Surface-mediated Organometallic Synthesis of $[\equiv SiO]^-[RhH_2(PMe_3)_4]^+$: the First Example of a Cationic Organometallic Complex attached to the Silica Surface by Ion Pairing

Susannah L. Scott, Pascal Dufour, Catherine C. Santini* and Jean-Marie Basset*

Laboratoire de chimie organométallique de surface, UMR CNRS-CPE 9986, Ecole Supérieure de Chimie-Physique-Electronique de Lyon, 43 blvd du 11 novembre 1918, 69616 Villeurbanne Cedex, France

The reaction of silica-supported bis(allyl)rhodium, $(\equiv SiO)(\equiv SiOX(Rh(\eta^3\text{-}C_3H_5)_2$ **1** (X = H, Si≡) with PMe_3 followed by H_2 yields $[RhH_2(PMe_3)_4]^+$, **2**, which is characterised by IR, solid-state ^{31}P NMR and elemental analyses and extracted quantitatively from the surface by ion-exchange with $Bu^n{}_4NCl$ in nitromethane; the counterion of **2** is presumed to be a siloxy group $[\equiv SiO]^-$ of the silica surface.

An interesting approach to homogeneous catalysis involves immobilizing organometallic complexes directly on surfaces.[1] It has been observed that surface-supported catalysts often have a considerable advantage over homogeneous analogues, in that unsaturated intermediates are readily formed and stabilized by the surface, which acts as a large and rigid ligand to trap them.[2] Although the supported organometallic complexes superficially resemble heterogeneous catalysts, their relatively uniform structure, reactivity and distribution on the support material make them essentially homogeneous in nature. In support of this idea, our recent investigations of the chemistry of surface organometallic complexes of Rh have revealed many similarities with molecular species and homogeneous reactions.[3]

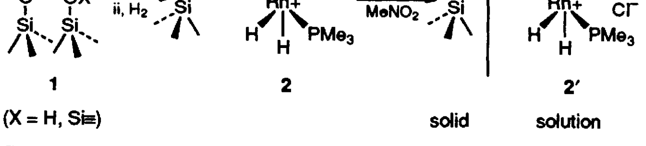
Several groups have observed that tris(allyl)rhodium reacts with the hydroxyl-terminated silica surface to give a well-defined bis(allyl)rhodium fragment, **1**, linked to the surface *via* a covalent bond to oxygen[4–6] (eqn. 1). The surface organometallic complex **1** probably attains an 18-electron configuration by coordination to a surface silanol or siloxane bridge.[6,7] We have examined the reactivity of **1** towards H_2,[8,9] CO[3] and PMe_3.[10] We here report that the reaction of **1** with PMe_3 followed by H_2 leads to the formation of a cationic rhodium dihydride which we have characterised on the surface and also extracted.

$$\equiv SiOH + Rh(\eta^3\text{-}C_3H_5)_3 \rightarrow \underset{\mathbf{1}}{(\equiv SiO)Rh(\eta^3\text{-}C_3H_5)_2} \quad (1)$$

The complex **1** on silica-200 was exposed to PMe_3 then H_2 without removing the excess PMe_3. After 48 h, the sample was evacuated to remove all volatile products and unreacted PMe_3 and H_2. In the IR spectrum, the bands characteristic of **1**[6] completely disappeared. In addition to bands due to PMe_3 [ν(C–H) 2967, 2905 cm^{-1}; $\delta(CH_3)$ 1422, 1295 cm^{-1}], a broad band appeared at 1938 cm^{-1}. When D_2 was used instead of H_2, the band at 1938 cm^{-1} was absent, and a band appeared instead at 1386 cm^{-1}. If the phosphine-containing sample was first treated with H_2, then evacuated and treated with D_2, a rapid (30 min) exchange occurred, indicated by the disappearance of the band at 1938 cm^{-1} and the appearance of the band at 1386 cm^{-1}. The proton-decoupled solid-state ^{31}P MAS NMR spectrum of the solid† contained two resonances at δ −11.9 and −24.7 [Fig. 1(*a*)]. Elemental analysis of the solid revealed 4.90% P and 4.02% Rh, for a ratio of P/Rh of 4.0.

