*Inorg. Chem.* **2002**, *41*, 7105–7112

Inorganic Chemistry
Article

# Silyl, Hydrido-Silylene, or Other Bonding Modes: Some Unusual Structures of $[(dhpe)Pt(SiHR_2)]^+$ (dhpe = $H_2P—CH_2—CH_2—PH_2$; R = H, Me, $SiH_3$, Cl, OMe, $NMe_2$) and $[(dhpe)Pt(SiR_3)]^+$ (R = Me, Cl) from DFT Calculations

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Received July 29, 2002

DFT (B3LYP) calculations have been carried out in order to quantitatively evaluate the energies and stereochemistry of the accessible structures of $[(dhpe)Pt(SiHR_2)]^+$ (dhpe = $H_2P–CH_2–CH_2–PH_2$; R = H, $CH_3$, $SiH_3$, Cl, OMe, SMe, $NMe_2$) and of $[(dhpe)Pt(SiR_3)]^+$ (R = $CH_3$, Cl). A number of different isomers have been located. The expected terminal silyl or hydrido-silylene complexes are often not the most stable complexes. An isomer in which an H or an R group bridges a Pt═SiHR or Pt═$SiR_2$ bond is found to compete with the terminal silyl or hydrido-silylene isomers. In some cases, isomers derived from cleavage of a C—H bond and formation of a silene or disilene ligand are obtained. The structures of the platinum silyls differ from that of the equivalent alkyl complex, calculated for $[(dhpe)Pt(CH_3)]^+$.

## Introduction

Silyl transition metal complexes have been studied extensively recently because of the number and variety of transformations that the metal silylalkyl group can undergo.[1] Understanding of the bonding is a prerequisite for understanding the reactivity patterns of this class of complexes relative to the related metal alkyl. For instance, the Si—H bond forms an a or b agostic bond more easily than does the C—H bond.[2−5] The Si—Si single bonds have been suggested to coordinate to a metal in an $\eta^2$ manner,[6] but this coordination is unknown, to our knowledge, for C—C single bonds. A Si—C agostic interaction has been suggested[7] whereas a C—C agostic interaction has been reported in the case of a heavily strained system.[8] It is currently accepted that Si-containing bonds are more reactive than the equivalent bond with carbon.[9] A silicon center is well-known for being able to increase its coordination up to 5 and even 6, that is, to become hypervalent, and this bonding situation is unfavorable for C.[10] The ability of Si to become hypervalent rationalizes some unusual structures in late transition metal

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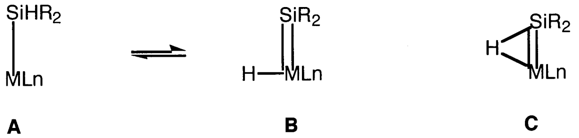
**Scheme 1**



complexes[11] and reactivity properties in lanthanide complexes.[12] From a computational point of view, the remarkable ability of Si−X σ bond to participate in agostic interactions has been the subject of many studies.[4,5,11,12] The comparison of the reactivity of silanes, alkanes, or alkylsilanes has shown that the presence of Si lowers the energy barrier for oxidative addition.[13]

In this paper, we start from the experimental fact that the silylene $[(dippe)Pt(H)(SiR_2)]^+$ (dippe = $^iPr_2P-CH_2-CH_2-P^iPr_2$; R = mesityl) derived from a 1,2 H shift on the associated $Pt(SiHR_2)$ complex observed by NMR.[14] It is possible that the two structures, silyl **A** and hydrido/silylene **B** (Scheme 1), could be two valence tautomers separated by a transition state (TS). The factors that favor tautomer **A** or **B** are the subject of this paper. In the carbon analogues, there is a reasonable understanding of the factors that stabilize a $M{=}CR_2$ double bond[15] and also of the factors that favor a carbene complex compared to other isomers.[16] Transition metal silylene complexes have also been the focus of a number of studies.[17] Computational studies of transition metal $SiH_2$ complexes have been carried out.[15,18] As expected, silylene and carbene complexes obey the same general bonding rules. However, the factors that control the relative energy of isomers **A** and **B** are not understood. Furthermore, the ability for Si to enter into unusual bonding modes derived from either agostic interaction or hypervalent situations might result in the occurrence of unexpected structures. Therefore, we have carried out DFT calculations on a homogeneous series of complexes $[(dhpe)Pt(SiHR_2)]^+$ (dhpe = $H_2P-CH_2-CH_2-PH_2$; R = H, $CH_3$, $SiH_3$, Cl, OMe, SMe, $NMe_2$) and $[(dhpe)Pt(SiR_3)]^+$ (R = $CH_3$, Cl). The $SiH_3$ and $CH_3$ complexes have been also compared so that the differences and similarities between silicon- and carbon-containing ligands may be delineated. In some key examples, the transition state structures connecting minima have been calculated. The key result of this work is that structures other than **A** and **B** are also minima and that the structural preferences of this family of $SiR_3$ complexes vary in an unusual way with R. The type and relative energies of the isomers for the various $SiHR_2$ complexes have been collected in Table 1, and the geometries with the atom numbering scheme are given in Figures 1−3.

