Metal−Silane Interaction in the Novel Pseudooctahedral Silane Complex *cis*-Mo(CO)(PH_3)$_4$(H···SiH_3) and Some Related Isomers: An *ab Initio* Study

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Abstract: *Ab initio* calculations at the second-order Mϕller-Plesset perturbation theory (MP2) level have been performed on the *cis* and *trans* isomers of the title model complex. For the *cis* isomer, the optimized structure shows a H···Si interaction distance of 1.813 Å, in close agreement with the experimental value of 1.769 Å for *cis*-Mo(CO)(depe)$_2$(H···$SiHPh_2$). Analysis of the density Laplacian ($\nabla^2\rho$) around the Mo−(H···Si) triangle reveals a predominantly covalent Mo−Si bond and a likely dative $H^- \rightarrow$Mo bond, with a heavily curved H···Si bond path, suggesting that the H···Si covalent interaction is severely weakened. The *trans* structure is 9.9 kcal/mol less stable than the *cis* isomer, caused by the competition of metal d-electrons between CO and H···Si, and is manifested by the shorter H···Si distance of 1.715 Å. The inability to locate a stable 7-coordinate structure with a H···Si distance greater than 2.5 Å suggests that a classical−nonclassical tautomerism analogous to that in some dihydrogen complexes seems not very likely, and the optimized structure for a pentagonal bipyramidal 7-coordinate isomer with H and Si not neighboring is 6.5 kcal/mol less stable than the observed *cis* isomer. Study of the rotation of the H···Si unit around the Mo−(H···Si) "bond" gives a rotation barrier of about 10 kcal/mol caused by the competition of Mo d-electrons for back-bonding similar to that for the *trans* isomer. On the basis of molecular orbital arguments, both the Mo complex and the widely studied piano-stool complexes Mn(Cp)(CO)$_2$(H···SiR_3) can be regarded as pseudooctahedral d^6-ML_6 which is a particularly stable class of complexes. The difference of the nature of bonding between H−H and H−Si complexes is also discussed in terms of orbital interaction.

Introduction

The subject of C−H bond activation has become an intensive area of research for more than three decades,[1] due to the tremendous interest in converting saturated hydrocarbons in petroleum to useful products, and a number of catalytic C−H cleavage processes involving transition metal complexes have been developed.[2] While the detailed reaction pathway is still not clear, extensive studies of the analogous BH_4^- [3] and $HSiR_3$[4] coordinations to transition metal centers have resulted in the understanding of the possible crucial reaction steps and intermediates for CH_4 coordination and activation. Gas phase studies of methane interaction with bare metal atoms show similarity with the well-known η^2- or η^3-BH_4^- complexes with M−H−B bridges (with or without M−B interactions),[5] while the agostic C−H interaction with metals suggests possible η^2-C−H σ coordination modes.[6] In this sense the recognition of η^2-H−SiR_3 complexes is extremely important since Si is in the same group as C.

Apart from serving as a model of C−H bond activation, η^2-H−SiR_3 complexes are also an important subject of organometallic catalysis in its own right.[7] In comparison with the widely studied "nonclassical" dihydrogen complexes,[4c,8] silane complexes with the H−Si σ bond coordinated to the metal center have long been suggested as possible intermediates of hydrosilation. The existence of H···Si interaction in hydrosilyl complexes has been recognized since 1969,[9] which was surprisingly earlier than the discovery of the first nonclassical dihydrogen complex W(CO)$_3$(P-*i*-Pr_3)$_2$(H−H) in 1984.[10] Since then a large number of piano-stool complexes (with cyclopentadienyl or arene ligands) with close H···Si[11] interaction distance of less than 2.5 Å[4,12] have been synthesized, and a few

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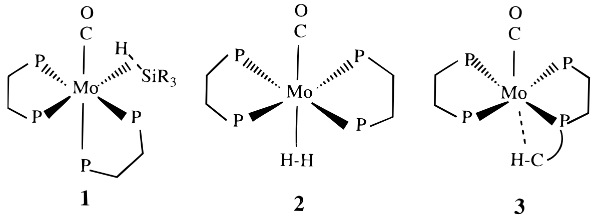

Figure 1. *cis* vs *trans* coordination of H−X (X = SiR_3, H, C) in the silane complex **1** and the dihydrogen complex **2** and the agostic C−H interaction in **3.**

were precisely characterized by neutron diffraction, confirming the short $H\cdots Si$ contact in these complexes. An extended Hückel theoretical study on the model system $MnCp(CO)_2(H\cdots SiH_3)$[13] suggested that a σ bonding−back-bonding model similar to the Dewar−Chatt model for the well-known π complexes can be applied to this group of piano-stool $H\cdots Si$ complexes.

