Synthesis and Partial Characterization of (Silica)rhodium Dihydrides: A New Catalyst for Olefin Hydrogenation

By MICHAEL D. WARD, THOMAS V. HARRIS, and JEFFREY SCHWARTZ*
(*Department of Chemistry, Princeton University, Princeton, New Jersey* 08544)

Summary The synthesis, characterization, and catalytic activity toward olefin hydrogenation of (silica)rhodium dihydrides is described.

WE recently reported that silica-supported zirconium hydrides are highly efficient olefin isomerization catalysts that possess modest olefin hydrogenation activity.[1] Further investigation of silica-supported transition metal hydrides has now resulted in the discovery of rhodium hydride species, catalysts that are effective for olefin hydrogenation and that exhibit high activity even toward hindered olefins.

When an excess of silica[1] (Aerosil, 300 m^2 g^{-1}) suspended in toluene is treated with tris(allyl)rhodium[2] (**1**), propene (1 equiv mol^{-1} Rh) is evolved (100% yield) and the golden yellow silica-supported bis(allyl) rhodium species (**2**) is formed (Figure). The evolved gases (propene and propane) were quantified using a calibrated manometer and were verified by g.c.–m.s. analysis. Hydrolysis of (**2**) with 2 N H_2SO_4 evolves two additional moles of propene (180% based on Rh), confirming the stoicheiometry shown for (**2**). When (**2**) is exposed to H_2 (1 atm), a colour change to dark brown is observed within 15 min and propane (1·3 equiv.) is evolved to give silica-supported rhodium dihydride (**3**) (*vide infra*).

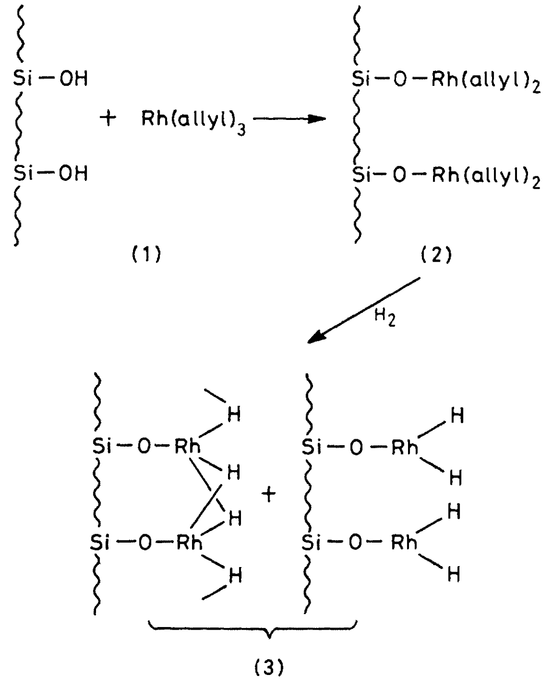

FIGURE. Other silica(oxygen) atom–Rh contacts may be present in (**3**).

Silica pellets of bis(allyl) species (**2**) exhibit i.r. absorptions at 3055 and 1473 cm^{-1}, indicative of allyl group vibrational modes.[3] When (**2**) is treated with H_2, these allyl group absorptions diminish, accompanied by the appearance of bands at 2080, 2003, and 1573 cm^{-1}. The two bands at 2080 and 2003 cm^{-1} are ascribed to a *cis* Rh^{III} dihydride unit analogous to $H_2RhCl(PPh_3)_2$[4] (ν_{Rh-H} = 2078 and 2013 cm^{-1}). Treatment of (**2**) with D_2 shifts these bands to 1450 and 1408 cm^{-1}, consistent with this assignment. The band at 1573 cm^{-1} is tentatively assigned to bridging hydride species (Rh–H–Rh) analogous to those observed for silica-supported zirconium hydrides.[1,5] This band falls within the range of frequencies reported for bridging hydride units of transition metal complexes.[6]

