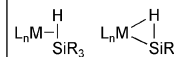


Structural and bonding characteristics in transition metal–silane complexes



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Received (in Cambridge, UK) 4th December 2001

First published as an Advance Article on the web 14th May 2002

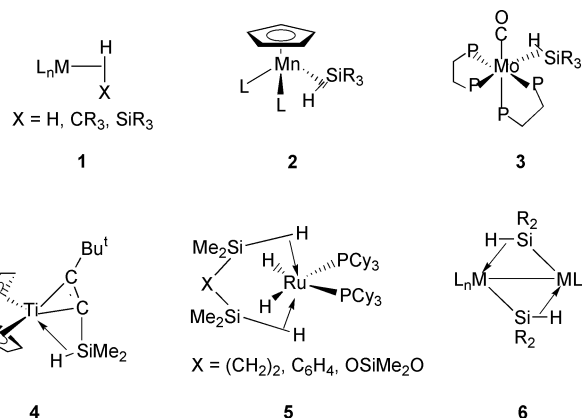
Transition metal–silane complexes containing metal– η^2 -H–Si coordination display different structural and bonding characteristics in comparison to other σ -complexes, such as dihydrogen and alkane (agostic) complexes. The different characteristics can be related to the strong σ^* -accepting properties of the η^2 -silane ligand(s) because of the weaker H–Si σ bond. Various examples of metal–silane complexes have been reviewed and their structural stabilities have been systematically discussed. Silyl–hydride complexes having substantial silyl–hydrido interactions have also been emphasized.

1 Introduction

The coordination chemistry of ligands to transition metal centers by η^2 σ bonds (see **1**) is of current interest in relation both to metal–ligand bonding and to the catalysis of reactions involving silanes.^{1–7} The study of these σ -complexes, also called ‘nonclassical’ or η^2 complexes, in particular has been driven by the ultimate goal of C–H bond activation, which is important to the understanding of many industrial processes. Typical σ -complexes include those of η^2 coordinated H–H, H–B, H–C (agostic) and H–Si bonds.^{3,7} Recently, considerable experimental and theoretical studies have been done in metal–silane σ complexes since they can serve as both a model for C–

H bond activation and possible intermediates in synthetically important hydrosilation reactions.^{5–7}

Earlier examples of nonclassical metal–silane complexes include mainly piano-stool type (**2**),² while recent syntheses and X-ray diffraction studies of the pseudo-octahedral molybdenum complexes Mo(CO)(P–P)₂(η^2 -HSiR₃) (**3**) (P–P = bidentate diphosphine ligands) provide the first examples of a non-piano-



stool mononuclear d⁶ octahedral complex containing metal–(η^2 -HSi) coordination.^{8,9} Although nonclassical complexes are more prevalent with mid-transition metals (Groups 6–8), early transition metal complexes can also possess such nonclassical interactions (see metallocene–acetylene complex TiCp₂(η^2 -*trans*-^tBuC \equiv CSiHMe₂) **4**).¹⁰ More recently, mononuclear complexes **5** containing two Ru–(η^2 -HSi) bonds were synthesized and characterized.¹¹ With the continuing effort in the area, dinuclear transition metal η^2 -silane complexes [L_nM(μ - η^2 -HSiR₂)₂] **6** have also been reported.^{5,12} Compared to other types of σ -complexes, transition metal silane complexes display special structural and bonding properties because of the much weaker H–Si bond and the ability of Si being hypervalent, *i.e.*, more than four electron pairs surrounding a Si center. In this article, we will provide detailed discussion and comments on the special structural and bonding feature based on various types of metal–silane complexes. Discussion will also be made to silyl–hydride complexes with substantial silyl–hydrido interactions.

2 The nature of the metal–silane interaction

The current understanding on the nature of metal–(η^2 -silane) interaction is based on the traditional Dewar–Chatt–Duncanson model for the well-known π complexes which emphasizes both ligand-to-metal σ bonding and metal $d\pi$ back-donation (see Fig. 1). Several studies of metal–silane interactions indicate that

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silane is a strong σ^* -accepting ligand because of the weaker H–Si σ bonding.^{13–15} Thus, the metal($d\pi$)-to-silane(σ^*) back-bonding interaction is deemed extremely important for the metal–(η^2 -silane) interaction.^{13–15}

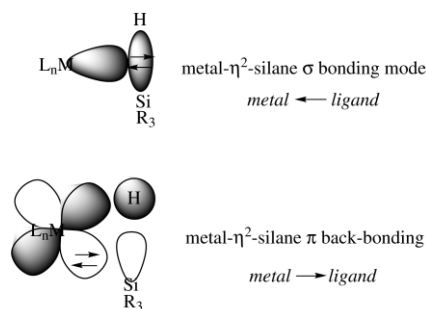
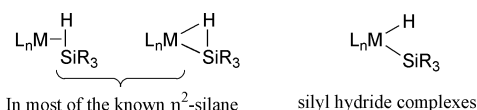


Fig. 1 The metal– η^2 -silane bonding interactions based on the Dewar–Chatt–Duncanson model.

