

## Supramolecular Approach to Metal–Support Interactions: Formation and Decarbonylation of Allyl Alcohol by an Oxide-supported ( $\sigma$ -Allyl)rhodium(III) Complex

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Silica- or alumina-supported bis(allyl)rhodium(III) reacts with  $\text{PMe}_3$ , producing an unstable mono(allyl)rhodium(III) fragment which undergoes C–O bond formation to give allyl alcohol which is then decarbonylated, as demonstrated by IR spectroscopy, isotopic labelling, elemental analysis and  $^{31}\text{P}$  solid-state MAS NMR.

The selectivity in the Fischer–Tropsch conversion of syn gas ( $\text{CO} + \text{H}_2$ ) towards either hydrocarbons or oxygenates (alcohols, aldehydes and carboxylic acids) depends strongly on the transition metal catalyst and the nature of the oxide support on which it is dispersed.<sup>1</sup> Hydrocarbons were suggested to be formed on fully reduced metal particles, while alcohols may be formed on ions.<sup>2,3</sup> It is known that CO exerts a strong disruptive effect on rhodium crystallites, leading to the formation of isolated and oxidized  $\text{Rh}^{\text{I}}(\text{CO})_2$  species.<sup>4</sup>

We wish to report that CO insertion is not necessary for the formation of alcohols, at least for discrete  $\text{Rh}^{\text{III}}$  complexes supported on silica or alumina. The implication is that for certain Rh/oxide systems, the surface of supported metal particles may contain oxidized rhodium species able to catalyse C–O bond formation without the intervention of CO.

We have studied the reactivity of an organometallic fragment of rhodium supported on various oxide surfaces in order to understand the mechanisms of heterogeneous catalysis. The reaction of oxide-bound bis(allyl)rhodium(III) with  $\text{PMe}_3$ <sup>5</sup> has already been reported. When bis(allyl)rhodium(I), **1**, grafted to a siloxy group<sup>6</sup> on the surface of silica-200,<sup>†</sup> is exposed to an excess of  $\text{PMe}_3$ , one equivalent of propene is liberated, Fig. 1.<sup>5</sup> A new surface organometallic complex, **2**,<sup>‡</sup> containing a  $\sigma$ -allyl ligand is formed.

We observed that **2** is not stable on silica-200. A few minutes after the addition of  $\text{PMe}_3$ , two small bands appeared in the IR spectrum at 1960 and 1643  $\text{cm}^{-1}$ , and ethane was detected in the gas phase. The IR band at 1960  $\text{cm}^{-1}$  increased in intensity with time and exposure to dynamic vacuum, Fig. 2. At the same time, the band at 1612  $\text{cm}^{-1}$  assigned to the  $\sigma$ -allyl ligand of **2** slowly decreased in intensity. Solid-state  $^{31}\text{P}$  MAS NMR spectra of aged samples of **2** contained a single very broad resonance at *ca.*  $\delta -11$ . Elemental analysis of the solid sample showed that the ratio P/Rh had decreased from 3 to 2. Allyl alcohol was extracted from the solid by washing with  $\text{H}_2\text{O}$ , and was detected by GC. The same observations were made on silica-550, but the reaction occurred much more slowly.

The IR band observed at 1960  $\text{cm}^{-1}$  is attributed to the  $\nu(\text{CO})$  mode of  $\equiv\text{SiORh}(\text{PMe}_3)_2(\text{CO})$ , **3**, by comparison to the IR and  $^{31}\text{P}$  NMR spectra of the molecular complex  $\text{ClRh}(\text{PMe}_3)_2(\text{CO})$ .<sup>§</sup> In order to confirm this assignment, 10 Torr  $^{13}\text{CO}$  (1 Torr  $\approx$  133.3 Pa) was added to **3** prepared by the reaction of **1** with  $\text{PMe}_3$ . The band shifted to 1917  $\text{cm}^{-1}$ , in agreement with the expected isotopic shift, eqn. (1).

