Haloalkyl Complexes of the Transition Metals. Part 3.[1] Reactions of Some Chloromethyl and Methoxymethyl Complexes of Molybdenum, Tungsten, Manganese, Rhenium, Iron, and Ruthenium with Some Tertiary Phosphine and Related Ligands

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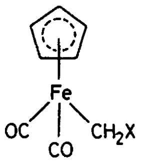
The reactions of some chloromethyl transition-metal complexes [M′–CH_2Cl] with PPh_3 have been investigated. For M′ = Fe(η^5-C_5H_5)$(CO)_2$ or W(η^5-C_5H_5)$(CO)_3$, cationic ylide complexes of the type [M′–CH_2PPh_3]$^+$ have been isolated, whereas for M′ = $Mn(CO)_5$ or Mo(η^5-C_5H_5)$(CO)_3$, chloro-complexes were obtained and for M′ = $Re(CO)_5$ or Ru(η^5-C_5H_5)$(CO)_2$, no ligand products were found under the reaction conditions used. The reactions have been investigated in methanol and acetonitrile. The reactions of [Fe(η^5-C_5H_5)$(CO)_2(CH_2Cl)$] with other ligands (L) have also been studied; cationic ylide complexes [Fe(η^5-C_5H_5)$(CO)_2(CH_2L)$]$^+$ have been obtained for L = PMe_2Ph, $PMePh_2$, PEt_2Ph, $PEtPh_2$, or $AsPh_3$ and disubstituted cationic complexes [Fe(η^5-C_5H_5)(CO)L_2]$^+$ where L = PMe_3, PMe_2Ph, PEt_2Ph, or $PEtPh_2$. Possible mechanisms for these reactions are discussed. The reactions of some methoxymethyl complexes [M′–CH_2OMe] with PPh_3 are also described.

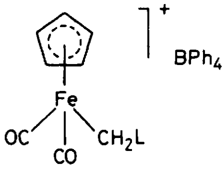
Transition-metal complexes containing halogenomethyl, methoxymethyl, or halogenoalkyl groups have potential as precursors for important classes of compounds including those with bridging methylene or polymethylene groups, terminal carbene groups, and a range of compounds of the type [ML_n(CH_2X)] (where M = transition metal, L_n = other ligands, and X = a nucleophile). Relative to main-group metal halogenomethyl compounds,[2] transition-metal halogenomethyl compounds have not been extensively studied.[1,3,4] We have previously reported that the reaction of PPh_3 with the [M′–CH_2Cl] complexes [where M′ = Fe(cp)$(CO)_2$ or W(cp)$(CO)_3$; cp = η^5–C_5H_5] gave cationic ylide complexes.[5] These results led us to examine, in more detail, the reactions of a series of [ML_n(CH_2Cl)] complexes (where L_n includes CO) with neutral donor ligands. Recently, reactions of tertiary phosphines with some [ML_n(CH_2X)] complexes (where L_n does not include CO; X = Cl, Br, or I) have been reported to give ylide products.[3,6,7]

The reactions of PR_3 ligands with [ML_n(CH_3)] complexes (where L_n includes CO) usually give rise to CO substitution by PR_3, with or without carbonyl insertion into the M′–CH_3 bond.[8] Other pathways are however available for the reactions of [ML_n(CH_2X)] complexes with similar ligands. There are at least three possible ways in which PR_3 ligands could react with [ML_n(CH_2X)] complexes (where L_n includes CO): (*i*) substitution of CO by one or more of the ligands L, with or without carbonyl insertion; (*ii*) nucleophilic attack by PR_3 at the carbon atom of the CH_2 group; and (*iii*) reactions which lead to displacement of the CH_2X group or formation of [M′–X] complexes.

We now report in detail on the reactions of some chloromethyl and methoxymethyl complexes of Mo, W, Mn, Re, Fe, and Ru with some tertiary phosphine ligands, $AsPh_3$ and $P(OMe)_3$, reactions which show some of the other pathways available to [ML_n(CH_2X)] complexes.



(1) X = Cl
(8) X = OMe



(2) L = PPh_3
(3) L = $PMePh_2$
(4) L = PMe_2Ph
(5) L = $PEtPh_2$
(6) L = PEt_2Ph
(7) L = $AsPh_3$

Results and Discussion

Reactions of [Fe(cp)$(CO)_2(CH_2Cl)$] *with Tertiary Phosphines,* $AsPh_3$, *and* $P(OMe)_3$.—We have studied the reactions of [Fe(cp)$(CO)_2(CH_2Cl)$] (1) with several tertiary phosphines and other ligands in both methanol and acetonitrile as solvents. Thus (1) reacts with PPh_3, $PMePh_2$, and $PEtPh_2$ in methanol under reflux to give, after work-up with $NaBPh_4$, cationic complexes of type [Fe(cp)$(CO)_2(CH_2L)$]BPh_4, *i.e.* (2), (3), and (5) (see Table 1 for reaction times, yields, and characterisation data). These complexes were isolated as yellow, air-stable BPh_4^- salts in yields of 54—74%. The BF_4^- salt analogous to (2) has been reported as the product of the reaction of [Fe(cp)$(CO)_2$(thf)]BF_4 (thf = tetrahydrofuran) with Ph_3P=CH_2.[9] We also find that complex (1) reacts with PPh_3 in methanol at room temperature over 3 d to give (2). In contrast, the reaction of PMe_2Ph with complex (1) gave (4) (after work-up with $NaBPh_4$) in only 8% yield after 3 d in methanol under reflux. The reaction of PEt_2Ph with (1) in methanol under reflux for 5 d gave a low yield of product. This product could not however be completely purified but the i.r. spectrum showed two strong ν(CO) bands (at 2 028 and 1 974 cm^{-1}), in similar positions to those observed for compounds (2)—(5), suggesting that (6) is the product. The reaction of (1) with $AsPh_3$ in methanol under reflux gave the yellow air-stable cation (7), isolated as the BPh_4^- salt. The reaction of $P(OMe)_3$ with (1) in methanol under reflux was attempted but after 4 d an i.r. spectrum of the reaction mixture showed only ν(CO) bands corresponding to [Fe(cp)$(CO)_2(CH_2OMe)$] (8).

