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# NEW MANGANESE, IRON, AND MOLYBDENUM CARBONYL CARBENE COMPLEXES

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## Summary

The carbene complexes $[Mn(CO)_3(L)_2CR(OMe)]PF_6$ ($L_2$ = 1,2-bis(diphenylphosphino)ethane, R = Me, $p$-$C_6H_4F$, $m$-$C_6H_4F$; L = $P(OMe)_3$, R = Me), $[Mn(CO)_4(PPh_3)CMe(OMe)]PF_6$, $[C_5H_5Fe(CO)(PPh_3)CMe(OMe)]PF_6$ and $[C_5H_5Mo(CO)_2(PPh_3)CMe(OMe)]PF_6$ have been prepared by alkylation of the appropriate acylmetal complex with $MeOSO_2F$, followed by metathetical anion exchange with $PF_6^-$. Reactions of the manganese compounds with phosphines occur to give phosphonium salts, and the acylmetal complex is recovered; this reaction reaffirms the oxonium formulation generally accorded to these complexes. Reaction of the manganese diphos complexes with methyl or $p$-chlorophenyl isocyanides results in carbene ligand displacement, giving $[Mn(CO)_3(diphos)CNR]PF_6$. With the analogous trimethylphosphite complexes, insertion of the isocyanide into the carbene—metal bond occurs.

## Introduction

Alkylation of acylmetal carbonyl species has been used extensively for the formation of metal carbonyl carbene complexes [1]. This method has been applied primarily when the acylmetal precursor is anionic; in these species the acyl oxygen basicity is relatively high and its reaction with an $R^+$ group (from such reagents as $R_3O^+$ or $ROSO_2F$) is favorable. The same reactions with the common uncharged acylmetal complexes [e.g. $RCOMn(CO)_5$] have not been reported, and it is possible that such reactions might not occur since the acyl oxygens of these species would be expected to be less basic.

It is known, however, that neutral acylmetal species possessing one or more donor ligands, such as phosphines substituted for carbon monoxide, can be alkylated [2]. This is a reasonable observation since in such a species the acyl oxygen should be more basic due to greater $\pi$-back donation to the acyl group from the metal. Carbene complexes of the formulas $[C_5H_5M(CO)(PPh_3)$-

$CMe(OR)]^+$ (M = Fe, Ru), $[C_5H_5Ru(CO)(L)CMe(OR)]^+$ (L = CO, $PCy_3$; Cy = $C_6H_{11}$) and $[C_5H_5Mo(CO)_2(PPh_3)CMe(OR)]^+$ (R = Me, Et) have been reported [2].

We have now prepared a number of manganese complexes by the same route, from the substituted acylmetal carbonyl compounds and $MeOSO_2F$ [3]. We also report several reactions of these species with donor ligands, and some interesting contrasts which developed in this work wherein the reactions were found to be dependent on the ligands present.

## Experimental

All reactions were carried out under nitrogen. The PMR data were obtained on a JEOL-NM-MH-100 spectrometer using acetonitrile-$d_3$ solutions unless otherwise noted and tetramethylsilane as an internal standard. Infrared spectra were taken on a Perkin—Elmer 457 instrument with suitable scale expansion, using dichloromethane solutions. Conductivity measurements were made on dichloromethane solutions between $4.0 \times 10^{-4}M$ and $6.0 \times 10^{-4}M$ with a Beckman conductivity bridge, Model RC-18-A and a Beckman conductivity cell with cell constant k = 0.20. Melting points were taken on a Kofler hot-stage and are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Published preparations of the following acylmetal complexes are cited: *m*- and *p*-$Mn(CO)_3(diphos)COC_6H_4F$ [4], $Mn(CO)_3(diphos)COMe$ [5], $Mn(CO)_3[P(OMe)_3]_2COMe$ [6], $Mn(CO)_4(PPh_3)COMe$ [7], $C_5H_5Fe(CO)(PPh_3)COMe$ [8], $C_5H_5Mo(CO)_2(PPh_3)COMe$ [9].

### *Preparations of carbene complexes*

The syntheses of the various carbene complexes were carried out by the following general method.

