

Alkane Activation by Oxide-Bound Organorhodium Complexes

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"Homogeneous" catalysis, or catalysis by discrete, soluble transition-metal complexes, is dominated by studies of the chemistry of such species in "soft"¹ ligand environments (for example, consisting of phosphines, sulfides, or carbonyls), and fascinating chemical processes, many of practical significance, have been developed through an understanding of their reactivity patterns.² Historically, one focus of research in "homogeneous" catalysis 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.¹ In this context, solid metallic oxides were chosen to provide this oxygen-based ligation.

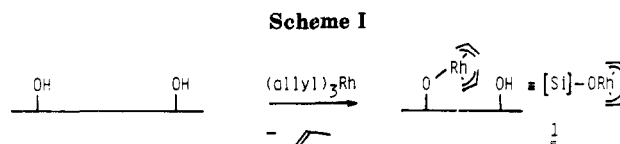
The chemistry of oxide-bound metal complexes of the "early" transition metals has been extensively studied by several groups³ and has been developed industrially, for example, to yield new types of olefin polymerization^{3e} or oxidation^{3c} catalysts. No such comparable body of work exists regarding the "late" metals. In that context, most work has focused on attachment of metal carbonyl clusters to oxide supports⁴ and on the creation of particulate metals attached to these oxides.⁵

The Chemistry of Oxide-Bound Rhodium Allyl Complexes

We chose to focus our attention 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 all of the reactions described below, we have used a variety of chemical procedures to characterize our complexes stoichiometrically to determine the nature of non-oxide ligation about the metal. We have also used several spectroscopic techniques to further characterize these species, but *details* of structure (for example, geometric relationships among the ligands and with regard to the metal) have not yet been determined.

Triallylrhodium reacts⁶ with hydroxyl groups of silica with evolution of 1 equiv of propylene to give Rh(III) species $[\text{SiO}]\text{Rh}(\text{allyl})_2$, 1. (We use the terminology $[\text{SiO}]$ simply to indicate covalent bonding between the oxide and the metal, but details of this interaction are not yet known. We do not know, for example, if more

than one oxygen atom interacts with the rhodium center at any time.) Chemical degradation of 1 yields 2 equiv of propylene, confirming the stoichiometric assignment as shown. These results prove that a chemical reaction has occurred between silica and triallylrhodium. This chemical deposition step is critical to the success of the reactions discussed below.



Hydrogen reacts slowly with 1 at room temperature. During this time 1 equiv of propane is evolved. Hydrogen uptake measurements correlated with the amount of propane thus obtained and these data are consistent, stoichiometrically, with the formation of $[\text{SiO}]\text{Rh}(\text{allyl})\text{H}$, 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}). Both of these hydride ligand bands are observable in vacuo. The latter band is quite broad, and it is possible that a fraction of the rhodium centers in 2 are bridged by hydride ligands. The allyl group of 2 is not removed by hydrogenation (1 atm, room temperature). The stoichiometry of 2 can be determined by chemical degradation using methanol (which liberates ca. 1 equiv of propylene) and by treatment with methyl iodide (which liberates ca. 1 equiv of methane). We note⁷ that if hydrogenation is attempted *before* chemical deposition has occurred (i.e., before formation of 1 is complete), triallylrhodium adsorbed on the oxide rapidly reacts to give a black material which shows no infrared transmission and which may be rhodium metal. In this context, triallylrhodium adsorbed on KBr (no chemical deposition occurs) and treated with hydrogen

(1) For a review of "hard" and "soft" character see: Pearson, R. G. "Hard and Soft Acids and Bases"; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.

(2) For example, see: Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980.

(3) (a) Ballard, D. G. H. *Adv. Catal.* 1973, 23, 263. (b) Zakharov, V. A.; Dudchenko, V. K.; Paukshtis, E. A.; Karakchiev, L. G.; Yermakov, Yu. I. *J. Mol. Catal.* 1977, 2, 421. (c) Yermakov, Yu. I.; Kuznetsov, B. N. *J. Mol. Catal.* 1980, 9, 13. (d) Yermakov, Yu. I.; Kuznetsov, B. N.; Zakharov, V.; "Catalysis by Supported Complexes"; Elsevier: Amsterdam, 1981. (e) Iwasawa, Y.; Yamagishi, M.; Ogasawara, S. *J. Chem. Soc., Chem. Commun.* 1980, 871. (f) Candlin, J. P.; Thomas, H. *Adv. Chem. Ser.* 1974, No. 132, 212. (g) Karol, F. J.; Karapinka, G. L.; Wu, C.; Dow, A. W.; Johnson, R. N.; Carrick, W. L. *J. Poly. Sci., Polym. Chem. Ed.* 1972, 10, 2621. G. L. Karapinka, U.S. Patent 37 709 853.

(4) For example, see: (a) Evans, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* 1984, 1123. (b) Psaro, R.; Ugo, R.; Zanderighi, G. M.; Besson, B.; Smith A. K.; Basset, J. M. *J. Organomet. Chem.* 1981, 213, 215.

(5) Ryndin, Y.; Hicks, R.; Bell, A.; Yermakov, Yu. I. *J. Catal.* 1981, 70, 287.