**Table 1.** Relative Energies of the Various Isomers or Transition States (TSs) for $[(dhpe)Pt(SiHR_2)]^+$ [a]

| R | type **A** $M-SiHR_2$ | type **B** $H-M{=}SiR_2$ | type **C** R bridged | type **C** H bridged | type **D**, **E** other |
|---|---|---|---|---|---|
| H | 3.1 | 3.8 TS | 0 | | |
| $CH_3$ | | 0 | 8.2 | 0.4 | |
| $SiH_3$ | | | | 15.2 | 0, 5.0 |
| Cl | 10.1 TS | 0 | 0.4 | | |
| OMe | 22.5 TS | 0, 2.4 | 13.9 | | |
| SMe | 23.9 TS | 1.9 | 0 | | |
| $NMe_2$ | 27.0 TS | 0 | 5.4 | | |

[a] Energies in $kcal \cdot mol^{-1}$. See Figures 1−4 for details.

## Computational Details

The calculations were carried with the Gaussian 98 suite of programs[19] within the framework of DFT with the B3LYP functional.[20a] The Hay and Wadt effective core potential ECP (quasirelativistic for Pt) was used to replace the 62 inner electrons of Pt,[21] and the 10 inner electrons of Si, S, P, and Cl.[22] The double ζ basis sets associated with the ECP were used for the valence shell of these atoms and were augmented by a d polarization shell for Si and P.[23] Atoms not directly bonded to Pt like H, C, N, O, S, and Cl were represented with a 6-31G basis set.[24] The H bonded to Si or to Pt was described with a 6-31G(d,p) basis set.[25] Unless mentioned, full optimization was carried out without symmetry restriction. The nature of all extrema was characterized by analytical frequency calculation. The topological properties of the electronic

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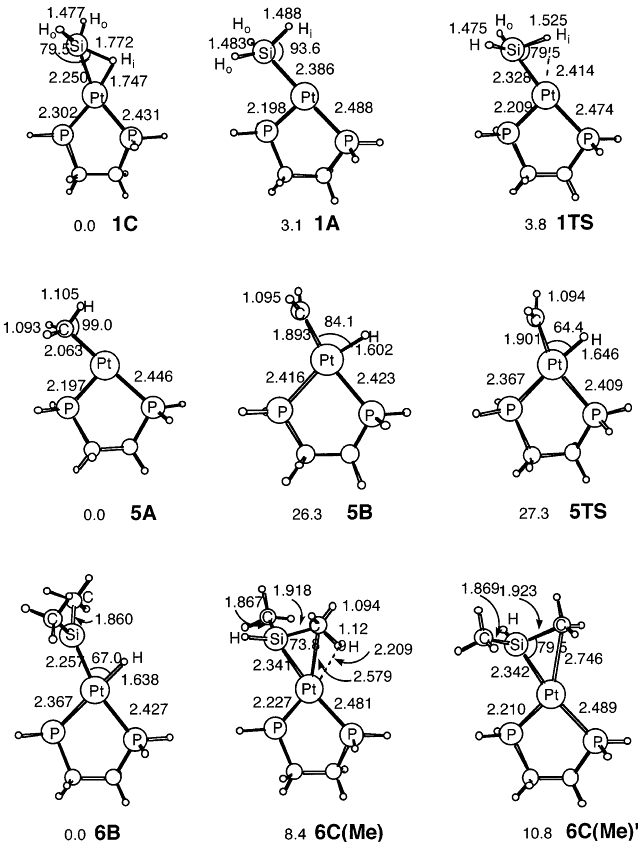

**Figure 1.** Optimized (B3LYP) structures for [(dhpe)Pt(SiHR$_2$)]$^+$ (dhpe = H$_2$P−CH$_2$−CH$_2$−PH$_2$; R = H, Me) and [(dhpe)Pt(CH$_3$)]$^+$. Relative energies in kcal·mol$^{-1}$. Selected geometrical parameters in Å and deg.

charge density[26] were investigated using Xaim[27] and a version of the AIMPAC package.[28] The basis sets in the density analysis were those used for the geometry optimization except for Si. For this atom, an all electron 6-31G(d) basis[29] set was used to avoid the difficulties associated with the ECP in the density analysis. CCSD(T) calculations[20b] on the DFT geometries were carried out for a more reliable evaluation of the relative energies of the extrema in selected cases.