*$[Mn(CO)_3(diphos)CMe(OMe)]PF_6$*. To a solution of $Mn(CO)_3$(diphos)-COMe (0.25 g, 0.43 mmol) in dry benzene (5 ml) was added methyl fluorosulfonate (Aldrich) (1 ml, excess) and the mixture stirred for 0.5 h at room temperature. The solution darkened a little during the reaction. The yellow oil obtained after evaporating the solvent was dissolved in 1/1 chloroform/acetone (10 ml) and a solution of $NH_4PF_6$ (0.5 g, excess) in acetone (10 ml) was added. After stirring the cloudy mixture for 0.5 h the solvent was again removed and the residue extracted with chloroform. Solvent removal gave a clear pale yellow oil which crystallized from acetone/ethyl ether on cooling, giving the product (0.25 g, 78%) as pale yellow prisms, m.p. 149-151° (dec.).

Found: C, 52.47; H, 4.43; P, 11.69. $C_{32}H_{30}F_6MnO_4P_3$ calcd.: C, 51.91; H, 4.08; P, 12.55%. IR: 2030s, 1976s(br), 1960s(br) [$\nu$(CO)]. PMR: $\tau$6.97 (s, 3H, OMe); 7.11 (s, 3H, Me); 6.83 (m, AA'BB', 4H, $CH_2$); 2.55 (m, 20H, Ph). $\Lambda_M$ = 43.3 $cm^2ohm^{-1}mol^{-1}$*.

*$[Mn(CO)_3(diphos)\{C(p\text{-}C_6H_4F)OMe\}]PF_6$*. Pale yellow prisms from acetone, 71% yield, m.p. 168-171°.

Found: C, 53.73; H, 4.05; P, 10.71. $C_{37}H_{31}F_7MnO_4P_3$ calcd.: C, 54.16; H, 3.81; P, 11.33%. IR: 2036s, 1982s(br), 1964s(br) [$\nu$(CO)]. PMR: $\tau$6.92 (s, 3H, OMe); 6.62 (m, AA'BB', 4H, $CH_2$); 2.86 (t, 2H) and 3.65 (d of d, 2H

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* For comparison, $4.86 \times 10^{-4}M$ $[n\text{-}Bu_4N]ClO_4$ gives a value for $\Lambda_M$ = 31.2 $cm^2ohm^{-1}mol^{-1}$.

second order pattern from $C_6H_4$); 2.50 (m, 20H, Ph). $\Lambda_M$ = 37.6 cm$^2$ohm$^{-1}$mol$^{-1}$.

$Mn(CO)_3(diphos)\{C(m\text{-}C_6H_4F)OMe\}]PF_6$. Pale yellow needles from acetone/diethyl ether, 77% yield, m.p. 157-160°.

Found: C, 54.13; H, 3.71; P, 11.20. $C_{37}H_{31}F_7MnO_4P_3$ calcd.: C, 54.16; H, 3.81; P, 11.33%. IR: 2026s, 1982s(br), 1963s(br) [$\nu$(CO)]. PMR: $\tau$6.91 (s, 3H, OMe); 6.60 (m, AA'BB', 4H, $CH_2$); 2.84-4.12 (br. m, 4H, $C_6H_4$); 2.48 (m, 20H, Ph). $\Lambda_M$ = 37.6 cm$^2$ohm$^{-1}$mol$^{-1}$.

The crystalline fluorosulfonate salt of this cation could be obtained directly from the reaction in essentially quantitative yield.

$[Mn(CO)_3(diphos)\{C(m\text{-}C_6H_4F)OMe\}]OSO_2F$. Yellow prisms from benzene, 100% yield, m.p. 111-114°.

Found: C, 59.15; H, 4.38. $C_{37}H_{31}FMnO_7P_2S$ calcd.: C, 58.81; H, 4.14%. IR: 2034s, 1984s(br), 1960s(br) [$\nu$(CO)]. PMR: Same as $PF_6$ salt. $\Lambda_M$ = 33.8 cm$^2$ohm$^{-1}$mol$^{-1}$.

$[Mn(CO)_3\{P(OMe)_3\}_2\{CMe(OMe)\}]PF_6$. Pale yellow prisms from methanol/diethyl ether, 79% yield, m.p. 88-90°.

