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Reactivity of main-group–transition-metal bonds

X *. The kinetics of iodination of compounds containing one, two, three or four tin–cobalt bonds

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Abstract

Rate coefficients are reported for the cleavage by iodine of tin–cobalt bonds in compounds $[Me_nSn\{Co(CO)_4\}_{4-n}]$ ($n = 0$–3) and $[Me_2ISnCo(CO)_4]$. The reactions are rapid with k_2 *ca.* 0.3–3000 $dm^3\ mol^{-1}\ s^{-1}$ in cyclohexane at 30°C. As the number of Sn–Co bonds increases the reactivity of the bonds decreases rapidly. Replacing a methyl group by a $Co(CO)_4$ group has roughly the same effect on the reactivity of Sn–Co bonds as replacing a methyl group by an iodine atom. The kinetic studies are hindered by the instability of the product $[Co(CO)_4I]$, which rapidly decomposes.

Introduction

As part of a study of the reactivity of metal–metal bonds in compounds containing several such bonds we have reported on the kinetics of cleavage by halogens of tin–transition-metal bonds in compounds containing two or three metal–metal bonds, such as $[Me_2Sn\{Mn(CO)_5\}_2]$ and $[Me_2Sn\{Mn(CO)_5\}\{Fe(Cp)(CO)_2\}]$ [1]. Cleavage of metal–metal bonds in these manganese derivatives by halogens is clean and quantitative, and structure–reactivity patterns can be ascertained. We have now extended this study to the reactions of tin–cobalt bonds in compounds containing one, two, three or four such bonds (compounds **1–4** respectively). The reactivity of the related compound $[Me_2ISnCo(CO)_4]$ (**5**) has also been examined. Halogenation of these compounds produces unstable cobalt carbonyl halides [2] as products, and acquisition of quantitative kinetic data is extremely difficult. Nevertheless we believe that the data reported here are reliable, and add to knowledge of structure–reactivity patterns of complexes containing more than one metal–metal bond.

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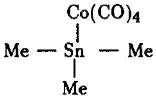
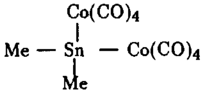
* For Part IX, see Ref. 1.



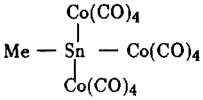
$$\mathrm{Me}-\underset{\mathrm{Me}}{\overset{\mathrm{Co(CO)_4}}{\mathrm{Sn}}}-\mathrm{Me}$$

1



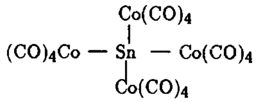
$$\mathrm{Me}-\underset{\mathrm{Me}}{\overset{\mathrm{Co(CO)_4}}{\mathrm{Sn}}}-\mathrm{Co(CO)_4}$$

2



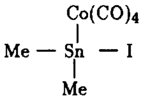
$$\mathrm{Me}-\underset{\mathrm{Co(CO)_4}}{\overset{\mathrm{Co(CO)_4}}{\mathrm{Sn}}}-\mathrm{Co(CO)_4}$$

3



$$\mathrm{(CO)_4Co}-\underset{\mathrm{Co(CO)_4}}{\overset{\mathrm{Co(CO)_4}}{\mathrm{Sn}}}-\mathrm{Co(CO)_4}$$

4



$$\mathrm{Me}-\underset{\mathrm{Me}}{\overset{\mathrm{Co(CO)_4}}{\mathrm{Sn}}}-\mathrm{I}$$

5

Experimental

Preparations

Complexes **1–5** were prepared by reaction of $[Co(CO)_4]^-$ with Me_3SnCl, Me_2SnCl_2, $MeSnCl_3$, $SnCl_4$, and Me_2SnI_2, respectively, in the appropriate molar quantities. Purification was by repeated recrystallisation and vacuum sublimation. Spectroscopic identification was consistent with assignments in the references in Table 1.

Kinetics

The iodination reaction of complex **1** was studied in a Durrum Stopped Flow spectrometer. Solutions of complexes **2–5** were placed in a capped 10 mm UV cell in a thermostatically controlled holder and allowed to reach the appropriate temperature. A small amount of iodine solution was added by syringe and after rapid mixing the absorbance chances were recorded on a chart recorder connected to a conventional UV spectrophotometer. In spite of scrupulous attention to degassing solvents and reagent purification, in some runs there was precipitation of decomposition products of cobalt carbonyl iodide. In these runs the absorbance–time data obtained before precipitation (corresponding to at least 30% of reaction) were used for the determination of (reproducible) rate coefficients.

