Reactivity of Main-group–Transition-metal Bonds. Part 8.[1] The Kinetics of Mercuration of Compounds containing Group 4B Elements bonded to Manganese, Iron, and Molybdenum: Effects of Structure on Reactivity

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The kinetics of cleavage by $HgBr_2$ of the main-group–transition-metal bonds in the following compounds are reported: $[Mn(CO)_5(MR_3)]$ (M = Sn, R = Et, Bu^n, or C_6H_{11}; M = Si or Ge, R = Me); $[Fe(cp)(CO)_2(MR_3)]$ (M = Sn, R = Bu^n or C_6H_{11}; M = Si or Ge, R = Me; cp = η-cyclopentadienyl); and $[Mo(cp)(CO)_3(SnBu^n{}_3)]$. The structure–reactivity patterns indicate that mercuration involves an S_E2(open) transition state. Mercury(II) bromide does not cleave the tin–transition-metal bonds in $[Mn(CO)_5(SnPh_3)]$ or $[Fe(cp)(CO)_2(SnPh_3)]$ but cleaves the phenyl–tin bonds in these compounds.

In recent papers we have reported on the kinetics and mechanism of the cleavage by iodine of the metal–metal bond in compounds containing Group 4B metals bonded to transition metals.[2-8] Reaction takes place by electrophilic attack on the transition metal, and proceeds through an intermediate akin to the σ complex found in electrophilic aromatic substitution. Cleavage of tin–transition-metal bonds by mercury(II) halides is similar to iodination, with the formation of an intermediate between the organometallic compound and the mercury halide prior to metal–metal bond cleavage [equation (1); X = Cl, Br, or I].[1]

$$HgX_2 + \text{organometallic} \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \text{intermediate} \xrightarrow[\text{slow}]{k_1} \text{products} \quad (1)$$

Here we report how structural variations in the main-group ligand, MR_3, attached to the transition element alter the rate of the reaction with mercury(II) bromide [equation (2): M′ = Mn, $n = 0$, $m = 5$; M = Si or Ge,

$$[M'(cp)_n(CO)_m(MR_3)]^* + HgBr_2 \xrightarrow[\text{dioxan or ethyl acetate}]{k_2^{\text{obs.}}} MBrR_3 + [M'(cp)_n(CO)_m(HgBr)] \quad (2)$$

* cp = η-Cyclopentadienyl.

R = Me; M = Sn, R = Me, Et, Bu^n, or C_6H_{11}; M′ = Fe, $n = 1$, $m = 2$; M = Si or Ge, R = Me; M = Sn, R = Me, Bu^n, or C_6H_{11}; M′ = Mo, $n = 1$, $m = 3$; M = Sn, R = Me or Bu^n]. The compound $[Mn(CO)_5(SnPh_3)]$ reacts with iodine to yield products resulting from both phenyl–tin and tin–manganese bond cleavage.[8] To further compare mercuration with iodination we have determined the nature of the products of the reaction of $[Mn(CO)_5(SnPh_3)]$ and $[Fe(cp)(CO)_2(SnPh_3)]$ with $HgBr_2$, and compared them with the analogous iodination reported earlier.[5,8] We have also examined how the introduction of a methyl group into the cyclopentadienyl ligand in $[Fe(cp)(CO)_2(SnMe_3)]$ alters the rate of mercuration.

RESULTS

Reactions of Mercury(II) *Bromide with* MR_3 (R = *alkyl*) *Derivatives of* Mn, Fe, *and* Mo (M = Si, Ge, *or* Sn).—*Product analyses.* None of the reactions reported here has been reported previously. The general method of product analysis has been described.[1] From mixtures of $HgBr_2$ and the organometallic compound in an appropriate solvent the mercury–transition-metal compound {$[Mn(CO)_5(HgBr)]$, $[Fe(cp)(CO)_2(HgBr)]$, or $[Mo(cp)(CO)_3(HgBr)]$} was identified by i.r. spectroscopy, and the bromide of the Group 4 element was identified either by mass spectroscopy or by g.l.c. analysis. No evidence for any other products was found, and details of the product analyses are given in Table 1. Infrared spectra of solutions from kinetic experiments confirmed that the mercurated transition-metal compounds were the only carbonyl-containing products formed under kinetic conditions.