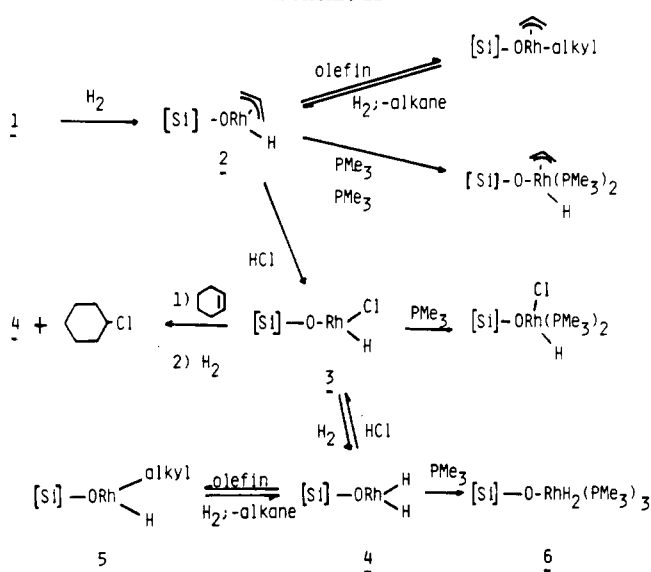
(6) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* 1981, 11, 397.

(7) Kitajima, N.; Schwartz, J. *J. Mol. Catal.* 1984, 26, 165.

(8) Dwyer, D., personal communication.

Jeffrey Schwartz was born in New York in 1945. He received the S.B. degree from MIT, where he did undergraduate research with George Whitesides and then the Ph.D. degree from Stanford University, where he was engaged in a joint research endeavor with Professors E. E. van Tamelen and John I. Brauman. He joined the faculty of Princeton University in 1970 and is now Professor of Chemistry. His research interests lie primarily in the development of novel organometallic reagent systems for use in organic synthesis and the study of oxide-bound organometallic complexes.

Scheme II



instantly gives black material showing a similar lack of infrared transmission. Thermolysis of 2 at 400 °C also gives a black material which shows no infrared absorption.

A series of XPS experiments was performed on 2 to corroborate its assignment as one of rhodium in an oxidized state relative to Rh metal. 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 °C followed by XPS analysis revealed that rhodium metal had been formed (oxidation potential at 307.25 eV).^{9a} XPS data obtained for 2 falls outside a range of values (308.4–311.3 eV)^{9b,c} which has been determined for Rh(III) salts, a range which overlaps with that for typical Rh(I) complexes (307.6–309.6 eV).^{9b} XPS data for covalent organometallic complexes, however, must be interpreted with caution:^{9c,d} although 2 is formally a complex of Rh(III), actual positive charge buildup on the metal in this hydride-ligated species may be quite low.

Treatment⁶ of 2 with excess gaseous HCl slowly leads to nearly complete removal of the allylic group, and infrared analysis of this material shows that a new rhodium hydride species (ν_{Rh-H} 2110 cm⁻¹) has been obtained. This material reacts with cyclohexane followed by hydrogen to yield cyclohexyl chloride, and we propose this compound to be [SiO]Rh(H)Cl, 3.

Treatment⁶ of 3 with hydrogen results in its conversion to a new species containing IR absorption bands at 2080 and 2020 cm⁻¹. This process can be followed readily by IR as can the reversion of 4 to 3 in the presence of gaseous HCl. An equilibrium constant of ~5 favoring 4 was noted, and the observation that 3 does not eliminate HCl in vacuo suggests that a pathway of reductive elimination of HCl followed by oxidative addition of H₂ is not responsible for this conversion process. Dihydrido species 4 reacts in the presence of excess olefin by uptake of 1 equiv of the

alkene to yield a new species [SiO]Rh(alkyl)H, 5, assigned as such on the basis of IR ($\nu_{Rh-H} = 2032$ cm⁻¹) and by subsequent hydrogenolysis of 5 to 4 with concomitant liberation of 1 equiv of the corresponding alkane (Scheme II).

A Unified Mechanistic Concept for Reactions of Supported Organorhodium Complexes with Hydrogen. The simple conversion of 1 to 2 using H₂ is an example of activation of hydrogen by a complex of formally Rh(III). Although analogous phenomena have been noted in aqueous medium,¹⁰ activation of hydrogen by Rh(III) species is not a common occurrence in the "soft" ligand chemistry of this metal in which hydrogen is activated by an "oxidative" process.¹¹ A similar process of hydrogen activation occurs in conversions of either 5 or 3 to give 4. The transformations 1 → 2, 2 → 3, and 4 → 5 are also interesting from the point of view of the nature of the products which are formed. For example, until recently organorhodium(III) hydride species had been considered unstable with regard to rapid reductive elimination; there now exist many examples of such species¹² as isolated entities (and of organoiridium(III) congeners¹³). Another interesting observation is that complex 3 can be prepared in the presence of excess HCl; typically, metal hydride ligands are labile to acids, such as HCl, to yield dihydrogen and salts.

The stability of 1, 2, 3, 4, and 5 to "reductive elimination" may be due to the presence of oxide ligation stabilization of Rh(III) relative to Rh(I) through stronger O–Rh bonding in the high-valent form. As a solid support, the oxide could also stabilize *coordinatively unsaturated* species such as 2, 3, and 4 against clusterification. That these rhodium species are unsaturated (or are highly labile toward deligation of μ -oxo centers of the oxide) can be demonstrated by noting their reactions with simple Lewis bases: 2, 3, and 4 react with small cone angle phosphines with stoichiometries predictable by normal rules of coordinative saturation. In other words, in these oxide-bound materials, the existence and number of "vacant" coordination sites can be determined or controlled in a predictable way as can be done in "homogeneous" organometallic chemistry (see Scheme II).

