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Silica-supported rhodium hydrides stabilized by triisopropylphosphine

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Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

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Abstract

The reaction of the silica-supported complex ($\equiv$SiO)($\equiv$SiOX)Rh(η^3-C_3H_5)$_2$, where X is H or Si, with excess P^iPr_3 leads to the formation of the chemisorbed bis(phosphine) Rh(I) complex [$\equiv$SiORh(P^iPr_3)$_2$]$_x$, proposed to be dimeric ($x = 2$) on the basis of the ^{31}P MAS NMR spectrum. The phosphine complex irreversibly binds H_2 to give a hydride complex, $\equiv$SiORh(P^iPr_3)$_2$(H)$_2$, characterized by IR and ^{31}P MAS NMR spectroscopy as well as D-exchange. The coordinatively unsaturated hydride complex is inferred to be the active site for hydrogenation of olefins under mild conditions.

Keywords: Silica; Surface organometallic chemistry; Olefin hydrogenation; Catalysis

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1. Introduction

Supported rhodium hydride complexes are potentially interesting recyclable hydrogenation catalysts. Reactions of surface organorhodium fragments with H_2 were initially proposed to give hydride complexes of unusual reactivity, capable of hydrogenating simple olefins [1] as well as arenes [2], and even activating methane [3]. However, the presence of particles of metallic rhodium in the system [4,5] raised the question of whether discrete rhodium hydrides were truly responsible for the observed reactivity. The assignment of a rhodium hydride vibration at 2048 cm^{-1} was also reevaluated [5,6]. Rhodium metal particles were shown to cause spontaneous decarbonylation of in situ generated allyl alcohol to give carbonyl ligands which absorb in the same spectral region [7].

Phosphine ligands have long been used to stabilize rhodium complexes in the presence of H_2, starting with Wilkinson's catalyst, ClRh(PPh_3)$_3$ [8]. Hydrogenation is initiated by dissociation of a phosphine ligand to produce a coordinatively unsaturated metal complex, which then undergoes oxidative addition of H_2 [9]. Unfortunately, it is precisely this lability which has foiled attempts to tether such catalysts to phosphinated solid supports such as polystyrene or silica [10], since many such systems experience serious leaching problems. Furthermore, catalytic activity may suffer from reduced access of the substrate to the heterogeneous

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active site [11]. An alternate strategy is the grafting of organometallic complexes directly onto high surface area oxide supports [12], which can result in well-defined surface organometallic fragments that experience strong interactions with an anionic surface “ligand”.

We previously reported the preparation of well-defined silica-supported analogues of Wilkinson’s catalyst and Vaska’s complex, $\equiv$SiORh(PMe$_3$)$_3$ and $\equiv$SiORh(PMe$_3$)$_2$(CO) [13,14], grafted via covalent Rh–O bonds directly to the silica surface. The carbonyl complex does not react with H_2, but does undergo oxidative addition of HCl to yield a discrete rhodium hydride complex. Coordinatively saturated $\equiv$SiORh(PMe$_3$)$_2$(CO)(H)(Cl) is unreactive towards olefins. In the presence of H_2, $\equiv$SiORh(PMe$_3$)$_3$ redistributes its phosphine ligands to yield the ion pair ($\equiv$SiO$^-$)[RhH$_2$(PMe$_3$)$_4$]$^+$, identified by ion exchange and extraction into solution [15]. Although the solid material catalyses olefin hydrogenation (and hydrogenolysis), the reactivity was attributed to the presence of metallic Rh. The formation of metal particles was suppressed when H_2 was added in the presence of excess PMe$_3$. Under these conditions, the cationic dihydride complex is formed quantitatively. Unfortunately, it also shows no reactivity towards olefins, presumably due to its coordinative saturation.

Molecular complexes of rhodium containing the bulky triisopropylphosphine ligand display enhanced reactivity in olefin hydrogenation [16], cyclooligomerization [17] and isomerization [18] as well as C–C coupling [19], the water gas shift reaction [20], alcohol and even alkane dehydrogenation [21,22]. In this contribution, we report the preparation of silica-supported rhodium(I) phosphine complexes using the triisopropylphosphine ligand. The reaction of silica-supported bis(allyl)rhodium(III), **1** [23,24], with P^{i}Pr$_3$ results in the formation of new surface rhodium–phosphine complexes which react with H_2 and olefins.

