Articles

Silyl, Hydrido Silylene or Alternative Bonding Modes: The Many Possible Structures of $[(C_5H_5)(PH_3)IrX]^+$ ($X = SiHR_2$ and SiR_3; $R =$ H, CH_3, SiH_3, and Cl)

Maria Besora,[†] Feliu Maseras,[†,‡] Agustí Lledós,*,[†] and Odile Eisenstein*,[§]

Unitat de Química Física, Edifici Cn, Universitat Autònoma de Barcelona, 08193 Bellaterra, Catalonia, Spain, Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans, 16, 43007 Tarragona, Catalonia, Spain, and LSDSMS (UMR 5636 CNRS-UM2), Institut Gerhardt, Université Montpellier 2, 34095 Montpellier Cedex 05, France

Received May 9, 2006

DFT calculations with the B3LYP functional are carried out on the systems $[Cp(PH_3)Ir(SiHR_2)]^+$ and $[Cp(PH_3)Ir(SiR_3)]^+$ ($Cp = C_5H_5$, $R =$ H, CH_3, SiH_3, Cl), which are representative examples of experimental complexes where the silylene ligand can exist. Geometry optimization for the different systems gives a large variety of structures, including the conventional silyl and hydrido silylene isomers, but also other less usual bridged structures, with a variety of groups taking a bridging position. Analysis of the large amount of data, together with those previously reported for $[(dhpe)Pt(SiHR_2)]^+$ and $[(dhpe)Pt(SiR_3)]^+$ ($dhpe = H_2P{-}CH_2{-}CH_2{-}PH_2$), leads to a better understanding of the general factors governing the relative stabilities of the possible isomeric forms.

Introduction

Organosilanes are involved in many catalytic transformations.[1] A number of transition metal complexes are able to catalyze the Si−H activation process, through oxidative addition, σ bond metathesis, and other mechanisms.[2] The coordination of the silicon atom to the metal is usually expected to produce species containing the formally simple silyl or silylene ligands. The case of the silylene ligands, with a double bond between the metal and the silicon, has received extensive attention in recent years.[3−12] Structures such as σ complexes containing the η^2 coordination of $H{-}SiR_3$ bonds[13−22] or an agostic H−Si bond[2,23,24] have also been characterized. An important amount of experimental work has been invested in the synthesis and characterization of transition metal complexes with silicon-based ligands in order to shed some light on the detailed mechanism of the Si−H activation and the factors affecting it.[1,9,10,25−28] However, the full structural characterization of the complexes may be prevented by the difficulty in locating hydrogen atoms by X-ray crystallography.

Systems related to Si−H activation by transition metal complexes have also been the subject of considerable computational work.[16,17,29−39] In particular, we studied computation-

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* Corresponding authors. E-mail: agusti@klingon.uab.es (A.L.); odile.eisenstein@univ-montp2.fr (O.E.).

[†] Universitat Autònoma de Barcelona.

[‡] ICIQ.

[§] Université Montpellier 2.

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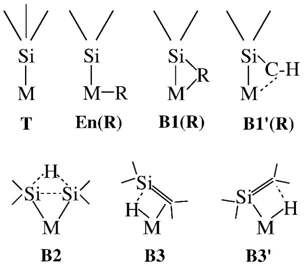

Figure 1. Schematic representation of the possible binding modes of a silyl group in a transition metal complex.

ally[33] the structural features of the platinum complexes $[(dhpe)Pt(SiHR_2)]^+$ and $[(dhpe)Pt(SiR_3)]^+$ (dhpe $= H_2P-CH_2-CH_2-PH_2$) with different R substituents. This study followed the synthesis and characterization of related platinum complexes.[26] Our computational study revealed a far more complicated situation than we expected. In addition to conventional terminal silyl (**T**) or doubly bonded silylene (**En**), a number of unusual bridged structures (**B**) were found as local or absolute minima. A schematic representation of the possible minima is shown in Figure 1.

The structural complexity of these systems was confirmed by subsequent studies. A computational study by Frenking and co-workers[34] of a tungsten complex,[7,40] $[Cp^*(dmpe)W(H_2SiMe_2]^+$ ($Cp^* = C_5Me_5$), found that the absolute minimum is a dihydride silylene structure, but four other structures with bridging hydrogen atoms are less than 5 kcal mol^{-1} above in energy. In a theoretical study of some Ir(V)/Ir(III) complexes bearing an SiH_3 group, a structure with a bridging hydrogen, **B1(H)**, has been located as a minimum.[41] Structures with bridging groups such as **B1(R)** have also been observed in experimental complexes by the group of Tilley.[42] Berry and co-workers reported a bridged structure of type **B3**.[43]

Inspired by the success of the predictions from our initial work,[33] we decided to extend the study to a different system. With this, we hope to be able to advance toward a systematization of available structures. Furthermore, by using a different metal and a different set of ligands we also expect to draw some conclusions on the properties of the metallic fragment ruling the relative stabilities of the different possible isomeric forms. The model systems we chose for this new study were based on the experimental iridium complexes $[(Cp^*)(PMe_3)Ir(HSiR_2)]^+$. The reactivity of this type of species has been investigated by Tilley and co-workers.[3−6] Evidence of an interconversion involving silene and silylene ligands in the coordination sphere of a transition metal complex was reported. Some of the products or intermediates were identified as complexes with bridging groups, as for $[(Cp^*)(PMe_3)Ir(\eta^2\text{-}CH_2SiMe_2)(H)]^+$, whose structure was determined by X-ray diffraction.[4]

The experimental complexes were modeled by $[Cp(PH_3)Ir(HSiR_2)]^+$ ($Cp = C_5H_5$) in our computational studies. The replacement of the cyclopentadienyl and phosphine methyl groups by hydrogen decreases considerably the computational time without altering significantly the electronic structures at the metal center. The nature of the silyl group was also modified by changing the nature of R (R = H, Me, SiH_3, and Cl). The $[Cp(PH_3)Ir(SiR_3)]^+$ systems, with SiR_3 instead of $HSiR_2$, were also computed for the sake of comparison.

