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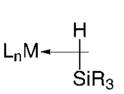
Going Beyond σ Complexation: Nonclassical Interligand Interactions of Silyl Groups with Two and More Hydrides[**]

Georgii I. Nikonov[*]



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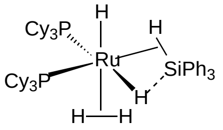
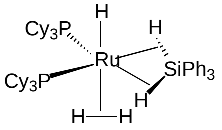
Transition metal silane σ complexes (**1**) are a well-documented class of nonclassical compounds in which the Si–H bond is considered to be at an intermediate stage in the oxidative addition to a metal center and a direct interaction between the silyl and hydride ligands is present.[1] The question as to whether the silyl ligand can interact simultaneously with more than one hydride has recently received a positive answer.

In 1990 the possibility that a silyl group could interact simultaneously with two hydride ligands was proposed for the first time by Crabtree and colleagues to describe the structure of the compound $[(PPh_3)_2ReH_6(SiPh_3)]$.[2] The presence of a $[H_2SiPh_3]^-$ ligand was postulated but the experimental evidence was scarce. Further progress in the identification of multicenter Si–H interactions came from the studies of other polyhydride diphosphane systems. The ruthenium fragment $[(PCy_3)_2RuH_2]$ (Cy = cyclohexyl) was shown to stabilize a variety of dihydrogen and silane σ complexes,[3] a useful entry into this chemistry being Chaudret's bis(dihydrogen) complex $[(PCy_3)_2Ru(H_2)_2H_2]$ (**2**).[4] The research group of Sabo-Etiennie and Chaudret showed that a reaction of **2** with $HSiPh_3$ affords the compound $[(\eta^2\text{-}H_2)(PCy_3)_2RuH_2(\eta^2\text{-}HSiPh_3)]$ (**3**)[5] which was originally formulated as a mixed dihydrogen and silane σ complex. However, its surprising structural features suggest an unusual type of interligand interaction. Firstly, in this complex the very bulky phosphane ligands unexpectedly occupy *cis* rather than the anticipated *trans* positions. Secondly, although the phosphanes lie *trans* to two supposedly different ligands, namely η^2-$HSiPh_3$ and hydride, the observed Ru–P bond lengths do not differ by very much (2.392(2) and 2.406(2) Å). Moreover, density functional theory (DFT) calculations on a model complex with much less sterically demanding phosphanes PH_3 ("$[(\eta^2\text{-}H_2)(PH_3)_2RuH_2(\eta^2\text{-}HSiPh_3)]$") show that the Ru–P bond lengths are also almost identical (2.370 and 2.367 Å), which suggests that an electronic factor is in operation.[5] Finally, the X-ray and DFT-calculated structures of **3** show that the silicon atom is bound almost equivalently to two hydride units (1.72(3) and 1.83(3) Å observed versus 1.946 and 2.071 Å calculated values) rather than one hydride as the silane σ-complexation model would imply; the 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 nonclassical bonding to the silyl.



3

versus



4

The unusual structural features of **3** were originally attributed to weak bonding between the hydride and silicon ligands which was regarded as "attractive nonbonded interactions".[5] While the nature of these interactions was not clearly defined, several bonding schemes were possible. For example, this unusual bonding between the silyl and hydride groups can be described in terms of an interaction between the fragment $[(PCy_3)_2RuH_2]^+$ and the dihydrosilyl ion $[H_2SiPh_3]^-$ (Figure 1), which leads to the nonclassical complex $[(\eta^2\text{-}H_2)(PCy_3)_2RuH(\eta^3\text{-}H_2SiPh_3)]$ (**4**), rather than the bonding model originally proposed in **3**. The molecular levels of $[H_2SiPh_3]^-$, analogous to the familiar $[H_3]^-$ ion, are shown on the right of Figure 1. Complexation of the $[H_2SiPh_3]^-$ ion to a metal center occurs by electron-density transfer from the orbitals ψ_1 and ψ_2 to metal-centered nonbonding orbitals of symmetry a and b, and back donation of the metal lone pair into ψ_3. This bonding scheme strongly resembles synergic

