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Long-Range Interaction between Nonbonded Hydrides: Attractive in the Case of Transition Metals?

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Abstract: Extended Hückel molecular orbital calculations give a positive Mulliken overlap population between cis nonbonded dihydride and trihydrides in transition-metal complexes (i.e., *cis*-$(H)_2Os(CO)_4$ and $CpIr(PH_3)(H)_3^+$). In contrast, isolobal organic systems (CH_4 and D_{3h} CH_5^+, respectively) show no tendency for such a positive long-range interaction. The results are interpreted in terms of variable electron transfer from the symmetry-adapted polyhydride H_n molecular orbitals into those of the metal or organic fragment. The cause of this variation can be traced to the local symmetry properties of the cylindrical-shaped LUMO. The results are consistent with the high fluxionality of polyhydrides as well as the recently discovered phenomenon of quantum mechanical exchange in NMR.

We have recently remarked on the electronic factors dominating the conformation of nonclassical H_2[1] coordinated cis to a hydride on mononuclear and dinuclear metal centers.[2,3] The conformation of H_2 is dominated by a combined interaction of σ^*_{HH} with a metal d orbital and a high-lying M–H σ orbital. The latter, the so-called cis interaction, leads to preferred alignment of the H–H bond with the M–H bond and manifests itself in an unusually high Mulliken overlap population (hereafter MOP) between the closest H center of H_2 and the cis hydride.

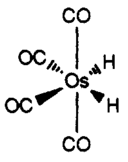
The occurrence of the cis interaction of hydrides has prompted us to investigate the interaction between two or more cis hydride ligands. We were interested in determining whether the effect was peculiar to complexes involving bicoordinated ligands (H_2,[2] ethylene[3]) or if it was a general feature of metal hydride complexes.

Dihydride Complexes

Extended Hückel molecular orbital calculations have been carried out on the known dihydride complex *cis*-$(H)_2Os(CO)_4$,[4] **1**, by using an idealized octahedral structure[5] with Os–H bond lengths of 1.65 Å (H···H distance of 2.33 Å). We have obtained a positive MOP between the H centers of 0.004. Clearly this value does not represent any form of chemical bond (the MOP between the H centers in a nonclassical H_2 complex is typically 0.5), yet it is indicative of some type of positive interaction between H's. The parameters used in the basis set for the hydride ligands in the initial calculation of **1** are actually a rather poor representation of the hydridic character of such H centers; a more suitable set of parameters involves the use of a more diffuse 1s orbital positioned at higher energy.[6] If these more "hydridic" parameters (hereafter Hyd parameters) are used, then the value of the MOP between the hydrides becomes more positive at 0.019 and clearly indicates a significant attraction between the two H centers. Hyd parameters have the effect of enhancing the cis interaction since they raise the energy of the metal hydride bond and make it more diffuse, but the large MOP cannot be an artifact of using such parameters since it also occurs with "normal" H parameters (hereafter Hyn parameters).

Table I. Comparison of Data from the FMO Analysis of **1** (Hyd Parameters) and **2** (Hyn Parameters)

	1	**2**
Frontier Orbital Energy (eV)		
a_1	−9.94	−12.31
b_2	−10.62	−11.40
σ^*	−10.13	−11.88
σ	−12.70	−14.87
Overlap between Frontier Orbitals		
$\langle b_2 \vert \sigma^* \rangle$	0.45	0.47
$\langle a_1 \vert \sigma \rangle$	0.41	0.61
Electron Density		
σ^*	0.95	1.04
σ	1.28	0.90



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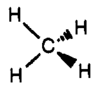

2

Methane, **2**, can be regarded as isolobal to **1** (since $Os(CO)_4^{2+}$ is isolobal to CH_2^{2+}), and one might expect to see similar effects in this "organic hydride." However, the MOP between two H's in **2** is negative at −0.038.[7] This suggests a stark contrast in the bonding of organic and inorganic hydrides. We have also performed the analogous calculation on the octahedral molecule *cis*-$(CH_3)_2Os(CO)_4$ where we find that the MOP between the methylic carbons is small and negative (−0.003). These results verify that the positive interaction obtained is peculiar to transition-metal hydrides.