The aim of this study is to evaluate, through geometry optimizations with the DFT computational method, the relative energies of isomers of the type **T**, **En**, and **B** shown in Figure 1. This classification used in our earlier work[33] needs further refinement. In the case of the terminal silyl group (**T**) there is only one type of isomer, but for the silylene structures derived from a $SiHR_2$ group, we have to envisage the silylene complex with H (**En(H)**) or R (**En(R)**) as terminal groups at the metal. A large number of bridging structures can be written. The bridging group between Ir and Si can be an atom such as H (**B1(H)**) or Cl (**B1(Cl)**) or R such as CH_3 or SiH_3 (**B1(R)**). With these latter systems, one can have β C−H or Si−H agostic interactions. These latter complexes will be labeled **B1′(R)**. Finally other structures with bridging groups will appear. Structure **B2**, with a hydrogen atom bridging two silylene type groups, can exist. When R = SiH_3 or R = CH_3, possible structures also include **B3** and **B3′**, where a silene group bonds in two different ways to the metal and interacts through either Si or C with a bridging hydrogen. These **B3** and **B3′** structures are formally related to β elimination products from CH_2-SiR_2H or SiR_2-CH_3 groups.

Computational Details

Calculations were performed with the Gaussian 98 series of programs.[44] Density functional theory (DFT)[45−48] was applied with the B3LYP hybrid functional.[49,50] A quasi-relativistic effective core potential (ECP) was used to replace the innermost electrons for the third-row elements Si, P, and Cl and the transition metal Ir. The Hay and Wadt ECP replaced 60 inner electrons of the Ir atom[51] and 10 of Si, P, and Cl.[52] The basis set used for the valence shell of these atoms was the standard double-ζ LANL2DZ contraction associated with the pseudopotentials.[44] For Si and P the basis set was augmented by a d polarization function.[53] A 6-31G(d,p) basis set was used for the H atoms attached to Si or to Ir.[54,55] For other

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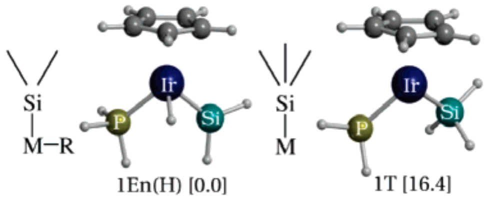

Figure 2. Optimized isomers for $[Cp(PH_3)Ir(SiH_3)]^+$, **1**. Relative energies (kcal mol^{-1}) are shown in square brackets.

H and for C, a 6-31G basis set was used.[54] All geometry optimizations were carried out without any symmetry restriction, unless otherwise stated. All computed minima were confirmed as such through analytical computation of the Hessian matrix. All discussions are carried out on the potential energies obtained from the SCF calculations. The charge analysis was carried out using the NBO approach.[56] The solvent effect was represented with the PCM scheme (DPCM).[57−59]

Results

$[Cp(PH_3)Ir(SiH_3)]^+$. The two minima optimized for $[Cp(PH_3)Ir(SiH_3)]^+$, **1**, are shown in Figure 2. The most stable structure is a silylene−hydrido complex, **1En(H)**. It has a three-legged piano-stool geometry, which sets the metal in an octahedral environment because the Cp ring can be viewed as a L_2X ligand set. The H−Ir−Si angle of 81.5° suggests the absence of through-space interaction between the hydride and the SiH_2 group. The hydride and SiH_2 exclusively interact with Ir, as confirmed by the Ir−H and Ir−Si bond distances of 1.596 and 2.228 Å, which are representative of Ir−H single bond and Ir−Si double bond distances. The silylene group is planar, with an Ir−Si−H angle of 125.5° (av). The plane containing the silylene group bisects the H−Ir−P angle and contains the approximate C_5 axis of the Cp ring. This orientation maximizes the $d_\pi-p_\pi$ interaction between the d^6 metal and the SiH_2 empty p orbital, as demonstrated by simple molecular orbital considerations for the isolobal $[CpFe(CO)_2(CH_2)]$ complex.[60]

The secondary minimum is 16.4 kcal mol^{-1} above **1En(H)**. It has a terminal SiH_3 group bonded to the metal and thus classifies as **1T**. It is a two-legged piano-stool with the silyl and PH_3 ligands as legs. The Ir−Si bond length of 2.394 Å, significantly longer than that in **1En(H)**, is consistent with a single bond between Ir and the silyl group. The three Si−H bonds are similar, but one Si−H bond is slightly longer than the two other ones (1.490 Å compared to 1.475 Å (av)). This suggests the possibility of a weak Ir···Si−H agostic interaction, which is consistent with the fact that $[Cp(PH_3)Ir(SiH_3)]^+$ is a 16 e$^-$ complex. Despite this weak agostic interaction, the presence of a nonbridging SiH_3 group is undisputable.

