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Electrophilic Chemistry of Oxide-Supported Rhodium Complexes. Activation of H–H and Alkane C–H Bonds

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Reactions between oxide-supported rhodium complexes and a variety of substrates, including phosphines, protic acids, H_2, and alkanes, can be described in terms of a general acid–base reactivity pattern.

Introduction

To attach a transition-metal complex to a metal oxide support can be accomplished by protolytic cleavage of an alkyl- (or allyl-) metal bond of the complex by hydroxyl groups of the oxide.[1-4] Often such supported complexes are prepared and routinely activated as catalysts by conversion to supported metal *particles* under vigorous conditions.[4] Were it possible to activate such species under *mild* conditions, it should be possible to characterize the resulting nonsoluble (but homogeneous) supported *complexes* more fully than is possible for typical "heterogeneous" systems, to understand their reactivity on the "molecular level", and to rationally develop new catalyst systems based on them as is typical for their "soluble" counterparts. An important feature which distinguishes oxide-bound supported complexes from phosphine- or carbonyl-ligated soluble or supported ones is the presence of "hard" ligation[5] by the metal–oxygen (oxide) bond. Thus, in the oxide-bound case, the support may exert medium effects (apart from simply stabilizing unsaturated species with regard to clustering) on the reactivity of the complex bound to it; for example, the presence of the "hard" metal–oxygen ligand bond may result in a preference for high oxidation states of the transition-metal center, since in these high oxidation states the strongest transition metal–oxygen (oxide) bonds should exist. Electrophilic activation of substrates by the metal center in these high oxidation state complexes may then occur.

Silica-bound rhodium complex [Si]–ORh(allyl)$_2$ (2) can be generated from Rh(allyl)$_3$ (1) and can be readily converted to [Si]–ORh(allyl)H (3) by hydrogenation under ambient conditions.[6-8] In the course of elucidating the chemistry of these species, a general pattern of reactivity has emerged in which the rhodium is maintained in the Rh(III) oxidation state and acts primarily as an active Lewis acid; its interactions with a reagent are governed by relative base properties of moieties within its ligand environment. This Lewis acidity is manifest through reactions of such Rh complexes with both conventional and unconventional "bases".

Results and Discussion

(1) Simple Reactions with Lewis Bases. Silica-bound complexes such as **3**, **5** and **6** are functionally coordinatively unsaturated,[9] as illustrated by the formation of phosphine adduct complexes of predictable stoichiometry.[7] Apparently an assignment of nominal coordination numbers about Rh can be operationally applied[9,10] and suggests that in **3**, two vacant coordination sites per Rh are present. In support of the concept of multiple coordinative unsaturation is the observation that **3** readily activates mono- and polycyclic arenes,[12] a process believed to require coordination of the substrate in at least η^4 fashion.[13-15] That *two* active sites are present is supported by the observation that addition of 1 equiv of PMe_3 completely quenches arene activation but leaves olefin activation (η^2 binding) intact.

(2) Electrophilic Cleavage of Ligands. Generation of a family of silica-bound rhodium hydrides from **3** was realized by protolytic removal of the allyl ligand to give [Si]–ORh(H)Cl (**5**), a species nominally coordinatively more unsaturated than either **2** or **3**. Although **3** was resistant to H_2SO_4, reaction with gaseous HCl proceeded, although *slowly*. Cleavage of the rhodium–allyl bond can be accomplished readily, however, by hydrolysis under basic conditions by addition of an excess of sodium methoxide (in methanol). Apparently then, the counteranion plays an important role in protonation of the allyl group of **3**. Nucleophilic "assistance" in the electrophilic cleavage of carbon–metal bonds has been postulated for other coordinatively unsaturated metal complexes which are characterized by nonpossession of metal-centered basic lone electron pairs, e.g., those of Hg(II),[16] Sn(IV),[17] or Zr(IV).[18]

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[8] Stoichiometric measurements conclusively demonstrate that one allyl ligand remains coordinated to Rh following hydrogenation and that the Rh-O bond remains intact. This was substantiated by the observation of ca. 1 equiv of C_3/Rh upon hydrolysis of **3** and by evoluation of ca. 1 equiv of CH_4/Rh by treatment of **3** with CH_3I.

[9] In this working definition, the allylic ligands are assumed to be η^3 and the Rh is assumed to be bound to the oxide via one oxide unit. Although μ-oxo units of the oxide support may coordinate[11] with the Rh, each coordination is assumed to be weak and the μ-oxo "ligands" are assumed to be easily replaceable.