The movement of the two H centers on a transition-metal complex toward each other generates a nonclassical H_2 complex. This operation has been carried out on **1** by using Hyn parameters in the basis set.[8] Figure 1 shows a plot of MOP between the two H centers as they move along the path shown. At all H–M–H

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(1) See, for example: (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organometallic Chem.* **1988**, *28*, 299.

(2) (a) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. F.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831. (b) Jackson, S. A.; Eisenstein, O. *Inorg. Chem.* In press.

(3) A related effect has been observed for ethylene coordinated cis to hydride ligands: Johnson, T. J.; Huffmann, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073.

(4) Vancea, L.; Graham, W. A. G. *J. Organomet. Chem.* **1977**, *134*, 219.

(5) We have used a regular structure to simplify the analysis. Previous results have shown that distortion around the metal center may change the conformation of nonclassical H_2,[2a] but such observations are probably unimportant with regard to interactions between spherical H 1s orbitals and are not considered here.

(6) For a normal (Hyn) H 1s orbital these parameters are $\zeta = 1.3$ and $H_{ii} = -13.6$ eV, whereas for a more hydride-like center (Hyd) they are $\zeta = 1.0$ and $H_{ii} = -11.6$ eV.[2,3]

(7) This MOP was calculated by using Hyn parameters; if Hyd parameters are used[6] this MOP is still negative at −0.054.

(8) The energy profile for this process is neither presented nor discussed here since the complex is a known dihydride and the closure of the H–H angle is energetically unfavorable.

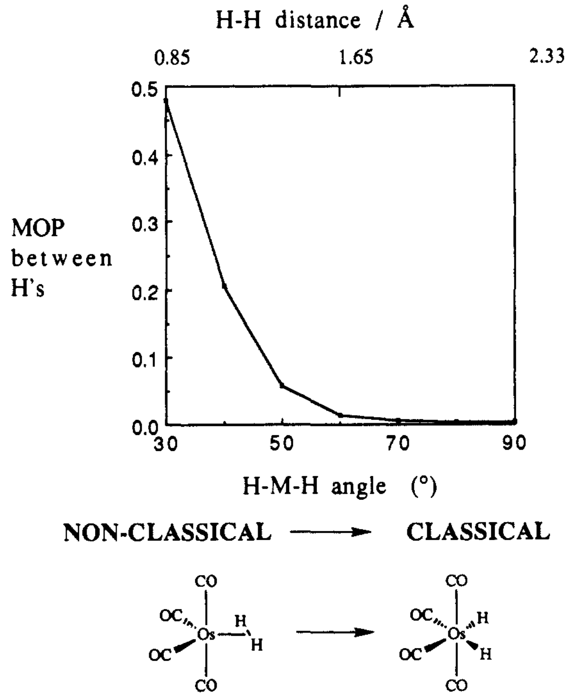

Figure 1. Plot of MOP between the two H's (Hyn parameters) in *cis*-$(H)_2Os(CO)_4$ versus the angle between them.

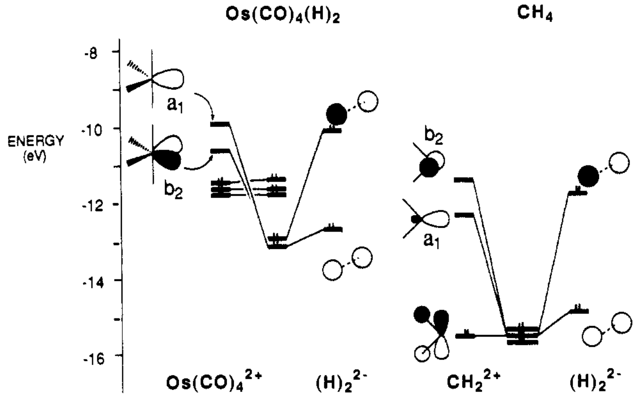

Figure 2. Interaction of the isolobal fragments $Os(CO)_4^{2+}$ (left) and CH_2^{2+} (right) with $(H^-)_2$ to form **1** (Hyd parameters) and **2** (Hyn parameters), respectively. The H···H distance and H parameters vary from **1** to **2** and cause a change in the position of the orbitals of isolated $(H^-)_2$. The three lower metal d-orbitals of $Os(CO)_4^{2+}$ are nonbonding.

