Reactivity of Main-group–Transition-metal Bonds. Part IV.[1] Kinetics of Iodination of Compounds containing Group 4B Elements bonded to Molybdenum, Manganese, and Iron: Effects of Structure on Reactivity

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Rate coefficients have been determined for the reactions in tetrachloromethane of iodine with $[Fe(cp)(CO)_2(MMe_3)]$ (M = Si, Ge, or Sn), $[Mo(cp)(CO)_3(SnR_3)]$ (R = Me, Bu, or Ph), $[Fe(cp)(CO)_2(SnR_3)]$ (R = Me, Bu, or Ph), $[Mn(CO)_5(SnR_3)]$ (R = Me, Et, or C_6H_{11}), $[Mn(CO)_5(MMe_3)]$ (M = Si, Ge, Sn or Pb), and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$. Alkyl groups on the Group 4B element influence reactivity as expected from their electronic properties rather than their steric effects. The reactivity of the compounds increases as silicon is replaced by germanium, tin, and lead. This is a consequence of vertical hyperconjugation and increasing stability of the MMe_3^+ ion (M = Si, Ge, Sn, or Pb).

We recently reported studies on the kinetics of scission by iodine of the bond between a Group 4 element (tin) and a transition metal (Cr, Mo, W, Mn, or Fe).[2,3] The process is one of electrophilic substitution at the transition metal [equation (1),† M = Sn], with the observed rate coefficient ($k_2^{\text{obs.}}$) as given by equation (2). The

$$[M'(cp)_n(CO)_m(MR_3)] + I_2 \xrightarrow{k_2^{\text{obs.}}} MR_3I + [M'(cp)_n(CO)_mI] \quad (1)$$

$$\text{Rate} = k_2^{\text{obs.}}[M'(cp)_n(CO)_m(MR_3)][I_2] \quad (2)$$

mechanism of the reaction is however, not simple, and probably involves one or more chemical intermediates. In an attempt to gain further information about this reaction we have carried out kinetic studies on a series of compounds in which systematic changes have been made in the organometallic substrate.

RESULTS

Product Analyses—These are given in some detail as most of the reactions studied have not been previously reported, and kinetic measurements are of no value unless they are based on an accurate knowledge of reaction stoicheiometry. Products were usually isolated from a 1 : 1 molar mixture of organometallic compound and iodine. For experimental convenience, kinetic measurements were usually made on systems containing an excess of the organometallic compound, but the products were confirmed to be identical with those isolated by recording i.r. and n.m.r. spectra of the solutions after reaction.

Reaction of $[Fe(cp)(CO)_2(SiMe_3)]$ *with Iodine in Tetrachloromethane*.—(a) *Product analysis*. A solution of $[Fe(cp)(CO)_2(SiMe_3)]$ (0.2393 g, 96 μmol) in CCl_4 (10 cm^3) was allowed to react with a solution of I_2 (0.2622 g, 146 μmol) in CCl_4 (10 cm^3) at room temperature. I.r. analysis of the resulting solution showed peaks in the carbonyl region at 2 042, 1 998, and 1 940 cm^{-1} {*cf.* $[Fe(cp)(CO)_2I]$ with peaks [4] at 2 044 and 2 000 cm^{-1} and $[Fe(cp)(CO)_2(SiMe_3)]$ with peaks [5] at 2 000 and 1 940 cm^{-1}}. The n.m.r. spectrum showed peaks at δ 5.02 and 5.65 p.p.m.‡ {$[Fe(cp)(CO)_2I]$ in $CDCl_3$ has a peak at δ 5.01 p.p.m.;[4] a prepared specimen in CCl_4 shows a peak at δ 5.03 p.p.m.; $[Fe(cp)(CO)_2(SiMe_3)]$, δ 5.65 p.p.m. (a prepared specimen)} and at δ 0.38 p.p.m. {$SiMe_3I$, δ 0.78 p.p.m.;[6] $[Fe(cp)(CO)_2(SiMe_3)]$, 0.38 p.p.m. (a prepared specimen)}. As $SiMe_3I$ is quite volatile, it may have evaporated from the solution before the n.m.r. spectrum was taken. These results indicate that reaction with iodine is not complete, but proceeds to a position of equilibrium as shown by equation (3). Comparison of intensities of n.m.r.

$$[Fe(cp)(CO)_2(SiMe_3)] + I_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(cp)(CO)_2I] + SiMe_3I \quad (3)$$

peaks showed that, under the conditions given in Table 1, *ca.* 50% of the iodine was converted into products.

(b) *Kinetics*. The kinetics of the reaction were studied under pseudo-first-order conditions {excess of $[Fe(cp)(CO)_2(SiMe_3)]$}, and the second-order rate coefficient, $k_2^{\text{obs.}}$ [equation (2)] was calculated from the observed first-order rate coefficient, $k_1^{\text{obs.}}$. The true rate coefficient, k_1, for a

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C \quad (4)$$

first-order reaction which proceeds to a position of equilibrium [equation(4)] can be calculated from the apparent half-time, $t_{\frac{1}{2}}^{\text{obs.}}$, by equation (5),[7] where α is the fraction of

$$k_1 t_{\frac{1}{2}}^{\text{obs.}} = \alpha[\ln(3-\alpha)]/(2-\alpha) \quad (5)$$

reaction at equilibrium. From the n.m.r. spectrum at equilibrium, $\alpha \approx 0.5$, hence $k_1 t_{\frac{1}{2}}^{\text{obs.}} = 0.305$. As $t_{\frac{1}{2}}^{\text{obs.}} = 0.693/k_1^{\text{obs.}}$, $k_1 = 0.305\ k_1^{\text{obs.}}/0.693$ and $k_2^{\text{obs.}} = 0.44\ k_1^{\text{obs.}}$ [complex].

