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Peculiar Hydride−Silyl Interactions in Group 5 Bent Metallocene Complexes, Studied by ab Initio Calculations

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The nature of possible H···SiR_3 interligand interactions in the complexes $MCp_2XH(SiR_3)$ (M = Nb, Ta; X = SiR_3, Cl, H, CH_3) has been studied by ab initio calculations at the MP2 level. The optimized structure of $NbCp_2(SiClH_2)H(SiClH_2)$ shows symmetric displacements of the silyl ligands about the hydride, with a H···Si distance of 2.180 Å, consistent with the experimental findings. Analysis of the Laplacian of the valence electron density ($-\nabla^2\rho$) reveals significant polarization of the electron density around H toward both silicon centers (without an observable H···Si bond path), indicating the presence of weak H···Si interaction. The extent of the H···Si interaction can be increased by replacing one of the SiR_3 ligands by a halide or CH_3 and using halide-substituted silyl ligands. An extreme case is $MCp_2ClH(SiCl_nH_{3-n})$, $n \geq 1$, with H···Si interaction distances less than 2.0 Å, and a curved H−Si bond path is observed in each of the respective Laplacian plots. Moreover, an in-plane Cl substituent on silicon causes a more drastic increase of the H···Si interaction than an out-of plane chloride due to favorable orbital interactions. For the tantalum analogue $TaCp_2(SiH_3)H(SiH_3)$, the theoretical results indicate a symmetric structure similar to $NbCp_2(SiClH_2)H(SiClH_2)$ rather than unsymmetric (with one H···Si distance of ~1.6 Å), as suggested by experimental X-ray results. Other theoretical evidences also support the symmetric C_{2v} structure of the complex. The "nonclassical" H···Si coordination in the Cl- and CH_3-substituted complexes suggest a new type of η^2-silane complexes stabilized by σ-withdrawing effects, without the presence of any strong π-acceptor like CO and PR_3.

Introduction

Transition metal hydrido−silyl complexes exhibiting short H···Si distances of less than 2.0 Å ("nonclassical" silane complexes) have attracted intensive synthetic, structural, and theoretical studies during the past 20 years,[1] both as possible intermediates in hydrosilation and a model for C−H bond activation.[2] Two extensively studied categories of such η^2-silane complexes are the group 7 pseudo-three-legged piano-stool complexes[1a−d] (e.g. **1**) and the groups 6−8 pseudooctahedral complexes[3] (e.g., **2**). The strong H···Si interactions in these complexes are manifested by the short (1.65~1.85 Å) H···Si distances, the unusually high $^1H-^{29}Si$ NMR coupling constants (70−90 vs 20−30 Hz for those systems considered to have separate H and SiR_3 ligands), and the strong preference for both **1** and **2** to adopt structures with strong H···Si interactions rather than alternative structures with separate hydride and silyl ligands. Detailed structural and theoretical studies have concluded that the groups 6−8 metals in both types of nonclassical silanes cause the t_{2g}-like metal d orbitals to be filled, and the presence of a strong π-acceptor ancillary ligand (carbonyl and phosphines) stabilizes the nonclassical structures.[1c,4] These conclusions are in line with those of the more extensively studied η^2-dihydrogen complexes.[1d,5] However, nonclassical η^2-silane complexes differ from η^2-dihydrogen complexes in that the H−Si σ-bond acts as a moderately strong σ^*-acceptor ligand, which can compete for back-bonding with the

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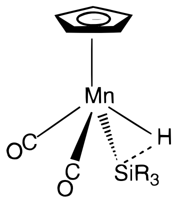

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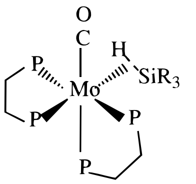

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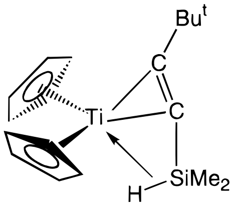

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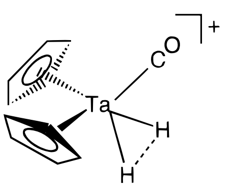

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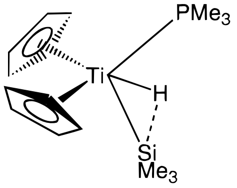

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strong π-acceptor (CO and PR_3), whereas the H−H bond shows much less σ^*-accepting character. This feature is elegantly demonstrated in the complex *cis*-Mo(CO)-$(depe)_2(H\cdots SiH_3)$ (**2**).[3b−c,4] (An analogous cationic fragment $Mn(CO)(depe)^+$ was recently reported to bind SiH_4 in the same manner.)[6]

Although nonclassical complexes are more prevalent with mid-transition metals (groups 6−8), early-transition-metal complexes can also possess such nonclassical interligand interactions. We have demonstrated that the group 4 metallocene−acetylene complex $TiCp_2(\eta^2$-*trans*-$^tBuC\equiv CSiHMe_2)$ (**3**)[7] involves severe competition between the H−Si σ^*- and the acetylene π^*-orbitals for metal back-bonding (and also possibly between the corresponding σ-bonding orbitals for ligand-to-metal donation),[8] resulting in a preferred trans configuration with both C≡C and H−Si bonds coordinated strongly to the metal center. The metal center is best described as having a d^2 configuration, which makes metal-to-(H−Si) back-bonding possible. Among the early-transition-metal complexes, the bent metallocene fragment MCp_2 is well-known for its versatility as a coordinating fragment to a wide variety of ligands[9] and its spectacular role in a number of catalytic processes, in particular Ziegler−Natta polymerization.[10] Possibilities of nonclassical interligand interactions arise naturally because of the forced planar arrangement of the ancillary ligands dictated by the frontier orbitals of the MCp_2 fragment.[11] Indeed, there are now a number of bent metallocene complexes having nonclassical η^2-ligands, including a rare example of an early transition metal η^2-dihydrogen complex $[TaCp_2(CO)(\eta^2\text{-}H_2)](BF_4)$ (**4**)[12] and a titanocene complex similar to **3**, $TiCp_2(PMe_3)(\eta^2\text{-}H\cdots SiMe_3)$ (**5**)[13] (but it is interesting to note that the Zr and Hf analogues[14] do not show any conceivable H···Si interaction). Each of these complexes **3**−**5** possess a strong π-acceptor like the group 6 and 7 pseudooctahedral counterparts **1** and **2**, thus it appears that the Dewar−Chatt-type back-bonding interaction[15] may also be responsible for their stability.