The combination of high oxidation state and coordinative unsaturation suggests that these rhodium complexes could be electrophilic. Consistent with this concept, we have noted only slow cleavage of organic ligands from these complexes under acidic conditions (for example, gaseous HCl) but rapid cleavage of these same groups under *basic* reaction conditions (for example, sodium methoxide in methanol). Apparently the presence of a coordinating counterion plays an important role in protonolysis of, for example, allylic groups of 2. This is reminiscent of the requirement for nucleophilic "assistance" in electrophilic cleavage of carbon–metal bonds of coordinatively unsaturated metal centers such as those of Hg(II),¹⁴ Sn(IV),¹⁵ or Zr(IV).¹⁶

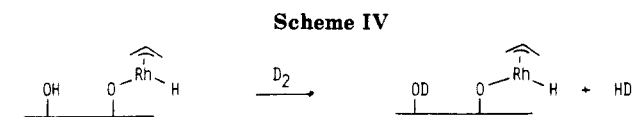
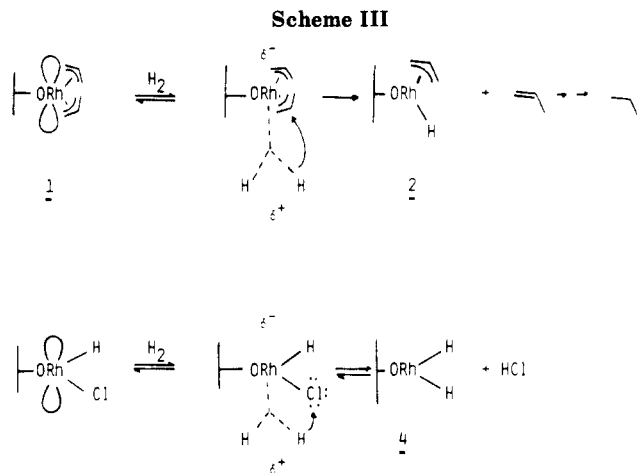
(9) (a) This value is within the range reported for Rh metal of varying particle size: Huzinga, T.; van't Blick, H. F. J.; Vis, J. C.; Prins, R.; *Surf. Sci.* **1983**, *135*, 580. (b) For a range of values for oxidized Rh species, as well as for Rh metal, see: Anderson, S. L. T.; Watters, K. L.; Howe, R. F. *J. Catal.* **1979**, *59*, 340; **1981**, *69*, 212. (c) Hamer, A. D.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1973**, 116. (d) Conner, J. A. "Handbook of X-Ray and UV Photoelectron Spectroscopy"; Heyden: Philadelphia, 1977; p 185.

(10) (a) Halpern, J.; James, B. R. *Can. J. Chem.* **1966**, *44*, 671. (b) James, B. R.; Rempel, G. L. *Can. J. Chem.* **1966**, *44*, 233.

(11) For example, see ref 2, Chapter 3.

(12) (a) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 562. (b) Perlana, R. A.; Bergman, R. G. *Organometallics* **1984**, *3*, 508.

(13) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. (b) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.



We believe that the postulated electrophilic nature of coordinately unsaturated Rh(III) species 2, 3, and 5 is responsible for their activation of hydrogen in ligand hydrogenolysis steps. Activation of H_2 has been observed by aqueous Rh(III)¹⁰ and by numerous metal oxides.¹⁷ In these cases, the concept of "heterolytic" activation of hydrogen has been developed: the coordinately unsaturated metal center acts as a sink for "H⁻", and a base in the environment of the metal center stabilizes the released proton. A comparable scheme has been suggested¹⁸ to explain hydrogenolysis of $(\eta^5-C_5H_5)_2Zr(R)X$ species in which the 16-electron Zr(IV) complex is proposed to form a molecular hydrogen complex followed by transfer of a "proton" from a Zr-H bond to the Zr-carbon bond. (A bona fide molecular hydrogen complex has now been prepared¹⁹ by reaction between a coordinatively unsaturated Mo species and H_2 .) For hydrogenolysis of 2, 3, or 5, coordination of molecular hydrogen followed by proton transfer to a ligand in the coordination sphere of the rhodium would yield the reaction products (Scheme III).

When 2 is exposed to D_2 , H-D exchange between the atmosphere and residual hydroxyl groups of the silica support is observed.²⁰ An infrared spectrum of 2 taken after a 10-min exposure to deuterium gas (1 atm, 20 °C) showed strong very broad absorption centered at 2600 cm^{-1} assigned to -OD vibrations consistent with the notion that in the presence of 2 H_2 or D_2 act as a source of H^+ or D^+ . In contrast to rapid exchange of protonic OH groups with D_2 , only slow exchange of the Rh-H group occurs with the atmosphere (Scheme IV). Until detailed structural information for 2 can be ascertained,

(14) Jensen, F. R.; Rickborn, B. "Electrophilic Substitution of Organomercurials", McGraw-Hill: New York, 1968.

(15) McGahey, L. F.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 4397.

(16) Labinger, J. A.; Hart, D. W.; Siebert, W. E., III; Schwartz, J. J. *Am. Chem. Soc.* **1975**, *97*, 3851.

(17) (a) Ozaki, A. "Isotopic Studies of Heterogeneous Catalysts"; Kodansha: Tokyo, 1977; pp 13-15. (b) Kokes, R. J.; Dent, A. L.; Chang, C. C.; Dixon, L. T. *J. Am. Chem. Soc.* **1972**, *94*, 4429. (c) Burwell, R. L., Jr.; Haller, G. I.; Taylor, K. C.; Read, J. F. *Adv. Catal.*, **1970**, *20*, 1.

(18) Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

(19) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

(20) Ward, M. D.; Schwartz, J. *Organometallics* **1982**, *1*, 1030.