No minimum corresponding to a bridged structure of type **B** was found for this complex. To evaluate the energy of such a structure, an optimization geometry in which the H−Ir−Si angle was frozen to 50.7° (the value calculated for platinum complexes presenting a structure with H bridging Ir and Si) was carried out. The resulting structure is found 4.6 kcal mol^{-1} higher than the most stable isomer, **1En(H)**. Relaxing this structure, leads to **1En(H)**, demonstrating that the structure with bridging hydrogen is not a minimum on the potential energy surface. Incorporating solvent by a PCM scheme with $\epsilon = 7.58$ to model THF does not modify the results.[61]

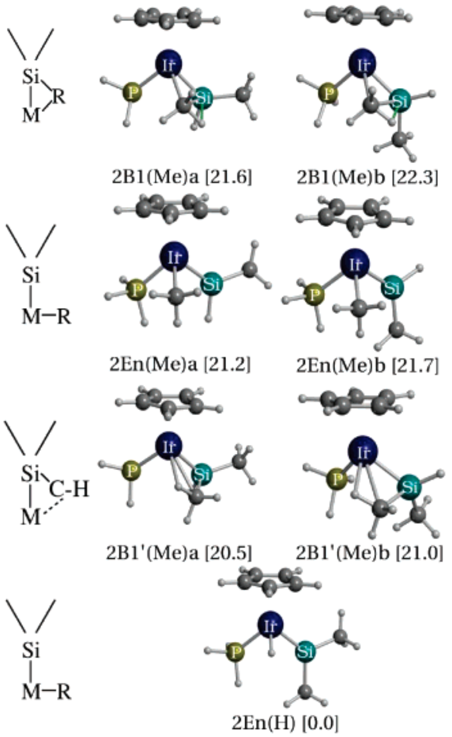

Figure 3. Optimized isomers for $[Cp(PH_3)Ir(SiH(CH_3)_2)]^+$, **2**. Relative energies (kcal mol^{-1}) are shown in square brackets.

$[Cp(PH_3)Ir(SiHR_2)]^+$ (R = CH_3, SiH_3, Cl). The structures of $[Cp(PH_3)Ir(SiHR_2)]^+$ (R = CH_3, **2**; R = SiH_3, **3**; and R = Cl, **4**) were optimized. The results are shown in Figures 3, 4, and 5 for **2**, **3**, and **4** respectively.

For **2**, seven isomers were located. The most stable isomer is the silylene−hydrido complex **2En(H)**. All other minima are at least 20 kcal mol^{-1} higher in energy. The main structural features of **2En(H)** (Ir−H = 1.592 Å, Ir−Si = 2.249 Å, and H−Ir−Si = 80°) and **1En(H)** are similar, which ascertains the nature of **2En(H)**. The six other isomers are close in energy and are grouped in three pairs. These pairs differ by the position of one methyl group, which either is bonded exclusively to the metal or takes various bridging positions between the metal and the silicon atom. The existence of a pair is associated with the exchange of the positions of the other methyl group and of the hydrogen, which are bonded to Si. The isomers of a pair are always close in energy.

A pair of structures with Me bonded to Ir and a SiHMe silylene group, identified as **2En(Me)a** and **2En(Me)b**, are 21.2 and 21.7 kcal mol^{-1} above **2En(H)**. The Ir−C distance of 2.170 Å (av) and the Ir−Si distance of 2.233 Å (av) are representative of single Ir−C and double Ir−Si bond distances. The existence of the pair derives from the position of the methyl group on the silylene, which is either *syn* or *anti* to the Cp ring. There is no interaction between the Me group bonded to Ir and the silylene Si, as shown by the C−Ir−Si angle equal to 88.5°. The **2En(Me)** isomers have a higher energy than **2En(H)** because

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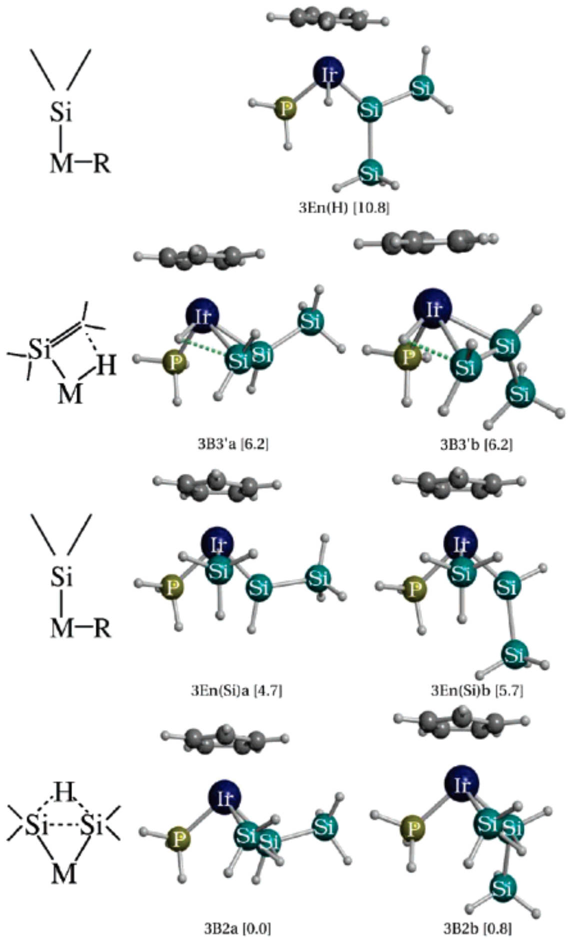

Figure 4. Optimized isomers for $[Cp(PH_3)Ir(SiH(SiH_3)_2)]^+$, **3**. Relative energies (kcal mol^{-1}) are shown in square brackets.