Found: C, 24.54; H, 3.87; P, 15.02. $C_{12}H_{24}F_6MnO_{10}P_3$ calcd.: C, 24.42; H, 4.10; P, 15.75%. IR: 2066s, 2022vw, 1989s(br) [$\nu$(CO)]. PMR: $\tau$5.61 (s, 3H, OMe); 6.98 (s, 3H, Me); 6.24 (t, $J$ = 5Hz, 18H, $P(OMe)_3$ in *trans* positions). $\Lambda_M$ = 59.0 cm$^2$ohm$^{-1}$mol$^{-1}$.

$[Mn(CO)_4(PPh_3)\{CMe(OMe)\}]PF_6$. Prepared in dichloromethane. Fine off-white needles from acetone/diethyl ether, 45% yield, m.p. 169-172°.

Found: C, 47.95; H, 3.40; P, 9.90. $C_{25}H_{21}F_6MnO_5P_2$ calcd.: C, 47.49; H, 3.35; P. 9.80%. IR: 2094m, 2028m, 2006s [$\nu$(CO)]. PMR: $\tau$5.99 (s, 3H, OMe); 7.09 (s, 3H, Me); 2.48 (m, 15H, Ph). $\Lambda_M$ = 41 cm$^2$ohm$^{-1}$mol$^{-1}$.

$[(C_5H_5)Fe(CO)(PPh_3)\{CMe(OMe)\}]PF_6$. Dark yellow prisms from acetone/diethyl ether, 84% yield, m.p. 170-173°. (The $BF_4$ salt of this complex is known [2].)

Found: C, 53.08; H, 4.36; P, 9.82. $C_{27}H_{26}F_6FeO_2P_2$ calcd.: C, 52.79; H, 4.27; P, 10.08%. IR: 2023w, 1976s(br) [$\nu$(CO)]. PMR: $\tau$5.85 (s, 3H, OMe); 7.66 (s, 3H, Me); 5.09 (s, 5H, $C_5H_5$); 2.50 (m, 15H, Ph). $\Lambda_M$ = 51.8 cm$^2$ohm$^{-1}$mol$^{-1}$.

$[C_5H_5Mo(CO)_2(PPh_3)\{CMe(OMe)\}]PF_6$. Prepared in dichloromethane. Bright yellow needles from acetone/diethyl ether, 62% yield, m.p. 126-129°. The complex is unstable in air, surface oxidation giving a green decomposition product. Acetone of crystallization could not be removed by drying under vacuum at 39° for 10 h.

Found: C, 50.49; H, 4.20; P, 8.81. $C_{28}H_{26}F_6MoO_3P_2\cdot$acet calcd.: C, 50.28; H, 4.36; P, 8.37%. IR: 1997m(br), 1916s(br) [$\nu$(CO)] and 1712 [$\nu$(C=O)]. PMR: $\tau$5.67 (s, 3H, OMe); 6.89 (s, 3H, Me); 4.57 (s, 5H, $C_5H_5$); 2.52 (m, 15H, Ph). $\Lambda_M$ = 54.7 cm$^2$ohm$^{-1}$mol$^{-1}$.

The compounds $Mn(CO)_5CO(m\text{-}C_6H_4X)$ (X = F, Cl), $Mn(CO)_5CO(p\text{-}C_6H_4F)$, $C_5H_5Fe(CO)_2CO(p\text{-}C_6H_4F)$, and $Co(CO)_3(PPh_3)CO(m\text{-}CH_2C_6H_4F)$ did not react under the conditions given and were recovered unchanged from the reaction mixtures.

### *Reactions of* $[Mn(CO)_3(diphos)C(m\text{-}C_6H_4F)OMe]PF_6$

*With triethylphosphine.* To a suspension of the carbene salt (0.15 g, 0.18

mmol) in dry benzene (20 ml) was added $PEt_3$ (0.024 g, 0.20 mmol). The mixture was stirred at room temperature for 10 min giving a yellow solution. The yellow oil obtained after removing solvent was crystallized by adding methanol. The yellow crystals had an infrared spectrum and melting point identical to that for the parent acetyl complex $Mn(CO)_3(diphos)CO(m\text{-}C_6H_4F)$. Careful crystallization, from acetone/diethyl ether, of the oil obtained from the filtrate after removal of the methanol gave $[PMeEt_3]PF_6$, identified by comparison of its infrared spectrum with that of an authentic sample.