The recent synthesis and X-ray diffraction study of the pseudooctahedral molybdenum complexes $Mo(CO)(P{-}P)_2(H\cdots SiR_3)$[14] **1** (P−P = depe, $SiR_3 = SiHPh_2$;[14a] P−P = dppe, $SiR_3 = SiH_3$[14b]) provide the first examples of a non-piano-stool mononuclear d^6 octahedral complex with a *single* $H\cdots Si$ interaction. The syntheses and characterizations of two analogous η^2-H_2 complexes with the same metal fragment[15] allow a useful comparison between $H\cdots H$ and $H\cdots Si$ coordination. An intriguing feature of the silane complexes **1** is that the $H\cdots Si$ moiety is *cis* to the carbonyl. This is in contrast to the known transition metal carbonyl dihydrogen complexes,[10,16] for example, $Mo(CO)(depe)_2(H_2)$, **2**, and complexes with agostic C−H interactions, e.g., $Mo(CO)(dppe)_2$, **3** (with Mo in close contact with one of the phenylic C−H bonds of about 2.8 Å),[17] where one carbonyl is always found to be *trans* to the σ-coordinated ligand (Figure 1). This indicates important differences of the nature of bonding between $H\cdots H$ and $H\cdots Si$ complexes.

In this work we provide *ab initio* studies of the model complex *cis*-$Mo(CO)(PH_3)_4H(SiH_3)$ and some of its hypothetical isomers. The structure, orbital interaction, and nature of the Mo−H−Si triangular interaction will be emphasized. The observation that only the *cis* isomer is formed will be explained. Comparisons with the widely studied pseudo-three-legged piano-stool silane complexes will be made, and the difference of the nature of bonding between dihydrogen and silane complexes will be discussed. We hope this work will arouse further interest in the study of silane coordination as a model of C−H bond activation.

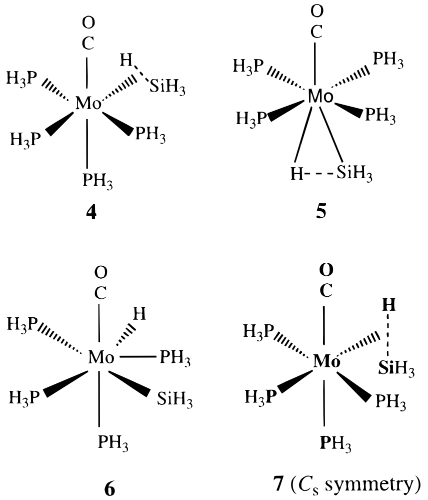

Figure 2. The four isomeric structures **4**−**7** of $Mo(CO)H(SiH_3)(PH_3)_4$ considered in this work.

Computational Details

Four isomers of the model complex $Mo(CO)(PH_3)_4H(SiH_3)$ were considered, as shown in Figure 2, where the two chelating diphosphines in the experimental complexes were replaced by four PH_3 ligands for theoretical simplicity. Some theoretical studies of the effect of using PH_3 instead of the realistic organic phosphines show that this simplification will lead to an error of 3 kcal/mol for the relative energies,[18,19] and thus the conclusions below will not be qualitatively affected by the above simplification. Structure **4** corresponds to the experimentally observed complex with the $H\cdots Si$ moiety *cis* to the carbonyl and with the two moieties mutually perpendicular, while $H\cdots Si$ was *trans* to CO in **5**. For the pentagonal bipyramidal structure **6** any possible $H\cdots Si$ interactions were precluded by the intervening phosphine. In structure **7**, an overall C_s symmetry was defined by the plane containing both CO and $H\cdots Si$ bonds, thus making the two moieties lie on the same plane.

Previous theoretical studies on polyhydride complexes have concluded that *ab initio* optimization at the second-order Mϕller−Plesset purturbation theory (MP2) level with effective core potentials (ECPs) and double-ζ valence basis sets provides reasonable predictions on the structures and stabilities of classical and nonclassical H_2 coordination for second- and third-row transition metal complexes.[18] In the present study the atoms Mo, Si, and P were described by the ECPs of Wadt and Hay[20] with a double-ζ valence shell, and the standard 6-31g basis sets were used for C, O, and H. A single unscaled d polarization function with exponent 0.262 was added to Si.[21] The basis set described here is assigned as BS1. Using this basis set, all geometries were optimized at the MP2 level involving all geometric parameters within the overall symmetries specified; i.e., no local symmetry or structural constraints were imposed.