Because of the significant back-bonding interaction, which weakens the H–Si interaction in the η^2 -silane unit, one has a series of structures ranging from nonclassical to the extreme case of classical silyl hydride complexes. Scheme 1 indicates



In most of the known η^2 -silane complexes or silane σ -complexes, the H–Si distances are normally in the range of 1.6 ~ 1.9 Å.

Scheme 1

that the commonly mentioned metal–silane σ -complexes or η^2 -silane complexes represent a wide range of structures in which the H–Si bonding is significantly weakened. Other types of σ -complexes such as metal–(η^2 -H₂) and metal–(η^2 -HC) (agostic) have relatively much smaller back-donation interactions and the coordinated H–C (or H–H) bond is only slightly weakened because the σ^* orbital of the coordinated H–C (or H–H) bond is much higher in energy. All the characterized dihydrogen and alkane σ -complexes are much closer to the nonclassical end with the H–H and C–H bond lengths (usually 0.8 ~ 0.9 Å and ~ 1.2 Å, respectively) approaching those of free H₂ (0.74 Å) and C–H (1.10 Å) bonds, although a few examples of dihydrogen complexes show intermediate distances of 1.10 ~ 1.3 Å.^{16,17} For metal– η^2 -silane complexes, the distances between the coordinated H and Si atoms have much wider range (1.6 ~ 1.9 Å) in comparison to the free H–Si σ bond (~ 1.5 Å).

3 Structural characteristics in mononuclear silane complexes

3.1 The *cis* arrangement in *cis*-Mo(η^2 -silane)(CO)(R₂PC₂H₄PR₂)₂

The complexes Mo(CO)(P–P)₂(η^2 -HSiR₃) **3** (P–P = depe, SiR₃ = SiHPh₂; P–P = dppe, SiR₃ = SiH₃) provide the first examples of a non-piano-stool mononuclear d⁶ octahedral complex with a single metal–silane interaction.^{8,9} The syntheses and characterizations of analogous η^2 -H₂ complexes with the same metal fragment allow a useful comparison between the H₂ and HSi coordinations. An intriguing feature of the silane complexes **3** is that the η^2 -HSi moiety is *cis* to the carbonyl while in the known transition metal carbonyl dihydrogen complexes, for example Mo(CO)(depe)₂(H₂), and complexes with agostic C–H interactions, for example Mo(CO)(dppe)₂, CO is always found to be *trans* to the σ -coordinated ligand (Fig.

2).^{18,19} This indicates important differences in the nature of bonding between η^2 -H₂ and η^2 -silane complexes.

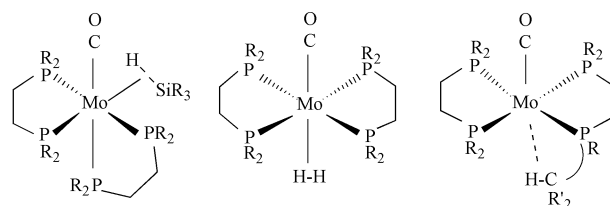


Fig. 2 Different structural arrangements among three σ -complexes based on Mo(CO)(P–P)₂ fragments.

In addition to the *cis* arrangement, the coordinated η^2 -HSi unit and CO are mutually perpendicular to each other. *Ab initio* quantum chemical calculations showed that the *trans* and *cis*-and-coplanar structural isomers are less stable by *ca.* 10.0 kcal mol^{–1} than the *cis*-and-perpendicular structure.¹³ The instability of the two structures has been explained by the competition for metal(d)-to-ligand(σ^*) π back-donation interactions in the structural arrangements (see Fig. 3).¹³ In contrast, the *cis*-and-

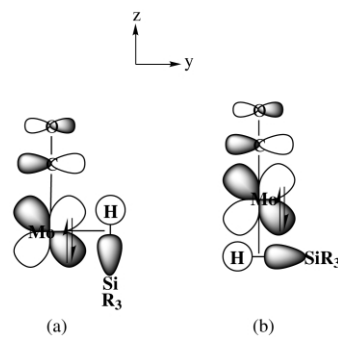


Fig. 3 Illustration of competing metal-to-ligand back-bonding interactions between the carbonyl and silane ligands in a *cis*-and-coplanar (a) and *trans* (b) arrangements.

perpendicular orientation gives no sharing of d orbitals in the π back-bonding interaction, leading to an optimal situation in which all the three t_{2g} orbitals (a d^6 electron configuration) interact with different empty orbitals of the CO (two) and η^2 -HSi (one) π^*/σ^* -accepting ligands. In other words, the *cis*-and-perpendicular arrangement of the CO and η^2 -HSi units avoids the competition for metal-to-ligand back-bonding interactions.

For the nonclassical dihydrogen and agostic metal complexes, the extent of metal-to-ligand back-bonding interactions is relatively limited and the competition is not dominant because of the high-lying σ^* orbitals of the coordinated H–H and H–C bonds. Therefore, *trans* structures are observed for these σ -complexes while the metal–silane complexes, also defined as σ -complexes, display different structural characteristics.

