Journal of Organometallic Chemistry, 421 (1991) 205-213
Elsevier Sequoia S.A., Lausanne
JOM 22186

Reactivity of Main-Group-transition-metal bonds

IX *. The kinetics of iodination of compounds containing two or more tin-transition-metal bonds

John R. Chipperfield *, Stephen Clark, David E. Webster and Halimahton Yusof
Department of Chemistry, The University, Hull HU6 7RX (UK)

(Received July 9th, 1991)

Abstract

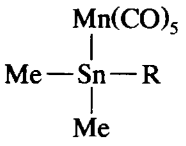
Rate coefficients are reported for the cleavage by halogens of tin-transition-metal bonds in compounds containing two or more such bonds. Bond reactivity with iodine is in the order Sn-Co ≈ Sn-Fe > Sn-Mo ≈ Sn-W > Sn-Mn. Rates of halogenation of compounds containing three tin-transition-metal bonds show that a subtle balance between steric and electronic effects determines bond reactivity.

Introduction

In a series of papers [1] we have quantitatively examined the reactivity of electrophiles with compounds such as [$Me_3SnMn(CO)_5$] which contain a group 14 element bonded to a transition metal. These compounds react smoothly and quantitatively with cleavage of the metal-metal bond, and the structure-reactivity behaviour can be accounted for by a balance of steric and electronic effects, with no evidence for special reactivity due to the metal-metal bond. A long term aim of the work is to investigate structure-reactivity relationships in metal cluster compounds, and so we have extended the previous work to cover compounds with more than one metal-metal bond. Although many such trimetallic compounds have been reported, there are no comparative reactivity data for them. In this paper we discuss the cleavage of tin-transition-metal bonds by iodine and bromine in compounds **1-8** where more than one tin-transition-metal bonds are present. We also present data on the related compounds **9-11** which contain a single tin-manganese bond.

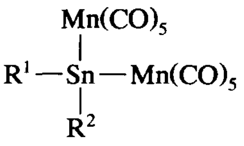
---

* For Part VIII see ref. 1.



$$\mathrm{Me{-}\overset{\overset{\textstyle Mn(CO)_5}{|}}{\underset{\underset{\textstyle Me}{|}}{Sn}}{-}R}$$

Complex	R
1	$Mn(CO)_5$
3	$Mo(Cp)(CO)_3$
4	$W(Cp)(CO)_3$
5	$Fe(Cp)(CO)_2$
6	$Co(CO)_4$
9	Cl
10	Br
11	I
13	Me



$$\mathrm{R^1{-}\overset{\overset{\textstyle Mn(CO)_5}{|}}{\underset{\underset{\textstyle R^2}{|}}{Sn}}{-}Mn(CO)_5}$$

Complex	R^1	R^2
1	Me	Me
2	Me	$Mn(CO)_5$
7	Cl	Cl
8	$Mn(CO)_5$	Cl
12	$Mn(CO)_5$	$Mn(CO)_5$

Experimental

Preparations

The complexes **1–11** were prepared in the usual way by treating the sodium salt of the appropriate transition-metal carbonyl with the appropriate organotin halide (see references in Table 1). Reactions were carried out in a THF solvent under nitrogen. The complexes **1** and **9–11** were recrystallised from pentane followed by

Table 1

Kinetic data for reactions of complexes 1-11 with X_2 (X = Br, I) in CCl_4 at 30.0 °C