Although the BS1 basis set reproduces, as will be shown later, experimental molecular geometries well, one might be concerned with the importance of polarization functions of phosphorus atoms (of the phosphine ligands) on the overall balance of

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Table 1. Bond lengths (Å), Bond Angles (deg), and Relative Energies (kcal/mol) for the Four Isomers of Mo(CO)(PH$_3$)$_4$H(SiH$_3$) Compared with those of the Experimental Complex **1**

	1 (exptl)	4	5	6	7
C≡O	1.189	1.229	1.217	1.234	1.215
Mo−C	1.932	1.944	1.988	1.932	1.973
Mo−P$_{cis}$	2.446−2.491	2.513−2.518	2.486−2.490	2.492−2.535	2.484
Mo−P$_{trans}$−HSi	2.548	2.551	N/A	N/A	2.540
Mo−P$_{trans}$−CO	2.549	2.569	N/A	2.555	2.578
Mo−Si	2.501	2.563	2.631	2.595	2.580
Mo−H	1.695	1.753	1.794	1.769	1.753
H···Si	1.769	1.813	1.715	4.041	1.754
C−Mo−Si	73.0	79.9	153.4	94.4	109.5
C−Mo−H	92.0	95.7	153.4	99.9	66.9
C−Mo−P$_{trans}$−CO	170.3	172.4	N/A	176.9	167.5
rel energy	N/A	0.0	9.9	6.5	10.7

bonding−back-bonding interactions. Therefore, a much better basis set (BS2), which supplements the BS1 basis set with polarization functions on those atoms directly attached to the molybdenum center (i.e., 6-31g** for C and H, and d functions of exponent 0.34 on all the P atoms[21]), was used to calculate the SCF electron density for use by the Laplacian analysis.

Ab initio calculations were performed using the *Gaussian 94* software[22] on a Silicon Graphics Onyx and a Hewlett-Packard 750/100 workstation, and electron density analysis was done with the AIMPAC package[23] on a Silicon Graphics Indigo2 workstation.

Results and Discussion

Structure and Molecular Orbital Analysis of *cis*-Mo(CO)(PH$_3$)$_4$H(SiH$_3$). The MP2-optimized structure for the model complex **4** is shown in Figure 2, which can be directly compared to the experimental complex *cis*-Mo(CO)(dppe)$_2$(H···SiHPh$_2$), in which the coordinated hydrogen atom is located by X-ray crystallography.[14a] The important bond lengths and angles are summarized in Table 1. All relative structural parameters in the experimental complex are preserved in the calculated structures: the phosphines *trans* to the carbonyl and H···Si moiety have larger Mo−P distances (~2.56 Å) than the others (~2.51 Å), which is indicative of the *trans* influence of the π-accepting carbonyl and the σ*-accepting[24] H···Si moiety. Of closer resemblance is the geometry of the Mo−(H···Si) triangle. The H−Mo−Si angle is about 45°, and the H···Si interaction distance is 1.813 Å, in very good agreement with the experimentally determined 1.769 Å. Therefore, one can have confidence in the reliability of MP2 optimization in reproducing the H···Si distance typical of the observed nonclassical hydrosilane complexes (1.65−1.85 Å).

A qualitative molecular orbital (MO) interaction diagram of the metal fragment and the H−SiH$_3$ moiety is presented in Figure 3. Both the experimental and the MP2 optimized geometries of the Mo(CO)(PH$_3$)$_4$ unit can be very well approximated by a square pyramidal d^6-ML$_5$ fragment derived from an octahedron, since all the L−M−L angles (except the OC−Mo−Si angle, which is significantly smaller than 90° as noted in Table 1) are close to 90°. The metal fragment provides a nonbonding "t_{2g}" set (two of them being stabilized by the two accepting π* orbitals of CO) and a hybridized a$_1$ frontier orbital directed toward the H···Si moiety.[25] If the silane is regarded as a single coordination unit, the H···Si moiety provides a σ bonding and an σ* antibonding orbital. As shown in Figure 3, the a$_1$ orbital interacts with the σ bonding orbital of H···Si, and the d$_{xy}$ orbital of the t_{2g} set interacts with the σ* orbital of H···Si, which is similar to the π* back-bonding orbital in the more familiar π complexes (with the π* replaced by the σ* orbital). Such back-bonding fills the σ* antibonding orbital of H···Si and tends to break the bond. In this sense the orbital interaction diagram bears a close relationship with the Dewar−Chatt model of π complexes.