## The Simplest System, [(dhpe)Pt(SiH$_3$)]$^+$, 1

Two minima, 3.1 kcal·mol$^{-1}$ apart, with a connecting transition state 3.8 kcal·mol$^{-1}$ above the most stable species have been found for [(dhpe)Pt(SiH$_3$)]$^+$ (Figure 1). Single point calculations of these structures at the CCSD(T) level give the corresponding energy values of 4.6 and 5.0 kcal·mol$^{-1}$. This indicates that DFT calculations give reliable results for this class of compounds. Only this method of calculation will be used for all other systems. In all extrema (minima or transition states), the dhpe ligand is not planar and takes its usual envelope shape. However, inversion of the envelope is essentially barrierless, and thus, deviation away from an ideal $C_s$ symmetry has no chemical meaning. For this reason, we will not discuss the difference between structural parameters that would be averaged by inversion of the envelope. One of the two minima is a silyl complex, can be assigned the type **A** structure, and is thus labeled **1A**. Complex **1A** has a T shape with one P trans to the empty Pt coordination site. The two arms of dhpe are thus different: the Pt−P bond trans to the empty site is short 2.198 Å whereas that trans to SiH$_3$ is longer (2.488 Å) because of a large trans influence. The three Si−H bonds are different, but the averaging of the envelope of dhpe results in only two different Si−H bonds: Si−H in (H$_i$) and out (H$_o$ and H$_{o'}$) of the molecular plane. The Pt−Si−H$_i$ angle is only 93.6° which puts H$_i$ 2.890 Å away from Pt. The average Pt−Si−H$_o$ angle is 113.8°. This may be indicative of, at best, a weak α agostic Si−H$_i$ bond although the lack of Si−H elongation (1.488 Å compared to the average Si−H$_o$ 1.485 Å) is in contrast to the usual elongation observed for an agostic Si−H bond.[2−5] The more stable minimum, 3.1 kcal·mol$^{-1}$ below **1A**, cannot be considered as representative of the type **B** species (Figure 1, Scheme 1) and is thus labeled **1C**. In **1C**, the Pt−Si bond (2.250 Å) is significantly shorter than in **1A** (2.386 Å); the H$_o$−Si−H$_{o'}$ moiety is essentially a planar silylene (angle sum at Si equal to 359.5°) coordinated to Pt. Despite the apparent formation of a silylene group, H$_i$ does not occupy a terminal position expected for a hydride. H$_i$ is almost equally bonded to Pt (1.747 Å) and also to Si (1.772 Å) and is best viewed as bridging the Pt−Si bond.

A transition state, **1TS**, connects **1A** and **1C**, and its nature is confirmed by the presence of an imaginary frequency of 149i cm$^{-1}$. **1TS** is 0.7 kcal·mol$^{-1}$ above **1A**, and the two species have similar geometries. They differ by the Pt−Si−H$_i$ angle (74.3° in **1TS** and 93.6° in **1A** to compare to 49.8° in **1C**). In **1TS**, the average Pt−Si−H$_o$ is equal to 109°, and the native silylene group is not yet planar (angle sum at Si = 352.7°). The other parameters of **1TS** intermediate between that in **1A** and **1C** deserve no specific comment.

No true hydride/silylene complex could be located as a minimum on the potential energy surface. To have an estimate of the energy of this type of structure, an optimization of a species with Si−Pt−H$_i$ angle fixed at 90° was carried out. This partially optimized structure of type **B** was found to be 3.4 kcal·mol$^{-1}$ above **1C** and is thus even higher in energy than **1A**. It is notable that the silylene moiety has the same metric parameters in the forced hydride/silylene complex (the same Pt−Si distance, and a planar silylene group) in **1C**; only the position of H$_i$ differs. Clearly, a terminal hydride is not favored in this system.

It is thus important to have a better understanding of the bonding in **1C**. For this, we have calculated (dhpe)Pt(SiH$_2$) and (dhpe)Pt(Me)(SiH$_3$). The first species is a model for the experimentally observed L$_2$Pt(SiR$_2$) (R = mesityl, L = PCy$_3$),[30] and the latter is a model for the experimentally

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observed (dippe)Pt(Me)($SiR_2$) (R = mesityl).[14] The geometry of these complexes is well reproduced by the calculations. In (dhpe)Pt($SiH_2$), the calculated Pt−Si bond length is 2.230 Å in the trigonal planar Pt(0) complex, close to the experimental value of 2.210 Å, and the silylene is perpendicular to the P−Pt−P plane as experimentally observed. In (dhpe)Pt(Me)($SiH_3$), the Pt−Si single bond length is calculated to be equal to 2.367 Å which is also close to the experimental value of 2.388 Å. On the basis of the good reproduction of the metric of complexes with well defined double and single Pt−Si bonds, we carried out an AIM study of these Pt(0) and Pt(II) complexes and complexes **1C**. The value of $\rho$ (0.1057) for the Pt−Si bond critical point is larger in (dhpe)Pt($SiH_2$) than in (dhpe)Pt(Me)($SiH_3$) ($\rho = 0.0936$), consistent with a double bond and a single bond, respectively. The $\rho$ value in **1C (**0.1014**)** suggests a bond closer to that in (dhpe)Pt($SiH_2$). The value of the ellipticity, $\epsilon$, in the Pt−Si bond ($\epsilon = 0.275$) in **1C**, slightly closer to that in (dhpe)Pt($SiH_2$) ($\epsilon = 0.475$) than in (dhpe)Pt(Me)($SiH_3$), ($\epsilon = 0.026$) is consistent with a $\pi$ Pt−Si bond in this unusual structure. This bonding scheme is very different from that which has been observed in transition metal complexes with an α agostic C−H bond with, in particular, the absence of any ring critical point.[31]

