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New types of non-classical interligand interactions involving silicon based ligands

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Dedicated to the great contribution of Professor M. Dewar to the theoretical organometallic chemistry and on the occasion of the 50th anniversary of his landmark paper

Abstract

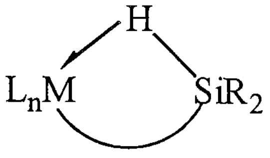
This review summarises recent findings and ideas about new non-classical interligand interactions in which at least one of the ligands has a silicon atom as an interacting centre. For many years the field of non-classical interactions was dominated by agostic and σ-complexes, bonding in which is often described in terms of electron-deficient 3c–2e interactions. In the case of silyl hydride compounds these early works resulted in the observation of η^2-$HSiR_3$ co-ordination mode. However, several recently reported systems can be rationalised as having more extended Si–H bonding, and ligands such as (η^3-H_2SiR_3) and even (η^4-H_3SiR_3) can be identified. Co-ordination of these complex ligands to the metal is still electron deficient. Another series of new discovered interligand interactions include donations from basic M–H (or M–Si) bond orbital onto suitable antibonding orbital of a neighbouring ligand ((Si–X)*, (C–O)*, etc). Different types of these hypervalent interactions are discussed and their relevance to migratory insertion reactions is traced. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Bond theory; Hydrido complexes; Hypervalent compounds; Non-classical interactions; Silicon

1. Introduction

Since the appearance of the classical Dewar's article in 1951 a tremendous success in the application of theoretical methods to organometallic chemistry has been made. MO theory is a particularly indispensable tool for understanding bonding situations in compounds with essentially delocalised bonds. Transition metal complexes with non-classical interligand interactions are examples of such compounds.

Non-classical interligand interactions between silicon based ligands and other groups are now known for almost 30 years [1], the most studied examples being the agostic (**1**) and silane σ-complexes (**2**). Bonding in these electron deficient systems is often regarded to as 3-centre–2-electron (3c–2e), although description in terms of Dewar–Chatt–Duncanson (DCD) type model is more appropriate (Fig. 1) [2]. As agostic we define a system in which a moiety participating in σ-complexation to the metal has an additional bridge to the metal (atoms or, in the limit of α-agostic case, just a single bond). A number of comprehensive reviews on silane σ-complexes have been published [1b,2]. However, several recently reported silicon substituted complexes cannot be described adequately using the conventional σ-bond complexation theory. This chemistry is reviewed here and possible bonding schemes for these non-classical systems are discussed.



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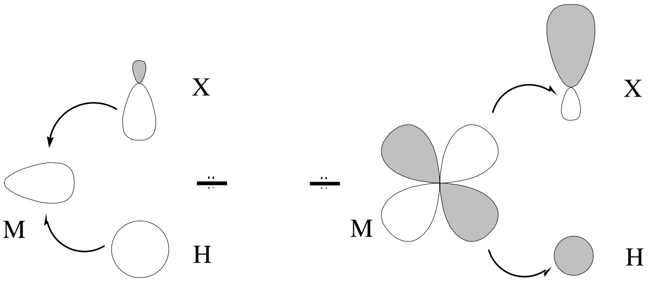


Fig. 1. Synergetic donation and back-donation interactions in σ-complexes.

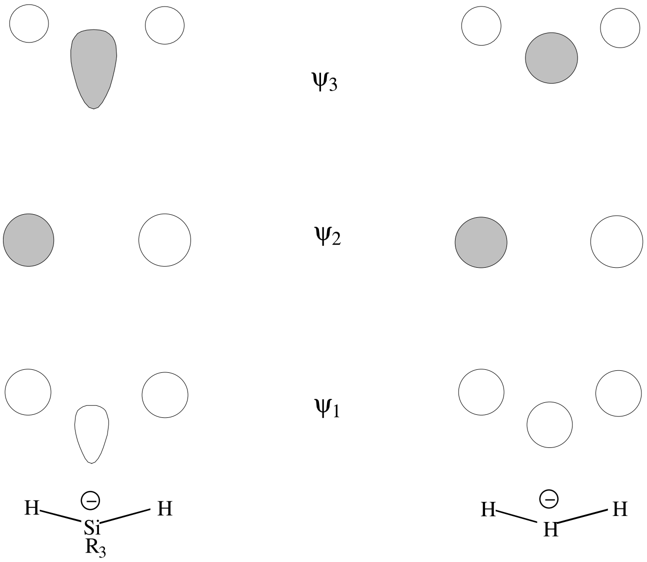
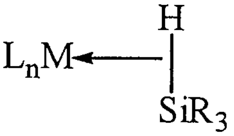


Fig. 2. Molecular orbital compositions of the $\{H_2SiR_3\}^-$ (left) and $\{H_3\}^-$ (right) ligands.



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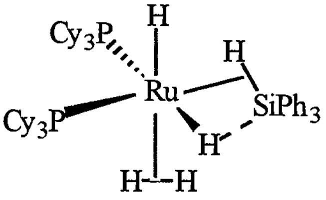
2. $(\eta^3\text{-}H_2SiR_3)^-$ ligand and related systems

Sabo-Etiennie at al. [3] have recently communicated an unusual ruthenium complex $[(\eta^2\text{-}H_2)(PCy_3)_2RuH_2(\eta^2\text{-}HSiPh_3)]$ (**3**) that was originally reported as a dihydrogen and silane σ-complex, as the formula suggested shows. However, its surprising structural features suggest an unusual type of interligand interactions. First, the authors noted that the very bulky phosphine ligands serendipitously occupy *cis* rather than intuitively preferred *trans* positions. Secondly, although the phosphines lie *trans* to such different ligands as reportedly η^2-$HSiPh_3$ and hydride, the observed Ru–P bonds do not differ much (2.392(2) and 2.406(2) Å). Moreover, the DFT calculated Ru–P distances in a model complex with much less encumbering phosphines PH_3, i.e. '$[(\eta^2\text{-}H_2)(PH_3)_2RuH_2(\eta^2\text{-}HSiPh_3)]$', are also almost identical (2.370 and 2.367 Å), suggesting that an electronic factor is in operation. Finally, the X-ray and DFT calculated structures of **3** show that the silicon atom is almost equivalently bound to two rather than one hydrogen as the silane σ-complexation picture would imply (1.72(3) and 1.83(3) Å observed versus 1.946 and 2.071 Å calculated values). Distance to the third hydride is much longer (X-ray: 2.40(3) Å, DFT: 2.116 Å). Therefore, **3** contains no more than one classical hydride, the other two are involved in the non-classical bonding with the silyl.



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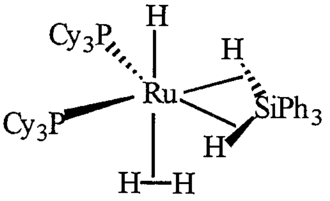

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The unusual structural features of **3** were originally attributed to the presence of weak interactions between the hydride and silicon ligands that were regarded as 'attractive non-bonded interactions'. As the exact nature of these interactions has not been specified, several bonding schemes can be invoked. One possibility is to consider this interaction as *electrostatic attraction* between the positively charged silicon atom and negatively charged hydride. With such a treatment the recognition of separated and weakly interacting unites (σ-complexed silane and hydride), as it was originally suggested, is logical. This view goes back to the suggested electrostatic interaction between the negatively charged hydride with the positively charged dihydrogen ligand identified in calculations of some hydrido–dihydrogen complexes [4]. However, interligand interactions in **3** are much stronger and structural distortions are more pronounced.

