g, 47 mmol) in 50 ml of ether was slowly added maintaining the flask at 0°. It was stirred at 0° for 0.5 hr and then refluxed for an additional hour. The solution was cooled and a saturated aqueous solution of NH_4Cl was slowly added to the flask with stirring. The ether portion was separated and washed with water until the ether was reasonably clear. The ether was removed by aspiration and the product dried under high vacuum and sublimed at 125°: 0.1-mm ir (4000-800 cm^{-1}) 3060 vvw, 3030 vvw, 1891 vw, 1582 vs, 1486 vs, 1451 w, 1387 m, 1292 m, 1225 vs (broad), 1195 m, 1150 vs, 1109 m, 1081 s, 1007 s, 930 vvw, 820 vs.

Synthesis of *cis*-$CH_3Mn(CO)_4L$ (L = PPh_3, 1a; $P(p\text{-}FC_6H_4)_3$, 1b; $P(p\text{-}CH_3C_6H_4)_3$, 1c). This synthesis has been reported for L = PPh_3.[4] The others were carried out analogously. A 1:1 mole ratio of $CH_3Mn(CO)_5$ (2.1 g, 10 mmol) and PPh_3 (2.6 g, 10 mmol) was refluxed in THF (100 ml) for 20 hr. The solvent was removed by aspiration and the product recrystallized from ether–hexane under nitrogen. Comparison of the carbonyl infrared spectrum with the reported absorptions[6] revealed we had the desired product, **1a**, $CH_3Mn(CO)_4PPh_3$. The yield for each (**1a**, **1b**, or **1c**) was about 80% after several successive crystallizations from the mother liquor.

The Synthesis of *cis*-$CH_3Mn(CO)_4P(OPh)_3$, 1e. $CH_3Mn(CO)_5$ (0.813 g, 3.9 mmol) and $P(OPh)_3$ (1.18 g, 1 ml, 3.8 mmol) were refluxed in 100 ml of THF under nitrogen for 18 hr. Removal of solvent by aspiration and chromatography with hexane-silica gel gave a very faint yellow band which crystallized from hexane–ether as white crystals, **1e**, $CH_3Mn(CO)_4P(OPh)_3$, in about 50% yield.

Internal Aromatic Metalation of $CH_3Mn(CO)_4PPh_3$, 1a. The title compound (0.25 g, 0.56 mmol) was refluxed in 25 ml of toluene for about 3 hr. The reaction was followed by monitoring the disappearance of a carbonyl stretching absorption in the infrared spectrum at 2055 cm^{-1} due to **1a.** The solvent was removed by aspiration and the brownish residue was applied to a silica gel–hexane chromatography column (1 × 18 in.) in a 10% benzene–hexane solution. The products were eluted by gradually increasing the percentage of benzene in hexane as described below.

The first band was pale yellow on the column but nearly colorless in solution. Recrystallization yielded 0.12 g (50%) of snow white crystals, **2a.** The compound is soluble in all organic solvents. It has been described previously.[2]

The second band was yellow and separated from the third band using 15% benzene–hexane. Recrystallization yielded about 0.02 g (10%) of bright yellow crystals, **3a.** The third band, orange-yellow, yielded about 0.03 g of gold crystals, **4a.** The fourth band consisted of a trace amount of a gold colored compound, **5a.** Under very concentrated reaction conditions, i.e., 2 g of **1a** in 10 ml, the yield of this product is raised in about 20%. The characterization of derivatives **3a**, **4a**, and **5a** as well as their analogs described below, is presented in the paper immediately following.[3]

The fifth and sixth bands were due again to trace constituents, and were shown to be products derived from the reaction of PPh_3 (**7a**) and CO (**6a**), respectively, on **2a**, see below.

Internal Aromatic Metalation of $CH_3Mn(CO)_4P(p\text{-}FC_6H_4)_3$, 1b. Compound **1b** (0.30 g, 0.60 mmol) was refluxed in 30 ml of toluene for 5 hr. The same monitoring and work-up procedure was used as with **1a**, to give the fluorine substituted analogs: **2b**, 0.13 g of white crystals (45%); **3b**, 0.04 g (13%) of gold crystals; **4b**, 0.03 g (10%) of orange crystals. These compounds are all slightly less soluble than their nonfluorinated analogs; compounds **3b** and **4b** are discussed in the following paper.[3]

