J. Am. Chem. Soc. 1986, 108, 6587-6592

Interaction between d^6 ML_5 Metal Fragments and Hydrogen: η^2-H_2 vs. Dihydride Structure

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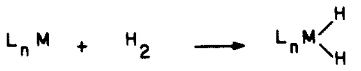
Received February 11, 1986

Abstract: The interaction of d^6 ML_5 fragment with H_2 to form either a η^2-H_2 coordinated or a dihydride complex is studied by means of Extended Hückel calculations. Both the H_2 approach toward the ML_5 fragment and the H–H bond cleavage leading to d^4 7-coordinated dihydride have been examinated. Whatever the nature of the metal and the ligands, H_2 approach leading to a η^2 type structure is an exothermic process, the strength of the interaction being larger for L = H^- (pure σ-donor) than for L = CO (π-acceptor). The ease of an eventual H–H cleavage to form the dihydride structure strongly depends on the electronic properties of the metal and ligands. It is shown to be related on the ability of the ML_5 fragment to populate $\sigma^*_{H_2}$. The formation of the dihydride is made more difficult by replacing a metal with high lying d orbitals (W for instance) by a metal with low lying d orbitals (Fe) and/or by replacing pure σ-donor ligands by π-acceptor ones. In complexes containing both σ-donor and π-acceptor ligands, the influence of the position of the π-acceptor ligands in the metal fragment is analyzed. In particular, it is shown that a carbonyl group trans to the incoming H_2 molecule favors the η^2 structure with respect to the case where this trans ligand is a pure σ-donor.

The nature of H–H bond interaction with a metal is a fundamental question because of its relevance to homogeneous catalysis. Just as for the C–H bond,[1] there is a sharp dichotomy in the way in which H–H bonds to the metal. Most often the H–H bond is broken, leading to the metal dihydride **1**. In this process, the oxidation number of the metal is formally increased by 2 (oxidative addition[2-10]). On the other hand, a series of complexes have been recently reported in which there is a novel type of bonding involving an η^2-dihydrogen structure **2** which retains the H–H bond.[11b,12-15]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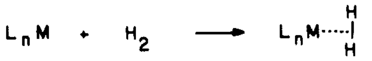
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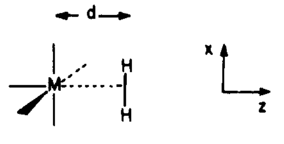
In this case, the oxidation number of the metal is not changed, as shown by the experimental values of the M–L force constants in complexes of type **2**.[13] These molecular H_2 complexes are intriguing since they may be regarded, at least from a geometrical point of view, as arrested forms of the oxidative addition of H_2 to metal. It is noticeable that most complexes of this type so far reported involve a d^6 ML_5 fragment interacting with H_2 (as in **3**). On the other hand, d^4 ML_5H_2 dihydride complexes are also



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well documented.[17-19] Therefore ML_5 fragment interacting with H_2 has the interesting capability to form either the η^2 molecular or the dihydride complex. Although numerous theoretical studies have been devoted to the understanding of the activation of C–H and H–H bonds,[16] the factors favoring the retention or the cleavage of a coordinated bond are not yet really understood. Let us first recall the available experimental data concerning the d^6 ML_5 + H_2 systems.

Well characterized ML_5H_2 dihydride structures are known: $MH_2(PMe_3)_5$ (M = Mo, W),[17] $MH_2(P(OMe)_3)_5$ (M = Cr,[18a] Mo,[19] W,[19] and Re$^+$ [19]). They are fluxional[18b] heptacoordinated complexes with a distorted pentagonal-bipyramidal geometry, known to be favorable for d^4 7-coordinated complexes.[20] On

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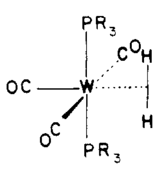
the other hand, side one bonded structures have been found for $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W (**4**); R = Cy, *i*-Pr),[12a,b] $Mo(CO)(dppe)_2(H_2)$[12c] (dppe = $PPh_2CH_2CH_2PPh_2$), $Cr(CO)_5(H_2)$,[13,14] $M(H)(dppe)_2(H_2)^+$ (M = Fe (**5**), Ru),[15a] and $(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(H_2)^+$.[15b] Here, the H–H bond is essentially retained: 0.75 Å (X-ray) and 0.84 Å (neutron diffraction) in **4**, 0.89 Å (X-ray) in **5** instead of 0.74 Å in isolated H_2. Furthermore, some complexes seem to be at the borderline between molecular hydrogen and dihydride form. In a recent work,[12c] Kubas et al. have shown that in solution, **4** contains an equilibrium fraction (15–30%) of the hydride complex, and their conclusion is that **4** should represent "a situation wherein the bonding of H_2 is at a near balance point between nondissociative and dissociative" and that "some of the known polyhydride complexes may contain equilibrium amounts of corresponding H_2 complexes". Heptacoordinated polyhydride complexes of osmium and iridium have been characterized,[21] but recent experiments suggest that in some Ir complexes an equilibrium between the two types of structure occurs under H_2 pressure.[10–11b] However, the dihydride loses readily H_2 in the absence of H_2 pressure,[10] an indication of the weakness of Ir–H_2 bonding. Finally, the unique hydride in **5** undergoes exchange with the two equivalent hydrogen atoms of the coordinated H_2 at temperature above −20 °C.[15a] If the mechanism involves H–H breaking and formation of a fluxional heptacoordinated complex, the activation energy (13.9 kcal/mol)[15a] would represent the energy barrier for the conversion of the molecular hydrogen complex **5** to a dihydride structure of type **1**.



