fraction) was sampled for an infrared spectrum.

Results and Discussion

The infrared studies show that silyl group exchange between chlorosilane and *N*-methyldisilazane is complete within 10 min at ambient temperature. No convergence of silyl group resonances is detectable in the NMR spectrum of a mixture of the two, allowing a lower limit of the half-time of exchange to be calculated according to the formula[10]

$$t_{1/2} = \frac{2^{1/2}}{2\pi(\nu_A - \nu_B)} \quad \text{(valid when resonances coalesce)}$$

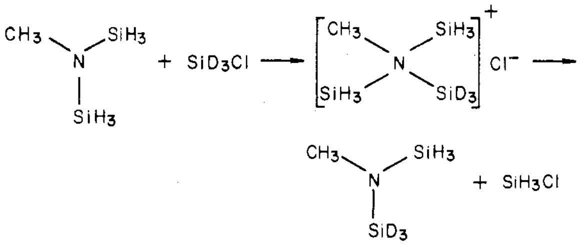
Since $\nu_A - \nu_B = 16.4$ Hz, the half-time of exchange at 40 °C is greater than 0.01 s.

An NMR spectrum of a mixture of SiD_3Cl and $(SiH_3)_2NCH_3$ showed immediate equilibration of silyl groups at −50 °C. However, no tendency toward coalescence of silyl group resonant frequencies was detectable at even 100 °C, indicating a very low activation energy for the exchange process.

In the SiD_3Cl–$(SiH_3)_3N$ system, no exchange of any type was detected at room temperature after 1 week at 25 °C. At elevated temperatures (73–93 °C) exchange was slow, and analysis of the infrared spectra of the chlorosilane fractions indicated the presence of partially deuterated species, suggesting hydrogen exchange. The possibility of silyl group transfer cannot be dismissed, however, as it was found in separate experiments that SiD_3Cl and SiH_3Cl slowly undergo hydrogen scrambling at comparable temperatures, as do $(SiD_3)_3N$ and $(SiH_3)_3N$. Thus silyl group exchange between SiD_3Cl and $(SiH_3)_3N$ could lead to a statistically scrambled mixture of partially deuterated chlorosilane moieties via either or both of the above routes.

The marked difference in the rates of silyl group exchange of chlorosilane with the two amines is further evidence for the increased basicity of$(SiH_3)_2NCH_3$ over $(SiH_3)_3N$. Any intermediate or transition-state complex involving a tetravalent nitrogen would require a lower activation energy in the case of $(SiH_3)_2NCH_3$ than in $(SiH_3)_3N$ if the lone pair of electrons on the nitrogen atom in the amines is involved in internal dative bonding to the 3d orbitals of the silicon atoms. The planarity of the Si_3N skeleton in $(SiH_3)_3N$[11] confirms the existence of such Si–N dπ–pπ bonding. The presence of three silyl groups would allow a more effective withdrawal of this electron density than would two, suggesting a greater energy of hybridization to form a tetravalent nitrogen atom.

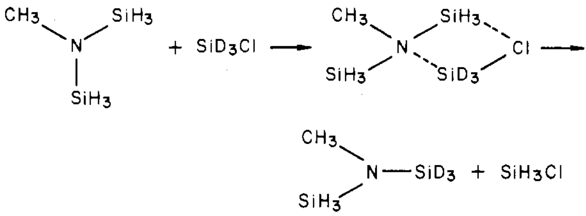
A mechanism involving the formation of a quaternary intermediate is conceivable (eq 1). Quaternary ammonium type compounds containing only one or two silyl groups such as silyltrimethylammonium iodide and disilyldimethylammonium chloride have been obtained,[5,12] although the disilyl-substituted species is unstable and decomposes readily.



(1)

Another possible mechanism would involve a four-center transition state followed by an unsymmetrical withdrawl (eq 2). Bimolecular complexes of $(SiH_3)_2NCH_3$ molecules involving five-coordinate Si and four-coordinate N atoms have been hypothesized[13] in the base-catalyzed decomposition of $(SiH_3)_2NCH_3$.

The former mechanism ought to be favored in a polar solvent. When deuterated acetonitrile was used as a solvent in a 2:1 mixture of SiH_3Cl and $(SiH_3)_2NCH_3$, the NMR spectrum again showed no tendency toward coalescence of the silyl hydrogen resonances.[14]



(2)

The mass spectral results show that the liquid phase is not necessary for silyl group exchange, in sharp contrast to a number of redistribution and elimination reactions involving compounds containing the silyl group attached to a group 5A element.[15–19]

These latter two factors both indicate a preference for the second mechanism. The rapidity of the exchange plus the lack of any detectable association in the gaseous phase shows the kinetic and thermodynamic instability of either proposed complex.

