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Organo-silicon and -tin Complexes of Ruthenium Carbonyl

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MANY transition-metal derivatives of the Group IVB elements have been characterised recently; some such as $Ph_2Sn[Mn(CO)_5]_2^{1}$ or $H_2Ge[Mn(CO)_5]_2^{2}$ contain a metal-atom sequence, while others are either known to have molecular structures with metal-atom clusters, *e.g.*, $Sn[Fe(CO)_4]_4$,³ or are reasonably assumed to have such structures, *e.g.*, $(Me_4N)_4[Pt_3Sn_8Cl_{20}]$.⁴ Herein we report the first compounds of what are apparently examples of both structural types derived from dodecacarbonyltriruthenium.⁵ Moreover, the reactions involving the ruthenium carbonyl or the anion $Ru(CO)_4^2$ -follow a different course to the analogous reactions with dodecacarbonyltri-iron or the anion $Fe(CO)_4^{2-}$.

Treatment of the anion $\operatorname{Ru}(\operatorname{CO})_4^{2-}$ at 0° in tetrahydrofuran with R_3 SnCl (R = Ph or PhCH₂) affords air-stable crystals of (Ph3Sn)2Ru(CO)4 (m.p. 180-182°) and the analogous benzyl complex [(PhCH₂)₃Sn]₂Ru(CO)₄. These complexes have a trans-arrangement of the R₃Sn groups, since only one strong carbonyl stretching mode is observed in the infrared spectrum. Reactions between $\operatorname{Ru}(\operatorname{CO})_4^{2-}$ and the halides $\operatorname{R}_3\operatorname{SnCl}$ $(R = Me, Et, Pr^n \text{ or } Bu^n)$ give compounds $(R_3Sn)_2$ -Ru(CO)₄. However, the infrared spectra of these complexes in the carbonyl stretching region show four bands. The band pattern observed in the spectrum of (Me₃Sn)₂Ru(CO)₄ (2084s, 2024s, 2012w, and 2003s cm.-1) is similar to that of (Me₃Sn)₂-Fe(CO)₄^{3b} and corresponds to a molecular structure with C_{2v} symmetry; the assignments being $A_1(1)$, B_2 , $A_1(2)$, and B_1 respectively. As R in $(R_3Sn)_2Ru(CO)_4$ changes from Et to Buⁿ, a band near 2010 cm.⁻¹ increases in relative intensity, indicating the formation of mixtures of *cis*- and *trans*-isomers. The iron compound $(Ph_3Sn)_2Fe-(CO)_4^6$ was prepared by the method used to obtain the ruthenium analogue. In contrast, however, its infrared spectrum showed four carbonyl stretching modes, corresponding to the *cis*-configuration.

The complexes (R₃Sn)₂Ru(CO)₄ are best prepared (60-70% yield) by heating dodecacarbonyltriruthenium and the hydride R₃SnH in hexane. A very minor product of this reaction analyses as $R_{10}Sn_4Ru_2(CO)_6$, for which structure (I) has been suggested.[†] The proton n.m.r. spectrum of (I; R = Me) shows two bands at τ 9.09 and 9.47, relative intensity approximately 2:3; the infrared spectrum has three carbonyl stretches, at 2036m, 2000s, and 1981m. Although the high resolution mass spectrum of (I; R = Me) does not show a molecular ion, there is a strong peak perhaps corresponding to $(P-2Me)^+$. Some evidence for this is provided by the mass spectrum of cis-(Me₃Sn)₂Ru- $(CO)_4$, which indicates that a methyl group is lost before a carbonyl group. The spectrum shows a weak molecular ion followed by strong peaks corresponding to $(P - Me)^+$, $(P - Me - nCO)^+$ (n = 1-4), $(P - 3Me - nCO)^+$, etc. The diamagnetism of (I), as evidenced by the sharp ¹H n.m.r. spectrum, requires spin pairing of the odd

[†] We are indebted to J. Dalton for this suggestion.





Reactions between $\operatorname{Ru}_3(\operatorname{CO})_{12}$ and organosilanes yield complexes of a different type. For example, trimethylsilane reacts to form, in high yield, trans- $Me_3Si \cdot Ru(CO)_4 \cdot Ru(CO)_4 \cdot SiMe_3$ (m.p. 129–131°), for which structure (II) is suggested on the basis of analysis, high-resolution mass spectrum $[M^+]$ at m/e 574; C₁₄H₁₈O₈Si₂¹⁰²Ru₂ requires 574], ¹H n.m.r. (singlet at τ 9.40), and infrared spectrum (ν_{ec} , 2041w, 2014vs, 2005sh,w). An identical band

pattern is shown by $trans-\operatorname{Bu}_3\operatorname{P}\cdot\operatorname{Mn}(\operatorname{CO})_4\cdot\operatorname{Mn}$ (CO)₄·PBu₃.⁷ Further evidence for the structure of (I) comes from the appearance in the mass spectrum of an ion attributable to $Me_3Si^{102}Ru(CO)_4^+$ at m/e287.

Under conditions similar to those used to obtain (II), dodecacarbonyltri-iron and trimethylsilane give no organosilicon(carbonyl)iron complex. further difference between the chemistry of the two carbonyls Ru₃(CO)₁₂ and Fe₃(CO)₁₂ occurs in their reactions with trichlorosilane. Recently it has been reported⁸ that Fe₃(CO)₁₂ and HSiCl₃ yield (Cl₃Si)₂Fe(CO)₄, whereas we have obtained Cl₃Si·Ru- $(CO)_4$ ·Ru $(CO)_4$ ·SiCl₃ as one product from the analogous reaction with the ruthenium carbonyl, and find no evidence for (Cl₃Si)₂Ru(CO)₄.

Compounds of type (II) would be expected to show a similar chemistry to that of the carbonyls of the manganese subgroup, and this appears to be the case. For example, the ruthenium-ruthenium bond in (II) may be cleaved to form an anion which on treatment with trimethyltin chloride gives cis-Me₃Si[•]Ru(CO)₄[•]SnMe₃. The mass spectrum of this complex also shows initial loss of a methyl group from the parent ion. Both Ru-Ru and Ru-Si bonds in (II) are broken in the reaction with trimethyltin hydride, which gives (I; R = Me) and cis-(Me₃Sn)₂Ru(CO)₄.

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- ¹ B. T. Kilbourn and H. M. Powell, Chem. and Ind., 1964, 1578; R. D. Gorsich, J. Amer. Chem. Soc., 1962, 84, 2486.
- ² A. G. Massey, A. J. Park, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1963, 85, 2021. ³ (a) P. F. Lindley and P. Woodward, *J. Chem. Soc.* (A), 1967, 382; (b) J. D. Cotton, S. A. R. Knox, I. Paul, and F. G. A. Stone, *J. Chem. Soc.* (A), 1967, 264.
 - ⁴ R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *Inorg. Chem.*, 1966, 5, 109.
 ⁵ M. I. Bruce and F. G. A. Stone, *J. Chem. Soc.* (A), 1967, 1238.
 ⁶ F. Hein and W. Jehn, *Annalen*, 1965, 684, 4.

 - ⁷ J. Lewis, A. R. Manning, and J. R. Miller, *J. Chem. Soc.* (A), 1966, 847. ⁸ W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 1967, **89**, 2773.