angles and H···H distances the MOP is positive. We note a sudden increase in MOP in the range of H···H distances of 1.2 Å which has previously been cited as a limit between classical/nonclassical complexes.[9]

In order to interpret why the inorganic and organic hydrides have opposite interactions between the two "hydrides" we have used a fragment molecular orbital (hereafter FMO) analysis and the isolobal analogy.[10] The $Os(CO)_4^{2+}$ fragment is isolobal with the inorganic fragment CH_2^{2+}; the two fragments have frontier orbitals with similar shapes, symmetry properties, and approximate energies and have the same number of electrons. If these fragments are allowed to interact with $(H^-)_2$ to give **1** or **2**, respectively, then we can compare and contrast the bonding in the two systems. The resulting interaction diagrams are shown in Figure 2.

Both $Os(CO)_4^{2+}$ and CH_2^{2+} have two empty frontier orbitals, a_1 and b_2, which interact with the $(H^-)_2$ σ_g and σ_u orbitals, respectively. Although no real H–H bond exists, we will denote $\sigma_g = \sigma$ and $\sigma_u = \sigma^*$ for the sake of simplicity. The interaction between b_2 and σ^* is similar in both **1** and **2** as demonstrated by the equivalent values of the overlaps between these FMOs (Table I) and the analogous energy gap between b_2 and σ^* in the two cases[11] (Figure 2). The resulting transfers of electrons from σ^* into b_2 are represented by the electron density remaining in σ^*. These are of the same order of magnitude (Table I), σ^* in **2** having only 0.09 electrons more than σ^* in **1**. This small difference originates from additional weak interactions of σ^* with higher orbitals of b_2 symmetry in **1**.

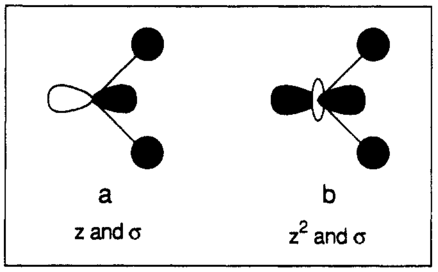

Figure 3. Diagrams showing the difference between the interaction of two separated H ligands with z and z^2 orbitals. In the case of z the overlap is good, but for z^2 the H's lie in the nodal cone and the overlap is poor.

The most striking differences in bonding arise in the interaction between a_1 and σ (Table I). In **2** σ is *less* occupied by 0.38 electrons than σ in **1**. This effect is derived from the large difference in the overlap $\langle a_1|\sigma\rangle$ between the two systems, 0.61 in **2** and 0.41 in **1**. This difference is due to the shapes of the acceptor orbitals. In **2** a_1 is a mixture of s and z, which both overlap well with σ (Figure 3a). In **1**, the analogous a_1 is a mixture of s, z, and z^2, with a large coefficient in z^2. The overlap between z^2 and σ is very small since the H's lie in the nodal cone of the metal orbital (Figure 3b). *It is this fundamental difference which lies at the heart of the contrast between the inorganic and organic systems.* It indicates that the effect is derived from the local topology of the z and z^2 and not from differences in atomic parameters.

Thus, when $(H^-)_2$ interacts with CH_2^{2+}, σ^* keeps more electrons than σ. Conversely, when $Os(CO)_4^{2+}$ interacts with $(H^-)_2$, σ keeps more electrons than σ^*. As a result of this, in **1** more electrons remain in an orbital which is *in phase* between the hydrides, while in **2** more electrons remain in an orbital which is *out of phase* between the hydrides. The fact leads to a net positive MOP between the transition-metal hydrides and a net negative MOP between the hydrogens in the organic system.

