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ORGANO-SILICON AND -TIN COMPLEXES OF OSMIUM CARBONYL

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Whereas the major product of the thermal reaction between dodecacarbonyl triruthenium and trimethylstannane is $(Me_3Sn)_2Ru(CO)_4$ [1], with trimethylsilane the binuclear ruthenium complex $[Me_3SiRu(CO)_4]_2$ is formed[2]. Further studies with $Fe_3(CO)_{12}$ and $Os_3(CO)_{12}$ have provided a greater insight into the nature of these and related reactions, through the characterisation of stable hydrido(carbonyl) complexes of osmium $Me_3M^{IV}Os(CO)_4H$ $[M^{IV} = Si, Sn]$.

In hexane at 80°, trimethylsilane and dodecacarbonyl triosmium afford the two complexes $(Me_3Si)_2Os(CO)_4$ ($\nu(CO)_{max}$ 2099w, 2031w, 2020w, 2011s cm^{-1}) and $[Me_3SiOs(CO)_4]_2$ ($\nu(CO)_{max}$ 2052m, 2012s, 2003(sh) cm^{-1}). The former compound is produced in highest yield, and, moreover, decomposes to give the latter compound when heated. If the reaction between trimethylsilane and dodecacarbonyl triosmium is carried out with ultraviolet irradiation, however, a third product, $Me_3SiOs(CO)_4H$, is obtained. This hydride is a volatile colourless liquid and exhibits the four carbonyl stretching absorptions of a *cis* isomer at 2119w, 2050w, 2036m and 2029s cm^{-1}. A high field proton NMR absorption is observed at τ 19.03 and the $\nu(Os{-}H)$ stretch has been identified at 1935 cm^{-1}. Like recently discovered $H_2Os(CO)_4$ [3], $Me_3SiOs(CO)_4H$ is of relatively high thermal stability. Decomposition is slow *in vacuo* at 50°, affording the two complexes $[Me_3SiOs(CO)_4]_2$ and $(Me_3Si)_2Os(CO)_4$. With Ph_3PAuMe, the hydride gives *cis*-$Me_3SiOs(CO)_4AuPPh_3$, a reaction which represents a new route to gold–transition metal complexes.

If a mixture of $Fe_3(CO)_{12}$ and Me_3SiH is irradiated no stable $Me_3SiFe(CO)_4H$ is obtained, but others[4] have observed the formation of $(Me_3Si)_2Fe(CO)_4$ in apparently infrared identifiable quantities only from a thermal reaction between an excess of the silane and the carbonyl. Ultraviolet irradiation of $Ru_3(CO)_{12}$ and Me_3SiH does not afford a new hydrido(carbonyl)–ruthenium complex but instead gives $[Me_3SiRu(CO)_4]_2$ as the main product (90% yield), together with a small amount of $(Me_3Si)_2Ru(CO)_4$, which was observed to decompose readily into the binuclear ruthenium species.

Ultraviolet irradiation of Me_3SnH and $Os_3(CO)_{12}$ in hexane gave only volatile colourless $Me_3SnOs(CO)_4H$, a liquid of comparable thermal stability to $Me_3SiOs(CO)_4H$, as shown by its formation, with $(Me_3Sn)_2Os(CO)_4$, from the reaction between $[Me_3SiOs(CO)_4]_2$ and Me_3SnH at 80°. In contrast, thermal reactions between Me_3SnH and $Os_3(CO)_{12}$ yield $(Me_3Sn)_2Os(CO)_4$. Previously, Me_3SnH and $Fe(CO)_5$ were observed to give $(Me_3Sn)_2Fe(CO)_4$ and traces of an unstable volatile substance believed to be $Me_3SnFe(CO)_4H$[5].

From the foregoing it appears that reactions between triorgano-silanes or -stannanes and the dodecacarbonyls of the iron triad involve an oxidative—addition process as the first step, producing $(R_3M^{IV})M(CO)_4H$ (M^{IV} = Si, Sn and M = Fe, Ru, Os). Only for osmium have the intermediate hydridocarbonyl species reasonable stability. When M^{IV} = Sn, the complexes $(R_3Sn)_2M(CO)_4$ are produced and are stable for all three transition elements. However, when M^{IV} = Si, the species $R_3SiM(CO)_4 \cdot M(CO)_4SiR_3$ (M = Ru, Os) are formed, probably via thermal decomposition of both $(R_3Si)_2M(CO)_4$ and $R_3SiM(CO)_4H$. Interestingly, this thermal transformation is more facile with ruthenium than with osmium and does not occur with the tin compounds $(R_3Sn)_2M(CO)_4$, the decomposition of which follows a different path[1]. The relative stability of the tin compounds is further supported by the observation that the species $[R_3SiM(CO)_4]_2$ (M = Ru, Os) react with trimethylstannane giving $(Me_3Sn)_2M(CO)_4$ and R_3SiH, in a reaction in which both Si—M and M—M bonds are broken.

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REFERENCES

1 J.D. Cotton, S.A.R. Knox and F.G.A. Stone, *J. Chem. Soc. (A)*, (1968) 2758.
2 J.D. Cotton, S.A.R. Knox and F.G.A. Stone, *Chem. Commun.*, (1967) 965.
3 F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 6 (1967) 2092.
4 O. Kahn and M. Bigorgne, *J. Organometal. Chem.*, 10 (1967) 137.
5 J.D. Cotton, S.A.R. Knox, I. Paul and F.G.A. Stone, *J. Chem. Soc. (A)*, (1967) 264.