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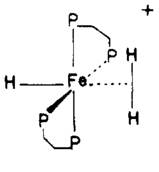

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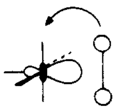
The factors which favor either the dihydride **1** or sideways-bonded hydrogen structure **2** clearly need to be delineated. *Steric factors* may be at work: as a matter of fact stable molecular complexes are found with bulky ligands. On the other hand, the *electronic factors*, related to the nature of the metal and that of the ligands, are also believed to play a role. In this paper, we will successively study, by means of Extended Hückel (E.H.) calculations, molecular hydrogen complexes **2** and the cleavage of H–H bond to form dihydride structure **1**, for M = W, Cr, Fe and L = H^-, CO.

Before analysing the results, let us briefly recall some general features of d^6 ML_5–H_2 interaction which operate both in **1** and **2**, even if it is at a different extent. H–H bond, as any σ bond, can act both as a σ-donor, through interaction between σ_{H_2} and a vacant d orbital on the metal, and as an acceptor by interaction of $\sigma^*_{H_2}$ with a filled metal orbital. In the case of d^6 ML_5 fragment, the main relevant orbitals on the metal center are the empty hybrid orbitals pointing toward the vacant site of ML_5 which interacts with σ_{H_2} (**6**) and the filled *xz* orbital which interacts with $\sigma^*_{H_2}$ (**7**) in a η^2 type coordination (this interaction would be zero in a η^1 complex which has been found to be less favorable[22]). Both of these two-electron interactions are stabilizing, and, as it has been discussed elsewhere,[22] they entail electron transfers between ML_5 and H_2 in opposite directions: H_2 toward M (M ← H_2) in **6** and M toward H_2 (M → H_2) in **7**. Both of these electron transfers weaken the H–H bond since σ_{H_2} is depopulated (as in **6**) or $\sigma^*_{H_2}$ is populated (as in **7**). Finally, note that this rough analysis does not take into account repulsive four-electron interactions between σ_{H_2} and the lower filled MOs of ML_5. In the remaining part of the study, we shall not discuss these four-electron interactions which have been found to be small[22] except for short distances of H_2 approach.



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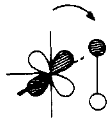

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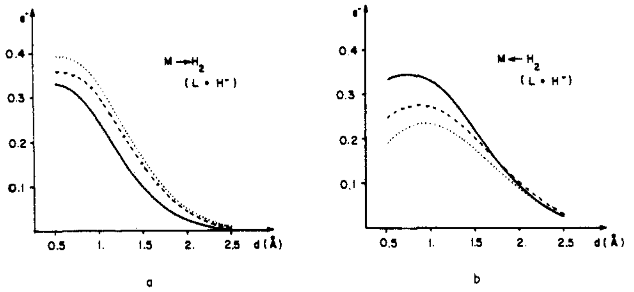

Figure 1. Evolution of the M → H_2 (a) and M ← H_2 (b) electron transfer between WH_5^{5-} (dotted line), CrH_5^{5-} (dashed line), FeH_5^{3-} (solid line), and H_2 as a function of the distance of approach of H_2.

η^2-Molecular Hydrogen Complexes. In the first set of calculations, η^2-H_2 complexes are studied. In these calculations, idealized geometries are used for ML_5 (cis L–M–L angles are equal to 90°), and the H–H bond is frozen to its value in isolated H_2 (0.74 Å). Therefore, our model involves only one geometrical parameter, *d*, the distance between the metal center and the middle of the H–H bond (**3**). Calculations were performed for M = Cr, W, Fe and L = H^-, CO in order to analyze the role of the metal nature and that of the surrounding ligands.

L = H^- (M = Cr, W, and Fe). We first study d^6 hydride fragments CrH_5^{5-}, WH_5^{5-}, and FeH_5^{3-} interacting with H_2, H^- modeling a pure σ-donor ligand. As the metal center is modified, the strength of interactions **6** and **7** as well as the amplitude of the associated electron transfers is changed (Figure 1). Back-donation from M to H_2 (**7**) is favored by high lying diffuse d oribtals, the energy gap between interacting MOs being smaller and their overlap larger. Both factors make W a better donor than Cr which in turn is better than Fe (Figure 1a) for all *d* distances. For the M ← H_2 electron transfer (**6**), the lowering of the metal hybrid orbital decreases the energy gap between interacting MOs but also corresponds to a smaller overlap with σ_{H_2} (less diffuse metal orbitals). At distances inferior to 1.7 Å, the energy factor is dominant (Figure 1b): Fe (energy of the hybrid orbital shown in **6**: $\epsilon_h = -10.22$ eV) is a better acceptor than Cr ($\epsilon_h = -8.88$ eV) which is better than W ($\epsilon_h = -8.41$ eV). The total stabilization energy results from both interactions **6** and **7**; some compensation occurs since a metal which is more favorable to one type of electron transfer is less favorable to the other one. The energy of the molecular complexes as a function of the distance *d* are reported in Figure 2. For all *d* distances, the order of energy stabilization is W > Cr > Fe; that is, it is controlled by the electron-donating capability of the metal fragment. Note that E.H. calculations lead to energy minima for very short