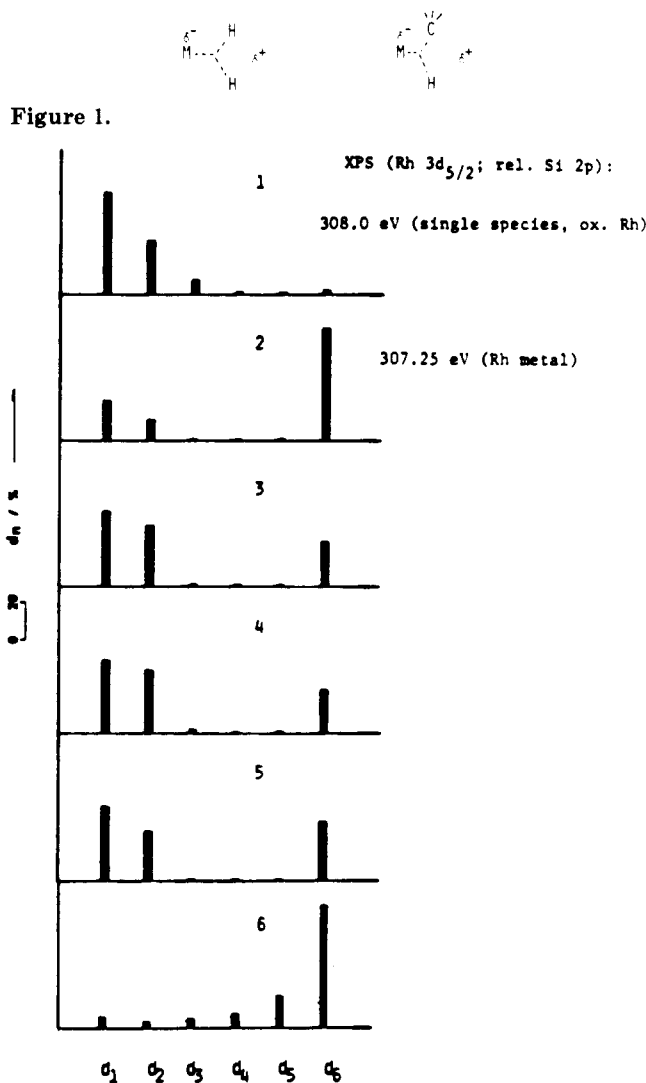


Figure 2. (1) -Rh(allyl)H/SiO₂. (2) Rh/SiO₂ prepared from -Rh(allyl)H/SiO₂ at 400 °C (1 atm of H₂). (3) Rh/SiO₂ prepared from RhCl₃ (aq) at 400 °C (1 atm of H₂). (4) Rh/SiO₂ prepared from RhCl₃ (methanol) at 150 °C (1 atm of H₂). (5) Rh/KBr prepared from Rh(allyl)₃/KBr at room temperature (1 atm of H₂). (6) Rh film (ref 23).

the origin of slow exchange of the hydride ligand in these systems cannot be explained convincingly. Complex 2 also catalyzes rapid (<1 min) equilibration of a 50:50 H_2 - D_2 mixture at room temperature.²⁰

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 experimentally²¹ and has been calculated to be facile *intermolecularly*.²² To probe interactions between alkanes and 2, we studied their reaction in the presence of D_2 gas. This led to H-D exchange in the alkane, and after long reaction times an equilibrium mixture of deuterated species was obtained.²⁰

It is well-known that many particulate metals will

(21) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(22) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625.

(23) Kembal, C. *Adv. Catal.* **1959**, *11*, 233.

Table I.
Rates for D₂/Alkane Exchange Catalyzed by
[SiO]-Rh(allyl)H

alkane	type*	turnover (mol/h-mol Rh)
CH ₄	α	- 0.0008
C ₂ H ₆	α, β	1.2
C ₃ H ₈	α, β	5.9
n-C ₄ H ₁₀	α, β	28.0
1-C ₄ H ₁₀	α, β	6.8
n-C ₅ H ₁₂	α, β	179.0
1-C ₅ H ₁₂	α, β	37.0
neo-C ₅ H ₁₂	α	- 0.0008

Catalyst amount = 50 mg (Rh = 0.012 mmol); alkane = 2.0 mmol;
D₂ = 4.0 mmol; reaction temperature = 100 °C.

NOTE: Chain branching slows the reaction: (1) → $\overset{\cdot}{\text{C}}$ by "H" abstraction
(2) → $\overset{\cdot}{\text{C}}$ by "H" abstraction
are NOT important processes here.

* Upon attack at a C_α-H bond, is there a C_β-H bond present?

catalyze exchange between alkanes and deuterium gas.²¹ For rhodium, this process usually results in an initially observable *polyexchange* of C-H bonds for C-D ones. In contrast, we note⁷ *sequential* H/D exchange occurred when **2** was used to catalyze this process between ethane, for example, and D₂ (see Figure 2, entry 1). Decomposition of **2** (heating at 400 °C under 1 atm of hydrogen for 4 h) gave a black species which showed no infrared absorptions attributable to Rh-H stretching modes. Not surprisingly this species showed catalytic activity for H/D exchange which was different from that of **2**. Noteworthy is the observation that whereas **2** gives rise to a distribution of deuterated ethanes relatively high in ethane-*d*₁ and low in ethane-*d*₆, this other black substance gives rise to a bimodal pattern showing a high degree of ethane-*d*₆ 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). As well, we note that overloading a silica sample with triallylrhodium relative to acidic -OH groups also gave a black material on treatment with hydrogen which catalyzed H/D exchange with ethane in a bimodal fashion analogous to either the pyrolysate or rhodium on silica prepared by conventional mechanisms; so did Rh(allyl)₃/KBr (no chemical deposition, see entry 5). We believe, therefore, that in the *absence* of chemical anchoring to the oxide, hydrogenation of the allyl-rhodium complex will give rhodium metal.²⁴ The bi-