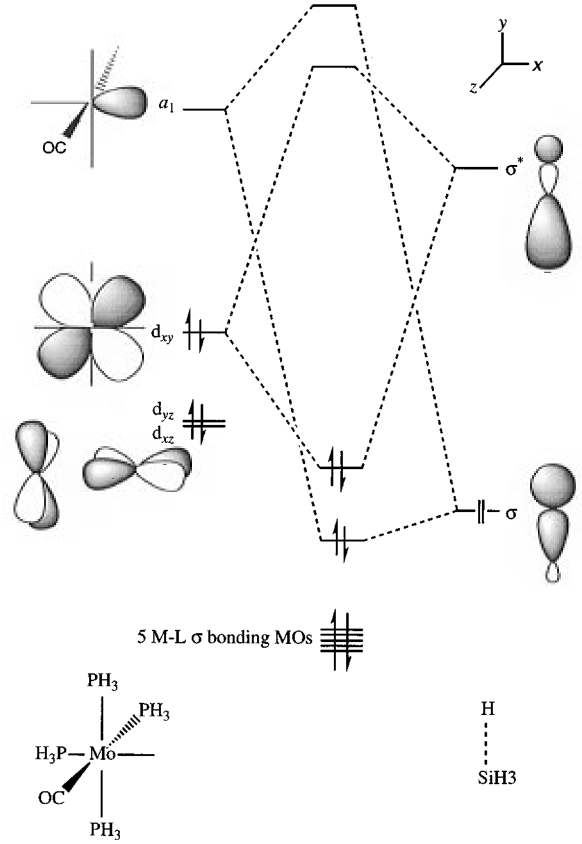

Figure 3. Qualitative molecular orbital interaction diagram for **1** (or **4**).

Coordination Environment around Si. When one treats the silicon to be bonded to four hydrogens and the molybdenum

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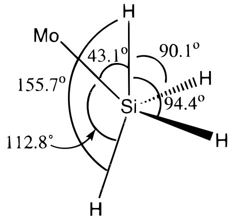

Figure 4. Coordination environment around Si in **4**.

center, a highly distorted trigonal bipyramid (TBP) results, typical of 5-coordination, with the coordinated H occupying one of the axial positions (Figure 4). A TBP coordination around Si is also observed in several hypervalent silicon compounds.[26] It has been recognized that, in such hypervalent compounds, the presence of one or more electronegative ligands allows the electrons in excess of the octet to be localized around the ligands, and hence they do not contribute to the valence shell of the central atom.[27]

To examine the significance of the hypervalence of Si in the H···Si interaction, we have reoptimized structure **4** with the d polarization function on Si removed. The H···Si interaction distance becomes 1.953 Å, which is significantly longer than that of the experimentally determined 1.769 Å, even allowing for experimental errors in the location of H. Thus, the d polarization function on Si is vital in the accurate determination of the H···Si distance, as is evident in theoretical studies of main-group hypervalent compounds.[28]

The tendency of Si to become "hypervalent" may be an important factor that discriminates silane Si−H coordination from either dihydrogen H−H or methane C−H. It has already been discussed that both η^2-H_2 and η^2-H−CH_3 correspond to "an early stage of oxidative addition".[4b] As C is in the second row, it strongly prefers 4-coordination, which obeys the octet rule. Indeed examples of stable molecules with 5-coordinated carbon are very rare.[29] This prevents the carbon from having strong interactions with five ligands, and hence η^2-methane complexes prefer to have the coordinated C−H bond essentially intact and have little metal−C interaction. In contrast, we have shown that Si has significant interactions (both ionic and covalent) with four hydrogens and the metal center, thus allowing the H−Si coordination to be "at a later stage of oxidative addition".

Electron Density Laplacian Analysis of the Mo−H···Si Interaction. To further elucidate the nature of the H···Si interaction, an electron density analysis based on the Laplacian ($\nabla^2\rho$) of the SCF valence electron density (hereafter referred to as the *density Laplacian*) of **4** was performed on the plane defined by the Mo−(H···Si) triangle, on the basis of Bader's atoms-in-molecules theory.[30] This kind of density Laplacian analysis has been extensively used to study the nature of chemical interactions,[31] in particular, the nature of bonding between "classical" and "nonclassical" dihydride complexes.[19,32] Figure 5 presents such a Laplacian plot for **4** based on the BS2 basis set. The Laplacian plot based on the BS1 basis set does not differ too much from the one presented in Figure 5. Therefore, one can conclude that a moderate size of basis set can provide a qualitatively correct result. In Figure 5, solid lines represent $\nabla^2\rho < 0$, indicating local electron density concentration, and dotted lines represent $\nabla^2\rho > 0$, i.e., local electron density depletion.

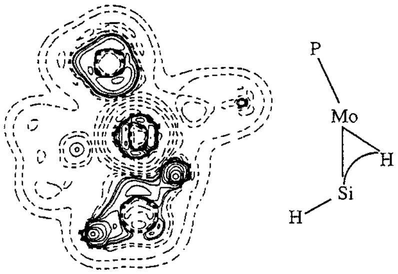

Figure 5. Laplacian ($\nabla^2\rho$) of the valence electron density of **4** on the plane defined by the Mo−H···Si triangle, with atom labels and bond paths on the right.