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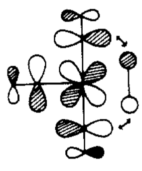
equilibrium distances (d = 0.8 Å). It is more meaningful to consider the stabilization energy obtained for more reasonable distances (between 1.5 and 1.7 Å, values found in **5** and **4**). For d = 1.7 Å, the stabilization energies are between 0.40 (M = Fe) and 0.75 eV (M = W). Finally, the influence of the bending of the M–H bonds lying in the plane of the incoming H_2 has been tested. In the isolated MH_5^{n-} fragments the bond angles are found close to 90°, in agreement with the experimental structure of d^6 $M(CO)_5$ complexes[23] and with previous theoretical calculations.[24] The bending remains small until short distances of approach of H_2 (88 and 85° for d = 1.7 and 1.4 Å, respectively), a result which is consistent with the experimental structures of **4** and **5**.

L = CO (M = Cr, W, and Fe). In the presence of π acceptor ligands, xz is stabilized and delocalized on the ligands by in-phase mixing with π^*_{CO} orbitals (**8**). These effects, which are larger for metal with high lying diffuse d orbitals (W > Cr > Fe), increase the energy gap between xz and $\sigma^*_{H_2}$ and reduce their overlap (despite some secondary in-phase overlap between π^*_{CO} and $\sigma^*_{H_2}$), making the interaction **7** weaker. Consequently, the donating ability of the metal fragment is reduced upon replacement of H^- by CO, this effect being larger in the order W > Cr > Fe. Calculations reported in Figure 3a actually show that in the field of five carbonyl groups the three metals W, Cr, and Fe transfer almost exactly the same amount of electron in $\sigma^*_{H_2}$. The contribution of interaction **7** to the stabilization energy is then expected to be nearly the same for all metals and lower than for L = H^-, especially for M = W and Cr.



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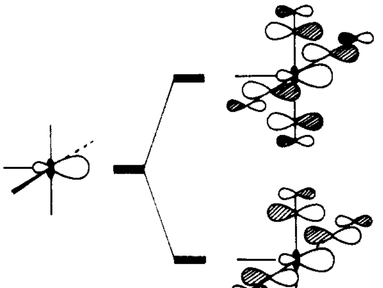
Let us now analyze the interaction **6** responsible for the electron transfer from H_2 to the metal. The metal hybrid orbital involved in **6** interacts with π^*_{CO} orbitals leading to bonding and antibonding combinations (**9** and **10**). Both **9** an **10** can now act as metal acceptor orbitals interacting with H_2. Calculations show that, whatever the metal, M ← H_2 is enhanced by the π–acceptor ligands (Figures 3b and 1b). As it was found for L = H^-, M ← H_2 increases in the order W, Cr, and Fe.



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The energies of the complexes as a function of the distance d (**3**) are reported in Figure 4. A consequence of the deactivation of early metals (W, Cr) toward electron transfer to $\sigma^*_{H_2}$ by carbonyl groups is that H_2 is less strongly bonded to the metal. For instance, for W the stabilization energy at d = 1.7 Å is 0.36 eV for L = CO and 0.75 eV for L = H^- (0.46 vs. 0.67 eV with Cr and 0.39 vs. 0.40 eV with Fe).

Let us now consider complexes such as $(PR_3)_2(CO)_3W(H_2)$ (**4**) which contains both π-acceptor and σ-donor ligands (PR_3). Experimental structure of complex **4** shows that the H_2 molecule is almost parallel to the P–W–P axis. Using the experimental values for d (1.70 Å) and H–H (0.84 Å),[12b] E.H. calculations on model systems **11** and **12** (PR_3 replaced by H^-), actually give structure **11** as being more stable by 2.1 kcal/mol at d = 1.7 Å, the same order of stability being found for any distance of approach. Electron transfer from H_2 to the metal involves the interaction of σ_{H_2} with the orbitals **13** and **14** which are respectively