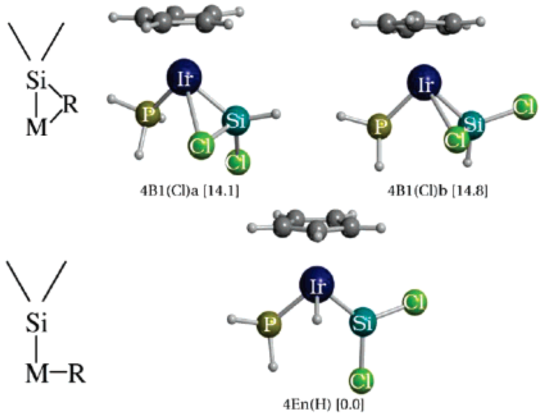

Figure 5. Optimized isomers for $[Cp(PH_3)Ir(SiHCl_2)]^+$, **4**. Relative energies (kcal mol^{-1}) are shown in square brackets.

the late transition metal tends to make a stronger bond to H than to Me[62] and because the electron-donating methyl groups stabilize the unsaturated sp^2 Si center and notably the empty p orbital of the silylene.

The other four isomers involve bridging methyl groups. The bridge can be with the carbon only or with a C−H bond. In the case of the pair **2B1(Me)a** and **2B1(Me)b**, the methyl group participates in the bridge through the carbon only, which leads to an acute Ir−Si−C angle of 61°. The bridging carbon atom is 2.190 and 2.176 Å from Si and 2.254 and 2.257 Å from Ir. In the other pair, **2B1′(Me)a** and **2B1′(Me)b**, the angle Ir−Si−C is larger (73.6°), the C−H bond is elongated to 1.140 Å, and the orientation shows the characteristics of an agostic C−H bond at the bridging methyl group. In other words, this latter structure can be viewed as having a bridging C−H bond. These **2B1′(Me)a** and **2B1′(Me)b** structures are 20.5 and 21.0 kcal mol^{-1} above the most stable isomer. The structures with a bridging C−H bond and a bridging carbon atom thus have similar energies.

Structures with a terminal $SiHMe_2$ group (**2T**) or with a hydrogen bridging the Ir−Si bond have not been found as local minima. Partial optimization, freezing some geometrical parameters, was carried out to estimate the energy of such structures. To search a **T** type structure, the Ir−Si−H and Ir−Si−C angles were frozen at 109°. This gave a structure 26 kcal mol^{-1} above **2En(H)**, showing that a terminal $SiHMe_2$ group is a highly unfavorable situation. To search for a **2B1(H)** structure, the H−Ir−Si angle was frozen at 50.7°. This gave a structure, only 5.9 kcal mol^{-1} above **2En(H)**, that reverted to **2En(H)** upon full optimization.

The geometry optimization of $[Cp(PH_3)Ir(SiH(SiH_3)_2)]^+$, **3**, lead to seven isomers, having either a terminal hydrogen, a terminal SiH_3 group, or a variety of bridging modes (Figure 4). In contrast to **2**, where the energies of the various isomers are spread over more than a 20 kcal mol^{-1} range, all isomers of **3** are much closer in energy and the energy difference between the most and least stable of the isomers is less than 11 kcal mol^{-1}. Another significant difference with **2** is that the silylene−hydrido complex **3En(H)** is the least stable of all the structures (10.8 kcal mol^{-1} above the absolute minimum). In **3En(H)**, Ir−H is equal to 1.592 Å, Ir−Si is equal to 2.256 Å, and H−Ir−Si is equal to 80.8°. These geometrical parameters are similar to those of **2En(H)**.

The most stable pair of isomers is **3B2a** and **3B2b**. As it was the case for **2**, the presence of a pair is associated with the exchange of position of H and SiH_3 bonded to Si(Ir). The isomers within a pair have very close structural features and energies. We either give average structural values or discuss only one member of the pair when more convenient. In the **3B2** pair, Ir is bonded to $SiH(SiH_3)$ and to a SiH_2 group with almost equal Ir−Si distances (2.332 and 2.350 Å). The distance between the two Si atoms bonded to Ir symmetrically is short, 2.340 Å. In addition, a hydrogen atom bridges the Si−Si bond symmetrically (Si−H = 1.680 Å, Si−Si−H = 41.7°). The pair of isomers, higher than **3B2**, is labeled **3En(Si)**. In these silylene−silyl complexes, the Ir−Si single bond of 2.45 Å (av) is significantly longer than the Ir−Si double bond of 2.240 Å (av). There is no through-space Si···Si interaction between the silyl and the silylene, as shown by the Si−Ir−Si angle of 86.5° (av). The next pair of isomers, in order of increasing energy, consists of **3B3′a** and **3B3′b**. These structures have the ligand $SiH(SiH_3){=}SiH_2$ where the substituted Si atom is bonded to the metal and where there is also a hydride ligand in a bridging position between SiH_2 and Ir. These structures can be viewed as deriving from a β-H elimination from $Ir{-}SiH(SiH_3){-}SiH_3$. The bridging H is close to both Ir (Ir−H = 1.601 Å (av)) and Si (Si−H = 2.197 Å (av)). The doubly bonded Si═Si group (Si−Si = 2.22 Å) is almost symmetrically coordinated to Ir (Ir−Si = 2.52 and 2.54 Å).

No structure with a terminal $SiH(SiMe_3)_2$ of type **T** could be located as a minimum. Partial optimization using the procedure previously described led to an energy of a model of **3T**, which lies 27 kcal mol^{-1} above the best isomer. A structure with bridging H is also missing as a minimum. Partial optimization

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[62] Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

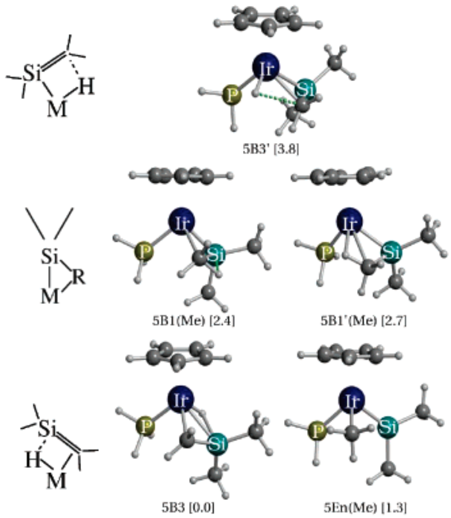

Figure 6. Optimized isomers for $[Cp(PH_3)Ir(Si(CH_3)_3)]^+$, **5**. Relative energies (kcal mol^{-1}) are shown in square brackets.