2. Experimental

The silica used in all experiments was non-porous Degussa Aerosil-200, with a surface area (derived from the Brunauer–Emmett–Teller (BET) adsorption isotherm) of ca. 200 m^2/g. The silica was calcined and partially dehydroxylated at 500 °C before reaction with Rh(η^3-C$_3$H$_5$)$_3$. The number of surface hydroxyl groups initially present on this silica, after 500 °C treatment, is 1.2 nm^{-2}. Experiments were performed in the absence of air and solvent in high vacuum all-glass reactors using breakseal techniques described previously [13]. Elemental analyses were performed by ICP.

Rh(allyl)$_3$ was synthesized according to the published procedure [25]. P^{i}Pr$_3$ (90%) was obtained from Aldrich and stored in a grease-free reactor equipped with a high vacuum Young valve. It was subjected to freeze–pump–thaw cycles to remove dissolved gases prior to use. H_2 (Air Products), D_2 (Matheson) and *cis*-2-butene (Matheson) were used as received.

Samples for solid-state NMR were sealed under vacuum in 5 mm × 30 mm pyrex NMR tubes placed inside zirconia rotors for magic angle spinning at 4 kHz. High power proton-decoupled ^{31}P spectra (frequency 81.0 MHz) were recorded on a Bruker ASX-200 instrument using a 4 μs 90° pulse. IR spectra were recorded on a Mattson Research Series FTIR equipped with a DTGS detector and a sample compartment purged with dry air generated by a Balston Purge Gas Generator. Spectra were obtained at 4 cm^{-1} resolution by coaddition of 32 scans.

3. Results and discussion

3.1. Preparation of (≡SiO)Rh(allyl)$_2$ and its reaction with P^{i}Pr$_3$

Sublimation of Rh(allyl)$_3$ at room temperature onto a silica pretreated at 500 °C results in evolution of propene and formation of a yellow solid whose surface contains bis(allyl)rhodium(III) fragments. The supported organometallic complexes have been described as 18-electron ($\equiv$SiO)($\equiv$SiOX)Rh(η^3-C$_3$H$_5$)$_2$, **1**, Eq. (1) [24].

$$\equiv\text{SiOH} + \equiv\text{SiOX} + \text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3 \rightarrow (\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2 + \text{C}_3\text{H}_6 \quad \mathbf{1}: \text{X is Si}\equiv; \quad \mathbf{1'}: \text{X is H} \tag{1}$$

After prolonged desorption of volatiles to a liquid N_2 trap, the Rh loading was measured to be 3.9 wt.% (0.34 mmol Rh/g silica). Since the quantity of surface hydroxyl groups initially present on silica treated at 500 °C is ca. 0.4 mmol/g [26], and since each $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$ reacts with precisely one surface hydroxyl group during grafting [24], the quantity of chemisorbed Rh corresponds to ca. 85% consumption of the surface protons. Accordingly, **1** is inferred to be the major product while **1′** is a minor product.

Addition of excess P^iPr_3 vapour to the silica-supported bis(allyl)rhodium(I) fragments results in the formation of 1,5-hexadiene, identified by GC. Phosphine thus induces reductive elimination of the allyl ligands from **1**, Eq. (2).

$$\underset{\mathbf{1}}{(\equiv\text{SiO})(\equiv\text{Si}_2\text{O})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2} + n\text{P}^i\text{Pr}_3 \rightarrow \underset{\mathbf{2}}{[\equiv\text{SiORh}(\text{P}^i\text{Pr}_3)_n]_x} + \text{CH}_2\text{=CH(CH}_2)_2\text{CH=CH}_2 + \equiv\text{SiOSi}\equiv \tag{2}$$