(24) The reaction between a silica allylrhodium species and H₂ has been reported to give silica/metallic rhodium: Foley, H. C.; DeCanio, S. J.; Tau, K. D.; Chao, K. J.; Onuferko, J. H.; Dybowski, C.; Gates, B. C. *J. Am. Chem. Soc.* 1983, 105, 3074. In striking contrast to **2** (which has a strong IR absorption at 2010 cm⁻¹ [ν(Rh-H)]), this other material shows no IR absorption in the region 2000-1050 cm⁻¹ in the absence of excess H₂; therefore this material is fundamentally different from **2**, and conclusions of that study are not germane to a discussion of the chemistry of **2**. Formation of rhodium metal in this other case may, in fact, be due to incomplete chemical deposition of the organometallic onto the oxide or to overloading of the support relative to available OH groups. Deposition stoichiometry was not reported in this case.

(25) Kitajima, N.; Schwartz, J. *J. Am. Chem. Soc.* 1984, 106, 2220.

modal distribution noted for H/D exchange catalyzed by rhodium metal obtained in the variety of ways described above may be related to the microscopic nature of active sites in particulate rhodium metal (particle size, number, nature of crystal faces, etc.), but in each case ethane-*d*₆ either predominates or is formed as a major component of the mixture (at low conversion) in contrast to that distribution resulting from use **2** (Figure 2).

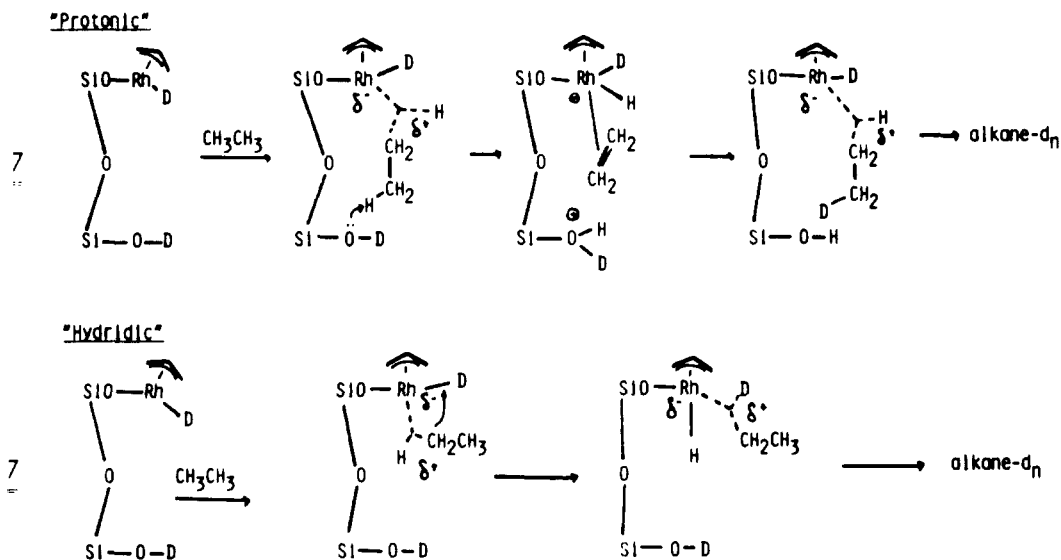
Mechanisms for H/D Exchange. The notion that **2** might act as an electrophilic site for activation of an alkane (or for dihydrogen) suggests that one possibility for H/D exchange involves hydride abstraction from the alkane. To probe this concept, we examined⁷ rates for H/D exchange of a series of alkanes catalyzed by **2**. As shown in Table I, steric factors are important in the H/D exchange process; however, alkanes amenable to activation by a hydride abstraction based route (branched species containing tertiary C-H bonds) reacted more slowly in the H/D exchange process than did their linear analogues. A radical-based H/D exchange reaction should also be favored by the presence of tertiary C-H bonds. Therefore, it seems that both hydride and H· abstraction pathways can be ruled out based on these relative rate measurements.

As shown in Table I, rates for H/D exchange of methane and neopentane are remarkably slow compared with those noted for the series of linear or branched hydrocarbons. In fact, it seems that alkanes demonstrating rapid H/D exchange are those capable of forming olefins; those alkanes examined which are incapable of olefin formation undergo slow H/D exchange. To understand mechanisms whereby complex **2** catalyzes H/D exchange, we performed a series of stoichiometric reactions. Deuterated species [Si(OD)-SiO]Rh(allyl)D (**7**) was obtained when **1** was treated with 1 atm of D₂. Species **7** reacts slowly with methane to give CH₃D and [SiO]Rh(allyl)H. The slow rate of this stoichiometric reaction is consistent with slow catalytic H/D exchange rates noted in Table I for methane, but it is not adequate to explain those higher rates noted for most other alkanes. When this same material (containing 0.08 mmol of Rh-D and 0.43 mmol of O-D) was heated with ethane under similar conditions, 0.35 mmol of deuterium incorporation, close to the equilibrium amount expected with regard to *total* deuterium content of **7** (deuteride and -OD sites) was detected in the ethane, as was a band in the infrared spectrum attributed to rhodium-hydride stretches.

