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Interaction between a σ bond and a d^n ML_n fragment: an MO analysis of the MnSiH three-center interaction in $CpMnL_2HSiR_3$ complexes

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Abstract

Two types of interactions between a σ bond and a d^n ML_n entity are generally considered: in the first type the σ bond is complexed to the metal atom, acting as a 2-electron ligand; in the second type, an oxidative addition reaction occurs, leading to a complex in which the σ bond is broken. The two different complexes resulting from two kinds of interactions can often be considered as two isomers. Extended Hückel calculations on compounds of the type $CpMnL_2HSiR_3$ show that the three center MnHSi interaction can be viewed as belonging to the first type, i.e. a σ H–Si bond coordinated to the d^6 $CpMnL_2$ fragment. Generalization for other d^n L_nMHSiR_3 complexes suggests that, when the H–Si bond is fully broken, the addition is not oxidative and that the bonding is better described as having a formally H^- and a formally SiR_3^+ ligand coordinated to a metal atom which has the same formal oxidation state as in the free ML_n fragment. The known experimental studies on these complexes are analysed on the basis of this MO analysis.

Introduction

The way a σ bond, namely H–H or C–H, interacts with a d^n ML_n unsaturated organometallic entity (such as, for example, d^6 ML_5 or d^8 ML_4) is now both experimentally and theoretically well understood [1–5]. Two general modes of coordination can be considered. In the first type, represented by **1**, the σ H–R bond (R = H, CR'_3 or any isolobal fragment) behaves as a 2-electron ligand towards the metal atom, generally allowing it to achieve its 18-electron configuration. The σ

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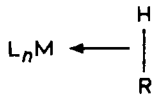
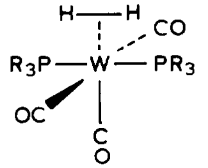


(1)



(2)

doublet in **1** is therefore delocalized over the three centers H, R and M. A typical example of this mode of coordination is the isolable molecular hydrogen complex $W(CO)_3(P\text{-}i\text{-}Pr_3)_2H_2$ (**2**) in which the H_2 ligand is bonded in a side-on fashion [3,4]. The bonding in this kind of complexes has been analysed by ab initio [2e] and extended Hückel [2d,27] methods.

A general frontier molecular orbital (FMO) interaction diagram for complexes of type **1** is given in Fig. 1a, with R = H for drawing simplicity. The ML_n fragment must necessarily possess a vacant FMO, symmetric with respect to the plane perpendicular to the MHR triangle which contains M. This FMO interacts with the occupied low lying σ orbital of H–R, generating the bonding 1*s* MO associated with the tricentric bond. This symmetric interaction gives the major contribution to the bonding between ML_n and H–R.

If the ML_n fragment also bears, like **2**, an occupied π-type FMO, antisymmetric with respect to the plane perpendicular to the MHR triangle which contains M, then its interaction with the vacant high lying σ^* orbital of H–R will increase the stability of **1** [2d,e]. In this case, complex **1** has two occupied MOs; the symmetrical

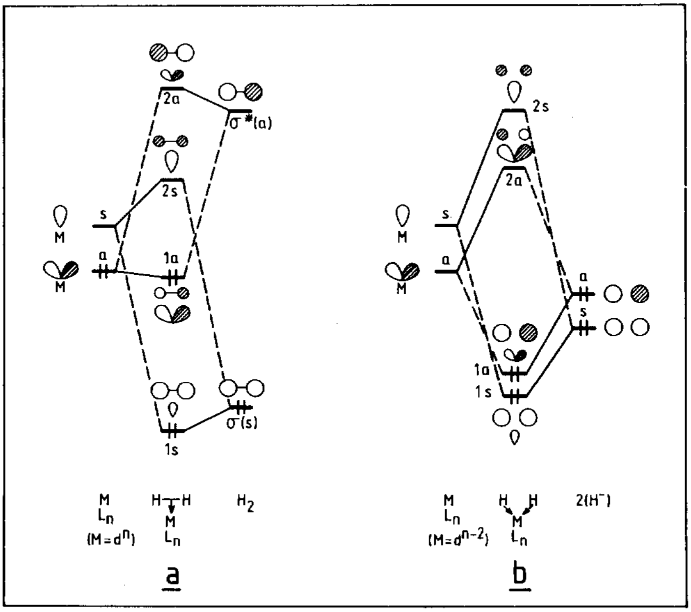
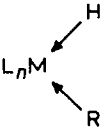


Fig. 1. General FMO interaction diagram for L_nMH_2 complexes: (a) H_2 acting as a 2-electron ligand; (b) complex resulting of an oxidative addition of H_2.

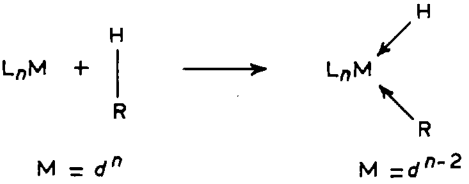
1*s*, predominantly HR localized, and the antisymmetrical 1*a*, predominantly metal localized.

Note that a linear M–H–R coordination mode is possible, but in this case the π-type (antisymmetric) interaction is totally absent [2d]. Coordination modes intermediate between linear and side-on are also possible [6 *].