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Registry No. Chlorosilane-d_3, 13637-82-6; *N*-methyldisilazane, 4459-06-7; trisilazane, 13862-16-3.

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A Molecular Orbital Analysis of the Oxidative Addition of Hydrogen to the Chlorotris(triphenylphosphine)rhodium(I) Complex

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The oxidative addition of molecular hydrogen to four-coordinate d^8 square-planar transition-metal complexes is an important reaction per se as well as in connection with homogeneous hydrogenation.[1,2] Spectroscopic results and kinetic

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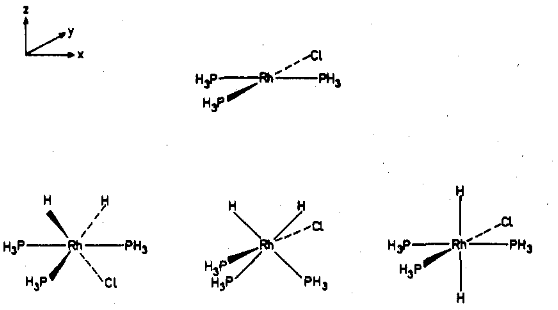


1 2 3

Figure 1. The parent $RhCl(PH_3)_3$ complex and the three octahedral stereoisomers of the dihydrido $H_2RhCl(PH_3)_3$ complex.

Table I. Total and Relative Energies of the Three Possible Octahedral Isomers of $H_2RhCl(PH_3)_3$ Obtained from ab Initio Calculations

isomer	total energy, au	rel energy, kcal/mol
1	−6159.5084	0
2	−6159.4896	11.8
3	−6159.4815	16.9

studies are consistent with the addition of H_2 being a concerted process leading to a cis adduct. The reaction is symmetry allowed[3,4] and in many cases it occurs rather readily (with $IrCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$ it is reversible with an activation energy of about 10 kcal/mol[5–7]) although breaking of a H–H bond—a highly endothermic process of 103 kcal/mol for the H_2 molecule[8]—is involved. Two possible ways for the activation of hydrogen were proposed many years ago, either transfer from bonding electrons of H_2 into a vacant d metal orbital[9] or transfer of electrons from an occupied metal d orbital to the antibonding orbital of H_2.[7,10] Surprisingly none of these proposals seems to have been studied so far theoretically. We hereafter present a molecular orbital analysis of the reaction

$$H_2 + RhCl(PH_3)_3 \rightleftarrows H_2RhCl(PH_3)_3$$

where $RhCl(PH_3)_3$ stands as a model[11] for the chlorotris(triphenylphosphine)rhodium(I), the well-known Wilkinson catalyst[7] (the oxidative addition of H_2 to $RhCl(PPh_3)_3$ is one of the possible first steps of the catalytic cycle leading to the hydrogenation of olefins[2]). Our qualitative conclusions are derived from a fragment molecular orbital analysis based on extended Hückel calculations.[15,16] Preliminary ab initio LCAO–MO–SCF calculations[21] have also been carried out in order to get more quantitative information.

Results and Discussion

For the dihydrido complex $H_2RhCl(PH_3)_3$ three octahedral stereoisomers **1**, **2**, and **3** are possible. They are shown on Figure 1 together with the parent complex $RhCl(PH_3)_3$. **1** and **2** can be viewed as the result of a cis addition of H_2 to $RhCl(PH_3)_3$ with bending of either the (PH_3)–Rh–Cl moiety or the (PH_3)–Rh–(PH_3) moiety, respectively. Isomer **3** would result from a trans addition of H_2 (which is symmetry forbidden[3,4]). The results of the SCF calculations (Table I) indicate that isomer **1** in which the hydrogen atoms are cis to each other and the phosphine ligands are in the *meridional* arrangement is the most stable one.[26] This is in agreement with the experimental results from NMR spectra[27–30] and from some X-ray crystal structures of closely related complexes, $[H_2Rh(CO)(PPh_3)_3]^+$ [31] and $[H_2Re(NO)(PPh_3)_3]$[32] (the higher stability of **1** can be traced to steric interactions when compared to **2** and to orbital interactions when compared to **3**[33]). According to these results the cis addition leading to isomer **2** is unlikely. In the following, we shall therefore restrict ourselves to the case of an oxidative addition leading to isomer **1**. Only the side-on approach (i.e., keeping H–H parallel to the *y* axis, see Figure 1) has been considered, although other pathways are possible: a rough determination of the potential energy surface (through extended Hückel calculations) indicates that, at the beginning of the reaction, the end-on approach (with H–H collinear to the *z* axis, see Figure 1) seems to be preferred over the side-on approach.[33,34]