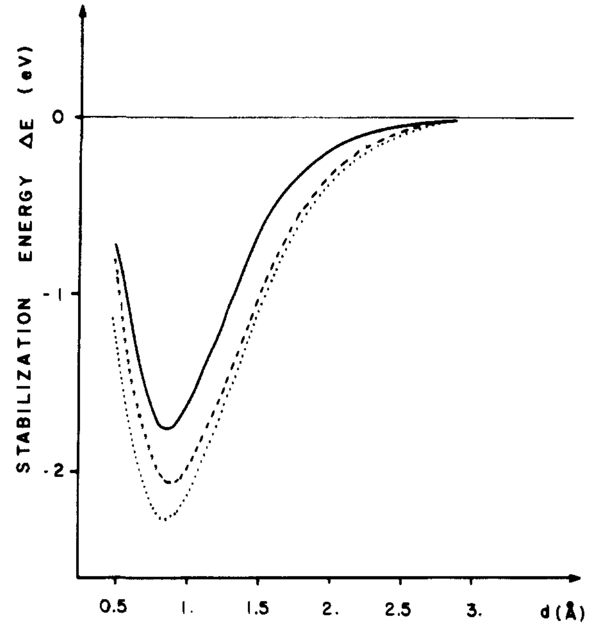

Figure 2. Stabilization energy (in eV) upon H_2 approach (H–H = 0.74 Å) toward WH_5^{5-} (dotted line), CrH_5^{5-} (dashed line), and FeH_5^{3-} (solid line).

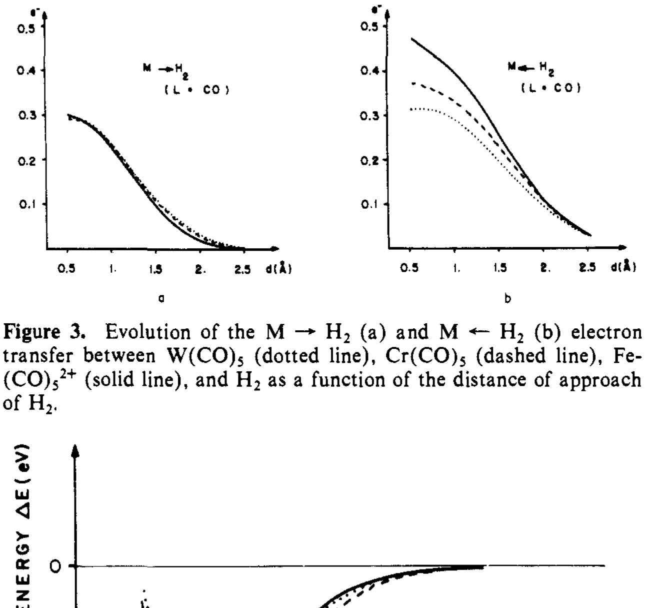

Figure 3. Evolution of the M → H_2 (a) and M ← H_2 (b) electron transfer between $W(CO)_5$ (dotted line), $Cr(CO)_5$ (dashed line), $Fe(CO)_5^{2+}$ (solid line), and H_2 as a function of the distance of approach of H_2.

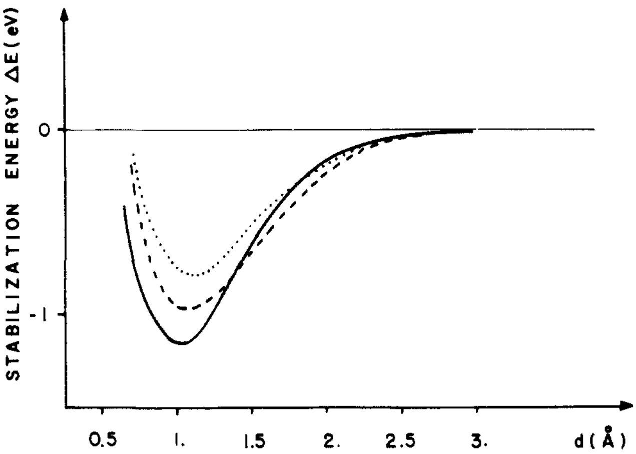

Figure 4. Stabilization energy (in eV) upon H_2 approach (H–H = 0.74 Å) toward $W(CO)_5$ (dotted line) $Cr(CO)_5$ (dashed line), and $Fe(CO)_5^{2+}$ (solid line).

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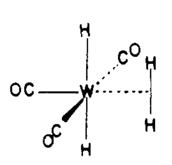

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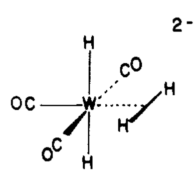

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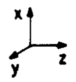

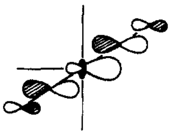

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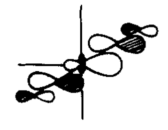

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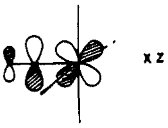
the bonding and antibonding combinations of the hybrid orbital carried out by the metal with the adjacent π^*_{CO} orbitals. Interaction with **13** favors structure **12** because of in-phase secondary overlaps while interaction with **14** favors structure **11** for the opposite reason. Some compensation occurs, but it is finally the interaction of σ_{H_2} with the orbital of lowest energy, **13**, which dominates: a slightly larger M $\leftarrow$ H_2 occurs in structure **12** (0.176 e$^-$ in **12** instead of 0.171 e$^-$ in **11**), thus favoring an H_2 approach parallel to the C–W–C axis (**12**). Consider now the interaction involving $\sigma^*_{H_2}$. In **11**, $\sigma^*_{H_2}$ interacts with xz (**15**), in **12** with yz (**16**). xz is stabilized by one π^*_{CO} orbital and yz by three.