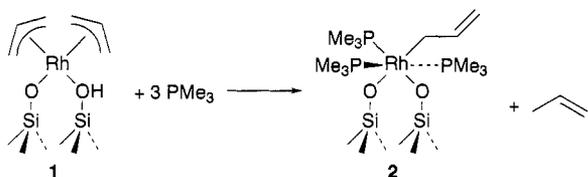
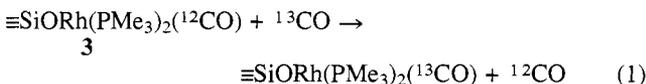
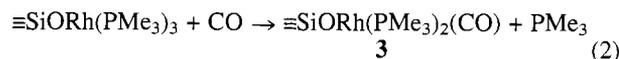


Fig. 1

Finally, **3** was prepared independently by reaction of  $\equiv\text{SiORh}(\text{PMe}_3)_3$  with CO, eqn. (2):



The product of eqn. (2) has IR [ $\nu(\text{CO})$  1960  $\text{cm}^{-1}$ ] and NMR ( $\delta -9.3$ ) properties very similar to those of **3** prepared by the reaction of **1** with  $\text{PMe}_3$ .

The origin of the carbonyl oxygen was suspected to be oxygen atoms of the silica surface. Therefore we partially exchanged the surface oxygen atoms with  $^{18}\text{O}$ , by repeated treatment of the silica with  $\text{H}_2^{18}\text{O}$  prior to dehydroxylation.<sup>7</sup> Subsequent reaction of the grafted bis(allyl)rhodium fragment with  $\text{PMe}_3$  gave two carbonyl peaks at 1957 and 1915  $\text{cm}^{-1}$ , corresponding to the isotopically different products of Fig. 3.

We interpret these results as the decomposition of **2** to give allyl alcohol, which is subsequently decarbonylated on the surface. The effect of the degree of surface dehydroxylation on the rate implies that surface hydroxy groups are involved. We propose the mechanism shown in Scheme 1.

The mechanism of C–O bond formation is depicted as a reductive elimination of a  $\sigma$ -allyl ligand with a siloxy ligand. Evidence for the formation of  $\equiv\text{SiOCH}_2\text{CH}=\text{CH}_2$  is seen in the IR spectrum as the small band at 1643  $\text{cm}^{-1}$ , assigned to  $\nu(\text{C}=\text{C})$ , which is distinct from the  $\nu(\text{C}=\text{C})$  band of **2** at 1612

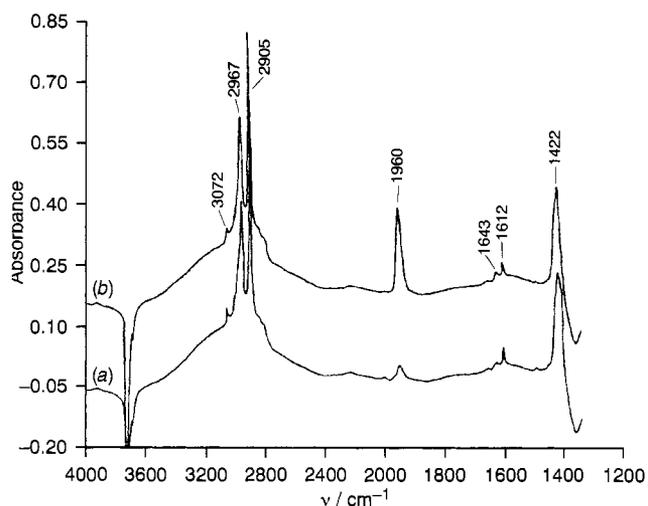


Fig. 2 IR transmission spectra of a self-supporting silica disc onto which  $\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_3$  has been grafted. The spectra were recorded after treatment of  $(\equiv\text{SiO})(\equiv\text{SiOH})\text{Rh}(\eta^3\text{-C}_3\text{H}_5)_2$ , **1**, with  $\text{PMe}_3$  followed by evacuation at room temp. for (a) 3 h (b) 16 h.