Reaction of $[Fe(cp)(CO)_2(GeMe_3)]$ *with Iodine in Tetrachloromethane*.—(a) *Product analysis*. A solution of $[Fe(cp)(CO)_2(GeMe_3)]$ in CCl_4 was allowed to react with an equimolar solution of I_2 at room temperature. I.r. analysis of the resulting solution showed peaks in the carbonyl region at 2 042 and 2 001 cm^{-1} {*cf.* $[Fe(cp)(CO)_2I]$}. N.m.r. analysis of the solution showed peaks at δ 5.01 and 1.05 {*cf.* $[Fe(cp)(CO)_2I]$, and $GeMe_3I$ (δ 0.98)[6]}. These results are in agreement with the reaction being described by equation (1) (R = Me, M = Ge, M′ = Fe, $n = 1$, $m = 2$).

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† cp = η-Cyclopentadienyl (C_5H_5).

‡ Proton shifts are in p.p.m. relative to $SiMe_4$.

[1] Part III, J. R. Chipperfield, J. Ford, and D. E. Webster, *J. Organometallic Chem.*, 1975, **102**, 417.

[2] J. R. Chipperfield, J. Ford, and D. E. Webster, *J.C.S. Dalton*, 1975, 2042.

[3] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Dalton*, 1975, 2048.

[4] R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, 1967, **1**, 451.

[5] T. S. Piper, D. Lemal, and G. Wilkinson, *Naturwiss.*, 1956, **43**, 129.

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[7] J. R. Chipperfield and G. E. Gould, *J.C.S. Perkin II*, 1974, 1331.

(b) *Kinetics.* The kinetics of the reaction were studied under pseudo-first-order conditions {excess of [Fe(cp)(CO)$_2$(GeMe$_3$)]}. The data, given in Table 1, fit rate equation (2).

Reaction of [Fe(cp)(CO)$_2$(SnBu$_3$)] *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of [Fe(cp)(CO)$_2$(SnBu$_3$)] (0.1736 g, 373 μmol) in CCl$_4$ (10 cm^3) was allowed to react with a solution of I$_2$ (0.0952 g, 375 μmol) in CCl$_4$ (10 cm^3). I.r. analysis of the resulting solution showed peaks in the carbonyl region at 2 042 and 2 001 cm^{-1} {*cf.* [Fe(cp)(CO)$_2$I]}. N.m.r. analysis showed a peaks at δ 5.01 p.p.m. {*cf.* [Fe(cp)(CO)$_2$I]}. These results are in agreement with the reaction being described by equation (1) (R = Bu, M = Sn, M′ = Fe, n = 1, m = 2).

TABLE 1

Reactions of Group 4 derivatives of molybdenum, manganese, and iron with iodine in CCl$_4$ at 30.0 °C

Compound	10^3[Compound] / mol dm^{-3}	10^3[I$_2$] / mol dm^{-3}	$k_2^{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}	Mean $k_2^{\text{obs.}}$ / dm^3 mol^{-1} s^{-1}	Method [a]
[Fe(cp)(CO)$_2$(SiMe$_3$)]	18.4	0.84	10.2	9.6	s.f.s.
	9.2	0.84	8.9		
	9.2	0.42	9.7		
[Fe(cp)(CO)$_2$(GeMe$_3$)]	6.9	0.50	126	116	s.f.s.
	6.9	0.25	120		
	3.45	0.25	103		
[Fe(cp)(CO)$_2$(SnMe$_3$)]				2 780 [b]	
[Fe(cp)(CO)$_2$(SnBu$_3$)]				3 000—5 000 [c]	s.f.s.
[Fe(cp)(CO)$_2$(SnPh$_3$)]	16.06	0.216	10.0	9.2 [d]	s.f.s.
	16.06	0.539	11.7		
	16.06	1.08	13.4		
	7.81	0.596	10.1		
	15.62	0.596	10.8		
[Mo(cp)(CO)$_3$(SnMe$_3$)]				226 [b]	
[Mo(cp)(CO)$_3$(SnBu$_3$)]	22.7	0.53	301	310	s.f.s.
	22.7	1.06	326		
	22.7	2.12	308		
	11.3	0.53	307		
[Mn(CO)$_5$(SiMe$_3$)]	21.4	1.17	5.1×10^{-6}	5×10^{-6}	u.s.
	12.2	0.69	4.8×10^{-6}		
[Mn(CO)$_5$(GeMe$_3$)]	21.8	0.60	1.03×10^{-4}	1.06×10^{-4}	u.s.
	9.0	0.38	1.1×10^{-4}		
[Mn(CO)$_5$(SnMe$_3$)]				0.0050 [b]	u.s.
[Mn(CO)$_5$(SnEt$_3$)]	28.6	0.84	0.0338	0.0328 [e]	u.s.
	11.6	0.84	0.0318		
[Mn(CO)$_5$(SnBu$_3$)]	27.9	0.874	0.0393 [f]	0.0388	u.s.
	24.8	0.801	0.0392 [f]		
	16.1	1.37	0.0380		
[Mn(CO)$_5${Sn(C$_6$H$_{11}$)$_3$}]	14.5	1.28	0.0285	0.0287	u.s.
	7.13	0.64	0.0272		
	7.08	0.64	0.0304		
[Mn(CO)$_5$(PbMe$_3$)]	14.4	0.694	0.147	0.146	u.s.
	48.7	0.694	0.151		
	7.65	0.694	0.143		
	22.8	0.694	0.141		

[a] s.f.s. = Stopped-flow spectrophotometer; u.s. = Unicam SP 500 spectrophotometer (see Experimental section); λ = 540 nm. [b] Ref. 2. [c] Estimated from $t_{\frac{1}{2}}$ as the reaction was very fast. [d] See text. [e] $k_2^{\text{obs.}}$ was shown to be independent of [I$_2$] at 40 °C. [f] Successive additions of I$_2$ to same [Mn(CO)$_5$(SnBu$_3$)] solution.