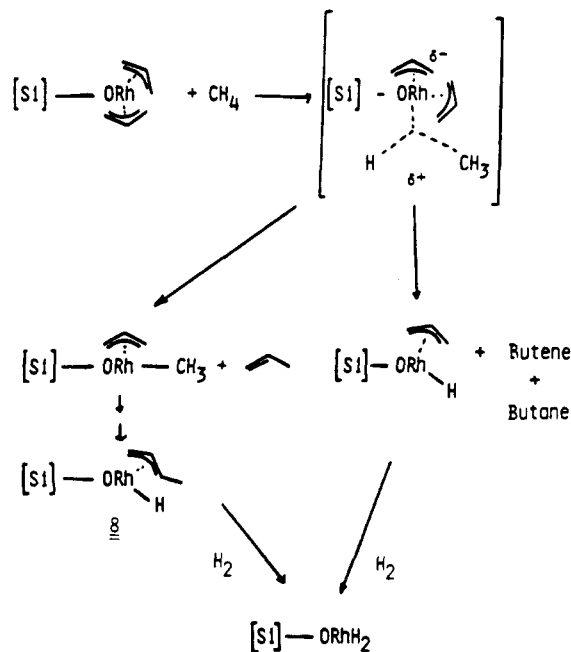
Given that exchange between ethane C-H bonds and protonic -OD centers is noted, we propose that two pathways exist for H/D exchange in ethane but that only a single one exists for H/D exchange in methane. We have called these pathways "hydridic" and "protonic" and they are shown in Scheme V. According to this scheme, activation of methane can be followed only by intramolecular ligand rearrangement to the hydridic center, analogous to our proposed mechanism for H₂ cleavage of Rh-allyl units. Coordination of an alkane such as ethane, however, provides another pathway for activation: electrophilic attack on an α-C-H bond acidifies β-C-H units and, therefore, deprotonation of the coordinated alkane can occur.

Activation of Methane. The notion that methane can be activated by an intramolecular ligand rear-

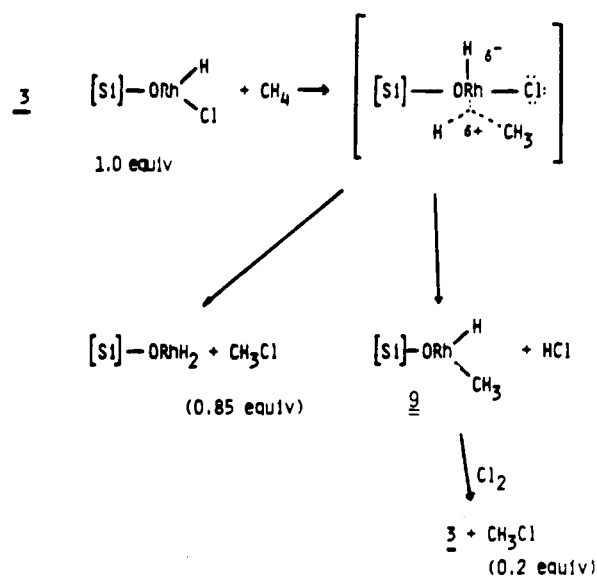
Scheme V.
Two Pathways Exist for H/D Exchange
("Protonic", Fast; "Hydridic", Slow)



Scheme VI



Scheme VII



rangement route from a two-electron, three-centered intermediate analogous to that one proposed for activation of H₂ was utilized to develop a pathway for a chemically interesting conversion of that species to an organic product. We have demonstrated that methane can replace hydrogen in *both* of the hydrogen activation steps shown in Scheme II. For example, when 1 is treated with H₂, 2 results. Similarly we found that when 1 was treated with methane (2 days, 100 °C), a mixture of hydride complexes 2 and 8 were obtained. Propylene and a small amount of butane and butene were also detected. Methanolysis of an aliquot of the resulting organorhodium species gave propane, *butene* and a small amount of hexane. Since protonolysis of 1 is known to yield propane and hexane, the reaction shown in Scheme VI can account for our data (methane activation was proven by use of ¹³CH₄).

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 (9; for the analogous [SiO]Rh(H)Bu, $\nu_{\text{Rh-H}} = 2010 \text{ cm}^{-1}$). Indeed when this material (8) was treated with chlorine, methyl chloride was obtained (0.2 equiv). These observations can be explained by the sequences shown in Scheme VII.

The stoichiometric reactions in Scheme VII suggested the possibility for a catalytic cycle for chlorination of methane using 3. Indeed we found this to be the case.²⁶ Complex 2 also served as the precursor for a catalyst for chlorination of methane (trichloropropane was also obtained). Neither Rh metal prepared from thermolyzed 2 nor conventionally prepared rhodium/silica (from RhCl₃·3H₂O) showed activity for methane chlo-

(26) Kitajima, N.; Schwartz, J. *Proc. Int. Congr. Catal.* 8th 1984, V, 453.

