Synthesis and Structure of $Cl_3SnRu_2(CO)_5Cl_3$

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TETRAHALIDES of germanium and tin have been reported to react with pentacarbonyliron to form *cis*-$(OC)_4Fe(X)MX_3$ (M = Ge, Sn; X = Cl, Br, I), which is transformed on warming into *cis*- or *trans*-$(OC)_4Fe(MX_3)_2$.[1] It was observed in the same study (although not reported) that dodecarbonyltri-iron afforded the same products under slightly more vigorous conditions. We report here the different course of the reaction in the case of dodecacarbonyltriruthenium.

At temperatures above 100°, $Ru_3(CO)_{12}$ reacts with MX_4 to form air-stable crystalline derivatives which analyse as $Ru_2(CO)_5MX_6$. Thus, its reaction with $SnCl_4$ (135° in xylene) affords $Ru_2(CO)_5SnCl_6$ in 90% yield as pale yellow crystals, m.p. 178°, with i.r. carbonyl stretching bands at 2154s, 2094s, 2084s, and 2031s cm.$^{-1}$ (CH_2Cl_2 solution). The molecular ion is observed in the mass spectrum at m/e 674; interestingly, a stronger peak due to $(P-SnCl_2)^+$ occurs at m/e 486.

The structure of $Ru_2(CO)_5SnCl_6$, as established by an X-ray crystallographic study, is shown in the Figure. Data were collected by counter methods; 886 unique non-zero reflections were refined by least-squares techniques to a final conventional residual of 6·4%. Each ruthenium atom is at the centre of a distorted octahedron, with the two octahedra sharing a face.

The structures of two other triply chlorine-bridged diruthenium molecules have recently been reported.[2,3] In both cases, the terminal positions were occupied by chlorine atoms and phosphine groups, and a shortening of bridging-chlorine–ruthenium distances *trans* to terminal chlorines was observed. The effect was attributed to the lower *trans*-effect of chlorine. In the present structure, bridging chlorines are equidistant from the ruthenium atoms, within error. The implication is that Cl_3Sn^- and CO have similar *trans*-effects, or, more precisely, that the *trans*-bond weakening effect of the two ligands as judged from this compound is the same.

Delocalization of the odd electron in $(Bu^n_3P)_4Ru_2Cl_5$ has been suggested[3] to account for the Ru–Ru distance[2] (3·115 Å); it is interesting that the Ru–Ru separation reported here is almost as short (3·157 Å), although no metal–metal interaction need be invoked. These distances are significantly shorter than the Ru–Ru separation in $(Et_2PhP)_5Ru_2Cl_4$ (3·367 Å) but much longer than the Ru–Ru bond in $Ru_3(CO)_{12}$ (2·848 Å).[4]

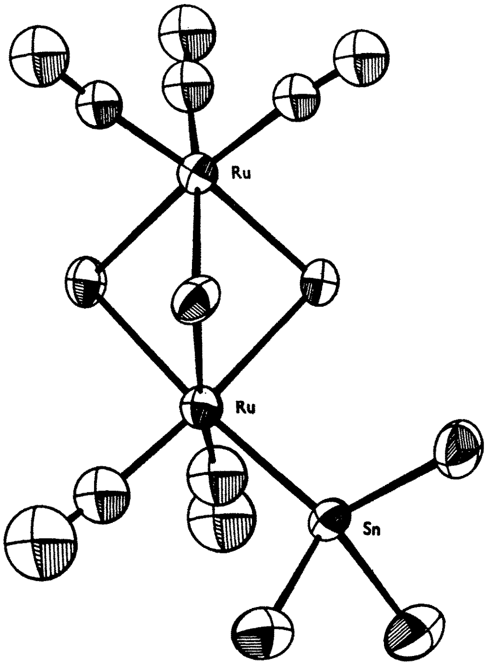
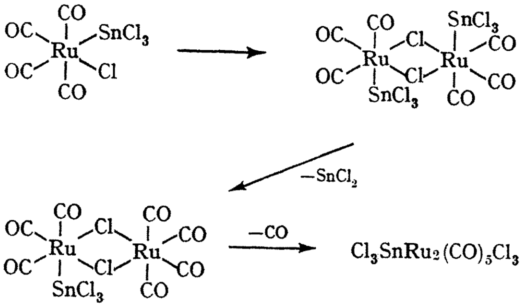


FIGURE. *Molecular structure of* $Cl_3SnRu_2(CO)_5Cl_3$. *Important bond lengths are*: Ru–Ru, 3·157(4); Ru–Sn, 2·565(4); Sn–Cl (*mean*), 2·347 (7); Ru–Cl (*mean*), 2·433(5) *Figures in parenthesis are standard errors or standard errors in the mean.*

At room temperature in benzene, $SnCl_4$ and $Ru_3(CO)_{12}$ react to form a yellow compound $Ru_3(CO)_{12},SnCl_4$ which exhibits carbonyl stretching bands at 2150m, 2120m, 2089sh, 2073s, 2057s, 2039w, 2019w cm.$^{-1}$ in dichloromethane. This resembles the spectrum reported for $Cl[Os(CO)_4]_3AuPPh_3$,[5] and a similar linear Ru–Ru–Sn backbone is assumed. In the high-temperature reaction, further cleavage of Ru–Ru bonds would form $(OC)_4Ru(Cl)$-$SnCl_3$; dimerization and loss of $SnCl_2$ according to the following scheme would form the product:



The expected quantity of $SnCl_2$ is recovered. When the reaction is carried out under 70 atmos. carbon monoxide, the product is *trans*-$(OC)_4Ru(SnCl_3)_2$ [ν(CO) at 2106 cm.$^{-1}$, dichloromethane]. The *trans*-form is stable in solution, in contrast to *trans*-$(OC)_4Fe(SnCl_3)_2$, which rapidly isomerizes to the *cis*-form.[1] These observations are reconciled if it is assumed that the Cl_3Sn group has almost the same π-acceptor capability as CO *when bonded to ruthenium*; then both *cis*- and *trans*-forms would be equally preferred from the electronic standpoint, and steric factors would determine the structure. Stone and his co-workers have applied similar arguments to the stereochemistry of $(OC)_4Ru(SnR_3)_2$ derivatives.[6]

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