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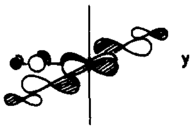

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Therefore, xz is above yz by 0.73 eV; its interaction with $\sigma^*_{H_2}$ is larger, and the M $\rightarrow$ H_2 electron transfer is greater in **11** than in **12** (0.119 and 0.107 e$^-$, respectively), favoring an H_2 approach parallel to H–W–H axis (**11**). The two types of interaction lead thus to opposite conformational preferences, but the latter induces a larger difference. Therefore H_2 is oriented such as to maximize the electron transfer from M to $\sigma^*_{H_2}$, just as a carbene ligand aligns its p acceptor orbital with the M–L bond (L = pure σ-donor ligand) in the $M(CO)_4L(CH_2)$ complex.[25] This result can be compared with recent ab initio calculations on the same complex.[26] In qualitative agreement with these calculations, we have found that both in **11** and **12** the larger electron transfer involves donation from H_2 to the metal: overall increases of electron density at the metal by 0.052 (**11**) and by 0.069 (**12**) electron are found, instead of 0.120 from ab initio calculations. In that sense, the primary interaction[26] in these complexes is that involving σ_{H_2} and the empty hybrid on the metal (**6**). However, our results suggest that the M $\rightarrow$ H_2 transfer which populates $\sigma^*_{H_2}$, is responsible for the greater stability of **11** compared to **12**. In ab initio calculations this electron transfer is very small, and accordingly the energy difference between **11** and **12** is only 0.3 kcal/mol.

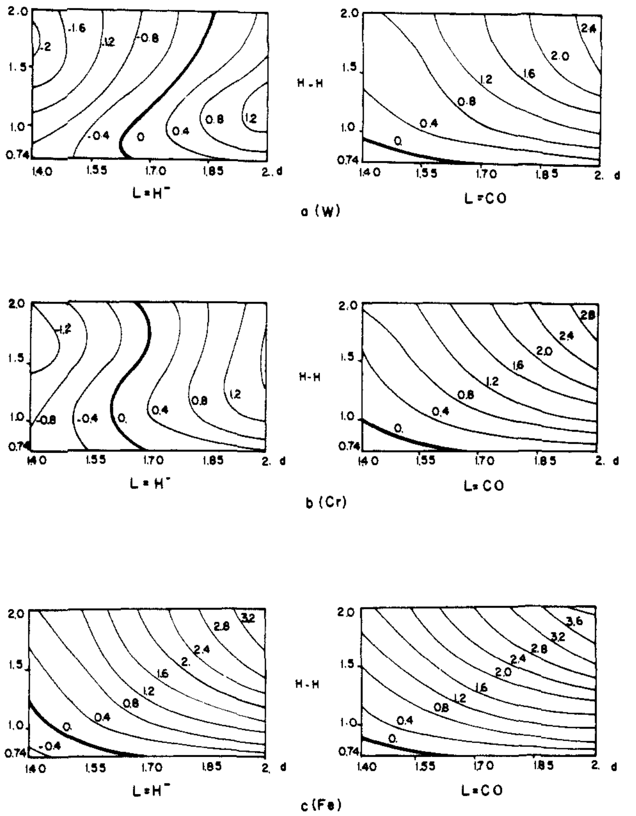

Figure 5. Potential energy surfaces computed for interaction of H_2 with ML_5 metal fragment, as a function of the distance of approach (d) and the length of H–H bond. On the left-hand side, complexes with L = H$^-$ are studied, with M = W (a), Cr (b), and Fe (c). On the right-hand side, H$^-$ ligands are replaced by CO. In each drawing, the potential energy curve corresponding to the energy of the η^2 molecular complex (H–H = 0.74 Å) at d $\simeq$ 1.7 Å is taken as origin and made thicker in order to vizualize the relative ease of H–H breaking upon the nature of the metal and that of the ligands.