In a continued effort for the study of the nature of H···Si interactions in various types of transition-metal complexes,[4,8] we encountered a peculiar metallocene disilyl complex $TaCp_2(SiMe_2H)H(SiMe_2H)$ (**6**)[16] which was reported to have an unsymmetric structure possessing a close H···Si interaction distance of ~1.83 Å. Structural and spectroscopic data indicated a similar type of nonclassical H···Si interaction as in **1** and **2**. This is an intriguing result because the silyl ligand is normally not considered a strong π-acceptor.[9] An analogous complex $NbCp_2(SiClMe_2)H(SiClMe_2)$ (**7**)[17a] was initially proposed to be unsymmetric like **6** with a close H···Si distance of ~1.63 Å, but the crystallographic data was later corrected,[17b] corresponding to the structure **7′** with symmetric displacements of the silyl ligands on both sides of the hydride, possessing an “intermediate” H···Si interaction distance of 2.056 Å. The situation is further complicated by the propositions that in **6** a “hydride shuffling” tautomerism was inferred from the chemical equivalence of the two silyl ligands, while in **7** the central hydride was proposed to act as a “hydrogen bridge” between the two silyls from the ^1H NMR shift value of the central hydride.

The seemingly contradictory structural features of these two complexes have prompted us to undergo a systematic theoretical study of the nature of the “long-range” hydrido−silyl interligand interactions in these metallocene−hydrido−silyl complexes. Our first goal is to resolve the apparent dilemma of symmetric vs unsymmetric structures for **6** and **7**/**7′** (Figure 1) and to elucidate the nature of the H···Si interaction in these complexes with possible long-range (>2.0 Å) hydrido−silyl interactions. Following that, the effects of varia-

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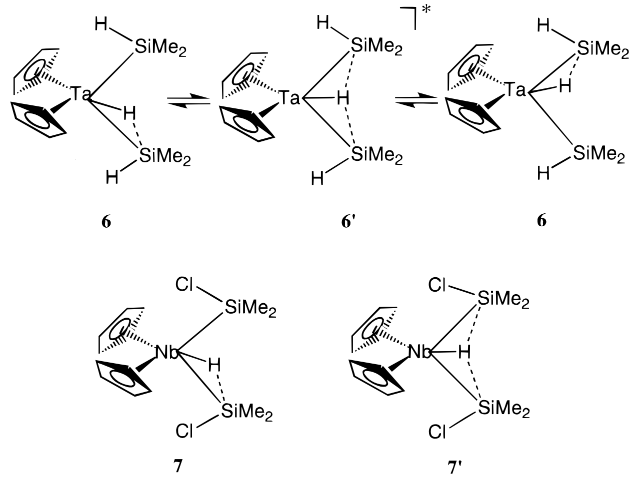

Figure 1. Apparently inconsistent structural features of the two group 5 metallocene complexes **6** and **7**.

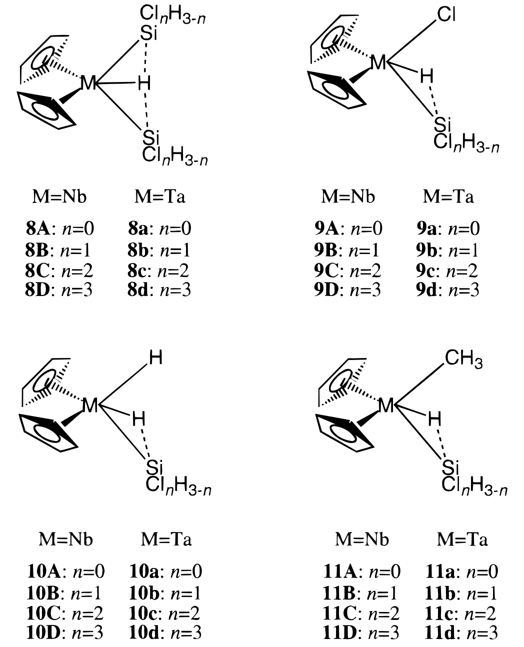

Figure 2. Model complexes **8**−**11** considered in this study. The symmetry plane contains the metal and the three ligand atoms directly bonded to M, and the in-plane silyl substituents also lie on the C_s plane.

tions in the electronic environments of the metal and silicon centers on the strength of H···Si interactions are studied by examining the structural and electronic features of other MCp_2XHSiR_3 systems with various terminal M−X ligands and chloride substitutions on the silyl ligand. Through these systematic theoretical studies, we attempt to build up a theoretical framework of the nature of H···Si interactions in group 5 bent metallocene complexes (specifically, this study focuses on neutral complexes with three discrete terminal ligands with neighboring H and SiR_3 units).

Computational Details

The model complexes considered in this study have a generic structure shown in Figure 2. Any alkyl or aryl ligands on silicon are replaced by H's for theoretical simplicity. The effects of variations of the electronic environment around the metal and Si centers are mimicked by various substitutions of the terminal M−X and the silyl Si−X ligands. For ease of specification of individual model complexes, the model systems are numbered from **8** to **11**, standing for complexes with terminal silyl, Cl, H, and CH_3 ligands, respectively. These terminal one-electron ligands were chosen as representatives of a moderate π-acceptor, strong σ-acceptor with π-donor character, and ligands with no appreciable π-bonding characteristics, respectively. The descriptors **A**−**D** denote niobocene complexes with silyl ligands containing 0−3 chloride substituents, and **a**−**d** are used for the corresponding Ta analogues.

Geometry optimizations were performed on the model systems **8**−**11** at the second-order Møller−Plesset perturbation theory (MP2) level with an overall C_s symmetry about a plane defined by the three terminal ligands. No other geometric constraints were imposed apart from the symmetry plane. To maintain this C_s symmetry, the ligand $SiClH_2$ has its Cl in the ligand plane and $SiCl_2H$ has two out-of-plane Cl's. The atoms H and C were described by the standard 6-31g basis set, and the Hay and Wadt effective core potentials (ECPs) with double-ζ valence basis sets[18] were used to describe all other heavy atoms (Nb, Ta, Si, and Cl). The three in-plane ligand atoms directly bonded to the metal center were augmented by single (d,p) polarization functions, i.e., 6−31g** for H and the Huzinaga d-polarization function[19] for Si and Cl.