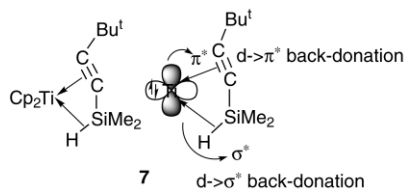
3.2 Competing for back-bonding interactions in TiCp₂(η^2 -*trans*-RC=CSiHR₂)

As mentioned above, most of the known metal– η^2 -silane complexes have H–Si bond lengths at 1.6 ~ 1.9 Å, significantly longer than the free silane H–Si bond length of 1.48 Å. Such lengthening is due to its low lying σ^* orbital, giving the η^2 -HSi moiety strong σ^* -accepting character. Therefore, a truly nonclassical H–Si complex can be expected only when there is no back-bonding, *i.e.*, a d^0 system. For example, the recently studied *ansa*-bridged rare earth disilylamide complexes having d^0 centers display the nonclassical feature.²⁰ The calculated H–Si distances are all shorter than 1.6 Å. In these complexes,

however, the metal-(η^2 -HSi) interaction is found to be quite weak and dominated by electrostatic effects.²⁰

There is an interesting complex $\text{TiCp}_2(\eta^2\text{-trans-}^t\text{BuC}\equiv\text{C-SiHMe}_2)$ **4** recently synthesized by Rosenthal *et al.*,¹⁰ which shows a drastic bending of the H-Si bond toward the metal center and undoubtedly indicates a very strong Ti-(η^2 -HSi) interaction. At one extreme, the complex could be formulated as a d^0 system if the acetylene is considered to withdraw 2 electrons from the metal (the metallacyclopropene formulation). Thus one would expect no back donation from Ti to the H-Si σ^* . The other extreme of a d^2 metal center for **4** (the π -complex formulation) would allow the two metal d electrons to participate in $d \rightarrow \sigma^*$ back donation. In view of the inherently weak metal(d^0)-(η^2 -HSi) interaction due to the lack of back-bonding, a d^0 metal center for **4** would lead to the apparent dilemma that the Ti-(η^2 -HSi) interaction is weak. Elucidation of the nature of Ti-(η^2 -HSi) interaction and the electronic configuration of the Ti center is thus very challenging.

Theoretical studies on the titanocene complex conclude that the complex is better formulated as a d^2 system with comparable back-bonding strengths of the acetylene and η^2 -HSi ligands (see **7**).¹⁴ The competition for back-donation interaction between the



two ligands is manifested by the structural characteristics. A number of *cis*- $\text{TiCp}_2(\text{RC}\equiv\text{CSiR}'_3)$ ($\text{R}' \neq \text{H}$) complexes, containing a silyl group attached to the acetylene but without possible Ti-(η^2 -HSi) interactions, shows significantly shorter Ti-C bond lengths of $\sim 2.1 \text{ \AA}$, compared with that of **4** (Ti-C = 2.162 \AA and 2.276 \AA). Their C \equiv C bond lengths are also slightly longer (1.28 \sim 1.31 \AA) than that of 1.275 \AA in **4**, which has the possibility of Ti-(η^2 -HSi) interaction. The calculated H-Si distance is *ca.* 1.65 \AA , close to the lower end of the H-Si distance range for metal-silane complexes. The titanocene complex discussed here provides an elegant example manifesting the different structural characteristics when compared to other types of σ -complexes.

3.3 Structural distortion in a few bis(silane) ruthenium complexes

Mononuclear bis(silane) complexes provide interesting examples to illustrate the structural characteristics. Recently, a few bis(silane) ruthenium complexes **5** possessing a near- C_{2v} symmetry were synthesized.^{11,21} The most interesting feature is the apparent *trans*-bis(η^2 -HSi) coordination. If each of the coordinated η^2 -HSi units is considered to be a fully $2e$ σ -donor, the parallel *trans* orientation of the two coordinated η^2 -HSi units would cause severe competition of the metal d-orbital for back-donation, similar to the hypothetical *trans* isomer of the complex $\text{Mo}(\text{CO})(\text{depe})_2(\eta^2\text{-HSiR}_3)$.

A theoretical study was done to provide some insight into the driving forces behind the stability of the apparently *trans*-bis(η^2 -HSi) coordination.¹⁵ Through the theoretical study, it was concluded that the chelating environment and the steric bulk of the experimental PCy_3 ligands prevent free distortion from the near- C_{2v} symmetry. In such a near- C_{2v} overall structural constraint, a 'slipping' distortion in which the two η^2 -HSi units move in a direction away from the phosphine ligands occurs to prevent the severe competition for metal(d)-to-ligand(σ^*) back-donation interaction between the two η^2 -HSi ligands.¹⁵ Fig. 4 shows a qualitative molecular orbital inter-