Complex	10^3[complex] (mol dm^{-3})	$10^4[X_2]$ (mol dm^{-3})	No. of runs	k_2 (dm^3 mol^{-1} s^{-1})	Preparation (refs.)
Reactions with iodine					
1	9.7–42	5–20	12	0.0219 ± 0.0005	2–4
2	2.2–10.6	2.4–5.2	9	0.0248 ± 0.0030	4
3	2.7–25	2.6–10	17	4.77 ± 0.12	5,6
4	1.6–8.3	2.6–10	12	4.68 ± 0.24	5
5	0.48–3.1	1.0–3.0	6	213.8 ± 1.3	this work
6	1.9–6.0	1.5–9.6	3	364 ± 1 [a]	7
7	see text			est. $< 1 \times 10^{-6}$	2,4
8	0.8–1.9	7.4–14.7	4	0.66 ± 0.05	4,6
9	27–83	5.2–9.9	8	$2.10 \pm 0.04 \times 10^{-4}$	8–11
10	15.7–60	5.2–9.9	9	$6.20 \pm 0.11 \times 10^{-4}$	8,9
11	17–67	5.0–9.3	9	$1.43 \pm 0.10 \times 10^{-4}$	8,11
13				5.1×10^{-3} [b]	
Reactions with bromine					
7	4–63	8–57	2	0.06 ± 0.02	2,4
9	3.7–4.1	38	4	5.08 ± 0.09	8,9
13				20.0 [c]	

[a] In cyclohexane $k_2 = 134.1 \pm 1.1$ dm^3 mol^{-1} s^{-1}. [b] Ref. 12. [c] Ref. 13.

vacuum sublimation at 80 °C (0.1 mmHg) onto a water-cooled probe. Complex **2** was recrystallised by cooling an extract of the crude material with hot light petroleum spirit (b.p. 40–60 °C), followed by sublimation as above at 90 °C. Complexes **3** and **4** were recrystallised from a 1 : 1 mixture of dichloromethane and light petroleum spirit (b.p. 40–60 °C). The $[Co(CO)_4]^-$ required for the preparation of complex **6** was prepared by dissolving dicobaltoctacarbonyl in methanol, and stirring the solution at 50 °C until CO evolution had ceased. The quantity of dicobaltoctacarbonyl required was based on eq. 1 [14].

$$3\,Co_2(CO)_8 + 2n\,CH_3OH \rightarrow 2[Co(CH_3OH)_n][Co(CO)_4]_2 + 8\,CO \qquad (1)$$

Complex **6** was recrystallised from pentane, complex **7** was vacuum sublimed at 120 °C, and complex **8** recrystallised from toluene/light petroleum spirit (b.p. 60–80 °C). The identity and purity of each of the above compounds was checked by comparing IR and NMR spectra with those in the literature, and these spectra together with mass spectra showed absence of impurities. The tin-iron-manganese complex **5** had not previously been prepared. A solution of $[\{Fe(Cp)(CO)_2\}_2]$ (1.89 g, 0.00560 mol) in anhydrous THF was stirred with sodium amalgam (1 g Na, 100 g Hg) at room temperature overnight under a nitrogen atmosphere. The THF solution was filtered through glass wool into a solution of $[ClMe_2SnMn(CO)_5]$ (2.6 g, 0.0069 mol) in THF. The mixture was stirred overnight under a nitrogen atmosphere. The solution was filtered and THF completely removed. The residue was extracted with light petroleum spirit (b.p. 40–60 °C), and this extract separated into three components on an alumina column. After elution of the centre (orange) band and removal of solvent, orange-red crystals of complex **5** were obtained with m.p. 49–50 °C. $\nu_{max.}(CO)$ 2084sh, 2080m, 2073sh, 2009sh, 1994vs, 1983s and 1943m cm^{-1} (CCl_4). $\delta(H)$ ($CDCl_3$) 0.73 (Me), 4.77 ppm (Cp) in ratio 6/5. m/z 522 (M^+, $C_{14}H_{11}O_7{}^{56}Fe^{55}Mn^{120}Sn$).

Kinetics

Kinetics were followed by UV spectrophotometry (either Unicam SP500 or Durrum stopped flow) as described previously [12]. Usually reactions were studied under pseudo-first-order conditions (at least ten-fold excess of the organometallic compound) and the plots of $\ln(A_t - A_\infty)$ against time were linear to > 80% reaction. Check studies were carried out under second-order conditions (slight excess of organometallic compound), and the expected rate coefficients obtained.

Results

Before kinetic measurements were made, reactions of the organometallic compounds with halogens were examined to establish the nature of the products, and to confirm that reactions were quantitative.