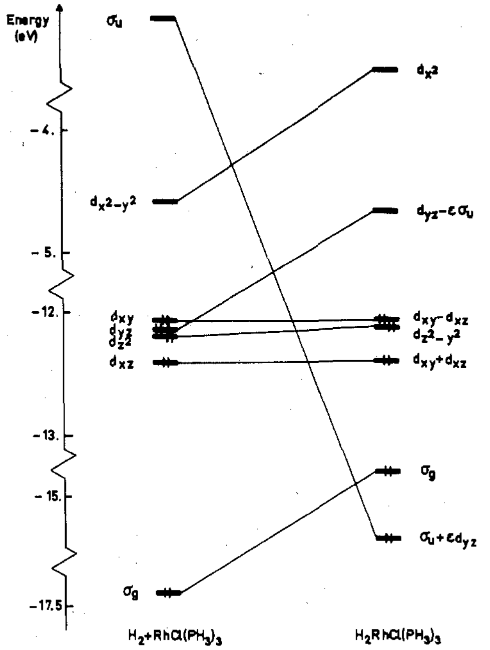
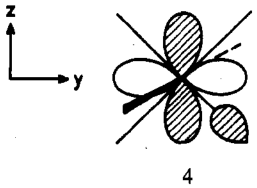


Figure 2. Correlation diagram (based on extended Hückel calculations) between the H_2 + $RhCl(PH_3)_3$ and $H_2RhCl(PH_3)_3$ systems.

When the incoming H_2 molecule approaches the square-planar complex, it is generally assumed that the two in-plane bonds (we refer here to the plane formed by Rh and H_2) bend away from the two hydrogen atoms, thus leading to the six-coordinate adduct of pseudo-O_h symmetry. Indeed extended Hückel calculations show this behavior. Our purpose here is not to discuss the path of the reaction (this will be done in a subsequent paper[33]) but to sort out the factors accounting for its feasibility. This is done with the aid of the correlation diagram (Figure 2) between the valence orbitals of the reactants H_2 + $RhCl(PH_3)_3$ and of the product $H_2RhCl(PH_3)_3$.

Three metal d orbitals of the occupied set of $RhCl(PH_3)_3$ (d_{xz}, d_{xy}, and d_{z^2}) do not change significantly in energy and form the occupied set of the $H_2RhCl(PH_3)_3$ complex. The d_{xz} and d_{xy} orbitals which were nonbonding (with respect to σ donation) in the square-planar complex remain nonbonding throughout the course of the reaction (with our chosen coordinate system they just mix each other). The d_{z^2} orbital which was metal–ligand σ antibonding in the square-planar complex becomes the $d_{z^2-y^2}$ nonbonding orbital in the octahedral complex (by mixing in the $d_{x^2-y^2}$ orbital). One would then expect a stabilization of this level. However the loss of the σ antibonding (**4**) is balanced by the gain in π antibonding (**5**) with the Cl π-donor orbital. The fourth metal d orbital (d_{yz}) which was nonbonding (with respect to σ donation) in



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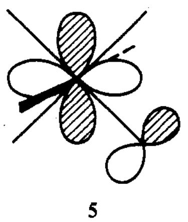

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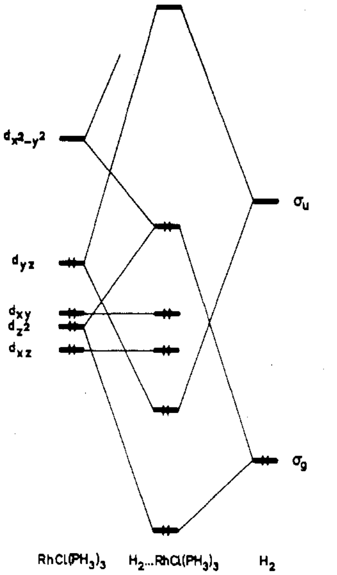
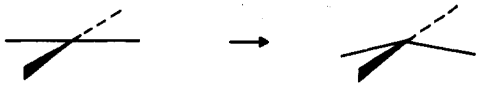


Figure 3. Interaction diagram for an intermediate point between the reactants and the product (see text for the corresponding geometries).

the square-planar complex becomes antibonding and is therefore highly destabilized.