The situation found for species **1C** is analogous to that of carbocations in which $H^+$ bridges a C=C bond. For this reason, a calculation of $C_2H_5^+$ (**2**), $Si_2H_5^+$ (**3**), and $CSiH_5^+$ (**4**) was carried out with the same method and level of calculations. The results are similar to these previously published on these systems.[32] Both $C_2H_5^+$, **2**, and $Si_2H_5^+$, **3**, have a $H^+$ bridging an essentially planar frame. In the case of the unsymmetrical $SiCH_5^+$, **4**, the optimized structure is that of a silylene bonded to a $CH_3$ group. No bridged $H^+$ is obtained, and the positive charge resides on the more electropositive center (Si vs C). The preference for a bridged versus unbridged cation has been the center of considerable discussions, and no further discussion in the case of **2**, **3**, and **4** is needed. Our concern is the reason platinum complex **1C** is bridged as in **2** or **3** but unlike **4**. In the case of a symmetrical species $X_2H_5^+$ like **2** or **3**, a bridged structure is found if the distances between the two X centers permit a good overlap with $H^+$ so that the partial bonds of $H^+$ with the two X centers are stronger than that of $H^+$ to a unique X center. In the case of unsymmetrical systems such as **4** and **1C**, the bond energy of $H^+$ to each center plays an important role. The electronegativity of the two centers is related to these bond energies. In **4**, $H^+$ prefers to make a bond to the more electronegative center. A bridged 2e−3c structure is preferred for **1C** which is compatible with the fact that the electronegativity difference is less between Si and Pt than between C and Si. It should be kept in mind that the nonbridged system **1A** is very close in energy to **1C**. The potential energy surface which describes this system is rather flat, and minor chemical changes at Si can easily modify the structural preferences.

To better understand the geometry of the Pt−$SiH_3$ complex relative to the Pt−$CH_3$ bond, the methyl complex (dhpe)Pt($CH_3$)$^+$ was calculated. The methyl complex and the hydrido-carbene complexes are both minima on the potential energy surface, the hydrido-carbene complex being 26.3 kcal·mol$^{-1}$ higher than the methyl complex. These two minima are both clear representatives of type **A** and **B** species and are labeled **5A** and **5B**. The geometry of the two structures presents no remarkable features. The T shaped methyl complex, **5A**, has no strong agostic C−H bond (C−$H_i$ is equal to 1.105 Å compared to the two other C−H bonds of 1.093 Å), and the hydrido-carbene complex, **5B**, presents no possible interaction between the hydride and the carbene (C−Pt−$H_i$ = 84.1°). The transition state, **5TS**, connecting the two minima is only 1 kcal·mol$^{-1}$ above the hydrido-carbene complex **5B**. Consequently, the geometries of **5TS** and **5B** are very similar; the only significant geometry change is the decrease of C−Pt−$H_i$ from 84.1° to 64.4° in **5TS**. The methyl complex is thus clearly the only accessible structure on the potential energy surface. A search was made for the structural equivalent of **1C**, but no minimum was found. The bonding preferences of $SiH_3$ and $CH_3$ in this Pt complex are thus fundamentally different.

### Substituted Systems [(dhpe)Pt($SiHR_2$)]$^+$, R = $CH_3$, 6

The structure of silyl complexes strongly depends on the nature of R, and calculations for representative R groups have been carried out. In this section, we consider the case of the methyl group. The geometry of the minima for this species contrasts with that found for the $SiH_3$ complex (Figure 1). The most stable minimum is a hydrido-silylene complex, which belongs to type **B** and is labeled **6B**. The Pt−$H_i$ distance (1.638 Å) is that of a terminal hydride. The Pt−Si bond is short, 2.257 Å, appropriate for a Pt−Si double bond, and the silylene group is perfectly planar (sum of angles around Si = 359.5°). This geometry appears to be different from **1C** as confirmed by further analysis. For instance, the Pt−Si distance is equal in **1C** and **6B**, and the angle Si−Pt−$H_i$ is 66.6° which puts $H_i$ 2.197 Å away from Si. This distance Si···$H_i$ is, however, too long to suggest any significant interaction as confirmed by an AIM analysis which shows no bond critical point between Si and $H_i$. Thus, **6B** is a true representative of species **B** of Scheme 1.

A complex representative of type **A** was not located as a minimum on the potential energy surface. Geometry optimization fixing the H−Si−Pt angle shows that an hypothetical $SiHMe_2$ complex would be more than 21 kcal·mol$^{-1}$ above **6B**. Furthermore, no structure with bridged H could be located as minimum. A secondary minimum situated 8.4 kcal·mol$^{-1}$ above **6B** has been located; it involves a $CH_3$ group occupying a bridging position between Pt and Si and is thus labeled **6C(Me)**. The Pt−Si bond, in **6C(Me)**, is not very short (2.341 Å) and is close to that in **1A**, 2.386 Å. The carbon of the bridging $CH_3$ is 1.918 Å from Si and 2.579

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Å from Pt. Remarkably, the C−H bond in the molecular plane is positioned to suggest some agostic interaction with a Pt···H distance of 2.209 Å and a C−H bond elongated to 1.129 Å, the average distance of the other two C−H bonds being 1.094 Å. A structure, **6C(Me)′**, with the same bridging $CH_3$ but without an agostic C−H interaction, has been located as a transition structure for exchange H in the bridging Me group, 2.4 kcal·mol$^{-1}$ above **6C(Me)**. The transition state for the transformation of **6B** into **6C(Me)** was not searched.

It thus appears that the two methyl groups significantly stabilize the hydrido-silylene complex by donating electrons to the silylene group through hyperconjugation. Furthermore, with the methyl group being not a very good candidate for a bridge bond, **6C(Me)** is only a secondary minimum.