The nature of the H···Si interactions in these model systems were studied by analysis of the Laplacian of the valence electron density ($-\nabla^2\rho$) on a plane defined by the metal, the terminal hydride ligand, and the Si atom of the silyl ligand, using Bader's atoms-in-molecules (AIM) theory.[20] This kind of density Laplacian analysis has been extensively used to study the nature of chemical interactions,[21] in particular, the nature of bonding between classical and nonclassical dihydride complexes.[22] The nature of H···Si interactions in some transition-metal complexes has also been rationalized with the use of AIM theory in our previous theoretical studies.[4,8] This approach has been shown to be productive in rationalizing (or "depicting") the relationship between the strength of the H···Si interaction and the electron configuration of the transition-metal center. The nature of the energy minima for the optimized model structures of **8a** and **8B** (corresponding to the experimental complexes **6** and **7**) was determined by calculation of their respective harmonic vibration frequencies at the MP2 level with the same basis set used for geometry optimizations.

Geometry optimizations and frequency analyses were performed with the Gaussian94 package[23] on Silicon Graphics (SGI) Onyx and SGI Challenge R10000 workstations, and electron density analysis was carried out with MOPLOT[24] on an SGI Indigo2 workstation.

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Table 1. Bond Lengths (Å) and Ligand Spreading Angle Si−H−Si (LSA, deg) of the Complexes $MCp_2(SiCl_nH_{3-n})H(SiCl_nH_{3-n})$[a]

	Nb					Ta			
	$n = 0$ (**8A**)	$n = 1$ (**8B**)	$n = 2$ (**8C**)	$n = 3$ (**8D**)		$n = 0$ (**8a**)	$n = 1$ (**8b**)	$n = 2$ (**8c**)	$n = 3$ (**8d**)
Nb−Cp	2.439	2.442	2.440	2.445	Ta−Cp	2.433	2.435	2.432	2.437
Nb−Si	2.641	2.588 (2.597)	2.589	2.564	Ta−Si	2.638 (2.633, 2.624)	2.585	2.590	2.566
Nb−H	1.770	1.791	1.794	1.786	Ta−H	1.776	1.796	1.783	1.789
Si···H	2.265	2.154 (2.056)	2.200	2.147	Si···H	2.288 (1.83, 2.48)	2.178	2.223	2.176
$Si-Cl_{in}$		2.179 (2.163)		2.151	$Si-Cl_{in}$		2.180		2.151
LSA	115.6	110.8 (104.3)	113.8	111.5	LSA	117.2 (109.9)	112.3	115.2	113.3

[a] Experimental values are enclosed in parentheses.

Results and Discussion

Silyl−Hydrido−Silyl Complexes $MCp_2(SiCl_nH_{3-n})$-$H(SiCl_nH_{3-n})$, M = Nb, Ta; n = 0−3: Structure and Systematic Trends. The MP2-optimized geometries of these model complexes **8** are listed in Table 1, and comparisons of the structural parameters of the models **8a** and **8B** with the experimental metallocene complexes **6** and **7′** are also made. The agreement of the theoretically determined bond distances with the experimental ones between heavy atoms are very good (to within 0.02 Å). Although the average metal to Cp-carbon distances are overestimated by about 0.06 Å and interligand Si···H distances by ~0.1 Å, these deviations do not qualitatively invalidate the conclusions below. The ligand spreading angles (Si−M−Si) are also overestimated by ~5°, but still within acceptable theoretical errors. The structures **8a** and **8B** possess a near-C_{2v} symmetry with the two silyl ligands displaced symmetrically about the central hydride. This is consistent with the corrected X-ray data for **7** (i.e., **7′**) but not for the reported unsymmetric (C_s) structure of **6**. Since there is an apparent discrepancy between the experimental and theoretical results for **6**, more theoretical evidences are necessary to confirm the symmetric structures of both **8a** and **8B**.

To determine whether the C_s-optimized model complexes **8a** and **8B** are really symmetric (i.e., they possess C_{2v} symmetry), both of the model systems were reoptimized at MP2 level with C_{2v} symmetry (where the M−H bond serves as the C_2 axis). Both of the C_{2v}-optimized structures turn out to be identical with the C_s-optimized counterparts in terms of total energy and structural parameters. In the investigation of possible unsymmetric isomers with nonclassical H···Si ligands (similar to the experimental structure of **6**), attempts to perform geometry optimizations in C_s symmetry using a highly unsymmetric starting geometry (with one H···Si distance at the uncoordinated silane distance of 1.48 Å) result in no unsymmetric nonclassical isomers of **8a** and **8B**. Rather, these highly unsymmetric starting geometries bounce back to the near-C_{2v} structures. On the other hand, relaxing the symmetry constraints altogether (i.e., full geometry optimization in C_1 symmetry) results in an optimized structure identical to the one with C_s symmetry. Therefore, a global C_s symmetry has been assumed for the following calculations, which is consistent with the fact that the three ancillary ligands of a bent metallocene complex are coplanar and perpendicular to the Cp−M−Cp plane.[11]

The most conclusive theoretical evidence for the stability of the (near-)C_{2v} structure for both complexes comes from an analysis of their respective harmonic vibration frequencies. The results of the frequency analysis for both **8a** and **8B** show no imaginary (negative frequency) vibration modes, and all low-frequency (<100 cm^{-1}) modes correspond exclusively to rotations of the Cp rings and symmetric Si−M−Si bending, thus indicating neither any tendency for the near-C_{2v}-optimized structures to distort in any way to the unsymmetric one nor rotations of the silyl ligands that would shift the in-plane Si−X bond.

One of the reviewers was concerned that density-functional methods, especially B3LYP, may give more reliable results than the often-used MP2 method. We have performed calculations of **8a** and **8B** (corresponding to the experimentally characterized complexes) using B3LYP with the same basis sets, which do give similar results as those from the MP2 calculations, namely, the symmetric C_{2v} structures for both **8a** and **8B** are the most stable, and the presence of an unsymmetric C_s tautomers are not very likely.