*With diphenylmethylphosphine.* To a solution of the carbene salt (0.25 g, 0.32 mmol) in 20 ml MeOH (or benzene) was added $PPh_2Me$ (0.065 ml, 0.35 mmol) and the mixture stirred at room temperature for 90 min. This reaction was slower than that with triethylphosphine but gave the acyl compound (93%) and $[PPh_2Me_2]PF_6$ (0.074 g, 100% as colorless needles from acetone/diethyl ether.)

*With triethylphosphite.* No reaction was observed between the carbene salt and $P(OEt)_3$. Starting material was recovered.

*With p-chlorophenyl isocyanide.* To a suspension of the carbene salt (0.14 g, 0.18 mmol) in dry benzene (10 ml) was added excess $CNC_6H_4Cl$ (0.10 g, 0.71 mmol) in benzene (5 ml) and the mixture was stirred at room temperature for 20 min. The yellow suspension appeared to dissolve, the solution turning red, and a pale yellow precipitate appeared. Filtration gave the product $[Mn(CO)_3(diphos)CNC_6H_4Cl]PF_6$ (0.121 g, 87%) as pale yellow needles which were recrystallized from acetone/diethyl ether, m.p. 176-178°.

Found: C, 52.58; H, 3.55; N, 1.57; P, 11.89. $C_{36}H_{28}ClF_6MnNO_3P_3$ calcd.: C, 52.74; H, 3.44; N, 1.71; P, 11.33%. IR: 2158s [$\nu$(CN)] 2083vw, 2038vs, 1966vs, 1986vs [$\nu$(CO)]. PMR: $\tau$6.79 (AA'BB' pattern, 4H, $CH_2$); 3.14 (AB pattern, $J$ = 8.5Hz, $J/\Delta\nu$ = 0.33, 4H, $C_6H_4Cl$); 2.40 (m, 20H, $C_6H_5$).

The same complex was obtained in 63% yield when *p*-chlorophenyl isocyanide was reacted with $[Mn(CO)_3(diphos)CMe(OMe)]PF_6$ in a similar manner.

*With methyl isocyanide.* In an analogous reaction to that above, the product $[Mn(CO)_3(diphos)CNMe]PF_6$ was obtained in 89% yield as off-white crystals which were recrystallized from acetone/diethyl ether giving yellow needles. m.p. 147-150°.

Found: C, 51.44; H, 3.99; N, 1.58; P, 11.88. $C_{31}H_{27}F_6MnNO_3P_3$ calcd.: C, 51.47; H, 3.76; N, 1.94; P, 12.85%. IR: 2210s [$\nu$(CN)], 2039vs, 1982vs(br) [($\nu$(CO)]. PMR: $\tau$7.32 (s, 3H, CNMe); 6.85 (AA'BB' pattern, 4H, $CH_2$); 2.38 (m, 20H, $C_6H_5$).

### *Reactions of* $[Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)]PF_6$

*With diphenylmethylphosphine.* To a solution of the carbene salt (0.25 g, 0.42 mmol) in MeOH (20 ml) was added $PPh_2Me$ (0.083 ml, 0.45 mmol). After 10 h stirring at room temperature, only starting material was recovered.

After 10 h in refluxing methanol, a small amount of starting material and some $[PMe_2Ph_2]PF_6$ (29% yield) were recovered, but no acetyl complex could be isolated. The latter had apparently decomposed under the harsh conditions employed.

*With methyl isocyanide.* To a solution of the carbene salt (0.25 g, 0.42 mmol) in dry benzene (10 ml) was added a solution of MeNC (0.025 ml, 0.5

mmol) in benzene (5 ml) and the mixture was stirred for 4.5 h at room temperature. The dark orange oil obtained after removal of the solvent was crystallized from methanol/diethyl ether, giving the product $[\mathrm{Mn(CO)_3\{P(OMe)_3\}_2\{C(NHMe)\text{-}C(OMe)_2Me\}}]\mathrm{PF_6}$ (0.075 g, 28%) as brown-orange crystals. Recrystallization from the same solvent gave off-white needles, m.p. softens 115°, melts 119-122°.