(**3**)

The second mode of coordination, **3**, is the result of an oxidative addition reaction of H–R on ML$_n$, shown in **4**. The H–R bond is broken to give formally two ligands H$^-$ and R$^-$. The H + R system has therefore gained two electrons in reaction **4**, taken from the metal atom which is formally oxidized, going from configuration d^n to configuration d^{n-2}.



(**4**)

A large number of reactions examplifying reaction **4** are known in which the reactive organometallic starting materials are various d^8ML$_4$ species [5].

A general FMO diagram for complexes of type **3** is given in Fig. 1b, with R = H. As for complex **1**, we have still an H + R system interacting with an ML$_n$ entity, so the FMO sets of these two interacting systems are similar. But this time, as the H–R bond is broken H and R are interacting very weakly, and consequently the σ and σ^* orbitals of HR are non bonding, almost degenerate when R = H, and lying at rather low energy. (Typically in extended Hückel calculations, the energy of a H$^-$ is -13.6 and -11.8 eV for a CH$_3$$^-$ lone pair). The double interaction (symmetrical and antisymmetrical) leads to the formation of two occupied bonding MOs, 1*s* and 1*a*, associated with the two M–H and M–R bonds. (This time ML$_n$ must necessarily possess two FMOs, one symmetrical and one antisymmetrical). MOs 1*s* and 1*a* are both predominantly localized on HR; it follows that the main difference between the electronic structures of **1** and **3** lies in the antisymmetrical orbital system: in **1**, the occupied 1*a* MO has a predominantly metal character and in **3** a predominantly HR character. The reason for this is that in **1**, FMO σ^* of HR lies at higher energy than the π-type ML$_n$ FMO and, conversely, at lower energy in **3**.

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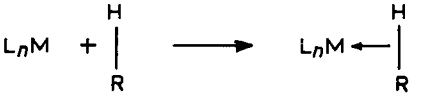
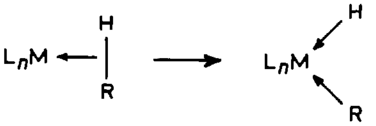
* Reference number with asterisk indicates a note in the list of references.



(5)

The total energy of the $ML_n + HR$ system decreases continuously during the complexation reaction 5. This is obvious from Fig. 2a which represents the schematic evolution of the crucial levels during this reaction: the two occupied levels (the σ orbital of HR and the π-type ML_n FMO) are both stabilized during the reaction by developing some bonding character with the other fragment.

On the other hand, an energy barrier is expected during reaction 4 [2a–d] due to an avoided crossing of the antisymmetrical levels as shown in Fig. 2b: the π-type ML_n occupied FMO correlates with the predominantly metal localized $2a$ vacant MO, and the σ^* vacant orbital of HR correlates with the occupied, predominantly HR localized $1a$ MO. In the case of R = alkyl another cause of the energy barrier is the reorientation of the alkyl group [2i].



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It is now easy to see that a similar energy barrier will be encountered during reaction 6, for in 1 the occupied $1a$ MO is predominantly metal localized and the

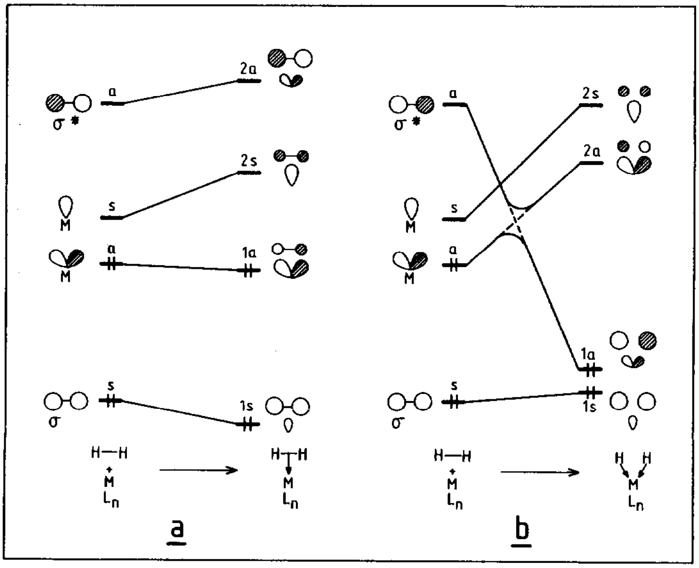


Fig. 2. Schematic evolution of the crucial MO levels during: (a) the reaction of complexation of H_2 on ML_n; (b) the oxidative addition reaction of H_2 on ML_n.