Similar eliminations of 1,5-hexadiene were reported previously for reactions of **1** with CO [27] and PMe_3 [13]. Upon evacuation of volatiles, the yellow solid **2** was found to contain 2.3 wt.% P (0.75 mmol P/g silica; 2.2 P/Rh). The major component of **2** is therefore inferred to have $n = 2$, i.e. $[\equiv\text{SiORh}(\text{P}^i\text{Pr}_3)_2]_x$. The reaction stoichiometry is different from the analogous reaction of **1** with PMe_3, for which the major product is $\equiv\text{SiORh}(\text{PMe}_3)_3$. The considerably greater steric size of P^iPr_3 (Tolman angle $\theta = 160^\circ$ versus 118° for PMe_3 [28]) is presumably responsible for the difference in stoichiometry. The observed value of the ratio $\text{P}/\text{Rh} > 2$ could be interpreted as evidence for the presence of a minor amount ($\leq 10\%$) of $\equiv\text{SiORh}(\text{P}^i\text{Pr}_3)_3$. Although $\text{HRh}(\text{P}^i\text{Pr}_3)_3$ is known, its structure is highly distorted [29], and $\text{ClRh}(\text{P}^i\text{Pr}_3)_3$ [30] has not been fully characterized [31].[1]

The in situ IR spectrum of **2** contains bands characteristic of the C–H stretching and deformation modes of P^iPr_3 at 2964, 2929, 2875, 1465, 1379 and 1366 cm^{-1}. A weak band at 1638 cm^{-1} is assigned to the ν(C=C) mode of allyl groups bound to siloxide sites on the silica surface, $\equiv\text{SiOCH}_2\text{CH=CH}_2$. This species was previously observed upon treatment of **1**, **1′** with PMe_3, along with traces of propene [13]. The analogous reaction of **1′** with P^iPr_3 is shown in Eqs. (3) and (4).

$$\underset{\mathbf{1'}}{(\equiv\text{SiO})(\equiv\text{SiOH})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2} + 2\text{P}^i\text{Pr}_3 \rightarrow \underset{\mathbf{3}}{(\equiv\text{SiO})_2\text{Rh}(\text{P}^i\text{Pr}_3)_2(\eta^1\text{-C}_3\text{H}_5)} + \text{CH}_2\text{=CHCH}_3 \tag{3}$$

$$\underset{\mathbf{3}}{(\equiv\text{SiO})_2\text{Rh}(\text{P}^i\text{Pr}_3)_2(\eta^1\text{-C}_3\text{H}_5)} \rightarrow \underset{\mathbf{2}}{\equiv\text{SiORh}(\text{P}^i\text{Pr}_3)_2} + \equiv\text{SiOCH}_2\text{CH=CH}_2 \tag{4}$$

A weak band at 1948 cm^{-1} is assigned to the ν(CO) mode of the minor product $\equiv\text{SiORh}(\text{P}^i\text{Pr}_3)_2(\text{CO})$, **4**, by comparison to the corresponding feature at 1940 cm^{-1} in the IR spectrum of $\text{ClRh}(\text{P}^i\text{Pr}_3)_2(\text{CO})$ [21]. The former is presumably the product of decarbonylation of allyl alcohol derived from $\equiv\text{SiOCH}_2\text{CH=CH}_2$. The analogous formation of $\equiv\text{SiORh}(\text{PMe}_3)_2(\text{CO})$ was observed during spontaneous evolution of $(\equiv\text{SiO})_2\text{Rh}(\text{PMe}_3)_3(\eta^1\text{-C}_3\text{H}_5)$ [7].

The ^{31}P MAS NMR spectrum of **2** is a complex one. The most intense signal is a multiplet centered at 56 ppm, a broad signal from 30 to 50 ppm and a clear doublet at 43 ppm (J_{RhP}: 180 Hz), Fig. 1a. Judging by its intensity, the multiplet is associated with the

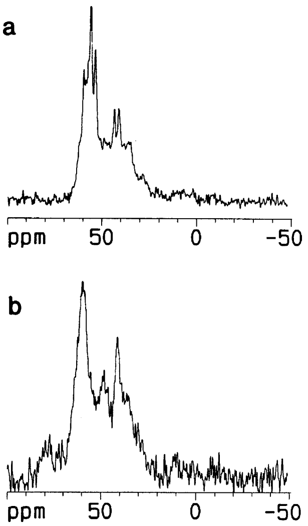

Fig. 1. ^{31}P MAS NMR spectra of $(\equiv\text{SiO})(\equiv\text{SiOX})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2$ (X is H or OSi≡) treated with (a) excess P^iPr_3, followed by evacuation of volatiles, then (b) H_2.