(b) *Kinetics.* The rate of reaction was so fast that a detailed study of the kinetics was impossible, even with a stopped-flow spectrophotometer. From semi-quantitative experiments, an estimate of the half-time of reaction was made and gave an approximate value of $k_2^{\text{obs.}}$ of between 3 000 and 5 000 dm^3 mol^{-1} s^{-1}.

Reaction of [Fe(cp)(CO)$_2$(SnPh$_3$)] *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of [Fe(cp)(CO)$_2$(SnPh$_3$)] (0.232 g, 442 μmol) in CCl$_4$ (10 cm^3) was allowed to react with a solution of I$_2$ (0.1102 g, 443 μmol) in CCl$_4$ (10 cm^3). I.r. analysis of the resulting solution showed peaks in the carbonyl region at 2 042 and 2 000 cm^{-1} {*cf.* [Fe(cp)(CO)$_2$I]}. N.m.r. analysis showed a peak due to cp at δ 5.04 p.p.m. {*cf.* [Fe(cp)(CO)$_2$I]}. The mass spectrum of the residue after removal of CCl$_4$ showed peaks at *m/e* values corresponding to the ions [Fe(cp)(CO)$_2$I]$^+$ and [SnPh$_3$I]$^+$. The breakdown pattern of [Fe(cp)(CO)$_2$I]$^+$ was the same as that of a prepared sample of [Fe(cp)(CO)$_2$I]. Thus the reaction may be described by equation (1) (R = Ph, M = Sn, M′ = Fe, n = 1, m = 2).

(b) *Kinetics.* The kinetics of the reaction were studied under pseudo-first-order conditions {excess of [Fe(cp)(CO)$_2$(SnPh$_3$)]}. The results in Table 1 show that $k_2^{\text{obs.}}$ increases with [I$_2$]. The most likely cause for this is the presence of a second term in the rate equation for a process involving two molecules of iodine [equation (6)]. Hence $k_2^{\text{obs.}}$ is given

$$\text{Rate} = k_2'[\text{C}][\text{I}_2] + k_3[\text{C}][\text{I}_2]^2 \qquad (6)$$

by (7). This means that a plot of $k_2^{\text{obs.}}$ against [I$_2$] should be

$$k_2^{\text{obs.}} = k_2' + k_3[\text{I}_2] \qquad (7)$$

a straight line with gradient k_3 and intercept k_2'. This is so. The values found are k_2' = 9.2 dm^3 mol^{-1} s^{-1} and k_3 = 4 × 10^3 dm^6 mol^{-2} s^{-1}.

Reaction of [Mo(cp)(CO)$_3$(SnBu$_3$)] *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of [Mo(cp)(CO)$_3$(SnBu$_3$)] (0.0358 g, 665 μmol) in CCl$_4$ (10 cm^3) was allowed to react with a solution of I$_2$ (0.0149 g, 587 μmol) in

[8] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

CCl_4 (10 cm^3). I.r. analysis of the resulting solution showed peaks in the carbonyl region at 2 044, 1 974, and 1 961 cm^{-1} {*cf.* $[Mo(cp)(CO)_3I]$ with peaks at 2 040, 1 968, and 1 955 cm^{-1};[8] we found peaks at 2 045, 1 975, and 1 960 cm^{-1} for a prepared sample}. N.m.r. analysis showed a peak from cp at δ 5.60 p.p.m. {*cf.* a prepared sample of $[Mo(cp)(CO)_3I]$ showed a peak at δ 5.60 p.p.m.}. These results are in agreement with the reaction being described by equation (1) ($R = Bu$, $M = Sn$, $M' = Mo$, $n = 1$, $m = 3$).

(b) *Kinetics.* The kinetics of the reaction were studied under pseudo-first-order conditions {excess of $[Mo(cp)(CO)_3(SnBu_3)]$} and the results (Table 1) fit rate equation (2) with $k_2^{obs.} = 310$ dm^3 mol^{-1} s^{-1}.

Reaction of $[Mn(CO)_5(SiMe_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mn(CO)_5(SiMe_3)]$ (0.013 g, 49 µmol) in CCl_4 (3.0 cm^3) was mixed with a solution of I_2 (0.001 g, 4 µmol) in CCl_4 (0.5 cm^3) and the reaction flask was kept at 20 °C in the dark. After 1 week the colour due to iodine was still present but an i.r. spectrum showed small peaks at 2 045 and 2 016 cm^{-1} due to $[Mn(CO)_5I]$ (peaks[9] at 2 125, 2 044, 2 016, and 2 003 cm^{-1}) in addition to those of starting material. G.l.c. analysis showed the presence of $SiMe_3I$ [$SiMe_3I$ for reference was prepared by the reaction of $SiMe_3(C_6H_4OMe\text{-}p)$ with I_2]. A slow reaction was taking place according to equation (1) ($R = Me$, $M = Si$, $M' = Mn$, $n = 0$, $m = 5$).

(b) *Kinetics.* The reaction was very slow, and was studied under pseudo-first-order conditions {$[Mn(CO)_5(SiMe_3)]$ in excess} over the first 15—25% of reaction. The optical density of the solution after reaction was taken to be that of a solution of $[Mn(CO)_5(SiMe_3)]$ alone. The reaction was first order in the concentration of each reagent, supporting rate equation (2), and values of $k_2^{obs.}$ are given in Table 1.

