

ALKANE ACTIVATION BY OXIDE-SUPPORTED ORGANORHODIUM COMPLEXES

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INTRODUCTION

"Homogeneous" catalysis, or catalysis by discrete, soluble transition metal complexes, is dominated by studies of such species in "soft" ligand environments (e.g., consisting of phosphines, sulfides or carbonyls). Historically, one focus of research in this field has been the elucidation of changes in reactivity of a complex which are effected by subtle modification of the ligand environment of the metallic center. It is of interest to us to determine how a gross change in this ligand environment affects the reactivity of a metal system bound to it; specifically, we aim to elucidate changes in rules of molecular reactivity which occur when the "soft" ligand environment of a transition metal complex is replaced by a "hard", oxygen-based one. In this context, solid metallic oxides were chosen to provide this oxygen-based ligation.

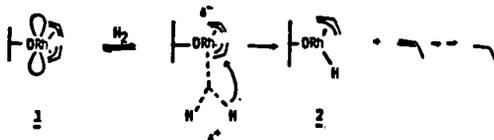
THE CHEMISTRY OF OXIDE-BOUND RHODIUM(ALLYL) COMPLEXES

We chose to focus our attention¹ on the chemistry of oxide-ligated rhodium complexes, given the many interesting and important reactions which exist for this metal in "classical", "soft-ligand"-based homogeneous catalysis. In our work we have used a variety of chemical and spectroscopic procedures to characterize our complexes.

Tris(allyl)rhodium reacts with hydroxyl groups of silica with evolution of 1 equiv of propylene to give Rh(III) species [SiO]Rh(allyl)₂, 1. (We use the terminology "[SiO]" simply to indicate covalent bonding between the oxide and the metal. Details of this interaction are not yet known, although preliminary results of EXAFS studies suggest that several oxygen atoms of the support interact with a given rhodium center.)



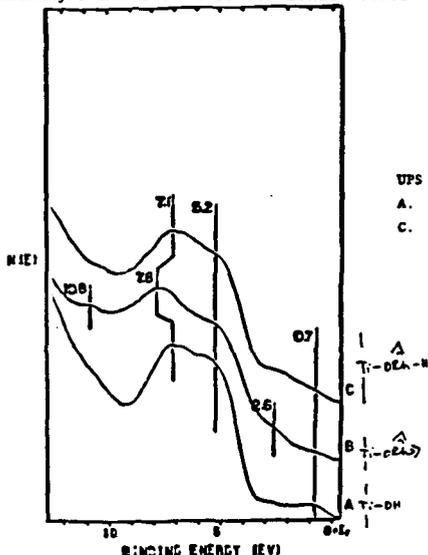
Hydrogen reacts slowly with 1 at room temperature. During this time 1 eq of propane is evolved. Hydrogen uptake measurements correlate with the amount of propane thus obtained and these data are consistent, stoichiometrically, with the formation of [SiO]Rh(allyl)H, 2. The infrared spectrum of 2 shows strong absorptions attributable to the allyl and hydride ligands ($\nu_{\text{Rh-H}} = 2010 \text{ cm}^{-1}$; weaker absorption at 1800 cm^{-1}). If hydrogenation is attempted before chemical deposition has occurred (i.e. before formation of 1 is complete) tris(allyl)rhodium adsorbed on the oxide rapidly reacts to give a black material which shows no infrared transmission, and which may be rhodium metal.



A series of XPS experiments was performed on 2 to corroborate its assignment. A single Rh species was found with an oxidation potential at 308.0 eV (Rh 3d 5/2 vs Si 2p). Thermolysis of this material at 400° followed by XPS analysis revealed

that rhodium metal had been formed (oxidation potential at 307.25 eV). XPS data obtained for 2 falls outside a range of values (308.4 eV to 311.3 eV) which has been determined for Rh(III) salts, a range which overlaps with that for typical Rh(I) complexes (307.6 eV to 309.6 eV). XPS data for covalent organometallic complexes, however, must be interpreted with caution: although 2 is formally a complex of Rh(III), actual positive charge build-up on the metal in this hydride-ligated species may be quite low.

To further probe the nature of the interaction between the metal complex and the oxide support, procedures were developed² for vapor phase deposition of tris(allyl)rhodium onto single crystal hydroxylated TiO₂ in ultra-high vacuum; deposition and a subsequent hydrogenolysis procedure were investigated through a series of UPS measurements made on the surface oxygens of the oxide. These demonstrated that attachment of the bis(allyl)rhodium moiety to TiO₂ was associated with a removal of electron density from the surface oxygens, consistent with the notion that this moiety is a strong electrophile (perhaps stronger than proton). Replacement of one of the allyl ligands by hydride revealed by UPS a build-up of charge on the surface oxygens. Thus the role of hydride as a strong donor ligand toward rhodium, mentioned above in discussions of XPS analyses, is corroborated by these UPS results. Variation in binding energies for surface oxygens as a function of other ligand changes in the coordination sphere of the rhodium demonstrate the covalent nature of the interaction between the metal complex and the oxide, which apparently behaves as a conventional "donor" ligand.