It appears that the interaction between the hydride ligands is related in some part to the spherical nature of the H 1s orbitals. By being less directional than other ligands, it allows for some build up of overlap, even if this is small for long H···H distances, between two adjacent hydrides while maintaining a strong M–H bond. This allows for a sharp increase of the MOP between two H centers without having to diminish the M–H overlap. It also means that nonspherical ligands such as alkyls being linked to the metal by a highly directional σ hybrid are not able to build up such long-range alkyl–alkyl positive interactions. This is supported by ^{13}CO NMR studies which have demonstrated scrambling of axial and equatorial CO's in these dihydride complexes which is not present in the analogous dimethyl complexes.[4,12] A related effect has been used to account for the favorable reductive elimination of H_2 relative to dialkyl.[13] This result implies that a nonclassical H_2 species is accessible to dihydride species and that the scrambling and H–H exchange processes may proceed via such an intermediate. Such an observation is supported by the recent observations of tautomeric nonclassical/classical equilibria[14] and nonclassical complexes with intermediate H···H bond distances.[15]

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(11) The energy difference, $E_{\sigma^*} - E_{b_2}$, is 0.49 and −0.48 eV in **1** and **2**, respectively.

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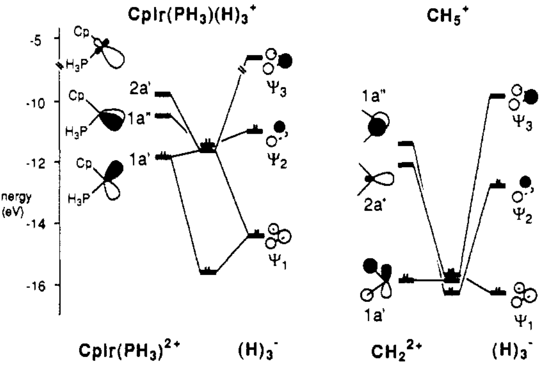


Figure 4. Interaction of the isolobal fragments $CpIr(PH_3)^{2+}$ (left) and CH_2^{2+} (right) with $(H)_3^-$ to form $\mathbf{5}^{hyd}$ and **6**, respectively. The H···H distances and parameters vary from $\mathbf{5}^{hyd}$ to **6** and causes a change in the position of the orbitals of isolated $(H)_3^-$. Note that two of the lower metal orbitals have been removed for the sake of simplicity.

Trihydride Complexes

We have also examined a number of other polyhydride complexes to determine whether such features are present in other ligand fields. There has recently been a large amount of activity in the area of so-called "trihydrogen" complexes. This was provoked, in part, by Burdett's suggestion that a coordinated H_3 ligand might be synthetically accessible.[16] The molecule $CpIr(PR_3)(H)_3^+$ (R = Me, Ph), **3**, was synthesized by Heinekey with this aim in mind,[17] but a neutron diffraction study showed that it was indeed a trihydride,[18] and it was demonstrated that the unusual NMR features observed for **3** were due to quantum mechanical exchange phenomena.[19] Although it is now certain that this species is not a trihydrogen complex we were interested in whether there may still be an interaction between the internal hydride (H_i) and each of the external hydrides (H_e) since this may shed some light on the NMR features.

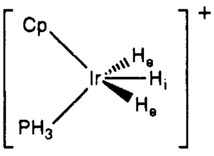
We have used the experimental neutron diffraction data as a basis for the geometry of $CpIr(PH_3)(H)_3^+$, **4**, in extended Hückel molecular orbital calculations in which the metal and the three H's are not coplanar and there is no mirror plane. In **4** the two H_e's are positioned at different distances from H_i. Using Hyd parameters[6] the MOPs between H_i and H_e are large and positive at 0.114 and 0.115. If Hyn parameters are used these values are still significantly positive at 0.032 and 0.048. These values are listed in Table II. There is a large amount of distortion in **4** which renders analysis of the molecular orbitals complicated, and we have carried out calculations on the symmetrical analogue of **4**, i.e., **5**.[5] In **5** all the Ir–H distances are 1.70 Å, and the molecule has a mirror plane bisecting the plane of the $(H)_3$ fragment which is coplanar with the metal. The MOP between H_i and H_e in **5** are of the same order of magnitude as in **4** (Table II), and it is **5** which has been used in the following discussion.