Reaction of $[Me_2Sn\{Mn(CO)_5\}_2]$ (1) with I_2

A solution of complex **1** (0.083 g, 0.154 mmol) in 5 cm^3 CCl_4 was mixed with 5 cm^3 of a solution of I_2 in CCl_4 (0.0309 mol dm^{-3}). After reaction was complete the solution had $\nu_{max.}(CO)$ 2127m, 2100m, 2043vs, 2034sh, 2012vs and 2003vs cm^{-1} and $\delta(H)$ 1.14 ppm. $[MnI(CO)_5]$ (authentic sample) has $\nu_{max.}(CO)$ 2125m, 2044vs and 2003vs cm^{-1} [15,16]. $[IMe_2SnMn(CO)_5]$ (**11**) has $\nu_{max.}(CO)$ 2099s, 2037m, 2013vs, and 2004vs cm^{-1} and δ(H) 1.12 ppm [8,11]. The mass spectrum of the residue after removal of solvent had peaks corresponding to the molecular ions of these two products and their breakdown products. Reaction can be described by eq. 2 ($M'L_n = Mn(CO)_5$).

$$[Me_2Sn\{Mn(CO)_5\}(M'L_n)] + I_2 \rightarrow [IMe_2SnMn(CO)_5] + [IM'L_n] \qquad (2)$$

Reaction of [MeSn{Mn(CO)₅}₃] (2) with I₂

A solution of complex **2** (0.0117 g, 0.0165 mmol) in CCl_4 (1 cm^3) was allowed to react with 1 cm^3 of a solution of I_2 in CCl_4 (0.0162 mol dm^{-3}). After reaction the solution had $\nu_{max.}$(CO) 2127m, 2116w, 2097w, 2052sh, 2044vs, 2030w, 2011vs, 2004vs, and 1979s cm^{-1} and δ(H) 1.17 ppm. This includes peaks from $[MnI(CO)_5]$ (see above) and $[IMeSn\{Mn(CO)_5\}_2]$. (The latter compound has not been reported, but by comparison with the reported spectra of $[Cl_2Sn\{Mn(CO)_5\}_2]$ [2,4] and $[Me_2Sn\{Mn(CO)_5\}_2]$ [2–4] it would be expected to have $\nu_{max.}$(CO) approx. 2116, 2097, 2052, 2030, 2011 and 1979 cm^{-1} and δ(H) 1.17 ppm). A mass spectrum of the residue after removal of solvent showed peaks from the molecular ions of $[MnI(CO)_5]$ and $[IMeSn\{Mn(CO)_5\}_2]$ and their breakdown products. Reaction can be described by eq. 3 (R = Me).

$$[RSn\{Mn(CO)_5\}_3] + I_2 \rightarrow [R(I)Sn\{Mn(CO)_5\}_2] + [IMn(CO)_5] \qquad (3)$$

Reaction of [Me₂Sn{Mn(CO)₅}{Mo(Cp)(CO)₃}] (3) with I₂

A solution of complex **3** (0.0199 g, 0.0338 mmol) in CCl_4 (1 cm^3) was allowed to react with 1 cm^3 of a solution of I_2 in CCl_4 (0.0309 mol dm^{-3}). After reaction the solution had $\nu_{max.}$(CO) 2100m, 2043vs, 2038sh, 2012s, 2004vs, 1976m and 1962sh, and δ(H) 1.11 and 5.61 ppm. These comprise peaks from $[IMe_2SnMn(CO)_5]$ (see above) and $[Mo(Cp)(I)(CO)_3]$ with $\nu_{max.}$(CO) 2045vs, 1975m and 1960sh cm^{-1} and δ(H) 5.60 ppm [17–19]. A mass spectrum of the residue after removal of solvent contained peaks from the molecular ions of $[Mo(Cp)(I)(CO)_3]$ and $[IMe_2SnMn(CO)_5]$ and their breakdown products. Reaction can be described by eq. 2 ($M'L_n = Mo(Cp)(CO)_3$).