Internal Metalation of $CH_3Mn(CO)_4P(p\text{-}CH_3C_6H_4)_3$, 1c. Compound **1c** (0.28 g, 0.58 mmol) was refluxed in 30 ml of toluene for 2 hr and worked up as with **1a** above. The methyl substituted analogs were found in the following yields: **2c**, 0.15 g (58%); **3c**, 0.024 g (8%); **4c**, 0.015 g (5%). Discussion of **3c** and **4c** is given in the following paper.[3]

Reaction of $P(o\text{-}CH_3C_6H_4)_3$ with $CH_3Mn(CO)_5$. $CH_3Mn(CO)_5$ (0.25 g, 1.2 mmol) and 0.36 g (1.2 mmol) of P(*o*-tolyl)$_3$ were refluxed in 50 ml of THF for 20 hr. During this time, the solution changed from white to yellow. Removal of solvent and column chromatography using hexane as eluent, followed by recrystallization yielded 0.38 g (80% based on $CH_3Mn(CO)_5$) of snow white crystals, **2d.** Since the product is colorless on the column, it was necessary to collect aliquots from the column and check them by infrared spectroscopy. No intermediate product $CH_3Mn(CO)_4$-P(*o*-tolyl)$_3$ could be observed.

Internal Aromatic Metalation of $CH_3Mn(CO)_4P(OPh)_3$, 1e. The title compound (0.415 g, 0.85 mmol) was refluxed in 25 ml of toluene for 3 hr. Removal of solvent by aspiration and chromatography with hexane on silica gel yielded two nearly colorless compounds.

The first fraction resulted in a very faint yellow oil (ca. 0.34 g, 85% yield), **2e**. Attempts to crystallize failed, and therefore elemental analysis was not obtained. The second band (colorless) yielded white crystals from hexane–ether, **7e** (ca. 0.05 g, 7.5%).

The Attempted Internal Metalation of $CH_3Mn(CO)_4L$, L = PEt_2Ph, 1f, and PMe_2Ph, 1g. Ten milligrams of $CH_3Mn(CO)_5$ was refluxed with an equivalent amount of PEt_3 and PMe_2Ph, respectively, in THF under nitrogen overnight. Removal of the solvent by aspiration yielded yellow oils **1f** and **1g**, respectively, which gave carbonyl infrared spectra analogous to those of the substituted methylmanganese complexes **1a–c**. Each oil was dissolved in toluene and allowed to reflux for 5 hr. An infrared spectrum of the reaction mixture revealed no absorptions which could be attributed to a metalation product. Removal of solvent, followed by column chromatography yielded primarily the starting material in each case and a trace of an unknown compound. Some decomposition was in evidence at the top of the column.

Carbonylation of $Ph_2\overline{P\text{-}\mu\text{-}C_6H_4\text{-}Mn}(CO)_4$, 2a. Compound **2a** (0.10 g, 0.23 mmol) was dissolved in 15 ml of diethyl ether and pressurized with CO (ca. 45 psi) in a 100-ml reaction bulb and allowed to stand for 1 week at room temperature. The solvent was removed and the residue recrystallized yielding 0.10 g of bright yellow crystals, **6a**. The same product may be obtained in high yield by bubbling CO through a toluene solution of **2a** at 40–50° for 10 hr or by pressurizing a benzene solution of **2a** with 100 psi of CO in a Hoke cylinder at 80° for 2–3 hr.

Attempted Decarbonylation of 6a. Compound **6a** (0.050 g, 0.11 mmol) was refluxed in 2 ml of octane for 1.5 hr and then cooled and applied directly to a chromatography column and eluted with 15% benzene–hexane solution first and finally a 40% benzene solution, yielded **2a** (10%) and recovered **6a** (85%).

Reaction of PPh_3 with 2a. Compound **2a** (0.110 g, 0.26 mmol) and an excess of PPh_3 (ca. 0.5 g) were dissolved in 25 ml of hexane under nitrogen and stirred at room temperature for 48 hr. No gas evolution was noted over the 48-hr period. A pale orange precipitate was isolated by filtration, washed several times with hexane, and dried under high vacuum. Attempts at recrystallization led only to a fine powder. The yield was 0.159 g of **7a** (95%).

When 0.02 g of **7a** was refluxed in 2 ml of toluene for 1.5 hr, the infrared spectrum revealed that the intensities of various bands were drastically changed and slight shifts were noted. Also a small amount of **2a** was seen in the spectrum (less than 10%). Again no gas evolution was observed. Analysis of this product showed it to be due to isomerization of **7a**, isolated above, and its infrared spectrum was identical with that of the compound isolated as the fifth fraction in the chromatography of the original reaction mixture described above.

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Supplementary Material Available. Figures A–F 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 JACS 75-3059.

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