

PRELIMINARY COMMUNICATION

TRICHLOROTIN DERIVATIVES OF OSMIUM CARBONYL AND OF OSMIUM CARBONYL HYDRIDES

J.R. MOSS and W.A.G. GRAHAM

Department of Chemistry, University of Alberta Edmonton, Alberta (Canada)

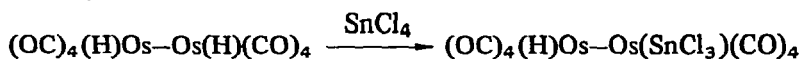
(Received June 23rd, 1969)

The reaction of tin tetrahalides with metal carbonyl complexes leads in a number of cases to trihalotin derivatives. Thus, $\text{Cl}_3\text{SnCo}(\text{CO})_4$ ¹, *cis*- $(\text{Cl}_3\text{Sn})_2\text{Fe}(\text{CO})_4$ ², and $\text{Cl}_3\text{SnRu}_2(\text{CO})_5\text{Cl}_3$ ³ have been prepared from tin tetrachloride and the corresponding metal carbonyl. We now find that this reaction with osmium carbonyls and carbonyl hydrides leads to trichlorotin derivatives of novel type.

The mononuclear carbonyl hydride of osmium, $\text{H}_2\text{Os}(\text{CO})_4$ ⁴, readily reacts with tin tetrachloride at room temperature to afford the new complex *cis*- $(\text{OC})_4\text{Os}(\text{H})\text{SnCl}_3$ as colorless, air-stable needles, m.p. 101–104°. The compound was characterized by elemental analysis and by the observation in the mass spectrum of a multiplet of the expected structure corresponding to the molecular ion. The trimethyltin analogue, *cis*- $(\text{OC})_4\text{Os}(\text{H})\text{Sn}(\text{CH}_3)_3$, has very recently been reported as the product of the reaction $(\text{CH}_3)_3\text{SnH}$ and $\text{Os}_3(\text{CO})_{12}$ ⁵.

The proton NMR spectrum of *cis*- $(\text{OC})_4\text{Os}(\text{H})\text{SnCl}_3$ in dichloromethane exhibits a singlet at τ 18.37, with spin-spin satellites corresponding to $J(^{119}\text{Sn}-\text{H}) = 136.0$ Hz and $J(^{117}\text{Sn}-\text{H}) = 129.5$ Hz. The tendency of SnCl_4 to react with only one Os-H bond is in contrast to the rapid and quantitative conversion of $\text{H}_2\text{Os}(\text{CO})_4$ to the dihalides by CCl_4 and CBr_4 ⁴.

The recently prepared dinuclear osmium carbonyl hydride, $\text{H}_2\text{Os}_2(\text{CO})_8$ ⁶, also reacts readily with tin(IV) chloride to afford colorless needles of $\text{H}(\text{Cl}_3\text{Sn})\text{Os}_2(\text{CO})_8$, m.p. 118–121°.



The eight bands observed in the carbonyl stretching region for the compound (Table 1) indicate a low symmetry. The NMR spectrum shows a singlet at τ 19.55 with no observable coupling to tin. The new dinuclear complex reacts readily with CX_4 to form $\text{Os}_2\text{X}(\text{SnCl}_3)(\text{CO})_8$ (X = Cl or Br) for which eight carbonyl stretching bands are observed.

We have also observed the reaction of triosmium dodecacarbonyl with tin tetrachloride at room temperature to form the adduct $\text{Os}_3(\text{CO})_{12} \cdot \text{SnCl}_4$; the infrared spectrum (Table 1) suggests that it has a linear $\text{Cl}_3\text{Sn}-\text{Os}(\text{CO})_4-\text{Os}(\text{CO})_4-\text{Os}(\text{CO})_4-\text{Cl}$ arrangement analogous to that recently reported for $\text{Ru}_3(\text{CO})_{12} \cdot \text{SnCl}_4$ ³. Other molecules of similar structure are $\text{Os}_3(\text{CO})_{12} \cdot \text{X}_2$ (X = halogen)⁷ and $\text{Os}_3(\text{CO})_{12} \cdot \text{Ph}_3\text{PAuCl}$ ⁸.

ACKNOWLEDGMENTS

We thank the National Research Council of Canada for financial support.

TABLE 1

Compound	Bands in ν (CO) region in n-heptane soln.
$\text{OsH}(\text{SnCl}_3)(\text{CO})_4$	2155m, 2095s, 2078vs, 2072s
$\text{Os}_2\text{H}(\text{SnCl}_3)(\text{CO})_8$	2142w, 2107vs, 2078s, 2065s, 2057 (sh), 2054s, 2043vs, 2032m
$\text{Os}_2\text{Cl}(\text{SnCl}_3)(\text{CO})_8$	2152w, 2118s, 2085vs, 2076s, 2067s, 2054vs, 2048 (sh), 2034m
$\text{Os}_2\text{Br}(\text{SnCl}_3)(\text{CO})_8$	2151w, 2118s, 2084vs, 2076s, 2067s, 2055vs, 2049m, 2035m
$\text{Os}_3(\text{CO})_{12}(\text{SnCl}_3)\text{Cl}^a$	2152m, 2124m, 2086(sh), 2069vs, 2049vs, 2030m, 2006m.

^a measured in CH_2Cl_2 solution.

REFERENCES

- 1 D.J. Patmore and W.A.G. Graham, *Inorg. Chem.*, 7 (1968) 771.
- 2 R. Kummer and W.A.G. Graham, *Inorg. Chem.*, 7 (1968) 1208.
- 3 R.K. Pomeroy, M. Elder, D. Hall and W.A.G. Graham, *Chem. Commun.*, (1969) 381.
- 4 F. L'Eplattenier and F. Calderazzo, *Inorg. Chem.*, 6 (1967) 2092.
- 5 S.A.R. Knox, C.M. Mitchell and F.G.A. Stone, *J. Organometal. Chem.*, 16 (1969) P67.
- 6 J.R. Moss and W.A.G. Graham, *Chem. Commun.*, (1968) in press.
- 7 B.F.G. Johnson, J. Lewis and P.A. Kilty, *J. Chem. Soc. A*, (1968) 2859.
- 8 C.W. Bradford and R.S. Nyholm, *Chem. Commun.*, (1968) 867.

J. Organometal. Chem., 18 (1969) P24–P25