Reaction of [Me₂Sn{Mn(CO)₅}{W(Cp)(CO)₃}] (4) with I₂

A solution of complex **4** (0.0214 g, 0.0316 mmol) in CCl_4 (1 cm^3) was allowed to react with 2 cm^3 of a solution of I_2 in CCl_4 (0.0309 mol dm^{-3}). After reaction the solution had $\nu_{max.}$(CO) 2100m, 2038vs, 2012sh, 2003vs and 1961m cm^{-1} and δ(H) 1.12 and 5.70 ppm. These comprise peaks from $[IMe_2SnMn(CO)_5]$ (see above) and $[W(Cp)(I)(CO)_3]$ with $\nu_{max.}$(CO) 2040vs and 1961 cm^{-1} and δ(H) 5.70 ppm [18]. A mass spectrum of the residue after removal of solvent showed peaks from the molecular ions of $[IMe_2SnMn(CO)_5]$ and $[W(Cp)(I)(CO)_3]$ and their breakdown products. Reaction can be described by eq. 2 ($M'L_n = W(Cp)(CO)_3$).

Reaction of [Me₂Sn{Mn(CO)₅}{Fe(Cp)(CO)₂}] (5) with I₂

A solution of complex **5** (0.0098 g, 0.0188 mmol) in CCl_4 (1 cm^3) was mixed with 1 cm^3 of a solution of I_2 (0.0152 mol dm^3). After 10 min the solution had $\nu_{max.}$(CO) 2099m, 2041vs, 2011vs, 2004vs and 2001vs cm^{-1} and δ(H) 1.12 and 5.00 ppm. This comprises peaks from $[Me_2ISnMn(CO)_5]$ (see above) and $[Fe(Cp)(I)(CO)_2]$ with

$\nu_{max.}$(CO) 2043vs and 2000vs cm^{-1} and δ(H) 5.01 ppm [18,20–22]. A mass spectrum of the reaction mixture (after removal of the solvent) showed peaks corresponding to the molecular ions of [IMe$_2$Sn{Mn(CO)$_5$}] and [Fe(Cp)(I)(CO)$_2$] and their breakdown products. Reaction can be described by eq. 2 (M'L$_n$ = Fe(Cp)(CO)$_2$).

Reaction of [Me$_2$Sn{Mn(CO)$_5$}{Co(CO)$_4$}] (6) with I$_2$

A solution of complex **6** (0.0160 g, 0.0311 mmol) in CCl$_4$ (1 cm^3) was allowed to react with 1 cm^3 of a solution of I$_2$ in CCl$_4$ (0.0310 mol dm^{-3}). After reaction was complete (judged by decoloration of the iodine and formation of a black precipitate from decomposition of [CoI(CO)$_4$]) the mixture was filtered. The filtrate had $\nu_{max.}$(CO) 2099m, 2012vs, and 2003vs cm^{-1}, and δ(H) 1.10 ppm. This agrees well with [IMe$_2$SnMn(CO)$_5$] (see above). The mass spectrum of the residue after removal of solvent corresponded to [IMe$_2$SnMn(CO)$_5$] and breakdown products. The other expected product, [CoI(CO)$_4$] is known to decompose rapidly [23] and is not detected by IR or mass spectroscopy. Reaction can be described by eq. 2 (M'L$_n$ = Co(CO)$_4$).

Reaction of [Cl$_2$Sn{Mn(CO)$_5$}$_2$] (7) with Br$_2$

After reaction of bromine (0.38 mmol) and complex **7** (0.41 mmol) in CCl$_4$ an IR spectrum of the solution had $\nu_{max.}$(CO) 2147w, 2126m, 2052s, 2045s, 2022w, 2011w,sh, 2000m and 1979w cm^{-1}. This agrees with that expected from [BrMn(CO)$_5$], a little [Br$_2$Mn$_2$(CO)$_8$] [15,16] and [Cl$_2$BrSnMn(CO)$_5$] (the latter assumed to have peaks of 2124, 2045, 2038 cm^{-1} by comparison with those of [Br$_3$SnMn(CO)$_5$] and [Cl$_3$SnMn(CO)$_5$]). Reaction can be described by eq. 4 (X = Br).