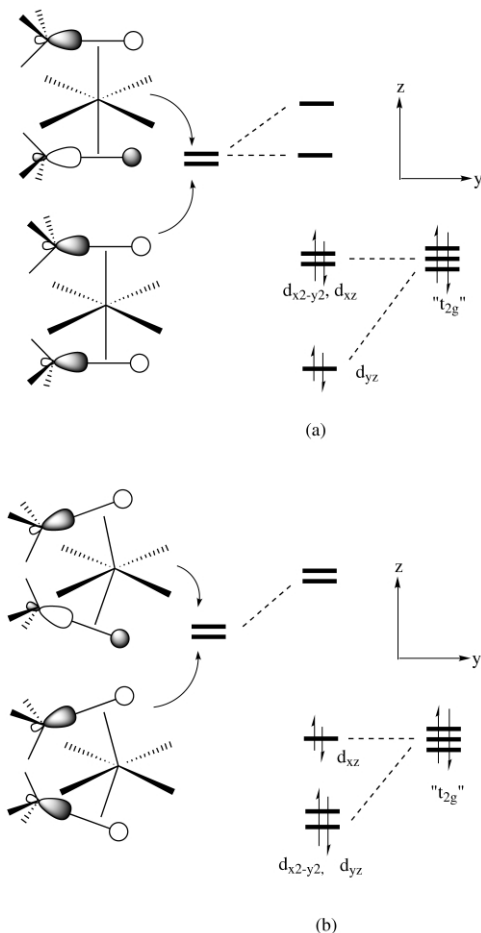
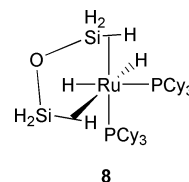


Fig. 4 Qualitative MO interaction diagram illustrating the competition of the two H-Si ' σ -bonds' for metal back-donation in (a), and the stabilization caused by the distortion in (b). (Adapted from M.-F. Fan and Z. Lin, *Organometallics*, 1999, **18**, 286).

action scheme illustrating how the competition is prevented by the 'slipping' distortion. In an 'idealized' 6-coordinate situation, where the two η^2 -HSi ligands act as simple $2e$ σ -donors, the metal d_{yz} orbital interacts simultaneously with the two *trans*- σ^* -orbitals, causing severe competition of metal-to-ligand(σ^*) back-donation (Fig. 4a). After the distortion, the resulting nearly *trans*-dihydride configuration enables the metal d_{yz} and $d_{x^2-y^2}$ orbitals to be utilized in favorable MO interactions with the HSi σ^* orbitals (Fig. 4b). As a result, the *trans*-bis(η^2 -HSi) structure of complexes **5** reflects the inherent stabilization of the complex through a particular distorted coordination of the two *trans*-(η^2 -HSi) units.

Ruthenium bis(silane) complex **8** has a bridging oxygen ($\text{X} = \text{O}$) in the chelating disilane ligand. Although the complex has not been structurally characterized, theoretical calculations

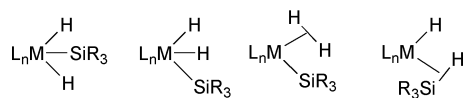


show that instead of a near- C_{2v} structure the complex adopts a structure in which the two η^2 -HSi units are *cis* to each other.²¹ Such kind of arrangement in the complex allows optimal metal(d)-to-ligand(σ^*) back-bonding interactions, *i.e.*, no competition exists as the two σ^* from the two coordinated η^2 -HSi units interact with different d orbitals from the metal center. The structural arrangement may be closely related to the lowest $J_{\text{Si-H}}$

values and the lowest barrier to activation for the hydride exchange process observed experimentally among the ruthenium bis(silane) complexes.²¹ The *cis* arrangement gives optimal back-bonding interaction, weakening the H–Si interaction significantly and leading to the lowest coupling constants. The more hydridic character of the hydrogens in the coordinated η^2 -HSi units because of the strong back-donation facilitates the relevant hydride exchange process. It should be noted that the calculated structural parameters reported in the literature²¹ do not correlate well with the argument given here.

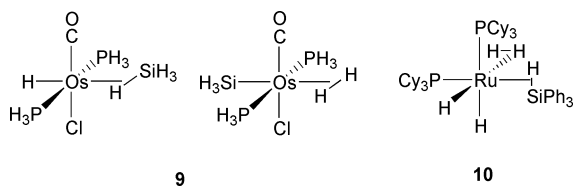
3.4 Isomeric preference in complexes when both η^2 -H₂ and η^2 -silane are possible

Many possible isomeric structural forms are possible for complexes of formula of L_nM'H₂SiR₃'. Scheme 2 shows several interesting isomeric forms, *i.e.*, classical forms and non-



Scheme 2

classical forms with η^2 -H₂ or η^2 -HSiR₃. Although a few L_nM'H₂SiR₃' systems have been studied, the factors influencing isomeric preferences have not yet been fully investigated. Theoretical calculations of [OsCl(CO)(PH₃)₂(H₂SiH₃)] predict the possible existence of two different stable σ -complexes **9**, [OsCl(CO)(PH₃)₂(SiH₃)(η^2 -H₂)] and [OsCl(CO)(PH₃)₂(H)(η^2 -H-SiH₃)] although a *T*₁ NMR measurement of [OsCl(CO)-(PⁱPr₃)₂(SiEt₃)(H₂)] suggests a nonclassical H₂ complex.^{22,23}

