TRIS(TETRACARBONYLCOBALT) TIN(IV) DERIVATIVES

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In earlier studies of metal-metal bonding,¹ we have reported the preparation and spectra of compounds $R_3MCo(CO)_4$, $R_2M[Co(CO)_4]_2$ and $X_2M[Co(CO)_4]_2$ (R = C_8H_5 , CH_3 ; X = Cl, Br, I; M = Ge, Sn, Pb). We give here a preliminary report on compounds of the type $RSn[Co(CO)_4]_3$, and some unexpected reactions encountered in this work. Several reactions afforded these compounds:

$$RSnCl_{3} + NaCo(CO)_{4} \rightarrow RSn[Co(CO)_{4}]_{3}$$
(1)

$$\operatorname{RSnCl}_{3} + \operatorname{Co}_{2}(\operatorname{CO})_{6} \to \operatorname{RSn}[\operatorname{Co}(\operatorname{CO})_{4}]_{3}$$
(2)

$$\operatorname{SnCl}_{4} + \operatorname{Co}_{2}(\operatorname{CO})_{8} \rightarrow \operatorname{ClSn}[\operatorname{Co}(\operatorname{CO})_{4}]_{3}$$
(3)

 $(R = CH_3, \underline{n}-C_4H_9, CH_2=CH, C_6H_5; X = Cl, Br, I)$

The methyl derivative, $CH_3 Sn[Co(CO)_4]_3$, (red crystals, mp 69-71°) showed carbonyl stretching frequencies (cm⁻¹) at 2101 (w), 2079 (s), 2040 (w), 2028 (wsh), 2020 (s), 2010 (s), 1992 (wsh), and 1961 (w) in cyclohexane solution.

Anal. Calcd. for $C_{13}H_3O_{12}SnCo_3$: C, 24.2; H, 0.5; O, 29.7. Found: C, 23.4; H, 0.4; O, 27.0.

The formulation $CH_3 Sn[Co(CO)_4]_3$ was confirmed by the occurance of the $CH_3 SnCo[Co(CO)_4]_3^+$ ion in the mass spectrum (MS-9). Fragments involving consecutive loss of CO and $Co(CO)_4$ from the molecular ion were also observed. A weaker series of fragments, $SnCo_3(CO)_4^+$ (x = 0 - 12) was also found. Mass spectra of the

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other derivatives were similar, although in the vinyl and halo compounds, the heaviest ion observed was $RSnCo_{3}(CO)_{11}^{+}$.

The mass spectrum of the butyl derivative was more complicated owing to the overlap of different fragments, but it was possible to identify the ions $C_4H_8SnCo(CO)_{12}^+$ and $C_4H_8SnCo_3(CO)_{11}^+$. This evidence, together with analytical data and the similarity of the infrared spectrum to the other derivatives, confirms that the product of reactions (1) and (2) $(R=\underline{n}-C_4H_9)$ is <u>not</u> the tris(<u>tri</u>carbonylcobalt) compound. We are thus unable to confirm the report² that reaction (2) gives rise to $\underline{n}-C_4H_9Sn[Co(CO)_3]_3$.

The latter compound, which would perhaps be expected in analogy with the known carbon^{3,4} and silicon⁵ derivatives of presumed structure I, is thus not formed. The type represented



by II is the stable product in the case of tin, and we have not been able thermally or by ultraviolet irradiation to effect the loss of carbonyl groups which would convert it to an analogue of I.

Reaction of cobalt carbonyl with tetravinylsilane⁵ yielded $CH_2=CHSi[Co(CO)_3]_3$, and in a further attempt to prepare the tricarbonylcobalt derivative of tin, we observed the following surprising results:

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$$(CH_2=CH)_4 Sn + Co_2(CO)_8 \begin{pmatrix} THF \\ Pentane \end{pmatrix} (CH_2=CH)_2 Sn[Co(CO)_4]_2$$
(5)

The product of reaction (4) was identical in properties and infrared spectrum with I, which has been obtained in a variety of other reactions.^{3,4} In the reaction, a vinyl group has evidently been converted to an ethylidyne group.

We have previously directed attention to proton-tin coupling constants in methyltin derivatives of transition metals.^{1,6} In $(CH_3)_3SnCo(CO)_4$ and $(CH_3)_2Sn[Co(CO)_4]_2$, values of $J(^{119}Sn-CH_3)$ are 52.6 and 45.7 c.p.s., respectively. For $CH_3Sn[Co(CO)_4]_3$, we now find a value of 33 c.p.s. (an average of ^{117}Sn and ^{119}Sn couplings, which are not resolved). This trend is understandable in terms of the distribution of the s-character of the tin atom among its four hybrid bonding orbitals. The smaller coupling constant implies reduced s-character in the Sn-CH₃ orbital, and therefore enhanced s-character in the tin orbitals bonding to cobalt.

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