Some features of interest in the Laplacian plot can be noted. Firstly, the Mo−P bond has local concentrations at P and depletions at Mo, indicating a dative bond through the lone pair of P (the other two Mo−P bonds *cis* to H···Si are out of the Mo−(H···Si) plane due to the tilting of the Mo−Si bond, and hence, the P centers are not shown in the plot). Focusing on the Mo−(H···Si) triangle, an ordinary covalent Mo−Si bond is revealed by one local concentration for each of Mo and Si; the Mo−H bond is essentially a dative H^-→Mo interaction, similar to P→Mo. The bond path of H···Si is significantly curved inward, with the turning point inclined toward Si, implying that the H−Si covalent bond is significantly weakened. This is in contrast to the situation in nonclassical dihydrogen complexes, where the H−H covalent bonding nature is essentially retained.[32]

Examining the area around Mo, there are four "corners" of concentrations bulging from the otherwise circular contour, corresponding to the metal d_{xy} orbital. One of the corners points almost directly to the electron concentration of the silicon, indicating the predominantly covalent Mo−Si interaction.

Density Laplacian analyses of classical and nonclassical forms of dihydride complexes[32] indicate that there is a high degree of electron density concentration between the two hydrogens for nonclassical complexes, but two M−H bonds for classical ones, which are consistent with the qualitative MO interaction scheme between the metal and the classical or nonclassical H_2 ligand.[8c] For the present silane complex we find an intermediate case: there are large degrees of density concentrations in both Mo−H and Mo−Si bonds, but there is still appreciable concentration between the H···Si moiety (although as noted the bond path is heavily curved inward).

Judging from the evidence of structure, MO interaction, and density Laplacian analysis, it is difficult to dichotomize the silane complex **1** (or **4**) into either classical or nonclassical as in the M−H_2 case. However, as stated above, the H···Si bond is severely weakened, the Mo−Si covalent bond is significant, and the H gains a large degree of hydride character. Thus, **1**

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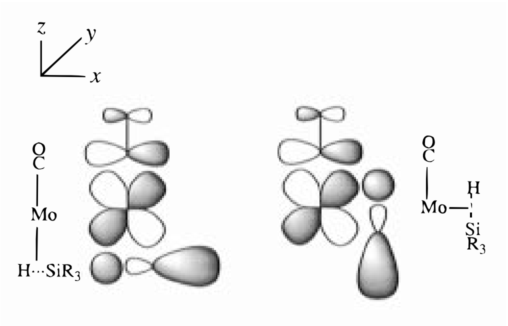


(a) for structure **5** (b) for structure **7**

Figure 6. Competition of the metal "t_{2g}" set of d orbitals in (a) the *trans* isomer **5** and (b) the C_s structure **7**.

(or **4**) lies closer to the classical extreme rather than nonclassical, the close contact of H and Si being facilitated by the ease of Si to form hypervalent coordination.

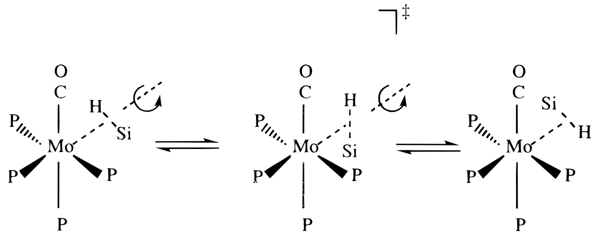
Stabilities of the *cis* and *trans* Isomers. In the experimental complexes **1**, only the *cis* isomer was formed by the addition of silane H−SiR_3 to the 5-coordinate complex **3**,[14] although the reaction leading to the formation of the *trans* isomer probably involves little molecular rearrangement and steric hindrance. Considering the ease of 5-coordinate complexes to undergo Berry pseudorotation, the reaction product is very likely to be thermodynamically controlled. This strongly suggests that the electronic structure of the *cis* form is much more favorable than the *trans* form. We have therefore calculated a hypothetical *trans* structure **5**, which is 9.9 kcal/mol higher than the *cis* form. With such a high energy, the *trans* structure would be too thermodynamically unfavorable with respect to the *cis* isomer.

The optimized structure of **5** shows signs of a smaller extent of M→H···Si σ^* back-bonding relative to the *cis* structure. The carbonyl bond length is 0.01 Å shorter, the H···Si distance is also shorter by 0.1 Å, and the Mo−H and Mo−Si bond lengths are significantly longer than those of the *cis* isomer. In terms of MO interaction, the destabilization of the *trans* isomer can be explained by the competition of the d electrons between the carbonyl and H···Si (Figure 6a). This competition results in a smaller extent of Mo d → H···Si σ^* back-bonding, and hence the H···Si distance becomes shorter. With the *cis* conformation, the carbonyl and H···Si interact with *different* d orbitals (the two CO π^* orbitals interact with d_{xz} and d_{yz}, and H···Si interacts with d_{xy}) of the t_{2g} set, and hence do not suffer from such destabilization due to the competition of metal d electrons. The preference of two π-accepting ligands to interact with different metal d orbitals is also evident in the *trans*-diolefin complex, in which the two C=C bonds are perpendicular to each other.[33]

Density Laplacian analysis of **5** also indicates a larger degree of H···Si interaction, namely, that the H···Si bond path is less curved, and the molybdenum d electron concentration points more to the center of the H···Si unit.