Kinetics. The reactions of the compounds with $HgBr_2$ were all first order in the concentration of compound, and all except those of manganese were first order in the concentration of $HgBr_2$ [equation (3)], and the values of $k_2^{\text{obs.}}$ found are given in Tables 2 and 3. Now for the scheme in

$$\text{Rate of mercuration} = k_2^{\text{obs.}}[\text{organometallic}][HgBr_2] \quad (3)$$

equation (1), $k_2^{\text{obs.}} = k_1K/(1 + K[HgBr_2])$.[1] For no reaction did $k_2^{\text{obs.}}$ decrease with increase of [HgBr] showing that $K[HgBr_2] \ll 1$. Low values for K are in accord with our previous mercuration studies. As mercurations of $[Mo(cp)(CO)_3(SnMe_3)]$ and $[Mn(CO)_5(SnMe_3)]$ in dioxan proceed according to equation (1) with K in the range 6—33 $dm^3\ mol^{-1}$,[1] we interpret the kinetics here in the same way. However, the kinetic results in this paper are equally consistent with a simple one-step bimolecular mercuration reaction, and the discussion is also valid for such a mechanism. $k_2^{\text{obs.}}$ for reactions of the manganese compounds increased slightly as $[HgBr_2]$ increased. We have attributed this to a polarity effect caused by the higher mercury(II) bromide concentrations (up to 4×10^{-2} mol dm^{-3}) necessary when

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[2] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J.C.S. Chem. Comm.*, 1975, 625.

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

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[7] J. R. Chipperfield, A. C. Hayter, and D. E. Webster, *J. Organometallic Chem.*, 1976, **121**, 85.

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

TABLE 1

Reactions of $HgBr_2$ with compounds containing Group 4B elements bonded to a transition metal: product analysis

Compound	I.r. peaks found (cm^{-1})	Mass spectrum ions identified	Solvent
$[Mn(CO)_5(SnEt_3)]$	2 110, 2 054, 2 019 [a]	$[SnBrEt_3]^+$, $[SnBrEt_2]^+$	Ethyl acetate
$[Mn(CO)_5(SnBu_3)]$	2 109, 2 052, 2 019 [a]	$[SnBrBu_3]^+$	
$[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$	2 110, 2 054, 2 020 [a]	$[SnBr(C_6H_{11})_3]^+$	
$[Fe(cp)(CO)_2(SnBu_3)]$	2 017, 1 969 [b]	$[SnBrBu_3]^+$	Dioxan
$[Fe(cp)(CO)_2\{Sn(C_6H_{11})_3\}]$	2 017, 1 971 [b]	$[SnBr(C_6H_{11})_3]^+$	
$[Fe(cp)(CO)_2(SiMe_3)]$	2 016, 1 970 [b]	*c*	
$[Fe(cp)(CO)_2(GeMe_3)]$	2 017, 1 971 [b]	*d*	
$[Fe(\eta\text{-}MeC_5H_4)(CO)_2(SnMe_3)]$	2 014, 1 965 [e]	$[SnBrMe_3]^+$	
$[Mo(cp)(CO)_3(SnBu_3)]$	2 017, 1 949, 1 933 [f]	$[SnBrBu_3]^+$	

[a] Literature values for $[Mn(CO)_5(HgBr)]$: 2 110, 2 055, and 2 020 cm^{-1} (P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1967, 1889). [b] Literature values for $[Fe(cp)(CO)_2(HgBr)]$: 2 018 and 1 972 cm^{-1} (M. J. Mays and J. D. Robb, *J. Chem. Soc.* (*A*), 1968, 329). [c] $SiBrMe_3$ identified by g.l.c. (using authentic $SiBrMe_3$). [d] $GeBrMe_3$ identified by g.l.c. (using authentic $GeBrMe_3$). [e] No literature values. The peaks are *ca.* 5 cm^{-1} lower than in the i.r. of $[Fe(cp)(CO)_2(HgBr)]$ and support $[Fe(\eta\text{-}MeC_5H_4)(CO)_2(HgBr)]$. Likewise the i.r. peaks of the starting material are shifted a little lower compared with those in the i.r. spectrum of $[Fe(cp)(CO)_2(SnMe_3)]$. [f] Literature values for $[Mo(cp)(CO)_3(HgBr)]$: 2 021, 1 950, and 1 933 cm^{-1} (see footnote *b* for reference).

