protons. If the ligands do not have directly bonded protons, spectra are obtainable for large ligands in relatively symmetrical environments. The chemical shifts are not large and are usually to high field. No simple rationalization of the shifts can be made; however, the constancy of values observed suggests that they are largely due to nonbonded effects. Coupling constants appear to be sharply dependent on the hybridization of the nitrogen and may afford a convenient measure of the s character of metal–nitrogen bonds.

Acknowledgment. This research was supported by Grant AM15707 from the National Institutes of Health and Grant GP-37025 from the National Science Foundation.

Registry No. $Rh(en)_3Cl_3$, 14023-02-0; $Rh(pn)_3Cl_3$, 14175-72-5; $Rh(tn)_3Cl_3$, 64175-36-6; $Rh(bpy)_3Cl_3$, 32680-72-1; $Rh(phen)_3Cl_3$, 27353-21-5; (*trans*-$Rh(en)_2Cl_2$)Cl, 15444-63-0; (*trans*-$Rh(py)_4Cl_2$)Cl, 14077-30-6; enH_2^{2+}, 22534-20-9; pnH_2^{2+}, 62063-19-8; tnH_2^{2+}, 61696-59-1; $phenH^+$, 22559-75-7; $bpyH^+$, 20755-72-0; pyH^+, 16969-45-2; en, 107-15-3; pn, 78-90-0; tn, 109-76-2; bpy, 366-18-7; phen, 66-71-7; py, 110-86-1; ^{15}N, 14390-96-6.

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(5) The abreviations used are: en = ethylenediamine; pn = 1,2-diaminopropane; tn = 1,3-diaminopropane; bpy = 2,2-bipyridine; phen = 1,10-phenanthroline; py = pyridine.

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Metalation of Acetyl- and Dimethylaminomethylferrocenes with Pentacarbonyl(methyl)manganese or -rhenium: Formation of Homoannular Metalated Ferrocenes and Ferrocenylmethylaminomethylene(tetracarbonyl)manganese[1,2]

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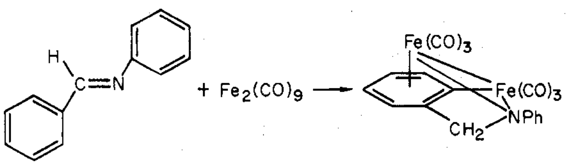
The homoannular metalation products tetracarbonyl(2-acetylferrocenyl)manganese (**3**) and -rhenium (**2**) and tetracarbonyl(2-dimethylaminomethylferrocenyl)rhenium (**9**) have been isolated and characterized. The cyclometalated product **3** is found to be much more labile to reaction with donor molecules than the phenyl analogue, tetracarbonyl(2-acetylphenyl)manganese. While **3** readily reacts with CO to form pentacarbonyl(2-acetylferrocenyl)manganese (**4**) the phenyl compound fails to show any reaction even at elevated temperature. While both species react with triphenylphosphine to form the phosphine-substituted facial tricarbonyl (e.g., *fac*-tricarbonyl(triphenylphosphino)-2-acetylferrocenylmanganese), **5**, the phosphine substitution occurs more rapidly for the ferrocenyl analogue. Treatment of benzoylferrocene with pentacarbonyl(methyl)manganese leads solely to metalation on the phenyl ring giving tetracarbonyl(2-ferrocenylcarbonylphenyl)manganese (**7**). The cyclometalated ferrocenylamine **9** undergoes electron oxidation with $FeCl_3$. Cyclic voltammetry indicates a reversible oxidation at +0.17 V (vs. SCE), lowered from that in the free amine (+0.43 V vs. SCE). The reaction of pentacarbonyl(methyl)manganese with dimethylaminomethylferrocene leads to a cyclometalation product involving the methyl group on nitrogen, i.e., tetracarbonyl(*N*-ferrocenylmethyl-*N*-methylaminomethylene)manganese (**10**).

Introduction

Up to the present study, the great majority of aromatic metalation reactions by transition metals have been observed for functionalized phenyl rings.[3] The present work was initiated to explore the metalation of substituted metallocenes, of which only a limited number of examples can be cited. It was earlier reported that FcCH=NPh [Fc = ferrocenyl, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4\text{–})$] failed to undergo metalation by $Fe_2(CO)_9$ analogous to that observed for PhCH=NPh (eq 1).[4]

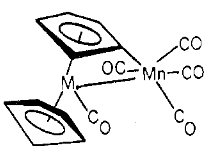


(1)

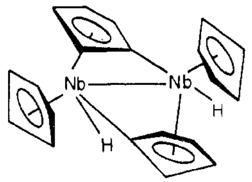
As suggested by these authors, the negative result for the metallocene is most likely due to the unavailability of the cyclopentadienyl ring π electrons for interaction with the second iron tricarbonyl moiety, a feature required in metalation by $Fe_2(CO)_9$ of the Schiff base.

That metallocene or metal–π-bonded arene rings can be σ metalated by transition-metal complexes has since been demonstrated by report of a variety of complexes, I–V,[5,6] while Seiwell[6f] has postulated metalated intermediates in the catalyzed H/D exchange in ferrocene and in cyclopentadienylrhodium compounds.

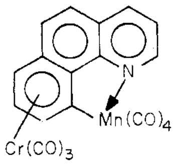
During the study described here and independently of it, Alper[7a] has reported the metalation of thiopivaloylferrocene with Na_2PdCl_4 giving product VI. More recently, Gaunt and Shaw[7b] have observed cyclometalation of dimethylaminomethylferrocene by $PdCl_4^{2-}$. It should be noted as well that lithiation, and to a lesser extent sodiation, of substituted ferrocenes has been extensively studied.[8] Through such metalated derivatives, transition-metal substituents may be brought in via the usual metathetical reactions; the mono- and bis[tris(η^5-cyclopentadienyl)uranium]ferrocenes[9] may be cited as examples of syntheses using such a pathway.



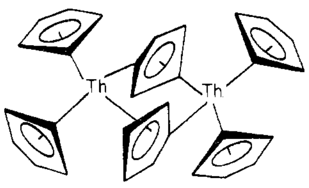
I, M = W, Mo[6a]



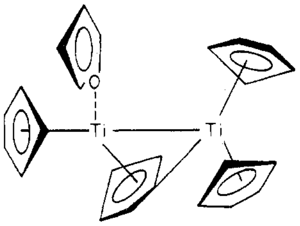
II[6b]



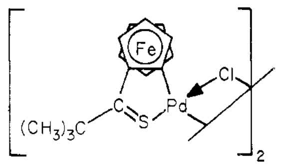
III[6c]



IV[6d]

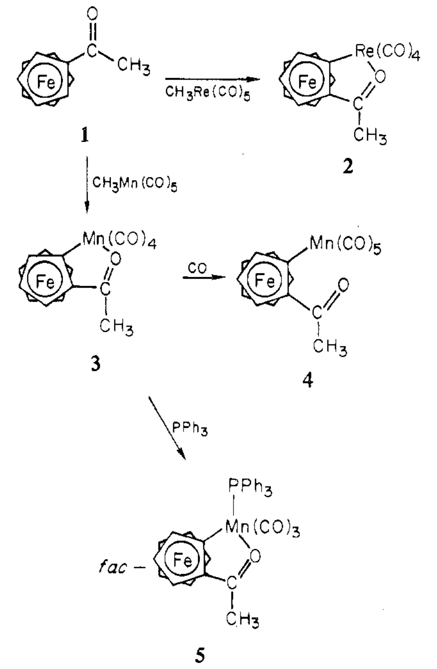


V[6e]

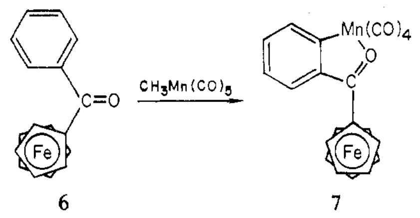


VI[7]

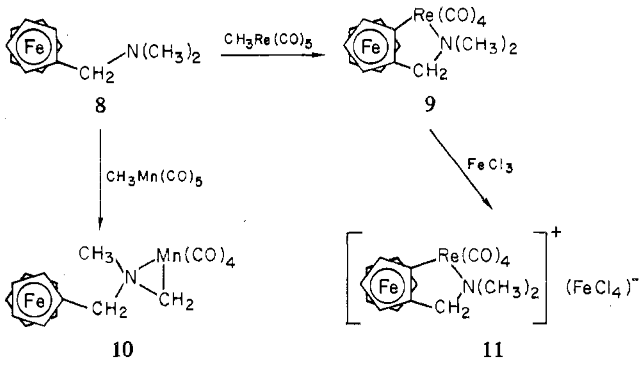
Scheme I



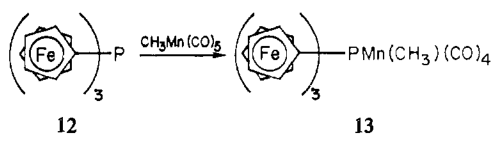
Scheme II



Scheme III



Scheme IV



Results and Discussion

The reactions studied in this work are summarized in Schemes I–IV to facilitate discussion of the spectral analysis and structural assignments of the new compounds described here.