In light of the possibility of a five-center, six-electron interligand interaction involving the central hydride ligand and the two in-plane Si−Cl bonds in **7**[17] and the apparent inconsistency of the assignment of a nonclassical structure for **6** with our theoretical results, we have carried out calculations of these model systems with progressively Cl-substituted silyl ligands. The results are again summarized in Table 1. All of these complexes adopt a symmetric C_{2v} structure like **8a** and **8B**, and hence a group 5 bent metallocene complex with a silyl−hydrido−silyl arrangement of the ancillary ligands is most likely to adopt the symmetric structures. Systematic trends in variations of structural parameters with the number of Cl-substitutions on the silyl ligands are observed from Table 1. The Si···H distances decrease from 2.265 to 2.147 Å for the niobocene complexes **8A−D** with increasing Cl substitution and from 2.288 to 2.176 Å for the Ta analogues **8a−d**. Moreover, the M−Si distance is shortened and the M−H distances becomes longer with the degree of Cl-substitutions. A notable exception occurs, however, for the case of two

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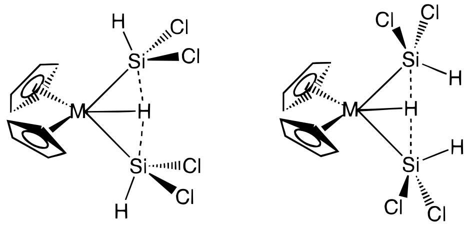
(24) Interactive MOPLOT: a package for the interactive display and analysis of molecular wave functions, incorporating the programs MOPLOT (D. Lichtenburger), PLOTDEN (R. F. W. Bader, D. J. Kenworthy, P. M. Beddal, G. R. Runtz, and S. G. Anderson), SCHUSS (R. F. W. Bader, G. R. Runtz, S. G. Anderson, and F. W. Biegler-Koenig), and EXTREM (R. F. W. Bader and F. W. Bieger-Koenig) by P. Sherwood and P. J. MacDougall, 1989.



8C **8C′**

Figure 3. The alternative silyl ligand orientations in **8C′** prohibit the Si centers to adopt the most favorable trigonal-bipyramidal coordination.

Cl-substitions (i.e., **8C** and **8c**) in which Si···H is longer than either of the one- or three-Cl-substituted cases. A similar reversal of trends can be found for the other structural parameters. It can, thus, be concluded that one in-plane Cl substituent exerts more influence than two out-of plane Cl substitutions on the strength of the H···Si interaction. Indeed the additional substitution of two out-of-plane Cl's on the monochloro-substituted complexes **8B** and **8b** to form **8D** and **8d** only causes an insignificant strengthening of the H···Si interaction, namely, a shortening of $\sim$0.005 Å for M−H and Si···H and a lengthening of $\sim$0.02 Å for M−Si. The role of the in-plane substituent on silicon will be discussed further in the following sections.

It may be argued that for the dichloro-substituted complexes **8C** and **8c**, steric repulsions between the out-of-plane Cl atoms keep the two silyl ligands apart. We have performed comparative calculations on some model systems with each of the silyl ligands rotated by 180°, forming structures such as **8C′** (Figure 3). The results indicate that **8C′** is 19.6 kcal/mol less stable than **8C.** The instability of **8C′** can be ascribed to the fact that the Si centers cannot attain a trigonal-bipyramidal (TBP) coordination, which is the most favorable for five-coordinate hypervalent silicon compounds.[11] For the model complexes **(9−11)C′**, the H···Si interaction distances are on overage $\sim$0.1 Å longer than those in **(9−11)C**, despite less interligand steric repulsions. These results further illustrate the spectacular role of the in-plane silyl substituent mentioned above.

Nature of Long-Range H···Si Interactions. To elucidate the nature of the long-range (Si···H distance > 2.0 Å) H···Si interactions for these complexes, Bader's atoms-in-molecules theory has been applied on the Laplacian of the valence electron densities $(-\nabla^2\rho)$ of the model complexes. This type of electron-density analysis has been used to elucidate the bonding in the model η^2-silane complexes *cis*-Mo(CO)$(PH_3)_4$(H···SiH_3)[4] and the complex $TiCp_2$(η^2-*trans*-HC≡$CSiH_3$).[8] The Laplacian plots are presented here for the niobocene complexes only (the plots for the Ta analogues have the same topological features). As seen in Figure 4, none of the complexes **8** show any observable H···Si bond paths, in comparison to the established nonclassical silane complexes. However, the electron density around H is severely polarized toward both silyl ligands, and the extent of polarization increases with shortening in H···Si interaction distance. The metal center exhibits a circular (or spherical in three-dimensions) electron-density pattern. The spherical appearance of the Laplacian around the metal center in the Laplacian plots are indications that the metal center (Nb or Ta) formally has a d^0 configuration, and this type of metallocene−disilyl complex is best regarded as a classical silyl−hydrido−silyl complex, with significant polarizing interactions of the silyl ligands for the central hydride; and while the theoretical results do not support the proposal of a five-center, six-electron interaction well, the in-plane silyl substituents do play a significant role in enhancing the extent of H···Si interaction.

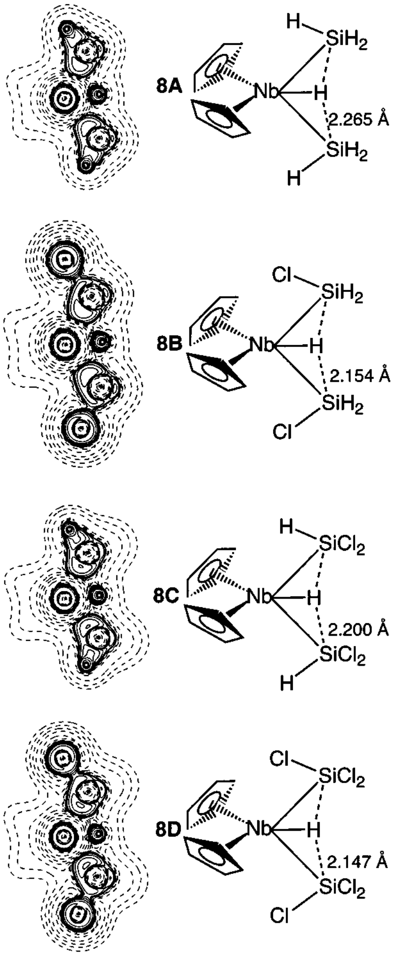


Figure 4. Plot of the Laplacian of valence electron density of **8** in a plane defined by M, Si, and the central hydride. Solid lines represent local electron density concentration $(-\nabla^2\rho > 0)$, and dashed lines represent local density depletion $(-\nabla^2\rho < 0)$. The density around the central hydride is observed to be symmetrically polarized toward both silyl ligands.