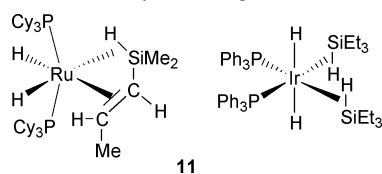


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The similar stability of the two structural forms has been attributed to the following reasons.²³ The η^2 coordination of H–SiR₃ to the [OsCl(CO)(PR₃)₂(H)] fragment is stronger than that of the H–H ligand to the [OsCl(CO)(PR₃)₂(SiR₃)] fragment by *ca.* 15 kcal mol⁻¹, a value that compensates almost exactly the superior strength of the H–H bond with respect to the H–SiR₃ bond. Another experimentally and theoretically studied system is TpRu(PPh₃)'H₂SiH₃'.²⁴ Various structural possibilities have been calculated theoretically. Supported by experimental NMR data, it was concluded that the η^2 -silane coordination is the stable structure. Recently, a remarkable complex RuH₂(η^2 -H₂)(η^2 -HSiPh₃)(PCy₃)₂ **10** bearing two different coordinated σ -bonds, η^2 -H₂ and η^2 -HSiPh₃, has been structurally characterized.²⁵ Theoretical calculations have also been done to give further support to the interesting structure.²⁵

In other related systems which have been experimentally studied, the η^2 -silane coordination seems prevalent. The bis(silane) complexes illustrated in Section 3.3 can in principle also have η^2 -H₂ coordination which is not observed experimentally. Two more examples illustrating the preference of the η^2 -silane coordination over η^2 -H₂ are given in **11**. The ruthenium



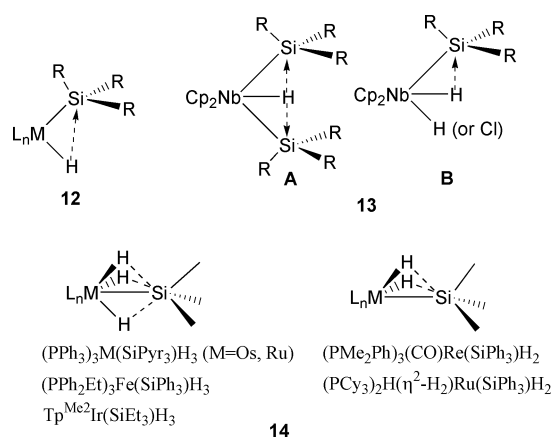
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complex has an X-ray structure while the structure of the iridium complex was proposed based on NMR experi-

ments.^{26,27} The reason for the preference may be related to the stronger metal–(η^2 -silane) interaction because of significant metal(d)-to-silane(σ^*) back-bonding discussed in Section 2 although more theoretical and experimental studies are necessary before a full picture can be drawn.

4 Silyl hydride complexes with substantial silyl–hydrido interactions

Transition metal silyl hydride complexes represent those in the classical end shown in Scheme 1. Because of the additional bonding ability due to its low electronegativity, silicon in the silyl group is normally able to attract electron density from adjacent hydride ligands. The type of interaction is illustrated in **12**, indicating the hypervalency around the Si center. The



hydride ligand tends to cap the triangle face formed by the metal center and two R groups. In other words, there are more than four electron pairs surrounding the Si center. Because of the different electronic property of Si in comparison to C, the silyl–hydrido interaction is always expected in silyl hydride complexes when the silyl and hydride ligands are *cis* to each other. The question is how strong is the interaction. If we define the metal– η^2 -silane complexes having the H–Si distances smaller than 1.9 Å, silyl hydride complexes having the distances between the hydride and silyl ligands in the range of 1.9 ~ 2.1 Å should possess significant silyl–hydrido interactions. Those with distances ranging from 2.1 ~ 2.5 Å are expected to have weaker interactions. Fig. 5 illustrates the different situations according to the distances between H and Si. It should be noted that the definition here is for the purpose of discussion, and not intended to be exact.

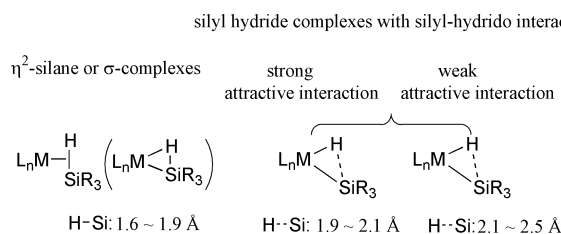


Fig. 5 Schematic illustration for different situations in metal–silane interactions. The definition here is not intended to be exact. The boundaries are not clear-cut in reality.

Through the work of Nikonov and his coworkers, many Cp-containing early transition metal silyl hydride complexes having strong silyl–hydrido interactions have been synthesized and structurally characterized.²⁸ These complexes have the structures shown in **13**. The substituents on Si include methyl, phenyl and halide groups. In **13A**, symmetric structures are

generally observed and a 5-center-6-electron bonding picture has been used to describe the structural feature. The distances between hydride and silyl ligands in these complexes are around 2.0 Å.