Another way to rationalise the interligand bonding in this compound is provided by application of the MO theory and explicitly implies *delocalised covalent interaction*. Consider the silyl and two hydrides as composing one molecular fragment bearing an effective negative charge and having the silicon atom in the centre of an open triangle. Molecular orbitals of such a moiety (Fig. 2, left) are analogous to those of the well-known trihydrogen anion $(H_3)^-$ (Fig. 2, right) [5], apart from the fact that the more electropositive silicon atom will contribute less to the lowest bonding orbital ψ_1. The structure of **3** can be now considered as an adduct (**4**) of $(H_2SiPh_3)^-$ with $[(\eta^2\text{-}H_2)(PCy_3)_2RuH]^+$. Compound **4** has a pseudo-octahedral geometry in which the classical hydride (the best σ-donor) is in a *trans* position with respect to the co-ordinated dihydrogen (the poorest donor), *cis*-phosphines lie in the equatorial positions *trans* to the two remaining co-ordination sites which are occupied by the $(\eta^3\text{-}H_2SiPh_3)^-$ ligand, with the silyl bridging the H–H edge. In such a co-ordination the good σ-donors (two phosphines and apical classical hydride), which also render the strongest *trans* influence, have the weakest σ-donors (dihydrogen and $\{H_2SiPh_3\}^-$) in the respective *trans* positions, and therefore the metal–ligand bonding is optimised. One positive sequence of the formation of $(H_2SiPh_3)^-$ upon interaction of H_{eq} with $HSiPh_3$ is that good σ-donors (phosphine and this equatorial hydride H_{eq}) are no longer in a mutual *trans* position and diminishing $M\text{–}H_{eq}$ interaction with the former hydride is compensated for by the $Si\text{–}H_{eq}$ interaction. Bonding of the $(H_2SiPh_3)^-$ ligand with the metal is provided by the overlap of ψ_1 with the metal centred non-bonding orbital of symmetry a, and ψ_2 finds a perfect match with the metal orbital b, which is phosphine antibonding amended by mixing with the Ru p orbital (Fig. 3). Bonding of the silicon atom to the lateral hydrogens in such a $(H_2SiR_3)^-$ ligand can be regarded as hypervalent (Fig. 2, left).

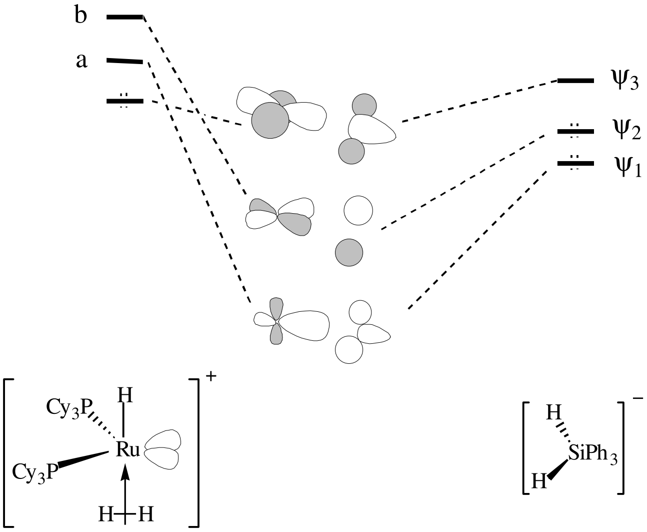


Fig. 3. Fragment MO interaction diagram for the complexation of $\{H_2SiR_3\}^-$ to $[(\eta^2\text{-}H_2)(PCy_3)_2RuH]^+$ to give **4**.

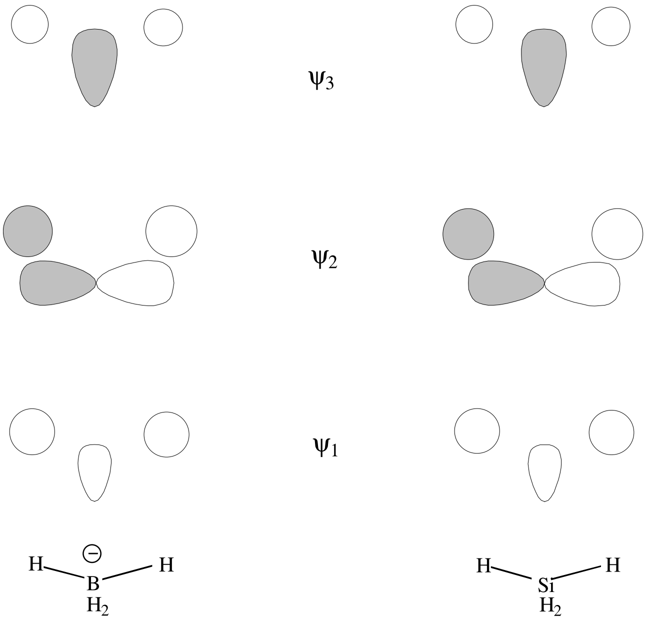


Fig. 4. Molecular orbital compositions of the $\{H_2BH_2\}^-$ (left) and $\{H_2SiH_2\}$ (right) ligands.

Taking into account the diagonal relationship between the silicon and boron it is worth comparing the $(H_2SiR_3)^-$ ligand with the abundant $(\eta^2\text{-}H_2BR_2)^-$ borate ligand. In η^2-borates the analogue of ψ_2 is stabilised considerably by the in-phase mixing of the unoccupied p orbital of boron (Fig. 4, left). For this reason, upon co-ordination of the $(H_2BR_2)^-$ moiety to a metal, back donation from the metal onto ψ_3 cannot break the B–H interaction completely as two bonding orbitals overweigh one antibonding; and the η^2-coordination mode of borates is often observed even in the case of electropositive early transition metals, amenable to strong back donation. If the boron atom bears substituents X with strong p-donor capabilities (OR, NR_2, etc) then the boron p orbital is populated and this stabilising effect of mixing p into ψ_2 is absent. For example, complexes $[Cp_2NbH_2(BC_8H_{14})]$ and $[Cp_2NbH_2\{B(O_2C_6H_4)\}]$ are structurally very different [6]. The first has a long Nb–B bond of 2.40(1) Å and was formulated as a η^2-borate complex $[Cp_2Nb(\eta^2\text{-}H_2BC_8H_{14})]$, while the latter exhibits a short Nb–B bond of 2.292(5) Å and is considered as a d^0 boryl complex without B–H interaction, analogous to classical niobocene dihydridosilyls $[Cp_2NbH_2(SiR_3)]$. Such a 'p-saturated' borate $(H_2BX_2)^-$ is thus analogous to $(H_2SiR_3)^-$. In the latter fragment the orbital ψ_2 is non-bonding with respect to the Si–H interaction (Fig. 2, left) and full back-donation from metal breaks the Si–H bonding completely, resulting in a classical dihydridosilyl system. Therefore, the non-classical $(H_2SiR_3)^-$ ligand can be formed within the co-ordination sphere of a transition metal only under conditions similar to those typical for more usual $(\eta^2\text{-}HSiR_3)$ σ-complexed silanes, i.e. when back-donation from the metal is not strong. Given this analogy and the unusual structure of **3**, one can predict that reaction of the compound $[(\eta^2\text{-}H_2)_2RuH_2(PCy_3)_2]$ with catechole borane, analogous to the reaction with $HSiPh_3$ leading to