The isolobal analogy of d^6 $(ML_5(H_2)$ with CH_5^+ written as C_{2v} $CH_3(H_2)^+$, **6'**, has been discussed previously.[16] The species CH_5^+ has been postulated on the basis of mass spectrometry experiments. However, reformulating CH_5^+ as D_{3h} $CH_2(H_3)^+$, **6**, which is only 11.7 kcal mol^{-1} higher in energy than **6'**,[20] has the advantage of putting the H centers in a geometry approximately equivalent to that of **5** and allows us to regard **6** as an organic trihydride. Thus $CpIr(PH_3)^{2+}$ is isolobal with CH_2^{2+}. The MOP between H_i and H_e in **6** is 0.019.[21] The H_i···H_e distance in **6** is 1.54 Å, compared to 1.70 Å in **5**. Thus the change in electron density between **5** and **6** is predominantly due to the difference in the interaction with the remaining fragment.

Table II. MOP Data between H_i and H_e for $CpIr(PH_3)(H)_3^+$ In Its Experimental Neutron Diffraction Structure **4** and Its Idealized Structure **5**[a]

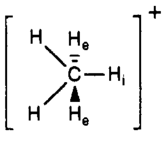
	H_i–H_e	H_i–H_e
Neutron Structure **4**		
distance H_i–H_e (Å)	1.71	1.68
MOP (Hyn) H_i–H_e	0.032	0.048
MOP (Hyd) H_i–H_e	0.114	0.115
Idealized Structure **5**		
distance H_i–H_e (Å)	1.70	1.70
MOP (Hyn) H_i–H_e	0.049	0.049
MOP (Hyd) H_i–H_e	0.146	0.146

[a] Results are given for two sets of parameters, Hyn and Hyd.



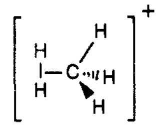
C_S SYMMETRY

5



D_{3h} SYMMETRY

6



C_{2v} SYMMETRY

6'

In both **5** and **6** we see a positive MOP between H_i and H_e which is significantly larger in **5**. A comparison of the interaction diagrams of **5** and **6** is shown in Figure 4. The H_3 symmetry-adapted molecular orbitals, in increasing energy order, are bonding Ψ_1 (1a′), nonbonding Ψ_2 (1a″), and antibonding Ψ_3 (2a′), using the C_s point group common to both **5** and **6**. The two lower orbitals are occupied if H_3 is regarded as a monoanionic fragment. The organic fragment CH_2^{2+} presents three orbitals for bonding, namely, 1a′, 2a′, and 1a″. When this fragment interacts with $(H_3)^-$ to form **6**, the 1a′ orbital remains nonbonding, the 1a″ interacts with Ψ_2 to bond with H_e and 2a′ participates in a typical three-orbital two-electron interaction with Ψ_1 and Ψ_3. In the metal fragment there are three occupied metal orbitals below two empty metal acceptor orbitals. The occupied orbitals undergo four electron destabilizing interactions with H_3^- which do not contribute to any bonding or electron transfer between fragments. Since we are looking for bonding interactions between fragments, we have simplified the diagram by removing two of these orbitals.[22] The bonding is then essentially very simple: the 2a′ empty frontier orbital bonds to H_i, via Ψ_1 and Ψ_3, while the 1a″ bonds to the two H_e via Ψ_2.

Thus the two bonding systems in **5** and **6** are analogous. The orbital Ψ_2 is nonbonding to H_i and will not contribute to any change in MOP between H_i and H_e. In order to explain the MOP between H_i and H_e, therefore, we need only to consider three orbitals: Ψ_1, 2a′, and Ψ_3. The comparison of *three* systems provides the most convenient way of explaining the bonding in these trihydrides. Table III shows data from FMO calculations of **5** with both Hyd (hereafter $\mathbf{5}^{hyd}$) and Hyn parameters (hereafter $\mathbf{5}^{hyn}$) and **6**.