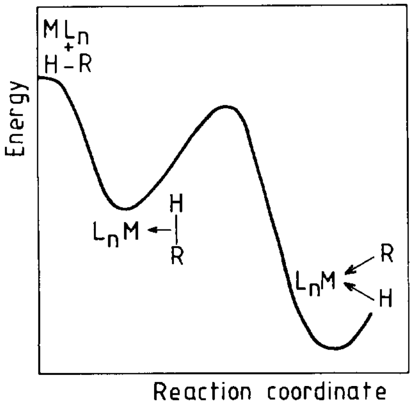


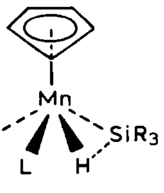
Fig. 3. Schematic energy profile of the reaction $ML_n + H{-}R \rightarrow \mathbf{1} \rightarrow \mathbf{3}$. The height of the energy barrier and the depth of the minimum are arbitrary (they depend of the system considered).

vacant $2a$ MO is mainly of HR character thus leading to a level crossing similar to the one of Fig. 2b. Therefore, as shown schematically in Fig. 3a, we have the infinitely separated ML_n + HR system, with complex **1** on one side of the energy barrier and complex **3** on the other. It thus appears that **1** and **3** are real isomers, and if they are both sufficiently stable and if the energy barrier is not too high, it should be possible to go from one to the other and vice versa.

At this point of the discussion, it should be noted that the existence of an avoided level crossing does not necessarily imply the existence of an energy barrier. Therefore, the possibility of a coordination mode intermediate between **1** and **3** can, not to be fully excluded, despite much evidence for a transition state between the **1** (or ML_n + HR) and the **3** systems [1–5]. Such a situation could occur in special cases; for example if there are, in addition to the two ML_n FMOs shown in Fig. 1 some other orbitals involved in the interaction with H–R.

There is a class of compounds in which the metal–σ bond interaction mode is not fully understood; it corresponds to a σ Si–H bond of a silane, $HSiR_3$, interacting with a $CpMnL_2$ entity. Structural, spectroscopic and chemical studies [7–11a] of the $CpMnL_2HSiR_3$ class of compounds lead to the conclusion that there is a peculiar MnSiH three-center interaction. For example, a neutron diffraction study of $CpMn(CO)_2HSiF(C_6H_5)_2$ [9a] showed unambiguously bonding Mn–Si and Mn–H distances of 2.53 and 1.56 Å, respectively, and a rather short Si · · H contact, 1.80 Å (the Si–H distance in free SiH_4 is 1.48 Å [12]).

The question posed in the paper, viz., Is there "a long Si–H or a short Si · · H bond non bond?", can be reformulated as "Is the coordination mode of type **1** or type **3**?". Other authors also propose a bonding scheme intermediate between **1** and **3** [8b,10].



(7)

In order to investigate the coordination in this class of compounds, we have undertaken extended Hückel calculations on the model compound CpMn(CO)$_2$-HSiH$_3$ [11].

Electronic structure of the CpMnL$_2$HSiR$_3$ compounds

The molecular geometry we first considered was based on the experimental structure of (CH$_3$C$_5$H$_4$)Mn(CO)$_2$HSiCl$_3$ [9b] (experimental crystallographic positional parameters were used) with the methyl group and the chlorine atoms replaced by hydrogen atoms, the experimental valence angles being preserved.

The FMO interaction diagram for CpMn(CO)$_2$HSiH$_3$ is shown in Fig. 4. The CpMn(CO)$_2$ fragment is of the well-known pseudooctahedral d^6 ML$_5$ class [13]; its FMO set is composed of one hybrid σ-type vacant orbital lying above a group of three occupied, mainly d-type, orbitals, viz., the "t_{2g}" set. The HOMO and LUMO of the distorted H· · SiH$_3$ fragment are the predominantly H-localized σ and the predominantly SiH$_3$ localized $\sigma^\star$ orbitals associated with the H· · Si "bond". Despite the rather long H· · Si distance (1.8 Å) and the fact that the "C_3 axis" of the SiH$_3$ group does not point towards the H-atom bonded to the metal but somewhere between this H-atom and the Mn-atom [9a,b], the $\sigma/\sigma^\star$ separation

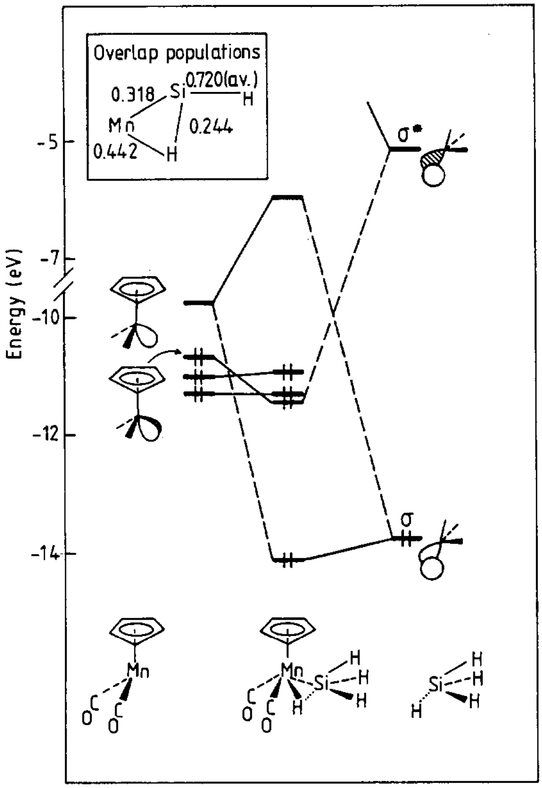
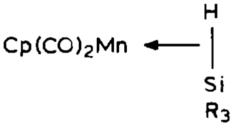


Fig. 4. FMO interaction diagram for CpMn(CO)$_2$HSiH$_3$ assuming a molecular structure extrapolated from the experimental geometry of a related complex (see text).

remains large (7.7 vs. 10.9 eV in the free tetrahedral SiH_4). Actually a rather strong $Si\cdot\cdot H$ bonding interaction remains. Our calculation on this distorted $H\cdot\cdot SiH_3$ fragment considered alone gives an $H\cdot\cdot Si$ overlap population of 0.56, compared to 0.74 for free tetrahedral SiH_4 (Si–H 1.48 Å). This partial conservation of bonding upon distortion can be related to the rather large diffuseness of the Si valence orbitals.