Interactions of a silyl group with two or more hydride ligands in some silyl polyhydride complexes have been highlighted and reviewed very recently.^{29,30} Crabtree and his coworkers in 1990 noticed this type of interaction in the structure of $(\text{PPh}_3)_2\text{ReH}_6(\text{SiPh}_3)$.³¹ A subsequent theoretical study on several silyl polyhydride complexes further confirms the existence of the interligand interactions.³² Several typical examples are illustrated in **14** showing that a silyl group interacts simultaneously with two or three hydride ligands. Complex **10** has also been considered to possess two silyl–hydrido interactions because the assumed hydride which is *trans* to a PCy_3 ligand shown in **10** is also found to have close contact with the silicon center.²⁹ This type of multiple silyl–hydrido interaction could have important implications in the determination of structural preference in some complexes. A recently reported $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{SiEt}_3)_3$ ($\text{Tp}^{\text{Me}_2} = \text{HB}(3,5\text{-Me}_2\text{-pz})_3$) complex adopts a capped octahedron in which the silyl group caps the triangle face formed by the three hydride ligands (see **14**).³³ However, the analogous $\text{Tp}^{\text{Me}_2}\text{IrH}_4$ is believed to have an edge-bridged octahedral structure because of the absence of silyl–hydrido interactions.³⁴

To understand these types of silyl–hydrido interactions, one starts with a classical picture and then considers the additional interligand interactions between hydride and silyl ligands. In contrast, the metal–silane complexes are normally described as σ -complexes with significant metal(d)-to-silane(H–Si's σ^*) back-donation interaction.

5 Effect of silicon's substituents on the interactions between metal and H–Si moieties

Studies of the substituent effect on the interactions between metal and H–Si moieties have been limited to two classes of complexes. One is related to the group 7 pseudo-three-leg piano-stool complexes (see **2**).³⁵ The other is the group 5 bent metallocene complexes (see **13**).³⁶ Both theoretical and experimental studies show that the H–Si distances are significantly influenced by the substituents on Si.

Fig. 6 shows the change of structural parameters of the NbHSi triangle with the number of chloride substituents on Si based on the systematic quantum chemical calculations on model complexes $\text{Cp}_2\text{M}(\text{SiCl}_n\text{H}_{3-n})_2(\text{H})$ ($\text{M} = \text{Nb}$ or Ta ; $n = 0 \sim 3$) having symmetric structures and $\text{Cp}_2\text{M}(\text{SiCl}_n\text{H}_{3-n})(\text{H})\text{X}$ ($\text{M} = \text{Nb}$ or Ta ; $n = 0 \sim 3$; $\text{X} = \text{H}$, Me or Cl) having asymmetric structures.³⁶ A halide substituent *trans* to the hydride is found to be most significant in strengthening the interaction between H and Si, indicating the hypervalent coordination around the Si center. The strongest interaction in these studied complexes has been found in $\text{Cp}_2\text{Nb}(\text{SiCl}_3\text{H})(\text{H})\text{Cl}$. With the increasing H–Si interactions, the Nb–H distances are lengthened slightly. From Fig. 6, one can see that the Nb–Si distances are also significantly shortened with the increasing number of chloride substituents. This behavior is remarkably different from other types of σ -complexes. In other types of σ -complexes $\text{L}_n\text{M}(\eta^2\text{-H-X})$ when the H-bonded atom in the X group is a second-row element, it is always expected that the M–X interaction will be the stronger, the H–X interaction the weaker. However, due to the tendency of the silicon center to be hypervalent, the commonly accepted viewpoint is not applicable here. Fig. 7 schematically illustrates the different structural behavior of metal–silane and other types of σ -complexes.

Based on the results shown in Fig. 6, one might conclude that a fluoride substituent should enhance the H–Si interactions even

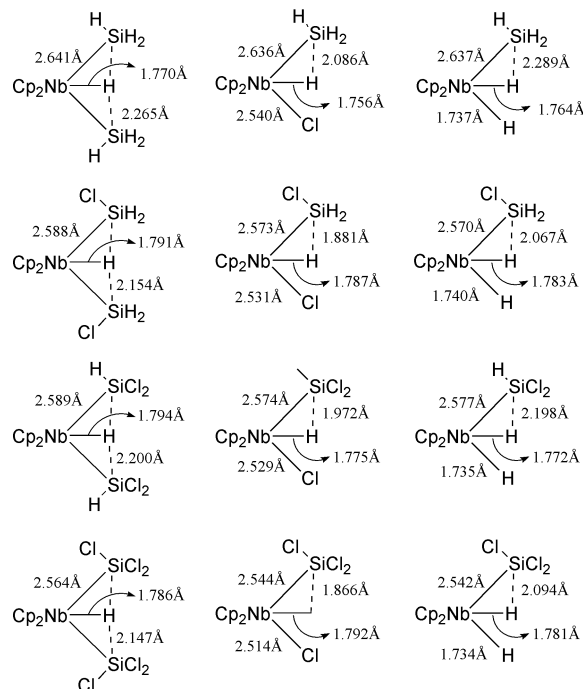


Fig. 6 The change of structural parameters of the NbHSi triangle with the number of chloride substituents on Si based on the results of MP2 quantum chemical calculations.