Examination of the solutions of complex (1) by i.r. and ^{1}H n.m.r. spectroscopy after standing in methanol show that a mixture of (1) and (8) is present. On addition of the phosphine ligand to this solution, only bands of (8) are seen suggesting that an equilibrium [equation (i)] may be set up and has been shifted to the right. On heating the reaction solution under

$$\underset{(1)}{[\mathrm{Fe(cp)(CO)_2(CH_2Cl)}]} + \mathrm{MeOH} \rightleftharpoons \underset{(8)}{[\mathrm{Fe(cp)(CO)_2(CH_2OMe)}]} + \mathrm{HCl} \quad \text{(i)}$$

Table 1. Data for products of the reaction of $[Fe(cp)(CO)_2(CH_2Cl)]$ with ligands in methanol

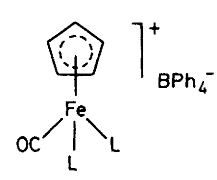
Compound	Reaction time	Yield (%)	M.p. (θ_c/°C)	$\tilde{\nu}$(CO) [a]/cm^{-1}	^{1}H N.m.r.[b] (δ/p.p.m.)	Analysis [c] (%)
(2) $[Fe(cp)(CO)_2(CH_2PPh_3)]BPh_4$	4 h	74	198—200 (decomp.)	2 032s, 1 981s	1.50 [d, 2 H, ^2J(PH) 12.5], 4.62 (s, 5 H), 6.93, 7.33, 7.63 (m, 35 H)	C 77.5 (77.75) H 5.45 (5.50) O 4.20 (4.15)
(3) $[Fe(cp)(CO)_2(CH_2PMePh_2)]BPh_4$	20 h	70	162—164	2 031s, 1 978s	1.15 [d, 2 H, ^2J(PH) 12.6], 1.97 [d, 3 H, ^2J(PH) 12.5], 4.72 (s, 5 H), 6.98, 7.35, 7.59 (m, 30 H)	C 75.7 (76.05) H 5.70 (5.70)
(4) $[Fe(cp)(CO)_2(CH_2PMe_2Ph)]BPh_4$	2 d	8	150—153	2 029s, 1 975s	1.26 [d, 2 H, ^2J(PH) 14.0], 1.58 [d, 6 H, ^2J(PH) 12.5], 4.70 (s, 5 H), 6.95, 7.50 (m, 25 H)	C 74.25 (74.2) H 5.90 (5.90) O 4.60 (4.95)
(5) $[Fe(cp)(CO)_2(CH_2PEtPh_2)]BPh_4$	5 h	54	178—180	2 030s, 1 977s	0.99 [dt, 3 H, ^3J(PH) 18.5, ^3J(HH) 7.7], 1.09 [d, 2 H, ^2J(PH) 12.6], 2.38 [dq, 2 H, ^2J(PH) 11.9, ^3J(HH) 7.7], 4.63 (s, 5 H), 6.93, 7.33, 7.60 (m, 30 H)	C 76.05 (76.25) H 5.85 (5.80)
(6) $[Fe(cp)(CO)_2(CH_2PEt_2Ph)]BPh_4$	5 d	Low	123—126	2 028s, 1 974s		Impure
(7) $[Fe(cp)(CO)_2(CH_2AsPh_3)]BPh_4$	3.5 h	66	194—196 (decomp.)	2 031s, 1 980s	[d] 2.50 (s, 2 H), 5.09 (s, 5 H), 6.88, 7.35, 7.80 (m, 35 H)	C 73.35 (73.55) H 5.15 (5.20)
(2a) $[Fe(cp)(CO)_2(CH_2PPh_3)]I$	7 d	17	194—200	2 025s, 1 972s	2.21 [d, 2 H, ^2J(PH) 12.5], 5.17 (s, 5 H), 7.70 (m, 15 H)	C 53.7 (53.8) H 3.75 (3.80)

[a] Measured in CH_2Cl_2. [b] Measured in CD_2Cl_2 unless otherwise stated; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; J values in Hz. [c] Calculated values in parentheses. [d] Measured in CD_3COCD_3.

reflux, the ν(CO) bands of (8) are replaced by bands consistent with formation of the respective cationic ylide products (2)—(7). Interestingly, (8) did not react with PPh_3 in methanol at room temperature over 6 d; however, when excess of aqueous HCl was added to the reaction solution, i.r. monitoring showed that (1) was rapidly formed followed by the cation (2). These results suggest that the iron complex that reacts with the phosphine is (1) rather than (8). Under different conditions (C_6H_6, u.v.; or reflux in CH_3CN for 4 d) the reaction of (8) with PPh_3 has been reported to give $[Fe(cp)(CO)(PPh_3)(CH_2OMe)]$[10] or $[Fe(cp)(CO)(PPh_3)(COCH_2OMe)]$[11] respectively. The difficulty with which (8) undergoes carbonyl insertion relative to $[Fe(cp)(CO)_2Me]$ is shown by the observation that $[Fe(cp)(CO)_2Me]$ reacts with PPh_3 in refluxing acetonitrile for less than 1 d to give an 80% yield of $[Fe(cp)(CO)(PPh_3)(COMe)]$.[11] Thus for complexes $[Fe(cp)(CO)_2(CH_2X)]$, the carbonyl-insertion reaction occurs less readily where X = the electron-withdrawing OMe group than where X = H.

Although (8) reluctantly reacts with PPh_3, we find that it does react with $[PPh_3H]I$ in methanol at room temperature, or under reflux, to give $[Fe(cp)(CO)_2(CH_2PPh_3)]I$ (2a) and i.r. monitoring suggests that this reaction proceeds *via* an intermediate which is probably $[Fe(cp)(CO)_2(CH_2I)]$.