The solid was washed with dry, O_2-free nitromethane saturated with $NaBPh_4$ or $Bu^n{}_4NCl$. The supernatant solution immediately acquired a yellow colour, while the solid was nearly completley decolourized. The IR spectrum of the solution contained a band at 1964 cm^{-1}. For NMR study, the nitromethane was evaporated and the yellow precipitate redissolved in D_2O. The proton-decoupled ^{31}P NMR of the D_2O solution contained two sets of resonances,‡ [Fig. 1(*b*)]. Each resonance is a doublet of triplets (δ −9.58, $^1J_{Rh-P}$ 70.0, $^2J_{P-P}$ 26.03 Hz; δ −21.09, $^1J_{Rh\mu P}$ 87.2, $^2J_{P-P}$ 26.35 Hz). Elemental analysis of the solid before and after the extraction indicated that 94% of the Rh and 95% of the phosphine passed into solution.§

Based on the IR spectra, we propose that the product is a rhodium hydride which exchanges its hydride ligands rapidly with D_2. The fact that this hydride species can be extracted quantitatively from the surface by ion exchange implies that there is no longer a covalent bond between Rh and silica. The extracted species was unambiguously identified as the *cis*-dihydridorhodium complex, **2′**, by comparison of its IR and ^{31}P NMR spectra with those of the known molecular complex, *cis*-$[RhH_2(PMe_3)_4]Cl$.¶ The *cis* geometry of **2′** is consistent with the ^{31}P solution spectrum, which shows two sets of two equivalent P atoms coupled to Rh. On the silica surface, the



Scheme 1 Surface synthesis and extraction of *cis*-dihydridotetrakis(trimethylphosphine)rhodium(III)

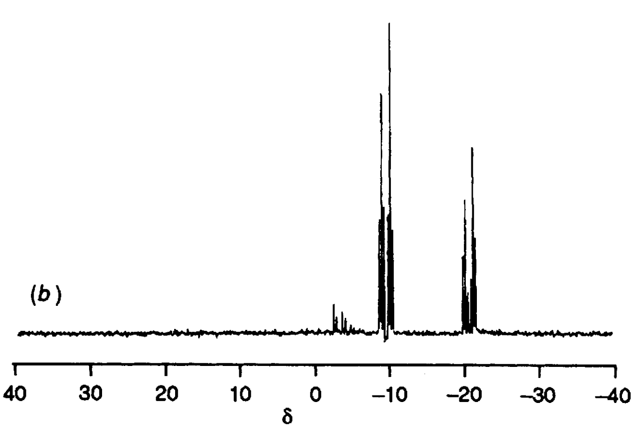


Fig. 1 Proton-decoupled ^{31}P NMR spectra of the cationic dihydride $[RhH_2(PMe_3)_4]^+$: (*a*) solid-state spectrum of the cation **2** on the silica surface, with counterion $\equiv SiO^-$ (spectrum obtained using magic angle spinning); (*b*) solution spectrum of the cation **2′** extracted from the silica surface with $Bu^n{}_4NCl$ in $MeNO_2$ and redissolved in D_2O

counterion for the cationic rhodium dihydride is probably the surface itself, which may contain deprotonated siloxy groups.

Additional evidence for the cationic nature of **2** is the 18-electron count of the extracted species **2′**, which renders unlikely the coordination of **2** to a surface ligand. The quantitative extraction of **2** rules out the possibility of disproportionation of a surface species to anionic and cationic complexes, as we have already observed in the adsorption of $Co_2(CO)_8$ on MgO, which gives $Co^{2+}[Co(CO)_4]^-{}_2$.[11] The formation of **2** is shown in Scheme 1.

It seems likely that the reaction of **1** with PMe_3 leads to the formation of a surface analogue of $ClRh(PMe_3)_3$, *i.e.* $(\equiv SiO)Rh(PMe_3)_3$. The reaction of this species with H_2 may give **2** by reactions which have precedent in molecular chemistry (eqn. 2–3).[12]

$$ClRh(PMe_3)_3 + H_2 \rightarrow [RhH_2(PMe_3)_4]Cl + \text{unidentified Rh products} \quad (2)$$

$$Cl[Rh(PMe_3)_4{}^+] + H_2 \rightarrow [RhH_2(PMe_3)_4]Cl \quad (3)$$

In eqn. (2), the cationic dihydride is formed even in the absence of excess phosphine, by a mechanism which requires a bimolecular redistribution of ligands. We have observed that **2** is formed on the silica surface even in the absence of excess phosphine, but in this case the reaction is not quantitative.[||]

The use of oxide surfaces in organometallic synthesis has already been applied to the preparation of neutral and anionic carbonyl clusters of Os,[13] Rh,[14,15] Ir[16] and Pt.[17] The rhodium dihydride complex **2** is, to our knowledge, the first example of the surface synthesis of a cationic organometallic complex, the anion being a surface siloxy group $\equiv SiO^-$.

S. L. S. thanks NATO and the Ministère des Affaires Etrangères (France) for postdoctoral support. We are grateful to Dr F. Lefebvre for recording the solid-state NMR spectra.