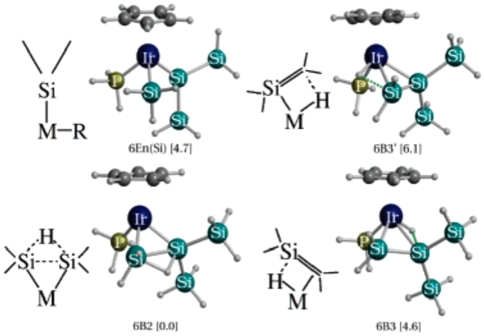

Figure 7. Optimized isomers for $[Cp(PH_3)Ir(Si(SiH_3)_3)]^+$, **6**. Relative energies (kcal mol^{-1}) are shown in square brackets.

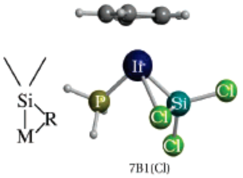

Figure 8. Optimized isomer for $[Cp(PH_3)Ir(SiCl_3)]^+$, **7**.

of a model of **3B(H)** gives an energy of 16 kcal mol^{-1} above the best isomer. These two structures revert to previously located minima upon full optimization.

The optimization of $[Cp(PH_3)Ir(SiHCl_2)]^+$, **4**, gives only three minima, covering an energy range of 15 kcal mol^{-1} (Figure 5). The most stable isomer is **4En(H)**. The structure is similar to the previously found silylene complexes (Ir−H = 1.591 Å, Ir−Si = 2.229 Å, and H−Ir−Si = 83°; Si−Cl = 2 Å). The higher structures come as a pair. They both have a chlorine atom bridging the Ir−Si bond (Ir−Cl = 2.617 Å (av) and Si−Cl = 2.201 Å (av)) and thus are labeled as **4B1(Cl)**. The members of the pair differ by the position of H and nonbridging Cl.

The energy of the missing minima was estimated by partial optimization as described previously. A model of **4T** was found to be at 24 kcal mol^{-1}. A model of silylene−chloride complex **4En(Cl)** (Cl−Ir−Si angle frozen at 90°) was found at 27 kcal mol^{-1}. A model of a complex with bridging H, **4B1(H)**, was found to be at 8.3 kcal mol^{-1}. It is remarkable that it is more stable than the secondary minimum with a bridging Cl, **4B1(Cl)**. However all these species reverted to those previously found upon full optimization.

$[Cp(PH_3)Ir(SiR_3)]^+$ (R = CH_3, SiH_3, Cl). The complexes without hydrogen on the silyl group were studied. The optimized structures are shown in Figures 6, 7, and 8 for R = CH_3, SiH_3, and Cl, respectively.

The optimization of $[Cp(PH_3)Ir(Si(CH_3)_3)]^+$, **5**, gives five isomers spread over an energy of 3.8 kcal mol^{-1}. The structure of lowest energy is **5B3**. The Si−C bond distance is equal to 1.799 Å, and the Si−C double bond is coordinated in a dihapto manner to Ir with Ir−Si and Ir−C distances equal to 2.224 and 2.555 Å, respectively. The bridging hydrogen is significantly closer to Ir (1.622 Å) than to Si (2.010 Å). However, the Ir−H distance is longer than for a pure terminal H (1.596 Å in **1En(H)**), and a Si−H distance of 2 Å is indicative of a significant interaction between Si and H. It is of interest to note that a structure **5B3′**, equivalent to **5B3** but where H bridges Ir and C in place of Ir and H, has been also located as a minimum. It is the least favorable of all isomers, although only 3.8 kcal mol^{-1} above **5B3**. In **5B3′**, the Ir−H distance is 1.582 Å and H is rather far from C. It is almost more appropriate to consider **5B3′** as having a dihapto-coordinated $Me_2Si{=}CH_2$ group and a hydride ligand with a *cis* interaction between the hydride and the π-bonded ligand.[63] The weaker interaction between the hydride and the π-bonded silene ligand accounts for **5B3′** being at higher energy than **5B3**. Another isomer, very close in energy to the absolute minimum, is **5En(Me)**, with a terminal methyl group (Ir−C = 2.161 Å) and a silylene (Ir−Si = 2.245 Å) substituted by two methyl groups. This structure is very similar to the pair of structures **2En(Me)**. The next pair of isomers has a methyl group bridging the Ir−Si bond via a carbon only (**5B1(Me)**, Ir−C = 2.253 Å and Si−C = 2.234 Å) or via a C−H bond (**5B1′(Me)**, C−H = 1.139 Å). These structures are very similar to **2B1(Me)** and **2B1′(Me)**. No structure with a terminal $SiMe_3$ group, **5T**, could be located as a minimum. Partial optimization gives a structure 10.3 kcal mol^{-1} above **5B3**, which disappears upon full optimization.

The solid-state structure of $[Cp^*Ir(PMe_3)(\eta^2\text{-}CH_2{-}SiMe_2)(H)]^+$, **4**, can be compared to the optimized structures found for **5**. The hydrogen atoms could not be detected in the X-ray diffraction, but IR and ^1H NMR spectroscopies showed that H was bonded to Ir. The X-ray diffraction shows the presence of a silene ligand where Ir−C is equal to 2.22(2) Å, Ir−Si is equal to 2.439(9) Å, and Si−C is equal to 1.84(2) Å. These parameters are close to that of the absolute minimum **5B3** or the highest local minimum **5B3′**. However the presence of a hole, for the hydrogen, between the phosphine ligand and $SiMe_2$ fits **5B3** best. Interconversion to a silylene−methyl group (only characterized as a base-stabilized complex) is suggested to occur via a structure containing a terminal $SiMe_3$ group. Our calculations, which give the base-free silylene−methyl complex **5En(Me)** only 1.3 kcal mol^{-1} above the silene complex **5B3** and a terminal silyl complex **5T**, 10 kcal mol^{-1}, although not a true minimum, agree well with the experimental findings.