TABLE 2

Reactions of Group 4 derivatives of Mn, Fe, and Mo with $HgBr_2$ at 30.0 °C

Compound	10^3[Compound] / mol dm^{-3}	$10^3[HgBr_2]$ / mol dm^{-3}	Solvent	λ / nm	$k_2^{obs.}$ / $dm^3\ mol^{-1}\ s^{-1}$
$[Mn(CO)_5(SnMe_3)]$			Ethyl acetate		0.059 [a,b]
$[Mn(CO)_5(SnEt_3)]$	0.16—0.22	10—40		300	0.011 9 [b,c]
$[Mn(CO)_5(SnBu_3)]$	0.2—0.4	5—40		300	0.006 4
$[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$	7.8—9.4	40			0.002 6 [d]
$[Fe(cp)(CO)_2(SnMe_3)]$			Dioxan		3.27 [a]
$[Fe(cp)(CO)_2(SnBu_3)]$	0.16—0.37	2—6		405	0.952
$[Fe(cp)(CO)_2\{Sn(C_6H_{11})_3\}]$	0.16—0.3	4—6		405	0.554
$[Fe(cp)(CO)_2(SiMe_3)]$	0.4—0.67	40—60		405	0.007 6
$[Fe(cp)(CO)_2(GeMe_3)]$	0.2—0.52	20—60		405	0.015 5 [e]
$[Fe(\eta\text{-}MeC_5H_4)(CO)_2(SnMe_3)]$	0.2—0.4	2—6		405	4.07
$[Mo(cp)(CO)_3(SnMe_3)]$					1.34 [a]
$[Mo(cp)(CO)_3(SnBu_3)]$	0.12—0.33	2—6		395	0.321

[a] Ref. 1. [b] Extrapolated to $[HgBr_2] = 0$ (see text and Table 3). [c] $\Delta H^\ddagger = 40.2 \pm 1.5$ kJ mol^{-1}, $\Delta S^\ddagger = -130.2 \pm 5.0$ J K^{-1} mol^{-1} over range 30—50 °C. [d] Kinetics measured by i.r. technique (see text). [e] $\Delta H^\ddagger = 44.2 \pm 1.6$ kJ mol^{-1}, $\Delta S^\ddagger = -133.6 \pm 5.8$ J K^{-1} mol^{-1} over range 30—50 °C.

studying the kinetics of the slow reactions of manganese compounds.[1] The value of 2.6×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ for $k_2^{obs.}$ for mercuration of $[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$ was obtained using an i.r. technique,[9] and it was not possible to carry out a systematic change in the concentration of $HgBr_2$. By comparison with other manganese compounds, we estimate for this compound a value of *ca.* 2.1×10^{-3} $dm^3\ mol^{-1}\ s^{-1}$ for $k_2^{obs.}$ at zero mercury(II) bromide concentration. Although the concentrations of $HgBr_2$ used in the mercuration of $[Fe(cp)(CO)_2(SiMe_3)]$ and $[Fe(cp)(CO)_2(GeMe_3)]$ were similar to those used for the manganese analogues, the values of $k_2^{obs.}$ were independent of mercury(II) bromide concentration, which suggests that these reactions are less sensitive to polarity changes.

TABLE 3

Values of $10^3k_2^{obs.}$ (in $dm^3\ mol^{-1}\ s^{-1}$) for reactions of $[Mn(CO)_5(SnR_3)]$ with $HgBr_2$ in ethyl acetate at 30 °C

	$10^3[HgBr_2]$/mol dm^{-3}			
R	5	10	20	40
Et		12.3	13.4	14.1
Bu	6.96	7.24	9.14	10.3