Received, 18th May 1994; COM. 4/02971B

Footnotes

[†] The sample was transferred to a zirconia rotor in an argon-filled glove bag. The solid-state ^{31}P spectrum was recorded on a Bruker MSL-300 spectrometer using magic angle spinning (3–4 kHz) and proton decoupling (pulse length 1 μ, recycle delay 1 s, number of scans 7300, line broadening 30 Hz before Fourier transform). Chemical shifts were referenced to 85% H_3PO_4; the error in the reported chemical shifts is *ca.* 0.3 ppm.

[‡] Referenced to H_3PO_4 in D_2O.

[§] The phosphine which remains on the surface may be $O{=}PMe_3$.

[¶] IR (Nujol): ν(Rh–H) 1965 cm^{-1}, ν(Rh–H)/ν(Rh–D) = 1.39.[18] ^{31}P NMR (CD_3NO_2): δ_{Pt} (axial) −11.08 (td, J_{Rh-P} 94.4, $^2J_{P-P}$ 28.0 Hz), δ_P (equatorial) −22.69 (br m, J_{Rh-P} 114.7 Hz).[12]

[||] In the absence of excess trimethylphosphine, the formation of **2** requires that surface complexes such as $(\equiv SiO)Rh(PMe_3)_4$ migrate and exchange phosphine ligands. The Rh which gives up its phosphines is then reduced to metallic Rh by H_2.[10]

References

1 S. L. Scott, J. M. Basset, G. P. Niccolai, C. C. Santini, J. P. Candy, C. Lecuyer, F. Quignard and A. Choplin, *New J. Chem.*, 1994, **18**, 115.

2 S. L. Scott and J. M. Basset, *J. Mol. Catal.*, 1994, **86**, 5.

3 P. Dufour, S. L. Scott, C. Santini, F. Lefebvre and J. M. Basset, *Inorg. Chem.*, 1994, **33**, 2509.

4 M. D. Ward and J. Schwartz, *J. Mol. Catal.*, 1981, **11**, 397.

5 H. C. Foley, S. J. DeCanio, K. D. Tau, K. J. Chao, J. H. Onuferko, C. Dybowski and B. C. Gates, *J. Am. Chem. Soc.*, 1983, **105**, 3074.

6 P. Dufour, C. Houtman, C. C. Santini, C. Nédez, J. M. Basset, L. Y. Hsu and S. G. Shore, *J. Am. Chem. Soc.*, 1992, **114**, 4248.

7 J. F. Halet and R. Hoffmann, *J. Am. Chem. Soc.*, 1989, **111**, 3548.

8 P. Dufour, C. C. Santini, C. Houtman and J. M. Basset, *J. Mol. Catal.*, 1991, **66**, L23.

9 P. Dufour, C. Houtman, C. C. Santini and J. M. Basset, *J. Mol. Catal.*, 1992, **77**, 257.

10 S. L. Scott, P. Dufour, C. Santini and J. M. Basset, submitted to *Inorg. Chem.*

11 N. Homs, A. Choplin, P. Piscina, L. Huang, E. Garbowski, R. Sanchez-Delgado, A. Théolier and J. M. Basset, *Inorg. Chem.*, 1988, **27**, 4030.

12 R. A. Jones, F. M. Real, G. Wilkinson, A. M. R. Galas, M. B. Hursthouse and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 511.

13 H. H. Lamb, A. S. Fung, P. A. Tooley, J. Puga, T. R. Krause, M. J. Kelley and B. C. Gates, *J. Am. Chem. Soc.*, 1989, **111**, 8367.

14 D. Roberto, R. Psaro and R. Ugo, *Organometallics*, 1993, **12**, 2292; R. Psaro, D. Roberto, R. Ugo, C. Dossi and A. Fusi, *J. Mol. Catal.*, 1992, **74**, 391.

15 J. M. Basset, A. Théolier, D. Commereuc and Y. Chauvin, *J. Organomet. Chem.*, 1985, **279**, 147; J. M. Basset, B. Besson, A. Choplin and A. Théolier, *Philos. Trans. Roy. Soc. London, A*, 1982, **308**, 115; A. Théolier, A. K. Smith, M. Leconte, J. M. Basset, G. M. Zanderighi, R. Psaro and R. Ugo, *J. Organomet. Chem.*, 1980, **191**, 415; A. K. Smith, F. Hugues, A. Théolier, J. M. Basset, R. Ugo, G. M. Zanderighi, J. L. Bilhou, V. Bilhou-Bougnol, and W. F. Graydon, *Inorg. Chem.*, 1979, **18**, 3104.

16 S. Kawi and B. C. Gates, *Inorg. Chem.*, 1992, **31**, 2939.

17 J. R. Chang, D. C. Koningsberger and B. C. Gates, *J. Am. Chem. Soc.*, 1992, **114**, 6460.

18 R. R. Schrock and G. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 2397.