UPS for Rh(allyl)(H) formation on titanium dioxide (001).
 A. 205L water/S' Ar+ B. 2420L tris(allyl)Rh/ (A)
 C. 3230L H₂/(B)

We suggest that coordinatively unsaturated 1 is electrophilic in its reactivity. Activation of H₂ has been observed by aqueous Rh(III) and by numerous metal oxides. In these cases, the concept of "heterolytic" activation of hydrogen has been developed; the coordinatively unsaturated metal center acts as a sink for "H⁻", and a base in the environment of the metal center stabilizes the released proton. When 2 is exposed to D₂, H-D exchange between the atmosphere and residual hydroxyl groups of the silica support is observed, consistent with the notion that in the presence of 2 H₂ or D₂ act as a source of H⁺ or D⁺. Complex 2 also catalyzes rapid (< 1 min) equilibration of 50:50 H₂-D₂ mixture at room temperature.



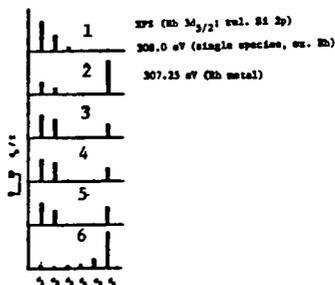
ACTIVATION OF ALKANES

Simple alkanes are conceptual analogs of dihydrogen in that they both should be able to form a two center, three electron bond with an unsaturated metal center utilizing electron pairs in bonding σ orbitals; analogous intramolecular C-H bond coordination is now well established experimentally and has been calculated to be



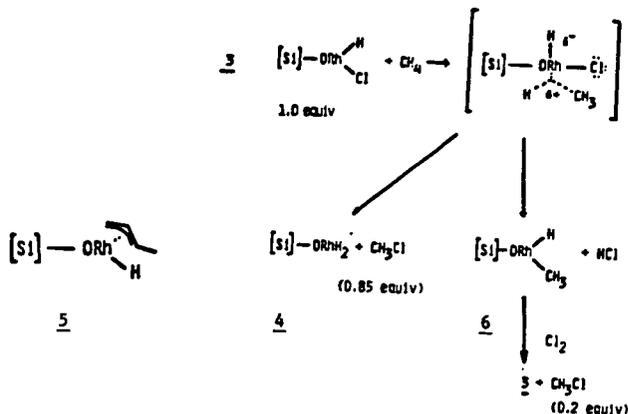
facile intermolecularly. To probe interactions between alkanes and 2, we studied their reaction in the presence of D_2 gas. Sequential H-D exchange occurred when 2 was used to catalyze this process between ethane, for example, and D_2 (see entry 1). Decomposition of 2 (heating at 400° under one atmosphere of hydrogen for 4 hrs) gave a black species which showed no infrared absorptions attributable to Rh-H stretching modes. This species showed catalytic activity for H-D exchange which was different from that of 2: whereas 2 gives rise to a distribution of deuterated ethanes relatively high in d_1 - and low in d_6 -ethane, this other black substance gives rise to a bimodal pattern showing a high degree of d_6 -ethane relative to d_1 (see entry 2). We had noted that simple thermolysis of 2 yields rhodium metal (by XPS analysis) and, therefore, we compared this black material with rhodium on silica obtained by conventional methods. Interestingly, rhodium on silica thus prepared behaves in a fashion similar to that noted for the pyrolysate (see entries 3 and 4).

- (1) -Rh(allyl)H/SiO₂
- (2) Rh/SiO₂ prepared from
-Rh(allyl)H/SiO₂ at 400° , 1 atm H₂
- (3) Rh/SiO₂ prepared from RhCl₃
(aqueous), 400° , 1 atm H₂
- (4) Rh/SiO₂ prepared from RhCl₃
(methanol), 150° , 1 atm H₂
- (5) Rh/KBr prepared from Rh(allyl)₃/KBr,
room temp., 1 atm H₂
- (6) Rh film