Hypervalent Coordination Around Silicon. The tendency of the silyl ligand in transition-metal complexes to participate in an additional interaction with a neighboring hydride (nonclassical H···Si interaction) has been attributed to the ease of Si to attain a hypervalent (in many cases five-coordinate) coordination environment,[25] and it is thus instructive to investigate the arrangement of the ligands around silicon. The hypervalent Si coordination in $NbCp_2(SiClH_2)H(SiClH_2)$ (**8B**) is shown in Figure 5 (which also includes the respective Si coordination environments in other classes of model systems studied here, i.e., **9B**, **10B**, and **11B**).

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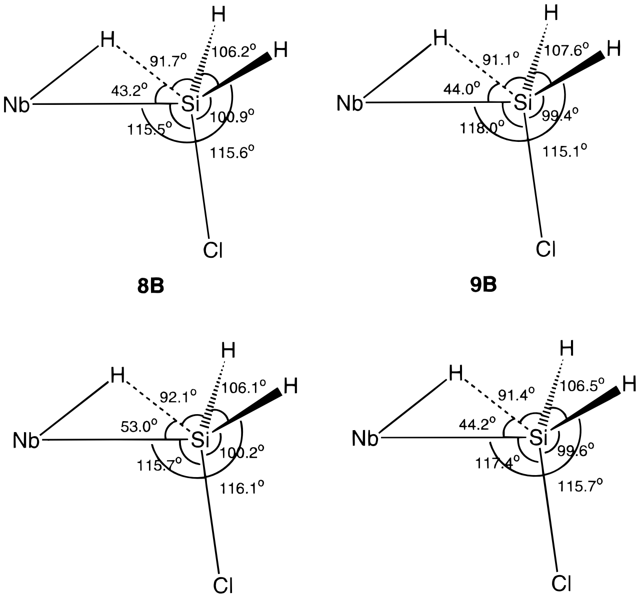
(25) (a) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989. (b) Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81. (c) Patai, S.; Rappoport, Z. *The Silicon-Heteroatom Bond*; Wiley: Chichester, U.K., 1991.



8B **9B** **10B** **11B**

Figure 5. The distorted trigonal-bipyramidal coordination environments in monochloro-substituted model complexes **8B**−**11B**. The (central) H−Si−Cl angle in all cases close to 180°, forming the "axle" of a trigonal bipyramid.

The Nb−SiClH$_2$ unit is highly distorted from the normal tetrahedral configuration, and the resulting coordination around silicon can be described as a distorted trigonal bipyramid (TBP). Such coordination, common among five-coordinate silicon compounds, is also found for the pseudooctahedral η^2-silane complex Mo(CO)(P−P)$_2$(H···SiH$_3$). Both the lengthening of the in-plane Si−X bond and the enhanced effect of the in-plane substituent on the strength of the H···Si interaction are quite common among trigonal-bipyramidal compounds involing hypervalence,[11] where the in-plane Cl substituent and the terminal H ligand (which forms a H···Si interaction with the silicon) form the axle of the TBP.

Chloro−Hydrido−Silyl Complexes MCp$_2$ClH(SiCl$_n$H$_{3-n}$), M = Nb, Ta; *n* = 0−3: Possibility of a Complex with Nonclassical η^2-Silane Coordination Character. Since a silyl−hydrido−silyl arrangement of ligands does not yield any nonclassical η^2-silane structure, we were interested in the possibility of a MCp$_2$XH(SiR$_3$) complex containing a prominent nonclassical H···Si interaction through a suitable choice of the terminal X ligand and silyl substituents, while at the same time further elucidating the factors governing the extent of the H···Si interaction in group 5 bent metallocene complexes. A terminal Cl ligand in place of one of the silyls provides a drastic change in the electronic environment around the group 5 metal center, and the results of the MP2-optimized geometries for model systems **9** are listed in Table 2. The corresponding electron density Laplacian ($-\nabla^2\rho$) plots for the niobocene complexes **9A**−**D** are shown in Figure 6. The most striking difference between **9** and **8** is the much shorter H···Si interaction distances, with the shortest one being 1.881 Å for **9D**, which is comparable with other recognized examples of nonclassical silane complexes. The *combined* action of a terminal M−Cl ligand and a Cl substituent on SiR$_3$ (especially an in-plane Cl) has drastically strengthened the H···Si interaction.

Before discussing the features of the Laplacian plots of **9**, it is useful to consider the relevant orbital interactions for the two extremes of the formulations of MCp$_2$ClH(SiR$_3$), where M is a group 5 metal, shown in Figure 7. In one extreme (Figure 7a), the H and SiR$_3$ ligands are considered as fully separated (i.e., no H···Si interaction), resulting in three terminal ancillary ligands; whereas the other extreme (Figure 7b) consists of an ideal nonclassical η^2-(H−SiR$_3$) ligand, considered as a single unit, thus giving two terminal ligands coordinated to the MCp$_2$ fragment. It is well-known[11] that the bent metallocene (MCp$_2$) fragment has three frontier orbitals available for interaction with additional ligands. In the classical extreme, the three frontier orbitals of MCp$_2$ (see the left column of Figure 7) interact with the three σ-orbitals of the three terminal ligands, giving three strong σ-bonding and three corresponding σ-antibonding MOs. The metal center, thus, possesses a formal d^0 configuration. In the nonclassical extreme, two of the three MCp$_2$ frontier orbitals interact with the two ligand σ-orbitals, forming two metal−ligand σ-bonds. The remaining lowest-lying MCp$_2$ "a$_1$"-orbital remains an essentially metal-centered d orbital (i.e., a formal "lone pair"). This lone pair d orbital acts as the HOMO of the complex as a whole, giving it a formal d^2 configuration. As will be shown below, analysis of the density Laplacian ($-\nabla^2\rho$) provides a direct manifestation of the nature of the H···Si interaction (or H···Si coordination to the MCp$_2$ fragment) between the classical and nonclassical extremes as described above.