Table II.
Metal-Catalyzed Chlorination of Methane

Catalyst Precursor	Metal Amount (mmol)	Time (h)	CH ₃ Cl (%)	CH ₂ Cl ₂ (%)	CHCl ₃ (%)	CCl ₄ (%)	Total Conversion	Turnover Number x 10 ⁴ (mol/mol-metal/sec)
SiO ₂	-	11	2.5	trace	trace	0	2.5	-
[Si]ORhHCl	0.024	11	12.6	1.1	trace	trace	13.7	1.7
[Si]OAlMe ₂	0.065	11	5.3	0.8	trace	0.4	8.1	0.38
[Si]O ₂ Zr(allyl) ₂	0.024	12	4.7	0.4	0.1	trace	5.2	0.60
[Si]O ₂ Zr(CHCMe ₃) ₂	0.033	11	5.0	trace	0.6	trace	6.2	0.57
*[Si]O ₂ Zr(CHCMe ₃) ₂	0.033	11	5.7	0.6	0.6	trace	6.9	0.63
[Si]O ₂ Mo(allyl) ₂	0.029	10	20.9	8.2	2.3	trace	12.2	3.7
•[Si]O ₂ Mo(allyl) ₂	0.029	10	23.3	17.6	12.5	2.3	55.7	6.4
[Si]O ₂ MoCl ₂	0.029	12	13.8	8.8	trace	trace	15.6	1.5
[Si]O ₂ MoO ₂	0.029	12	23.7	9.6	2.4	trace	35.7	3.4

* Catalyst treated with Cl₂ before adding CH₄/Cl₂ mixture.

Cl₂ = 4 mmol; CH₄ = 1.2 mmol; at 100°C

Catalyst amount = 100 mg

riation. Although the mechanism for the metal-catalyzed reaction has not yet been proven, we believe that it parallels the steps noted in the stoichiometric cases shown in Scheme VII and involves the metal acting as a Lewis acid.

As shown in Scheme VII, the Lewis acidic metal center coordinates a C-H bond and competitive migration of either proton or the alkyl fragment to a ligand in the coordination sphere of metal generates the mixture of products obtained. (Although free radical based chlorination of methane at low conversions also gives a distribution which is high in methyl chloride and low in carbon tetrachloride, relative rates for chlorination of C₁ compounds are different from those reported²⁷ for the free radical case. For example, using 3 relative rates²⁵ for chlorination of CH₄, CH₃Cl, CH₂Cl₂, and CH₃Cl are in the order 1.0, 1.6, 0.5, and 0.4. For free radical chlorination, these relative rates are reported²⁷ to be 1.0, 1.8, 1.3, and 0.6. In both cases, therefore, methyl chloride is more reactive than is methane; for the free radical route, so is methylene chloride. In our case, although methyl chloride is more reactive than is methane, methylene chloride is less reactive than is CH₄.) Using 3 as catalyst, methane conversion to chlorinated products is found to be first with respect to methane, zero order with regard to chlorine pressure, consistent with a mechanism in which alkane activation (either in the coordination step or in the intramolecular rearrangement step) is rate determining and in which chlorine attack upon rhodium complexes is relatively fast.

The mechanism for CH₄ activation shown in Scheme VII does not involve oxidation state changes for the metal in the course of the chlorination sequence. Rather, it simply involves the metal acting as a Lewis acid. Therefore, it seemed likely that other metallic species capable of acting as Lewis acids should also be able to catalyze methane chlorination. Rates would vary according to the electrophilicity of the metal and the ability of the "methane complex" to undergo intramolecular rearrangement. In fact, platinum species in acidic media are well-known to activate alkanes,²⁸ and

we found²⁶ that a variety of silica-bound halometal complexes could catalyze methane chlorination. The most active of these used molybdenum; zirconium(IV) complexes (d⁰), and even an aluminum one ([SiO]AlCl₂) could suffice. The possibility that methane conversion in these sequences results simply from interligand reorganization is tantalizing. It should be possible to replace chloride with other ligands in the coordination sphere of the metal; hence this sequence could provide the basis for conversion of methane to a variety of other interesting organic products formed according to the ligand substitution capabilities of the metal center (Table II).

State of the "Art": Characterization of Complexes

"Homogeneous" catalysis has been greatly abetted by the development of solution NMR techniques which enable details of complex structure to be elucidated. Up to the present, we have had to rely on stoichiometric determinations and primarily vibrational spectroscopic techniques to determine compositions of complexes which we have prepared. Detailed characterization has been hampered by their nonsoluble nature and by their low concentration on the oxide support. Our ability to structurally characterize these species is, therefore, at a stage comparable to that which existed in the "classical" era of structure determination of organometallic compounds before the advent of facile NMR for use in the solution phase in this area. "Magic-angle" NMR techniques may become of use in the future elucidating such structures.²⁹ We have recently found it possible³¹ to obtain some structural information concerning [SiO]-ORhH₂(PMe₃)₃, 6, a nonsoluble analogue of ClRhH₂(PPh₃)₃, by ³¹P NMR investigation of it as a colloidal suspension in benzene. Using Aerosil 300, 6 was prepared containing approximately 4% P by weight. Fourier transform ³¹P {¹H} NMR of this material gave a spectrum containing broad absorptions at

(29) EXAFS may also be useful here. Recently, the structure of (OC)₂Rh/Al₂O₃ was shown to contain three Rh-O interactions (van't Blick, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. *J. Am. Chem. Soc.* 1985, 107, 3139. This structure may be valid for a species of similar composition prepared³⁰ from (allyl)₂Rh/Al₂O₃.

(30) Huang, T.-N.; Schwartz, J.; Kitajima, N. *J. Mol. Catal.* 1984, 22, 389.

(31) Ward, M. D. Ph.D. Thesis, Princeton University, 1981.

(27) Goldfinger, P.; Huybrechts, Martens, G. *Trans. Faraday Soc.* 1961, 57, 2210.

(28) Gol'dschleger, N. F.; Eskova, V. V.; Shilov, A. E.; Shteinman, A. A. *Russ. J. Phys. Chem. (Engl. Transl.)* 1972, 46, 785.