Despite the total absence of symmetry in $CpMn(CO)_2HSiH_3$, a rather strong pseudosymmetry is preserved in the FMO sets, and two major interactions are observed: one "symmetrical", between σ_{SiH} and the vacant hybrid of $CpMn(CO)_2$, and one "antisymmetrical", between $\sigma^{\star}_{SiH}$ and the in plane π-type occupied FMO of $CpMn(CO)_2$. The two other FMOs of the "t_{2g} set" remain almost unperturbed. Clearly, this interaction diagram is similar to the one of Fig. 2a, since the $\sigma^{\star}_{SiH}$ lies 6.6 eV above the π-type "antisymmetrical" metal FMO. Thus the coordination mode can be assigned unambiguously to the general type **1**, namely **8**.



(**8**)

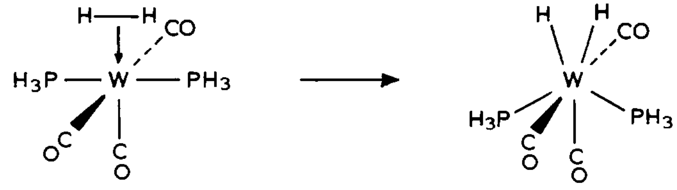
The large difference between the energies of the two interacting "antisymmetric" FMOs is highly significant, but we nevertheless decided to test this result. The H_{ii} parameters of Mn and Si were allowed to vary over a range of ±2 eV, while in all our calculations $\sigma^{\star}_{SiH}$ remained at significantly higher energy than the metallic π-type FMO. A similar result was obtained with three Cl atoms in place of the three silyl H atoms and also with a molecular geometry taken from the averaged neutron structure of $(CH_3C_5H_4)Mn(CO)_2HSiF(C_6H_5)_2$ [9a] and other standard structures. Introduction of $3d$ Si atomic orbitals in the calculations does not affect significantly the results.

The significantly weakening of the $H\cdot\cdot Si$ bond in **8** (the corresponding overlap population in the complex (Fig. 4) is 0.24) is the consequence of the two main interactions:
(i) the symmetrical interaction corresponds to the delocalization of the σ_{SiH} bonding pair on the Mn atom, leading to a loss of SiH bonding character (the corresponding charge transfer is of 0.37 electron [14 *]).
(ii) the antisymmetrical interaction corresponds to the delocalisation of a metal π lone pair into the antibonding $\sigma^{\star}_{SiH}$ orbital, leading to a gain of SiH antibonding character (the corresponding charge transfer is of 0.39 electron).

At this stage of the discussion, the similarity between **8** and **2** has to be pointed out; In both cases we have a σ bond coordinated as a 2-electron ligand to a d^6 ML_5 fragment in a side-on fashion. In both cases the σ bond is weakened upon coordination but significantly more in **8** than in **2** where the H–H separation is 0.84 Å, according to neutron diffraction data [3] (compared with 0.74 Å in free H_2).

Can a $CpMnL_2HSiR_3$ compound exist with a fully broken SiH bond?

We can now ask ourselves whether, if **8** and **2** are of the coordination type **1**, there is a possibility for them to give, via reaction **6**, their oxidatively added isomer of type **3**.



(9)

An evaluation of the energy profile of reaction **9** is plotted on Fig. 5. Because extended Hückel calculations are not suitable for full geometry optimisation, we only allowed angular variations during the process, and the results have to be considered as only indicative. From the starting point of an averaged geometry for **2**, but with simpler phosphines, we found the energy minimum for the oxidatively added product of type **3** at an H· · H distance of 1.8 Å. Consistently, an energy barrier, of 0.5 eV, associated with the avoided level crossing is found. At our level of accuracy, isomers **1** and **3** are equally probable for our model $W(CO)_3(PH_3)_2H_2$. In the case of the real compound **2**, one can only suggest that the steric hindrance of the bulky phosphine groups accounts for the fact that only the isomer of type **1** has been observed [3]. Moreover, eighteen-electron $L_5M(H)_2$ complexes have been shown to exist in their d^4 dihydro form [4g]. Furthermore, some compounds closely related to **2**, of general formula $L_4MH(H_2)$ ($M = d^6$), exhibit in solution at rather low temperatures fluxional behaviour showing exchange between the hydride atom and the two equivalent hydrogens [4b,c]. Such a process suggests the existence of the type **3** d^4 $L_4M(H)_3$ trihydride form, in equilibrium with its d^6 type **1** isomer [4c]. Related tetrahydride complexes exhibit a similar fluxional behaviour [4k]. More recently, Kubas et al. [4h] and Upmacis et al. [4i] have evidenced the $\mathbf{1} \rightleftarrows \mathbf{3}$ equilibrium for d^6 $L_5M(H_2)$ complexes.