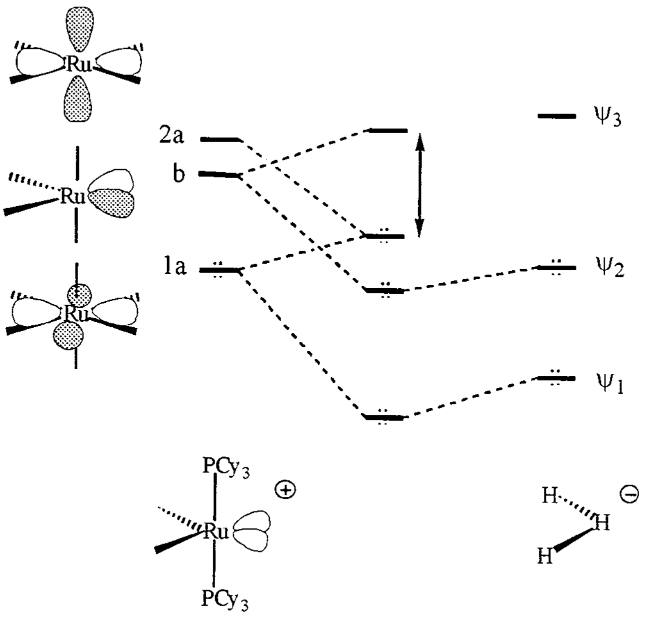
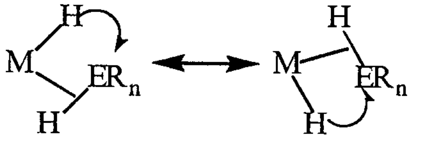


Fig. 5. Fragment MO interaction diagram for the complexation of $\{H_3\}^-$ to a, an octahedral complex of ruthenium. The arrow shows the energy gap between the HOMO and LUMO formed upon interaction of the metal orbital b with ψ_2.

3, should give the η^2-borate complex $[(\eta^2\text{-}H_2)(\eta^2\text{-}H_2Bcat)RuH(PCy_3)_2]$, although usually complete oxidative addition of HBcat to the late transition metal centres occurs affording hydrido(boryl) derivatives [7].

The alternative (and equivalent way) to describe the interligand interactions in **3** is to consider electron density transfer from the M–H bonding orbital onto the (Si–H)* antibonding orbital of a σ-complexed silane (η^2-HSiPh$_3$) (**5**). The idea of the M–H → (H–H)* and M–C → (H–H)* donations goes back to the work of Brintzinger [8] on what we now call σ-bond metathesis reactions [9]. These exchange reactions are frequent in the chemistry of d^0 early transition metal complexes where structures like **5** are believed to be either reactive intermediates or more likely the transition states [9b]. In this case the absence of back-donation from metal onto the $(H_2ER_3)^-$ group (pure 4c–4e interaction) makes the ligand–metal interaction very weak and these compounds are not isolable. Analogous long-range *covalent* interaction M–H → (H–H)* between the hydride and dihydrogen ligands was initially suggested by Eisenstein et al. [10], although later studies favoured electrostatic description in terms of attraction between the positively charged H atom of the dihydrogen moiety and negatively charged hydride [4]. These interactions apparently determine the unusual molecular shape of the chelated bis(η^2-Si–H) complexes of ruthenium of the type $[\{(\eta^2\text{-}HSiR_2)_2X\}RuH_2(PCy_3)_2]$ [11]. Another relevant example can be found in hydride chemistry. Bonding of the trihydrogen ligand $(H_3)^-$ to transition metal complexes was theoretically addressed by Burdett et al. [12] while analysing the co-ordination chemistry of polyhydrogens. (H_3) complexes were postulated as intermediates in the exchange reactions of hydrides with dihydrogen ligands and in polyhydride systems [2a,12,13], but thorough theoretical investigations showed that these species are better described as transition states [14]. Also, the co-ordinated $(H_3)^-$ ligand was initially postulated to account for the unusual NMR coupling (now viewed as quantum mechanical exchange coupling) in some transition metal trihydrides [15] but later studies ruled out this possibility [16]. However, in light of the recent results achieved by the research group of Sabo-Etiennie and Chaudret the existence of the co-ordinated $(H_3)^-$ should be revived within a new context. Thus, in addition to the (H_2SiR_3) complex **4** discussed above, this group has reported recently a remarkable ruthenium compound $[(PCy_3)_2(\text{ph–py})Ru(\eta^2\text{-}H_2)(H)]$ (ph–py-2-pyridinylphenyl) (**6**) presenting the first example of an exchange coupling between a hydride and dihydrogen ligand [17]. The hydride and dihydrogen ligands are in exchange with the barrier of 39.8 kJ mol^{-1}. The authors suggested that "a weak interaction between the hydride and the co-ordinated dihydrogen molecule" (like the hydride–silane interaction in **5** and the hydride–dihydrogen interaction in the above-mentioned work of Eisenstein [10]) could explain these observations. The crystal structure of **6** provides a clue in understanding this behaviour. Like **4**, **6** is pseudo-octahedral, with phosphines occupying the apical cites and hydride and dihydrogen ligands lying in the equatorial plane *trans* to the ph–py ligand (H *trans* to the nitrogen atom of pyridine and (H_2) *trans* to the carbon atom of phenyl, i.e. the part of the ph–py ligand with the strongest *trans* influence). Noteworthy is that the hydride–dihydrogen distance (1.34(7) Å) is quite comparable with the H–H bond length within the (H_2) ligand (1.09(4) Å). When thinking about an open form of the trihydrogen ligand $(H_3)^-$ one should take into account that this moiety should *not necessarily be symmetrical* with the two H–H distances equal. In fact upon co-ordination to a metal, it can be distorted by the second-order Jahn–Teller (SOJT) effect [18]. Fig. 5 shows how this can happen. $(H_3)^-$ binds to an octahedral complex by interacting with the appropriate metal based orbital, labelled assuming a local C_2 symmetry. Orbitals 1a and ψ_1 undergo 4e–4c interaction that would be repulsive unless stabilised by mixing in of the upper orbital 2a. If interaction of the metal orbital b with ψ_2 is not effective then the energy gap (shown by the arrow) between the HOMO (of the a symmetry) and LUMO (of the b symmetry) can be small. This leads to an interaction of these two levels with the B vibrational mode creating an SOJT distortion of the ligand. In the extreme case of a strong interaction, the $(H_3)^-$ unit separates into isolated hydrido and dihydrogen ligands. The absence of the C_2 symmetry in a real compound like **6** does not affect these arguments much, as going from the C_2 case to **6** does not change the topological properties of the orbitals, hence the underlying electronic reasons for the SOJT distortion are retained. SOJT in **6** creates an asymmetric double well for the movement of the central hydrogen between two lateral cites. This movement (classical or tunnelling) coupled with the rotation (again classical or tunnelling) of the dihydrogen moieties, formed at both sides of the molecule, equalise all three hydrogen atoms at high temperature, as is observed in the ^{1}H-NMR spectrum of **6**. At low temperature, when decoalescence occurs, tunnelling probably prevails and 'appearing' coupling between two different proton signals is observed exactly as is the case in other hydride systems with quantum-mechanical exchange couplings [16]. Again, as for the silicon compound **4** interligand bonding in **6** can be considered alternatively in terms of electron density transfer from the M–H bond orbital onto the (H–H)* antibonding orbital of the co-ordinated dihydrogen [10]. It is a question of convenience whether to regard the compound as having SOJT distorted $(H_3)^-$ ligand or to think about it as a complex with interacting hydride and (H_2) ligands. Both bonding schemes are in fact equivalent but when this interaction is weak and a distinct dihydrogen ligand can be recognised clearly, the latter approach is more visual than the trihydrogen formulation shown in Fig. 5.



