

Reduction of Silica-supported Bis-allyl Rhodium by H₂: Characterization by ¹H N.M.R. Spectroscopy

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Surface ¹H n.m.r. spectroscopy provided details of the reaction of the SiO₂-supported complex SIL-O-Rh(allyl)₂ with H₂ at 298 K, leading to propene, propane, and highly dispersed supported Rh metal, which was catalytically active for toluene hydrogenation.

New reactivity and catalytic activity of organometallic complexes may result from their bonding to surfaces; surface-bound complexes are industrial catalysts for alkene polymerisation.¹ The need for improved methods to characterise the structure and reactivity of surface-bound organometallic species led us to use surface ¹H n.m.r. spectroscopy to investigate the SiO₂-supported complex SIL-O-Rh(allyl)₂ [prepared from SiO₂ and Rh(allyl)₃²] and its reactions with H₂ and CO.

The n.m.r. spectrum of the supported complex has just one signal, at δ 1.2 relative to SiMe₄ (external) (Figure 1, spectrum A), arising from the protons of the allyl ligands bound to Rh. The full width at half the maximum height is only 1.7 p.p.m., which suggests that all the allyl protons experienced nearly the same average environment and confirms that the Rh nuclei in the allyl complexes were present in discrete (molecular) entities on the support.²

The reaction of the complex with H₂ at 298 K resulted in gradual and ultimately complete elimination of the allyl groups. N.m.r. spectra collected during the reaction (Figure 1, spectrum B) show two resonances, a decreasing one due to the allyl protons, and an increasing one at δ 4.7, which was rapidly

removed by evacuation of the sample at 298 K and 6.67×10^{-2} N m⁻². The gaseous products were identified by their mass spectra as propane and propene. After evacuation of the sample, each of the following was adsorbed: propene, propane, and water. The following resonances were observed in the ¹H n.m.r. spectrum: propene, δ 4.6 and 1.0; propane, δ 0.3; and water, δ 4.1. Therefore, we attribute the resonance at δ 4.7 [observed during the reaction of SIL-O-Rh(allyl)₂ with H₂] to adsorbed propene and possibly water. A new resonance became evident during the reaction with H₂, extending from δ ca. 15 to ca. -5 (Figure 1, spectrum C); it is assigned to protons of surface -OH groups.³ Reaction with D₂ led to the same spectral changes observed for H₂, except that no broad resonance was observed for SIL-OD groups, which are ¹H n.m.r. silent.

The ¹H n.m.r. spectra showed that there was no reaction between CO and the SIL-O-Rh(allyl)₂ sites at 298 K and 1.01×10^5 N m⁻². After the sample had been exposed to CO, it was exposed to H₂ at 298 K, and the above mentioned reactions with H₂ failed to occur. To investigate this inhibition by CO, we exposed the material to CO and observed i.r. bands

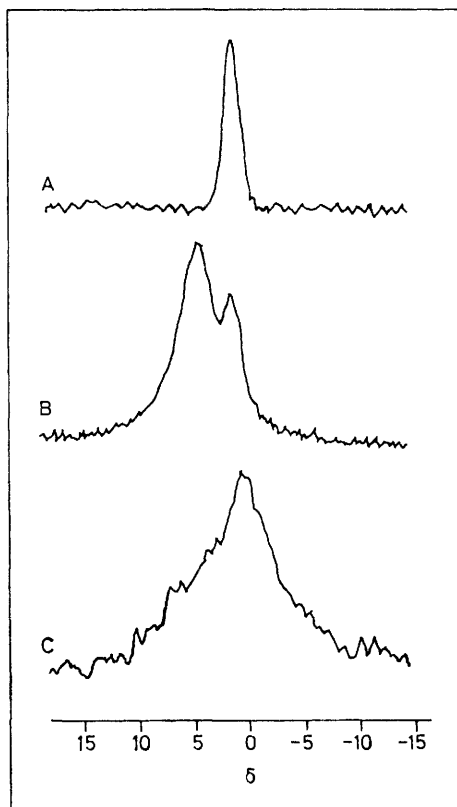


Figure 1. ^1H N.m.r. spectra of SIL-O-Rh(allyl)_2 at 298 K (spectrum A); after exposure of SIL-O-Rh(allyl)_2 to H_2 at 298 K and $1.01 \times 10^5 \text{ N m}^{-2}$ for $1.8 \times 10^3 \text{ s}$ (spectrum B); and for $1.8 \times 10^4 \text{ s}$, followed by evacuation (spectrum C).

indicating that a surface dicarbonyl rhodium species, $\text{Rh}^{\text{I}}(\text{CO})_2$, had formed (ν_{CO} 2105, 2090, and 2035 cm^{-1}). Evidently, CO adsorption occurred at sites different from SIL-O-Rh(allyl)_2 . We infer that the aforementioned reaction with H_2 had occurred at these other sites and that hydrogen had spilled over⁴ as protons to the support. These protons presumably were responsible for further protolysis of the SIL-O-Rh(allyl)_2 species, generating Rh^{III} ions and propene. After extended reaction with H_2 , the Rh was reduced to metal, whose presence was suggested by the blackening of the sample and by results of an X-ray photoelectron spectroscopic experiment showing a shift in the binding energy of the Rh $3d_{5/2}$ electron from 308.9 to 307.6 eV. We infer that the observed propane had formed by hydrogenation of propene on the Rh metal.

In a catalysis experiment with H_2 and toluene vapour at 298 K as the feed to a flow reactor containing particles of SIL-O-Rh(allyl)_2 , a short induction period of negligible catalytic activity was observed, followed by high, stable activity, as Rh metal particles formed from the initial, presumably inactive complex.

These results illustrate the potential of ^1H n.m.r. spectroscopy for the elucidation of surface organometallic chemistry.

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