

Bis(triethylsilyl)dihydro(pentamethylcyclopentadienyl)rhodium: an Organo-rhodium(v) Complex

Maria-Jesus Fernandez and Peter M. Maitlis*

Department of Chemistry, The University, Sheffield S3 7HF, U.K.

The rhodium(v) complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\text{H})_2(\text{SiEt}_3)_2]$ is formed by reaction of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2\text{Cl}_4]$ and HSiEt_3 .

Although the higher oxidation states of the platinum metals are usually achieved only with oxide or fluoride as ligands,¹ we were recently able to prepare organometallic complexes of iridium(v)² and of rhodium(iv)³ when the $\eta^5\text{-C}_5\text{Me}_5$ ligand⁴ was present. We now report that $\eta^5\text{-C}_5\text{Me}_5$ can even stabilise rhodium(v) and without fluoride or oxide ligands.

The Rh^{V} complex (3) was obtained during a study of the hydrosilation-dehydrogenation reaction recently reported.⁵ It can be easily prepared (50% yield) by reaction of $[(\text{C}_5\text{Me}_5)_2\text{Rh}_2\text{Cl}_4]$ (1) with excess of triethylsilane in 1,2-dichloroethane, preferably in the presence of triethylamine. Complex (3) crystallises in colourless plates, is hydrocarbon-soluble, and can be purified by column chromatography. It has been characterised by microanalysis, its molecular weight (osmometry in toluene, 465; mass spectrum shows the expected molecular ion peak at m/e 470), and n.m.r. spectroscopy. The ^1H n.m.r. spectrum (400 MHz, C_6D_6) showed four resonances, at δ 1.70 [q, 15H, C_5Me_5 , $J(\text{Rh}-\text{Me}) \simeq J(\text{Me}-\text{hydride}) = 0.6$ Hz], 1.09 [t, 18H, SiCH_2CH_3 , $J(\text{CH}_3-$

$\text{CH}_2) = 7.8$ Hz], 0.89 [q, 12H, SiCH_2CH_3 , $J = 7.8$ Hz], and -13.85 [broad d with satellites, 2H, hydride, $J(\text{Rh}-\text{H}) = 36.9$ Hz, $J(\text{Si}-\text{H}) = 7.8$ Hz]. The $^{29}\text{Si}\{^1\text{H}\}$ [δ 38.33, d, $J(\text{Rh}-\text{Si}) = 15.9$ Hz] and $^{13}\text{C}\{^1\text{H}\}$ n.m.r.† spectra confirmed the structure, but final proof for the presence of two hydride ligands came from the ^{103}Rh n.m.r. spectrum which showed a triplet at $\delta -1714$ p.p.m. (with respect to 3.16 MHz = 0 p.p.m.) with $J(\text{Rh}-\text{H}) = 36.6$ Hz. On irradiation at the hydride frequency this collapsed to a singlet (Figure 1). The i.r. spectrum in cyclohexane showed a single, rather broad peak, with some evidence of shoulders, at 2020 cm^{-1} , due to a terminal $\nu(\text{Rh}-\text{H})$. We therefore suggest that the

† The $^{13}\text{C}\{^1\text{H}\}$ n.m.r. spectrum (C_7D_8 , 25 MHz), δ 9.5 (SiCH_2CH_3), 11.0 (SiCH_2), 11.2 (C_5Me_5), and 101.4 [C_5Me_5 , $J(\text{C}-\text{Rh}) = 3.5$ Hz] p.p.m. showed no significant change over the temperature range -50 to $+30$ °C indicating the C_5Me_5 ring to be η^5 -bonded.

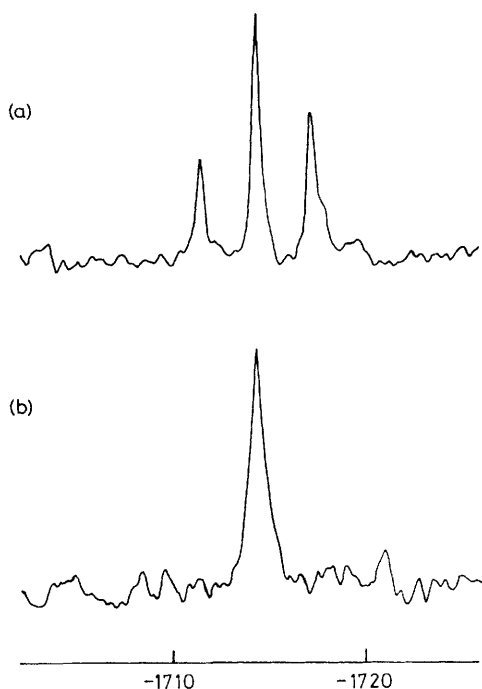


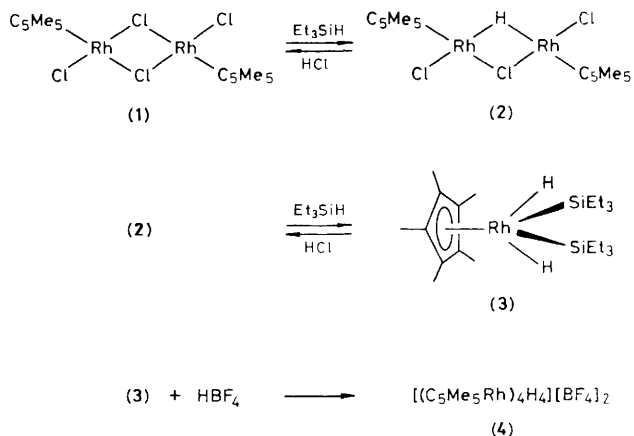
Figure 1. The ^{103}Rh n.m.r. spectrum of complex (3): (a) no decoupling; (b) with irradiation at the hydride frequency.

hydrides are probably *trans*- in the basal plane of a square pyramid.

When the reaction to form (3) was followed by ^1H n.m.r. spectroscopy, an intermediate could be isolated and identified as the purple μ -hydrido complex $[(\text{C}_5\text{Me}_5\text{Rh})_2\text{HCl}_3]$ (2).⁶ The reaction sequence (1) \rightarrow (2) \rightarrow (3) could be reversed by treating (3) with HCl.

The complex (3) is air-stable but moderately sensitive to protonic acids; for example, it reacts with HBF_4 in methanol to give the dark green tetranuclear tetrahydride (4),⁷ identified by its characteristic ^1H n.m.r. spectrum.

The precise mechanism by which (3) is formed is not yet clear but it could well involve some type of double oxidative addition of Si-H to Rh. Although Si-H bonds readily add to low-valent metal complexes, a reductive elimination step



usually occurs when higher oxidation state species are involved.⁸

This work shows that higher oxidation states are relatively easily accessible for Rh as well as for Ir; as a consequence it will therefore be necessary to consider their involvement in catalytic processes.

We thank Dr. B. E. Mann for the n.m.r. spectra and the S.E.R.C. for support.

Received, 21st December 1981; Com. 1446

References

- 1 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley-Interscience, New York, 4th Edn., 1980, pp. 934 *et seq.*
- 2 K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 808.
- 3 K. Isobe, D. G. Andrews, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 809.
- 4 For a recent review, see P. M. Maitlis, *Chem. Soc. Rev.*, 1981, 10, 1.
- 5 A. Millan, E. Towns, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 673.
- 6 C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1973, 1901.
- 7 P. Espinet, P. M. Bailey, P. Piraino, and P. M. Maitlis, *Inorg. Chem.*, 1979, 18, 2706.
- 8 C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Adv. Organomet. Chem.*, 1973, 11, 253.