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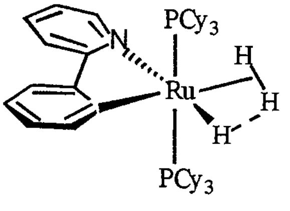

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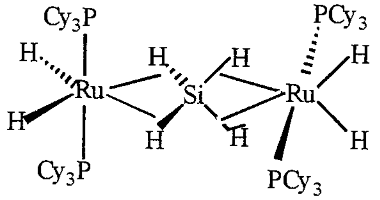
Analogous SOJT distortion may be observed for the $(H_2SiR_3)^-$ ligand too, but this ligand is expected to be a stronger π-acceptor than trihydrogen (as long as σ-complexed silane is a stronger π-acceptor than dihydrogen [19]) and therefore a stronger back-donation from the metal and a weaker SOJT distortion should occur. Indeed, in the compound **4**, related to **6**, the silicon atom interacts almost equivalently with both hydrogens. The recognition of a $(H_2SiR_3)^-$ ligand within the co-ordination sphere of ruthenium in **4** does not rule out the possibility of an additional weak interaction between the silicon atom and genuine hydride originally suggested by the authors [3]. This interaction may be either electrostatic or covalent (for example, $H \rightarrow (H_2SiR_3)^*$ donation similar to the donations suggested by Eisenstein et al.) as discussed above, but according to all data is weaker than bonding to the two other hydrogens.

The proposed $(H_2SiR_3)^-$ ligand is neither new nor recent. For the first time this ligand was postulated in 1990 by Crabtree and Ephritikhine et al. to explain the properties of rhenium polyhydride silyl derivative $[ReH_6(SiPh_3)(PPh_3)_2]$ [20]. Several structural features of this compound indirectly supported the presence of interligand interactions; the observation of short Si–H contacts (1.76 and 1.96 Å) and decreased fluxionality, usual for seven-co-ordinate and polyhydride complexes, were consistent with this view. Analogous suggestion was made for the related compound $[ReH_2(SiPh_3)(CO)(PPh_3)_3]$ [21]; however, in both cases the NMR data did not support this idea as no Si–H coupling was observed [21]. Furthermore, a classical structure was observed for the compound $[ReH_6(SiEt_3)(PPh_3)_2]$ by neutron diffraction [22]. The story took an unexpected turn when Lin and Hall calculated at the RHF level of theory that model complexes $[ReH_2(SiH_3)(CO)(PH_3)_3]$ and $[ReH_6(SiH_3)(PH_3)_2]$ can have interligand Si–H interactions [23]. Optimised hydride positions resulted in relatively small Si–H contacts (2.1–2.3 Å) and Laplacian analysis of electron density was also suggestive of interligand interactions. However, no rationalisations of the nature of these interactions were drawn.

Related bonding situation occurs in the unique bimetallic ruthenium complex $[\{(PCy)_2RuH_2\}_2(\eta^3,\eta^3,\mu\text{-}SiH_4)]$ (**7**) also recently reported by the group of Chaudret and Sabo-Etienne [24]. This compound has a tetra(σ-Si–H)-complexed SiH_4 ligand occupying a bridging position between two ruthenium atoms and having two pairs of Si–H bonds σ-complexed to each of them. Two Si–H bonds and Ru lie in one plane as is observed in **4**. In further comparison of **7** with **4**, one should take into account that η^3-SiH_4 ligand is neutral, and therefore on going from the structural type **4** to the type **7** one has to replace the (η^2-H_2) ligand with a hydride. In **7** each Ru centre is pseudo-octahedral, with the (η^3-SiH_4) ligand occupying one of the edges, analogously to what we observed in **4**. An important difference is that in the absence of the (η^2-H_2) ligand the two hydrides, having the strongest *trans* influence, lie *trans* to the (η^3-SiH_4) ligand whereas phosphines occupy the apical cites. Four electrons of the two Si–H bonds form an orbital pattern (Fig. 4, right) which to a great extent resembles that shown in Fig. 2. The only amendment to be made is to add a vacant p orbital on Si to the molecular orbital ψ_2, since in SiH_4 the silicon atom has four substituents in contrast to five in $(H_2SiPh_3)^-$ (Fig. 4, right). This bonding scheme is thus analogous to the one in borates $(\eta^2\text{-}H_2BR_2)^-$ discussed above.



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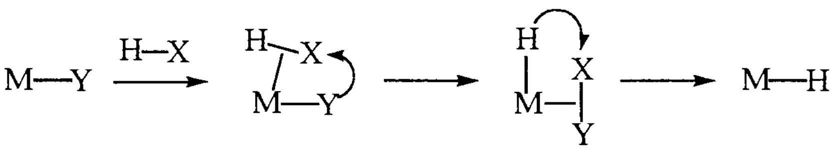
In light of these results achieved by the research group of Sabo-Etiennie and Chaudret the existence of other $(H_2SiR_3)^-$ and $(H_3)^-$ complexes seems plausible. Apart from the theoretical interest these compounds are important as models of the heterolytic splitting of dihydrogen and silanes on the M–Y bonds (Eq. (1)).