We have also investigated the reactions of $[Fe(cp)(CO)_2(CH_2Cl)]$ (1) with tertiary phosphines in acetonitrile as solvent, at room temperature in the dark. Thus complex (1) with PPh_3 gave (2) after work-up with $NaBPh_4$; the analogous PF_6^- salt (2b) was also prepared. The reaction of (1) with $PMePh_2$ resulted in the isolation of complex (3). The same cationic products were thus obtained with these ligands in methanol and acetonitrile although the reactions in acetonitrile, which were carried out at a lower temperature, took longer. A mixture of two products, *viz.* (4) and (9), was isolated from the reaction of (1) with PMe_2Ph (1 : 1 molar ratio of reactants) in acetonitrile for 17.5 h. If the reaction was carried out for a longer period (5 d) with an excess of PMe_2Ph, then (9) was the only product isolated (81% crude yield); these results suggest that (4) is converted into (9). From the reactions of (1) with PMe_3 or PEt_2Ph were isolated (10) and (11) respectively as air-stable, yellow crystalline BPh_4^- salts. The phosphonium salt $[PMeEt_2Ph]BPh_4$ was also isolated from the reaction of (1) with PEt_2Ph in acetonitrile. For details of reaction times, yields, and characterisation of the products of the reactions of (1) with ligands L in acetonitrile see Table 2. The PF_6^- salt analogous to (10) has recently been reported as the product of heating $[Fe(cp)(CO)(PMe_3)Br]$ with PMe_3 in toluene under reflux and the I^- salt analogous to (10) from the reaction of $[Fe(cp)(CO)_2(PMe_3)]I$ with PMe_3 under reflux in acetonitrile for 2 h.[12] The reaction of (1) with $PEtPh_2$ in acetonitrile gave a yellow solid on work-up with $NaBPh_4$. This product was not



(9) L = PMe_2Ph (10) L = PMe_3
(11) L = PEt_2Ph (12) L = $PEtPh_2$

Table 2. Data for some products of the reactions of $[Fe(cp)(CO)_2(CH_2Cl)]$ with tertiary phosphines in acetonitrile

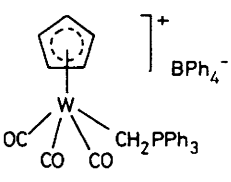
Compound	Reaction time (t/d)	Yield (%)	M.p. (θ_c/°C)	$\tilde{\nu}$(CO) [a]/cm^{-1}	^{1}H N.m.r.[b] (δ/p.p.m.)	Analysis [c] (%)
(2b) $[Fe(cp)(CO)_2(CH_2PPh_3)]PF_6$	1.8	42	202—205 (decomp.)	2 028s, 1 976s	1.82 [d, 2 H, ^2J(PH) 12.5], 4.93 (s, 5 H), 7.66 (m, 35 H)	C 52.5 (52.2) H 3.75 (3.7) F 18.35 (19.05)
(9) $[Fe(cp)(CO)(PMe_2Ph)_2]BPh_4$	5	81	193—196 (decomp.)	1 967	[d] 1.65 [pseudo-triplet, 6 H, $\lvert J(PH) + J(P'H)\rvert$ 10.0], 1.83 (pseudo-triplet, 6 H, $\lvert J(PH) + J(P'H)\rvert$ 10.0], 4.96 [t, 5 H, ^3J(PH) 1.4], 6.87, 7.36, 7.53 (m, 30 H)	C 73.8 (74.2) H 6.35 (6.35)
(10) $[Fe(cp)(CO)(PMe_3)_2]BPh_4$	2	32	>250 (decomp.)	1 971	1.39 [pseudo-triplet, 18 H, $\lvert J(PH) + J(P'H)\rvert$ 10.0], 4.56 [t, 5 H, ^3J(PH) 1.9], 6.96, 7.30 (m, 20 H)	C 69.7 (69.7) H 7.10 (7.0)
(11) $[Fe(cp)(CO)(PEt_2Ph)_2]BPh_4$	3	15	140—142	1 962	0.93, 1.65 (br m), 4.52 [t, 5 H, ^3J(PH) 2.0], 6.97, 7.35 (m, 30 H)	C 75.8 (75.0) H 7.05 (6.9)
(12) $[Fe(cp)(CO)(PEtPh_2)_2]BPh_4$	5			1 962		Impure
$[PMeEt_2Ph]BPh_4$	3	17	200—201		[e] 1.29 [dt, 6 H, ^3J(HH) 7.5, ^3J(PH) 19.5], 2.05 (d, 3 H, ^2J(PH) 13.0], 2.42 [dq, 4 H, ^2J(PH) 13, ^3J(HH) 7.5], 6.92, 7.37, 7.78 (m, 25 H)	C 84.2 (84.0) H 7.6 (7.6)

[a] Measured in CH_2Cl_2. [b] Measured in CD_2Cl_2 except when otherwise stated; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; J values in Hz. [c] Calculated values in parentheses. [d] Measured in CD_3COCD_3. [e] Measured in CD_3NO_2.

obtained in a pure state, however its i.r. spectrum shows one ν(CO) band (1 962 cm^{-1}) suggesting that it is (12). Trimethyl phosphite did not react with (1) over 6 d in acetonitrile.

Since the same products are isolated, at least in some cases, in methanol and acetonitrile then similar reaction pathways may be followed in both solvents (although the reactions of chloromethyl complexes in methanol can be more complicated due to the formation of methoxymethyl complexes). In acetonitrile, less nucleophilic ligands tend to give cationic ylide complexes whereas more nucleophilic ligands give $[Fe(cp)(CO)L_2]^+$ species.