Reaction of $[Mn(CO)_5(GeMe_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mn(CO)_5(GeMe_3)]$ (0.020 g, 64 µmol) in CCl_4 was mixed with a solution of I_2 (0.001 g, 4 µmol) in CCl_4 at 20 °C. After 6 weeks the colour due to I_2 remained but an i.r. spectrum showed peaks at 2 044 and 2 016 cm^{-1} {due to $[Mn(CO)_5I]$} in addition to those from starting material. After evaporation of CCl_4 the mass spectrum of the residue was recorded and showed peaks corresponding to the molecular ion of $GeMe_3I$. A low source temperature was necessary as $GeMe_3I$ is volatile.

(b) *Kinetics.* The reaction was slow and was studied under pseudo-first-order conditions {$[Mn(CO)_5(GeMe_3)]$ in excess} over the first 30—45% of reaction. The optical density of the solution after reaction was taken to be that of a solution of $[Mn(CO)_5(GeMe_3)]$ alone. The reaction was first order in the concentration of each reagent [supporting equation (2)] and values of $k_2^{obs.}$ are given in Table 1.

Reaction of $[Mn(CO)_5(SnEt_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mn(CO)_5(SnEt_3)]$ (0.015 g, 37 µmol) in CCl_4 (1 cm^3) was allowed to react with a solution of I_2 (0.001 g, 4 µmol) in CCl_4 (0.25 cm^3). The i.r. spectrum of the resulting solution had bands in the carbonyl region at 2 126, 2 045, and 2 016 cm^{-1} in addition to those of the starting materials {*cf.* $[Mn(CO)_5I]$}. A second solution of $[Mn(CO)_5(SnEt_3)]$ (0.015 g, 37 µmol) in CCl_4 (1 cm^3) was allowed to react with I_2 (0.011 g, 43 µmol) in CCl_4. After evaporation of CCl_4 the mass spectrum of the residue was recorded and showed peaks from the molecular ion $SnEt_3I$ and its breakdown products. The reaction can thus be described by equation (1) ($R = Et$, $M = Sn$, $M' = Mn$, $n = 0$, $m = 5$).

(b) *Kinetics.* The kinetics of the reaction were studied under pseudo-first-order conditions with $[Mn(CO)_5(SnEt_3)]$ in excess. The reaction was first order in the concentration of each reagent [confirming equation (2)] and values of $k_2^{obs.}$ are given in Table 1. Activation parameters are given in Table 3.

Reaction of $[Mn(CO)_5(SnBu_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mn(CO)_5(SnBu_3)]$ (0.040 g, 83 µmol) in CCl_4 (3 cm^3) was allowed to react with a solution of I_2 (0.002 g, 8 µmol) in CCl_4 (0.5 cm^3). An i.r. spectrum of the solution showed peaks at 2 045 and 2 016 cm^{-1} {*cf.* $[Mn(CO)_5I]$} in addition to peaks from starting material. After removal of CCl_4 a mass spectrum of the residue showed peaks at *m/e* values corresponding to $SnBu_3I$. The reaction may be described by equation (1) ($R = Bu$, $M = Sn$, $M' = Mn$, $n = 0$, $m = 5$).

(b) *Kinetics.* The kinetics of the reaction were studied under pseudo-first-order conditions {excess of $[Mn(CO)_5(SnBu_3)]$}. When a reaction was complete a second portion of iodine was added. $k_2^{obs.}$ Values for consecutive runs were similar, indicating that the reagents contained no significant impurities, and support rate equation (2).

The Reaction of $[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$ (0.025 g, 44 µmol) in CCl_4 (3 cm^3) was allowed to react with 0.5 cm^3 of a solution of I_2 (0.012 g, 47 µmol) in CCl_4 (10 cm^3). The i.r. spectrum of the resulting solution had bands (in addition to those of starting material) at 2 126, 2 044, 2 016, and 2 001 cm^{-1} (*cf.* $[Mn(CO)_5I]$ and a small peak at 2 033 cm^{-1} possibly from $[\{Mn(CO)_4I\}_2]$ formed by slow decomposition of $[Mn(CO)_5I]$; $[\{Mn(CO)_4I\}_2]$ has peaks at 2 087, 2 033, 2 009, and 1 976 cm^{-1}).[9] After removal of CCl_4, a mass spectrum of the residue showed peaks at *m/e* values corresponding to the molecular ion of $Sn(C_6H_{11})_3I$ and its breakdown products. The reaction can be described by equation (1) (R = cyclohexyl, $M = Sn$, $M' = Mn$, $n = 0$, $m = 5$), followed by the very slow reaction $2[Mn(CO)_5I] \longrightarrow [\{Mn(CO)_4I\}_2] + 2CO$.

(b) *Kinetics.* The kinetics were studied under pseudo-first-order conditions as usual and in the time scale of the rate studies formation of $[\{Mn(CO)_4I\}_2]$ can be ignored. The reaction was first order in the concentration of each reactant confirming rate equation (2) and values of $k_2^{obs.}$ are given in Table 1. Rate coefficients were measured over the range 30—50 °C and activation parameters are given in Table 3.