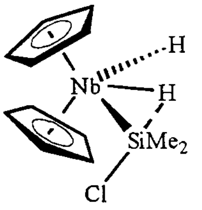


(1)

X = H, SiR$_3$

3. Interligand hypervalent interaction (IHI) in silylhydrides of niobocenes

As has been mentioned already, the dihydridosilyl derivatives of Group 5 metalocenes are different from **4** in that there is an effective back-donation from the high lying metal orbital a_1 onto the antibonding orbital ψ_3 of $(H_2SiR_3)^-$, thus breaking the Si–H interactions. With the R groups being alkyl and/or aryls only, the resultant complexes are classical monosilyl dihydrides without any significant Si–H interaction [25]. However, in case there is a good leaving group X at the silicon centre another type of interligand interaction becomes possible (see **8**) [26]. This stems from the electron density transfer from the electron-rich M–H bond orbital onto the (Si–X)* antibonding orbital (Fig. 6). An interligand hypervalent interaction (IHI) emerges and the silicon atom adopts a pseudo-trigonal bipyramidal environment, in which the hydride and substituent X occupy the apical cites. Population of the (Si–X)* renders the Si–X bond longer, while more silicon s character goes to bonding with the most electropositive equatorial substituent (in this case ML_n), thus making the M–Si bond shorter. Short interligand Si–H contacts of 1.80–2.05 Å are also observed. NMR relaxation [26d], neutron diffraction [26d] and DFT calculation [26c] revealed that the interacting metal–hydride bond elongates which, first, is a result of electron density depletion and, second, allows a better overlap of the M–H bond orbital with the (Si–X)* antibonding orbital. In the monosilyl systems like $[Cp_2Nb(SiMe_2Cl)H_2]$ IHI can be classified as 3c–4e interligand interaction (M)H → (Si–Cl)* in the co-ordination sphere of a transition metal. Another type of IHI is possible in the mono(hydride) bis(silyl) derivatives in which the hydride occupies a bridging position between two silyls and interacts with both of them (**9**). This IHI is a 5c–6e interligand interaction in the co-ordination sphere of a transition metal, the structural sequences and environment of each silicon atom are the same as in the previous case but structural distortions are less pronounced.



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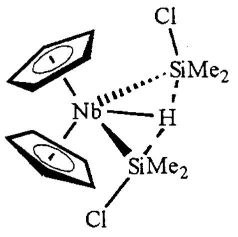
3c-4e



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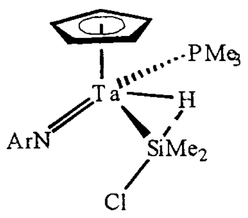
5c-6e



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3c-4e

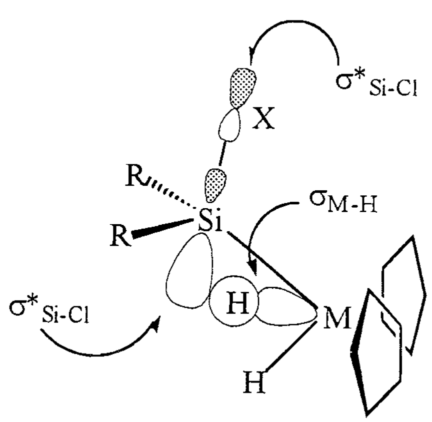


Fig. 6. M–H bond donation onto the (Si–Cl)* antibonding orbital upon formation of 3c–4e IHI in **8**.

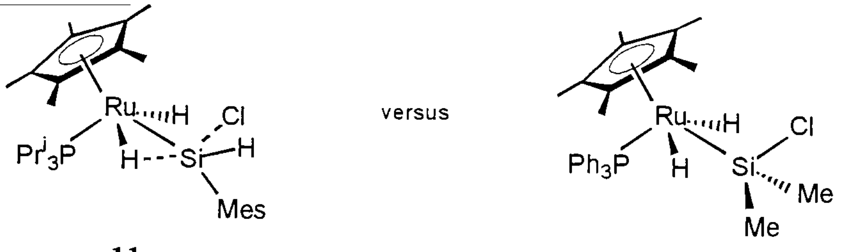
Lin and Fan calculated models of complexes **8** and **9** (H atoms in place of Me) at the MP2 level of theory and did not observe a bond path between the silyl and hydride ligands in the Laplacian maps of the resultant electron density [27]. Based on this observation, they suggested that "this type of metallocene disilyl complex is best regarded as a classical silyl–hydrido–silyl complex, with significant polarising interactions of the silyl ligands for the central hydride" [28]. However, independent calculation of the same systems at the DFT level does show a bond path for the compound **8** but not for **9** [26c]. In the latter case the interligand bonding is more delocalised and the bond path must be severely curved, eventually collapsing into isolated M–Si and M–H bonds. This observation suggests that care should be taken in the interpretation of Laplacian analysis of a compound with relatively weak interligand interactions because the result can depend crucially on the quality of electron density produced by calculations. Moreover, analysis [26c] of structural trends in the calculations of Fan and Lin is more in accordance with the presence *covalent interaction* between the silyl and hydride ligands, which is further supported by the experimental results [26d,26e].

Finally, it should be mentioned that interligand hypervalent interactions in **8** and **9** should be differentiated from the hydrogen–silicon–hydrogen hypervalency observed in **3**. While the $(H_2SiR_3)^-$ ligand does include six-co-ordinate silicon atom with hydrogens occupying the apical sites, both of these apical substituents are involved in bonding with the metal. In contrast, in **8** and **9** only one apical group (the hydride) has a bond to the metal. Moreover, **8** and **9** are the products of *complete* oxidative addition of silanes and the silicon atom is bound to the metal via a strong single bond, whereas in **3** bonding of $SiPh_3$ to Ru is delocalised and electron deficient.

4. Other examples of IHI

The first 3c–4e IHI between one silyl and one hydride in the non-metallocene environment was found in the tantalum complex **10**, which is an isolobal analogue [29] of the niobocenes **4** and **5** [30]. This time the NMR properties of the metal allow the Si–H coupling constant to be determined (niobium has a nuclear spin of 9/2 with large Larmor frequency, which leads to a broadening of signals thus hiding their splitting for **8** and **9**). In **10** the Si–H coupling constant of 33.3 Hz was measured. This value is noticeably less than the usual value observed in the silane σ-complexes [2b] (40–70 Hz) but still shows that a significant silicon s character participates in bonding with the hydride. Were the silicon in an ideal TBP environment, the bonding to a hydride would be by pure silicon p orbital and the direct coupling due to the Fermi contact would be zero [26c].

Another example of IHI can be found examining the structure of the ruthenium complex $[\mathrm{Cp^*(P^iPr_3)RuH_2(SiHMesCl)}]$ [31] (**11**) reported by Tilley et al. [32]. This compound also has the Cl and one of the hydrides in mutual *trans* positions relatively to silyl. The long Si–Cl (2.170(4) Å) and surprisingly short Ru–Si (2.302(3) Å) bonds are consistent with the IHI. The latter bond is even shorter than that one in the related ruthenium silylene derivative $[\mathrm{Cp^*(PMe_3)_2Ru(SiPh_2^*MeCN)}]^+$ (2.328 (2) Å) [33]. Because the IHI directly depends on the basicity of the hydride, and the latter depends on the electron-richness of the metal effected by the ligands, the interligand interaction in **11** can be easily tuned. The simplest way to achieve this is to change the basicity of the phosphine. Indeed, the crystal structure of the related triphenylphosphine complex $[\mathrm{Cp^*(PPh_3)RuH_2(SiMe_2Cl)}]$ shows it to be the classical dihydridosilyl [32].