An examination of the density Laplacian plots in Figure 6 indicates that, except for **9A** and **9a** (with no chloride substituent on silicon), all complexes display a curved H−Si bond path similar to that observed in *cis*-Mo(CO)(PH$_3$)$_4$(H···SiH$_3$) (**2**).[4] The electron density around the metal center has a square appearance, indicating a *noticeable contribution* of the resonance electronic structure with a formal d^2 configuration. With a "nearly perfect" formal d^2 configuration, four "corners" of local electron density concentrations would appear as in the previously studied complex TiCp$_2$(η^2-*trans*-HC≡CSiH$_3$) (**3**).[8] The chloro−hydrido−silyl metallocene systems can thus be described as having the character of a nonclassical η^2-silane complexes, but are apparently less nonclassical than **2** or **3** due to the more severe breaking of the H···Si "bond" (H···Si distance ~1.9−2.0 Å). The complexes **9** lie further away from the nonclassical end (in particular, **9A** and **9a**, having no H−Si covalent bond path, can be said to be essentially classical) of the orbital interaction pattern in Figure 7.

The systematic trend of structural variations with the degree of Cl-substitution on silicon resembles that of the silyl−hydrido−silyl case above. Notably, a single in-plane Cl-substituion on silicon results in a ~0.2 Å shortening in the H···Si interaction distance, which is more drastic than the disilyl complexes **8**. The ligand spreading angle (LSA) is on average 5° larger than that of **8**, and the nonbonding Cl···H distances are more or less constant with variations in Cl-substitution on silicon. These structural features probably mean that the close proximity of the hydride and the silyl ligands and the variation in H···Si distance with Cl-substitution

Table 2. Bond Lengths (Å) and Ligand Spreading Angle (deg) of the Complexes $MCp_2ClH(SiCl_nH_{3-n})$

	Nb					Ta			
	$n = 0$ (**9A**)	$n = 1$ (**9B**)	$n = 2$ (**9C**)	$n = 3$ (**9D**)		$n = 0$ (**9a**)	$n = 1$ (**9b**)	$n = 2$ (**9c**)	$n = 3$ (**9d**)
Nb−Cp	2.456	2.455	2.456	2.458	Ta−Cp	2.451	2.448	2.450	2.451
Nb−Cl	2.540	2.531	2.529	2.514	Ta−Cl	2.532	2.520	2.519	2.515
Nb−H	1.756	1.787	1.775	1.792	Ta−H	1.765	1.794	1.782	1.795
Nb−Si	2.636	2.573	2.574	2.544	Ta−Si	2.640	2.577	2.580	2.548
Ch···H	2.583	2.606	2.596	2.595	Cl···H	2.594	2.605	2.599	2.591
Si···H	2.086	1.881	1.972	1.866	Si···H	2.112	1.889	2.004	1.888
$Si-Cl_{in}$		2.204		2.171	$Si-Cl_{in}$		2.202		2.168
LSA	123.4	118.9	121.7	118.8	LSA	124.6	119.2	122.8	119.5

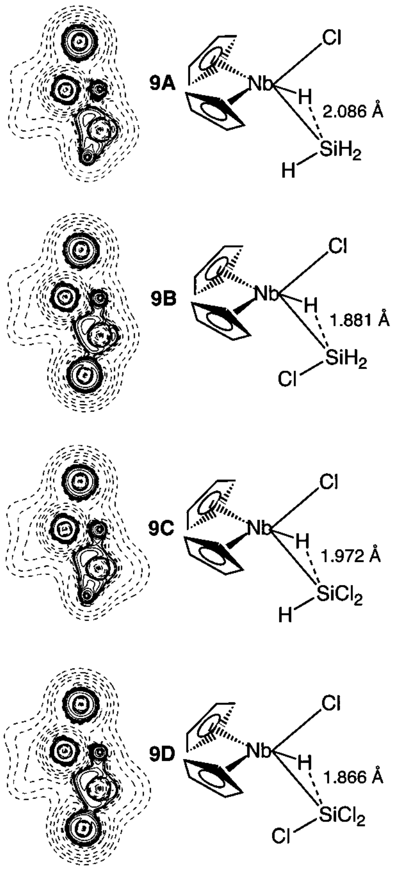
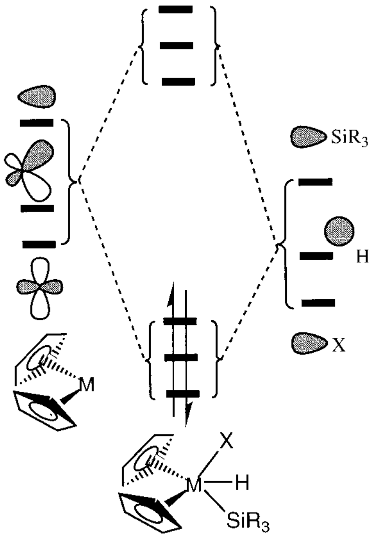


Figure 6. Laplacian plot of **9**. Note the presence of a H−Si bond path (except **9A**) and the square appearance of the density around metal center.

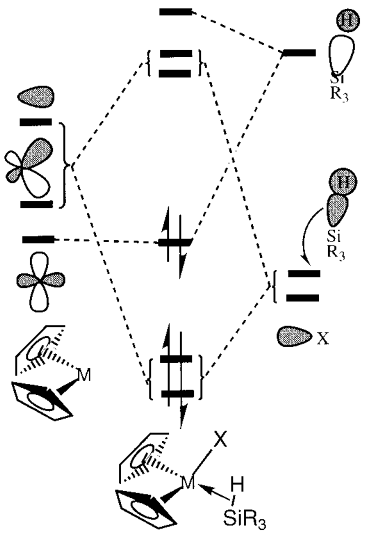
are not "forced" by the steric repulsion between Cl and H.