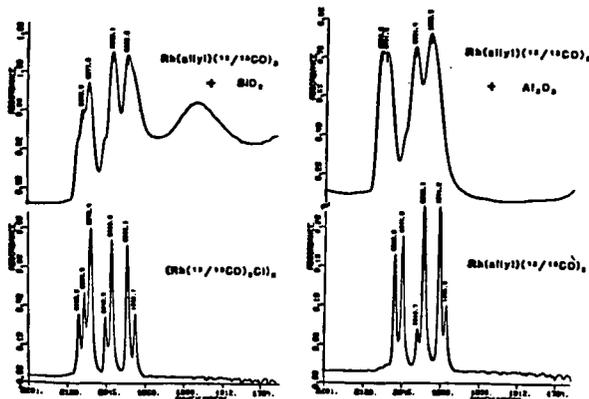
ACTIVATION OF METHANE

We proposed that methane could be activated by an intramolecular ligand rearrangement route from a two-electron, three-centered intermediate analogous to that one proposed for activation of H₂, and we have demonstrated that methane can replace hydrogen in the hydrogen activation step shown in Scheme 2. For example, when 1 is treated with H₂ 2 results; similarly we found that when 1 was treated with methane, a mixture of hydride complexes 2 and 5 were obtained. Hydrogen also reacts with hydrido-chloride complex 3 to give dihydride 4, and therefore 3 was treated with methane. This results in the formation of methyl chloride (0.85 equiv); activation of methane was confirmed by use of ¹³CH₄. Here, infrared analysis performed on rhodium-containing materials showed the presence of dihydride 4, and broadened absorption centered at 2040 cm⁻¹ suggested that 4 could be contaminated with another hydride species, perhaps a (methyl)rhodium(hydride) complex 6; (for the analogous [SiO]Rh(H)Bu, $\nu_{Rh-H} = 2010$ cm⁻¹). Indeed when this material (6) was treated with chlorine, methyl chloride was obtained (0.2 equiv). These observations can be explained³ by the sequences shown below.



OXIDE-DEPENDENT DEPOSITION AGGREGATION

Although we had noted that a variety of oxides could be used for chemical attachment of organorhodium complexes, we had not originally studied how variation in the oxide itself affects the structure or reactivity of complexes bound thereto, and deposition control was attained only by adjusting total content of hydroxyl groups on the oxide. The subtle notion was not considered that relative locations might vary of reactive hydroxyl groups on oxides of different structure, although this distribution of reactive sites would control deposition of one equivalent of an organometallic with regard to another. Silica and alumina are among the most commonly used oxides, in general, for chemical attachment to reactive organometallic complexes, and we found⁴ that an interesting oxide-dependent deposition phenomenon distinguishes these two materials: although for both we utilize samples containing a large excess of acidic hydroxyl groups relative to total rhodium deposited, we note that for silica, deposition of rhodium complexes occurs selectively to generate dimers; on alumina (of comparable total acidity) monomers are formed.



Rhodium carbonyl compounds bound to silica are not structurally stable under hydrogen⁴. This can be demonstrated by noting changes in the infrared spectrum of carbonyl compounds formed on deposition and after subsequent treatment with H₂. Specifically, we note a relative decrease in intensity attributable to terminal carbonyl ligation and an increase in intensity attributable to bridging or "semi-bridging" carbonyl groups. We note that rhodium hydride species (2 or 4) on silica are also structurally unstable under H₂ with regard to clusterification. When these reactions were followed by infrared spectroscopy evidence was obtained for the presence of intermediary molecular hydrogen adducts. Thus, although it is a commonly held assumption that degradation under hydrogen of catalytically active complexes to metallic particles occurs first by reduction of the complex to the metal and then by aggregation, our data suggest that a complementary route, namely aggregation followed by degradation, must also be considered. It is interesting to note that dihydride or dicarbonyl complexes of rhodium bound to either alumina or titanium dioxide do not demonstrate any evidence for analogous clusterification under H₂. Clearly the surface properties of all of these oxides must be better elucidated to understand differences in reactivity imparted to the covalently bound complexes by their various oxide ligands.

1. Alkane Activation by Oxide-Bound Organorhodium Complexes, Schwartz, J. *Acc. Chem. Res.*, 1985, 18, 302-308, and references cited therein.
2. Investigation of a Model Catalytic System in Ultrahigh vacuum: The Adsorption of Rh(allyl)₃ on the TiO₂ (001) Surface, Smith, P.; Bernasek, S. L.; Schwartz, J.; McNulty, G. S. *J. Am. Chem. Soc.* 1986, 108, 5654-5655.
3. Activation of Alkanes by Oxide-Supported Organorhodium Complexes, Kitajima, N.; Schwartz, J. *Proceedings of the Fourth International Symposium on Homogeneous Catalysis - Fundamental Research in Homogeneous Catalysis, Volume III*, 1986, 1003-1014.
4. Oxide-Dependent Deposition and H₂-Promoted Aggregation of Organorhodium Complexes, McNulty, G. S.; Cannon, K.; Schwartz, J. *Inorg. Chem.* 1986, 25, 2919-2922.