Characterization. The mass spectra obtained for the new compounds are summarized in Table I.[10] Each includes the expected parent ion peak and peaks associated with loss of up to n CO's, where n is the number of metal carbonyls in the molecule. In each case, the $[P - nCO]^+$ peak is more intense than the $[P]^+$ or any of the $[P - xCO]^+$ peaks (where $x < n$).

Infrared absorptions of the terminal metal carbonyl stretching region of each of these new compounds are given in Table II. The patterns observed are consistent with n CO's and with the stereochemistry indicated for each of the new derivatives in the above schemes.[11]

Ferrocenyl Metalation. The following three compounds have been identified as products of homoannular ferrocenyl metalation: tetracarbonyl(2-acetylferrocenyl)rhenium (**2**), tetracarbonyl(2-acetylferrocenyl)manganese (**3**), tetracarbonyl(2-dimethylaminomethylferrocenyl)rhenium (**9**). Absorptions in the terminal M–CO region of the infrared spectrum of these and the other compounds isolated here are summarized in Table II. These are consistent with a cis tetracarbonyl moiety in each case (see also Figure 1).[10] Acyl-to-metal coordination is indicated in the IR spectra of **2** and **3** by the approximately 150 cm^{-1}[12] shift of the C═O stretch, from 1675 cm^{-1} in the free ketone to 1520 cm^{-1} in the complexes (see Table II).

The NMR spectra of **2** and **9** are shown in Figure 2. The peak positions are given in the Experimental Section. These spectra no longer contain the CH_3–M resonance of the pentacarbonyl(methyl)manganese or -rhenium at or above Me_4Si. The relative ratio of resonances in the cyclopentadienyl and methyl regions confirms the loss of a cyclopentadienyl proton as a result of metalation. The intense sharp singlet at τ 5.90–6.15 in these spectra confirms that one cyclopentadienyl ring remains unsubstituted and therefore that metalation has occurred homoannularly. As is indicated near the lower trace in Figure 2, the methylene protons and the methyl groups of **9** are nonequivalent since the environments above and below the plane of the metallocyclic ring are different. Thus the NMR spectrum of **9** includes an AB quartet with a geminal coupling of 13 Hz for the methylene protons and a singlet for each of the two methyl groups.

Competition for metalation by a phenyl vs. ferrocenyl group was explored in the reaction of benzoylferrocene, **6**, with $CH_3Mn(CO)_5$. The product, **7**, obtained in 62% yield, is shown by mass spectral and infrared data to be the metalated ketone. Its NMR spectrum shows phenyl and cyclopentadienyl resonances in relative ratio 4:9 indicating phenyl rather than ferrocenyl metalation. Indeed this spectrum is essentially a composite of those obtained for tetracarbonyl(2-acetyl-

Table II. Terminal Metal Carbonyl and Acyl Stretching Frequencies

Compd	$\nu_{C\equiv O}$,[a] cm^{-1}	$\nu_{C=O\rightarrow M}$,[b] cm^{-1}
2	2092 m, 1986 s, 1976 s, 1939 s	1530
3	2060 m, 1994 s, 1986 s, 1947 s	1530[c]
7	2079 m, 1993 s, 1988 s, 1943 s	1500
9	2084 m, 1978 s, 1968 s, 1933 s	
10	2055 m, 1970 m, 1944 vs, 1936 s	
16	2058 m, 1967 m, 1951 vs, 1937 s	
4[d]	2117 w, 2060 m, 2024 s, 2014 s, 1991 s	
5[e]	2002 s, 1902 m, b, 1897 m, b	1531
9[f]	2087 m, 1980 s, 1977 s, 1926 s	
11[f]	2095 m, 1996 s, 1986 sh, 1951 s	
13	2052 m, 1976 m, 1963 s, 1945,[g] 1930 m, b	
15	2014 vs, sh, 1934 s, b, 1909 s, b	1538
17	2058 m, 1967 m, 1951 vs, 1937 s	

[a] Cyclohexane solution unless otherwise specified in footnotes *e* and *f*, below; intensities are designated by w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, b = broad. [b] KBr mull; for reference, the carbonyl stretching frequencies in the free ketones are observed as follows: **1**, 1645 cm^{-1} (1675 cm^{-1} in cyclohexane); **6**, 1620 cm^{-1}. [c] A value of 1520 cm^{-1} in heptane solution. [d] Acyl absorption, 1658 cm^{-1}. [e] CS_2 solution. [f] THF solution. [g] Variable intensity due to the trans isomer; see text.

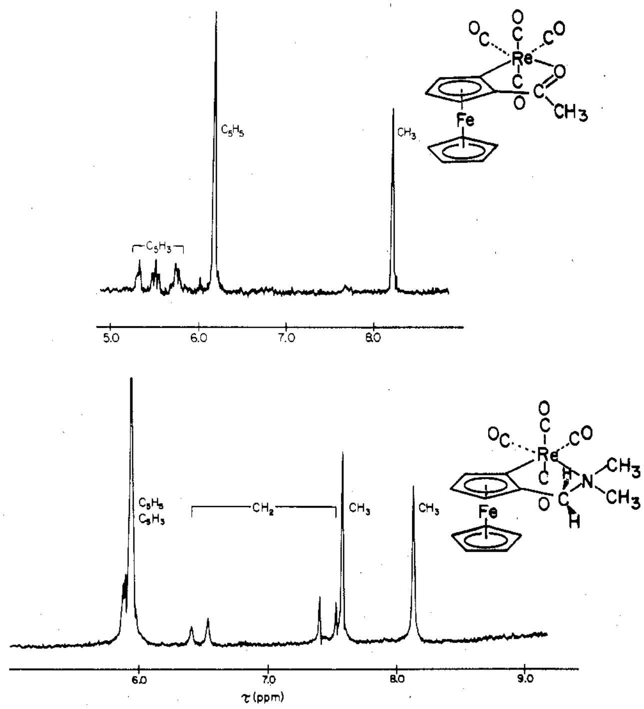


Figure 2. ^1H NMR spectra, benzene-d_6 solution, Varian A60D spectrometer: **2**, top scan; **9**, lower scan.

phenyl)manganese and acetylferrocene, neglecting methyl resonances, as is shown in Figure 3. A small solvent shift of the phenyl protons is also observed (see Experimental Section for a listing peak positions).

Thus metalation of the phenyl ring in benzoylferrocene is preferred, resulting no doubt from the strain involved in fusing two five-membered rings,[4] either in the kinetics of the reaction or in the thermodynamic stability of products (or both). Product composition could also be derived in part from relative product stabilities; the yield in the metalation of acetylferrocene was 32% while that for metalation of acetophenone was about 60%.[12] The relative instability of products containing a metalated cyclopentadienyl ring correlates with their increased reactivity, discussed below.