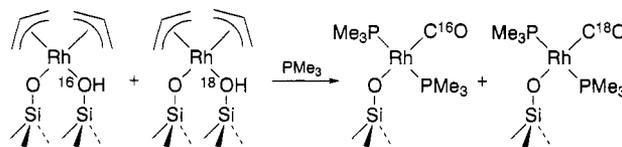
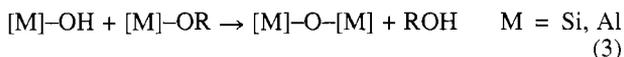


Fig. 3

$\text{cm}^{-1}$ .|| Allyl alcohol may be formed by reaction of the silyl ether with surface silanol groups. This reaction is well known in the synthesis of glasses, eqn. (3).<sup>9</sup>

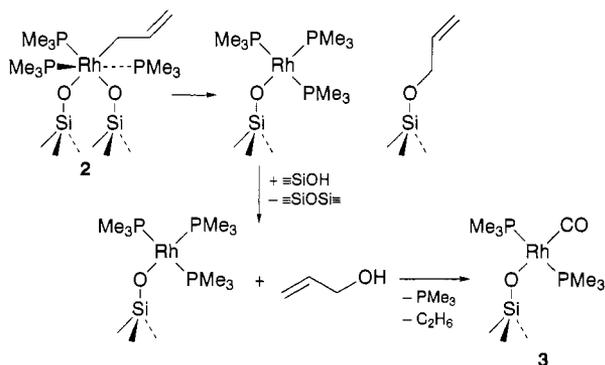


Decarbonylation of allyl alcohol by the tris(phosphine)rhodium(I) complex then leads to the observed product, **3**. A similar reaction was reported between allylic alcohols and  $\text{CIRh}(\text{PPh}_3)_3$ , yielding  $\text{CIRh}(\text{PPh}_3)_2(\text{CO})$  and substituted ethanes.<sup>10</sup>

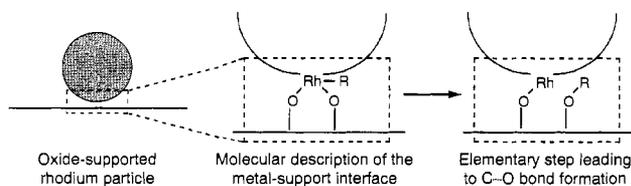
On alumina, treatment of grafted bis(allyl)rhodium with  $\text{PMe}_3$  gave initially an IR band at  $1612 \text{ cm}^{-1}$ , corresponding to  $[\text{AlO}]_2\text{Rh}(\text{PMe}_3)_3(\text{CH}_2\text{CH}=\text{CH}_2)$ , **2'**, which was replaced with time by a peak at  $1966 \text{ cm}^{-1}$ , corresponding to  $[\text{Al}-\text{O}]\text{Rh}(\text{PMe}_3)_2(\text{CO})$ , **3'**. The proposed decarbonylation of allyl alcohol shown in Scheme 1 was investigated by preparing  $[\text{Al}-\text{O}]\text{Rh}(\text{PMe}_3)_3$  on alumina-550.\*\* Addition of excess allyl alcohol to **2'** resulted in the appearance of  $[\text{Al}-\text{O}]\text{Rh}(\text{PMe}_3)_2(\text{CO})$ , **3'**, as judged by the increased intensity of the band at  $1966 \text{ cm}^{-1}$  band. New bands at  $1750$  and  $1570 \text{ cm}^{-1}$  were also observed, and are thought to be due to ester and carboxylate species produced by subsequent reactions of **3'** with allyl alcohol. The nature of these products is under investigation.<sup>11</sup>

The formation and decarbonylation of allyl alcohol subsequent to the reaction of **1** with  $\text{PMe}_3$  is reminiscent of the reaction of **1** with  $\text{H}_2$ . In that chemistry, reduction to rhodium metal is accompanied by formation of allyl alcohol, which was proposed to be responsible for the formation of CO adsorbed on the metal particles.<sup>††7</sup> Here we believe that decarbonylation occurs exclusively on discrete surface organometallic complexes, since the elemental analysis, IR and NMR spectra of **3** correspond closely to those of the molecular analogue  $\text{CIRh}(\text{PMe}_3)_2(\text{CO})$ , and are not consistent with Rh metal partially covered by CO. The presence of strongly electron-donating trialkylphosphine ligands is probably responsible for maintaining surface-bound rhodium in a monomeric, oxidized form.