Initial reaction of a ligand, L, with complex (1) may involve nucleophilic attack at the carbon atom of the $M'{-}CH_2Cl$ group to give $[Fe(cp)(CH_2L)]^+$ by a S_N2 reaction analogous to the quaternisation of tertiary phosphines by alkyl halides.[13] Alternatively, this reaction could involve the intermediacy of the carbene cation $[Fe(cp)(CO)_2(CH_2)]^+$, a methylene species which has previously been proposed as a reaction intermediate and recently characterised in the case of the substituted derivative $[Fe(cp)(Ph_2PCH_2CH_2PPh_2)(CH_2)]^+$.[14] Others have found that reactions of some $[M'{=}CHR]^+$ complexes (where R = H or Me) with PR'_3 ligands give complexes of the type $[M'{-}CHRPR'_3]^+$.[15–17] Since it appears that $[Fe(cp)(CO)_2(CH_2L)]^+$ may be converted into $[Fe(cp)(CO)L_2]^+$ (at least where L = PMe_2Ph) and no evidence in any of the reactions was obtained for a species of type $[Fe(cp)(CO)L(CH_2L)]^+$, then a possible sequence of reactions leading to the disubstituted product may involve migration of L from carbon to iron by a 1,2 shift, followed by substitution of CH_2 by L, *i.e.* $[(OC)M'{-}CH_2L]^+ \xrightarrow{-CO} [LM'{=}CH_2]^+ \xrightarrow{L} [M'L_2]^+$ (where M' = metal and other ligands). The migration of a tertiary phosphine ligand from carbon to a metal in an $[M'{-}CR_2{-}PR'_3]$ type of complex has been observed previously.[16,18,19] Alternatively, the ligand L may displace the ylide followed by CO substitution, *i.e.* $[(OC)M'{-}CH_2L]^+ \xrightarrow[-CH_2L]{L} [(OC)M'{-}L]^+ \xrightarrow{L} [M'L_2]^+$. No products of the type $[Fe(cp)(CO)_2L]^+$ were observed in any of the reactions, however the phosphonium cation $[PMeEt_2Ph]^+$, isolated in the reaction of (1) with PEt_2Ph, may result from protonation of the displaced ylide $CH_2{=}PEt_2Ph$.



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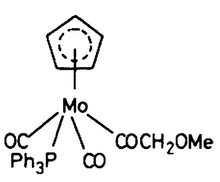

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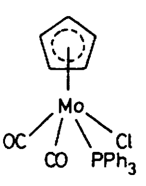

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Reactions of Some Chloromethyl Complexes of Ru, Mo, *and* W *with* PPh_3.—In contrast to the reaction of (1) with PPh_3, $[Ru(cp)(CO)_2(CH_2Cl)]$ gave only $[Ru(cp)(CO)_2(CH_2OMe)]$[1] after heating in methanol under reflux with PPh_3 for 5 d. The reaction of $[W(cp)(CO)_3(CH_2Cl)]$ with PPh_3 on heating in methanol under reflux for 4 h gave the cationic ylide complex $[W(cp)(CO)_3(CH_2PPh_3)]^+$ isolated as the Cl^- salt in a crude yield of 80%; this complex was obtained as a yellow, air-stable crystalline solid. This cationic complex, isolated as the BPh_4^- salt (13), was also obtained (20% yield) from the reaction of $[W(cp)(CO)_3(CH_2Cl)]$ with PPh_3 in acetonitrile at room temperature in the dark for 34 d; see Table 3 for characterisation data for complexes of W and Mo. Different types of products were identified from the reaction of $[Mo(cp)(CO)_3(CH_2Cl)]$ with PPh_3. Thus, the reaction of $[Mo(cp)(CO)_3(CH_2Cl)]$ with PPh_3 in acetonitrile for 28 d at room tempera-

Table 3. Data for some products of the reactions of chloromethyl and methoxymethyl complexes of Mo, W, and Mn with PPh_3

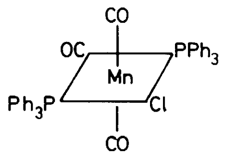
Compound	M.p. (θ_c/°C)	$\tilde{\nu}$(CO) [a]/cm^{-1}	^{1}H N.m.r.[b] (δ/p.p.m.)	Analysis [c]
(13) $[W(cp)(CO)_3(CH_2PPh_3)]BPh_4$	192—198	2 036s, 1 952 (sh), 1 933s	[d] 1.81 [d, 2 H, ^2J(PH) 15.5], 5.25 (s, 5 H), 6.93, 7.53 (m, 35 H)	C 65.3 (65.95) H 4.85 (4.55)
(13a) $[W(cp)(CO)_3(CH_2PPh_3)]Cl$	173—180	2 030s, 1 940 (sh), 1 926s	2.80 [d, 2 H, ^2J(PH) 16.0], 5.98 (s, 5 H), 7.62, 7.90 (m, 15 H)	C 48.6 (50.3) H 3.4 (3.45) Cl 5.7 (5.5)
(14) $[Mo(cp)(CO)_2(PPh_3)(COCH_2OMe)]$	118—119	1 938m, 1 857vs, 1 627m	3.34 (s, 3 H), 4.24 (s, 2 H), 5.02 (s, 5 H), 7.46 (m, 15 H)	C 60.55 (60.9) H 4.8 (4.55)
(16) $[Mn(CO)_3(PPh_3)_2Cl]$	136—180 (decomp.)	2 038w, 1 950vs, 1 917m		
(17) *cis*-$[Mn(CO)_4(PPh_3)(COCH_2OMe)]$	104—106	2 070m, 2 040w, 1 965s, 1 933m, 1 640m	3.26 (s, 3 H), 3.70 (s, 2 H), 7.46 (m, 15 H)	C 60.15 (59.8) H 4.05 (4.0)
(18) *cis*-$[Mn(CO)_4(PPh_3)(CH_2OMe)]$	90—92	2 062m, 1 982 (sh), 1 967vs, 1 936s	[d] 3.07 (s, 3 H), 3.63 [d, 2 H, ^3J(PH) 6.8], 7.45 (m, 15 H)	C 60.8 (60.75) H 4.3 (4.25)
(19) *trans*-$[Mn(CO)_3(PPh_3)_2(CH_2OMe)]$	160—163	2 010w, 1 921s, 1 885m	2.52 (s, 3 H), 3.13 [t, 2 H, ^3J(PH) 7.5], 7.39, 7.65 (m, 30 H)	C 70.8 (70.7) H 5.25 (5.0)