Reaction of $[Mn(CO)_5(PbMe_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.** A solution of $[Mn(CO)_5(PbMe_3)]$ (0.030 g, 67 µmol) in CCl_4 (3 cm^3) was allowed to react with I_2 (0.0015 g, 7 µmol) in CCl_4 (0.4 cm^3). The i.r. spectrum of the resulting solution had bands in the carbonyl region (in addition to those of starting material) at 2 126, 2 044, and 2 016 cm^{-1} {*cf.* $[Mn(CO)_5I]$}. A second solution of $[Mn(CO)_5(PbMe_3)]$ was allowed to react with half the amount of I_2 required for complete reaction. N.m.r. analysis of this solution showed a peak at δ 1.20 p.p.m. {from $[Mn(CO)_5(PbMe_3)]$}, peaks assigned as methyl-lead halides, and a peak at δ 2.14 p.p.m. corresponding to MeI. A small amount of a white precipitate was formed in the n.m.r. tube. This is probably $PbMe_2I_2$, formed after scission of the

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* Clark and his co-workers reported reaction of $[Mn(CO)_5(PbMe_3)]$ with excess of I_2 to give PbI_2.[10]

[9] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, 1962, **1**, 933.

[10] M. R. Booth, D. J. Cardin, N. A. D. Carey, H. C. Clark, and B. R. Sreenathan, *J. Organometallic Chem.*, 1970, **21**, 171.

Pb–Mn bond [equation (1); R = Me, M = Pb, M′ = Mn, $m = 5$, $n = 0$) by the $PbMe_3I$ reacting further with the strong iodine solution used for the n.m.r. experiment. It is not likely that $PbMe_3I$ reacts with I_2 in dilute solutions as Pilloni and Tagliavini[11] have studied the kinetics of the iodinolysis of $PbMe_4$ in CCl_4, and reported no secondary reaction of $PbMe_3I$.

$$PbMe_4 + I_2 \xrightarrow{CCl_4} PbMe_3I + MeI \qquad (8)$$

(b) *Kinetics.* The kinetics were studied under pseudo-first-order conditions as usual. The reaction was first order in the concentration of each reactant confirming rate equation (2) and values of $k_2^{obs.}$ are given in Table 1. On mixing solutions of $[Mn(CO)_5(PbMe_3)]$ with I_2, the initial optical density was less than that calculated for the iodine solution alone {$[Mn(CO)_5(PbMe_3)]$ does not absorb at 540 nm}. This suggests that formation of a charge-transfer complex between I_2 and $[Mn(CO)_5(PbMe_3)]$ is occurring.[2,12]

Reaction of $[Mo(cp)(CO)_3(SnPh_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.** A solution of $[Mo(cp)(CO)_3(SnPh_3)]$ (0.7267 g, 1.21 mmol) in CCl_4 (10 cm^3) was allowed to react with a solution of I_2 (0.3119 g, 1.21 mmol) in CCl_4(10 cm^3) (at room temperature). The i.r. spectrum of the solution contained peaks in the carbonyl region at 2 044, 2 016, 1 974, 1 955, and 1 919 cm^{-1} {a specimen of $[Mo(cp)(CO)_3I]$ had peaks at 2 045, 1 975, and 1 960 cm^{-1}, (lit.,[8] 2 040, 1 968, and 1 955 cm^{-1}) and $[Mo(cp)(CO)_3(SnPh_3)]$ has peaks[14] at 2 004, 1 934, and 1 909 cm^{-1}}. N.m.r. analysis showed peaks due to cp at δ 5.58 and 5.38 p.p.m. {*cf.* $[Mo(cp)(CO)_3I]$, δ 5.60; $[Mo(cp)(CO)_3(SnPh_3)]$, δ 5.55 p.p.m.[14]}. G.l.c. analysis showed the presence of PhI. A mass spectrum was recorded for the residue left after the CCl_4 had been removed. It showed the presence of $[Mo(cp)(CO)_3I]$ and also $[Mo(cp)(CO)_3(SnPh_2I)]$ and other iodine-containing derivatives.

The above i.r. data contain peaks at 2 016 and 1 919 cm^{-1} that are unassigned, and the n.m.r. band at δ 5.38 p.p.m. is also unassigned. The presence of PhI in the solution indicates that Ph–Sn bonds have been cleaved and it is likely that the unassigned peaks are due to $[Mo(cp)(CO)_3(SnPh_2I)]$ (which was seen in the mass spectrum). The i.r. and n.m.r. spectra of $[Mo(cp)(CO)_3(SnPh_2I)]$ have not been published, but the i.r. spectrum of $[Mo(cp)(CO)_3(SnI_3)]$ shows peaks at 2 035, 1 970, and 1 943 cm^{-1}.[15] As there is a linear relation between carbonyl-stretching frequencies and $\Sigma\sigma^*$ for R groups attached to Sn in compounds of type $[Mo(cp)(CO)_3(SnR_3)]$,[7] the i.r. bands of $[Mo(cp)(CO)_3(SnPh_2I)]$ can be calculated. Bands at 2 012, 1 944, and 1 920 cm^{-1} are predicted, and 2 012 and 1 920 cm^{-1} compare favourably with those found at 2 016 and 1 919 cm^{-1}. The peak at 1 944 cm^{-1} is not detected probably because of overlap with the 1 960 cm^{-1} peak of $[Mo(cp)(CO)_3I]$ to give the peak at 1 955 cm^{-1}.