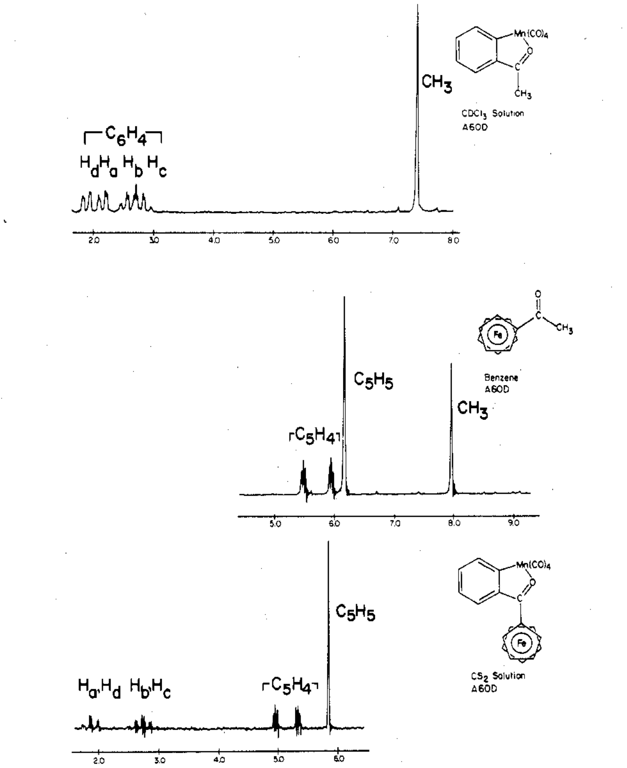


Figure 3. NMR spectra of (top) tetracarbonyl(2-acetylphenyl)manganese (**14**), (middle) acetylferrocene (**1**), and (bottom) tetracarbonyl(2-ferrocenylphenyl)manganese (**7**).

Reactivity of Tetracarbonyl(2-acetylferrocenyl)manganese (3). The title compound displays increased reactivity compared with the phenyl analogue, tetracarbonyl(2-acetylphenyl)manganese (**14**) (see Figure 3). Thus while **14** fails to undergo any discernible reaction when heated for 36 h at 60–70 °C under 3 atm of CO pressure, **3** reacts readily with CO at room temperature and 3 atm of pressure. Indeed, when CO is passed through a hexane solution of **3** at room temperature, spectral changes in the M–CO region of the infrared indicate conversion to **4**, pentacarbonyl(2-acetylferrocenyl)manganese. This is obtained in 80% yield. The appearance of the molecular ion peak at *m/e* 422 in the mass spectrum corresponds to addition of CO to **3** (28 + 394). Mass spectral peaks attributable to loss of up to five CO's are also present with $[P - 5CO]^+$ being most intense (see Table I).[10] This indicates five metal carbonyls. Furthermore, the C=O stretch in this derivative occurs at an IR frequency attributable to an uncoordinated ketone (Figure 4)[10] as required by the assigned structure. The M–CO IR spectrum of **4** (Figure 5) shows *five* metal carbonyl absorptions. This is a considerable departure from the usual $M(CO)_5$ spectrum which contains two A_1 modes and one E mode in the infrared.[11] It is apparent that in the present derivative, the degeneracy of the intense E mode has been lifted (two strong bands) and what must be the Raman-active B_1 mode between the highest energy A_1 and the split E modes has gained considerable intensity. These features indicate that the C_4 symmety of the radial carbonyl groups has been appreciably lifted. The acetyl group on the cyclopentadienyl ring bonded to manganese is no doubt exerting considerable steric influence to achieve such an observable difference.

The NMR spectrum of **4** (Figure 5) is similar to that of **3** and indicates a homoannularly disubstituted ferrocene as is expected for the assigned structure.

The formation of **4** clearly indicates lability of the manganese-to-oxygen bond in the metalated acetylferrocene, **3**. This is one of the few cases where a cyclometalation ring has been opened up by an incoming donor group. Only two other such ring openings are known to us, that reported for a

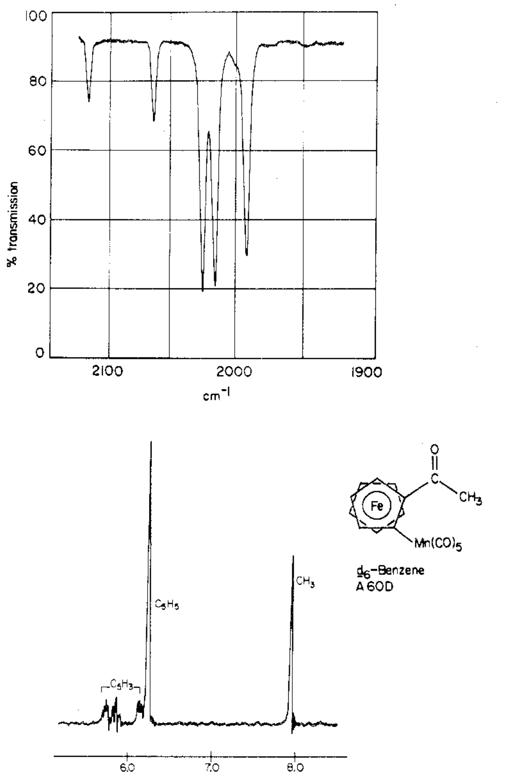


Figure 5. For 4: (top) terminal metal carbonyl infrared absorptions, cyclohexane solution, Beckman IR-4; (bottom) NMR spectrum, benzene-d_6, Varian A60D spectrometer.

phenylazophenyl derivative of palladium in which substitution by PEt_3 leads to a simple σ-bonded phenylazophenyl group[13a] and those for *N*,*N*-dialkyl-*o*-aminobenzyl derivatives of platinum which are opened by soft ligands such as dimethylphenylphosphine or CO to give the corresponding σ-bonded *o*-benzyl or acyl complexes.[13b] These previous ring opening reactions are each on square-planar complexes.

Compound **3** also undergoes a much more facile reaction with triphenylphosphine than does tetracarbonyl(2-acetylphenyl)manganese (**14**). While the reaction of **3** with triphenylphosphine occurs readily at room temperature and is completed within 15 min under hexane reflux to form **5**, compound **14** reacts with triphenylphosphine only at elevated temperatures and requires 4 h under hexane reflux to achieve complete reaction, forming *fac*-tetracarbonyl(triphenylphosphino)-2-acetylphenylmanganese (**15**).

Spectral data clearly indicate that products **5** and **15** are analogues of one another. Thus the mass spectrum of each (Table I)[10] includes a parent ion peak attributable to the triphenylphosphine substituted tricarbonyl. In addition, peaks corresponding to loss of three molecules of carbon monoxide from the parent ion of each molecule are seen, although the mass spectral peaks indicating loss of one or two metal carbonyl groups are not observed in either case. As expected for such species, an IR absorption characteristic of $C{=}O{\rightarrow}M$ is observed (see Table II and Figure 6). The geometry about manganese is deduced from the absorption pattern in the M–CO IR terminal region. Three equal-intensity maxima are observed in each case. This pattern of absorptions is that expected for a facial metal tricarbonyl in which the noncarbonyl ligands are not identical.[11]

The ^1H NMR spectra of **5** (Figure 6) exhibits the expected features. This spectrum includes an unusually long range ^{31}P to ^1H coupling for the CH_3 resonance also observed in **15**. Although typical "long range couplings" between ^{31}P and ^1H are reported for nuclei separated by three chemical bonds,[14a] a number of examples of coupling through five or more bonds have been reported involving other nuclei[14b] and there is at least one report of ^{31}P to ^1H coupling through five bonds.[15] Such coupling is found in systems of the type $(CH_3O)_2P(Y)N(CH_3)PCl_2$, Y = S or O, and $(CH_3O)_2P(S)N(CH_3)P(S)(C_4H_9)_2$ and is of the order of $^5J(PNPOCH_3)$ = 0.2–0.45 Hz.[15] The coupling observed here is 2 Hz in each case.

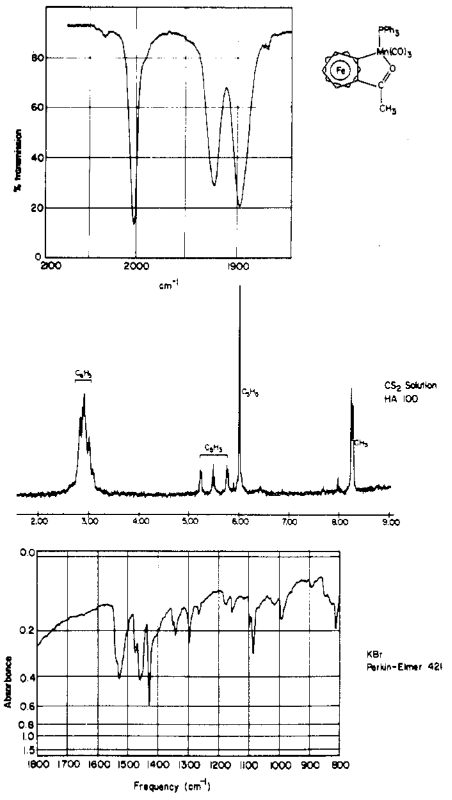
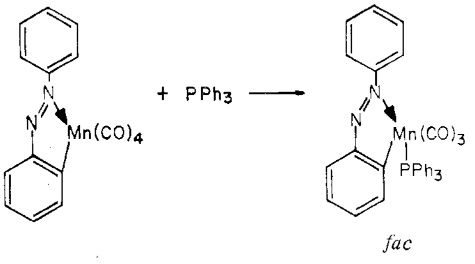


Figure 6. For 5: (top) terminal metal carbonyl region of the infrared, CS_2 solution, Beckman IR-4; (middle) NMR spectrum, CS_2 solution, Varian HA100 spectrometer; (bottom) infrared spectrum, KBr pellet, Perkin-Elmer 421 (grating).