Reactions of Triphenyltin Derivatives of Mn *and* Fe *with* $HgBr_2$.—We investigated the products formed by the reaction of $HgBr_2$ with $[Fe(cp)(CO)_2(SnPh_3)]$ and $[Mn(CO)_5(SnPh_3)]$. Samples of $[Fe(cp)(CO)_2(SnPh_3)]$ were mixed with $HgBr_2$ (1 : 1, 1 : 2, 1 : 3, or 1 : 6 molar ratios) in ethyl acetate. The solutions rapidly became orange and an orange precipitate formed. After 1 h the solvent was removed, the residue extracted with chloroform, and an i.r. spectrum recorded. For each sample only peaks at 2 011 and 1 963 cm^{-1} were present {*cf.* $[Fe(cp)(CO)_2(SnBrPh_2)]$ with peaks[10] at 2 010 and 1 963 cm^{-1}}, and there was no evidence for products of scission of tin–iron bonds such as $[Fe(cp)(CO)_2(HgBr)]$. The results of similar experiments with $HgBr_2$ and $[Mn(CO)_5(SnPh_3)]$ are shown in Table 4.

TABLE 4

Reactions of $HgBr_2$ with $[Mn(CO)_5(SnPh_3)]$ in ethyl acetate at 20 °C

Molar ratio $[HgBr_2]$: $[Mn(CO)_5(SnPh_3)]$	I.r. peaks (cm^{-1}) found [a] (in CH_2Cl_2)	Carbonyl present,[b] $[Mn(CO)_5(SnB_nrPh_{3-n})]$			
		$n = 0$ [c]	$n = 1$	$n = 2$	$n = 3$
1 : 1	2 118w, 2 107, 2 096w, 2 048w, 2 029w, 2 015, 2 000	l	m	l	
2 : 1	2 118, 2 107w, 2 060, 2 030		t	m	
3 : 1	2 127w, 2 118, 2 060w, 2 044w, 2 030			m	t
6 : 1	2 127, 2 118, 2 062w, 2 031			m	t

[a] Reference spectra given in J. Ford, Ph.D. Thesis, University of Hull, 1972; W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2217; and S. Onaka, T. Miyamoto, and Y. Sasaki, *Bull. Chem. Soc. Japan*, 1971, **44**, 1851. J. Ford reported a peak at 2 058 cm^{-1} (not at 2 034 cm^{-1} as in S. Onaka *et al.*) for $[Mn(CO)_5(SnBr_2Ph)]$. [b] m = Main product, l = small amount, t = trace. [c] Starting material.

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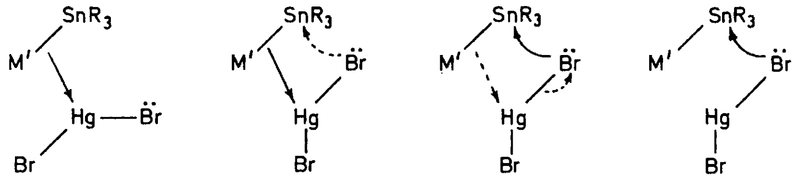
[10] R. E. J. Bichler, H. C. Clark, B. K. Hunter, and A. T. Rake, *J. Organometallic Chem.*, 1974, **69**, 367.

The mixtures were allowed to react for 3 d at room temperature before removing the solvent. The white residue {absence of any yellow colour precludes the presence of [Mn-Br$(CO)_5$]} was dissolved in dichloromethane, and an i.r. spectrum was recorded. Again there was no evidence for tin–manganese bond cleavage. The dibromo-derivative [Mn$(CO)_5$($SnBr_2Ph$)] was the favoured product.

DISCUSSION

Substituent Effects.—We have studied the rates of mercuration of a number of trialkyltin (SnR_3) derivatives of Mn, Fe, and Mo (Table 2). The general pattern of reactivity is (R =) Me < Et < Bu^n < C_6H_{11}, and this order is independent of the solvent (dioxan or ethyl acetate) used. Abraham [11] recently critically analysed the interpretation of such substituent effects. He noted that for S_E2 reactions two series of substituent effects may be found: (*a*) the ' electronic ' order, Me < Et < Bu^n, where the increasing inductive effect of longer alkyl chains enhances reactivity; and (*b*) a ' steric ' order, Me > Et > Bu^n, where reactivity decreases as the size of the substituent increases. Although substituents can exert both a steric and a polar effect, it seems that for most reaction series one will dominate giving rise to series (*a*) or (*b*). Abraham proposed two different reaction paths. When the ' steric ' sequence of substituent effects is found the reaction proceeds *via* an ' S_E2 (open) ' mechanism with a transition state [structure (1) for mercuration] where electrons in the tin–transition-metal bond attack the electrophilic mercury atom, with minimal interaction between the lone pairs of electrons of bromine and the tin atom. The ' electronic ' sequence is found when reaction proceeds *via* an ' S_E2 (co-ord.) ' mechanism with a transition state shown in structure (4) where there is interaction between bromine's electron pairs and the electrophilic tin atom. Of course, for many reactions neither of these extreme transition states [(1) or (4)] occurs, but reaction proceeds *via* cyclic transition states [(2) or (3)] where emphasis is on either electrophilic attack by mercury [structure (2)] or nucleophilic attack by bromine [structure (3)].