The n.m.r. band at δ 5.38 p.p.m. can also be assigned to $[Mo(cp)(CO)_3(SnPh_2I)]$. The compound $[Mo(cp)(CO)_3(SnPh_3)]$ therefore reacts with I_2 in two ways [equations (9) and (10)].

$$\begin{aligned} & \nearrow^{k_2} \; SnPh_3I + [Mo(cp)(CO)_3I] && (9) \\ [Mo(cp)(CO)_3(SnPh_3)] + I_2 & \xrightarrow{k_2'} [Mo(cp)(CO)_3(SnPh_2I)] + PhI && (10) \end{aligned}$$

(b) *Kinetics.* The kinetics of the reaction with I_2 were studied under pseudo-first-order conditions {excess of $[Mo(cp)(CO)_3(SnPh_3)]$}, and values of $k_2^{obs.}$ are given in Table 2; $k_2^{obs.}$ will equal $k_2 + k_2'$. The n.m.r. spectrum of the products showed peaks at δ 5.58, $[Mo(cp)(CO)_3I]$, and 5.38 p.p.m., $[Mo(cp)(CO)_3(SnPh_2I)]$, with relative intensities of 3 : 2. The rate constant, k_2, for bond cleavage will be 0.6 $k_2^{obs.}$. Activation parameters calculated from the variation of $k_2^{obs.}$ with temperature over the range 30—45 °C are $\Delta H^\ddagger = 39 \pm 3$ kJ mol^{-1} and $\Delta S^\ddagger = -136 \pm 8$ J K^{-1} mol^{-1}. Although $k_2^{obs.}$ is composite, these parameters are of a similar magnitude to $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the similar reactions given in Table 3 where bond breaking takes place.

TABLE 2

Reactions of $[Mo(cp)(CO)_3(SnPh_3)]$ and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$ with iodine in CCl_4 at 30.0 °C

Compound	10^3[Compound] / mol dm^{-3}	$10^3[I_2]$ / mol dm^{-3}	$k_2^{obs.}$ / dm^3 mol^{-1} s^{-1}	Fraction of metal–metal bond cleavage	k_2 / dm^3 mol^{-1} s^{-1}	Method *
$[Mo(cp)(CO)_3(SnPh_3)]$	17.3	0.88	0.362 } 0.371	0.6	0.223	s.f.s.
	17.3	0.44	0.310			
	17.6	0.22	0.325			
	8.8	0.44	0.415			
$[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$	6.7	0.28	1.16	0.5	0.58	s.f.s.

* See footnote *a* (Table 1); λ = 540 nm.

TABLE 3

Activation parameters for the reaction of $[Mn(CO)_5(SnR_3)]$ with I_2 in CCl_4

R	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
Me	50.5 ± 4 *	−122 ± 10 *
Et	44.6 ± 2.6	−126 ± 8
C_6H_{11}	50.1 ± 4.2	−109 ± 10

* Ref. 2.

Reaction of $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$ *with Iodine in Tetrachloromethane.*—(a) *Product analysis.* A solution of $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$ (1.2 mmol) in CCl_4 (10 cm^3) was allowed to react with an equimolar solution of I_2 in CCl_4 (10 cm^3). The i.r. spectrum of the solution showed

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* This reaction has been reported by Clark and his co-workers,[13] who observed similar products in $CHCl_3$ at room temperature after 12 h.

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peaks at 2 041, 2 013, 1 972, 1 952, and 1 915 cm^{-1} {*cf.* [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_3$)] with peaks at 2 003, 1 932, and 1 906 cm^{-1}}. Introduction of a Me group on to the cyclopentadienyl ring lowers the i.r. bands of [Mo(cp)(CO)$_3$(SnPh$_3$)] by at most 4 cm^{-1}. Hence the peaks at 2 041 and 1 972 cm^{-1} are probably due to [Mo(η-C$_5$H$_4$Me)(CO)$_3$I] {*cf.* [Mo(cp)(CO)$_3$I] with peaks at 2 045, 1 975, and 1 960 cm^{-1}}. By comparison with the reaction of [Mo(cp)(CO)$_3$(SnPh$_3$)], the peaks at 2 013 and 1 915 cm^{-1} are probably due to [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_2$I)]. The peak at 1 952 cm^{-1} results from overlap of bands from [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_2$I)] and [Mo(η-C$_5$H$_4$Me)(CO)$_3$I] {*cf.* the peak at 1 955 cm^{-1} in the spectrum of the product of the reaction of [Mo(cp)(CO)$_3$(SnPh$_3$)] and I$_2$}.

N.m.r. analysis of the reaction solution showed peaks at δ 1.52 and 1.23 p.p.m. (from Me in the C$_5$H$_4$Me ligand) and δ 5.60, 5.45, and 5.35 p.p.m. (from C$_5$H$_4$ ring) {*cf.* [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_3$)] with peaks at δ = 5.20, 5.03, and 1.25 p.p.m. (and 7.35 for Ph)}. By comparison with the reaction of [Mo(cp)(CO)$_3$(SnPh$_3$)] with I$_2$, we expect two main molybdenum-containing products, [Mo(η-C$_5$H$_4$Me)(CO)$_3$I] and [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_2$I)]. The i.r. spectrum (above) confirms this and peaks from both products were found in a mass spectrum of the residue from the reaction after removal of CCl$_4$; PhI was detected by g.l.c. analysis. The reaction scheme is, therefore, as given by equations (9) and (10), with η-C$_5$H$_4$Me replacing cp therein.

(b) *Kinetics.* The kinetics of the reaction were measured as for [Mo(cp)(CO)$_3$(SnPh$_3$)] and $k_2^{\text{obs.}}$ is given in Table 2. The relative concentrations of products [Mo(η-C$_5$H$_4$Me)(CO)$_3$(SnPh$_2$I)] and [Mo(η-C$_5$H$_4$Me)(CO)$_3$I] are 1 : 1 (n.m.r. analysis) and therefore $k_2 = k_2^{\text{obs.}}/2 = 0.58$ dm^3 mol^{-1} s^{-1}.