Possibility of Classical−Nonclassical Tautomerism Analogous to That of Dihydrogen Complexes. To investigate whether a truly classical 7-coordinate isomer with neighboring H and Si exists, and hence a classical−nonclassical tautomerism as suggested by the original authors is possible,[14b] we started geometry optimizations without any structural constraints with two of the possible geometries for 7-coordination: a pentagonal bipyramid and a capped octahedron[34] (with the hydride in the capping position). In both cases the optimized structures turn out to be the same as the one based on the experimental pseudooctahedral structure (i.e., **4**). Therefore, the classical−nonclassical equilibrium as suggested by the presence of two isomeric forms in solution seems not very likely. The failure to obtain a truly classical isomer for such systems with close H···Si contact is also described in a previous theoretical study with pseudo-three-legged piano-stool complexes.[13] Moreover, the experimental evidence that the two tautomers are of similar energy denies the possibility that the observed equilibrium is of the *cis* ⇄ *trans* type.

Scheme 1. Enantiomeric Interconversion of **1**, Passing through the Assumed C_s "Transition" State **7**, with the Atoms Defining the Symmetry Plane in Bold



4 **7** **4'**

However, we are able to obtain an optimized 7-coordinate pentagonal bipyramidal structure **6**, in which the H and Si are *not* adjacent, but with an intervening PH_3, thus precluding any possible H···Si interactions. We find that this isomer lies 6.5 kcal/mol above the most stable structure (i.e., **4**). It is surprising that the destabilization caused by the competition of metal d electrons (as shown by the relative energy of 9.9 kcal/mol for **5**) is more severe than the disruption of the H···Si interaction in **6**, which suggests that the covalent H···Si interaction in **5** (and more so in **1** or **4**) is severely diminished.

Given the experimental evidence that the "tautomerism" observed in solution has an interconversion barrier of about 10 kcal/mol (judging from the variable temperature NMR spectrum), and the two tautomers have similar structures (also based on the solution NMR spectrum), we propose that the rotation of the H···Si unit about the Mo−(H···Si) "bond" may be a possible mechanism of the interconversion of the two forms of **1**.

Rotation of H···Si. Facile rotation of the H···Si moiety about the axis through the metal and perpendicular to H···Si has been observed in several hydrosilyl complexes,[35] which is an important aspect of the dynamics of such complexes. To estimate the activation barrier and to investigate the cause of such a barrier in the presently studied complex, we have calculated a hypothetical optimized transition structure for the interconversion of the two enantiomers of **4** (Scheme 1). The assumed transition structure **7** has a global C_s symmetry with the symmetry plane defined by Mo, CO, the PH_3 *trans* to CO, and the H···Si moiety. It represents a molecular geometry which the enantiomeric interconversion is likely to pass through.

Structure **7** has an energy 10.7 kcal/mol higher than that of **4**, which is similar to the value of 9.9 kcal/mol in **5**. Examination of the structural parameters of **5** in Table 1 shows resemblance of **7** to the *trans* isomer **5**, namely, that the carbonyl and H···Si bond lengths are similar. In terms of MO interaction, similar competition of metal d electrons as in **5** occurs (Figure 6b), but in this case it is the orientation of the H···Si moiety that forces the sharing of one of the metal d orbitals with carbonyl.

The experimentally observed tautomerism process could be related to the above process of H···Si rotation about the Mo−

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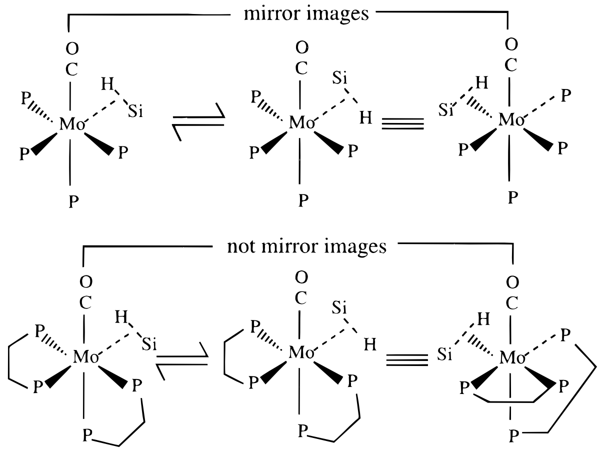

Figure 7. Relationship between the rotational isomers of **1**, demonstrating the loss of enantiomeric character due to chelation.