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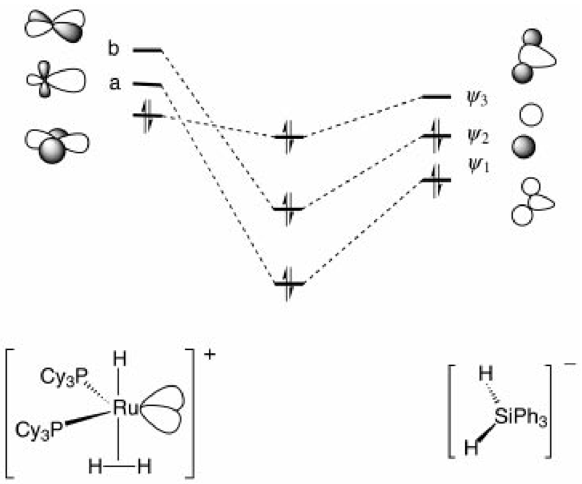
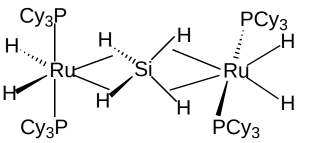


Figure 1. Qualitative fragment MO interaction diagram for the complexation of $[H_2SiR_3]^-$ to $[(\eta^2\text{-}H_2)(PCy_3)_2RuH]^+$ to give **4**.

donation/back-donation interactions responsible for the complexation of σ bonds to metals and clearly implies bonding between the silyl and hydrides. Formation of the $[H_2SiPh_3]^-$ ligand within the ruthenium coordination sphere allows **4** to avoid an unfavorable situation when ligands with a strong *trans* influence are in mutually *trans* positions. In **4** the hydride, the ligand with the strongest *trans* influence, is *trans* to the weakest σ donor—dihydrogen—whereas other ligands with strong *trans* influence—the phosphanes—lie *trans* to the $[H_2SiPh_3]^-$ ion. The absence of the Si–H interaction and any other arrangement of the ligands would bring two or more ligands with strong *trans* influence into positions *trans* to each other. In addition, formation of the Si–H bond compensates for the weakening of the Ru–H bond. The driving force for the formation of nonclassical complex **4** is the poor back donation from the metal d level into the (H-Si-H)* antibonding orbital (it is this effect which is responsible for the whole range of silane and dihydrogen σ complexes formed with this system) and optimization of the ligand-to-metal bonding. Similar "secondary" Si–H interactions were identified in the chelate bis(silane) complexes $[\{\eta^4\text{-}(H\text{-}SiR_2)_2X\}Ru(PCy_3)_2H_2]$ (X = bridging ligand) reported by the same group.[3c]

Another type of multicenter H-Si-H interaction was found in a dimetallic ruthenium complex $[\{(PCy)_2RuH_2\}_2(\eta^3,\eta^3,\mu\text{-}SiH_4)]$ (**5**) obtained serendipitously by the reaction of **2** with $H_2SiMePh$.[6] This compound has a tetra-(σ-Si–H)-complexed SiH_4 group, which bridges two ruthenium moieties, and is the first example of a complex in which two H–Si bonds originating from the same silane are coordinated to one metal center, two pairs of the silane Si–H bonds are coordinated to each of the two ruthenium atoms. Two Si–H bonds and an Ru center lie in the same plane as observed in **4**. However, the essential difference between **5** and **4** is that the η^3-SiH_4 ligand is neutral and, therefore, in going from **4** to **5** the η^2-H_2 ligand must be replaced with a hydride. In **5**, each Ru center is pseudo-octahedral, with the η^3-SiH_4 ligand occupying one of the equatorial edges, analogous to the situation in **4**. The weakest *trans*-influence ligands to be positioned *trans* to the hydride groups are now the Si–H bonds of the η^3-SiH_4 ligand. Phosphanes, which have a weaker *trans* influence than hydrides, occupy the apical sites. Again, as in **4**, the metal–ligand bonding is perfectly optimized. Neglecting the ruthenium centers, the silicon atom in **5** has only four substituents in contrast to the five groups in **4**. Therefore the Si–H bonding in **4** and **5** is different: in **5** it does not differ much from that in the bis(silane) σ complexes, whereas in **4** the bonding of the silicon center to the hydrides is in a sense hypervalent.