Why a structure similar to **1C** is not located as a minimum on the potential energy surface, especially because H$^+$ is such a good candidate for bridging bonds, has no clear explanation. A possible explanation is that the methyl groups on silylene give more electron density to the Si center which in turn polarizes the Pt−Si $\pi$ bond toward Pt. This favors H$^+$ to get closer to Pt and to become a hydride. Why the methyl group assumes a bridging position and why there is no $SiMe_2H$ complex of type **A** is also unclear. The agostic $\beta$ C−H interaction from the bridging Me group in **6C(Me)** is not the only reason for the stability of this structure because removing the agostic C−H interaction costs only 2.4 kcal·mol$^{-1}$ and keeps the Me group at the same position. Species **6C(Me)** and **6C(Me)′** have truly bridging Me groups.

## Case of [(dhpe)Pt(SiMe$_3$)]$^+$, 7

How is the bonding of the commonly used trimethylsilyl group related to that of $SiMe_2H$ and that of $SiH_3$? The results are shown in Figure 2. The number of isomers is large because one can cleave a C−H bond to form a C−Si double bond or a C−Si bond to form a silylene group. The most stable structure results from the cleavage of a C−H bond. The resulting $CH_2{=}SiMe_2$ group is bonded to Pt, and the remaining H center bridges the Pt−Si bond. This complex does not belong to any of the previously defined structural types and is thus labeled **7D**. In **7D**, the $CH_2{=}SiMe_2$ is almost planar. The Pt−C bond (2.174 Å) is within the range found for olefin complexes. The Pt−Si bond (2.646 Å) is long especially compared to that in **1C**. The distance of the bridged H to Pt and Si is around 1.7 Å and is thus very similar to that in **1C**.

Another minimum, essentially at the same energy as **7D** (0.2 kcal·mol$^{-1}$ higher), has a Me group bridging a $Pt{=}SiMe_2$ group and is thus labeled **7C(Me)**. As in the case of **6C(Me)**, which it resembles, the ground state has a C−H bond interacting with Pt. The transition state, **7C(Me)′**, for rotating the methyl group to remove the agostic interaction, is 2.1 kcal·mol$^{-1}$ above **7C(Me)**. The situation for **7C(Me)** and **7C(Me)′** is thus very similar to that for **6C(Me)** and **6C(Me)′**. The next higher minimum, **7E**, is a hydride/$SiMe_2{=}CH_2$ complex with H cis to the carbon center. It is 14.1 kcal·mol$^{-1}$ above **7D**. The binding of the $SiMe_2{=}CH_2$ is slightly more symmetrical with respect to Pt than that in **7D**. The Pt−H bond is typical of a terminal hydride.

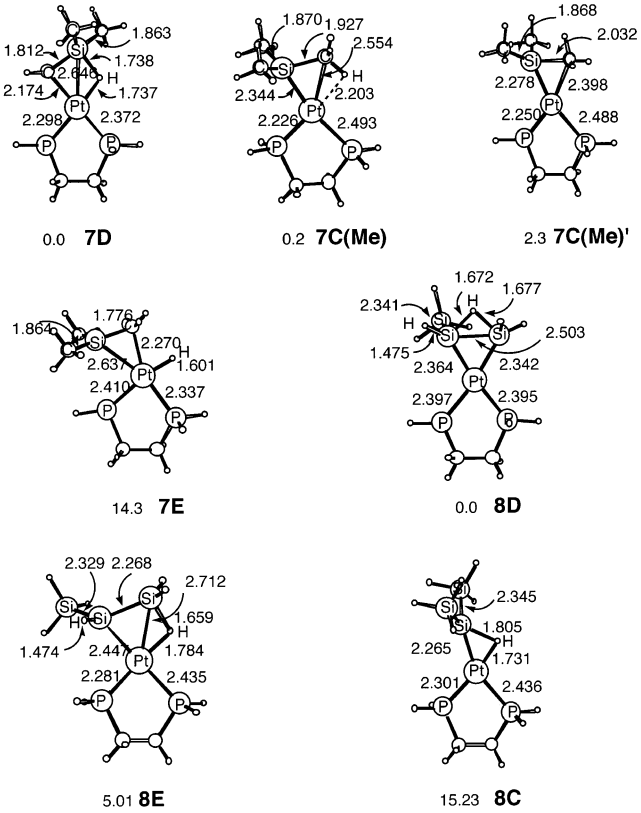
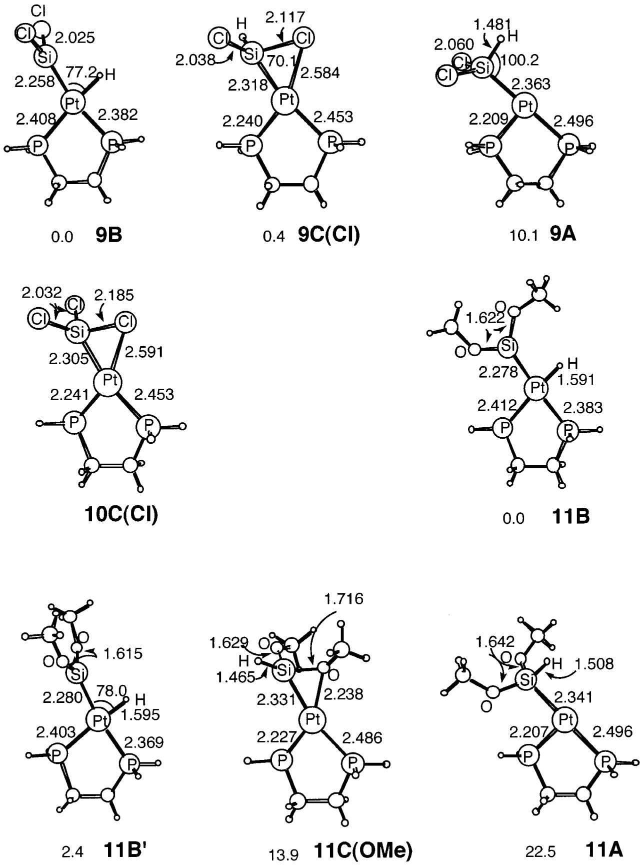