The facial substitution observed in **5** is analogous to that observed for substitution into the (phenylazophenyl)manganese tetracarbonyl, reaction 2.[16]



(2)

Metalation of a Methyl Group of Dimethylaminomethylferrocene. Reaction of dimethylaminomethylferrocene with $CH_3Mn(CO)_5$ afforded the product **10**, characterized by its mass spectrum as a one-to-one adduct of the two starting materials less 1 mol each of CO and CH_4. The four-band M–CO IR of **10**, Table II and Figure 7b,[10] suggests a cis tetracarbonyl. Its pattern, however, is quite unlike that of previously characterized metalated ferrocenyl–$M(CO)_4$ compounds **2**, **4**, and **9** (see Figure 1),[10] which are similar to each other. The structure of **10** is clearly suggested by its NMR spectrum, Figure 8. The resonances in the region τ 5.76–6.18 due to the cyclopentadienyl protons are of combined relative area 9.0, indicating that no cyclopentadienyl substitution has occurred from the parent amine to **10**. The AB quartet at τ 7.0 (geminal coupling of 13.5 Hz) is assigned to

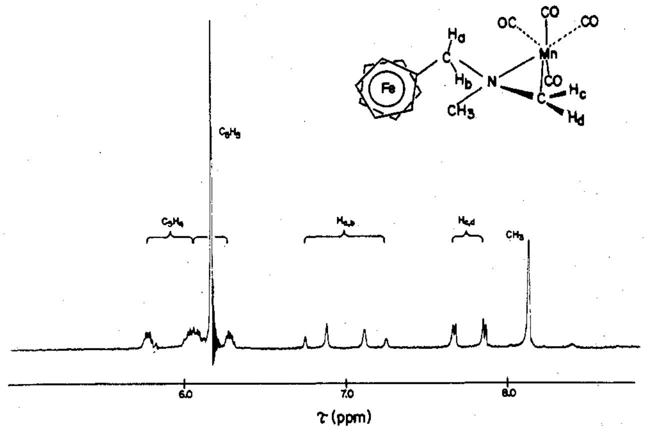
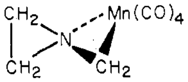


Figure 8. ^{1}H NMR spectrum of compound **10**, benzene solution, Varian HA100 spectrometer.

the methylene protons between Fc and N. There remain three higher field resonances of relative area 1:1:3, indicating loss of a proton from one of the methyl groups in the starting amine to yield a new methylene group with magnetically different protons. Compound **10** is thus identified as the methyl metalation product tetracarbonyl(*N*-ferrocenylmethyl-*N*-methylaminomethylene)manganese. The Fc–CH_2–N protons are expected to be nonequivalent as the result of an asymmetric center at nitrogen. The chemical shift of the $-CH_2-$ group bound to Mn is at high field, analogous to the resonance in $CH_3Mn(CO)_5$ which is found near τ 10. The nonequivalence of these protons (H_c, H_d) is again a result of different environments on the two sides of the plane of the metallocyclic ring (Figure 8). The structure of **10** has been determined.[17]

Our observation of the M–N–C metallocycle has been paralleled by reports of similar constructs obtained in other chemical systems and by different chemical routes. A series of dialkylaminomethylene complexes including η^2-aziridinylmethyl(tetracarbonyl)manganese (**16**) have been synthesized by treatment of the pentacarbonyl halides of manganese or rhenium with aminomethyl(trialkyl)tin derivatives.[18] Other η^2- and η^1-dialkylaminomethylene derivatives have been synthesized by the reaction of iminium salts with carbonyl anions[19] or zerovalent complexes of nickel[20] and a methylsalicylaldiminium complex of nickel was obtained through a proton transfer reaction in the treatment of $Ni(1,5\text{-}C_8H_{12})_2$ with salicylaldimine.[21]



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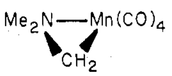
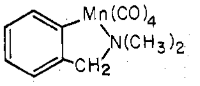


17

Independently, we have prepared η^2-dimethylaminomethyl(tetracarbonyl)manganese (**17**) for comparison with **10**. The carbonyl absorption in the infrared for these two derivatives is shown in Figure 7.[10] The resemblance between these two is quite remarkable as is their distinct difference with the other cis tetracarbonyl derivatives synthesized in the present work (**2**, **4**, and **9**; see Figure 1[10]). The $-CH_2-$ protons in **17**, like the analogous protons in **10**, resonate at high field.

The formation of **10** rather than a manganese analogue of **9** is likely another indication of the strain in the metallocyclic ring fused to a cyclopentadienyl ring. It is not unreasonable to assume that rhenium with its larger atomic radius should prefer a five-membered ring while the smaller manganese atom forms the three-membered ring in metalation of the methyl group in preference to the ferrocenyl group. In reaction of $CH_3Mn(CO)_5$ with dimethylbenzylamine, metalation does take place on the phenyl ring forming tetracarbonyl(2-dimethylaminomethylphenyl)manganese (**18**), the x-ray crystal structure of which has been reported.[22] No report of the preparation and spectral characterization of **18** has appeared; experiments in these laboratories have confirmed that **18** is the principal product in the metalation of dimethylbenzylamine with $CH_3Mn(CO)_5$. The preparation and isolation of **18** was accomplished following the general procedure for metalation reactions (see the Experimental Section). In fact there was no evidence for any methyl–metalated product. These findings suggest that in metalations with $CH_3Mn(CO)_5$ formation of systems in which a five-membered ring is fused to a six-membered ring is preferred to formation of a three-membered ring which is preferred to formation of systems of two fused five-membered rings.



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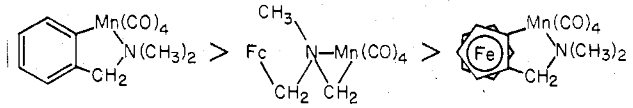


Oxidation of 9. The oxidation of the metalated ferrocene **9** is readily effected by $FeCl_3$ in ether at room temperature. Since similar chemical oxidation of **18** failed to proceed under these conditions, one-electron oxidation of the ferrocenyl portion of **9** to ferrocinium is implicated here. This conclusion is corroborated by cyclic voltammetry which shows a reversible oxidation of the free amine, **8**, at +0.43 V vs. SCE which is lowered to a potential of +0.17 V vs. SCE in the metalated species due to the presence of the electron releasing metal carbonyl substituent. Indeed, investigations of the electrochemistry of ferrocene and substituted ferrocenes by others[23] have shown that the ferrocenyl–ferrocinium couple is lowered by electron-donating groups on ferrocene while electron-withdrawing substituents increase the potential of that couple. As expected, the cyclic voltammogram of the oxidized metalated ferrocene, **11**, also shows a reversible process at 0.17 V vs. SCE, but in this case at negative potential and in the form of a reduction. The reduction wave is accompanied by a second irreversible reduction which is attributed to the tetrachloroferrate counterion. $FeCl_3$ oxidation of ferrocene to produce ferrocinium tetrachloroferrate has been reported by others.[24]

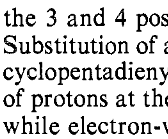
The M–CO IR spectrum of **11**, like the decrease of the oxidation potential from **8** to **9**, indicates interdependence of the ferrocenyl and metal carbonyl portions of the molecule. The pattern of absorptions in the terminal metal carbonyl region of the infrared is very similar for the parent compound, **9**, and for the oxidized form, **11**, but is shifted to higher energy in **11** (Figure 9).[10] This is as expected for compounds differing chiefly in the amount of positive charge in the complex of which only a small amount is present on the manganese atom bearing the carbonyl groups. The positive charge should decrease the amount of metal-to-carbonyl back-bonding and thereby increase the frequency of $\nu_{C\equiv O}$.