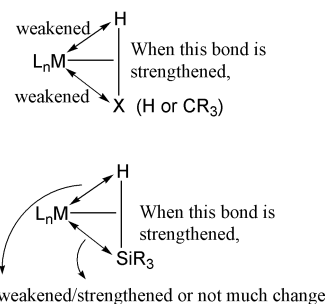
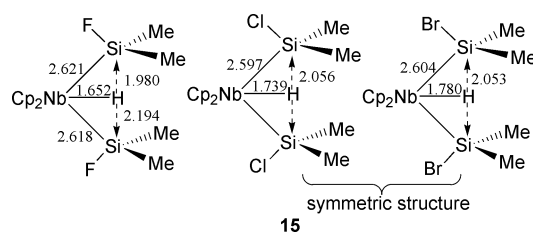


Fig. 7 Schematic illustration of the different structural behavior of metal–silane and other types of σ -complexes.

more and that a bromide substituent should have the opposite effect, because the fluoride is more electronegative and the bromide less. Experimental structures shown in **15** do not



entirely support this conclusion.²⁸ If one takes the average H–Si distance (2.087 Å) for the fluoride complex, one sees not much difference in the H–Si distances among the three halide complexes. It is also unexpected that the Nb–Si distances for the fluoride complex are much longer than those of the other two analogs. To account for the unexpected trend in the Nb–Si bond distances, an additional electronic factor called the theory of interligand hypervalent interaction (IHI) was proposed,²⁸ emphasizing the different structural changing behavior with respect to the change in the electronic properties of different substituents. In fact, if we carefully examine the Nb–H bond distances, one can see that the fluoride complex has a much shorter Nb–H distance. The stronger Nb–H interaction may

result in the weakening of the Nb–Si bonds. In theory, the Nb–Si distances in the bromide complex should be even longer when compared to those in the chloride complex. The noticeably longer Nb–H bond makes the Nb–Si bonds shorter. Comparing the detailed structural characteristics among these complexes, one has to consider the structural parameters in the MHSi triangle as a whole and cannot isolate them.

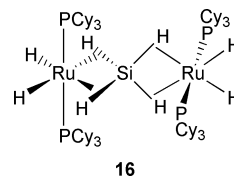
The group 7 pseudo-three-leg piano-stool complexes $\text{Cp}(\text{CO})_2\text{M}\{(\eta^2\text{-HSi}(\text{Cl}_n\text{H}_{3-n}))\}$ ($\text{M} = \text{Mn, Tc}$ and Re ; $n = 1 \sim 3$) have also been studied more thoroughly.³⁵ Experimentally, it was found that the η^2 -silane ligand dissociates more slowly for complexes with electron-rich metal centers or more electronegative substituents on silicon. Based on the commonly accepted viewpoint that the stronger H–Si interaction in the η^2 -silane ligand weakens the interaction between the metal center and the coordinated η^2 -silane ligand, and therefore, could facilitate the dissociation process, it was inferred that the H–Si interaction should be weaker for complexes with more electronegative substituents on silicon. Theoretical calculations on $\text{Cp}(\text{CO})_2\text{M}\{(\eta^2\text{-HSi}(\text{Cl}_n\text{H}_{3-n}))\}$ ($\text{M} = \text{Mn, Tc}$ and Re ; $n = 1 \sim 3$) do not support the inference.³⁵ On the contrary, the calculated results show that the H–Si distances decrease slightly with the number of chloride substituents. The increase of chloride substituents on Si also significantly shortens the M–Si bond distances. Therefore, the higher dissociation energies for complexes with more electronegative substituents are not related to the H–Si interaction but to the strong metal–silicon interaction. The different behavior is again associated with the silicon's lower electronegativity and ability to be hypervalent.

6 Dinuclear complexes containing bridging μ - η^2 -HSi units

Many dinuclear transition metal complexes containing bridging μ - η^2 -HSi units have been synthesized and structurally characterized over the past few years because of their catalytic importance.^{5,12} Structurally, the majority of these dinuclear η^2 -silane complexes have an unsymmetrical and planar $[\text{M}(\mu\text{-}\eta^2\text{-HSi})]_2$ moiety with different M–Si distances (see **6**) although there are situations in which the $[\text{M}(\mu\text{-}\eta^2\text{-HSi})]_2$ moieties are almost orthogonal.³⁷ Formally, if we assign a metal–metal bond for each of these dinuclear complexes, the 16-electron (for Pt/Pd metal centers) or 18-electron rule (for non-Pd/Pt centers) is met.