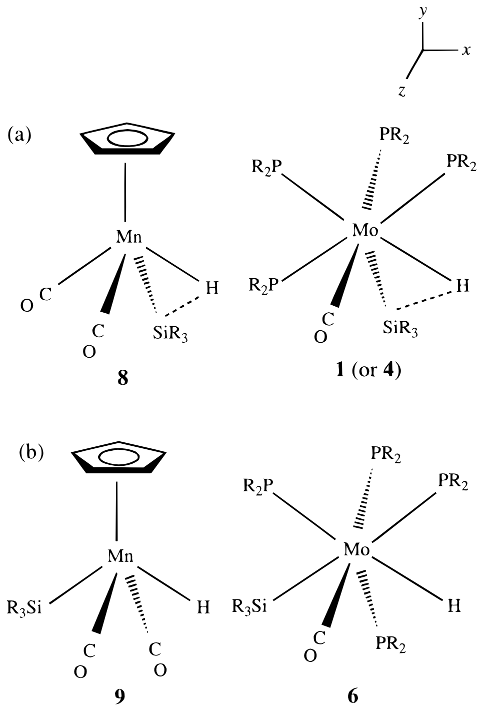

Figure 8. Structural analogies between the piano-stool and pseudooctahedral complexes.

(H···Si) axis. In the absence of chelations (of the phosphine ligands), the 180°-rotation product is an enantiomeric isomer. However, for the experimentally studied molybdenum complex **1**, the two forms corresponding to **4** and **4′** are no longer enantiomers due to the chelation (Figure 7), thus resulting in significantly different NMR spectra and relative energies for the two isomeric forms. The rotation barrier of about 10 kcal/mol is consistent with the variable temperature NMR spectrum.

Although the above postulation is consistent with both the experimental results and our present theoretical calculations, it still requires further experimental and theoretical confirmation.

Comparisons with Pseudo-Three-Legged Piano-Stool $MCpL_2(H\cdots SiR_3)$. The complex $MnCp(CO)_2(H\cdots SiR_3)$ is the first recognized class of complexes with close H···Si interactions,[4] and there are close structural similarities between the piano-stool complex **8** and the presently studied pseudooctahedral complex **1**, as shown in Figure 8a. Electronically, if the cyclopentadienyl ligand is viewed as a 6-electron ligand occupying three coordination sites, this group of complexes can be treated as d^6 octahedral, which is similar to the presently studied molybdenum complex, and hence there is also close similarity between the MO interactions of the two types of complexes.[13] In the piano-stool complexes it was concluded that electron-donating ligands tend to lengthen the H···Si distance, and this can be explained by the generic d^6-ML_6 orbital interaction diagram. The electron-donating ability of the t_{2g} set is increased by the π-donating ligands, which in turn populates the σ^* orbital of H···Si and weakens the interaction.

The 7-coordinate classical isomer **6** can be compared with the "*trans*" conformation **9** (where the H and SiR_3 ligands occupy opposite vertices of the square base) of the piano-stool structures (Figure 8b). For piano-stool hydrosilane complexes with second-row transition metals, it has been shown that the isomer with close H···Si contact (the "*cis*" form) is more stable than the *trans* form (in which the hydride and silyl ligands occupy opposite vertices of the square base).[4b] The present study also shows that the H···Si form **4** is more stable than **6** with H and Si not in contact. This is an indication that the H···Si interactions in these two types of complexes are still significant in providing additional stabilization to those complexes that can form close H···Si contact.

The presently studied system provides an additional flexibility not present in the piano stools: a π-accepting ligand such as CO can be placed *trans* to H···Si, while this is not possible with the piano-stool complexes.

It seems likely that an important driving force for the H···Si interaction is the strong tendency for a transition metal complex to become d^6 6-coordinate whenever the electronic structure allows. Indeed to our knowledge there are examples neither of pseudo-5-coordinate hydrosilane complexes with close H···Si contact nor 7-coordinate classical hydrosilane complexes with H and Si more than 2.5 Å apart (there are two 7-coordinate mononuclear complexes with neighboring $H\cdots SiR_3\cdots H$ ligands,[36] and for one of them[36b] it has been shown that a weak H···Si interaction still exists for a H−Si distance of about 2.3 Å[37]). Hence, the stabilization due to the H···Si interaction is not strong enough to compensate for the destabilization caused by the unfavorable orbital interactions of 5- or 7-coordination.