Conversely, in the case of $CpMn(CO)_2HSiH_3$, any attempt to find a stable geometry, **10**, in which the H atom and the SiH_3 group are far from each other, failed. The FMO interaction diagram corresponding to a typical calculation on **10**, where the H · · Si distance is 2.5 Å, is represented in Fig. 6. As the H atom and the SiH_3 group are this time not significantly interacting, the FMO set of the H + SiH_3

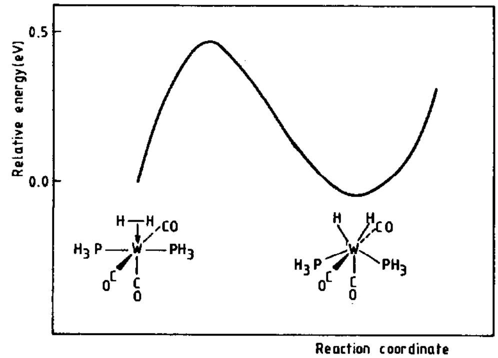


Fig. 5. Evaluation of the energy profile of the oxidative addition **6** for the compound $W(CO)_3(PH_3)_2H_2$.

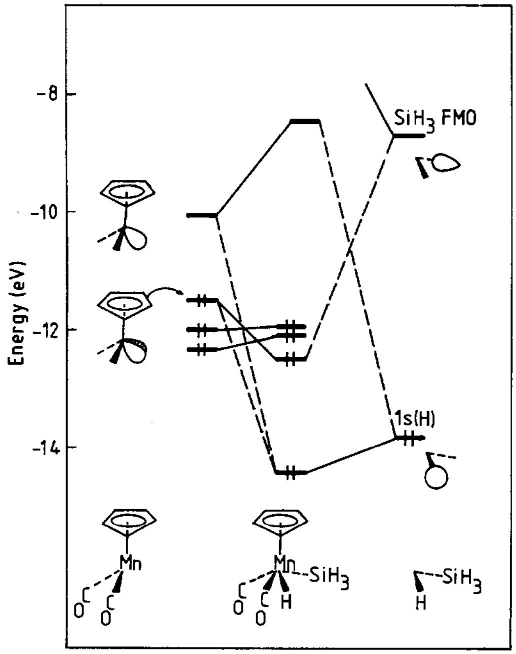
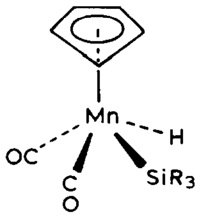


Fig. 6. FMO interaction diagram for $CpMn(CO)_2HSiH_3$ in which the H–SiH_3 bond is broken (H ··· Si 2.5 Å).

system involves two non-bonding orbitals: the 1*s* atomic orbital of the H atom and a hybrid Si orbital. It is important to note that this Si orbital lies 2.7 eV above the metal π-type FMO. This is a crucial similarity with **8**, in which the σ^{*}_{SiH} orbital, preponderantly of Si character, lies also above the π-type metal FMO (Fig. 4).



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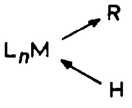


(11)

Because of the absence of symmetry (an pseudosymmetry) in **10**, a rather important intermixing of the four FMOs occurs. Nevertheless, as for **8**, the two major interactions are the interaction between the σ-type metallic FMO and the lowest orbital of the $H + SiH_3$ system and the interaction between the π-type metallic FMO and the highest orbital of the $H + SiH_3$ system.

Clearly, the MO diagrams of Figs. 4 and 6 are closely related. It is evident that the formal oxidation state of the Mn atom is the same in **8** and **10**. A general representation for **10**, which can be seen as a d^6 ML_5 entity interacting with formally H^- and $R^+ = SiH_3{}^+$ fragments, is given in **11**. Of course, because of the strong covalency, the calculated charges are rather different from the formal ones (-0.23 for the H ligand and $+0.16$ for SiH_3) [15 *].

The transit **8** → **10** occurs without any avoided level crossing, and consistently no energy barrier was found during the process, only a significant increase in energy. Even the reorientation of the SiH_3 group does not causes the emergence of a transition state during the transit. The result is that **10** is not an isomeric form of **8** but just a destabilized geometry.

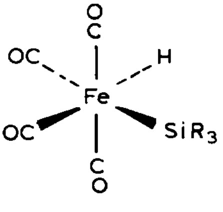
We can generalize the preceding discussions in the following way:

The interaction of a σ bond H–R with a d^n ML_n entity bearing a half occupied set of two FMOs (one of σ type and one of π type) can lead to various modes of coordination. Two general cases have to be considered [16 *]. In the first case, the frontier orbital of the R fragment lies below the metallic π-type FMO; in this situation the coordination modes **1** or **3** are the more probable; the existence of one of them (**1** or **3**) does not a priori exclude the possibility of existence of the other (**3** or **1**) which can exist as an alternative isomeric form. In the second case, the frontier orbital of R lies above the metallic π-type FMO, and so an oxidative addition of HR on ML_n is impossible and only one type of coordination, corresponding to the MO diagram of Fig. 2a, is allowed. This coordination mode can be represented either by **1**, **11** (which can be considered as two limit formulas), or an intermediate form, depending whether the intensity of the H · · R bonding interaction is rather strong, very weak or intermediate. The bonding scheme adopted in such a case is a result of a compromise between the loss of H–R bonding, the gain of M–H and M–R bonding, and the geometrical flexibility of the ML_n fragment. This last parameter probably plays an important role in the case of compounds of the $CpMnL_2HSiR_3$ family in which the $CpMnL_2$ fragment is rather rigid, i.e. the supplementary bending of this fragment required by a full breaking of the H–SiR_3 bond is energetically too disfavored, relative to the poor improvement of its bonding abilities with the H + SiR_3 system.

In the related $CpRe(CO)_2HSi(C_6H_5)_3$ compound, the SiH separation is larger, ~ 2.2 Å according to an X-ray study [17]. This is consistent with the fact that there is more room in the coordination sphere of the Re atom and that its π-type FMO lies at higher energy. Indeed, a smaller difference between the metal π orbital and the SiR_3 FMO favor coordination type **11**, whereas a larger separation will favor coordination type **8**. This is also consistent with the fact that *trans* isomers exist in the family of compounds $CpRe(CO)_2HER_3$ (E = Si, Ge) [8c, 7b]. Our calculations on the model $CpRe(CO)_2HSiH_3$, using the experimental structure of $CpRe(CO)_2$-$HSi(C_6H_5)_3$, in which the separation between the two "antisymmetrical" FMOs is 3.6 eV, lead to still significant H · · Si overlap population of 0.14 electron.

ML_4HSiR_3 18-electron complexes

On the other hand, in the family of the octahedral *cis*-$Fe(CO)_4HSiR_3$ compounds **12**, the H and SiR_3 groups are considered independent [18]. This is



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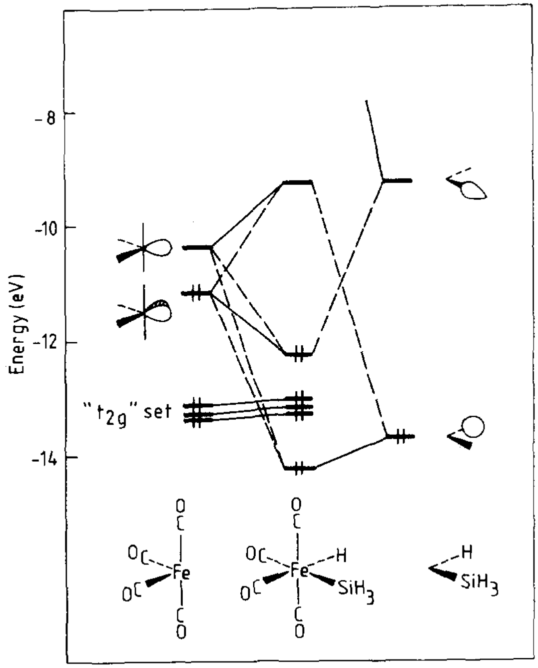
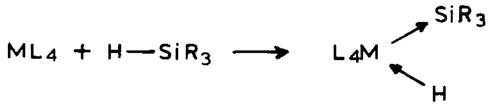


Fig. 7. FMO interaction diagram for the octahedral *cis*-$Fe(CO)_4HSiH_3$ complex.

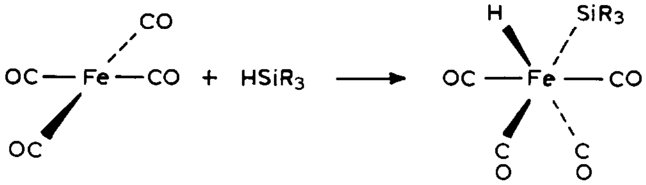
consistent with the high energy of the π lone pair of the C_{2v} d^8 $Fe(CO)_4$ fragment in **12** [19]. Our calculation on the octahedral *cis*-$Fe(CO)_4HSiH_3$ model, in which the H · · Si distance is 2.8 Å, leads to an FMO diagram (Fig. 7) very similar to the one of Fig. 6 (The SiH_3 frontier orbital lies 1.9 eV above the $Fe(CO)_4$ π lone pair level). Thus the coordination mode corresponds to **11**. Here also a strong covalency is observed, due to the small difference between the energies of the SiH_3 FMO and the π-type metallic orbital. The calculated charges are -0.30 for H and $+0.11$ for SiH_3.

Since the Si–H bond has not oxidatively added in compounds **12** no significant activation energy is expected for reaction **13** [20 *], providing the d^8 ML_4 π lone pair still lies below the SiR_3 FMO. Indeed, reaction **13** is known for Ir^IL_4 complexes [21] and small $\Delta H^\star$ values (~ 6 kcal/mol) [21a] have been observed. A rough determination of the energy profile of this type of reaction was evaluated by calculating the variation of the total electronic energy during transit **14**, in which the arbitrary starting point is a planar $Fe(CO)_4$ and a tetrahedral SiH_4 with Fe · · · H 1.6 Å. No energy barrier was observed; this is consistent with the small activation enthalpies observed which can be associated with the first stage of the reaction, not taken in account in transit **14**. Indeed, the early approach of the two interacting molecules is repulsive [2a–d]. Consistently, for the same transit **14**, but with CH_4 in place of SiH_4, the usual energy barrier (0.8 eV) associated with an oxidative addition process was observed.