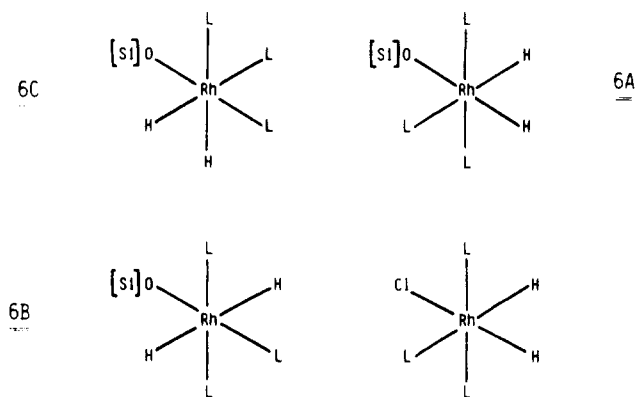


Figure 3. Possible structures for $[\text{SiO}]\text{-RhH}_2\text{L}_3$.

-11.2 and +1.2 ppm (vs. 85% H_3PO_4 as an external reference), and ($\Delta\nu_{1/2} = \sim 400$ and ~ 500 Hz, respectively) in a ratio of 1.8:1, suggesting the presence of two equivalent (upfield) and one unique (downfield) P nuclei (a small amount (ca. 5%) of free PMe_3 was also present). The difference in chemical shifts between free and rhodium-coordinated PMe_3 (ca. 52 ppm) is within the range of values reported for soluble analogues.³²⁻³⁴ The difference between the two coordinated phosphine absorptions ($\Delta\delta = 12.4$ ppm) is also within the range observed for the two types of nonequivalent P nuclei of $\text{ClRhH}_2(\text{PPh}_3)_3$.³² Large phosphorous-rhodium coupling is anticipated, and restricted molecular motion leading to non-average static interactions may likely be the major contribution to line broadening. However, the possibility that a variety of Si-OH sites exist in the support suggests that a family of comparably ligated complex species may be present: these complexes might be similar with regard to ligation geometry about rhodium, but may be different in terms of their local environment on the oxide surface.

These data obtained for the suspension, as imperfect as they are, may be of use in enabling a proposal for the structure of 6. The trans influence of ligands trans to P has been shown to effect relative ^{31}P chemical shifts.^{32,33} Generally, the chemical shift of ^{31}P moves downfield for the series of trans ligands $\text{Cl} > \text{P} > \text{H}$. Thus, structure 6A should exhibit a spectrum in which the unique P nucleus is *upfield* of the trans pair as is reported for $\text{ClRhH}_2(\text{PPh}_3)_3$.³² We prefer 6c as it obviates the unfavorable presence of trans dihydride ligands (assuming that $[\text{SiO}]$ is approximately equal to Cl in the "trans influence" series). Structure 6c may be preferable to 6A (a formal, supported analogue of ClRhH_2L_3 in which the oxide replaces Cl) for steric reasons, as interactions of the PMe_3 ligands with the bulky "silica ligand" are minimized in the former structure (Figure 3).

Homogeneous or Heterogeneous? Throughout this discussion little attention has been paid to the relegation of our oxide-bound complexes to either the classical

"homogeneous" or "heterogeneous" categories. Conventionally, the criterion of *solubility* is that which is used to categorize classical "homogeneous" and "heterogeneous" systems, and these classical contexts in fact refer to reactions from the perspective of the chemist, i.e., the presence of catalyst and substrate in one or more phases. Another perspective on the reaction is that one from the point of view of the substrate molecule: does it encounter one type of active site or does it encounter many? A better consideration for defining a catalyst as "homogeneous" therefore may be that one relating to its possessing only a single type of active site, and in fact, we prefer to describe these species as "homogeneous, yet insoluble" entities.

A "Marriage of Convenience". Does the use of an oxide support simply constitute a "marriage of convenience"? Such marriages exist when catalyst species are reversibly bound to an insoluble support: the catalyst species perform their role in solution and are removed from the reaction medium upon reattachment to that support.³⁵ The oxide-bound complexes described herein do not fit this "definition" of a marriage of convenience in that they perform their role *chemically bound* to the oxide;³⁹ they are complexes in an oxygen-based ligand environment:

This environment apparently stabilizes the metal in its "harder" or higher valent form.

The oxide ligand can immobilize bound complexes (and facilitate recovery from a reaction medium) and inhibit clusterification; this can be used to advantage, for example, for olefin^{6,36} or, especially, arene^{36,37} hydrogenation.

A high-valent complex in a coordinatively unsaturated environment is apparently electrophilic; this, in turn, can be put to advantage in the context of alkane activation.

To create an "ensemble catalyst" by attaching an active metal complex to a support which itself is structurally modifiable is an especially appealing concept. As in any good "marriage" synergy, here the interplay between reactivity patterns for the bound metal complex and physical properties of the support, can be exploited to maximize reactivity or selectivity for the couple in ways not possible to accomplish for the partners acting alone.³⁸ It is perhaps this aspect of oxide-bound metal complexes which holds the greatest allure for future research endeavors in this field.

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(32) Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* 1974, 96, 2762.

(33) Brown, T. H.; Green, P. J. *J. Am. Chem. Soc.* 1970, 92, 2359.

(34) Grim, S. O.; Wheatland, D. A. *Inorg. Chem.* 1969, 8, 1716.

(35) For example, see: Gates, B. C. *J. Catal.* 1975, 40, 255.

(36) Huang, T.-N.; Schwartz, J. *J. Am. Chem. Soc.* 1982, 104, 5244.

(37) Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* 1981, 103, 5253.

(38) For one such example, in the case of zeolite-encapsulated catalyst complexes, see ref 34.