Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

PRELIMINARY NOTE

Rhodium–silicon complexes

Complexes containing direct metal–silicon bonds have been reported for several transition metals, but none are known for metals of the second long period. We now report the isolation of the first silyl derivatives of rhodium.

Initial attempts to prepare silyl derivatives of rhodium or iridium by reaction of the compounds $(Ph_3P)_2M(CO)Cl$ with an alkali metal derivative of a silane (*cf.* the known silyl derivatives of platinum[1,2] or gold[2]) failed to produce readily-characterised products. The oxidative addition reaction of a d^8 complex has been used to prepare iridium–silicon compounds *e.g.*, the reaction[3] of silanes R_3SiH with $(Ph_3P)_2Ir(CO)Cl$ gives the complexes $(Ph_3P)_2Ir(CO)ClH(SiR_3)$ [$R_3 = Cl_3$, Cl_2Ph, Cl_2Et, $(OEt)_3$, but not alkyl or aryl] which are considerably dissociated in solution and quantitatively decomposed to starting materials when heated. This alternative approach also failed when applied to the compound $(Ph_3P)_2Rh(CO)Cl$, presumably because of the higher energy of oxidation of rhodium(I). Replacement of carbon monoxide by triphenylphosphine might be expected to facilitate reaction, and in accord with this the complexes $(Ph_3E)_3RhX$ ($X = Cl$, Br; $E = P$, As, or Sb)[4] have been found to react with an excess of trichlorosilane or of triethoxysilane to give the bright yellow rhodium(III) derivatives $(Ph_3E)_2RhXH(SiR_3)$; the displaced ligand Ph_3E was recovered from its solution in the excess of the silane. These products do not dissociate in solution, and satisfactory molecular weights corresponding to monomers have been obtained. The presence of a direct rhodium–hydrogen bond is indicated by infra-red absorption in the range 2040–2080 cm^{-1}, values comparable to those reported for the compounds $(Ph_3P)_2Ir(CO)ClH(SiR_3)$[3], $(Ph_3P)_2Ir(CO)ClH_2$[5] and $(Ph_3E)_2RhClH_2$[4].

The chloro-complexes are not sufficiently soluble to give good NMR spectra, but the complex $(Ph_3P)_2RhBrHSi(OEt)_3$ in dichloromethane gives a sharp, well-resolved spectrum showing at high field two sets of overlapping double triplets (23.6 τ and 24.6 τ; both sets give $J(Rh\text{–}H) = 24.0$ cps and $J(P\text{–}H) = 14.3$ cps). The total integrated intensity of these peaks, relative to those due to the silane and phosphine, corresponds to one proton per rhodium atom. Studies at two frequencies (60 and 100 Mcps) establish that the two sets of peaks are due to two species with different chemical shifts. The peaks due to the CH_2-groups of the silane are also slightly split (1.5 cps) in the 100 Mcps spectrum. The two species are almost certainly isomers, possibly produced by coordination of the solvent; studies with other solvents are in progress. Solvent coordination has been postulated[4] in other $(Ph_3P)_2RhClXY$ systems, but well resolved spectra were not obtained owing to the presence of a paramagnetic impurity. Neither the NMR spectra nor the IR spectra of the complexes give any evidence for the presence of the free silanes.

A solution of the complex $(Ph_3P)_2RhClHSiCl_3$ in dichloromethane reacts with carbon monoxide to give $(Ph_3P)_2Rh(CO)Cl$, thus demonstrating that the lack of reaction between the last compound and trichlorosilane is caused by thermodynamic and not kinetic factors.

The rhodium(I) complex $(Ph_3P)_3RhCl$ catalyses the addition of triethylsilane and of triphenylsilane to hex-1-ene to give the corresponding n-hexylsilane. Under comparable conditions the reaction of triphenylsilane is the more rapid.

Acknowledgements

We gratefully acknowledge the award of a Central Electricity Generating Board Scholarship to D.J.P.

Department of Chemistry,
The University of Manchester
Institute of Science and Technology,
Manchester, 1 (Great Britain)

R. N. HASZELDINE
R. V. PARISH
D. J. PARRY

1 J. CHATT, C. EABORN AND S. IBEKWE, *Chem. Commun.*, (1966) 700.
2 M. C. BAIRD, *J. Inorg. Nucl. Chem.*, 29 (1967) 367.
3 A. J. CHALK AND J. F. HARROD, *J. Am. Chem. Soc.*, 87 (1965) 16.
4 J. A. OSBORN, F. H. JARDINE, J. R. YOUNG AND G. WILKINSON, *J. Chem. Soc.* (A), (1966) 1711; J. T. MAGUE AND G. WILKINSON, *J. Chem. Soc.* (A), (1966) 1736.
5 L. VASKA AND J. W. DILUZIO, *J. Am. Chem. Soc.*, 84 (1962) 679.

Received April 27th, 1967