Comparisons with Pseudooctahedral $ML_5(H_2)$ Complexes. Theoretical studies with this class of dihydride complexes show that the nonclassical dihydrogen form is favored by the presence of a late transition metal, which has contracted d orbitals, and strong π-acceptor ligands *trans* to H_2.[8c] Similarities can also be found in the H···Si complexes. In the transition metal nonclassical hydrosilane complexes theoretically studied thus far, the H···Si interaction distance is less than 2.5 Å, and at least one carbonyl ligand is present. However, the *cis* arrangement of CO and H···Si causes the coordinated H−Si bond to become elongated, and thus H−Si lies closer to the classical end (to our knowledge there are as yet no examples of H···Si complexes with CO *trans* to H···Si).

The extent of metal→H−X σ^* back-bonding is the most important factor in determining the structures and stabilities of the nonclassical forms of H−X coordination. In the dihydrogen case, the H−H σ^* orbital lies high in energy, and it is not quite susceptible to M→σ^* back-bonding. The presence of a *trans* π-acceptor ligand like CO further prevents such back-bonding, and keeps the H−H distance close to that of uncoordinated H_2. With H···Si coordination, however, the σ^* orbital lies at lower energies, so it is able to form M→σ^* back-bonding. When the carbonyl and H···Si are *trans* to each other, there will definitely be competition between them for the metal d electrons, since

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there are two carbonyl π^* orbitals available for back-bonding. The better σ^*-accepting ability of the H···Si moiety actually destabilizes the *trans* orientation.

In transition metal dihydride complexes, the nonclassical form (with a H−H distance of ∼0.8 Å) has the two hydrogens *trans* to carbonyl, while the classical form (with a H−H distance >1.7 Å) prefers the *cis* position. This is also the case for the hydrosilane complex: the *cis* form has a longer H···Si distance (1.813 Å) than that of the *trans* form (1.715 Å). However, unlike the dihydride analogs, the *cis* form does not become completely classical due to the additional stabilization of silicon hypervalent coordination.

It should be emphasized that back-bonding from the metal d orbitals to the π^* or σ^* orbitals of the accepting ligands causes the stabilization of the complex *as a whole* due to the removal of electron density from the electropositive metal center (as shown by the stability of **1** or **4** relative to the other isomers), but the nonclassical *trans*-CO−(H···Si) isomer is destabilized due to the competition of metal d electrons.

Conclusions

The H−Si σ bond in silanes SiHR$_3$ serves as a moderately strong σ^* acceptor ligand in transition metal complexes. The σ^*-accepting character is manifested in the structure of the pseudooctahedral complex **1**, namely, that the Mo−P bond length *trans* to H···Si is lengthened to a similar extent as that *trans* to CO.

An analysis of the density Laplacian around the Mo−(H···Si) triangle reveals that the H is essentially hydridic in character, its close approach to the Si center being facilitated by the ease of silicon to become hypervalent. The covalent bonding between the metal ML$_5$ fragment and the H···Si unit is mainly through silicon. This is in sharp contrast to the η^2-H$_2$ complexes in which there is a marked density concentration between the two hydrogens.

The *cis* preference of the molybdenum complex can be explained by molecular orbital interaction arguments. In the *cis* orientation **4** with C≡O and H···Si bonds perpendicular to each other, the completely filled metal t_{2g} set of d orbitals interacts with different antibonding orbitals of the two ligands (two with CO and one with H···Si). In both the *trans* orientation **5** and the *cis* one, with C≡O and H···Si parallel, **7**, there is competition between the antibonding ligand orbitals with one of the metal d orbitals. The resulting destabilization is estimated to be about 10 kcal/mol for both isomeric structures, which is significantly greater than the loss of the H···Si interaction in the 7-coordinate isomer **4**.

There are close structural and electronic similarities between the presently studied pseudooctahedral complexes and the widely investigated pseudo-three-legged piano-stool complexes. Both can be regarded as a d^6 6-coordinate system, which has been recognized as a particularly stable class of complexes.[35]

We can summarize the difference between H−Si and H−H coordination as follows: In η^2-silane complexes the coordinated H−Si bond is weakened significantly, with the main covalent bonding of the metal to silicon; thus, it lies closer to the classical hydridosilyl extreme. In η^2-H$_2$ complexes the H−H bond remains essentially unperturbed by the M→H$_2$ σ^* back-bonding, and it lies closer to the nonclassical dihydrogen extreme.

Finally, we note that there are examples of silane complexes with H···Si distances approaching the H−Si distance in the uncoordinated silane ligands, including the apparently 8-coordinate complex Ir(PR$_3$)$_4$H$_2$(SiR$_3$)$_2$,[38] and the recently synthesized bent titanocene "agostic Si−H" complex TiCp$_2$(*trans*-*t*-BuC≡CSiHMe$_2$).[39] Thus, the structural variety of silane complexes may be as rich as the dihydrogen complexes, and further experimental and theoretical studies would result in a more thorough understanding of the nature of H−Si coordination, and hence the important process of C−H bond activation.

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