The chloride ligand is well-recognized for its strong σ-accepting (due to its very high electronegativity) and π-donating capabilities. The existence of an η^2-silane coordination in a complex without any strong π-acceptor is thus a surprising result. This strongly suggests that the factors governing the strength of the H···Si interaction in these group 5 metallocene complexes are very different from those of the more familiar mid-transition-metal pseudooctahedral η^2-silane complexes, with the nature of the H···Si interaction being well described by Dewar−Chatt-type synergic σ-bonding−π-back-bonding model. In the present case of early-transition-metal metallocene complexes with three discrete terminal ligands, the σ-withdrawing effect of the electronegative Cl (both as a terminal M−X ligand and a silyl substituent) probably dominates the bonding picture. We believe that the electronic environment around the metal center plays a crucial role in determining the extent of the H···Si interaction in early (groups 3−5) transition-metal complexes. The presence of Cl substituents on silicon pull electron density away from Si, enhancing the electrostatic attraction between the H and SiR_3 ligands (and hence polarizing the hydride electron density toward Si). As mentioned in the Introduction, the complex $TiCp_2(PMe_3)(\eta^2\text{-H}\cdots SiMe_3)$ possesses a prominent η^2-silane coordination character



Classical Structure

(a)



Non-classical Structure

(b)

Figure 7. Orbital interaction diagrams for the two extremes of $MCp_2ClH(SiR_3)$: (a) classical and (b) nonclassical.

Table 3. Bond Lengths (Å) and Ligand Spreading Angle (deg) of the Complexes $MCp_2HH(SiCl_nH_{3-n})$

	Nb					Ta			
	$n = 0$ (**10A**)	$n = 1$ (**10B**)	$n = 2$ (**10C**)	$n = 3$ (**10D**)		$n = 0$ (**10a**)	$n = 1$ (**10b**)	$n = 2$ (**10c**)	$n = 3$ (**10d**)
Nb−Cp	2.440	2.439	2.439	2.440	Ta−Cp	2.435	2.433	2.433	2.434
Nb−H^1	1.737	1.740	1.735	1.734	Ta−H^1	1.749	1.749	1.745	1.744
Nb−H^2	1.764	1.783	1.772	1.781	Ta−H^2	1.774	1.792	1.780	1.787
Nb−Si	2.637	2.570	2.577	2.542	Ta−Si	2.636	2.571	2.582	2.549
H^1···H^2	1.806	1.867	1.864	1.834	H^1···H^2	1.860	1.912	1.843	1.860
Si···H^2	2.289	2.067	2.198	2.094	Si···H^2	2.296	2.070	2.223	2.131
LSA	120.8	117.0	119.1	117.5	LSA	122.7	118.4	120.8	119.1

Table 4. Bond Lengths (Å) and Ligand Spreading Angle (deg) of the Complexes $MCp_2(CH_3)H(SiCl_nH_{3-n})$

	Nb					Ta			
	$n = 0$ (**11A**)	$n = 1$ (**11B**)	$n = 2$ (**11C**)	$n = 3$ (**11D**)		$n = 0$ (**11a**)	$n = 1$ (**11b**)	$n = 2$ (**11c**)	$n = 3$ (**11d**)
Nb−Cp	2.453	2.451	2.451	2.452	Ta−Cp	2.448	2.445	2.446	2.446
Nb−C	2.330	2.325	2.327	2.325	Ta−C	2.311	2.305	2.307	2.305
Nb−H	1.768	1.795	1.779	1.793	Ta−H	1.773	1.799	1.782	1.793
Nb−Si	2.640	2.569	2.572	2.537	Ta−Si	2.642	2.570	2.578	2.543
C···H	2.264	2.314	2.272	2.294	C···H	2.278	2.318	2.274	2.290
Si···H	2.205	1.960	2.072	1.945	Si···H	2.221	1.965	2.111	1.985
LSA	121.3	116.5	118.8	116.1	LSA	122.7	117.2	120.4	117.6

(H···Si distance ~1.8 Å). It shifts to the classical end (with H···Si distance > 2.3 Å) by merely switching the first-row Ti to second- or third-row Zr or Hf. The higher electron-releasing tendency for second- and third-row transition-metal atoms alone has qualitatively changed the nature of the bonding in these group 4 metallocene complexes. It is also possible that the dihydrogen complex $[TaCp_2(CO)(\eta^2\text{-}H_2)](BF_4)$ (**4**) can allow for nonclassical H_2 coordination due to its cationic nature.

It is worth comparing the nature of bonding between $TiCp_2(\eta^2\text{-}trans\text{-}^tBuC{\equiv}CSiHMe_2)$ (**3**) and $MCp_2ClH(SiCl_nH_{3-n})$ (**9**). In the titanium complex, the emphasis is placed on the competition of π-back-bonding between the acetylene π^*-orbital and the H−Si σ^* orbital for the MCp_2 $1a_1$ orbital back-bonding, and the d^2 configuration for the metal center makes this back-bonding feasible. In the niobocene case, one *starts* with a classical description with three discrete ancillary ligands, in which the π-bonding character of the individual ligands is relatively unimportant, and the metal has a formal d^0 configuration. The terminal Cl ligand makes the metal (Nb or Ta) center electron-deficient, so that the metal d → (H···Si) σ^* back-donation is significantly reduced, and a formal d^2 metal center is, therefore, preferred. Moreover, the Cl substituents on the silyl ligand enhance the H···Si "bond" strength through an electron-density withdrawing effect. The enhancing effect of the in-plane Cl substitutent is more pronounced due to its "apical" position in a pseudotrigonal-bipyramidal Si coordination. It is, therefore, possible for a group 5 metallocene fragment to maintain a nonclassical η^2-ligand coordination by either a σ-withdrawing effect or Dewar−Chatt-type π-back-bonding interactions.

Dihydrido−Silyl Complexes $MCp_2HH(SiCl_nH_{3-n})$ and Methyl−Hydrido−Silyl Complexes $MCp_2(CH_3)H(SiCl_nH_{3-n})$, M = Nb, Ta; n = 0−3: Role of Terminal M−X and Silyl Si−X Substituents. Hydride and methyl are representatives of ligands of moderate electronegativity with little π-bonding characteristics because the antibonding orbitals are not quite accessible. The H ligand serves as a potential competitor against SiR_3 for nonclassical η^2-interaction with the central hydride to the metal center; while to date there is no example of a discrete nonclassical alkane (H···CR$_3$) complex.[2j] The results of MP2 optimizations of the model complexes **10** and **11** are shown in Tables 3 and 4, respectively.