$$[\mathrm{Cl_2Sn\{Mn(CO)_5\}_2}] + \mathrm{X_2} \rightarrow [\mathrm{Cl_2XSnMn(CO)_5}] + [\mathrm{XMn(CO)_5}] \qquad (4)$$

Reaction of complex 7 with I$_2$

In CCl$_4$ reaction was very slow, and neither reliable kinetics, nor product identification was possible. It is probable that the first step is similar to that described by eq. 4 (X = I).

Reaction of [ClSn{Mn(CO)$_5$}$_3$] (8) with I$_2$

After reaction of iodine (0.00149 mol dm^{-3}) and complex **8** (0.00147 mol dm^{-3}) in CCl$_4$ for 2 h an IR spectrum of the solution had $\nu_{max.}$(CO) 2127w, 2119w, 2094s, 2054sh, 2045s, 2029s and 2000br. This agrees with that expected from [IMn(CO)$_5$] and [Cl(I)Sn{Mn(CO)$_5$}$_2$]. The IR of the latter compound has not been reported, but in view of the tiny effect of change of halogens on the $\nu_{max.}$(CO) in [XSn{Co(CO)$_4$}$_3$] [24] it is likely to be close to that of complex **7**. Reaction can be described by eq. 3 (R = Cl).

Reaction of [ClMe$_2$SnMn(CO)$_5$] (9) with I$_2$

A solution of complex **9** (0.0236 g, 0.0621 mmol) in CCl$_4$ (2 cm^3) was allowed to react with 2 cm^3 of a solution of I$_2$ (0.0289 mol dm^{-3}). After reaction the solution had $\nu_{max.}$(CO) 2127m, 2088m, 2044vs, 2033vs, 2003vs and 1977m cm^{-1}, and δ(H) 1.24, 1.44, and 1.64 ppm. [MnI(CO)$_5$] has $\nu_{max.}$(CO) 2125, 2044 and 2003 cm^{-1} and it readily forms the dimer [{MnI(CO)$_4$}$_2$] with $\nu_{max.}$(CO) 2087m, 2033vs and 1976m

cm^{-1} [15,16]. The NMR spectrum arises from $Me_2Sn(Cl)I$ and the compounds Me_2SnCl_2, and Me_2SnI_2 which will form from $Me_2Sn(Cl)I$ by scrambling. A mass spectrum of the residue after removal of solvent showed the presence of molecular ions from $[MnI(CO)_5]$ and Me_2SnI_2 and their breakdown products. Reaction can be described by eq. 5 (X = Cl).

$$[XMe_2SnMn(CO)_5] + I_2 \rightarrow [XMe_2SnI] + [IMn(CO)_5] \qquad (5)$$

*Reaction of $[BrMe_2SnMn(CO)_5]$ (**10**) with I_2*

A solution of complex **10** (0.0266 g, 0.0628 mmol) in CCl_4 (2 cm^3) was allowed to react with 2 cm^3 of a solution of I_2 in CCl_4 (0.0289 mol dm^{-3}). After reaction the solution had $\nu_{max.}(CO)$ 2127m, 2088m, 2044vs, 2033vs, 2004vs and 1976m cm^{-1}, and $\delta(H)$ 1.44, 1.52 and 1.64 ppm. The IR spectrum tallies with that expected from a mixture of $[MnI(CO)_5]$ and $[\{MnI(CO)_4\}_2]$ (see above). The NMR spectrum arises from $Me_2Sn(Br)I$ together with Me_2SnBr_2 and Me_2SnI_2 formed by scrambling. The mass spectrum of the residue after removal of solvent contains peaks from the molecular ions of $[MnI(CO)_5]$ and Me_2SnI_2 and their breakdown products. Reaction can be described by eq. 5 (X = Br).