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[1] Early synthetic attempts were carried out under N_2, prior to the recognition of rhodium's propensity to form dinitrogen complexes in the presence of P^iPr_3.

major product, $[\equiv SiORh(P^iPr_3)_2]_x$. The structure with $x = 1$ would be analogous to the monomeric (three-coordinate) form of molecular $ClRh(P^iPr_3)_2$, which does not exist to an appreciable extent either in solution [32] or in the solid state [33]. Furthermore, we can confidently exclude the presence of mononuclear sites stabilized by additional coordination of a siloxane oxygen, i.e. $(\equiv SiO)(\equiv Si_2O)Rh(PR_3)_2$, since the ^{31}P signals of analogous molecular compounds $(\eta^2\text{-}CF_3CO_2)Rh(P^iPr_3)_2$ (δ: 69.8 ppm, d, J_{RhP}: 208.4 Hz [34]) and $(\eta^2\text{-}O_2S(O)Me)Rh(P^iPr_3)_2$ (δ: 70.2 ppm, d, J_{RhP}: 212.2 Hz [35]) occur at significantly lower fields. (In addition, these complexes are reported to be red or violet [35], unlike **2** which is yellow). In contrast, the ^{31}P signal of dimeric $[Rh(P^iPr_3)_2(\mu\text{-}Cl)]_2$ occurs at 57.1 ppm (d, J_{RhP}: 197 Hz) [32]; the ^{31}P chemical shift of orange $[Rh(P^iPr_3)_2(\mu\text{-}OH)]_2$ is similar at 61.3 ppm (d, J_{RhP}: 183 Hz) [36]. We therefore propose a dimeric structure for **2**, $[Rh(P^iPr_3)_2(\mu\text{-}OSi\equiv)]_2$. The multiplet signal at 56 ppm appears to be an overlapping doublet of doublets or "pseudo-triplet", indicating that the siloxide bridges are asymmetrical and the phosphines are disposed as *cis* pairs.

Dimerization implies mobility of supported Rh complexes, Eq. (5), a phenomenon with precedent in the chemistry of $\equiv SiORh(CO)_2$, which associates rapidly on silica to give $[Rh(CO)_2(\mu\text{-}OSi\equiv)]_2$ [27].

$$2(\equiv SiO)Rh(P^iPr_3)_2 \leftrightarrows \underset{\mathbf{2}}{[Rh(P^iPr_3)_2(\mu\text{-}OSi\equiv)]_2} \qquad (5)$$

Mobility may be caused by the facile migration of surface hydroxyls [37], or by "degrafting" of a cationic intermediate such as $[Rh(P^iPr_3)_3]^+$ formed in the presence of excess phosphine [14]. A cationic species such as $(\equiv SiO^-)[Rh(P^iPr_3)_3]^+$, **5**, may be responsible for the signal at 43 ppm. In further support of this hypothesis, the ^{31}P spectrum recorded in the presence of excess P^iPr_3 shows, in addition to the sharp signal at 19 ppm due to free P^iPr_3, enhanced intensity of the peak at 41 ppm, Fig. 2a. Similar ion pair formation was reported in the treatment of $\equiv SiORh(PMe_3)_2(CO)$ with excess PMe_3, Eq. (6) [14]:

$$\equiv SiORh(PMe_3)_2(CO) + PMe_3 \leftrightarrows (\equiv SiO^-)[Rh(PMe_3)_3(CO)]^+ \qquad (6)$$

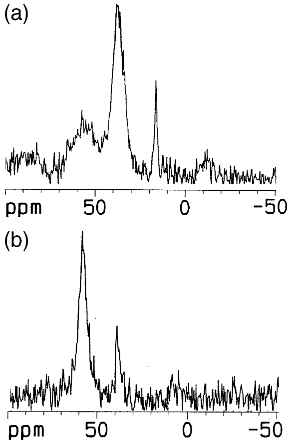


Fig. 2. ^{31}P MAS NMR spectra of $(\equiv SiO)(\equiv SiOX)Rh(\eta^3\text{-}C_3H_5)_2$ (X is H or $OSi\equiv$) treated with (a) excess P^iPr_3, without evacuation of volatiles, then (b) addition of H_2 in the presence of excess P^iPr_3, followed by evacuation.