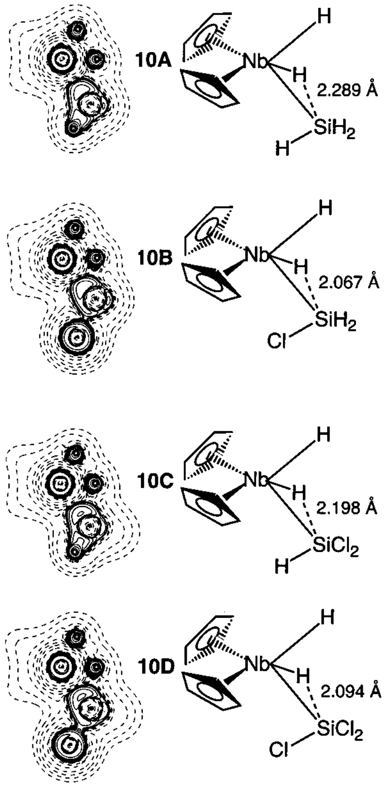


Figure 8. Laplacian plot of **10**. Note the absence of a H−Si bond path for any of the model systems, the severe polarization of the electron density around Si toward the central hydride, and the nonexistence of observable H···H interactions.

For the dihydrido complexes **10**, neither an η^2-H_2 nor an η^2-H···SiR_3 coordination is observed in the density Laplacian ($-\nabla^2\rho$) plot (Figure 8) and the density around the metal center has a rather circular pattern. This shows that the complexes **10** are most appropriately regarded as "totally classical" dihydride and hydrido−silyl systems. While there is no appreciable polarization of the electron density between the hydrides, the density of the central H is seen to be significantly polarized toward SiR_3, thus indicating a similar degree of H···Si interaction as those of the disilyl complexes **8**, and this is also manifested by the similar H···Si interligand distances in **8** and **10.** These results conform to the general observation that H···Si interactions are preferred to H···H interactions when both of them are allowed in the molecular structure.[26] The complexes **11** can thus be considered as the classical end of the group 5 metallocene complexes in terms of H···Si interactions.

The methyl−hydrido−silyl complexes **11** turn out to be intermediate between **10** and **9** regarding its structure and degree of H···Si interaction. It is interesting to observe that the one- and three-chloride-substituted complexes **11B/b** and **11D/d** possess a curved H−Si bond path in the Laplacian plot, while that of non- and two-Cl-substututed cases **11A/a** and **11C/c** do not. By surveying the H···Si interaction characteristics of **8**−**11** and using the criterion of Bader's atoms-in-molecules theory, a "boundary" between nonclassical η^2-silane and classical hydridosilyl complexes can be placed at a H···Si distance of ~2.0 Å (an attempt has also been made to set the maximum H···H distance of an η^2-H_2 complex at ~1.4 Å).[27] The CH_3 ligand probably serves a similar role as Cl electron withdrawal when it is bonded to a metal center, although a much weaker one. The combined action of electron-withdrawing effects from M and Si has once again enhanced the strength of the H···Si interaction as in **9**.

Conclusions

In this study we have analyzed the structure and bonding of group 5 bent metallocene complexes with neighboring H and SiR_3 ligands. The complexes $MCp_2(SiCl_nH_{3-n})H(SiCl_nH_{3-n})$ (**8**) are shown to exclusively attain the symmetric C_{2v} structures, thus confirming the corrections made for the X-ray data of $NbCp_2(SiClMe_2)H(SiClMe_2)$ (**7**), and a number of theoretical examinations indicate that the complex $TaCp_2(SiMe_2H)H(SiMe_2H)$ (**6**) is most likely to adopt the symmetric C_{2v} structure. The failure to obtain a stable nonclassical η^2-H···Si structure through MP2 optimizations further suggests that complex **6** is not very likely to possess an unsymmetric nonclassical η^2-silane structure, as suggested by X-ray data, and the possibility of a hydride shuffling tautomerism is not very high. Nevertheless, the significant long-range (H···Si distance > 2.0 Å) H···SiR_3 interligand interaction is confirmed by the presence of a severe polarization of the electron density from the central hydride toward both silyl ligands. The symmetric arrangement of the silyl−hydrido−silyl ligands is obtained for complexes with any number of Cl-substituents on silicon, and in no case was a H−Si bond path observed.

From the systematic study of the electronic effects of the MCp_2 fragment and the Si atom on the strength of the H···Si interaction, we have arrived at a rather unexpected ligand environment capable of forming a nonclassical H···Si coordination without the presence of any strong π-acceptor, namely, $MCp_2ClH(SiCl_nH_{3-n})$ (**9**) (M = Nb, Ta; $n = 1-3$) and $MCp_2(CH_3)H(SiCl_nH_{3-n}$, $n = 1, 3$) (**11**). From the consideration of orbital interactions and comparisons with carbonyl-type metallocene complexes containing η^2-coordinated ligands, e.g., **5** and **6**, it is possible that the major factor controlling the extent of nonclassical interligand interactions is the electronic deficiency of the metal and silicon center, induced by electronegative ligands, with metal-to-ligand π-back-bonding enhancing the stabilizing effect.

Systematic trends of variations in structure with the number of Cl-substitutions on silicon are consistent across all structural types of MCp_2 model complexes **8**−**11**. Both the M−Si and M−X (X = Cl, H, and CH_3) distances decrease and the M−H (the central MCp_2 hydride ligand) distance increases with the number of Cl-substituents on silicon. In particular, the in-plane Si−Cl bond exerts a more powerful effect than out-of-plane Cl's in enhancing the strength of the H···Si interaction, which can be viewed as a trans effect of the trigonal-bipyramidal coordination. The σ-withdrawing effect of a chloride substituent couples with that of the terminal M−Cl ligand in enhancing the attracting interaction between the central hydride and the SiR_3 ligand.

The bent metallocene fragment provides a platform for novel bonding possibilities. The complexes **9** and **11**, while they still have not been synthesized to date, present real potential targets for exploration by synthetic and structural chemists. We hope this theoretical study will provide an impetus for the possible new research area of nonclassical σ-bond coordination in transition-metal complexes stabilized by σ-interactions.

Acknowledgment. This work is supported by the Research Grants Council of Hong Kong.

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