Owing to the non-transparency of the SiO_2 support in (narrow) bands centred at 1860 and 1630 cm^{-1} and to continuous absorption below 1400 cm^{-1}, i.r. spectra of the supported species are of limited value in this region. We find that this problem can be somewhat alleviated by the use of Raman spectroscopy, as the silica support is transparent in the regions noted above. In the Raman spectrum of (**2**), peaks tentatively assigned to Rh–O vibrations were observed at 447, 481, and 505 cm^{-1} (these bands are absent in a spectrum of the silica support). A Kr laser (6764 Å) was employed on the powdered sample contained in a glass capillary tube. Bands attributed to Rh–H vibrations were not observed in Raman spectra taken under these conditions. Thus the combination of i.r. and Raman spectroscopic measurements allows partial characterization of oxide-supported species over a wide range of frequencies.

Observation of propane upon hydrogenation of (**2**) suggested that (**3**) may be an olefin hydrogenation catalyst. Indeed, we have found that (**3**) catalyses the hydrogenation of mono-, di-, tri-, and tetra-substituted olefins efficiently. The catalyst is not air or water sensitive and samples of it exposed to the atmosphere for two days retained *ca.* 50% catalytic activity. Also, little catalytic activity is lost even after hydrogenation of several thousand equiv. of olefin. The Table lists the observed rates for hydrogenation of a series of representative olefins. It is significant that hydrogenation of the tetra-substituted species 2,3-dimethylbut-2-ene is competitive with that of cyclo-hexene. This result is contrary to that noted for olefin hydrogenations catalysed by soluble species such as $RhCl(PPh_3)_3$.[7] The efficiency of (**3**) as a catalyst for hydrogenation of the tetra-substituted olefin and the narrow range of rates shown in the Table may be due to a relative lack of appreciable steric hindrance about the metal, especially when compared with $RhCl(PPh_3)_3$ or with polymer-supported rhodium (phosphine) catalysts.[8] The ability of silica-supported zirconium hydrides to isomerize an olefinic double bond past the tertiary carbon centre of methylenecyclohexane was attributed to this steric characteristic.[1]

TABLE. Rates of hydrogenation of olefinic substrates by (**3**); initial [olefin] = 0·22 M; H_2 = 1 atm; 0·01 mmol RhH_2 on 25 mg silica (4% Rh by weight); in 9 ml hexane.

Olefin	Rate/10^3 l mol^{-1} min	Relative rate
But-1-ene	5·20	8·62
cis-But-2-ene	3·74	6·20
trans-But-2-ene	3·63	6·02
2-Methylbut-2-ene	3·28	5·44
2,3-Dimethylbut-2-ene	0·60	1·00
Cyclohexene	3·39	5·62
1-Methylcyclohexene	2·88	4·78

Hydrogenation of olefins catalysed by (**3**) showed zero order dependence on olefinic substrate concentration. First order dependence in H_2 was observed when studied over the range $P(H_2)$ = 0·95—0·60 atm. A minimal isotope effect was measured [$k(H_2)/k(D_2) = 0{\cdot}92$]. Species (**3**) is a poor olefin isomerization catalyst; only seven turnovers of but-1-ene were isomerized over 24 h.

We thank Halcon Research and Development Corporation and the National Science Foundation, for generous support of this work.

(*Received*, *24th January* 1980; *Com.* 079.)

[1] J. Schwartz and M. D. Ward, *J. Mol. Catal.*, in the press.

[2] J. Powell and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1966, 323.

[3] T. B. Chenskaya, L. A. Leites, V. T. Aleksanyan, A. S. Ivanov, and A. Z. Rubezhov, *Akad. Nauk U.S.S.R. Bulletin*, 1974, 1931.

[4] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[5] V. A. Zakharov, V. K. Dudchenko, E. A. Paukshtis, L. G. Karakchiev, and Yu. I. Yermakov, *J. Mol. Catal.*, 1977, **2**, 421.

[6] S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, 1971, **93**, 4594; J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D; Kaesz, *ibid.*, 1975, **97**, 3947; C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *J. Chem. Soc., Chem Commun.*, 1971, 734. G. K. Barker, M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *ibid.*, 1976, 671.

[7] F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1574.

[8] R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, 1971, **93**, 3062.