**Figure 2.** Optimized (B3LYP) structures for [(dhpe)Pt(SiMe$_3$)]$^+$ and [(dhpe)Pt(SiHR$_2$)]$^+$ (dhpe = $H_2P{-}CH_2{-}CH_2{-}PH_2$; R = $SiH_3$). Relative energies in kcal·mol$^{-1}$. Selected geometrical parameters in Å and deg.

The several extrema $SiMe_3$ complexes can be understood from the previous results. When H is near a Pt−SiR$_2$ bond, it has a preference for a bridging position (like in the Pt−SiH$_3$ complex) whereas when it is near a $CH_2$ group it prefers to make a unique bond to C or to Pt (like in the Pt−CH$_3$ complex), or to favor the formation of a methyl bridging group.

## Case of [(dhpe)Pt(SiH(SiH$_3$)$_2$)]$^+$, 8

The remarkable differences between $CH_3$ and $SiH_3$ ligands in these Pt complexes lead us to calculate the PtSiH(SiH$_3$)$_2$ ligand and to compare it to the PtSiHMe$_2$. The results are shown in Figure 2. The most stable structure, **8D**, has a H bridging the Si═Si double bond. The next higher structure, **8E**, (5 kcal·mol$^{-1}$ above **8D**) has a SiH(SiH$_3$)═SiH$_2$ ligand and H bridging the Pt−Si bond. The highest energy structure, **8C**, 15.2 kcal·mol$^{-1}$ above **8D**, has a Si(SiH$_3$)$_2$ group and bridging H. The geometries of these systems have no surprising metric parameters compared to the previous structures presented in this work, and they will not be discussed further. It is noteworthy that the disilene species is nonplanar, suggesting electron donation from Pt to the Si−Si $\pi$* orbital. The energy pattern is interesting. The silylene group is not stabilized by a group like $SiH_3$ resulting in the silylene isomer being higher in energy. In contrast, the methyl group is a stronger donor through $\pi_{CH_3}$ (hyperconjugation) than $SiH_3$. The silylene group can thus be

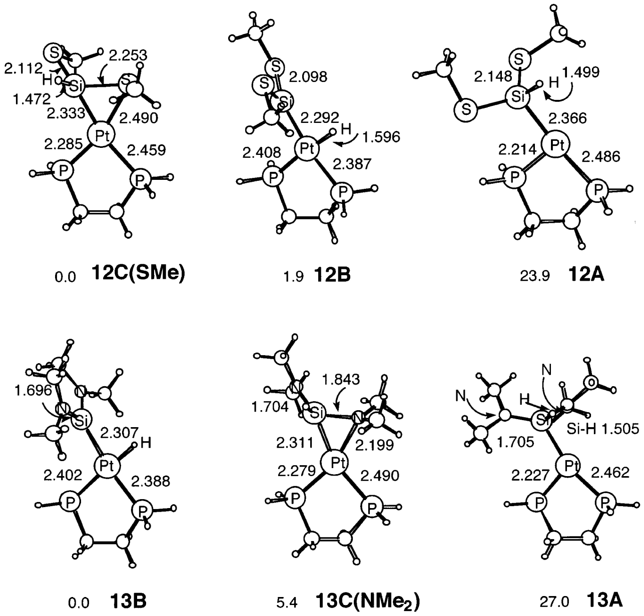


0.0 **9B** 0.4 **9C(Cl)** 10.1 **9A**

**10C(Cl)** 0.0 **11B**

2.4 **11B'** 13.9 **11C(OMe)** 22.5 **11A**

**Figure 3.** Optimized (B3LYP) structures for $[(dhpe)PtH\ (SiHR_2)]^+$ (dhpe = $H_2P-CH_2-CH_2-PH_2$; R = Cl, OMe) and $(dhpe)Pt(SiCl_3)$. Relative energies in kcal·mol$^{-1}$. Selected geometrical parameters in Å and deg.



0.0 **12C(SMe)** 1.9 **12B** 23.9 **12A**

0.0 **13B** 5.4 **13C(NMe$_2$)** 27.0 **13A**

**Figure 4.** Optimized (B3LYP) structures for $[(dhpe)PtH\ (SiHR_2)]^+$ (dhpe = $H_2P-CH_2-CH_2-PH_2$; R = SMe, $NMe_2$). Relative energies in kcal·mol$^{-1}$. Selected geometrical parameters in Å and deg.

stabilized by the $CH_3$ group and not by $SiH_3$. Thus, a complex with a Si═Si bond receiving electron density from the Pt(0) center is favored. The small energy preference for H bridging the Si═Si bond compared to a Pt−Si bond has no obvious origin.

It clearly appears from this first set of calculations that the presence of a Pt−silylene bond favors the formation of a bridge with various other groups or atoms. Such features are not present for the analogous carbon complexes.