*Reaction of $[IMe_2SnMn(CO)_5]$ (**11**) with I_2*

A solution of complex **11** (0.0320 g, 0.0680 mmol) in CCl_4 (2 cm^3) was allowed to react with 2 cm^3 of a solution of I_2 in CCl_4 (0.0289 mol dm^{-3}). After reaction the solution had $\nu_{max.}(CO)$ 2127m, 2088m, 2044vs, 2033s, 2003vs and 1976m cm^{-1}, and $\delta(H)$ 1.64 ppm. The IR spectrum tallies with that expected from a mixture of $[MnI(CO)_5]$ and $[\{MnI(CO)_4\}_2]$ (see above) and the NMR spectrum agrees with that of Me_2SnI_2 (see above). The mass spectrum of the residue after removal of solvent contains peaks from the molecular ions of $[MnI(CO)_5]$ and Me_2SnI_2 and their breakdown products. Reaction can be described by eq. 5 (X = I).

Halogen cleaves tin–transition-metal bonds cleanly in the reactions reported; no side reactions were detected. It was possible to make kinetic studies readily by following the loss of halogen. These showed that halogenation reactions are second order, eq. 6 (X = Br or I).

$$d[\text{product}]/dt = k_2[\text{organometallic}][X_2] \qquad (6)$$

The values of k_2 obtained are shown in Table 1. There was no kinetic evidence for any reaction intermediates, or multiple order in halogen as is sometimes found in halogenations.

Discussion

After the first tin–manganese bond is cleaved in the reaction of $[Me_2Sn\{Mn(CO)_5\}_2]$ (**1**) there is the possibility that the remaining tin–manganese bond will be more reactive than the first. However, products arising from the cleavage of two bonds were never observed. This is supported by the low k_2 value for the iodine cleavage of the tin–manganese bond in $[Me_2(I)Sn\{Mn(CO)_5\}]$ (**11**) (the product of cleavage of the tin–manganese bond in **1**). This occurs much more slowly ($k_2 = 0.000143$ dm^3 mol^{-1} s^{-1}) compared with $k_2 = 0.0219$ dm^3 mol^{-1} s^{-1} for the iodination of **1** so further molecules of **1** react rather than the tin–

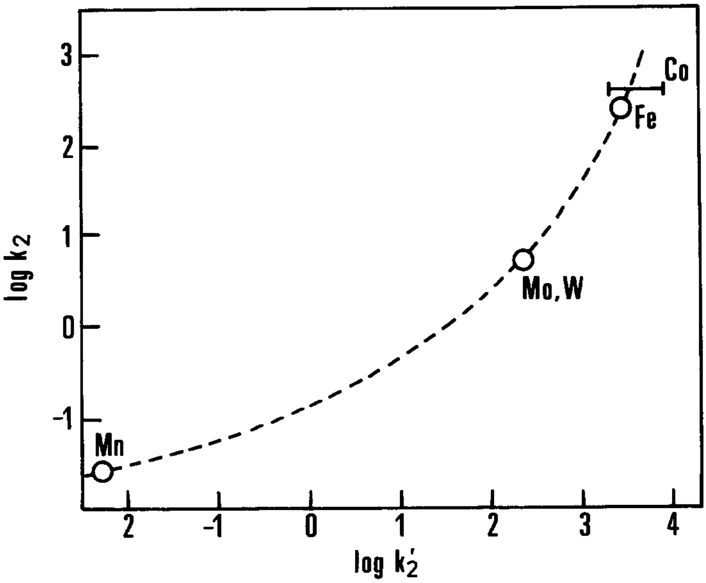


Fig. 1. Plot of log k_2 for reaction of I_2 with $[Me_2Sn\{Mn(CO)_5\}(ML_n)]$ against log k_2' for reaction of I_2 with Me_3SnML_n, where $ML_n = Mn(CO)_5$, $Mo(Cp)(CO)_3$, $W(Cp)(CO)_3$, $Fe(Cp)(CO)_2$, and $Co(CO)_4$; CCl_4, 30.0 °C.