The minor products $(\equiv SiO)_2Rh(P^iPr_3)_2(\eta^1\text{-}C_3H_5)$, **3**, and $\equiv SiORh(P^iPr_3)_2(CO)$, **4**, are expected to give rise to signals close to those of "T"-square pyramidal $HRh(P^iPr_3)_2Cl_2$ (δ: 45.7 ppm, d, J_{RhP}: 97 Hz [38]) and $ClRh(P^iPr_3)_2(CO)$ (δ: 49.8 ppm, d, J_{RhP}: 117.5 Hz [32]). Both are candidates to contribute to the broad signal at 30–50 ppm.

3.2. Reaction of $(\equiv SiO)Rh(P^iPr_3)_x$ with H_2/D_2

The reaction of **2** with 53 kPa H_2 results in a deepening of the yellow colour and the appearance of two new bands in the IR spectrum at 2162 and 2043 cm^{-1}, Fig. 3a. These bands are stable under dynamic vacuum at room temperature. Their assignment as ν(Rh–H) modes was confirmed by evacuation of the reactor and addition of D_2. The new bands disappeared, while two new bands at 1560 and 1488 cm^{-1} appeared, Fig. 3b. For comparison, the calculated H/D isotope shifts based on the simple harmonic oscillator approximation are 1529 and 1445 cm^{-1}, respectively.

The position of the higher frequency ν(Rh–H) mode, at 2162 cm^{-1}, resembles bands reported for the molecular complexes $(\eta^2\text{-}CF_3CO_2)RhH_2(P^iPr_3)_2$, at 2150 cm^{-1} [16], $RhH_2Cl(P^iPr_3)_2$ at 2140 cm^{-1} [39] and $(\eta^2\text{-}CH_3S(O)O_2)RhH_2(P^iPr_3)_2$ at 2165 and 2135 cm^{-1} [35]. Therefore, we propose that oxidative addition of H_2 to $[\equiv SiORh(P^iPr_3)_2]_2$ generates the

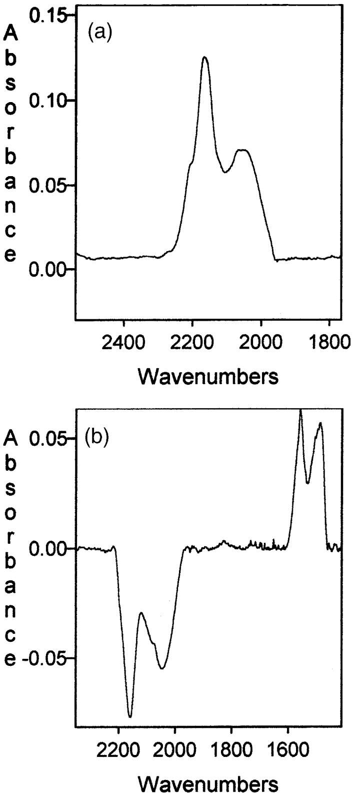


Fig. 3. Difference IR spectra of silica-supported rhodium hydrides, obtained by the reaction of (≡SiO)(≡SiOX)Rh(η^3-C_3H_5)$_2$ (X is H or OSi≡) with P^iPr_3 followed by (a) H_2, then (b) D_2. The spectrum of the silica before addition of H_2 was subtracted from (a), followed by a baseline correction. Similarly, the spectrum of the silica before addition of D_2 was subtracted from (b).

dihydride, **6**, Eq. (7).

$$\underset{\mathbf{2}}{[(\equiv SiO)Rh(P^iPr_3)_2]_2} + 2H_2 \rightarrow 2\underset{\mathbf{6}}{\equiv SiORh(P^iPr_3)_2(H)_2} \quad (7)$$