## Introducing Strong $\pi$ Donors Cl, OMe, SMe, NMe$_2$

We will now discuss the structures for $[(dhpe)Pt(SiHX_2)]^+$ (X = Cl, OMe, SMe, $NMe_2$) and $[(dhpe)Pt(SiCl_3)]^+$. The results are shown in Figures 3 and 4.

The X groups that are introduced on Si carry lone pairs that make them good candidates for bridging positions. They are also efficient at stabilizing the silylene group through $\pi$ donation into the empty p orbital of $SiR_2$. These two factors should favor the silylene structure (**B** type) or the unusual bridge structure (**C** type) and disfavor the silyl **A** type complex.

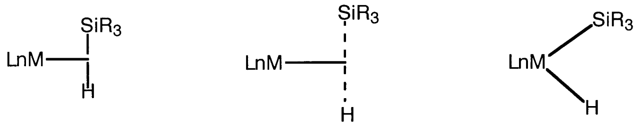
The preferred structure of $[(dhpe)Pt(SiHCl_2)]^+$ is the hydrido-silylene complex, **9B**, but at almost the same energy (0.4 kcal·mol$^{-1}$ above) is a structure with Cl bridging the Pt−Si(H)(Cl) bond, **9C(Cl)**. The geometrical structure of **9B** is unremarkable. The structure of **9C(Cl)** shows a Cl equally bridging Si and Pt. For the transition state, **9A**, (10.1 kcal·mol$^{-1}$ above **9B**) between **9B** and **9C(Cl)** the $SiHCl_2$ group has no bridging atom. The replacement of the unique H by Cl in $(dhpe)Pt(SiHCl_2)^+$ leads to complex **10C(Cl)**, that has a bridged Cl. No other isomer could be located on the potential energy surface; only type **C** structures are found for this system.

The preferred structure of $[(dhpe)Pt(SiH(OMe)_2)]^+$ has many more minima due to some additional conformational possibilities associated with the OMe group. The most stable group of structures is of the hydrido-silylene **B** type. In the most stable arrangement, **11B**, the O−Si−O plane is in the molecular plane. Another minimum, **11B′**, with the O−Si−O plane perpendicular to the P−Pt−P plane is 2.4 kcal·mol$^{-1}$ above **11B**, and the transition state between these two rotamers is 2.9 kcal·mol$^{-1}$ above **11B**. There is clearly easy rotation of the $Si(OMe)_2$ group. The next group of structures, **11C(OMe)**, 14 kcal·mol$^{-1}$ higher than **11B**, has an OMe group bridging the Pt−Si(H)(OMe) bond. The transition state, **11A**, between the bridged OMe species, **11C(OMe)**, and the hydrido-silylene complex, **11B**, has a $SiH(OMe)_2$ group with no bridging group and is found 22.5 kcal·mol$^{-1}$ above **11B**. A transition state of comparable nature and energy to **11A** was found to exchange the bridging and terminal methoxy groups.

When OMe is replaced by SMe, the most important change compared to OMe is that the bridged SMe species, **12C(SMe)**, becomes 1.9 kcal·mol$^{-1}$ more stable than the hydrido-silylene complex, **12B**, where the silylene is stabilized by two SMe groups. The transition state, **12A**, between **12C(SMe)** and **12B**, with a nonbridging $SiH(SMe)_2$ group is 23.9 kcal·mol$^{-1}$ above **12C(SMe)**. The more diffuse orbitals of S compared to O make it an especially good bridging group.

In the case of two $NMe_2$ groups, the hydrido-silylene complex, **13B**, is the most stable structure in accord with the strong $\pi$ donating ability of N compared to O. The

**Scheme 2**



structure with a bridged NMe$_2$ group, **13C(NMe$_2$)**, is 5.4 kcal·mol$^{-1}$ above **13B**. The transition state, **13A**, between **13B** and **13C(NMe$_2$)** with a nonbridging SiH(NMe)$_2$ group is 27 kcal·mol$^{-1}$ above **13B**.

## Discussion

Our results generalize the results found for SiHR$_3$ to the case of the SiH$_3$ group itself. In the case of SiR$_3$−H, three different structural types (Scheme 2) have been found depending on the degree to which the hydride and the silyl group interact.[5,11] In our case, the degree of Si−H bonding also varies; the difference between SiR$_3$−H and the present case is that the former corresponds to a change of oxidation state to the metal while the latter is not associated with a redox process if the silylene is considered as a neutral ligand. No such behavior is seen in carbon chemistry where the bridged case is usually not found. As mentioned previously, the bridging hydrogen atom in carbon chemistry is very well documented in carbocation chemistry but not in transition metal alkane, alkyl, or alkylidene species. When H forms a bridge, it requires that the partial bonds to the bridge atoms must be sufficiently strong to overcome the classical situation when a H atom is bonded to a single carbon or silicon atom. The strong C−H bond (100−110 kcal·mol$^{-1}$) disfavors such a situation because the bond to the other atom would be considerably weaker when the other atom is a transition metal. The Si−H bond energy, around 90 kcal·mol$^{-1}$,[33] is closer to that of a M−H bond.[34] These energy considerations account for the occurrence of a bridging situation like **C** type, but these considerations do not say it will occur. They do not give direction for when it does occur. Why is the bridge situation favored with the SiH$_3$ group and not with SiHMe$_2$? The electron donating ability of Me probably stabilizes the silylene group. This is consistent with the same effect seen with all other $\pi$ donating groups (Cl, OR, SR, NR$_2$) considered in this work. However, in each case, bridged structures appear as alternate minima. This is the case for groups which are known to form bridge bonds by utilizing their lone pairs. The ability for CH$_3$ and SiH$_3$ groups to take a bridging position with the silyl ligand is remarkable. Recently, Tilley et al. have found a Ta complex in which the SiMe$_2$H group of a CH$_2$−SiMe$_2$−SiMe$_2$H chain is shown to be bridging the metal center and also forming a $\gamma$ Si−H interaction,[35] a structure which is said to be unprecedented.[1b] Although the Ta complex is different from the systems studied here, they both illustrate the ability of the SiH$_3$ group to take a bridging position.