Cleavage of H–H bond. Study of H–H bond breaking by E.H. method requires some cautions because this method is known to be inadequate for bond lengths optimization. Since neither the H–H bond in η^2-molecular complexes nor M–H bonds in dihydrides can be optimized, a different strategy has to be used in the context of E.H. calculations. Our choice for the study of dihydride formation is based on the following theoretical and experimental data: (i) Reliable ab initio calculations of H_2 addition to organometallic complexes have shown that H–H cleavage occurs only when H_2 is close to the metal.[27-29] A reason for this is that interaction of type **7** which pours electrons in $\sigma^*_{H_2}$ is large only for short distances of approach;[30] (ii) Experimental structures of η^2-molecular complexes **4** and **5** show that H_2 can approach close to the metal center (1.7–1.5 Å) without being noticeably lengthened. (iii) Finally, in the related problem of C–H activation by metal center, and its eventual breaking, the structures reported so far show that the C–H bond can also approach close to the metal without large stretching.[31] On this basis, we decided to study the formation of dihydride complexes **1** by computing two-dimensional potential energy surfaces, the geometrical parameters being the H–H bond length, varied from 0.74 (molecular complex) to 2.0 Å (dihydride), and the distance d (**3**) between the metal center and the middle of the H–H bond in the range 2.0–1.4 Å. At each point of the surface, the bending of the ML bonds lying in the plane of incoming H_2 has been optimized. Since the E.H. method is not reliable for bond energies, such calculations cannot give a definitive answer about the relative stability of the molecular or dihydride complexes for a *given system*. In the following discussion, we will therefore focus on the trends which are found when the nature of the metal and that of the ligands are changed and not on the absolute energies. The potential energy surfaces computed for the various ML_5 fragments (M = W, Cr, Fe; L = H$^-$, CO) are reported in Figure 5. In each case, the origin of the energy is that of the molecular complex (H–H = 0.74 Å) at a distance of approach $\simeq$ 1.7 Å in order to visualize

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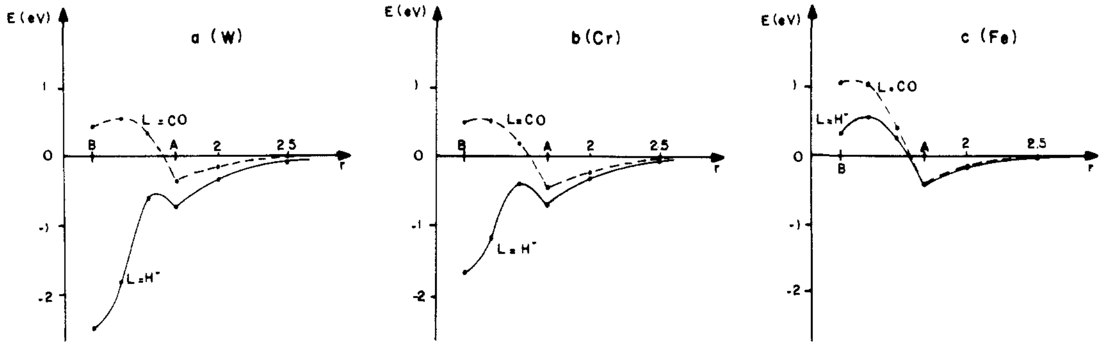

Figure 6. Cuts through the two-dimensional potential energy surfaces calculated for the addition of H_2 to d^6 ML_5 metal fragments (Figure 5), according to a two-step mechanism: approach of molecular hydrogen (H–H = 0.74 Å) toward the metal fragment until d = 1.7 Å (point A), followed by H–H breaking (point B), the M–H distances being kept constant at 1.74 Å. In full line are given the energy curves for L = H^-, in dotted line those for L = CO, for M = W (a), Cr (b), and Fe (c).

more clearly how the ease of H–H cleavage depends on the nature of the metal and ligands.

As the H–H cleavage proceeds, both interactions 6 and 7 are enhanced because σ_{H_2} is destabilized and $\sigma^*_{H_2}$ is stabilized. However, the stabilization of $\sigma^*_{H_2}$ is much larger than the destabilization of σ_{H_2}, and the general shape of the potential energy surfaces reported in Figure 5 can be rationalized by correlating the ease of H–H cleavage with the ability of ML_5 fragment to populate $\sigma^*_{H_2}$, as it has already been found for the addition of H_2 to other metal complexes.[27,30,32] Another characteristic of these surfaces is the fact that even in the most favorable case (M = W, L = H^-), the H–H bond breaking cannot occur at a too large distance of approach of H_2. The reaction mechanism can therefore be approximately described by a two-step reaction path: approach of H_2 rather close to the metal center followed by the H–H breaking. Cuts through the potential energy surfaces which correspond to this two-step mechanism are reported in Figure 6. A molecular η^2 complex is formed at d = 1.7 Å, and, in a second step, H–H is broken keeping the M–H distance constant (1.74 Å), these values being chemically more reasonable than the optimum values given by E.H. calculations.

L = H^- (Figure 5, Left-Hand Side and Figure 6, Full Line Curves). The metal fragment is surrounded by pure σ-donor ligands, which is favorable for M → H_2 electron transfer. Breaking of H–H bond is a bit easier for W than for Cr because d orbitals of W are higher in energy and more diffuse than those of Cr. A large change occurs for M = Fe: despite the nature of the ligands, FeH_5^{3-} resists the formation of the dihydride upon interaction with H_2 much more than WH_5^{5-} and Cr_5^{5-} because Fe atom is by itself a poor electron donor. This trend is in qualitative agreement with the dihydride structures found for ML_5 = $W(PMe_3)_5$,[17] $Mo(PMe_3)_5$,[17] $Cr(P(OMe)_3)_5$,[18a] $W(P(OMe)_3)_5$,[19] and $Re(P(OMe)_3)_5^+$ and with the molecular structure of $(\eta_5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)(H_2)^+$ [15b] and $Fe(H)(dppe)_2(H_2)^+$ [15a] (**5**). Note however that in the latter, steric factors (dppe ligands) may also favor the molecular form.