Found: C, 27.58; H, 4.79; N, 2.11; P, 13.98. $\mathrm{C_{15}H_{31}F_6MnNO_{11}P_3}$ calcd.: C, 27.16; H, 4.71; N, 2.11; P, 14.01%. IR: 2050m, 1967vs, 1942vs, 1912w(sh) [$\nu$(CO)], 1584m [$\nu$(CN)]. PMR ($\mathrm{CDCl_3}$): $\tau$8.74 (s, 3H, COMe); 6.75 (s, 6H, OMe); 6.26 (s, 3H, NMe); 6.21 (m, 18H, $\mathrm{P(OMe)_3}$); —0.35 (v. br. s, 1H, NH?).

*With p-chlorophenyl isocyanide.* In a similar reaction, pale yellow well-formed crystals of $[\mathrm{Mn(CO)_3\{P(OMe)_3\}_2\{C(NHC_6H_4Cl)C(OMe)_2Me\}}]\mathrm{PF_6}$ were obtained in 20% yield, m.p. 107-109°. There was too little material for an analysis. The infrared spectrum indicated that isocyanide insertion had occurred.

IR: 2067s, 2053s, 1975vs(br), 1956vs(sh) [$\nu$(CO)], 1552s [$\nu$(CN)]. PMR ($\mathrm{CDCl_3}$): $\tau$8.58 (s, 3H, CMe); 6.67 (s, 6H, OMe); 6.20 (18H, $\mathrm{P(OMe)_3}$); 2.57 (AB pattern, 4H, $\mathrm{C_6H_4}$). N—H resonance not located.

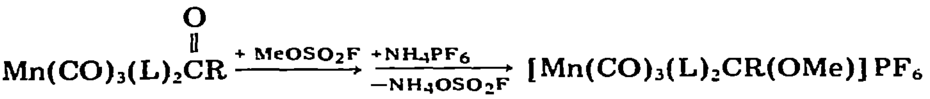
### *Alkyl group exchange*

Because of the oxonium-like chemical behavior of these carbene complexes, we considered the exchange of these groups between two acyl complexes to be feasible. One reaction was carried out which confirmed our expectations.

*Reaction of [Mn(CO)₃(diphos)C(m-C₆H₄F)OMe]PF₆ and Mn(CO)₃(diphos)-COMe.* Equimolar amounts of the two reagents were placed in an NMR tube, and the solvent $\mathrm{CD_3CN}$ added, along with tetramethylsilane as an internal standard. The reaction was observed by NMR integrated intensities (35°), following the disappearance of the $\tau$6.91 (OMe) and 8.20 (C-Me) resonances of the carbene complex and the $\mathrm{Mn(CO)_3(diphos)COMe}$ complex respectively. At the same time the intensities of the resonances of the new complex $[\mathrm{Mn(CO)_3(diphos)CMe(OMe)}]\mathrm{PF_6}$ at $\tau$7.11 (C-Me) and 6.97 (O-Me) were measured. After about 14 h no further change was observed. Conversion to the products, based upon integrated starting material—product intensities, was 82%.

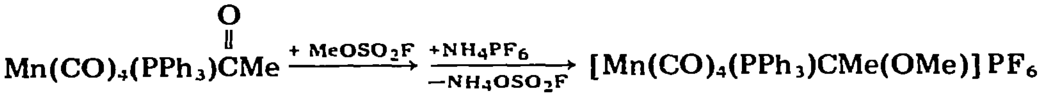
## Discussion

The complexes described here were prepared by the reactions shown below:

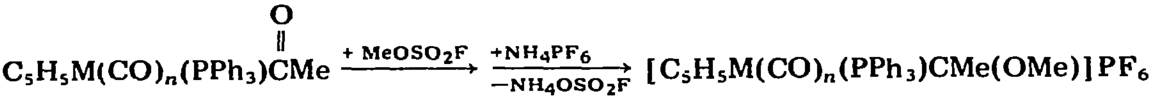


$$\mathrm{Mn(CO)_3(L)_2}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R}\xrightarrow{+\mathrm{MeOSO_2F}}\xrightarrow[-\mathrm{NH_4OSO_2F}]{+\mathrm{NH_4PF_6}}[\mathrm{Mn(CO)_3(L)_2CR(OMe)}]\mathrm{PF_6}$$