The optimization of $[Cp(PH_3)Ir(Si(SiH_3)_3)]^+$, **6**, gives four isomers over an energy range of 6 kcal mol^{-1}. The most stable isomer, **6B2**, is similar to that found for **3B2**. It has $Si(SiH_3)_2$ and SiH_2 groups (Ir−Si = 2.35 Å (av)) bonded to the metal, these two groups being themselves relatively close to each other (2.52 Å) and being symmetrically bridged by H (Si−H = 1.47 Å (av)). Two other structures, 4.6 and 6.1 kcal mol^{-1} above **6B2**, have a $SiH_2Si(SiH_3)_2$ silene ligand coordinated η^2 to the metal and bridged by a hydrogen atom on one of the Ir−Si bonds. When the Si atom next to the bridging H has two SiH_3

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[63] Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073.

Table 1. Relative Energies (kcal mol^{-1}) for the Isomers of $[Cp(PH_3)Ir(SiHR_2)]^+$ (R = H, CH_3, SiH_3, and Cl; 1−4) and $[Cp(PH_3)Ir(SiR_3)]^+$ (R = CH_3, SiH_3, and Cl; 5−7)[a]

		T	En		B1		B2	B3	
silyl			(H)	(R)	(H)	(R)		B3	B3′
SiH_3	1	16.4	**0.0**		(4.6)				
$SiH(CH_3)_2$[b]	2	(26.0)	**0.0**	21.2/21.7	(5.9)	20.5/21.0 21.6/22.3			
$SiH(SiH_3)_2$	3	(27.4)	10.8	4.7/5.7	(16.0)		**0.0**/0.8	6.2/6.2	
$SiHCl_2$	4	(24.0)	**0.0**	(27.3/27.7)	(8.3)	14.1/14.8			
$Si(CH_3)_3$[b]	5	(10.3)		1.3		2.4 2.7		**0.0**	3.8
$Si(SiH_3)_3$	6	(27.6)		4.7			**0.0**	4.6	6.1
$SiCl_3$	7	(7.4)		(10.0)		**0.0**			

[a] Values separated by a slash sign indicate a pair of isomers differing by exchange of the substituents at the Si atom bonded to Ir. Values in parentheses indicate isomers obtained by partial optimization while freezing selected internal coordinates. These isomers are not true minima. [b] Values on the first line indicate a **B1** type isomer (bridging CH_3 group through C only); values on the second line indicate a **B1′** type isomer (bridging CH_3 group through a C−H bond).

Table 2. Relative Energies (kcal mol^{-1}) for the Isomers of $[(dhpe)Pt(SiHR_2)]^+$ (R = H, CH_3, SiH_3, and Cl) and $[(dhpe)Pt(SiR_3)]^+$ (R = CH_3, SiH_3, and Cl)[33] [a]

	T	En		B1		B2	B3	
silyl		(H)	(R)	(H)	(R)		B3	B3′
SiH_3	3.1	(3.4)		**0.0**				
$SiH(CH_3)_2$[b]	(15.6)	**0.0**	(21.5/21.5)	(0.4)	8.2/8.4 10.8/10.8			
$SiH(SiH_3)_2$	(20.3)	(18.3)	(12.0/12.1)	15.2		**0.0/0.0**	5.0/5.0	
$SiHCl_2$	(10.4)	**0.0**	(19.9)	(2.8)	0.4/0.4			
$Si(CH_3)_3$	(7.4)		(9.9)		0.2/2.3		**0.0**	14.3
$Si(SiH_3)_2$	(22.8)		(11.6)			**0.0**	4.4	4.7
$SiCl_3$	(8.4)		(15.8)		**0.0**			

[a] Values separated by a slash sign indicate a pair of isomers differing by exchange of the substituents at the Si atom bonded to Pt. Values in parentheses indicate isomers obtained by partial optimization while freezing selected internal coordinates. These isomers are not true minima. [b] Values on the first line indicate a **B1** type isomer (bridging CH_3 group through C only); values on the second line indicate a **B1′** type isomer (bridging CH_3 group through a C−H bond).

substituents, the isomer is labeled **6B3**, and when it has two H substituents, it is the **6B3′** isomer. In both species, the Si−Si distance is that of a double bond (2.223 Å (av)) coordinated in a dihapto manner to Ir (Ir−Si = 2.603 Å (av)). The hydride is 1.641 Å (av) from Ir. The last isomer is **6En(Si)**, 4.7 kcal mol^{-1} above **6B2**. This silylene−silyl complex has no remarkable differences from the previous silylene complexes discussed in this work (Ir−Si(silyl) = 2.445 Å, Ir−Si(silylene) = 2.259 Å). A structure with a terminal $Si(SiH_3)_3$ group, **6T**, could not be located as a minimum, and partial optimization gave an energy of 27.6 kcal mol^{-1}.

The optimization of $[Cp(PH_3)Ir(SiCl_3)]^+$, **7**, gave one minimum, **7B1(Cl)**. In this structure, a chlorine atom is bridging the Ir−Si bond (Ir−Si = 2.293 Å, Ir−Cl = 2.622 Å, and Si−Cl = 2.207 Å). No structures with a terminal $SiCl_3$ group, **7T**, and with a silylene group and a terminal chlorine, **7En(Cl)**, could be located as minima. Using the partial optimization procedure, they were estimated to be at 7.4 and 10 kcal mol^{-1} above **7B1(Cl)**, respectively.