manganese bond of the iodination product. In compounds where tin is bonded to two different metals the reactivity of the compounds is in line with that expected from the previous studies on compounds containing a single tin–transition-metal bond. This general order is $Fe \approx Co > W \approx Mo > Mn$ [12,25]. So compounds containing a tin–manganese and a tin–M (M = Fe, Co, W, Mo) will react with iodine and break the Sn–M bond, and not the Sn–Mn bond. For the reactions of complexes **1–6** with iodine, a plot of log k_2 against log k_2' for the iodination of the analogous compound containing a methyl group in place of pentacarbonylmanganese (e.g. $[Me_3SnMn(CO)_5]$ (**13**), $[Me_3SnMo(Cp)(CO)_3]$, etc.) is not the expected straight line *. In both series the general order of rate coefficients is (M =) $Fe \approx Co > Mo \approx W > Mn$.

Introduction of a second $Mn(CO)_5$ group in place of a methyl group on tin in $[Me_3SnMn(CO)_5]$ (**13**) causes a ten-fold increase in k_2. With no difference in electronic factors between a methyl group and $Mn(CO)_5$ a doubling would be expected on statistical grounds as either of the two Sn–Mn bonds can react. Introduction of a third $Mn(CO)_5$ group has only a slight effect upon reactivity. It could be that the expected (another tenfold) increase in reactivity is compensated for by steric effects of the bulky $Mn(CO)_5$ group. The reactivity of $[ClSn\{Mn(CO)_5\}_3]$ (**8**) with iodine is 30-fold greater than $[MeSn\{Mn(CO)_5\}_3]$ (**2**), although the introduction of an electronegative chlorine in place of a methyl would be expected to

---

* k_2' for the reaction of $[Me_3SnCo(CO)_4]$ was reported as 780 $dm^3\ mol^{-1}\ s^{-1}$ (cyclohexane, 30 °C) [25]. It decomposes readily in solution and further work has indicated that this value is 3–4 times too low. With a suitable allowance for solvent effect (see Table 1) the estimate for k_2' in CCl_4 is about $7.6 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$. The bar line on Fig. 1 shows the uncertainty in k_2'.

retard bond cleavage. The smaller chlorine (compared with methyl) must make the tin–manganese bonds more accessible.

In the series of compounds {$Me_2XSnMn(CO)_5$] where X = Cl (**9**), Br (**10**), I (**11**), and Me (**13**) the reactivity order is I < Cl < Br < Me. If electronic effects were dominant we would expect Cl < Br < I < Me (as increasing electron withdrawal is expected to retard electrophilic substitution). The observed order again probably arises from a combination of steric and electronic factors.

The value of k_2 for the reaction of compound **1** is almost invariant with temperature over the limited range 30–45 °C. This implies a low $\Delta H^{\ddagger}$ (of the order of -3.3 kJ mol^{-1}) and a high negative $\Delta S^{\ddagger}$ (around -290 J K^{-1} mol^{-1}). This is in line with activation parameters for the reactions of compounds containing a single tin–transition-metal bond, and suggests that the reaction mechanism is more complex than the simple kinetics indicate.

The compound [$Cl_2Sn\{Mn(CO)_5\}_2$] (**7**) is far less reactive with iodine than [$Me_2Sn\{Mn(CO)_5\}_2$] (**1**) and reacts at a measurable rate with bromine. Introduction of chlorine atoms in place of methyl groups generally inhibits tin–manganese bond cleavage by halogens, and the tin–manganese bond in [$Cl_3SnMn(CO)_5$] is completely resistant to attack by any halogen [17]. The tin–manganese bond in [$Me_3SnMn(CO)_5$] (**13**) reacts with bromine some 2000 times faster than with iodine. Introduction of a chlorine in place of a methyl group, compound **9**, while reducing halogenation rates increases the relative rates of bromination to iodination to 24000.