[10] Although [Si]–ORh(H)Cl(PMe$_3$)$_2$ is nominally a 16-electron complex (excluding μ-oxo group ligation), a third phosphine ligand did not coordinate (strongly) to the rhodium center. π-Donation from chloride to rhodium though may labilize this third phosphine ligand toward dissociation. Replacement by hydride of the allyl ligand of **3** or the chloride ligand of **5** enabled net coordination of a third equivalent of PMe_3.

[11] A similar interaction has been suggested for a silica-bound (allyl)nickel species. See: Yermakov, Yu. I.; Kuznetsov, B. N. *Kinet. Katal.* **1972**, *13*, 1355.

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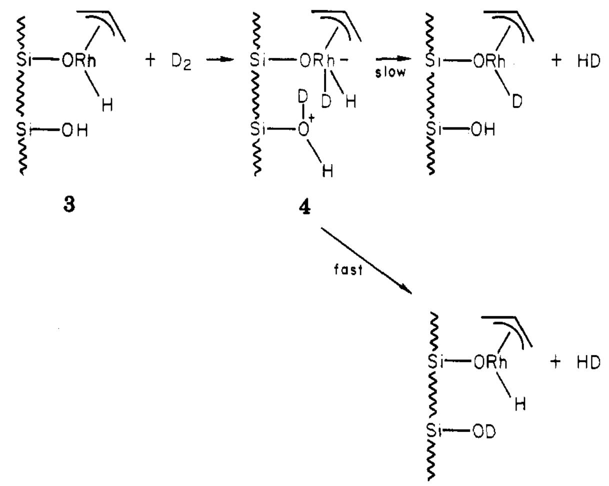
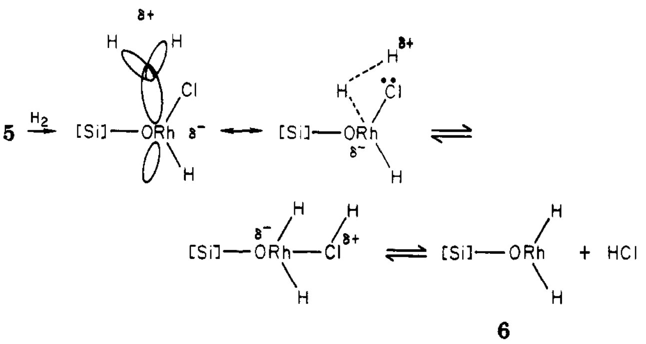
Scheme I. H-D Exchange Reactions Involving 3



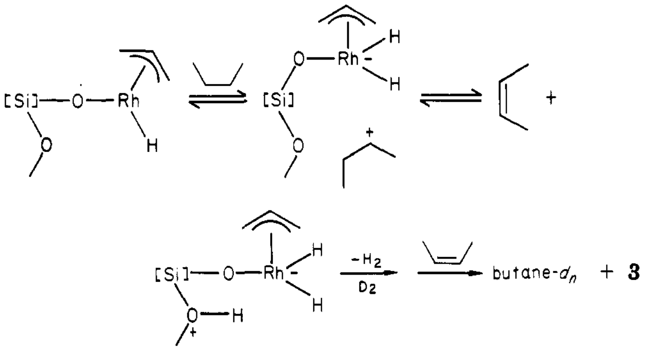
(3) Electrophilic Activation of Less Typical "Bases". Dihydrogen. (i) Ligand Hydrogenolysis. We have proposed[7] that H_2 is activated heterolytically by Rh(III) in the hydrogenolysis of rhodium allyl or rhodium alkyl species. Heterolytic activation of H_2 has been observed[19,20] in studies of $RhCl_6^{3-}$ and has been proposed for $[(\eta^5\text{-}C_5Me_5)RhCl_2]_2$ and for numerous metal oxides (Cr_2O_3, Co_3O_4, NiO, ZnO, Al_2O_3).[23-25] In each case an electrophilic metal center is suggested to abstract "H^-"; a basic oxygen atom stabilizes the released proton.[26-29] A comparable scheme has been forwarded to explain hydrogenolysis of $(\eta^5\text{-}C_5H_5)_2Zr(R)X$ (X = H or Cl)[30] in which the proton is transferred to the metal–carbon bond. For hydrogenolysis of 2, the "proton" would ultimately attack the metal–carbon bond of the allyl ligand to generate 3 and propylene. Hydrogenolysis, therefore, is "ligand" assisted as is protonolysis.