Initially, there are two electrons in Ψ_1 which are transferred into 2a′ which in turn occupy Ψ_3 in a typical three-orbital in-

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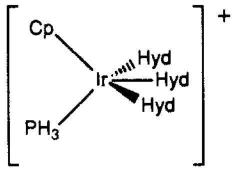
(21) Hyn parameters have been used for calculations on **6**; if Hyd parameters[6] are used for the three "hydridic" H's then the MOP between H_e and H_i is 0.038. These values may be artificially high due to the unusually close approach of H_i and H_e in **6**.

(22) These interactions do have the effect of raising the energy of the molecular orbitals of **5** by mixing with orbitals of the same symmetry. This mixing is most obvious in the HOMO of **5** which is very close to the nonbonding set, but since this does not contribute to the bonding it is not considered in-depth here.

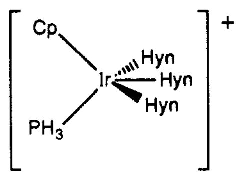
Table III. Comparison of Data from the FMO Analysis of 5^{hyd}, 5^{hyn}, and **6** (Hyn Parameters)

	5^{hyd}	5^{hyn}	**6**
	Electron Density		
ψ_3	0.28	0.73	0.40
ψ_2	1.01	1.40	1.10
ψ_1	1.56	1.61	0.80
	Overlap between Frontier Orbitals		
$\langle\psi_3\|2a'\rangle$	0.03	0.03	0.40
$\langle\psi_2\|1a''\rangle$	0.30	0.27	0.72
$\langle\psi_1\|2a'\rangle$	0.40	0.37	0.39
	MOP between Central Atom and H_i and H_e		
H_e	0.43	0.46	0.59
H_i	0.38	0.43	0.70
	MOP between H_i and H_e		
	0.146	0.049	0.019
	Energy (eV)		
ψ_3	−5.7	−10.6	−9.8
ψ_2	−11.0	−13.4	−12.8
ψ_1	−14.4	−15.6	−16.2

teraction. Both of these processes weaken H_i and H_e interaction and are dependent on the overlaps between the frontier orbitals and their energy differences. In **6** the overlaps $\langle\Psi_1|2a'\rangle$ and $\langle\Psi_3|2a'\rangle$ are strong, and there is a large amount of electron density transferred into Ψ_3 (0.40) from Ψ_1 where only 0.80 electrons remain. Both of these effects contribute toward H_i–H_e interaction weakening (i.e., a small MOP). Both 5^{hyd} and 5^{hyn} show very small $\langle\Psi_3|2a'\rangle$ overlaps compared to $\langle\Psi_1|2a'\rangle$ and thus less electron density transferred into Ψ_3. More electrons remain in Ψ_1 (1.56 in 5^{hyd} and 1.61 in 5^{hyn}), and a strong positive interaction is present between H_i and H_e in **5** relative to **6**. The difference in overlaps between the organic and inorganic fragment acceptor orbitals and Ψ_1 and Ψ_3 is derived from the same effect as described above for the dihydride (Figure 3); it is a function of the presence of d orbital participation in the 2a′ acceptor orbital and the fact that the H centers are located in the nodal plane of the metal orbital.



5^{hyd}



5^{hyn}

The change in H parameters from 5^{hyd} to 5^{hyn} results in a large variation in electron transfer but not in overlap (Table III). This arises from the change in the position of the trihydride energy levels, especially Ψ_3, which changes the magnitude of any electron transfer. This means that electron transfer from 2a′ to Ψ_3 is much less important for trihydrides with higher lying Ψ_3 (0.28 electrons for Ψ_3 for Hyd parameters with a high-lying Ψ_3 compared to 0.73 for Hyn parameters with a lower lying Ψ_3). As expected more electronegative centers (Hyn) tend to accumulate electrons into deeper orbitals. This explains why the H_e···H_i MOP is higher in 5^{hyd}.