The formation of allyl alcohol by the surface reaction of an alkylrhodium(III) complex in the absence of CO has probable implications for the mechanism of C–O bond formation at the interface between metal particles and oxide surfaces; Scheme 2.



Scheme 1



Scheme 2

In this respect, it is interesting to note that the selectivity of Rh/oxide catalysts for alcohol synthesis increases with metal dispersion.<sup>12</sup> The 'chemical anchoring' of metal particles to oxide surfaces *via* oxidized surface metal atoms has been proposed to stabilize metal particles in a highly dispersed state.<sup>13</sup>

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## Footnotes

† The silica used in these experiments is Degussa Aerosil, a pyrogenic silica with a specific surface area of  $200 \text{ m}^2 \text{ g}^{-1}$ . The designation silica-200 indicates that the silica was pretreated at  $200 \text{ }^\circ\text{C}$  under dynamic vacuum ( $10^{-4}$  Torr) for 16 h in order to remove adsorbed water and partially dehydroxylate the surface. For IR experiments, approx. 15 mg of silica was pressed into a self-supporting wafer with diameter 16 mm.

‡ The surface organometallic complex **2** was characterised by elemental analysis (3 P/Rh), reaction with  $\text{H}_2$  (liberation of 1 equiv. of propene), IR [ $\nu(\text{C}=\text{C})$   $1612 \text{ cm}^{-1}$ , characteristic of  $\sigma$ -allyl ligands coordinated to transition metals] and solid-state  $^{31}\text{P}$  MAS NMR ( $\delta$   $-13.2$ ,  $-24.3$  relative to  $\text{H}_3\text{PO}_4$ ). The  $\sigma$ -allyl ligand of **2** also undergoes CO insertion and reductive elimination with a siloxy ligand to give the silyl ester  $\equiv\text{SiOC}(\text{O})\text{CH}_2\text{CH}=\text{CH}_2$ .

§ IR:  $\nu(\text{CO})$   $1960 \text{ cm}^{-1}$ ;  $^{31}\text{P}$  NMR:  $\delta$   $-10.22$  (d).<sup>14</sup>

¶  $\equiv\text{SiORh}(\text{PMe}_3)_3$  can be prepared by the reaction of  $\text{CH}_3\text{Rh}(\text{PMe}_3)_3$  with silica-200, or by the reaction of  $\text{Rh}(\text{allyl})_3$  with silica-550, followed by treatment with excess  $\text{PMe}_3$ . In the latter case, 1,5-hexadiene is formed by reductive elimination from **1**. However, some propene is also produced, *i.e.* **2** is also present.

|| In a blank experiment, allyl alcohol was adsorbed at room temp. on silica-200. The IR spectrum revealed a  $\nu(\text{C}=\text{C})$  band at  $1642 \text{ cm}^{-1}$ .

\*\* The alumina used in these experiments is Degussa C, with a specific surface area of  $200 \text{ m}^2 \text{ g}^{-1}$ . Alumina-550 was prepared by calcination under flowing oxygen at  $550 \text{ }^\circ\text{C}$  followed by dehydroxylation under dynamic vacuum ( $10^{-4}$  Torr).

†† Two  $\nu(\text{CO})$  bands were observed at  $2048$  and  $1870 \text{ cm}^{-1}$ , characteristic of terminal and bridging CO adsorbed on a metal surface. The position of the high frequency band is sensitive to CO coverage.

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