(ii) H_2–D_2 Exchange Catalyzed by 3. When 3 was exposed to D_2, H–D exchange between the atmosphere and residual hydroxyl species of the silica support was observed. An infrared spectrum of 3 taken after 10 min of exposure to D_2 (1 atm, 20 °C) showed a strong, very broad absorption assigned to OD vibrations centered at 2600 cm^{-1} (see Scheme I) which suggests that a proton (or D^+) may be transferred to an oxygen atom of the support on activation of hydrogen (or D_2). This spectrum also showed that the Rh–H absorptions remained, although they appeared to decrease slightly in intensity; an increase in absorption in the 1450-cm^{-1} region was also observed and may be attributed to the development of Rh–D species (the intensity of the absorption at 1800 cm^{-1} decreased at a faster rate than did that of the 2010-cm^{-1} band). That 3 catalyzes H–D exchange between D_2 and residual hydroxyl group protons of the support faster than it undergoes hydride ligand exchange with the atmosphere suggests that hydride ligands of intermediate 4 are not equivalent.[31,32]

Scheme II. H_2-HCl Exchange



Scheme III



In another experiment it was found that when a 50:50 H_2–D_2 mixture was added to 3 at room temperature (H_2–D_2:3 = 40:1), an equilibrium mixture of H_2, HD, and D_2 (1.2:2:1) was obtained within 1 min. (This time span was the shortest possible one for measurement by methods available to us.) The rate of HD formation from an H_2:D_2 mixture catalyzed by 3 is at least 20 turnovers min^{-1} Rh^{-1} under subambient conditions (20 °C (600 mmHg)). This rate is *at least* 2000 times faster than is allyl ligand hydrogenation of bis(allyl) species 2, which suggests that hydrogenolysis of the residual allyl ligand of 3 may be difficult due to ineffective *kinetic* competition. That is, following hydrogen activation, recombination may be so fast that attack of the proton on the metal–carbon bond of the allyl moiety is insignificant under the conditions studied.

(iii) H_2–HCl Ligand Exchange. Reaction of [Si]–O-Rh(H)Cl, 5, with H_2 gives $[Si]\text{–}ORhH_2$, 6, presumably with evolution of HCl(g) (which would be difficult to detect under the reaction conditions).[7] Since 5 does not lose HCl spontaneously in vacuo, a mechanism similar to that proposed above is suggested in which Rh(III) activates H_2 heterolytically; the released proton attacks the chloride ligand (Scheme II). This process is directly analogous to "classical" heterolytic activation of hydrogen by MCl_6^{3-} (M = Ru, Rh). It is interesting to note that 5 does not react with HCl to give the dichloride complex; the intensity of the absorption attributed to ν_{Rh-H} of 5 did not decrease upon prolonged exposure to HCl. This behavior may result from kinetic competition between protonation of the Rh–H bond and the chloride ligand in 5. In other words, de-

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[22] This species was catalytically active toward olefin and arene hydrogenation through Rh(I) intermediates.

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[31] No evidence for incorporation of deuterium into the allyl ligand of 3 was found by infrared spectroscopic analysis.

[32] While alternative explanations for H–D exchange can not be entirely discounted, the fact that neither propane nor propene were observed in the course of these experiments argues against pathways involving reduced rhodium(I) or rhodium(III) *polyhydride* species.

Table I. Deuterium Distribution in Butane from the Reaction of Butane-d_0 and 3^a with D_2

butane-d_n	% distribution 20 °C	% distribution 100 °C
d_0	92	20
d_1	5	5
d_2	3	7
d_3	0	8
d_4	0	14
d_5	0	15
d_6	0	14
d_7	0	10
d_8	0	4
d_9	0	2

[a] Reaction conditions: 3 (0.1 g, 0.04 mmol of Rh), butane (1 mmol), D_2 (1 atm), no solvent.

generate exchange occurs more rapidly than does productive exchange, similar to that competition proposed for H_2 between the allyl–Rh and Rh–H bonds of **3**. These results suggest that the kinetic basicity of these ligands toward proton decreases in the order Cl > H > allyl; the relative susceptibility of these ligands to protonation determines the outcome of a potential hydrogenolysis reaction.