Synthesis of Tetracarbonyl(triferrocenylphosphino)methylmanganese (13). In preparation for future attempts toward the metalation of triferrocenylphosphine by $CH_3Mn(CO)_5$, the above-mentioned substitution product was synthesized requiring 5.5 h under THF reflux. This reaction thus resembles that of triphenylphosphine with $CH_3Mn(CO)_5$. Under THF reflux the latter system affords *cis*-tetracarbonyl(triphenylphosphino)methylmanganese (**19**).[25] Heating of **19** in refluxing toluene results in metalation of the phenyl group.[26] Preliminary investigation shows that heating of **13** in refluxing octane produces new spectral features in the M–CO IR spectrum with liberation of some triferrocenylphosphine. Time did not permit further investigation into this system in this work.

The carbon–hydrogen combustion analysis of **13** confirms the molecular formula of the substitution product and the parent ion peak, though weak, can be observed in the mass spectrum. The M–CO IR and NMR spectra of **13** (Figure 10)[10] indicate the presence of both cis and trans isomers. Since the intensity of the M–CO absorption at 1945 cm^{-1} varies with respect to the other M–CO absorptions, it is assigned to the trans isomer while the other absorptions are due to the cis isomer. The presence of two isomers is also indicated by the resonances in the M–CH_3 region of the NMR spectrum. A doublet ($J_{\mathrm{P-H}}$ = 8 Hz) is observed due to the predominant cis isomer, accompanied by a single weaker resonance at τ 9.96 which is taken as representing the trans isomer. Surprisingly, no other peak accompanied this signal within the region ca. 90 Hz above and below the resonance which was investigated.

Attempt to Metalate Tricarbonyl(η^5-acetylcyclopentadienyl)manganese, "Acetylcymantrene". Under the conditions employed, acetylcymantrene failed to be metalated by $CH_3Mn(CO)_5$ or $CH_3Re(CO)_5$. Comparison of the C=O stretch in acetophenone, acetylferrocene, and acetylcymantrene (1687, 1675, and 1682 cm^{-1}, respectively, in hydrocarbon solution) clearly indicates that the donor power of the cymantrene ketone should be adequate to promote metalation. However, ferrocene is a strong electron donor while cymantrene is less so with respect to substituents on Cp.[27] This may have an influence in the metalation. Like cymantrene, ruthenocene is only moderately electron donating,[27] so that an attempt to metalate acetylruthenocene may test this hypothesis. In any case, clear distinction is found for the reactivities of acetylcymantrene and acetylferrocene with respect to metalation.

On the Question of Homoannular vs. Heteroannular Metalation. All of the metalated 2-substituted ferrocenes observed to date have been of the homoannular type. This is reasonable in view of structural studies of [3]-ferrocenophanes. Those studies have shown that the cyclopentadienyl rings are tilted from parallel by angles of 8.8, 10, and 10.6° in compounds **20**,[28a] **21**,[28b] and **22**,[28c] respectively. Thus the failure to observe heteroannular metalation of ferrocenes is likely a result of the strain which would be caused by a three-membered bridge.



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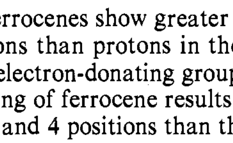

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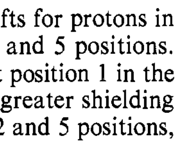

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^{1}H NMR Assignments for Protons in Substituted Cyclopentadienyl Rings. Recent NMR studies[29] of monodeuterated monosubstituted ferrocenes show greater shifts for protons in the 3 and 4 positions than protons in the 2 and 5 positions. Substitution of an electron-donating group at position 1 in the cyclopentadienyl ring of ferrocene results in greater shielding of protons at the 3 and 4 positions than the 2 and 5 positions, while electron-withdrawing substituents deshield protons at positions 3 and 4 more than those at positions 2 and 5. The presence of two types of substituents whose relative magnitudes of this effect are not now known prohibits specific assignment of the NMR resonances for the protons of the substituted cyclopentadienyl ring in the compounds discussed in this work. Correct assignment would require deuteration studies in these cases.

Experimental Section

Materials. The sources of some of the specialty chemicals mentioned frequently in the text are given as follows: silica gel for chromatography, J. T. Baker; "Florisil", Matheson Coleman and Bell; alumina, E. Merck; $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$, Pressure Chemical Co., Pittsburgh, Pa.; $Mn_2(CO)_{10}$ was also prepared in these laboratories following the method of Podall et al.[30] as modified by Calderazzo;[30b] acetylferrocene, benzoylferrocene, and dimethylaminomethylferrocene, Alfa; tricarbonyl(η^5-cyclopentadienyl)manganese, Ethyl Corp. Pentacarbonyl(methyl)manganese was prepared by a modification of the method of Closson, Kozikowski, and Coffield[31] using anhydrous ether as solvent. Methyl iodide, which has been purified by passage through a 7 mm × 20 cm column of activity I neutral alumina, was used to methylate the intermediate $NaMn(CO)_5$. The $CH_3Mn(CO)_5$ was purified by chromatography on silica gel using pentane as eluent or by sublimation under static vacuum at 30–40 °C. Pentacarbonyl(methyl)rhenium was prepared by the method of Hieber and Braun[32] and was purified by sublimation at 55 °C (10–20 μ). Tetracarbonyl(2-acetylphenyl)manganese (**14**) was prepared according to the method of McKinney et al.[12] Tetracarbonyl(2-dimethylaminomethylphenyl)manganese (**18**) was prepared by the method of Abel and Rowley.[18b] Tricarbonyl(η^5-acetylcyclopentadienyl)manganese (**23**) was prepared by G. Firestein of these laboratories according to the method of Cotton and Leto.[33] Triferrocenylphosphine, **12**, was prepared using Freidel–Crafts conditions as described by Sollott and Peterson:[34] IR (KBr) (cm^{-1}) 1103 (s, sharp) and 1025 (sh) (substituted ferrocene),[35] 1308 (vw) and 1018 (s) (Fc–P),[35] 1048 (vw) (P=O,[35] from a slight Fc_3PO impurity); NMR ($CDCl_3$) τ 5.70 (m), 5.80 (m), 5.92 (s) (lit.[36] ($CDCl_3$) τ 5.16, 5.26, and 5.39).

All common solvents and reagents were from the usual commercial vendors. The sources of other specific materials are given where mentioned in the text below.

Procedures. Anhydrous diethyl ether (ether, Mallinckrodt) was obtained in metal containers and used immediately after opening. THF was dried by distillation from CaH_2 under nitrogen. Nitrogen was purified by passage over BTS catalyst (Badische Anilin-Soda-Fabrik A.G.) to remove trace amounts of oxygen, followed by drying over $CaSO_4$ and then molecular sieves (Linde 5A). Solvents other than THF were deoxygenated by bubbling nitrogen for 10–15 min prior to use. Stirring of reaction mixtures was accomplished by magnetic stirring bars. Solvents were removed under aspiration using a Büchi rotary evaporator.

Analytical Procedures. All melting points were taken in capillaries using a Thomas-Hoover melting point apparatus or oil bath and are uncorrected. Capillaries were sealed in vacuo except where noted.

Infrared spectra of the terminal metal carbonyl region (1850–2150 cm^{-1}, M–CO IR) were recorded on a Beckman IR-4 spectrophotometer equipped with a LiF prism. Spectra were obtained in 1-mm path length CaF_2 cells except where noted and calibrated to ±1 cm^{-1} using the 2138.6-cm^{-1} peak of cyclohexane. These absorptions are designated as vs = very strong, s = strong, m = medium, w = weak, and sh = shoulder. Infrared spectra at other frequencies were recorded on a Perkin-Elmer 421 grating spectrophotometer. The functional assignment of reported absorptions follows the wavelength.

Proton magnetic resonance spectra were obtained on a Varian A 60 D or, where noted, on a HA 100 spectrometer using tetramethylsilane (Me_4Si) as an internal reference. Chemical shifts are reported in parts per million on the τ scale and the data are reported in the order chemical shift, multiplicity (where s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant, integration, and interpretation. HA 100 spectra were recorded by Dr. Kai Fang of the UCLA Chemistry Department.