Although, as already mentioned, these bridging situations are unprecedented for alkyl/carbene complexes, it is worth mentioning that related structures can be found in the chemistry of transition metal boryl complexes.[36]

In the case of the SiMe$_3$ group, the calculations have shown the presence of several isomers that are close in energy. In our system, the least stable isomer is a Pt−methyl−SiMe$_2$ complex. At lower energy are isomers with a silylene group with a bridged or terminal H depending on the position of H relative to the silylene and also a Pt−SiMe$_3$ complex with a bridged Me group. The existence of these nearly isoenergetic isomers is fully consistent with the observation of a silene−silylene rearrengement in a cationic iridium complex.[37] It is also consistent with the observation of a H elimination of an aliphatic C−H bond from a silyl ligand to generate a silene complex of Ru(II).[38] Likewise, the redistribution of the Me group between silicon centers in the bis-silyl tungsten complex attributed to the presence of a silylene/silyl intermediate is probably related to our finding.[39a] The small calculated difference in energy between the various isomers in our Pt complexes can easily be modified by changing the metal and ligands. These points require further studies. Our very different results on the Pt−SiH$_3$ and Pt−CH$_3$ complexes are also consistent with the noted propensity for silyl complexes to undergo 1,2-rearrangement. These migrations have been found to be especially facile when a comparison is made to the behavior of the corresponding alkyl derivatives.[39b]

The ability of a $\pi$ donor group to function as a bridging group is no surprise. Our results for the SR substituted silyl group are fully consistent with the formation of [*cis*-(PEt$_3$)$_2$-Pt($\mu$-S$^t$Bu) (HSi(S$^t$Bu)]$^+$ from [*cis*-(PEt$_3$)$_2$Pt(H)Si(S$^t$Bu)$_2$]$^+$.[40] These two complexes, of type **C** and **A** according to our classification, are calculated to be only 1.9 kcal·mol$^{-1}$ apart. A reversible 1,2 H-transfer was observed at low temperature in the experimental system. The transition state for this process has been calculated to be over 20 kcal·mol$^{-1}$ above the two minima. This rather high transition state may be stabilized by coordination of OEt$_2$ at the Pt empty site.

The groups that favor a stable silylene complex (i.e., a minimum on the potential energy surface) are $\pi$ donors either with their lone pairs (Cl, OR, SR, NR$_2$) or because of efficient hyperconjugation. Thus, the silylene complex is not a minimum for R = H and SiH$_3$. However, there is no simple rationale for understanding the relative energies of the nonbridged and bridged Pt−silylene complexes because the

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two situations can be stabilized by the occupied orbitals of the R groups.

The very high sensitivity of the silyl complexes to small chemical changes shown in this work shows that special care must be exercised when choosing the model for carrying out calculations when an accurate geometrical minimum is the goal. This could be a limitation for using calculations for determining the absolute minimum in this family of complexes. The electronic property of the phosphine ligand, its steric influence, as well as the presence of a counterion could all influence the geometry of the Pt$-$SiR$_3$ moiety and need to be included in the calculations. A similar conclusion was reached in a study of silyl groups interacting with a lanthanide metal center.[41] A general conclusion that emerges from our studies is that special care should be taken when using computational studies for determining the absolute minimum of silicon-containing transition metal complexes. They are probably more sensitive to the nature of all elements of the complex than equivalent carbon complexes. For instance, the geometry of the molecule which initiates the work, $[(\mathrm{dippe})\mathrm{Pt(H)(SiR_2)}]^+$ (dippe $=$ $^i$Pr$_2$P$-$CH$_2$$-$CH$_2$$-$P$^i$Pr$_2$; R $=$ mesityl), needs to be calculated with the complete diphosphine ligand and the two mesityl groups. The work is in progress using QM/MM methology.

## Conclusions

The (diphos)Pt$-$silyl complexes reveal structural features that are unusual and unprecedented in equivalent alkyl complexes. Unusual bridged structures appear as possible minima in addition to or in replacement of the traditional silyl or silylene complexes that are derived from the analogy with the analogous carbon complexes. Even groups such as CH$_3$ and SiH$_3$ are candidates for bridging position in addition to the usual groups Cl, OR, SR, and NR$_2$ for such position. The nature of the minima depends strongly on the precise nature of the ligands, suggesting that considerable caution should be taken when modeling transition metal silicon-containing complexes.

**Acknowledgment.** Financial support from the Spanish DGES (Project PB98-0916-C02-01) and the Catalan DURSI (Project 1999 SGR00089) is acknowledged. F.M. thanks also the support of DURSI, which has allowed the stay of M.B. in Montpellier.

IC025911J

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