[a] Measured in CH_2Cl_2. [b] Measured in $CDCl_3$ except where otherwise stated; s = singlet, d = doublet, t = triplet, and m = multiplet; *J* values in Hz. [c] Calculated values in parentheses. [d] Measured in CD_2Cl_2.

ture in the dark gave $[Mo(cp)(CO)_2(PPh_3)Cl]$ (15) in 71% yield. If the same reactants were heated under reflux in methanol, then three products were identified depending on the reaction time. Thus after 30 min the main product isolated was $[Mo(cp)(CO)_2(PPh_3)(COCH_2OMe)]$ (14). This product is presumably formed by the reaction of $[Mo(cp)(CO)_3(CH_2OMe)]$ with PPh_3; in a separate experiment, we have shown (by i.r. monitoring) that methanol reacts with $[Mo(cp)(CO)_3(CH_2Cl)]$ to give $[Mo(cp)(CO)_3(CH_2OMe)]$. With longer reaction times, $[Mo(cp)(CO)_3(CH_2Cl)]$ and PPh_3 in methanol gave mainly $[Mo(cp)(CO)_2(PPh_3)Cl]$ with some $[Mo(cp)(CO)(PPh_3)_2Cl]$. The reluctance of $[Mo(cp)(CO)_3(CH_2Cl)]$ to undergo carbonyl insertion has previously been noted, thus no reaction was found to occur between this chloromethyl complex and cyclohexyl isocyanide.[20] It is interesting to note that the reaction of $[Mo(cp)(CO)_3Me]$ with triphenylphosphine gives both $[Mo(cp)(CO)_2(PPh_3)Me]$ and $[Mo(cp)(CO)_2(PPh_3)(COMe)]$ in tetrahydrofuran or hexane solvents.[21]

From the intensities of the ν(CO) bands in the i.r. spectra, complex (14) can be assigned the *trans* isomer and (15) the *cis* isomer.[22]

Reactions of Some Chloromethyl and Methoxymethyl Complexes of Mn *and* Re *with* PPh_3.—The product of the reaction of $[Mn(CO)_5(CH_2Cl)]$ with PPh_3 in methanol or acetonitrile at room temperature in the dark was $[Mn(CO)_3(PPh_3)_2Cl]$ (16),[23] which we also obtained from the reaction of $[Mn(CO)_5Cl]$ with PPh_3 in acetonitrile at room temperature. The reaction of $[Mn(CO)_5(CH_2Cl)]$ with PPh_3 probably goes *via* initial formation of $[Mn(CO)_4(PPh_3)Cl]$ which then under the reaction conditions gives the disubstituted product. In contrast, $[Re(CO)_5(CH_2Cl)]$ did not react with PPh_3 in acetonitrile under similar conditions.



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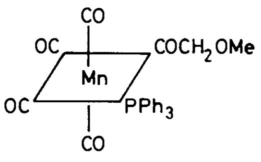
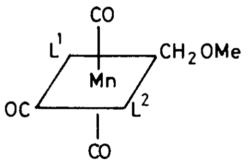


(17)



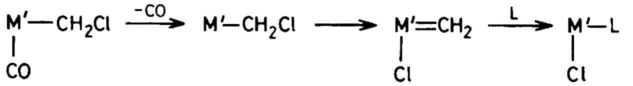
(18) L^1 = CO, L^2 = PPh_3
(19) L^1 = L^2 = PPh_3

The reaction of $[Mn(CO)_5(CH_2OMe)]$ with PPh_3 in acetonitrile at room temperature for 5 d in the dark gave *cis*-$[Mn(CO)_4(PPh_3)(COCH_2OMe)]$ (17). The *cis* configuration was assigned on the basis of four ν(CO) bands in the i.r. spectrum; see Table 3 for characterisation data for manganese complexes. It is interesting to note that the reaction of $[Mn(CO)_5Me]$ with PPh_3 in thf gives *cis*-$[Mn(CO)_4(PPh_3)(COMe)]$ in 72% yield after stirring for several hours.[24] In contrast, $[Re(CO)_5(CH_2OMe)]$ did not react with PPh_3 under similar conditions.

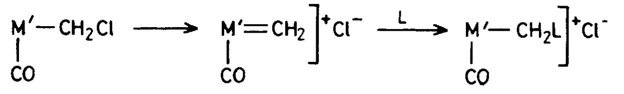
Reaction of $[Mn(CO)_5(CH_2OMe)]$ with PPh_3 (1 : 1 molar ratio of reactants) in methanol under reflux gave *cis*-$[Mn(CO)_4(PPh_3)(CH_2OMe)]$ (18) in 74% yield. When an excess of PPh_3 was used, then (18) was formed initially but longer reaction times resulted in formation of *trans*-[$Mn(CO)_3(PPh_3)_2(CH_2OMe)$] (19) in *ca.* 25% yield with (18) still the major product of the reaction. The *trans* configuration for (19) is assigned on the basis of three ν(CO) bands in the i.r. spectrum and a 1 : 2 : 1 triplet seen in the ^1H n.m.r. spectrum for the CH_2 protons of the methoxymethyl group.