Mass spectra of solids were recorded by Ms. Elizabeth Irwin of the UCLA Chemistry Department on an AE1 MS9 spectrometer. Only peaks corresponding to the parent ion ($[\mathrm{P}]^+$), loss of ligand(s) from the parent ion ($[\mathrm{P} - x\mathrm{L}]^+$), and ligand molecular ions greater than m/e 200 are reported. These peaks are reported in units of m/e and are followed by their assignment.

Carbon and hydrogen combustion analyses were performed by Ms. Heather King of the UCLA Chemistry Department.

Metalation of Substituted Metallocenes by $CH_3M(CO)_5$. General Procedure. The substituted metallocene and $CH_3M(CO)_5$ (M = Mn or Re) were added to a deaerated hydrocarbon in a 50- or 100-mL Schlenk flask. The mixture was heated with stirring to reflux. After refluxing for 2–5 h under nitrogen, the mixture was allowed to cool to room temperature under nitrogen. The solution volume was then reduced to less than 5 mL at room temperature (ca. 50 °C to remove decane) on a vacuum line equipped with a liquid-nitrogen trap. The reaction mixture was then transferred to a 2 × 25 cm column of activity

V (15% water) neutral alumina and eluted with hexane. Chromatography of metalated acetylferrocenes was carried out in dim light since the free ketone shows surface reaction with light during chromatography. The first material to elute was $M_2(CO)_{10}$ (M = Mn or Re). This was followed by the metalated ferrocene. The third band was the starting substituted ferrocene and was orange. A fourth pink band remained at the top of the column in the metalations of acetylferrocene and has not been identified. The eluent containing the metalated product was collected and evaporated to dryness at room temperature.

All of the new compounds reported in this chapter are slightly air sensitive. Solutions of these materials begin to form hexane-insoluble solids within a few hours on exposure to air, and solids show noticeable decomposition after a few days in air.

Early attempts at purification of these compounds by column chromatography on silica gel, "Florisil", or activity III neutral alumina resulted in extensive decomposition, and no pure products could be isolated. Chromatography on activity V neutral alumina resulted in good separation with little decomposition. Some specific examples follow.

Reaction of $CH_3Re(CO)_5$ with Acetylferrocene (1). $CH_3Re(CO)_5$ (0.354 g, 1.04 mmol) and **1** (0.241 g, 1.05 mmol) were dissolved in 25 mL of deaerated decane. The solution was heated to reflux for 2 h and then cooled to room temperature. Isolation was carried out as above to yield 0.214 g (40% based on starting $CH_3Re(CO)_5$) of a purple solid **2**: mp 127.5–129.5 °C; NMR (benzene-d_6) τ 5.24 (m), 5.45 (m), 5.68 (m) (combined area 3.1, C_5H_3), 6.11 (s, 5.0, C_5H_5), 8.15 (s, 2.9, $-CH_3$). Attempts to prepare an analytically pure sample of this material either by multiple recrystallizations from hexane solution or by sublimation at 90 °C (10–20 μ) were unsuccessful.

Reaction of $CH_3Mn(CO)_5$ with 1. Following the general metalation procedure 0.248 g (1.09 mmol) of **1** and 0.730 g (3.48 mmol) of $CH_3Mn(CO)_5$ in 20 mL of deaerated heptane were refluxed for 2 h. Chromatography yielded 0.138 g (32% based on starting **1**) of a dark red solid, **3**.

Analytically pure **3** could be obtained by successive recrystallizations from hexane. Crystals were collected, washed with pentane, and dried (22–23 °C (10–20 μ)): mp 126–127.5 °C; NMR (benzene-d_6) τ 5.07 (m), 5.35 (m), 5.52 (m) (combined area 2.9, C_5H_3), 6.00 (s, 5.1, C_5H_5), 8.22 (s, 3.1, $-CH_3$).

Anal. Calcd for $C_{16}H_{11}O_5FeMn$: C, 48.77; H, 2.81. Found: C, 49.14; H, 2.99.

A 17.4% yield of **3** (based on starting $CH_3Mn(CO)_5$) was obtained when 0.503 g (2.40 mmol) of $CH_3Mn(CO)_5$ and 0.607 g (2.66 mmol) of **1** were heated at reflux in 40 mL of deaerated octane for 2 h and the product isolated as above.

Despite the continued presence of starting materials (as indicated by M–CO and C=O stretches of the infrared), the reaction of $CH_3Mn(CO)_5$ with **1** failed to proceed to completion except in the presence of a large excess of $CH_3Mn(CO)_5$. In fact, the reaction unaccountably seemed not to proceed beyond the point it had reached after about 2 h under reflux.

Reaction of $CH_3Mn(CO)_5$ with Benzoylferrocene (6). Following the general metalation procedure above, 0.312 g (1.08 mmol) of **6** and 0.213 g (1.01 mmol) of $CH_3Mn(CO)_5$ were heated together in 30 mL of deaerated heptane for 6.5 h. Upon chromatography and solvent removal from the eluent, 0.306 g (62% based on $CH_3Mn(CO)_5$) of a scarlet viscous oil, **7**, was isolated. This material was very soluble in common organic solvents (hexane, acetone, THF, ether, and CCl_4) and could not be induced to crystallize. Solid was obtained only when water was added to solutions of the material in acetone, methanol, or THF. As a result, no attempt at carbon–hydrogen analysis was made: NMR (CS_2) τ 1.91 (t of d, $J_{H_aH_b} = J_{H_cH_d} = 7.5$, $J_{H_aH_b} = J_{H_bH_d} = 1.5$ Hz, 2.0, aromatic), 2.80 (quintet of d, 2.0, aromatic), 5.00 (virtual triplet, $J_{A_2B_2} = 2.0$ Hz, 2.0) (C_5H_4), 5.92 (s, 5.1, C_5H_5); NMR (acetone-d_6) aromatic region consists of τ 1.61 (d of d), 1.93 (d of d), 2.59 (quintet of d).

Reaction of $CH_3Re(CO)_5$ with Dimethylaminomethylferrocene (8). As described in the general metalation procedure 0.304 g (0.89 mmol) of $CH_3Re(CO)_5$ and 0.15 mL (0.81 mmol) of **8** were heated under reflux in 30 mL of deaerated octane for 2.5 h. The product, **9**, a red-orange solid, was isolated in 50% yield (0.214 g) based on starting $CH_3Re(CO)_5$. It was recrystallized by dissolving in a minimal amount of ether, adding an equal amount of hexane, and reducing the solution volume in a stream of nitrogen until crystallization began. The solution was then warmed to dissolve the crystals. Slowly cooling the solution to −20 °C resulted in crystal formation. A second such recrystallization followed by washing with pentane and drying (22–23 °C (10–20 μ)) afforded analytically pure material: mp 115–117 °C; NMR (benzene-d_6, HA 100) τ 5.88 (s, C_5H_3), 5.92 (br s, C_5H_3 and C_5H_5) (combined area 8.0), 6.90 (AB quartet, $J_{AB} = 13$ Hz, $\delta_A = \tau$ 7.39, $\delta_B = \tau$ 6.41, $-CH_2-$), 7.50 (s, $-CH_3$) (combined area 5.1), 8.05 (s, 2.9, $-CH_3$).

Anal. Calcd for $C_{17}H_{16}O_4NFeRe$: C, 37.79; H, 2.98. Found: C, 37.91; H, 3.23.

Reaction of $CH_3Mn(CO)_5$ with 8. This reaction was carried out and the product isolated as in the general metalation procedure by using 0.220 g (1.05 mmol) of $CH_3Mn(CO)_5$ and 0.402 g (1.65 mmol) of **8** in 40 mL of deaerated heptane and refluxing for 5 h. The product was a yellow solid, **10** (0.162 g, 38% based on $CH_3Mn(CO)_5$), which was twice recrystallized from hexane to obtain analytically pure material: mp 107.5–110 °C; NMR (benzene, HA 100) τ 5.76 (m), 6.06 (m), 6.28 (m, C_5H_4), 6.18 (s, C_5H_5) (combined area 9.0), 7.00 (AB quartet, $J_{AB} = 13.5$ Hz, $\delta_A = \tau$ 7.17, $\delta_B = \tau$ 6.83, 2.2, $FcCH_2N-$), 7.67 (d, $J_{\text{gem H-H}} = 2$ Hz, 1.0) 7.86 (d, $J_{\text{gem H-H}} = 2$ Hz, 1.0) (both due to $\overline{\mathrm{NCH_2M}}\mathrm{n}$), 8.14 (s, 3.0, $-CH_3$).