The same trends in the metal d levels are observed in the four-coordinate complex $RhCl(PH_3)_3$ for the pseudo-D_{4h} → pseudo-C_{2v} (**6**) distortion, namely, destabilization of the d_{yz} level and insensitivity to the distortion of the other occupied levels. This has also been noted by Elian and Hoffmann when comparing the $M(CO)_4$ and MCl_4 systems.[35]



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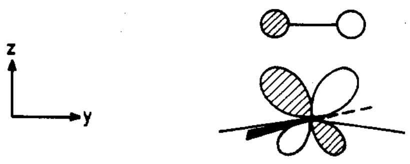
Of the two orbitals of the incoming ligand H_2, the σ_g bonding orbital is destabilized since the H–H distance has increased. For the same reason the σ_u antibonding orbital is stabilized. Furthermore the two-electron bonding interaction of σ_u with d_{yz} (**7**) adds to the stabilization (see below). The correlation diagram of Figure 2 indicates that the σ_u orbital would cross the d_{yz} orbital. However, these two orbitals do overlap and are therefore strongly mixing in as shown on the interaction diagram of Figure 3 between a stretched H_2 fragment (H–H = 1.5 Å) and a $RhCl(PH_3)_3$ complex distorted toward a pseudo-C_{2v} symmetry (∠Cl–Rh–P = 130°), the Rh–H distance being 1.8 Å. Consequently the crossing is avoided.[36] Whether or not this avoided crossing of the two orbitals leads to a small barrier[37] is difficult to decide on the basis of extended Hückel calculations only.[38] Calculations carried out on discrete points located on the reaction path seem to indicate that the corresponding barrier, if any, will be rather small.



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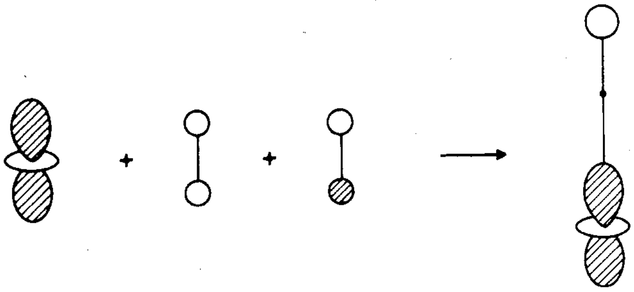
Indeed the mixing of the d_{yz} and σ_u orbitals is the key point for the activation of the hydrogen molecule, since the corresponding interaction (see Figure 3) is a two-electron stabilizing interaction. Two factors should be considered in this respect: (i) increasing the H⋯H distance lowers the σ_u level of the H_2 fragment; (ii) distorting the $RhCl(PH_3)_3$ fragment, as shown in **6**, in addition to reducing the steric repulsion with the incoming H_2, destabilizes and hybridizes the d_{yz} orbital (see **7**) in such a way that its overlap with σ_u is increased.[39] Therefore due to larger overlap and better energy match, the interaction between the two orbitals is enhanced and the $d_{yz} + \sigma_u$ combination stabilized further.

Concurrently with the two-electron stabilizing interaction there is a four-electron destabilizing interaction between the d_{z^2} orbital of $RhCl(PH_3)_3$ and the σ_g orbital of H_2. This also appears clearly from the interaction diagram of Figure 3 and we trace the barrier of the reaction to this interaction. However, the antibonding combination $d_{z^2}-\sigma_g$ is somewhat stabilized through the interaction with $d_{x^2-y^2}$. This interaction was already present in the distorted $RhCl(PH_3)_3$ fragment but to a lesser extent: because of a better energy match between $d_{x^2-y^2}$ and $d_{z^2}-\sigma_g$ this interaction is larger, leading to a $d_{z^2-y^2}$ nonbonding orbital and hence a moderate energy barrier. Note that if the d_{z^2} orbital is higher in energy, its interaction with σ_g will be lessened and a decrease in the energy barrier is therefore expected. This is in agreement for instance with a greater reactivity of iridium complexes[40] where the d orbitals are higher in energy (moreover since d_{yz} is also higher in energy in the iridium complexes, its stabilizing interaction with σ_u will be enhanced). The same type of argument can be used to predict that the cis addition leading to isomer **2** might have a greater activation energy: bending the (H_3P)–Rh–(PH_3) moiety could lead to a stabilization of the d_{z^2} level since there is no balance in the loss of σ antibonding. A greater destabilizing interaction between d_{z^2} and σ_g is therefore expected. This may be balanced, however, by a greater stabilizing interaction between the σ_u and d_{xz} orbitals (the addition taking place in the *xz* plane, see Figure 1) since the d_{xz} orbital is more destabilized and hybridized by two σ donors like PH_3.