Conclusions

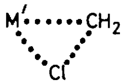
From this study we can make certain observations and generalisations. (*i*) Reactions of PR_3 ligands with the [$M'–CH_2OMe$] complexes are similar to those of the analogous [$M'–CH_3$] complexes in that [$M'(PR_3)(CH_2OMe)$] or [$M'(PR_3)(COCH_2OMe)$] complexes are formed although the reactions of the methoxymethyl complexes are slower. (*ii*) Complexes of the type [$M'–CH_2X$] (X = Cl or OMe) where M is a first-row transition-series metal appear to be more reactive towards PPh_3 than where M is a second- or third-row transition metal. (*iii*) Complexes [$M'–CH_2Cl$] show different reaction pathways to [$M'–CH_3$] on reaction with PR_3 ligands and in no case did we observe simple CO substitution by PR_3, or carbonyl-insertion products. (*iv*) Two types of products seem to be formed initially in reactions of [$M'–CH_2Cl$] complexes with ligands L, *viz.* [$M'(L)Cl$] or [$M'–CH_2L$]$^+$. These products may be rationalised on the basis of initial chlorine migration from the carbon of the CH_2Cl group. There are two possible cases to be considered. (*a*) Where a CO ligand can readily dissociate to generate a co-ordinatively unsaturated species then a 1,2 shift of chlorine (an α-chlorine transfer) can occur from carbon to the metal; substitution of the CH_2 group could then lead to the product as in Scheme 1. Other examples of 1,2 shifts of halogen from carbon to metal have been reported.[7,25–27] (*b*) Where a CO ligand is not readily lost, then migration of chloride outside the co-ordination sphere of the metal could occur followed by nucleophilic attack at the carbon of the cationic carbene complex (Scheme 2). In the absence of a ligand L, nucleophilic attack of chloride at the metal could occur with displacement of a CH_2 group as has been found in some reactions of [$Fe(cp)(CO)_2(CH_2Cl)$] [28] and [$Fe(cp)(CO)(PPh_3)(CH_2Cl)$].[10] The 1,2 chlorine shift may go *via* a three-centre transition state (see below) as has been proposed for other 1,2 shifts from carbon to metals (and the reverse reaction, a 1,2 shift from metal to carbon), *e.g.* decomposition of halogenoalkyl compounds of mercury,[29] the 1,2 hydrogen shift in cyclopentadienyltungsten methyl complexes,[16] and the carbonyl-insertion reaction.[8] The generation of a co-ordinatively unsaturated species has been suggested as an important step in providing a low energy pathway for the β-hydride transfer reaction for transition-metal alkyl complexes.[30,31]



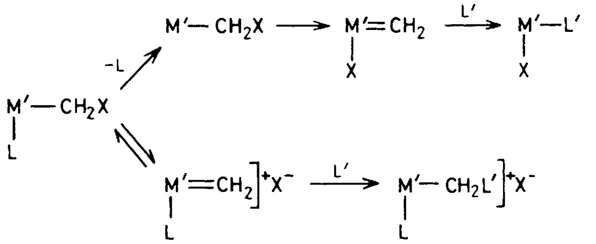
Scheme 1.



Scheme 2.



On the basis of the pathways suggested above, the formation of *cis*-[$Pt(PPh_3)_2(CH_2PPh_3)Cl$]I from the reaction of *cis*-[$Pt(PPh_3)_2(CH_2Cl)I$] with PPh_3[7] may be suggested to go *via* the carbene intermediate [$Pt(PPh_3)_2(CH_2)Cl$]$^+I^-$. A possible scheme for the reaction of [$M'(L)(CH_2X)$] complexes with ligands L′ may be written showing the two pathways (Scheme 3).



Scheme 3.

We are at present investigating other examples of these types of reactions and attempting to obtain more information on their mechanisms.

Experimental

All reactions were performed under nitrogen using standard Schlenk-tube techniques. The following methoxymethyl and chloromethyl complexes were prepared by reported methods: [$Fe(cp)(CO)_2(CH_2X)$] (X = Cl or OMe),[32] [$M(cp)(CO)_3(CH_2X)$] (M = Mo or W; X = Cl or OMe),[32,33] and [$Mn(CO)_5(CH_2OMe)$].[34] Tertiary phosphines (Strem Chemicals Inc. and BDH Chemicals Ltd.) and $AsPh_3$ (Merck) were used without further purification; PMe_3 was synthesised by the method of Mann and Wells.[35] Microanalyses were performed by the microanalytical laboratories at the University of Cape Town or by F. and E. Pascher, Bonn, Germany. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer and ^1H n.m.r. spectra on a Varian XL100 or a Bruker WH 90 spectrometer using tetramethylsilane as internal reference. Melting points were obtained on a Kofler hot-stage microscope and are uncorrected.

Reactions of [$Fe(cp)(CO)_2(CH_2Cl)$] (1) *with* PPh_3, $PMePh_2$, PMe_2Ph, $PEtPh_2$, PEt_2Ph, *and* $AsPh_3$ *in Methanol; Synthesis of Compounds* (2)—(7).—*General procedure.* Compound (1) was heated under reflux in methanol (10 cm^3) with the ligand (slight excess of 1 mol). For reaction times, see Table 1. Monitoring the reaction by i.r. spectroscopy in the ν(CO) region showed that, irrespective of the ligand, (1) was in equilibrium with [$Fe(cp)(CO)_2(CH_2OMe)$] (8). This was followed by the appearance of bands due to the respective products. When the reaction had gone to completion, as judged by the i.r. spectra, the yellow reaction solution was cooled and the product precipitated by addition of a solution of an excess of $NaBPh_4$ in methanol. These precipitates were recrystallised from acetone–diethyl ether or dichloromethane–diethyl ether to give the products (2)—(7) as yellow, air-stable crystalline solids. For yields and characterisation data for the complexes see Table 1.

Reaction of [Fe(cp)(CO)$_2$(CH$_2$OMe)] (8) *with* [PPh$_3$H]I.—The salt [PPh$_3$H]I (0.67 mmol) (synthesised from PPh$_3$ and HI in hexane) was added to a solution of (8) (0.056 mmol) in methanol (8 cm^3). The reaction mixture was allowed to stand for 7 d. Periodic monitoring by i.r. spectroscopy showed that the ν(CO) bands of (8) diminished fairly rapidly to give new bands at 2 025 and 1 972 cm^{-1} (CH$_2$Cl$_2$ solution). This new species was in turn partially converted into a new product (shoulders appeared on the bands at 2 025 and 1 972 cm^{-1}). Orange crystals formed, which were separated from the mother-liquor and identified as [Fe(cp)(CO)$_2$(CH$_2$PPh$_3$)]I (17%). Treatment of the mother-liquor with NaBPh$_4$ gave [Fe(cp)(CO)$_2$(CH$_2$PPh$_3$)]BPh$_4$ (2) (16%).