11

3c-4e IHI

classical

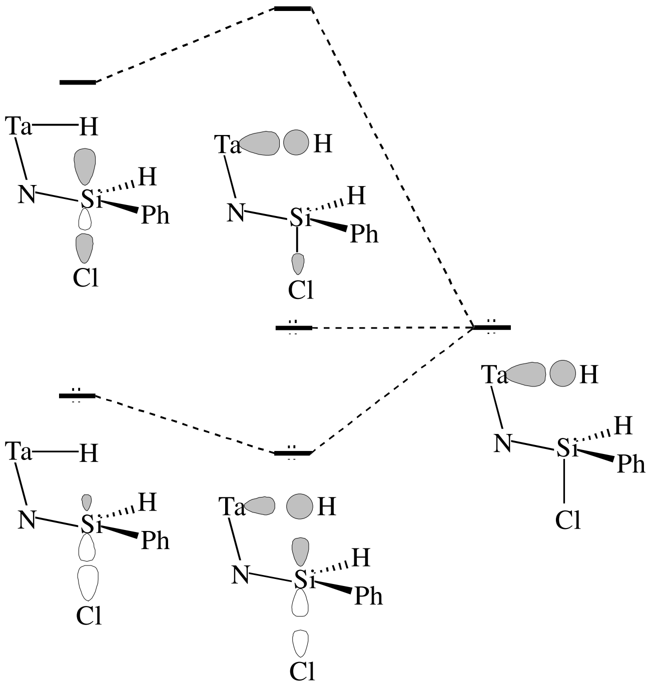
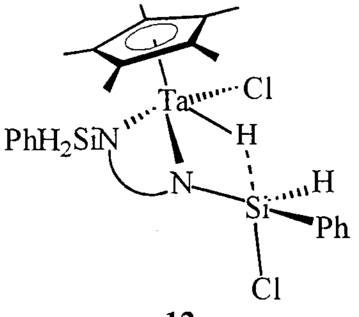


Fig. 7. MO description of the interligand bonding in **12**.

Hypervalent interligand interaction between a hydride and β-positioned silicon atom of a silyl substituted amide was reported by Gountchev and Tilley for the tantalum complex [Cp*Ta(η^2-PhSiH$_2$N(C$_{14}$H$_{12}$)-NSiHClPh)(H)(Cl)] (**12**) [34]. The existence of Si–H interaction was derived from the elongation of the Si–Cl bond lying *trans* to the hydride, low Ta–H stretching frequency and large value (6 Hz) for the formally $^4J_{H-H}$ coupling constant between the hydride and silicon-bound hydrogen in the ^{1}H-NMR spectrum. This kind of non-classical interligand bonding can be called β-IHI. The authors recognised this by describing the Si–H bonding in terms of resonance structures, one of which included a hypervalent five-coordinate Si centre. Alternative MO description, typical for hypervalent compounds and analogous to the one for **8** [26c], can be easily elaborated upon (Fig. 7).



12

A surprising case of interligand interaction of one silyl with three hydrides was discovered by Hübler and Roper et al. [35] for the Ru and Os complexes [(PPh$_3$)$_3$M(SiPyr$_3$)H$_3$] (**13**) bearing three electron-withdrawing pyrrolyl substituents at silicon. A very high Si–H coupling constant of 47.4 Hz was observed in the ^{29}Si-NMR spectra of the Ru compound (29.2 Hz for Os). Low-temperature NMR experiment revealed no temperature dependence of the spectrum and absence of fluxionality down to − 85°C. It appears unlikely that a fast equilibrium between two classical hydrides and one η^2-silane ligand, equalising three hydrides on the NMR time scale, could exist at such a low temperature. Although hydride positions could not be established from the X-ray structure of the Os complex, DFT calculations showed these to be *trans* to each phosphine ligand and *trans* to each Si–N bond. NBO analysis revealed two types of interligand interactions [35]. The first one was the donation of electron density from the M–H bonding orbital onto the (Si–M)* antibonding orbital, whereas the second consisted in the donation of electron density from three M–H bonding orbitals onto three *trans* Si–N antibonding orbitals. The latter interaction is in sense an IHI of the type H–Si–N that thus can be called a triple IHI. Calculation of a series of model compounds having the H, NH$_2$ and Pyr substituents at silicon (all substituents of the same sort) showed that both types of interligand interactions increase on going from H to Pyr, i.e. in the order of raising electronegativity of the substituent [35]. Given the energy of both donations provided by NBO, the authors considered the first donation, M–H → (Si–M)*, as the main one. However, several observations contradict this conclusion. Were the M–H → (Si–M)* donation significant, population of the (Si–M)* orbital would cause lengthening of the Si–M bond. In contrast, the authors pointed out that the M–Si bond is very short whereas the Si–N bond is long, both features being characteristic for IHI. Secondly, the calculations clearly show that the *trans* positions of the hydrides and pyrrolyl ligands are crucial for the Si–H interaction to occur and that rotation of the silyl around the Si–M axis is a very unfavourable process. This points against the predominance of the M–H → (Si–M)* donation because, due to the cylindrical symmetry of the M–Si bond, such a donation should be indifferent to rotation. It is noteworthy that rotation causes lengthening of the Os–Si bond, consistent with the loss of three IHI's M–H → (Si–N)*. From the energetic point of view the M–H → (Si–M)* donation was very strong for all model compounds calculated, both classical and non-classical. Taking into account that the idea of NBO is to ascribe the best possible Lewis structure to a compound and then consider the rest of electron density as different hyperconjugative contributions, this appearing M–H → (Si–M)* donation could be, in fact, an artefact, intrinsic for NBO, thus reflecting the inability of NBO to consider the hydride and silyl as totally independent units. If this is the case, then significant back-donation

Si–M → (M–H)* must also be observed (these data were not reported) as was found in the calculations of classical and non-classical (with IHI) niobocene silylhydrides [26c].

Another way to understand the interligand bonding in **13** is to consider the interaction of the complex $[(R_3P)_3M]^{2+}$ with the fragment $\{H_3SiR_3\}^{2-}$. The MO's of the latter can be easily obtained by mixing MO's of the closed form of trihydrogen anion $\{H_3\}^-$ with the MO of the silyl anion$\{SiR_3\}^-$ (Fig. 8). Since the silyl hydride orbital lies higher in energy than the combination of s orbitals of hydrogens (at large H–H distances three levels of $\{H_3\}^-$ do not differ much in energy from the 1s orbital of the hydrogen atom), clear orbital stabilisation can be seen. Further stabilisation of this double-charged unit occurs upon co-ordination to the cationic osmium (ruthenium) complex. The Si–H interaction in **13** will be retained provided the back-donation from metal onto the $\{H_3–Si\}^*$ antibonding orbital is not complete. This description implies that in the resultant neutral compound the oxidation state of the metal is intermediate between 2 and 4 (classical trihydridosilyl structure would implied OS 4) and the putative $\{\eta^4\text{-}H_3SiR_3\}^{2-}$ ligand is a relative of the $\{\eta^2\text{-}HSiR_3\}$ and $\{\eta^3\text{-}H_2SiR_3\}^-$ ligands discussed above. Since the silicon atom in $\{H_3SiR_3\}^{2-}$ is hypervalent the importance of *trans* disposition of the substituents at Si becomes clear.