It is now well-known that alkane C–H bonds are easily oxidatively added to d^8 CpML reactive species photochemically generated in the reaction medium [5b]. An earlier theoretical study [2d] showed that the energy barrier associated with the oxidative addition avoided level crossing (see Fig. 2b), is rather low because of the

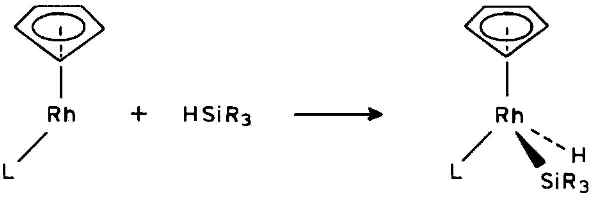


(13)



(14)

high energy [19] of the d^8 CpML π lone pair. An estimate of the energy profile of reaction **15**, with M = Rh, L = CO and R = H, shows a small barrier of 0.2 eV although the π lone pair of CpRh(CO) is still 0.68 eV below the SiH_3 FMO. With CH_4 in place of SiH_4 we found a significant energy barrier of 0.7 eV, in agreement with a previous study [2d].



(15)

The exchange reaction of $HSiR_3$ with a 2-electron ligand in $CpMn(CO)LHSiR_3$ complexes

The kinetics of the exchange reaction **16** have been extensively studied [7a,22]. Mechanism **17** was first suggested by Hart–Davies and Graham [7a], who proposed the energy profile of Fig. 8 (solid line). This mechanism is not fully consistent with

$$\begin{array}{ll} CpMn(CO)LHSiR_3 + L' \rightarrow CpMn(CO)LL' + HSiR_3 & \\ \quad L = CO, \text{phosphine} \qquad\qquad L' = \text{phosphine} & \end{array}$$

16

our results. Since reaction **17a** is of type **5**, no energy barrier is expected for it. For similar reasons (no avoided level crossing) reaction **17b** is also expected to occur without an energy barrier. According to these arguments, the free CpMn(CO)L

$$\text{(a)} \quad CpMn(CO)LHSiR_3 \overset{\text{slow}}{\rightleftarrows} CpMn(CO)L + HSiR_3$$

$$\text{(b)} \quad CpMn(CO)L + L' \overset{\text{fast}}{\rightleftarrows} CpMn(CO)LL'$$

17

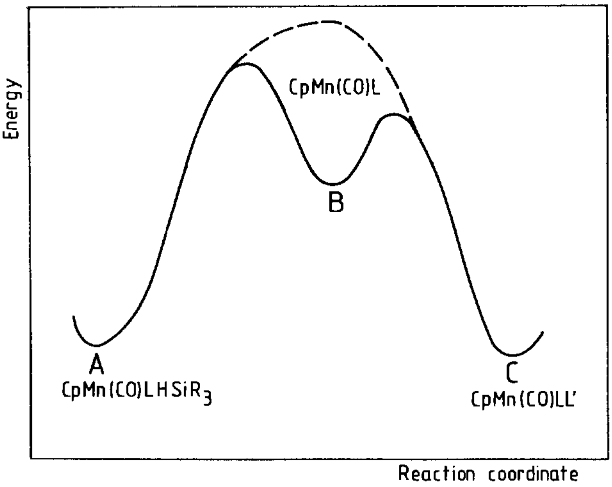
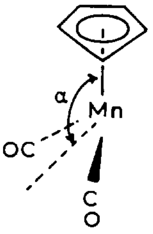


Fig. 8. Schematic energy profile of reaction **16**: solide line: assuming mechanism **17**; dashed line: assuming CpMn(CO)L is the only transition state in the reaction.

species must be a transition state, not a reaction intermediate, thus corresponding to a maximum on the energy profile curve, as shown by the dashed line in Fig. 8.

In order to test the above qualitative arguments, an evaluation of the energy profile of reaction **17a** and **17b** was undertaken using as a model CpMn(CO)LHSiR$_3$ with L = PH$_3$. We first optimized the α angle of the free CpMn(CO)$_2$ species **18**. As expected [13], the minimum energy was found for $\alpha = 152°$, a value close to the ideal pseudooctahedral one (144.7°) and to the experimental one observed in



(18)

CpMn(CO)$_2$HSiR$_3$ complexes (for example 142° in (CH$_3$C$_5$H$_4$)Mn(CO)$_2$-HSiF(C$_6$H$_5$)$_2$ [9a]. There is then no significant change in the geometry of the CpMn(CO)L entity during reaction **16**. When this optimized geometry for CpMn(CO)$_2$ was assumed, no energy barrier was found, as expected, for reactions **17a** and **17b**. Actually, reaction **17a** was found to be exothermic; this incorrect prediction is not surprising, and is attributable to the overestimation by extended Hückel calculations of the loss of Si–H bonding energy upon complexation (where the Si–H distance goes from 1.48 to 1.80 Å).