The bonding and structural features of a series of these bis(μ - η^2 -silane) complexes $[\text{L}_n\text{M}(\mu\text{-}\eta^2\text{-HSiR}_2)]_2$ have recently been studied using density functional theory calculations.¹² Based on the theoretical calculations, it was found that these dinuclear silane complexes display noticeably shorter H–Si distances (1.6 ~ 1.7 Å) in the $[\text{M}(\mu\text{-}\eta^2\text{-HSi})]_2$ units when compared with mononuclear η^2 -silane complexes. The shorter H–Si distances in the metal-(η^2 -silane) interactions suggest that these dinuclear complexes are more non-classical than mononuclear ones. The more non-classical feature has been explained as a result of weaker metal(d) to H–Si(σ^*) back-donation interactions due to the presence of a metal substituent on silicon. In the $\text{L}_n\text{M}(\mu\text{-}\eta^2\text{-HSiR}_2)_2\text{ML}_n$ complexes **6**, the metal centers can be considered as substituents on Si. The metal substituent, which is very electropositive, makes the Si center more electron-rich, and therefore weakens the back-donation interactions. It is not yet known how other substituents on Si affect the metal-(η^2 -HSi) interactions in these dinuclear complexes. It will be interesting in the future to examine the effect of electronegative substituents such as halides. It should be also noted that no such type of bridging η^2 -HC analogs have been reported up to date based on the knowledge we have.

The bimetallic ruthenium complex $[\{\text{PCy}_3\}_2\text{RuH}_2]_2(\eta^3, \eta^3, \mu\text{-SiH}_4)$ **16** contains a bridging SiH_4 molecule in which all the



four H–Si bonds are coordinated to the metal centers.³⁸ It is expected that the metal(d)-to-ligand(σ^*) back-donation for each H–Si bond is limited because one has four simultaneous back-bonding interactions to the central SiH_4 moiety. Therefore, it is not surprising that the H–Si bond distances (1.685 Å from DFT/B3LYP and 1.69 ~ 1.72 Å from X-ray data) are at the shorter end when compared to those in other ruthenium η^2 -silane complexes.

7 Summary

Although the traditional Dewar–Chatt–Duncanson model for the well-known π complexes is commonly used to describe the bonding of various types of transition metal σ -complexes $\text{L}_n\text{M}(\eta^2\text{-HX})$ **1** containing η^2 -HX ligand(s), η^2 -silane complexes differ considerably from others in terms of structural and bonding characteristics.

(1) Because of the weaker H–Si bond, η^2 -silane ligands possess strong σ^* -accepting properties. The metal(d)-to-ligand(σ^*) back-bonding interactions are significant. Therefore, metal- η^2 -silane complexes show much longer H–Si distances (1.6 ~ 1.9 Å) in comparison to the free H–Si σ bond (~ 1.5 Å). Truly nonclassical metal–silane complexes having H–Si distances close to those in free silanes exists only in d^0 systems. The metal–silane interactions in these truly nonclassical complexes are mainly electrostatic.

(2) The significant metal(d)-to-ligand(σ^*) back-bonding interactions make metal–silane complexes show different structural preference. The η^2 -silane ligand in these complexes orients itself in such a way that competition for back-donation against other π -accepting ligands can be avoided. In carbonyl-containing complexes, the η^2 -HSi unit prefers to be *cis* and perpendicular to a carbonyl ligand.

(3) When geometrical constraints such as chelations do not allow an arrangement for optimal metal(d)-to-ligand(σ^*) back-bonding interactions, special structural arrangements are necessary. The titanium metallocene complex and the ruthenium bis(silane) species discussed in Section 3 provide showcases for this type of scenario.

(4) Regarding the structural preference of η^2 -silane vs. $\eta^2\text{-H}_2$ for complexes when both coordination modes are allowed, the η^2 -silane mode seems more prevalent although more studies are necessary before a final conclusion can be made.

(5) Silyl hydride complexes with significant silyl–hydrido interactions are those having the distances between hydride and silyl ligands in the range of 1.9 ~ 2.1 Å. The silyl–hydrido interactions are considered as an H→Si dative bond to make the Si center hypervalent. Complexes with silyl and hydride ligands being *cis* to each other are always expected to have silyl–hydrido interactions. Those with distances ranging from 2.1 ~ 2.5 Å are considered to have weaker interactions. The distance ranges defined here are for the purpose of discussion and are not clear-cut.

(6) The structural parameters, *i.e.*, the M–Si, H–Si and M–H bond distances, involving the metal- η^2 -HSi interactions are indicators of how strong the metal–silane interactions are. The changes of these structural parameters with different substituents on silicon are interesting. Electronegative substituents could enhance both the M–Si and H–Si interactions. The situation cannot be true for other metal- η^2 -HX complexes in

which enhanced M–X interaction is generally at the expense of a weakened H–X one.

(7) Dinuclear transition metal complexes containing bridging μ - η^2 -HSi units display noticeably shorter H–Si distances (1.6 ~ 1.7 Å). These dinuclear complexes are more non-classical than mononuclear ones. The more non-classical feature is a result of weaker metal(d) to H–Si(σ^*) back-donation interactions due to the presence of a metal substituent on silicon. Further studies can be done on the substituent effect as well as on multinuclear clusters containing η^2 -HSi bridging units.

8 Acknowledgements

I'd like to thank my co-workers for their contribution to the work reported here: Man-Fai Fan, Sai-Heung Choi, and Wai-Han Lam. The Research Grants Council of Hong Kong and the Hong Kong University of Science and Technology are thanked for their financial support.

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