Discussion

The relative energies for the various isomers of $[Cp(PH_3)Ir(SiHR_2)]^+$ (R = H, CH_3, SiH_3, Cl; **1**−**4**) and $[Cp(PH_3)Ir(SiR_3)]^+$ (R = CH_3, SiH_3, Cl; **5**−**7**) are shown in Table 1, where values in parentheses correspond to species, which are not true minima. The most remarkable result is that a terminal silyl group is never a favored structure in these 16 e$^-$ species. In most cases, this is not even a true minimum. While the silyl group is certainly stable in many complexes,[2] the occurrence of an empty coordination site seems associated with a structural reorganization of the silyl group aimed at the use of the empty coordination site for additional bonding. Note that square planar 16 e$^-$ complexes have stable silyl groups with classical terminal silyl structure because there is no low-lying empty metal d orbital in such systems.[64] The silylene−hydrido form (**En(H)**) is relatively favorable. It corresponds to a true minimum for all $SiHR_2$ groups, and it is the best structure for π electron donor R groups (CH_3 and Cl). In the silylene−hydrido complex, the metal has no empty coordination site, but the unsaturation present at the silylene group is not fully compensated by electron donation from the silicon substituents. For this reason, silylene complexes are usually stabilized by bases, tosylate and ethers for instance.[6,25,54] The silylene group appears also as a possible isomer with terminal methyl (**5En(Me)**) and silyl (**3En(Si)**) ligands. The same bonding situation is found for (**2En(Me)**), but this structure is at high energy with respect to other isomers of **2**. In the case of **3**, the silylene−silyl form **3En(Si)** is in fact at a lower energy than the silylene−hydrido isomer **3En(H)**. The silyl group, which is a strong σ electron donor, moves to the metal and leaves a $=Si(H)(SiH_3)$ silylene ligand. In absence of more precise thermodynamic information on the metal−silyl bonds, it is not easy to understand in detail the origin of these preferences since in addition the energy difference between the two silylene isomers is relatively small. The rule appears to be that strong σ donor groups (H, CH_3, SiH_3) can be terminal ligands in association with silylene groups stabilized by moderate π donors (CH_3, SiH_3, and Cl). The same argument accounts for the lack of a silylene−chloride complex even when the silylene is substituted by two chlorine atoms (complex **7**). The chloride does not take a terminal position but prefers a bridged position.

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(64) Chan, D.; Duckett, S. B.; Heath, S. L.; Khazal, I. G.; Perutz, R. N.; Sabo-Etienne, S.; Timmins, P. L. *Organometallics* **2004**, *23*, 5744.

Table 3. NBO Analysis of the Ir═Si π Bond

complex	R/silylene	population Ir(d)	population Si(p)
1En(H)	H/SiH_2	1.792	0.340
2En(H)	$H/SiMe_2$	1.822	0.327
3En(H)	$H/Si(SiH_3)_2$	1.777	0.406
4En(H)	$H/SiCl_2$	1.796	0.499
5En(Me)	Me/SiHMe	1.793	0.327
6En(Si)	$SiH_3/SiH(SiH_3)$	1.798	0.396

An NBO analysis was carried out for all silylene complexes (Table 3), although caution should be used when performing such an analysis for transition metal complexes.[65] The Ir═Si π bond is strongly polarized: $Ir^{(-\delta)}Si^{(+\delta)}$; the population on the Ir 5d orbital involved in the interaction with the Si 3p atomic orbital is occupied by around 1.8 e^-, while the Si 3p orbital is occupied by an average of 0.37 e^-. Furthermore, the electron population in this Ir d orbital varies little with the nature of the substituents on Si. It is the smallest for $Si(SiH_3)_3$ (1.78) in **3En(H)** and the highest for $SiMe_2$ (1.82) in **2En(H)**, which follows the electron-donating ability of the silicon substituents. In contrast, the electron population on the Si 3p orbital varies more: it is the smallest for $SiH(CH_3)$ and $Si(CH_3)_2$ (0.32) in **5En(H)** and **2En(H)** and the largest for $SiCl_2$ (0.50) in **4En(H)**. This is because the Si 3p orbital receives some electron density from π-donating atoms such as Cl. Because of the interaction with the neighboring atomic orbital, the sum of the electron densities in the Ir 5d orbital and the Si 3p orbital is not equal to 2. However this sum is not far from 2, which suggests that the Ir−Si π interaction dominates over the interactions with the Si substituents. This π interaction and the planar silylene geometry both indicate the presence of an Ir−Si π bond, in contrast to what occurs in the nonplanar H_2EEH_2, where E is a heavy group 14 element (Si to Pb).[66] However the very high polarity of the Ir−Si π bond is also probably an indicator that the silicon is strongly electron deficient. Other structures such as the bridged structures are thus preferred.

These calculations show the remarkable dominance of bridged structures. All the groups (H, CH_3, SiH_3, and Cl) that have been studied can occupy a bridging position. The hydrogen atom appears to be less versatile in its ability to take a bridging position. For instance, it does not bridge the metal and a silylene; **B1(H)** is never found as a stable isomer. The H favors a bridging position of type **B3**. In other words, H prefers a position deriving from a β-H migration than from an α-H migration. However, **B2** type structures where H bridges two neighboring Si atoms is an absolute minimum, and therefore it does not seem that there is any intrinsic difficulty in the H going to the bridging position. It should be mentioned however that structures of type **B2** have not yet been observed experimentally. Although the calculations have been carried out for SiH_3 groups, which ignore steric effects, the possibility of observing this interesting bridging structure should not be excluded.

