Chemical Communications

NUMBER 19/1967 4 OCTOBER

Organo-silicon and -tin Complexes of Ruthenium Carbonyl

By J. D. COTTON, S. A. R. KNOX, and F. G. A. STONE*
(*Department of Inorganic Chemistry, The University, Bristol* 8)

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 $Fe(CO)_4^{2-}$.

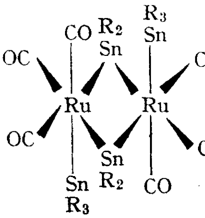
Treatment of the anion $Ru(CO)_4^{2-}$ at 0° in tetrahydrofuran with R_3SnCl ($R = Ph$ or $PhCH_2$) affords air-stable crystals of $(Ph_3Sn)_2Ru(CO)_4$ (m.p. 180—182°) and the analogous benzyl complex $[(PhCH_2)_3Sn]_2Ru(CO)_4$. These complexes have a *trans*-arrangement of the R_3Sn groups, since only one strong carbonyl stretching mode is observed in the infrared spectrum. Reactions between $Ru(CO)_4^{2-}$ and the halides R_3SnCl ($R = Me$, Et, Pr^n or Bu^n) give compounds $(R_3Sn)_2Ru(CO)_4$. However, the infrared spectra of these complexes in the carbonyl stretching region show four bands. The band pattern observed in the spectrum of $(Me_3Sn)_2Ru(CO)_4$ (2084s, 2024s, 2012w, and 2003s cm.$^{-1}$) is similar to that of $(Me_3Sn)_2Fe(CO)_4$[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 Bu^n, 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 $(R_3Sn)_2Ru(CO)_4$ are best prepared (60—70% yield) by heating dodecacarbonyltriruthenium and the hydride R_3SnH 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*-$(Me_3Sn)_2Ru(CO)_4$, 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

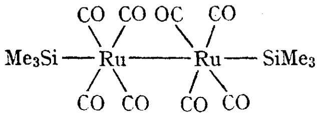
---

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

electron on the ruthenium atoms, possibly *via* the bridging tin atoms.[3a] Although iron carbonyls and trimethyltin hydride afford *cis*-$(Me_3Sn)_2Fe(CO)_4$, the organotin(carbonyl)iron cluster complexes also produced[3b] have different molecular formulae from (I).



(I)



$$\begin{array}{c}\mathrm{CO\ \ CO\ \ OC\ \ \ CO}\\ \mathrm{Me_3Si{-}Ru{-}Ru{-}SiMe_3}\\ \mathrm{CO\ \ CO\ \ \ CO\ \ CO}\end{array}$$

(II)

Reactions between $Ru_3(CO)_{12}$ 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; $C_{14}H_{18}O_8Si_2{}^{102}Ru_2$ requires 574], ^1H n.m.r. (singlet at τ 9·40), and infrared spectrum (ν_{CO}, 2041w, 2014vs, 2005sh,w). An identical band pattern is shown by *trans*-$Bu_3P{\cdot}Mn(CO)_4{\cdot}Mn(CO)_4{\cdot}PBu_3$.[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/e 287.

Under conditions similar to those used to obtain (II), dodecacarbonyltri-iron and trimethylsilane give no organosilicon(carbonyl)iron complex. A further difference between the chemistry of the two carbonyls $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$ occurs in their reactions with trichlorosilane. Recently it has been reported[8] that $Fe_3(CO)_{12}$ and $HSiCl_3$ yield $(Cl_3Si)_2Fe(CO)_4$, whereas we have obtained $Cl_3Si{\cdot}Ru(CO)_4{\cdot}Ru(CO)_4{\cdot}SiCl_3$ as one product from the analogous reaction with the ruthenium carbonyl, and find no evidence for $(Cl_3Si)_2Ru(CO)_4$.

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*-$Me_3Si{\cdot}Ru(CO)_4{\cdot}SnMe_3$. 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*-$(Me_3Sn)_2Ru(CO)_4$.

One of us (S.A.R.K.) thanks the S.R.C. for a research studentship. We thank the U.S. Army through the European Research Office for support.

(*Received, July* 31*st*, 1967; *Com.* 804.)

---

[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.