DISCUSSION

Effect of changing the Alkyl Groups on Tin.—The iodine cleavage of the tin–transition-metal bond in [Mo(cp)(CO)$_3$(SnMe$_3$)], [Mn(CO)$_5$(SnMe$_3$)], and [Fe(cp)(CO)$_2$(SnMe$_3$)] has been studied in detail[2] and is shown to be an electrophilic substitution. The effect on the reaction of changing the alkyl groups (R) on tin reported here supports this conclusion. The reactivity towards iodine can be influenced by a combination of steric and polar features of the different R groups. In a bimolecular electrophilic reaction increase in the electron-donating power of R should enhance reactivity, whereas increase in the size of R would tend to reduce reactivity.[16] The rate of iodination of [Mn(CO)$_5$(SnEt$_3$)] relative to [Mn(CO)$_5$(SnMe$_3$)] is 6.7 : 1. This ratio is close to that for the electrophilic substitution of SnPhR$_3$ by iodine in tetrachloromethane where the relative rate coefficients are 5.1 (R = Et) and 1 (Me).[17] However, this latter reaction is second order in the iodine concentration, so rate coefficients are not directly comparable with those for [Mn(CO)$_5$(SnR$_3$)]. A butyl group is expected to be a little more electron donating than ethyl, and [Mn(CO)$_5$(SnBu$_3$)] is 7.9 times as reactive as its methyl analogue. The relative reactivities of [Mo(cp)(CO)$_3$(SnBu$_3$)] and [Fe(cp)(CO)$_2$(SnBu$_3$)] compared with their methyl analogues are, however, much lower, namely 1.4 and 1.5 respectively, indicating that the effect of a cyclopentadienyl group on the transition metal may moderate electronic effects from other parts of the molecule.

The rate-enhancing effect of increase in size of the alkyl group, both here and in the iodination of SnPhR$_3$ in the non-polar solvent tetrachloromethane, may be contrasted with the reverse effect for iodination of SnPhR$_3$ in the polar solvent methanol where the relative reactivities are 0.244 (R = Bu) and 1 (Me).[18] In the polar solvent the steric effects of R are dominant, large R groups preventing adequate solvation in the transition state.

The lower reactivity of SnPh$_3$ derivatives of molybdenum and iron compared with their methyl analogues is in line with the reduced reactivity of SnPh$_4$ compared with SnMe$_3$Ph with iodine in tetrachloromethane, where the reduction in rate [1.8×10^{-2} (R = Ph), 1 (Me)] [17] is similar to that for [Mo(cp)(CO)$_3$(SnR$_3$)] [10^{-3} (R = Ph), 1 (Me)] and [Fe(cp)(CO)$_2$(SnR$_3$)] [0.3×10^{-2} (R = Ph), 1 (Me)]. These reductions in rate reflect a genuine electron-withdrawing effect of the phenyl group, as the related cyclohexyl compounds Sn(C$_6$H$_{11}$)$_3$Ph and [Mn(CO)$_5${Sn(C$_6$H$_{11}$)$_3$}] react, respectively, 5.3 [17] and 5.9 times faster with iodine than their methyl-substituted analogues, although the phenyl and cyclohexyl groups are of similar size.

The effect of changing the alkyl group on tin on the activation parameters is quite small (Table 3). This is further evidence that electronic rather than steric effects are dominant so far as the alkyl group is concerned.

Effect of changing the Main-group 4 Element.—The rates of reaction of analogous compounds of silicon, germanium, tin, and lead towards electrophilic substitution have been measured for only one reaction, protodemetallation (acid-catalysed hydrolysis) of M(alkyl)$_3$(aryl) compounds, where the relative reactivities are 1 (M = Si), 36 (Ge), 3.5×10^5 (Sn), and 2×10^8 (Pb).[19]

In Table 1 the relative rates of reaction of [Mn(CO)$_5$(MMe$_3$)] with iodine are 1 (M = Si), 21 (Ge), 10^3 (Sn), and 3×10^4 (Pb), and of [Fe(cp)(CO)$_3$(MMe$_3$)] with iodine are 1 (Si), 12 (Ge), and 290 (Sn). The rates of protodemetallation (p) and of our reaction correlate well; a plot of log $k_{\text{rel.}}^{\text{p}}$ against $k_2^{\text{obs.}}$ is almost linear,[20] even though the two studies use different solvents, aqueous alcohol and tetrachloromethane, and different electrophiles (H$^+$ and I$_2$). The range of observed reactivity of the Group 4 metal–transition-metal bond with iodine is some 10^5 lower than that of the Group 4 metal–phenyl bond with protons. It is not easy to obtain a second-order rate coefficient for the protodemetallation of MPhR$_3$ as the concentration of H$^+$ used is not readily available for the strong acidic media used. The k_2 value for the reaction with PbEt$_3$Ph can be calculated as 1.77 dm^3 mol^{-1} s^{-1} with all other phenyl–metal bond cleavages being very much slower. Thus the reactions of our compounds with

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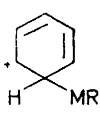
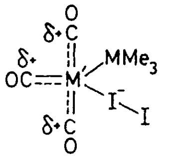
iodine are much faster than protodemetallations. The smaller range of reactivity found here probably reflects the unselective nature of iodine compared with the solvated proton. Fast rates and lack of selectivity generally accompany each other.

The order of protodemetallation is interpreted in terms of the electron-releasing ability of the MMe_3 groups and stabilisation of intermediates such as (I) by structure (II) involving vertical hyperconjugation.[21-24] Vertical hyperconjugation involves delocalisation of σ electrons of the phenyl–metal bond into the π orbitals of the phenyl ring, as shown in (II). The correlation of our reaction with protodemetallation suggests that vertical hyperconjugation is also important here. We have postulated the formation of intermediates (III) in our reaction,[3] and this can be stabilised by conjugation of the σ electrons of the transition-metal–Group 4 metal bond with the π orbitals of the carbonyl groups as shown in (IV). The increase in rate from silicon to lead is a reflection of the increasing stability of the $[MMe_3]^+$ ion as the group is descended.