S_E2 (open) — S_E2 (cyclic) — S_E2 (co-ord.)

(1) (2) (3) (4)

In our studies of iodination of compounds containing tin–transition-metal bonds we found the ' electronic ' sequence,[5] and suggested a cyclic transition state.[3] The nature of the solvent can alter reaction mechanisms, and hence change the relative effect of substituents. For example, in the reaction of bromine with tetra-alkyltin compounds the ' steric ' series was found in dimethylformamide and acetic acid,[12] whereas the ' electronic ' series was found for the same reaction in the much less polar chlorobenzene.[13]

We suggest that mercuration of our organometallic compounds with $HgBr_2$ proceeds *via* an ' S_E2 (open)' transition state similar to structure (1), or possibly *via* a cyclic structure (2) with little interaction between the bromine and tin atoms. The structure of the intermediate [equation (1)] should be like that of isolable adducts of mercury(II) halides with such compounds as [Co(cp)$(CO)_2$]. These are also similar to (1) with the mercury atom co-ordinated to the transition metal.[14]

The rates of mercuration of [FeL$(CO)_2$($SnMe_3$)] (L = cp or η-C_5H_4Me) are insensitive to the presence of the methyl substituent on the cp ligand, probably because the substituent is far from the reaction centre.

Effect of changing the Main-group 4 Element.—We have already shown [2] that the relative rates of iodination of analogous manganese derivatives [Mn$(CO)_5$(MMe_3)] (M = Si, Ge, Sn, or Pb), $k_{rel.}^{IMn}$, correlate well with the relative rates of protodemetallation [15] of MR_3R' (R = alkyl R' = aryl), $k_{rel.}^{H}$. A plot of log $k_{rel.}^{IMn}$ against log $k_{rel.}^{H}$ is almost linear.[2] Similarly the relative rates of iodination of iron derivatives, [Fe(cp)$(CO)_2$(MMe_3)], $k_{rel.}^{IFe}$, also correlate well with $k_{rel.}^{H}$.[2] In both these logarithmic plots the point for the germanium-substituted compound is not quite on the expected line: iodinations of the germanium compounds are about three times faster than predicted from protodemetallation rates.

The relative rates of reaction of $HgBr_2$ with [Fe(cp)-$(CO)_2$(MMe_3)], $k_{rel.}^{HgFe}$, are (M =) Si 1, Ge 2.1, and Sn 443. The Figure shows log $k_{rel.}^{HgFe}$ plotted against (*a*) log $k_{rel.}^{H}$ and (*b*) log $k_{rel.}^{IFe}$. The correlation of mercuration with protodemetallation is quite good, but the point for the germanium derivative shows that it reacts *ca.* 1.5 times more slowly than would be expected from protodemetallation. The transition states in protodemetallation (Wheland intermediate) and in mercuration [S_E2 (open), see above] are similar, whereas for iodination a

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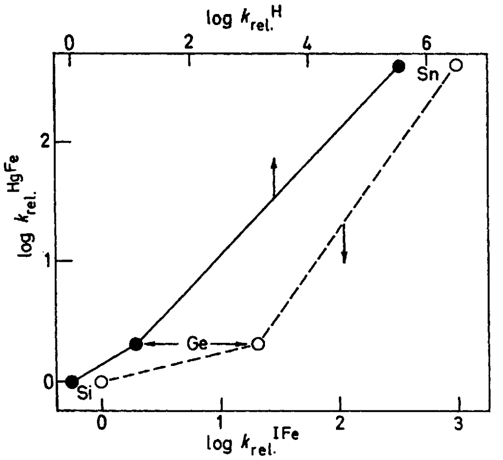
cyclic transition state is likely. Also both protodemetallation (aqueous ethanolic perchloric acid) and mercuration (dioxan and ethyl acetate) were studied in solvents which are more polar than that used for iodination (tetrachloromethane).