Nevertheless, assuming the general shape of the energy profile proposed by Hart–Davies and Graham (Fig. 8, solide line), we can suggest two other mechanisms:

(i) the B minimum does not correspond to free CpMn(CO)L but rather to CpMn(CO)L complexing a molecule of solvent. (Even in a saturated solvent like n-heptane, a σ C–H bond could be complexed.) In this case B must be a shallow minimum between two maxima lying at the same energy, both corresponding to the free CpMn(CO)L transition state.
(ii) the B minimum corresponds to a Si–H bond complexed in a end-on fashion (our calculations indicate that a linear Mn · · Si · · H coordination is also stable) [23 *]. In this case the first energy barrier, associated with a rotation of the Si–H bond, should be mainly of steric origin and especially sensitive to the sizes of R, L and the eventual substituents on the Cp ligand. The first energy maximum should be lower or equal to the second, which corresponds to the free CpMn(CO)L species. This interpretation is in agreement with a mechanistic proposal for reaction **16** based on NMR studies advanced by Colomer et al. [8b].

Though none of these proposed mechanisms fits perfectly with Hart–Davies and Graham's experimental results [9a], our orbital arguments strongly suggest that CpMn(CO)L is the highest reaction coordinate energy point. If this is the case, then the activation enthalpy of reaction **16** is directly related to the energy difference between CpMn(CO)L and CpMn(CO)LHSiR$_3$. According to recent experiment [22], the $\Delta H^\star$ value increases with increasing electron donor ability of L. This is consistent with the fact that if L is a strong donor, the π lone pair of CpMn(CO)L is also destabilized is this molecule. However this is not the case for CpMn(CO)LHSiR$_3$, in which this destabilizing effect is balanced by the gain of MnSiH bonding.

Finally, we note that a recent structural and spectroscopic study, by one of us, of various CpMnL$_2$HSiR$_3$ complexes [24] is in excellent agreement with our calculations: A very broad valley exists in which there is Mn, H, Si three-center bonding. On changing the substituents or ligands, only the degree of Mn–H, Si–H or Si–Mn bonding is changed. The opening of the Si–H bond is favored by the use of electron donating ligands and/or electronegative substituent R, both reducing the energy difference between the metallic π-lone pair and the SiR$_3$ FMO. However in no case is complete separation of H and SiR$_3$ reached.

Appendix

The calculations were carried out within the extended Hückel formalism [25] using the weighted H_{ij} formula [26]. The atomic parameters utilized are listed in Table A1. When not specified in the text, the following bond distances (Å) and angles (°) were used: Mn–CO 1.8 ; Mn–C(Cp) 2.13; Mn–H 1.6; Mn–Si 2.3; Fe–CO 1.8; Fe–H 1.6; Fe–Si 2.3; Fe–CH$_3$ 1.9; W–CO 2.0; W–P 2.5; W–H 1.75; Rh–CO 1.9; Rh–C(Cp) 2.2; Rh–H 1.7; Rh–Si 2.4; Rh–CH$_3$ 1.95; C–O 1.15; C–H 1.09. Si–H 1.48; Si · · · H 1.8; P–H 1.4; H–C–H = H–Si–H = H–P–H = 109.47; M–C–O 180.

Unless otherwise specified, octahedral symmetry was systematically assumed around the metal atom. i.e. L–M–L 90 or 180° and Cp centroid–M–CO 125.26°.

The variation of the total electronic energy of the considered systems during transits **9**, **14** and **15** was determined from an hypothetical reaction coordinate based on a linear transit between the geometries of the starting and the final points. In all these transits the M–H distances were kept constant (1.75 in **9**; 1.6 in **14**. 1.7 in **15**).

Table A1

Parameters used in extended Hückel calculations [a]

Orbital		H_{ii} (eV)	ζ_1	ζ_2	C_1	C_2
H	1*s*	−13.6	1.30			
C	2*s*	−21.4	1.625			
	2*p*	−11.4	1.625			
O	2*s*	−32.3	2.275			
	2*p*	−14.8	2.275			
P	3*s*	−18.6	1.75			
	3*p*	−14.0	1.30			
Si	3*s*	−17.3	1.383			
	3*p*	−9.20	1.383			
Mn	4*s*	−9.75	1.80			
	4*p*	−5.89	1.80			
	3*d*	−11.67	5.15	1.70	0.514	0.693
Fe	4*s*	−9.10	1.90			
	4*p*	−5.32	1.90			
	3*d*	−12.60	5.35	1.80	0.536	0.667
Rh	5*s*	−8.09	2.135			
	5*p*	−4.57	2.099			
	4*d*	−12.50	4.29	1.97	0.580	0.5685
Re	6*s*	−9.22	2.398			
	6*p*	−4.45	2.372			
	5*d*	−11.29	5.443	2.277	0.636	0.567
W	6*s*	−8.26	2.341			
	6*p*	−5.17	2.309			
	5*d*	−10.37	4.982	2.068	0.694	0.5631

[a] The *d* orbitals are formed by a linear combination of two simple Slater functions.

The H–W–H and P–W–P bond angle values corresponding to the mimimum energy of Fig. 5 are 61 and 148° respectively.

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