L = CO (Figure 5, Right-Hand Side and Figure 6, Dotted Line Curves). The replacement of H^- by CO dramatically changes the shape of the potential energy surfaces computed for M = W and Cr because, as it has been shown in the study of η^2 molecular complexes, the carbonyl groups deactivate W and Cr complexes toward electron donation to $\sigma^*_{H_2}$. As a matter of fact, the potential energy surfaces resemble that computed for FeH_5^{3-}, the dihydride formation being much more difficult for L = CO than for L = σ-donor, a trend in agreement with the η^2 molecular structures of ML_5 = $Cr(CO)_5(H_2)$[13,14] and the dihydride structure of $MH_2(PMe_3)_5$ (M = Mo, W)[17] and $MH_2(P(OMe)_3)_5$ (M = Cr,[18] W,[19] and Re^+ [19]).

Complexes with Both σ-Donor and π-Acceptor Ligands (Figures 7 and 8). As we have just seen, pure σ-donor ligands are more favorable than π-aceptor ones for the formation of the dihydride structure **1**. Mixed ligand (σ-donor and π-acceptor) complexes are thus very interesting because the influence of carbonyl groups on the ease of H–H cleavage may depend on its position in the metal fragment. Calculations have been performed in the way described above with complex **17** (two CO cis with respect to H_2 and trans to each other) and **18** (one CO trans to H_2). The potential energy surfaces are reported in Figure 7, the cuts corresponding to the two-step mechanism in Figure 8. Interaction of H_2 with **17** can be made either with H–H parallel to the H–Cr–H axis (Figures 7a–8a) or to the OC–Cr–CO axis (Figure 7b–8b). In the latter, $\sigma^*_{H_2}$ interacts with yz which is deactivated toward electron donation by interaction with the $\pi^*_{CO}(z)$ orbitals, and the breaking of H–H bond is made more difficult than with five-donor ligands (Figures 5b left-hand side and Figure 7b). However, if H_2 approaches parallel to H–Cr–H axis, $\sigma^*_{H_2}$ interacts

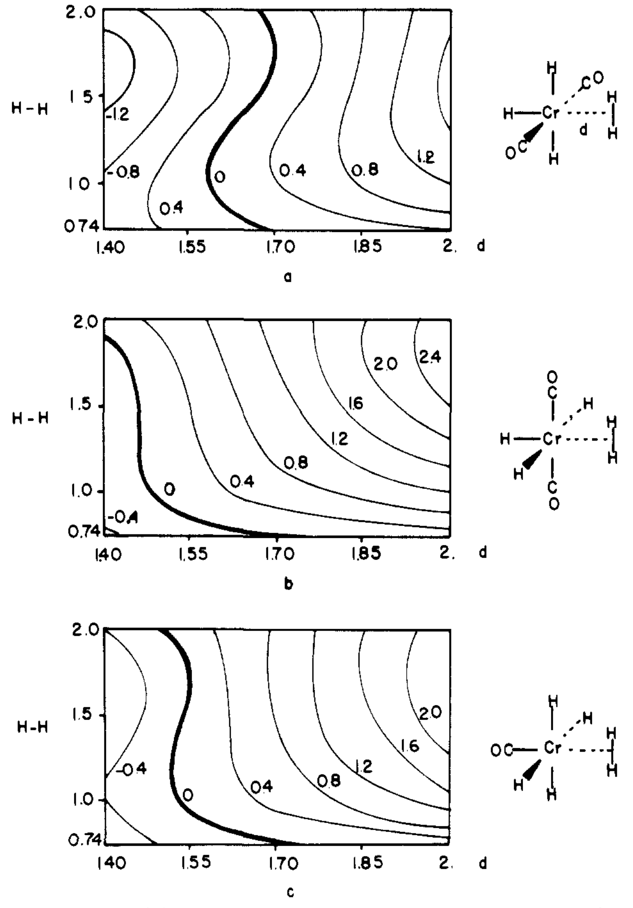

Figure 7. Potential energy surfaces computed for the interaction of H_2 with metal fragments **17** and **18**, as a function of the distance of approach (d) and the length of H–H bond. The energy curve corresponding to the energy of the η^2 molecular complex (H–H = 0.74 Å) at $d \simeq 1.7$ Å is taken as the origin and made thicker, in order to visualize the influence of the various ligands on the ease of H–H breaking.