($\mathrm{L = P(OMe)_3}$; R = Me; $\mathrm{L_2}$ = diphos, R = Me, $m\text{-}\mathrm{C_6H_4F}$, $p\text{-}\mathrm{C_6H_4F}$)



$$\mathrm{Mn(CO)_4(PPh_3)}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Me}\xrightarrow{+\mathrm{MeOSO_2F}}\xrightarrow[-\mathrm{NH_4OSO_2F}]{+\mathrm{NH_4PF_6}}[\mathrm{Mn(CO)_4(PPh_3)CMe(OMe)}]\mathrm{PF_6}$$



$$\mathrm{C_5H_5M(CO)_{\mathit{n}}(PPh_3)}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Me}\xrightarrow{+\mathrm{MeOSO_2F}}\xrightarrow[-\mathrm{NH_4OSO_2F}]{+\mathrm{NH_4PF_6}}[\mathrm{C_5H_5M(CO)_{\mathit{n}}(PPh_3)CMe(OMe)}]\mathrm{PF_6}$$

(M = Fe, $n$ = 1; M = Mo, $n$ = 2)

The reactions were carried out in dichloromethane, and an oil was generally observed to form as the reaction progressed. Crystalline hexafluorophosphate salts were obtained directly upon metathetical reaction with $NH_4PF_6$.

All the carbene salts above are air-stable crystalline solids except for the molybdenum complex which decomposed slowly in air. Conductivity studies in dichloromethane showed them to be 1/1 electrolytes.

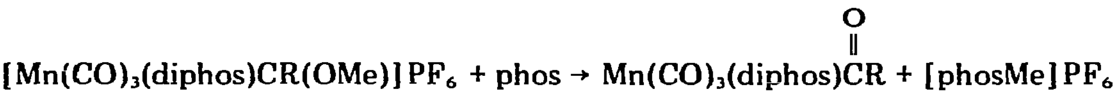
In all probability the diphos complexes, $[Mn(CO)_3(diphos)CR(OMe)]PF_6$ possess a different geometry around the metal than that for the phosphite complexes. The carbonyl stretching patterns are clearly different, with $[Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)]PF_6$ having two major absorptions, the diphos complexes having three. Moreover, the triplet pattern of phosphite methyl protons in the PMR is suggestive of a *trans* arrangement of these groups. If this is so then the phosphite complex should probably be assigned to a *mer* configuration (*trans L*), whereas the diphos complexes assume the *fac* configuration.

Methyl fluorosulfonate, first reported by Alder et al. [10], is an active alkylating agent, comparable to trimethyloxonium fluoroborate. Its use to prepare other carbenemetal complexes has been noted [3].

Alkylation of the unsubstituted acyl complexes $Mn(CO)_5COR$ (R = Me, $p$-$C_6H_4F$, $m$-$C_6H_4F$, $m$-$C_6H_4Cl$) and $C_5H_5Fe(CO)_2CO(p$-$C_6H_4F)$ was unsuccessful under the reaction conditions employed. The strong electron-withdrawing properties of the carbon monoxide ligands appear to reduce the basicity of the acyl carbonyl oxygen sufficiently to prevent electrophilic attack by $Me^+$.

It is now generally assumed that the cationic carbenemetal complexes can be better regarded as "onium" complexes [2,11]. Thus the complexes derived from alkylation of acylmetal complexes behave as if there is a substantial positive charge on oxygen. Thus the transfer of the group bonded to oxygen as $R^+$ to various basic reagents is rationalized [11].

We have looked at several such reactions here. The various cationic manganese carbene complexes having diphos as a ligand are quickly and smoothly dealkylated in the presence of phosphines at room temperature:



$$[Mn(CO)_3(diphos)CR(OMe)]PF_6 + phos \rightarrow Mn(CO)_3(diphos)\overset{\overset{\displaystyle O}{\|}}{C}R + [phosMe]PF_6$$

(R = Me, $m$-$C_6H_4F$, $p$-$C_6H_4F$; phos = $PEt_3$, $PPh_2Me$)

Interestingly, the phosphite complex, $[Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)]PF_6$, did not react in this manner. In fact, no reaction with these phosphines was observed at room temperature; at higher temperatures decomposition was noted.

It is appropriate to comment that the dealkylation reaction noted above took precedence over either carbonyl or carbene displacement. Both modes of reaction are seen in other systems [12,13].