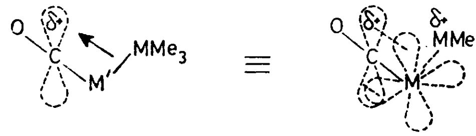


(I)

(II)



(III)



(IV)

M = Group 4 metal, M′ = transition metal; only representative CO groups have been included

Effect of changing the Ligand attached to the Transition Metal.—We have already noted that compounds containing a cyclopentadienyl ligand {$[Mo(cp)(CO)_3(SnMe_3)]$, $[Fe(cp)(CO)_2(SnMe_3)]$} react more readily with iodine than $[Mn(CO)_5(SnMe_3)]$, and suggested that this may arise from cyclopentadienyl being a better donor ligand than carbon monoxide.[2] Attaching a methyl group to a cyclopentadienyl ligand should further enhance its electron donor properties if the methyl group displays its usual inductive effect. The compound $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$ reacts with iodine 2.6 times more readily than $[Mo(cp)(CO)_3(SnPh_3)]$ (Table 2), showing that, as expected for an electrophilic-substitution reaction, electron supply does enhance reactivity. This large rate enhancement supports a mechanism where the electrophilic attack at the transition metal [*i.e.* formation of the intermediates (III)] is the rate-limiting step in the overall reaction. There is a spread of values of $k_2^{obs.}$ for $[Mo(cp)(CO)_3(SnPh_3)]$ (Table 2) but all values are substantially below those found for $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$

EXPERIMENTAL

Preparations.—The compounds containing Group 4 elements bonded to a transition metal were prepared by the usual route of allowing the sodium salt of the appropriately substituted transition-metal anion to react with an appropriate halide MR_3Cl (R = Me, Et, Bu, Ph, or cyclohexyl; M = Si, Ge, Sn, or Pb). Reactions were carried out in tetrahydrofuran (thf) at room temperature under an atmosphere of nitrogen. Further details of the preparation of $[Mn(CO)_5(SnMe_3)]$, $[Mo(cp)(CO)_3(SnMe_3)]$, and $[Fe(cp)(CO)_2(SnMe_3)]$ have been given.[2] The compound $[Fe(cp)(CO)_2(SiMe_3)]$[4] was sublimed under reduced pressure (0.2 mmHg)* at 60 °C; $[Fe(cp)(CO)_2(GeMe_3)]$[24] was distilled under reduced pressure (0.2 mmHg) on to a probe cooled to −78 °C; $[Fe(cp)(CO)_2(SnBu_3)]$[25] was recrystallised from CH_2Cl_2, and then distilled under reduced pressure (0.5 mmHg) at 180 °C; $[Fe(cp)(CO)_2(SnPh_3)]$[26] was extracted with CH_2Cl_2, and recrystallised from hexane; $[Mo(cp)(CO)_3(SnBu_3)]$ was recrystallised from CH_2Cl_2; $[Mn(CO)_5(SnEt_3)]$[27] was purified by dry-column chromatography[28] using an alumina column and n-hexane as eluant. [The product was finally sublimed under reduced pressure (0.1 mmHg) at 0 °C on to a probe at −78 °C]; $[Mn(CO)_5(SnBu_3)]$[27] was purified similarly;

TABLE 4

I.r. and n.m.r. data for the new compounds

Compound	I.r. (in CCl_4) [ν(CO)/cm^{-1}]			N.m.r. (in CCl_4) (δ/p.p.m.)
$[Mo(cp)(CO)_3(SnBu_3)]$	1 990	1 918	1 890	cp 5.27, Bu 1.25
$[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$	2 003	1 932	1 906	Me 1.25, cp 5.03 and 5.20, Ph 7.35
$[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$	2 083	1 987		

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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$[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$ was recrystallised from light petroleum (b.p. 40—60 °C); $[Mn(CO)_5(PbMe_3)]$ [29] was recrystallised from light petroleum (b.p. <40 °C) and then sublimed under reduced pressure (0.2 mmHg) on to a probe cooled to −78 °C; $[Mo(cp)(CO)_3(SnPh_3)]$ [13] was recrystallised from light petroleum (b.p. 40—60 °C)–dichloromethane (1 : 4); $[Mo(\eta\text{-}C_5H_4Me)(CO)_3(SnPh_3)]$ was recrystallised from light petroleum (b.p. 40—60 °C)–dichloromethane (1 : 1); $[Mn(CO)_5(SiMe_3)]$ was prepared by heating $[Mn_2(CO)_{10}]$ with $SiMe_3H$ in a Carius tube as described by Berry and MacDiarmid,[30] and recrystallised from CH_2Cl_2; and $[Mn(CO)_5(GeMe_3)]$ [31] was purified by recrystallisation from pentane. I.r. and n.m.r. data for new compounds are given in Table 4.

Kinetics.—Kinetic runs were carried out as described earlier.[2,3] Either a stopped-flow spectrophotometer (s.f.s., Tables 1 and 2) or a Unicam SP 500 spectrophotometer (u.s., Table 1) were used as appropriate. For some fast reactions, the SP 500 spectrophotometer was used in the 'direct read out' mode and connected to a chart recorder. In this way absorbance could be measured 10 s after mixing the reagents.

[5/1477 *Received, 28th July,* 1975]

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