The same qualitative conclusions emerge from our SCF calculations carried out on discrete points of the energy surface. These calculations also indicate that the end-on approach is preferred over the side-on approach at the beginning of the reaction;[41] in this approach the σ_u orbital of H_2 and the antibonding combination $d_{z^2}-\sigma_g$ are allowed to mix giving rise to a $d_{z^2} - \epsilon\sigma_g + \epsilon\sigma_u$ nonbonding level (**8**).[42] The SCF calculations (like the extended Hückel calculations) yield, however, H⋯H distances which seem to be too short (between 0.8 and 0.9 Å), especially near the transition state. This may be due to a poor description of the wave function along the reaction path by a single determinant, since the single determinant wave function may be schematically described (considering only the in-plane valence orbitals) as $(d\sigma)^2(d_{yz})^2(\sigma_g)^2$ for the reactants and as $(d\sigma)^2(\sigma_u)^2(\sigma_g)^2$ for the product. A DC-SCF wave function with these two configurations would certainly be a better description of the wave function. Work along these lines is now in progress.[33] It is interesting to note, however, that little H–H bond breaking in the transition state for the addition reaction H_2 + $IrCl(CO)(PPh_3)_2$ has been suggested[1b] on the basis of a small kinetic isotope effect[28] when D_2 is added instead of H_2. Furthermore the geometry of the transition state is expected



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to be close to the one of the reactants for this exothermic reaction.[43]

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Registry No. **1**, 71213-98-4; **2**, 71213-97-3; **3**, 71171-41-0; $RhCl(PH_3)_3$, 71171-40-9; $RhCl(PPh_3)_3$, 14694-95-2.

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(41) For a Rh–H distance of 2.2 Å and a H–H distance of 0.8 Å (these two distances may be considered as representative of the beginning of the reaction) and a planar $RhCl(PH_3)_3$ entity the SCF energies of the linear end-on and perpendicular side-on geometries were computed to be −6159.5245 and −6159.5046 au, respectively, i.e. a difference of 12.5 kcal/mol.

(42) This is essentially a polarization effect. Some S_N2 type of addition of RX or trans addition of HX in polar solvent could be accounted for by the end-on approach and this polarization effect.

(43) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

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Reaction of 1,8-Bis(dimethylamino)naphthalene, a Highly Basic and Weakly Nucleophilic Amine, with Several Polyboranes and with Boron Trifluoride

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Whereas strong bases such as OH^-, H^-, CH_3^-, and $(C_6H_5)_3P{=}CH_2$ readily deprotonate $B_{10}H_{14}$, weaker bases, L, such as acetonitrile and dialkyl sulfides react with this polyborane to form the bis adduct $L_2B_{10}H_{12}$ accompanied by the liberation of H_2.[1] There is some suggestion that the intermediate base strength tertiary amines deprotonate $B_{10}H_{14}$[2] although further reaction can also take place[3] to give $[R_3NH]^+[R_3N{-}B_{10}H_{13}]^-$ and eventually $(R_3N)_2B_{10}H_{12}$ with the liberation of hydrogen.[4,5] The outcome of B_2H_6 reactions with amines is considerably dependent on the nature of the base. Ammonia promotes the formation of the salt[6] $[(H_3N)_2BH_2^+][BH_4^-]$ whereas simple trialkylamines combine with B_2H_6 to give only the borane adduct $R_3N{\cdot}BH_3$.[7] Certain chelating species in which donor sites are favorably disposed such as in the N-methylated *o*-phenylenediamine produce salts from diborane[8] similar in structure to the salt obtained from ammonia and diborane.

1,8-Bis(dimethylamino)naphthalene is a remarkably strong base, pK_a = 12.3, for an aromatic amine, with steric factors dictating weak nucleophilic behavior. Relief of molecular strain in the neutral molecule upon protonation, as well as intramolecular hydrogen bonding, is thought to contribute to the high pK_a.[9–11] The present study examines the reactions of 1,8-bis(dimethylamino)naphthalene with a cross section of polyboranes, B_2H_6, B_5H_9, and $B_{10}H_{14}$, as well as with BF_3 in order to establish competitive preferences of this amine toward adduct formation, proton abstraction, or amine-complexed boronium ion/borohydride ion salt formation.

Experimental Section

Materials. 1,8-Bis(dimethylamino)naphthalene (sold as proton sponge) was obtained from Aldrich Chemical Co., $B_{10}H_{14}$ from K and K Laboratories, B_5H_9 from Callery Chemical Co., and B_2H_6 from Olin Mathieson Chemical Corp.

Nuclear Magnetic Resonance Data. Both the ^1H and ^{11}B NMR spectra were obtained on a HA-100 spectrometer operating at 100 and 32.1 MHz, respectively; boron-11-decoupled ^1H spectra at 100 MHz were observed while irradiation was done at 32.1 MHz by using