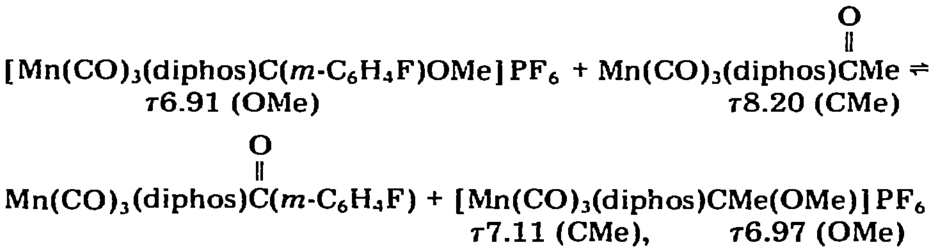
Perhaps the easiest way to view the reactions cited above is in the acid—base sense. The acid is the donor of the $Me^+$ group and can react with any base (in an equilibrium) to give a new acid, the conjugate acid of the original base, and the conjugate base of $MeOSO_2F$, the fluorosulfonate ion; viz:

$$MeOSO_2F + B \rightleftharpoons MeB^+ + OSO_2F^-$$

The equilibrium will favor the weaker acid and base, according to Brønsted theory.

The fact that substituted acyl manganese carbonyl complexes are sufficiently strong bases to add a $Me^+$ group nearly quantitatively, whereas the unsubstituted metal acyls are not, is of some interest in two respects. First, there is the fact that there is a substantial enough difference to actually determine reactivity or non-reactivity. This is somewhat surprising, for although the increased back-donation from metal to the acyl group on substitution of carbonyls is generally acknowledged, and documented by the shift in the acyl carbonyl stretching frequencies upon substitution, the effect usually is small. Second, it also becomes clear why some of these carbene complexes exhibit reactivity resembling oxonium behavior. It should not be surprising to find that these carbene complexes are reasonably good acids (i.e. $Me^+$ donors) in their own right.

With the realization that these carbene (or carboxonium) complexes should be $Me^+$ donors, an obvious reaction is suggested. This is the possible alkyl group exchange between one acyl complex and another, the alkylation of one acyl complex by a carbenemetal complex. We have observed the following reaction:



$$\underset{\tau 6.91\ (\mathrm{OMe})}{[\mathrm{Mn(CO)_3(diphos)C}(m\text{-}\mathrm{C_6H_4F})\mathrm{OMe}]\mathrm{PF_6}} + \underset{\tau 8.20\ (\mathrm{CMe})}{\mathrm{Mn(CO)_3(diphos)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Me}} \rightleftharpoons$$

$$\mathrm{Mn(CO)_3(diphos)}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}(m\text{-}\mathrm{C_6H_4F}) + \underset{\tau 7.11\ (\mathrm{CMe}),\qquad \tau 6.97\ (\mathrm{OMe})}{[\mathrm{Mn(CO)_3(diphos)CMe(OMe)}]\mathrm{PF_6}}$$

After 14 h an approximate 82% conversion (based on integrated NMR intensities) of reactant products (on right) was found; no further reaction past this point occurred. It is possible that this system had achieved some equilibrium distribution at this time. More work is needed to define this possibility, however.

The reactions of these manganese carbene species with methyl and *p*-chlorophenyl isocyanides were also studied, and remarkably, the reactions that occurred for the diphos and phosphite complexes also differed. In the case of the diphos complexes, carbene displacement occurred; viz:

$$[\mathrm{Mn(CO)_3(diphos)CR(OMe)}]\mathrm{PF_6} + \mathrm{R'NC} \rightarrow [\mathrm{Mn(CO)_3(diphos)CNR'}]\mathrm{PF_6}$$

($R' = Me$, $R = m\text{-}C_6H_4F$; $R' = p\text{-}C_6H_4Cl$; $R = Me$, $m\text{-}C_6H_4F$)

However the reaction of $[Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)]PF_6$ with these isocyanides (in methanol) resulted in insertion into the carbene carbon—metal bond, accompanied by methanol addition:

$$[\mathrm{Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)}]\mathrm{PF_6} + \mathrm{R'NC} \xrightarrow{(+\mathrm{MeOH})} [\mathrm{Mn(CO)_3\{P(OMe)_3\}_2\text{-}C(NHR')C(OMe)_2Me}]\mathrm{PF_6}$$

Similar isocyanide insertion reactions have been observed by Fischer et al. [14] with (neutral) carbenechromium complexes which, parenthetically, are also noted not to behave chemically as oxonium ions or $R^+$ donors.

## Acknowledgement

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