The measured value of k^{HgFe} for the germanium derivative is about six times smaller than predicted from a linear free-energy relation between k^{HgFe} and k^{IFe}. It is likely that this arises from steric effects. Silicon and germanium have similar sizes (covalent radii, 117 and 122 pm respectively). While steric effects are unlikely to be dominant for iodination in tetrachloromethane (the 'electronic' order of substituent effects is found), the transition state for mercuration in dioxan and ethyl acetate shows evidence of crowding ('steric' order of substituent effects). Also $HgBr_2$ is a larger electrophile than iodine. Thus mercuration rates are very dependent on the sizes of the Group 4 atoms in these compounds and the silicon and germanium derivatives have similar reactivities.



Logarithmic plots of relative rates of mercuration of [Fe(cp)-$(CO)_2(MMe_3)$] against protodemetallation of MR_3R' (R = alkyl, R' = aryl) (——) and iodination of [Fe(cp)$(CO)_2(MMe_3)$] (M = Si, Ge, or Sn) (– – – –)

Reactions of Triphenyl Derivatives of Fe *and* Mn *with* $HgBr_2$.—When iodine reacts with an excess of $[Mn(CO)_5(SnPh_3)]$ or $[Fe(cp)(CO)_2(SnPh_3)]$ products arising from both metal–metal and phenyl–tin bond cleavage are found.[5,8] Mercury(II) bromide does not break the metal–metal bond in these compounds, but causes phenyl–tin bond scission. These reactions can be understood using the concepts of hard and soft acids and bases.

Both aromatic carbon atoms and low-oxidation-state transition metals are soft bases, but a transition metal with filled *d* orbitals is softer than aromatic carbon. The very soft electrophile iodine attacks both the transition metal and aromatic carbon. Reaction with the harder electrophile chlorine occurs solely at the aromatic centre with no metal–metal bond cleavage.[8] The hydrogen halides are hard electrophiles, and do not break the metal–metal bonds in $[Mn(CO)_5(SnMe_3)]$ and similar compounds but give halogeno(methyl)tin derivatives.[10,16] Mercury(II) bromide, although usually considered a soft electrophile, is harder than iodine and attacks at the aromatic carbon rather than the soft transition metal.

In $[Mn(CO)_5(SnPh_3)]$, replacement of phenyl groups by iodine strengthens the remaining phenyl–tin bonds and $[Mn(CO)_5(SnPhI_2)]$ reacts with iodine with metal–metal rather than phenyl–tin bond cleavage. When $[Fe(cp)(CO)_2(SnPh_3)]$ and $[Mn(CO)_5(SnPh_3)]$ react with $HgBr_2$ the remaining phenyl–tin bonds become stronger as phenyl groups are replaced by bromine and become resistant to further electrophilic attack. Thus $[Mn(CO)_5(SnBr_2Ph)]$ is the favoured manganese product and $[Fe(cp)(CO)_2(SnBrPh_2)]$ does not react further with $HgBr_2$. The electron-attracting halogen atoms attached to tin make the remaining aromatic groups less susceptible to electrophilic attack.

EXPERIMENTAL

The preparations and purification of the compounds containing Group 4 elements bonded to a transition metal have already been described.[5] The kinetics of the reactions were examined using a Unicam SP 500 spectrophotometer at the wavelengths given in Table 2 as already described. Reactions were studied under pseudo-first-order conditions (excess of $HgBr_2$) and a second-order rate coefficient, $k_2^{\mathrm{obs.}}$, was calculated by dividing the measured first-order rate coefficient by the concentration of $HgBr_2$. No measureable changes in the u.v. spectrum of $[Mn(CO)_5\{Sn(C_6H_{11})_3\}]$ could be seen when it reacted with $HgBr_2$ and the kinetics were followed by an i.r. technique.[9]

[6/1837 *Received*, 30*th September*, 1976]

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