Corey and Braddock-Wilking mentioned the continuing evolving types of bonding interactions for the silyl transition metal complexes.[2] The diversity is even more striking when several silyl groups are present, and the constant theme is the increasing number of highly diverse bridging situations. Thus $SiH(CH_3)_2$, **2**, and $SiH(SiH_3)_2$, **3**, have different bonding pictures, with more bridging structures for the latter. The ability for Si to become hypervalent is the reason for this behavior. As a group bonded to a transition metal, the silyl type group has been noted to eventually interact in a nonclassical manner with other ligands.[2,16,17,22,39] The chlorine atom also has a large preference for occupying a bridging position and, as mentioned earlier, for stabilizing the silylene group. The presence of chlorine significantly reduces the number of possible isomers.

The calculations show that the difference in energy between the various isomers is sometimes rather small, especially in the case of polysilyl ligands. The relative order of isomers can thus be easily modified by other factors such as the metal itself. It is therefore of interest to compare the results obtained for Ir to those previously obtained for $[(dhpe)Pt(SiHR_2)]^+$ and $[(dhpe)Pt(SiR_3)]^+$.[33] Table 2 summarizes the published results using the present notations. The main result is that silylene isomers (**En(R)**) are not as favored with Pt as with Ir. For instance, in the case of Pt, an isomer with a silylene group of type **B1(H)** is found as a true minimum only for $SiHMe_2$ and $SiHCl_2$. No silylene complexes with terminal CH_3 or terminal SiH_3 could be located as minima. The empty Si p orbital of the silylene can receive electron density from the metal, and this back-bonding interaction is necessary to stabilize the silylene group. Ir(III) is a better electron donor via back-bonding than Pt(II) and thus stabilizes the silylene more efficiently. Another way to present the argument is to view nonstabilized silylene groups as X_2 type ligands. They are thus well suited to interact with metal centers easily amenable to a formal two-unit oxidation. This is the case for Ir(III), since Ir(V), although not highly frequent, is a known oxidation state of Ir. In contrast, Pt(IV) is much rarer and in particular not reported with a square planar coordination. There is thus an increased possibility to isolate a stable silylene free from Lewis base stabilization with $[CpLIr(SiHR_2)]^+$ or $[CpLIr(SiR_3)]^+$ type complexes than with the square planar Pt derivatives. Electron-donating groups at the metal for instance by changing L[67] or the Cp type ligand could also favor the occurrence of the silylene group.

Another interesting result is that isomers with terminal silyl are not as unfavorable with Pt as they are for Ir. The **T** type isomers are closer in energy to the other structures for Pt than they are for Ir, and a **T** isomer has been even located as a true minimum for $[(dhpe)Pt(SiH_3)]^+$. This increases the possibility of trapping a complex with a silyl group. For instance, platinum bisphosphine silyl hydride complexes have been characterized.[64] Although various isomers with bridging groups have been obtained in the case of Pt, the general pattern is that structures with an empty site at the metal (**T**) are more favored for ML_3 d^8 Pt(II) than for ML_5 d^6 Ir(III).

Conclusions

The $[Cp(PH_3)Ir(SiHR_2)]^+$ and $[Cp(PH_3)Ir(SiR_3)]^+$ (R = H, CH_3, SiH_3, and Cl) complexes have been studied with DFT calculations. They present a large variety of isomers, some of them being close in energy. The structures vary from the classical terminal silyl to the silylene complexes with one of the groups (H or R) from the original silyl $SiHR_2$ or SiR_3 groups being coordinated to the metal. Between these two extremes situations, one finds a variety of nonclassical structures with unusual bridging situations. The terminal silyl complex is not a favorable isomer in these 16 e^- complexes. It is found as a stable secondary minimum only for R = H and with a relatively high energy. In contrast, silylene−hydrido, silylene−silyl, and silylene−methyl complexes are found to be among the most favorable isomers. To be a favorable isomer, the silylene requires π electron donor groups on Si (CH_3, Cl) and strong σ electron donor groups on the metal (H, SiH_3, CH_3). The diversity of the

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[67] Perrin, L.; Clot, E.; Eisenstein, O.; Loch, J.; Crabtree, R. H. *Inorg. Chem.* **2001**, *40*, 5806.

bridging situations is large and increases with the number of silyl groups involved. All groups have the ability to become a bridge between the metal and either the silicon or the carbon. The case of chlorine is special because it favors strongly the bridging situation. Bridges can occur between Ir and the Si atom in the first coordination sphere or between Ir and an atom in a β position relative to the metal. Hydrogen favors the latter situation. Hydrogen is also found to bridge two silicon atoms in a structure, which has not yet been found experimentally. The CH_3 and Cl groups bridge between Ir and the Si atom in the first coordination sphere. Comparison of the results with those obtained previously for $[(dhpe)Pt(SiHR_2)]^+$ and $[(dhpe)Pt(SiR_3)]^+$ shows that a wide variety of bonding patterns is found for both metals. However, the calculations show that the silylene type isomer is more favored for Ir than Pt, a result that can be attributed to the stronger back-donating ability of Ir(III) compared to Pt(II). These studies lead to a better systematization of the diversity of the structural features in silicon-containing transition metal complexes.

Acknowledgment. Financial support from the Spanish MEC (projects CTQ2005-09000-CO1-01, CTQ2005-09000-CO1-02), the Catalan DURSI (projects 2005SGR00715, 2005SGR00896), and the ICIQ foundation is acknowledged. We are grateful to Dr. Eric Clot (Montpellier) for helpful discussions.

Supporting Information Available: List of Cartesian coordinates and energies (au) for all optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0603971