In another experiment, complex (8) was heated under reflux with an excess of [PPh$_3$H]I in methanol for 1 h. Addition of NaBPh$_4$ to the reaction mixture gave (2) (75%).

Reaction of [Fe(cp)(CO)$_2$(CH$_2$Cl)] (1) *with* PPh$_3$, PMePh$_2$, PMe$_2$Ph, PMe$_3$, *and* PEtPh$_2$ *in Acetonitrile; Synthesis of Compounds* (2)—(4) *and* (9)—(12).—*General procedure.* A solution of compound (1) in acetonitrile (10 cm^3) was reacted with the tertiary phosphine ligand ($\geqslant$2 mol) at room temperature in the dark. The course of the reaction was monitored by i.r. spectroscopy in the ν(CO) region. In all cases except the reaction with PPh$_3$, the reaction mixture became deep red and ν(CO) bands of [{Fe(cp)(CO)$_2$}$_2$] were observed in the i.r. spectra as well as bands due to products. The solvent was removed under reduced pressure, the residue dissolved in methanol, and a methanol solution of an excess of NaBPh$_4$ was immediately added. The resulting air-stable, yellow precipitate was filtered off and recrystallised. Data for compounds not listed in Table 1 appear in Table 2. The following compounds were also obtained from the reaction of (1) with the appropriate ligand in acetonitrile (reaction time, yields, and other departures from general procedure noted in parentheses): [Fe(cp)(CO)$_2$(CH$_2$PPh$_3$)]BPh$_4$ (2) (2 d, crude yield 52%, 1 mol equivalent PPh$_3$); [Fe(cp)(CO)$_2$(CH$_2$PMePh$_2$)]BPh$_4$ (3) (5 d, 33%); a mixture of [Fe(cp)(CO)$_2$(CH$_2$PMe$_2$Ph)]BPh$_4$ (4) and [Fe(cp)(CO)(PMe$_2$Ph)$_2$]BPh$_4$ (9) separated by fractional recrystallisations [17.5 h, 1 mol equivalent PMe$_2$Ph, products identified by i.r. spectroscopy in ν(CO) region and ^{1}H n.m.r. spectra].

Preparation of [Fe(cp)(CO)$_2$(CH$_2$PPh$_3$)]PF$_6$ (2b). A solution of complex (1) (0.67 g, 2.96 mmol) and PPh$_3$ (0.77 g, 2.94 mmol) in acetonitrile (10 cm^3) was allowed to stand at room temperature in the dark for 42 h. The solvent was removed under reduced pressure and the resulting yellow oil dissolved in methanol (5 cm^3). Addition of a solution of [NBu$^n_4$]PF$_6$ (1.11 g, 2.94 mmol) in methanol (15 cm^3) caused precipitation of a yellow crystalline solid. Recrystallisation from dichloromethane–hexane gave the product as yellow platelets. For yield and characterisation data see Table 2; the equivalent conductance for a *ca.* 10^{-3} mol dm^{-3} solution (C$_6$H$_5$NO$_2$) was 31.7 Ω^{-1} cm^2 mol^{-1}.

Reaction of (1) *with* PEt$_2$Ph *in acetonitrile.* A solution of complex (1) (0.341 g, 1.51 mmol) in acetonitrile (8 cm^3) was treated with PEt$_2$Ph (0.583 g, 3.51 mmol) and the mixture allowed to stand for 3 d in the dark. The red solution was evaporated to dryness and the residue dissolved in methanol. Addition of an excess of NaBPh$_4$ in methanol gave a mixture of yellow platelets and white needles. This mixture was dissolved in acetone and light petroleum (b.p. 60—80 °C) added slowly. On cooling, white needles (0.30 g, 40%) were deposited and identified as [PMeEt$_2$Ph]BPh$_4$ (see Table 2). Further addition of light petroleum gave yellow platelets (0.17 g). This product could not be completely separated from the white needles but was identified as [Fe(cp)(CO)(PEt$_2$Ph)$_2$]BPh$_4$ (11) on the basis of data given in Table 2.

Reactions of [W(cp)(CO)$_3$(CH$_2$Cl)] *with* PPh$_3$.—*In acetonitrile: synthesis of compound* (13). A solution containing [W(cp)(CO)$_3$(CH$_2$Cl)] (0.346 g, 0.90 mmol) and PPh$_3$ (0.276 g, 1.05 mmol) in acetonitrile (10 cm^3) was allowed to stand in the dark at room temperature for 34 d. The solvent was removed from the orange-red solution under reduced pressure. The residue was dissolved in methanol, filtered, and an excess of a solution of NaBPh$_4$ in methanol was added, when yellow needles of [W(cp)(CO)$_3$(CH$_2$PPh$_3$)]BPh$_4$ (13) (0.170 g, 20%) precipitated (see Table 3 for characterisation data).

In methanol. A solution containing [W(cp)(CO)$_3$(CH$_2$Cl)] (0.197 g, 0.515 mmol) and PPh$_3$ (0.162 g, 0.618 mmol) dissolved in methanol was refluxed for 3.25 h. The solvent was removed under reduced pressure and the resulting residue solidified on addition of hexane. This solid (0.274 g) was filtered off and washed with hexane then recrystallised from dichloromethane–hexane to give yellow needles of [W(cp)(CO)$_3$(CH$_2$PPh$_3$)]Cl (13a) (0.117 g, 35%) (see Table 3 for characterisation data). This formulation of this product was confirmed by its reaction with NaBPh$_4$ which gave a product with identical colour, m.p., and i.r. and ^{1}H n.m.r. spectra to (13).