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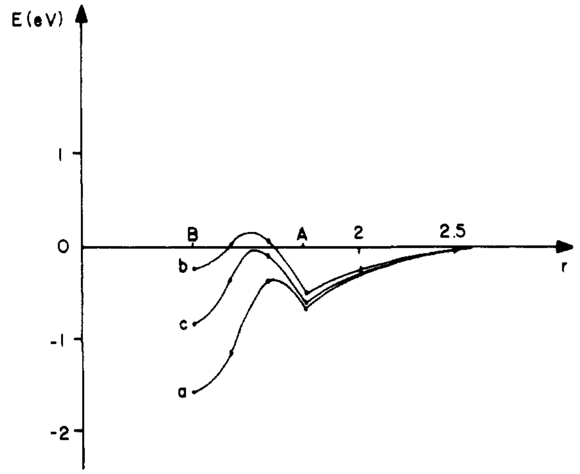
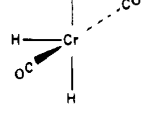


Figure 8. Cuts through the two-dimensional potential energy surfaces calculated for the addition of H_2 to complexes **17** and **18** (Figure 7), according to a two-step mechanism with intermediate formation of a η^2 molecular complex (H–H = 0.74 Å) at d = 1.7 Å. Curves (a) and (b) correspond to the addition of H_2 to **17**, with H–H either parallel to H–Cr–H axis (a) or to OC–Cr–CO axis (b). Curve (c) is associated with the addition of H_2 to **18**.

with xz which is not affected by the carbonyl groups: the potential energy surface (Figure 7a) is almost identical with that computed with five σ-donor ligands (Figure 5b, left-hand side). Therefore, the carbonyl groups in **17** are not efficient in favoring the molecular complex with respect to the dihydride because H_2 can approach parallel to M–σ-donor bonds. The molecular complex can be favored by carbonyl groups cis to H_2 only if π^*_{CO} orbitals interact with both xz and yz. This can be realized by putting three or four carbonyl groups in that position or only two but cis to each other. In complex **18**, CO is trans to H_2, and whatever the way in which H_2 approaches, $\sigma^*_{H_2}$ interacts with a d orbital (xz, yz, or a combination of both) which mixes with a π^*_{CO} orbital. Therefore, the η^2 molecular complex tends to be more favored with a π-acceptor ligand trans to the incoming H_2 than with a pure σ-donor one[36] (Figures 7c and 8c), a trend which is in agreement with the available experimental data: dihydride structure for $M(PMe_3)_5(H_2)$ (M = Mo, W),[17] equilibrium M–η^2-H_2 $\leftrightarrow$ H–M–H in $W(CO)_3(PR_3)_2(H_2)$[12c] (in that complex, H_2 is parallel to the P–W–P axis so that only the carbonyl trans to H_2 favors the dihydrogen structure), and molecular hydrogen complex for $Mo(CO)(dppe)_2(H_2)$.[12c] In the latter, dppe ligands could also be at work in favoring the H_2 form through steric constraint.



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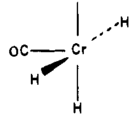

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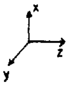

As a conclusion of this study, we have shown that the replacement of pure σ-donor ligand by π-acceptor ones weakens the interaction between d^6 ML_5 fragments and H_2 in η_2 molecular complexes and makes the dihydride formation more difficult because the amplitude of M $\rightarrow$ H_2 electron transfer, through interaction 7, is reduced. Changing a metal with high lying d orbitals (W) in a metal with low lying d orbitals (Fe) also disfavors the dihydride formation. In complexes in which both σ-donor and π-acceptor ligands are present, the latter are effective in stabilizing the η^2-molecular complex with respect to the dihydride one only if the π^*_{CO} orbitals can interact with the d orbital which populates $\sigma^*_{H_2}$. A carbonyl group trans to incoming H_2 always plays that role. Finally, the existence of a new type of bonding between metal fragment and H_2, in which the H–H bond is essentially retained, mainly arises from the stabilization energy associated with H_2 approach before H–H breaking. In d^6 ML_5 complexes, the low lying orbital pointing toward H_2 is empty, and the four electron repulsions are small. Consequently, the two-electron stabilization dominates. The situation may be different for the addition of H_2 with planar d^8 ML_4 complexes in which the z^2 orbital is full, entailing a four-electron repulsion with σ_{H_2} upon H_2 approach. Burdett and Lee[37] have recently analyzed this d^6 vs. d^8 problem by using the method of moments, showing that the d^6 ML_5 complexes are more likely to form η^2-molecular complexes with H_2 than planar d^8 ML_4 ones.

Acknowledgment. Dr. A. Sevin is gratefully acknowledged for helpful discussions. We thank the Ambassade de France in Algeria and the Ministère des Relations Extérieures for financial support. We are grateful to the CIRCE for providing computing facilities.

Appendix

The calculations were of Extended Hückel type, and the weighted H_{ij}'s[33] were used. Idealized geometries were assumed: M–H = 1.75, M–C = 1.95, C–O = 1.14 Å. Unless specified, angles at the metal were taken to be 90° in the ML_5 fragment. The atomic parameters for each metal were taken from earlier work: W,[34] Cr,[35] Fe.[35]

Registry No. CrH_5^{5-}, 103438-03-5; WH_5^{5-}, 103438-04-6; FeH_5^{3-}, 103438-05-7; $Cr(CO)_5$, 26319-33-5; $W(CO)_5$, 30395-19-8; $Fe(CO)_5^{2+}$, 103438-06-8; H_2, 1333-74-0.

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