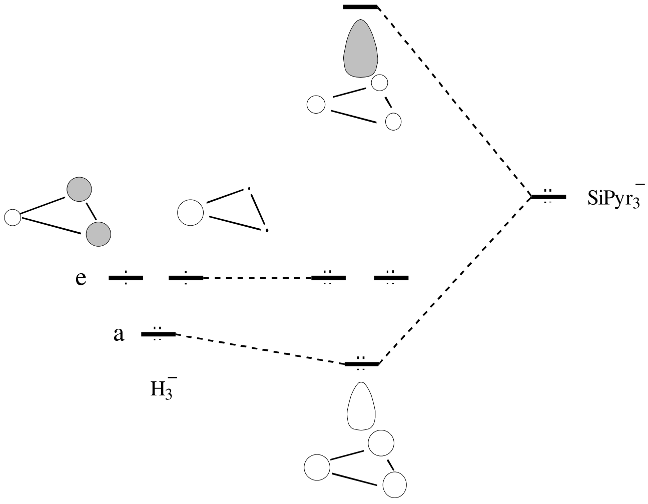
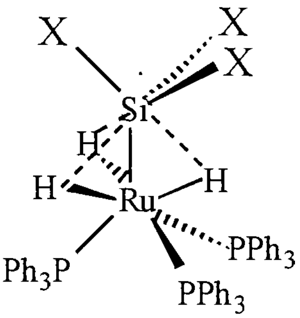


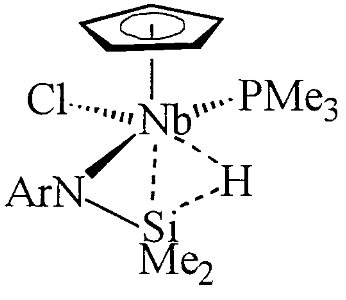
Fig. 8. Formation of $\{H_3SiR_3\}^{2-}$ upon interaction of $\{H_3\}^-$ with $\{SiR_3\}^-$.



13

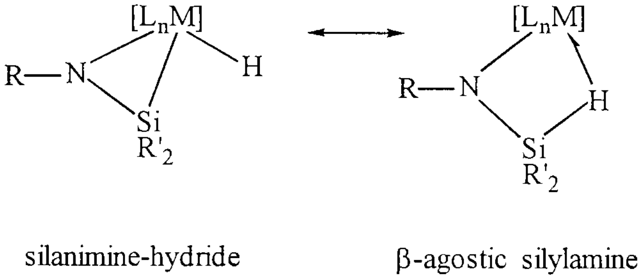
5. New Si–H → M agostic interactions

In mononuclear complexes Si–H → M agostic interactions have become available only recently and are known now only for the β- [30,36–38] and δ-positioned [39] silicon atoms; bonding in the latter case does not differ much from that in the silane σ-complexes. For the β-Si–H → M agostic interactions carbon [36], phosphorus [37] and nitrogen [30,38] bridges are known. Until very recently, the β-Si–H → M agostic interactions in the silylated amide derivatives were observed only for the d^0 species. In these compounds, where no back-donation is possible and the Si–H bond is virtually unstretched, the existence of the Si–H-to-metal complexation was inferred primarily from the spectroscopic data. In the IR spectra of the d^0 agostic silylamides the Si–H stretching bands are usually observed about 1950 cm^{-1} and in few instances down to 1800 cm^{-1}, approximately 150–300 cm^{-1} closer to the low-frequency end from the usual bands of uncoordinated Si–H bonds. In the ^{1}H-NMR spectra the Si–H protons exhibit upfield shifts and the Si–H couplings are reduced down to about 110 Hz (normal range for the $^1J_{Si–H}$ constants is 160–200 Hz) [38b]. The most impressive structural sequence of this Si–H → M agostic interaction is the diminished Si–N–M bond angle, which can be as low as 92.1(1)° in the Sm complex [38d].



14

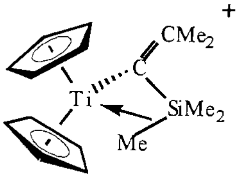
In the d^0 systems the silicon-bound hydrogen, by no means, can be considered as a hydride, and the β-Si–H → M agostic interaction cannot be classified as an interligand. It is, however, of interest as a limiting form in considering interligand interactions in the d^n ($n \geq 2$) systems. The first example of β-Si–H → M agostic interaction in a d^n ($n \geq 2$) silylamide has been recently found for the formally d^2 niobium complex $[Cp\{\eta^3\text{-}(C_6H_3^iPr_2)N–SiMe_2–H\}Nb(Cl)(PMe_3)]$ (**14**) [30]. In this case a significant back-donation onto the (Si–H)* antibonding orbital occurs, which results in a noticeable rupture of the Si–H interaction. In **14** the Si–H stretching frequency exhibits further bathochromic shift to 1620 cm^{-1} that is close to the typical region for the ν(Nb–H) in niobocene hydrides (1650–1750 cm^{-1}). The X-ray refined position of the hydride gave the Nb–H and Si–H distances of 1.91(5) and 1.52(5) Å, respectively, which is in good accordance with the DFT calculated structure. The first value is longer then the typical Nb–H bond (range ca. 1.60–1.81 Å), whereas the Si–H distance is noticeably longer than the previously reported free or d^0 β-agostic Si–H bonds (range ca. 1.42–1.50 Å). Interligand bonding in **14** can be described as a resonance between the 3c–2e agostic interaction (Si–H donation only, A) and classical silanimine–hydride structure (with complete back-donation, B). The diminished (in comparison with the d^0 cases) $^1J_{Si-H}$ constant of 96.6 Hz explicitly shows that bonding situation in **14** lies in between these extremes. Finally, it is interesting to note that **14** is produced in a reaction analogous to that one leading to the non-classical tantalum complex **10**, i.e. by the interaction of $[Cp(ArN)M(PMe_3)_2]$ with $HSiMe_2Cl$. This surprising difference in reactivity is apparently caused by the greater propensity of tantalum to exist in the oxidation state 5, in which silane is completely added to the metal and interaction of the silyl with hydride occurs by a hypervalent mode. In contrast, the oxidation state of niobium in **14** is intermediate between 4 and 5.