Reactions of [Mo(cp)(CO)$_3$(CH$_2$Cl)] *with* PPh$_3$.—*In acetonitrile.* A solution containing [Mo(cp)(CO)$_3$(CH$_2$Cl)] (0.400 g, 1.36 mmol) and PPh$_3$ (0.373 g, 1.42 mmol) dissolved in acetonitrile (5 cm^3) was allowed to stand in the dark at room temperature for 28 d. The orange crystalline solid (0.496 g, 71%) which precipitated was filtered off and washed with acetonitrile (2 × 2 cm^3) and hexane (10 cm^3). Recrystallisation of this solid from dichloromethane–hexane gave orange-red prisms, m.p. 178—192 °C; ν(CO) (CH$_2$Cl$_2$) 1 971vs and 1 883m cm^{-1}. The i.r. and ^{1}H n.m.r. spectra of this product were identical to those of a sample of [Mo(cp)(CO)$_2$(PPh$_3$)Cl] (15) prepared from [Mo(cp)(CO)$_3$(Cl] and PPh$_3$.[36,37]

In methanol. A solution containing [Mo(cp)(CO)$_3$(CH$_2$Cl)] (0.165 g, 0.56 mmol) and PPh$_3$ (0.176 g, 0.67 mmol) dissolved in methanol (15 cm^3) was heated under reflux for 30 min. The solvent was removed under reduced pressure to give an orange solid which was washed with hexane then recrystallised from benzene–hexane to give orange microcrystals of [Mo(cp)(CO)$_2$(PPh$_3$)(COCH$_2$OMe)] (14) (0.16 g, 52%) (for characterisation data see Table 3).

In a separate experiment [Mo(cp)(CO)$_3$(CH$_2$Cl)] was allowed to stand in methanol solution for 2 h. After this time the solvent was removed under reduced pressure and an i.r. spectrum of the residue showed ν(CO) at 2 026s, 1 950s, and 1 933s cm^{-1} (cyclohexane) identical to the ν(CO) i.r. spectrum of [Mo(cp)(CO)$_3$(CH$_2$OMe)].

In another experiment [Mo(cp)(CO)$_3$(CH$_2$Cl)] (0.184 g, 0.63 mmol) and PPh$_3$ (0.197 g, 0.75 mmol) as a solution in methanol (15 cm^3) were heated under reflux for 4 h. The solution was cooled to −10 °C when orange-red crystals (0.138 g) precipitated. These were shown to be mainly [Mo(cp)(CO)$_2$(PPh$_3$)Cl] but with some [Mo(cp)(CO)(PPh$_3$)$_2$Cl] and [Mo(cp)(CO)$_2$(PPh$_3$)(COCH$_2$OMe)] by comparison of i.r. and ^{1}H n.m.r. spectra with those of authentic samples.[36,37]

Reaction of [Mn(CO)$_5$(CH$_2$Cl)] *with* PPh$_3$.— A solution of [Mn(CO)$_5$(CH$_2$Cl)][1] (0.106 g, 0.44 mmol) and PPh$_3$ (0.291 g, 1.10 mmol) dissolved in acetonitrile (4 cm^3) was allowed to stand at room temperature in the dark for 7 d. The yellow needles which formed were filtered off and washed with acetonitrile and hexane to give the product (0.144 g, 47%), m.p. 136—180 °C (decomp.). This had an i.r. spectrum, m.p., and colour identical to those of a sample of [Mn(CO)$_3$(PPh$_3$)$_2$Cl] [23] (16) prepared from the reaction of [Mn(CO)$_5$Cl] and PPh$_3$ in acetonitrile at room temperature in the dark for 5 d.

In a separate experiment, a solution of [$Mn(CO)_5(CH_2Cl)$] (0.186 g, 0.76 mmol) and PPh_3 (0.207 g, 0.79 mmol) in methanol (10 cm^3) was allowed to stand in the dark at room temperature for 6 d. The yellow precipitate (0.090 g, 33% based on PPh_3) which formed had an identical i.r. spectrum to that shown by [$Mn(CO)_3(PPh_3)_2Cl$] (16).

Reaction of [$Mn(CO)_5(CH_2OMe)$] *with* PPh_3.—The complex [$Mn(CO)_5(CH_2OMe)$] (0.140 g, 0.58 mmol) was allowed to stand in acetonitrile (4 cm^3) with PPh_3 (0.150 g, 0.56 mmol) for 5 d at room temperature in the dark. The solvent was removed under reduced pressure and the resulting yellow oil washed with hexane to give *cis*-[$Mn(CO)_4(PPh_3)(COCH_2OMe)$] (17) as yellow microcrystals (0.090 g, 30%) (see Table 3 for characterisation data).

In a separate experiment, a solution containing [$Mn(CO)_5(CH_2OMe)$] (0.320 g, 1.33 mmol) and PPh_3 (0.356 g, 1.36 mmol) dissolved in methanol (10 cm^3) was heated under reflux for 50 min. The solvent was removed under reduced pressure to give a yellow oil which was then dissolved in hexane, filtered, and cooled to −10 °C when *cis*-[$Mn(CO)_4(PPh_3)(CH_2OMe)$] (18) precipitated as clusters of yellow needles (0.470 g, 74%).

In another experiment, [$Mn(CO)_5(CH_2OMe)$] (0.550 g, 2.28 mmol) and PPh_3 (1.38 g, 5.27 mmol) as a solution in methanol were heated under reflux for 5 h. The reaction mixture was cooled and the precipitate was filtered off to give *trans*-[$Mn(CO)_3(PPh_3)_2(CH_2OMe)$] (19) (0.420 g, 26%). The product was then purified by two recrystallisations from benzene–hexane. After filtering off the precipitate of (19), the solvent was removed under reduced pressure from the filtrate. This residue was dissolved in hexane and cooled to −10 °C to give pale yellow crystals (0.825 g) which contained (18) as the only metal carbonyl compound, but contaminated with triphenylphosphine.

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