Anal. Calcd for $C_{17}H_{16}O_4NFeMn$: C, 49.91; H, 3.94. Found: C, 49.86; H, 3.89.

Reaction of $BrMn(CO)_5$ with $(CH_3)_2NCH_2Sn(n\text{-}Bu)_3$ (25). The tin compound was obtained from the following sequence of reactions (Bu = butyl)

$$(CH_3)_2NH + PhSH + CH_2O(aq) \xrightarrow[\Delta]{} \underset{\textbf{24}}{PhSCH_2N(CH_3)_2}$$

$$(n\text{-}Bu)_3SnCl + Li \rightarrow (n\text{-}Bu)_3SnLi$$

$$(n\text{-}Bu)_3SnLi + PhSCH_2N(CH_3)_2 \rightarrow \underset{\textbf{25}}{(n\text{-}Bu)_3SnCH_2N(CH_3)_2}$$

Phenyl dimethylaminomethyl sulfide (**24**) was prepared according to the method of Grillot and Thompson[37] using lithium tri-*n*-butyltin in THF prepared by the procedure of Tamborski et al.[38] $(n\text{-}Bu)_3SnLi$ in THF and $PhSCH_2N(CH_3)_2$ were combined as described by Peterson.[39] The details of these procedures are also given in ref 2. $BrMn(CO)_5$ was prepared by the action of excess Br_2 on $Mn_2(CO)_{10}$ in CCl_4 and used without further purification.

A solution of 0.295 g (1.07 mmol) of $BrMn(CO)_5$ and 0.39 g (1.15 mml) of **25** in 30 mL of dry deaerated THF was heated under reflux for 3 h. After cooling under nitrogen, the THF was removed and the residue transferred to a 30 × 2 cm column of activity V neutral alumina. Elution with hexane resulted in a single yellow band, which was collected and concentrated to an orange-yellow oil, **17**; NMR (benzene) τ 7.95 (s, 2.0, $\overline{\mathrm{NCH_2Mn}}$) and 8.05 (s, 6.0, $-N(CH_3)_2$).

Reaction of $CH_3Mn(CO)_5$ with Triferrocenylphosphine (Fc_3P), 12. A solution of 0.223 g (0.40 mmol) of **12** and 0.72 g (1.39 mmol) of $CH_3Mn(CO)_5$ in 100 mL of dry deaerated THF was heated under reflux in a nitrogen atmosphere. The reaction was monitored by TLC (silica gel plates eluted with benzene). The Fc_3P was found to be consumed after 5.5 h of reflux. After this period of time the reaction mixture was allowed to cool to room temperature under nitrogen. Solvent was removed. The resulting orange solid was dissolved in a minimal volume of CH_2Cl. Hexane was added (50% by volume) and solvent was removed under aspiration until solid began to form. Cooling resulted in orange crystals of **13** (0.95 g, 30%) which were washed with 50:50 CH_2Cl_2–hexane and dried (22–23 °C (10–20 μ)); mp 194 °C (with decomposition); NMR (CD_2Cl_2) τ 5.49 (m), 5.83 (s), 5.94 (s) (combined area 26.9, C_5H_4 and C_5H_5), 9.96, 10.12, 1.30 ($J_{\text{cisP-H}} = 2$ Hz, combined area 2.8, $-CH_3$).

Anal. Calcd for $C_{35}H_{30}O_4PFe_3Mn$: C, 54.73; H, 3.94. Found: C, 54.54; H, 4.06.

Heating of **13** in refluxing octane led to changes in the M–CO IR spectrum, which were complete within 4 h. Cooling of the hot octane solution led to crystallization of an orange solid, which is thought from R_f on TLC and melting point measurements to be triferrocenylphosphine. This material showed only a small absorption in the M–CO region of the IR spectrum probably due to an impurity. Column chromatography of the mother liquor on activity III neutral alumina afforded small amounts of three compounds. These materials have not been characterized, except for the following M–CO IR data (compounds are numbered in the order in which they eluted from the column): compound I, 2055 (m), 1984 (m), 1962 (s), 1953 (sh), 1945 (m), and 1935 cm^{-1} (m); compound II, three equal-intensity absorptions at 2004, 1924, and 1983 cm^{-1}; compound III, 1947 cm^{-1}.

Reaction of 3 with CO. A solution of 0.092 g (0.23 mmol) of **3** in 20 mL of hexane was transferred to a Hoke bomb, and the contents were degassed by freezing with liquid nitrogen, evacuating, and thawing and repeating the cycle twice. While at −178 °C the bomb was then pressurized with 3 atm of CO and allowed to warm to room temperature. After 20 h the pressure was released and the solution removed by syringe. Concentrating the clear brown solution in a stream of CO to 1 mL and cooling resulted in 0.078 g (80%) of a red-brown crystalline solid, **4**, which was washed with pentane and dried (22–23 °C (10–20 μ)). Alternatively this material could be isolated by chromatography on activity V neutral alumina: mp 104–106 °C (with decomposition); NMR (benzene-d_6) τ 5.77 (m), 5.90 (m), 6.18 (m) (C_5H_4), 6.29 (s, C_5H_3) (combined area 8.2), and 7.98 (s, 2.9, $-CH_3$).

Anal. Calcd for $C_{17}H_{11}O_6FeMn$: C, 48.38; H, 2.68. Found: C, 48.42; H, 2.83.

Reaction of 3 with Triphenylphosphine. A solution of 0.179 g (0.45 mmol) of **3** in 5 mL of hexane was bubbled with nitrogen for 5 min and then heated near reflux under nitrogen. To the above hot solution was added a deaerated solution of 0.120 g (0.45 mmol) of triphenylphosphine in 15 mL of hexane, over 3 min. After heating under reflux for 30 min (M–CO indicated that the reaction was complete after 15 min), THF (ca. 3 mL) was added to dissolve the dark brown solid which had formed. The mixture was allowed to cool to room temperature. Upon further cooling 0.178 g (58%) of dark brown microcrystals, **5**, was obtained: mp 185–188 °C; NMR (CS_2, HA 100) τ 2.90 (m, 15.6, aromatic), 5.23 (m, 1.1), 5.48 (m, 1.0), 5.78 (m, 1.1) (C_5H_3), 6.02 (s, 4.5, C_5H_5), 8.24 (d, J_{P-H} = 2 Hz, $-CH_3$). An analytical sample was obtained by dissolving in ether, diluting with hexane (20% by volume), reducing the solution volume by ca. 30%, and cooling. The dark brown crystals which formed were collected, washed with 50:50 ether–hexane, and dried (22–23 °C (10–20 μ)).

Anal. Calcd for $C_{33}H_{26}O_4PFeMn$: C, 63.08; H, 4.17. Found: C, 63.01; H, 4.14.

Attempted Reaction of 14 with CO. A solution of 0.195 g (0.68 mmol) of **14** in 40 mL of heptane was syringed into a Hoke bomb. The bomb and contents were degassed and pressurized with 3 atm of CO as described above. After warming to room temperature, the bomb was heated at 60–70 °C for 36 h. At that time it was allowed to cool to room temperature and was then vented through a bunsen flame to burn the CO as it escaped. The clear, yellow solution was syringed from the bomb. Metal–carbonyl IR spectra showed only absorptions attributable to starting material, **14**.

Reaction of 14 with Triphenylphosphine. A 0.177-g (0.62 mmol) sample of **14** was refluxed with 0.329 g (1.26 mmol) of triphenylphosphine in 25 mL of deaerated hexane. The progress of the reaction was monitored by M–CO IR spectra which indicated three new absorptions. Some unreacted **14** remained after 4 h. After an additional 3 h of reflux, the reaction had proceeded no further and the mixture was allowed to cool under nitrogen. This was chromatographed on a 2 × 35 cm "Florisil" column. After eluting with hexane to remove unreacted **14** and triphenylphosphine, a red to yellow band was eluted with 50% benzene–hexane. This band was collected and evaporated to a red solid. Recrystalliztion of this solid by dissolving in a minimal amount of dry THF and adding heptane to cloud the solution and cooling gave 0.280 g (90%) of *fac*-tricarbonyl(triphenylphosphino)-2-acetylphenylmanganese (**15**). Analytically pure material was obtained by a second recrystallization from THF–heptane. Crystals were washed with pentane and dried (22–23 °C (10–20 μ)): mp 166 °C (d, open capillary); NMR (CS_2) τ 2.05 (m, aromatic), which collapsed to a singlet upon ^{31}P irradiation, 2.82 (m, aromatic) (combined area 19.0), and 8.00 (d, J_{P-H} = 2.5 Hz, 3.0, $-CH_3$).