The compound [$Sn\{Mn(CO)_5\}_4$] (**12**) has been reported by two groups [26,27] and we had hoped to include it in our studies. The IR spectra given [26,27] do not tally, and despite many attempts using the reported methods and variations, we have been unsuccessful in preparing it. No great difficulty was anticipated as the much more sterically crowded compound [$Si\{Mn(CO)_5\}_4$] has been reported [28].

Conclusions

Compounds **1–8** contain more than one metal–metal bond but undergo clean reactions with halogens, and kinetic evaluation of structure–reactivity relationships can be made. In the compounds studied reactivity patterns can be accounted for by electron accepting/donating powers of ligands together with steric effects. There is no evidence for enhanced or reduced reactivity of metal–metal bonds caused by metallic bonding. Replacement of tin–methyl bonds by tin–halogen bonds greatly reduces the reactivity of the bond between the tin atom and a transition metal.

References

1 J.R. Chipperfield, A.C. Hayter and D.E. Webster, J. Chem. Soc., Dalton Trans., (1977) 921.
2 R.D. Gorsich, J. Am. Chem. Soc., 84 (1962) 2486.
3 W. Jetz, P.B. Simons, J.A.J. Thompson and W.A.G. Graham, Inorg. Chem., 5 (1966) 2217.
4 J.A.J. Thompson and W.A.G. Graham, Inorg. Chem., 6 (1967) 1365.
5 H.R.H. Patil and W.A.G. Graham, J. Am. Chem. Soc., 87 (1965) 673.
6 R.E.J. Bichler, M.R. Booth, H.C. Clark and B.K. Hunter, Inorg. Synth., 12 (1970) 61.
7 G.M. Bancroft and K.D. Butler, J. Chem. Soc., Dalton Trans., (1973) 1694.
8 N.A.D. Carey and H.C. Clark, Inorg. Chem., 7 (1968) 94.
9 S. Onaka, T. Miyamoto and Y. Sasaki, Bull. Chem. Soc. Jpn., 44 (1971) 1851.

10 K. Triplett and M.D. Curtis, Inorg. Chem., 15 (1976) 431.
11 W.A.G. Graham, Inorg. Chem., 7 (1968) 315.
12 J.R. Chipperfield, J. Ford and D.E. Webster, J. Chem. Soc., Dalton Trans., (1975) 2042.
13 J.R. Chipperfield, J. Ford, D.J. Lee, A.C. Hayter and D.E. Webster, J. Chem. Soc., Dalton Trans., (1976) 1024.
14 W. Hieber, J. Sedlmeier and W. Abeck, Chem. Ber., 86 (1953) 700.
15 J.C. Hileman, D.K. Huggins and H.D. Kaesz, Inorg. Chem., 1 (1962) 933.
16 H.D. Kaesz, R. Bau, D. Hendrickson and J.M. Smith, J. Am. Chem. Soc., 89 (1967) 2844.
17 J.R. Chipperfield, J. Ford and D.E. Webster, J. Organomet. Chem., 102 (1975) 417.
18 T.E. Sloan and A. Wojcicki, Inorg. Chem., 7 (1968) 1268.
19 T.S. Piper and G. Wilkinson, J. Inorg. Nucl. Chem., 3 (1956) 104.
20 R. Ugo, S. Cenini and F. Bonati, Inorg. Chim. Acta, 1 (1967) 451.
21 B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1956) 3030.
22 A.N. Nesmeyanov, I.F. Leshcheva, I.V. Polovyanyuk, Yu.A. Ustynyuk and L.G. Makarova, J. Organomet. Chem., 37 (1972) 159.
23 E.W. Abel and G.V. Hutson, J. Inorg. Nucl. Chem., 30 (1968) 2339.
24 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 5 (1966), 2222.
25 J.R. Chipperfield, A.C. Hayter and D.E. Webster, J. Organomet. Chem., 121 (1976) 185.
26 G.K. Madomedov and L.V. Morozoba, Koord. Khim., 7 (1981) 381.
27 M. Bigorne, C. R. Acad. Sci. Paris Ser. C., (1968) 695.
28 B.J. Aylett and M.T. Taghipour, J. Organomet. Chem., 249 (1983) 55.