Table 1

Second-order rate coefficients, k_2, for the reaction of complexes **1–5** with I_2 in cyclohexane at 30.0°C

	Complex	k_2 ($dm^3\ mol^{-1}\ s^{-1}$)	Reference for preparation
$[Me_3SnCo(CO)_4]$	(1)	3000 [a]	3
$[Me_2Sn\{Co(CO)_4\}_2]$	(2)	26.6 ± 2.8	3
$[MeSn\{Co(CO)_4\}_3]$	(3)	25.7 ± 1.6	4
$[Sn\{Co(CO)_4\}_4]$	(4)	0.33 ± 0.05	5
$[Me_2ISnCo(CO)_4]$	(5)	14.2 ± 0.7	6

[a] Intensive purification of compound **1** and re-examination of the kinetics of iodination have led to this increased value of k_2 over the value previously reported [7], (see Ref. 1).

Results and discussion

These iodination reactions (eq. 1, $m = 0$, $n = 0$–3; $m = 1$, $n = 3$) produce $[Co(CO)_4I]$, which is unstable in solution [2,8].

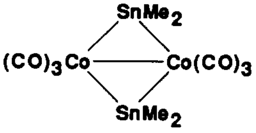
$$[Me_{n-m}I_mSn\{Co(CO)_4\}_{4-n}] + I_2 \xrightarrow{k_2} [Me_{n-m}Sn\{Co(CO)_4\}_{3-n}I_{m+1}] + [Co(CO)_4I] \qquad (1)$$

A black precipitate is readily formed and both product identification and kinetic studies are hampered. This made detailed IR analysis of the products impossible, but mass spectrometry of the filtered product solution from the reaction of iodine with complexes **1**–**5** showed evidence for the formation Me_3SnI, $[Me_2Sn\{Co(CO)_4\}I]$, $[MeSn\{Co(CO)_4\}_2I]$, $[Sn\{Co(CO)_4\}_3I]$, and Me_2SnI_2 respectively, as expected for reaction according to eq. 1.

Kinetics of the iodinations were studied under pseudo-first-order conditions with the cobalt complexes (0.4–11×10^{-3} mol dm^{-3}) in at least an eightfold excess over the iodine (0.5–10×10^{-4} mol dm^{-3}). Over the limited concentration ranges studied reaction was first order in both iodine and cobalt complex, and second-order rate coefficients, k_2, are given in Table 1.

When a methyl group in the related manganese compound $[Me_3SnMn(CO)_5]$ is replaced by a second $Mn(CO)_5$ group, the rate of iodine cleavage of Sn–Mn bonds rises by a factor of 6 [1]. However when a methyl group in complex **1** is replaced by a second $Co(CO)_4$ group the rate of iodine cleavage of Sn–Co bonds is reduced a hundredfold. Introduction of a second $Co(CO)_4$ group has a similar effect to replacement of a methyl group in complex **1** by iodine as in complex **5**. Replacing methyl groups by halogens in $[Me_3SnMn(CO)_5]$ leads to strengthening of the metal–metal bond to the extent that the Sn–Mn bond in $[I_3SnMn(CO)_5]$ cannot be broken by halogens [9]. These observations are in line with the fact that $Co(CO)_4$ is more electron-attracting than $Mn(CO)_5$. The relative electron-attracting ability of these two groups can be seen from the relative acidities of carbonyl hydrides: the hydride $[Mn(CO)_5H]$ is a much weaker acid than $[Co(CO)_4H]$ [10]. The latter, according to measurements of pK_a values in acetonitrile, is not quite as strong an acid as HI, whereas $[Mn(CO)_5H]$ has a pK_a some 7 units higher [11]. Replacement of a further methyl group by another $Co(CO)_4$ group has little effect on the rate. The extra electron-withdrawing power is balanced to some degree by the statistical factor (three Sn–Co bonds to attack rather than two). In compound **4** although there are four Sn–Co bonds to attack the iodination rate is again decreased, and perhaps steric hindrance also reduces the reactivity as well as the additional electron-withdrawing power. In compounds containing Sn–$Mn(CO)_5$ [1] and Sn–$Co(CO)_4$ bonds the reactivity of tin–transition-metal bonds with halogens parallels the acidity of the transition-metal hydrides. This provides further confirmation that any interactions between empty 5*d* orbitals on tin and filled 3*d* orbitals on the transition metal must be very small in these compounds.

We have shown that quantitative reactivity studies can, with difficulty, be made on these compounds containing several heteroatomic metal–metal bonds. The results give no evidence for any special features associated with metal–metal bonding, and provide a sound basis for examining the reactivity of clusters such as complex **6** [12,13] containing more complex metal–metal bonding.



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