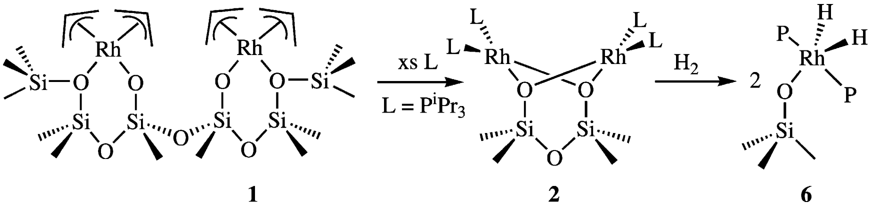
The structure of **6** may be pseudo-trigonal bipyramidal, as are other very stable complexes of the form RhH_2ClP_2 [32,38]. However, we cannot rule out additional coordination of a siloxane oxygen, as in (≡SiO)(≡Si_2O)$RhH_2(P^iPr_3)_2$, analogous to the pseudo-octahedral (η^2-O_2Z)$RhH_2(P^iPr_3)_2$. Both are consistent with the observed ν(Rh–H) frequency. Although two bands are expected by symmetry, they are not always resolved, as the spectra of the molecular analogues show. The origin of the second ν(Rh–H) mode at 2043 cm^{-1} is not presently known, but it is much too low in frequency to assigned to **6**. The only molecular analogue with a hydride vibration in this region is $Rh_2H_4(P^iPr_3)_4$, for which ν(Rh–H) was reported at 2040 cm^{-1} [40].

The major signal in the ^{31}P MAS NMR spectrum is deshielded upon hydrogenation of **2**, appearing as a broad signal at 61 ppm with no resolved coupling, Fig. 1b. It is assigned to **6**, by comparison to the chemical shifts of $RhH_2Cl(P^iPr_3)_2$, 62.9 ppm [32] and (η^2-O_2CCF_3)$RhH_2(P^iPr_3)_2$, 61.8 ppm [16]. The signals at 48 and 42 ppm may arise from minor products such as **4**, **5**, $Rh_2H_4(P^iPr_3)_4$ and $(\equiv SiO)_2RhH(P^iPr_3)_2$ (by hydrogenation of **3**). The ^{31}P shift of a molecular analogue of the last complex, $RhHCl_2(P^iPr_3)_2$, is 45.7 ppm [38]. However, its ν(Rh–H) vibration occurs at 1946 cm^{-1}, well outside the range of the hydride stretching modes shown in Fig. 3b.

When H_2 was added in the presence of excess P^iPr_3, the ^{31}P spectrum was even simpler, Fig. 2b. The signal at 61 ppm is assigned to the major product **6**, while the minor peak at 42 ppm may be assigned to residual **5**.

3.3. *Reaction of silica-supported rhodium hydrides with cis-2-butene*

Exposure of **6** (and its accompanying minor products) to 24 Torr *cis*-2-butene in the presence of excess H_2 led to the formation of butane (70% conversion in 15 min at room temperature, in the presence of 0.5 mg Rh). Significantly, no other hydrocarbons were detected. This observation rules out the presence of traces of Rh metal, which would catalyze the hydrogenolysis of butane under these conditions. The reactivity of **6** contrasts with the lack of hydrogenation activity of coordinatively saturated ($\equiv SiO^-$)$[RhH_2(PMe_3)_4]^+$ [15]. It is possible that the activity of **6** derives from coordinative unsaturation (i.e. five-coordination), as in $RhH_2Cl(P^iPr_3)_2$, or that a siloxane ligand readily decoordinates from a pseudo-octahedral form of the complex to allow olefin binding. Ligand dechelation was presumed responsible for the styrene hydrogenation activity of the related molecular complexes (η^2-O_2Z)$RhH_2(P^iPr_3)_2$ [16].



Scheme 1.

4. Conclusion

The use of rigid unmodified silica as a support for rhodium phosphine complexes is not sufficient to prevent their mobility, but in the case of P^{i}Pr$_3$ complexes, it allows the preparation of discrete chemisorbed rhodium hydride complexes, Scheme 1, which are active in olefin hydrogenation, without concomitant formation of Rh metal particles.

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