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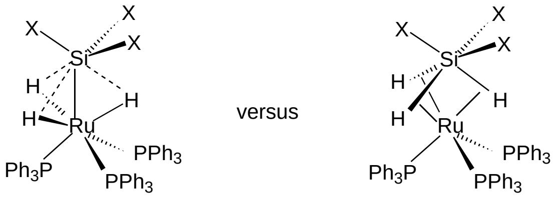
A unique case of interligand interaction between one silyl and three hydride groups was discovered by Hübler and Roper and co-workers for the complexes $[(PPh_3)_3M(SiPyr_3)H_3]$ (**6**; M = Ru, Os) bearing three electron-withdrawing pyrrolyl (Pyr) substituents on the silicon center.[7] Very high Si,H 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 experiments revealed no temperature dependence of the spectrum and the absence of fluxionality down to −85 °C. It appears unlikely that a fast equilibrium between two classical hydrides and one η^2-silane ligand, equalizing the three hydrides on the NMR time scale, could exist at such a low temperature. Natural bond order (NBO) analysis suggested that Si–H interactions in **6** stem from electron-density donation from the M–H bonding orbitals into the (Si–M)* antibonding orbital.[7] The main disadvantage of this bonding scheme is that it cannot explain the strong dependence of the molecular parameters of **6** on the value of the H-Si-Pyr angle. DFT calculations show that rotation of the silyl group around the Si–M axis, which breaks the optimal *trans* position of the hydride and the pyrrol with regard to the silicon atom, is a very unfavorable process.[7] In contrast, the proposed M–H→(Si–M)* donation must be unaffected to rotation because of the cylindrical symmetry of the M–Si bond.



6

NBO analysis of **6** also identified another type of nonclassical Si-H interaction which arose from electron-density transfer from the M–H bonding orbital into the (Si–N)* antibonding orbital.[7] This bonding is analogous to the interligand hypervalent interaction (IHI), H⋯Si–X (where X = halide), first discovered in basic transition metal hydrides having halosilyl groups SiR_2X in a position *cis* to the M–H bond.[8] Noteworthy is that a sharp rise in energy upon rotation of the $SiPyr_3$ group in **6** is accompanied by significant lengthening of the M–Si bond, consistent with the loss the IHI stabilization. The *trans* positions of the H and X (X = N, halogen etc) groups relative to the Si atom is a prerequisite for IHI and, therefore, the occurrence of IHI in this system can, in principle, explain the dependence of the energy on the rotation of the silyl group. However, the presence of IHI requires the ruthenium center in **6** to be in the less favorable oxidation state (+IV).

An alternative approach to rationalize the Si–H bonding in **6** is to consider the interaction of the complex $[(R_3P)_3M]^{2+}$ with the fragment $\{H_3SiR_3\}^{2-}$. The qualitative molecular orbitals (MOs) of the latter can be easily obtained by mixing MOs of the closed form of trihydrogen ion $[H_3]^-$ with the MO of the silyl ion $[SiR_3]^-$ (Figure 2). Since the silyl hybrid orbital lies at higher energy than the combination of s orbitals of hydrogens (at large H–H separations three levels of $[H_3]^-$ do not differ much in energy from the 1s orbital of hydrogen atom), orbital stabilization can be seen. Further stabilization of this doubly charged unit occurs upon coordination to the cationic osmium (ruthenium) complex, where the a and e levels find perfect matches. The Si–H interaction in **6** will be retained provided the back donation from the metal to the $(Si-H_3)^*$ antibonding orbital is not complete. This description implies that in the resultant neutral compound the oxidation state of the metal is intermediate between II and IV (a classical trihydridosilyl structure would imply Os^{IV}) and the proposed $\{\eta^4\text{-}H_3SiR_3\}^{2-}$ 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 reason for the *trans* disposition of the substituents at Si becomes clear.

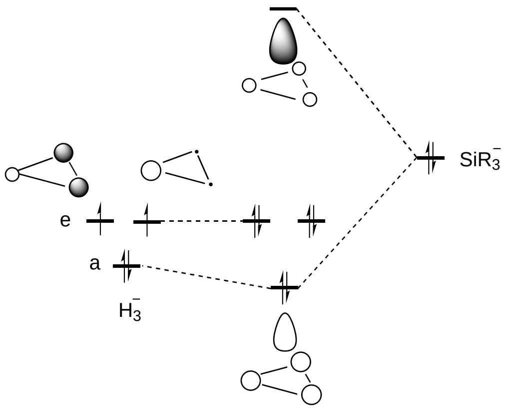


Figure 2. Formation of $\{H_3SiR_3\}^{2-}$ upon interaction of $[H_3]^-$ with $[SiR_3]^-$.

These recent examples of $(H)_2-Si$ and $(H)_3-Si$ interactions show that studying nonclassical Si–H interactions now goes beyond the more usual silane Si–H σ complexes. Other types of multicenter Si–H interactions such as Si_3-H are feasible and offer a challenge for both the synthetic and theoretical chemists.

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