Anal. Calcd for $C_{29}H_{22}O_4PMn$: C, 66.93; H, 4.26. Found: C, 67.05; H, 4.09.

Attempts to reproduce this reaction at room temperature failed.

Reaction of 9 with FeCl₃. To a solution of **9** (0.088 g, 0.16 mmol) in dry ether in an oven-dried 100-mL Schlenk flask under nitrogen was added 0.197 g (1.21 mmol) of $FeCl_3$ in 10 mL of dry ether. The mixture immediately turned olive green and precipitate formed. After 30 min of stirring the olive green solid, **11**, was collected by suction filtration. This material was recrystallized by adding ether to a CH_2Cl_2 solution until clouding began and then cooling to afford 0.083 g (70%) of **11**. Analytically pure material was obtained from a second crystallization: mp 111–113 °C (open capillary); M–CO IR (THF) 2095 (m), 1996 (s), 1986 (sh), and 1951 cm^{-1} (s).

Anal. Calcd for $C_{17}H_{16}NO_4Fe_2ReCl_4$: C, 27.67; H, 2.19. Found: C, 27.71; H, 2.24.

Attempted Reaction of 14 with FeCl₃. A 0.351-g (2.16 mmol) portion of $FeCl_3$ was weighed into a nitrogen-filled vial and transferred under nitrogen to an oven-dried 100-mL Schlenk flask, and 10 mL of anhydrous ether was added. A solution of 0.216 g (0.75 mmol) of **14** in 20 mL of anhydrous ether was added and the mixture was allowed to stir at room temperature. During this time, a small amount of brown solid precipitated but there was no other evidence of reaction. After stirring for 6 h the mixture was extracted with three 15-mL portions of H_2O. The ether layer was dried ($MgSO_4$) and evaporated to dryness leaving a yellow solid. This material was chromatographed on a 2 × 35 cm silica gel column with hexane as eluent and 0.184 g (85%) of starting material **14** was collected and identified by M–CO IR and NMR spectra. Despite an odor of acetophenone from the solid before chromatography, no free C=O stretch could be seen in the IR spectrum.

Cyclic voltammograms of compounds **8**, **9**, and **11** were obtained with the help of Dr. Timm E. Paxson on an instrument designed and built by Dr. R. J. Wiersema.[41] The voltammograms were recorded vs. the saturated calomel electrode (SCE) in CH_2Cl_2 solution with $(n\text{-Bu})_4NPF_6$ as supporting electrolyte. The following couples were observed: $\mathbf{8} \rightarrow \mathbf{8}^+ + e^-$, +0.43 V (reversible); $\mathbf{9} \rightarrow \mathbf{9}^+ + e^-$, +0.17 V (reversible); $\mathbf{11} + e^- \rightarrow \mathbf{11}^-$, −0.17 V (reversible) accompanied by −0.03 V (irreversible).

Attempted Reaction of CH₃Re(CO)₅ with Tricarbonyl(η⁵-acetylcyclopentadienyl)manganese (23). This reaction was carried out as described in the general metalation procedure above, using 0.112 g (0.54 mmol) of $CH_3Re(CO)_5$ and 0.250 g (1.01 mmol) of **23** in 20 mL of deaerated decane at 150–160 °C. IR spectra recorded after 2 and 4 hr of heating showed no new M–CO absorptions. After 4 h only those absorptions due to unreacted **23** could be seen. The ketone stretch of **23** remained and there was no indication of the stretch due to a coordinated acyl. Thus no metalation reaction occurs.

Attempted Reaction of CH₃Mn(CO)₅ with 23. This reaction was attempted by G. Firestein of these laboratories following the general procedure described above.

A solution of 0.12 g (0.57 mmol) of $CH_3Mn(CO)_5$ and 0.104 g (0.42 mmol) of **23** in cyclohexane was refluxed for 8 h. M–CO IR spectra of the reaction mixture after 2, 4, and 8 h of heating showed no change from the spectrum recorded at time zero due to starting $CH_3Mn(CO)_5$ and **23**. Thus no reaction appeared to have taken place.

In a second attempt, 0.123 g (0.58 mmol) of $CH_3Mn(CO)_5$ and 0.101 g (0.41 mmol) of **23** were heated together at reflux in *p*-dioxane for 6 h. Solvent was then removed by aspiration and the IR spectrum of the M–CO region was recorded (cyclohexane). This spectrum showed absorptions attributable to $Mn_2(CO)_{10}$ and unreacted **23** with no indication of metalated products.

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Registry No. **1**, 1271-55-2; **2**, 56665-70-4; **3**, 56708-99-7; **4**, 64175-40-2; **5**, 64175-39-9; **6**, 1272-44-2; **7**, 64175-38-8; **8**, 1271-86-9; **9**, 56708-97-5; **10**, 56725-20-3; **11**, 64188-88-1; **12**, 1292-82-6; **13** (cis isomer), 64188-86-9; **13** (trans isomer), 64281-56-7; **14**, 50831-23-7; **15**, 64175-37-7; **16**, 52638-18-3; **17**, 52638-14-9; **18**, 38162-89-9; **23**, 12116-28-8; **25**, 26285-62-1; $CH_3Re(CO)_5$, 14524-92-6; $CH_3Mn(CO)_5$, 13601-24-6; $BrMn(CO)_5$, 14516-54-2; CO, 630-08-0; PPh_3, 603-35-0; $FeCl_3$, 7705-08-0.

Supplementary Material Available: Mass spectral data (Table I) and IR spectra (Figures 1, 4, 7, 9, and 10) (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This is part 12 in a series on metalation reactions; for part 11 see B. T. Huie, C. B. Knobler, R. J. McKinney, and H. D. Kaesz, *J. Am. Chem. Soc.*, in press.

(2) This paper is taken from the Ph.D. dissertation of S. A. S. Crawford, University of California, Los Angeles, 1975.

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Crystal and Molecular Structure of *N*-Ferrocenylmethyl-*N*-methylaminomethylene(tetracarbonyl)manganese[1]

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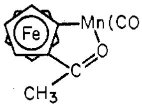
The crystal and molecular structure of *N*-ferrocenylmethyl-*N*-methylaminomethylene(tetracarbonyl)manganese, $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)CH_2(CH_3)\overline{NCH_2Mn}(CO)_4$, has been determined by a three-dimensional x-ray diffraction study. The compound forms yellow crystals which are of the primitive space group $P2_12_12_1$, of the orthorhombic system, with $a = 10.152$ (2), $b = 21.348$ (4), and $c = 8.104$ (1) Å. Diffraction data were collected using Mo Kα radiation and a Syntex $P\bar{1}$ automated diffractometer. The structure was solved by use of Patterson and Fourier summations and was refined by full-matrix least-squares techniques to a conventional discrepancy factor $R = 0.057$ for 1271 unique nonzero reflections with $2\theta < 55°$. All atoms were located. The novel $\overline{\mathrm{Mn{-}N{-}C}}$ metallocycle is best viewed as an aminomethylene group acting as a three-electron donor to the manganese atom. The principal distinguishing features are a C–N bond length of 1.42 (1) Å and a C–N–C bond angle of 110.4° for the groups bonded to the nitrogen atom. These parameters are similar to those found in the related $\overline{\mathrm{Ni{-}N{-}C}}$ metallocycle obtained in the reaction of an iminium salt with a Ni^0 complex. The two cyclopentadienyl rings in the title compound are in an *eclipsed* conformation.

Introduction

A recent communication from these laboratories reported the metalation of acetylferrocene (**1**) and dimethylaminomethylferrocene (**2**) with pentacarbonylmethylmanganese (**3**) and -rhenium (**4**).[2] The product of each of these reactions, except that of **2** and **3**, was the homoannular metalation of ferrocene, i.e., product **5**. The metal–carbonyl infrared stretching vibrations and proton magnetic resonance indicated that the reaction of **2** with **3** had resulted in metalation of a methyl group to form a compound presumed to be **6**. Both prior and concurrent structural reports of metal–nitrogen–



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