(iv) H–D Exchange between Butane and D_2 Catalyzed by 3. In an experiment conceptually related to H_2–D_2 exchange, **3** was found to catalyze exchange of C–H bonds of *butane* with D_2 (100 °C, 1 atm of D_2)(see Table I). This process may involve hydride abstraction from the alkane by Rh(III)[33] leading to a carbonium ion which is either stabilized or deprotonated by the oxide support. If the latter reactivity mode is operative, D_2 addition to the resulting olefin would account for the noted atmospheric label incorporation into the alkane. Indeed, when olefins were treated with D_2 in the presence of **3**, a range of deuterio isomers was observed. For example, reaction of 1-butene with D_2 resulted in the formation of butane-d_n (n = 0–4) in the following amounts: $d_0 = 0.22$, $d_1 = 0.28$, $d_2 = 0.26$, $d_3 = 0.14$, $d_4 = 0.10$. A minimal isotope effect, $[k(H_2)/k(D_2)] = 0.92$, was observed.

Conclusion

Reactivity of the oxide-bound rhodium complexes noted above can be described by a pattern of acid–base chemistry: coordinatively unsaturated, electrophilic Rh(III) and the presence of basic sites in its ligand sphere facilitate heterolytic activation of reagent species. This behavior is reminiscent of that found for several soluble metal complexes and metal oxides for activation of H_2; it may be that this electrophilic pathway is a general one which accounts for important processes for activation of C–H bonds, such as the allylic oxidation of olefins, which are carried out over oxide-based catalyst systems.[34]

Experimental Section

Preparation of starting materials and techniques used in this area have been reported.[7]

Reaction of [Si]-ORh(H)Cl with H_2. (1) Hydrogen was added to a pressure of 1 atm (10 mmol) to a 250-mL flask containing [Si]–ORh(H)Cl (0.5 g, 0.2 mmol). The reaction was left to stand for 2 days; the atmosphere of the flask was removed periodically and was refilled to ensure completeness of reaction and was checked by infrared analysis (disappearance of 2110-cm^{-1} band of **5** and appearance of doublet at 2080 and 2020 cm^{-1}).

(2) Pellets of [Si]–ORhH$_2$ were prepared similarly for infrared study by treatment of **5** with 1 atm of hydrogen, either in a flask or directly in the infrared cell.

Reaction of [Si]-ORhH$_2$ with HCl. (1) Silica-supported species **6** (0.5 g, 0.19 mmol of Rh) was added to a 600-mL flask. The flask was evacuated at 10^{-6} mmHg and refilled with gaseous HCl (1 atm). After 5 days the atmosphere was removed and was collected (after passage through a KOH trap followed by a –196 °C trap). Calibrated manometer and mass spectral analysis found H_2 (0.13 mmol, 0.7 equiv/equiv of Rh).

(2) This reaction was also carried out on a pressed pellet of **6** in an infrared cell and was observed directly spectrally. Removal of the HCl atmosphere by evacuation followed by refilling with H_2 (1 atm) regenerated **6**. This cycle was repeated numerous times wihout noticeable decomposition of either species (judged from the intensities of the infrared absorptions).

H–D Exchange between H_2 and D_2 Catalyzed by 3. A 1:1 mixture of H_2 and D_2 was prepared by using an apparatus consisting of two flasks joined by a stopcock. The volumes of the flasks were calibrated (with CO_2), and pressures were established by manometer.

Hydrogen (580 mmHg, 7.88 mmol) was added to one of the previously evacuated flasks. Then D_2 (700 mmHg, 7.91 mmol) was added to the other flask. The gases were mixed thoroughly by opening the stopcock between them and alternative cooling (–196 °C) and warming (room temperature) one of the flasks several times. The H_2–D_2 mixture was added to **3** (0.10 g, 0.04 mmol of Rh) in a preevacuated 50-mL flask; the flask was closed immediately after the pressure equalized (460 mmHg). After ca. 30 s the gas mixture was removed from the flask via Toepler pump to collect 1.5 mmol of gas in the collection chamber. The total exposure time was approximately 1 min. The collected gas mixture was analyzed by MS to give H_2, HD, and D_2 in a 1.2:2:1 ratio, respectively.

In a control experiment it was found that the metallic source parts of the MS instrument slowly catalyzed H–D exchange of a 50:50 H_2–D_2 mixture. Under conditions identical with those used for sample analysis, only 5–10% HD was produced in the mass spectrometer.

H–D Exchange between *n*-Butane and D_2 Catalyzed by 3. To a 50-mL flask containing **3** was added *n*-butane (2 mmol). Then D_2 (8.5 mmol) was added from a 200-mL bulb (1 atm), and the flask was heated to 100 °c. After 2 days, collection of the volatiles gave *n*-butane (2 mmol) by calibrated PV trap. GC/MS analysis showed extensive deuterium incorporation.

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Registry No. **1**, 12082-48-3; H_2, 1333-74-0; HCl, 7647-01-0; *n*-butane, 106-97-8; 1-butene, 106-98-9.

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