14A **14B**

6. C–Si → M agostic interactions

The non-classical interligand interactions of the silicon based ligands are not restricted to hydrides only. The neutron diffraction study and DFT calculations of the formally γ-agostic C–H complexes $[Cp^*(C_6H_3^tBu_2O)YCH(SiMe_3)_2]$ and $[Cp^*Ln\{CH(SiMe_3)_2\}_2]$ revealed that the metal centre interacts mainly with the Si_β–C_γ bond rather than with the γ-C–H bonds [40]. An analogous interaction was observed in the cationic complexes $[Cp_2Ti(\eta^3\text{-}C(CMe_2)SiMe_2\text{–}Me)]^+$ (**15**) [41] and its *ansa*-bridged zirconium relative $[Cp'_2Zr(\eta^3\text{-}C(CMe_2)SiMe_2\text{–}Me)]^+$ (Cp'_2- 1,2-bis(indenyl)ethylene) [42]. Recent re-investigation into the nature of β-agostic C–H → M interactions suggests that this can be a general phenomenon since these interactions were found to have mainly a β-C–M bonding character rather than the C–H-to-metal donations [43]. Presumably the same happens for the 'β-agostic $SiC_\beta\cdots M$ interaction' recently reported by Jordan et al. for a zirconocene cationic complex $[Cp_2Zr(THF)(\eta^2\text{-}CH_2CH_2SiMe_3)]^+$ (**16**) [44]. In this system the $SiMe_3$ group lies *trans* to the metal and has no direct Si–M contact; therefore this interaction cannot be classified as an interligand.



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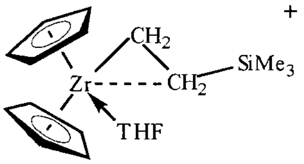
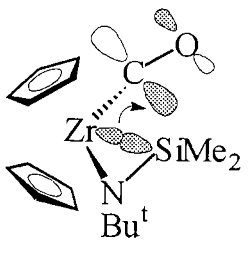


16

7. Interligand hypervalent interactions in non-hydride compounds

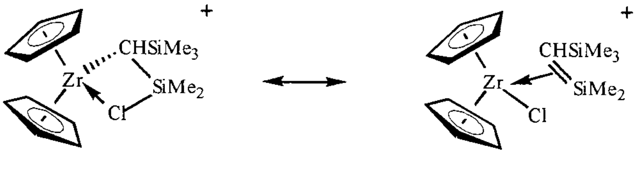
An important case of interligand interaction was discovered by Berry et al. These authors argued that X-ray structure determination and ZINDO calculation of the silanimine carbonyl complex $[Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(CO)]$ (**17**) are consistent with the presence of a long-range Si···C (C in the co-ordinated carbonyl) interaction [45]. Such an interaction can be viewed as stemming from the electron density transfer from the high lying M–Si bonding orbital onto the (C–O)* antibonding orbital. This suggestion helps to explain the observation of a low C–O stretching frequency (1797 cm^{-1}) for a formally d^0 complex and increased formally $^2J_{Si-C}$ coupling constant of 24.1 Hz. This interligand interaction could be considered as an initial stage of the silicon migration onto the co-ordinated carbonyl ligand. Indeed, on heating **17** in the presence of phosphine the Si–C bond coupling occurs. A number of other silicon atom migrations were observed in the reactions of the related compound $[Cp_2Zr(\eta^2\text{-}Me_2Si{=}N^tBu)(PMe_3)]$ with unsaturated molecules (ketones, alkenes, alkines, CO_2, CS_2). It might be postulated that analogous (M–Si) → (C–X)* (X = C, O, S) interactions occur during the intermediate stages of these reactions [46].



17

Very similar Si–C interligand bonding was identified in the tantalum silyl carbonyl complex $[Cp^*(2,6\text{-}C_6H_3^iPr_2\text{-}N)Ta(CO)(Si(SiMe_3)(H)]$ based on the low ν_{CO} stretching frequency, acute Si–Ta–C bond angles and elongated Ta–Si bonds [47]. Again, silyl migration from tantalum onto carbonyl ligand was observed as an extension of this non-classical interligand interaction. These findings are very important because they shed more light on the nature of other silyl-to-carbonyl migrations [48–53].

Unique Si–Cl interactions were found in the *ansa*-indenyl complex of zirconium $[C_2H_4(indenyl)_2Zr(\eta^2\text{-}CH(SiMe_3)SiMe_2\text{–}Cl)]^+$ (**18**) [54]. Bonding of the chlorine to metal and silicon was described by a resonance of two forms. The first one (**18A**) considers co-ordination of chlorine to metal as the Cl lone pair donation, whereas bonding to silicon is by a single bond. In the second form (**18B**) the Si–Cl bond is split and the silicon ligand is viewed as a co-ordinated silene. This description implies that this system can be rationalised as having non-classical interligand interaction of chlorine with the silene. In line with the previous discussion, this interaction can be considered as a donation of the Cl lone pair onto the Si–C antibonding orbital (no metal back donation in this d^0 system is possible). This bonding mode is reminiscent to what we observed above for **3** and co-ordinated trihydrogen. It is interesting that **18** was formed by the Si–C bond activation in the presumably $Si_\beta\text{–}C_\gamma$ agostic complex $[Cp'_2Zr(\eta^3\text{-}CH(SiMe_3)SiMe_2\text{–}Me)]^+$, having Me in the place of chlorine, and resembling the titanium complex **15** mentioned above. Similar to **18**, this agostic $C_\gamma\text{–}Si_\beta\cdots M$ bonding can be considered as a donation of electron density from the Zr–C bond onto the Si–C antibonding orbital of the co-ordinated silene.



18A **18B**

8. Summary

Study of interligand interactions is an emerging field of research that contributes a lot to our understanding of transition metal mediated transformations of organic molecules and provides further development to the theory of chemical bond. The theory of σ-complexation allowed us to gain an incredibly useful insight into the nature of oxidative addition/reductive elimination reactions. Further examples of electron deficient σ-complexations and agostic interactions appear in the literature (complex **14**, for instance). However, there is a growing series of non-classical structures that cannot be satisfactorily described as σ-complexes or agostic systems. Some of them, like Ru complex **3**, are electron deficient systems, in which interligand Si–H interaction can be viewed as bonding in the unusual $(\eta^3\text{-}H_2SiR_3)^-$ ligand. Others appear to be electron-rich systems with different modes of IHI. In the chemistry of silylhydrides IHI was detected in the form of 3c–4e interaction M–H → Si–X (in **8**, **10**–**12**), 5c–6e interaction X–Si ← (M)H → Si–X (**9**) and possibly triple 3c–4e interaction $M(\text{–}H \rightarrow Si\text{–}X)_3$ in complex **13**. A common feature of these interactions is the electron density transfer from the basic M–H bond onto the silicon based antibonding orbital (Si–X)* where X is a good leaving group. Such a transfer can be viewed as intramolecular complexation of a Lewis base (σ-base) to a Lewis acid (σ*-acid). In a sense, analogous situation happens in hydride-free compounds like **17**. Here electron density is transferred from an electron rich M–Si bond onto a ligand based antibonding orbital of an unsaturated moiety (e.g. carbonyl). It can be foreseen that at least some types of these interactions should not be restricted to silicon based ligands only and, in principle, could be found for other main-group element substituted complexes. In silyl chemistry the most likely next candidate to be found is a compound having IHI of two hydrides with one silicon atom. A complex with three silyls interacting with one hydride ('inverted' analogue of compound **13**) is also quite feasible.

Interligand hypervalent interactions considered in this article have a direct relevance to the migratory insertion reaction, and the link between some non-classical interactions and insertion reactions has been established.

Acknowledgements

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