In trihydrides it appears that there should always be a significant number of electrons remaining in a very deep hydride bonding orbital (Ψ_1), and thus a long-range attraction should occur between the cis nonbonded hydrides. The extent of this interaction depends on the amount of electron transfer from Ψ_1 into Ψ_3.

The electron density in the nonbonding Ψ_2 orbital also shows a large change between the organic and inorganic trihydrides. In **5** the most electron density lies in the bonding Ψ_1 orbital, but in **6** the nonbonding orbital has the highest electron density. This does not contribute to the cis hydride interaction but manifests itself in a stronger bond (a higher MOP) from the carbon to the central hydrogen in **6**, where Ψ_1 is dominating, compared to a weaker bond from metal to the central hydride in **5** where Ψ_2 dominates (Table III).

Table IV. Extended Hückel Parameters Used in Calculations

		H_{ii} (eV)	ζ_1	ζ_2	c_1	c_2
Os	6s	−8.17	2.452			
	6p	−4.81	2.429			
	6d	−11.84	5.571	2.416	0.63719	0.55980
Ir	6s	−8.60	2.500			
	6p	−4.90	2.200			
	6d	−12.17	5.796	2.557	0.66982	0.58600

[a] *c* is the expansion coefficient in the double ζ-wave function.

Our results show positive interactions between adjacent hydrides in **5**. Such a result is consistent with the large amplitude anisotropic thermal motion of the hydrides in the H···H direction (ca. 0.03 Å) in the neutron structure of **3**[18] which suggests that a structure with shorter H···H distances is thermally accessible. The same positive interactions might be expected for other analogous trihydride species.[23]

Conclusions

We conclude that although isolobal "organic hydrides" may show no positive interaction between adjacent hydrogens, there might always be a positive long-range interaction between cis nonbonded hydride ligands coordinated to a metal center. We have demonstrated that this effect is present in both cis dihydride and trihydride complexes. This does not imply that such transition-metal hydrides are nonclassical, in the sense of a weak bond between the hydrides, but merely that the hydrides are "aware" of each others presence. Such a result is not found with ligands other than hydrides, such as alkyls. The unique behavior of hydrides is associated with the spherical nature of the 1s orbital of hydrogen which results in a good overlap between transition-metal fragments and polyhydride ligands as well as within the polyhydride set. These nascent bonds between hydrides should facilitate the exchange processes which are so often observed in dihydride[4,12,14,15] and trihydride complexes.[14,23,24] Such a process might also have implications in the quantum mechanical exchange which has been invoked to explain the unusual NMR features of some trihydride complexes,[19] with the caveat that our results are qualitative and cannot be linked in a quantitative manner to NMR data or the activation energies of exchange processes.

The difference between "organic" and "inorganic" hydrides is derived from a reversal in the occupation of H_n polyhydride orbitals. In organic hydrides the orbital which is *out of phase* between adjacent hydrides is more occupied, whereas in inorganic hydrides more electrons occupy that orbital which is *in phase* between adjacent hydrides. The difference in behavior between the two species cannot be understood in terms of the isolobal analogy. We have to trace it back to the local symmetry properties of the cylindrically shaped LUMO. In inorganic fragments this orbital is predominantly z^2, while in organic fragments it is mostly z. The presence of the nodal cone in z^2 contributes to a considerable decrease in overlap between the acceptor orbital and the symmetry-adapted orbital of H_n. We have demonstrated that this causes more electrons to remain in orbitals which are bonding between cis hydrides in inorganic compounds.

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Appendix

The calculations have been carried out by using the extended Hückel method with the weighted H_{ij} formula.[25] The idealized octahedral structure of **1** assumed Os–C, C–O, and Os–H distances of 1.92, 1.14, and 1.65 Å, respectively.[26] The geometry of **5** was adapted from ref 18 and has Ir–Cp(center), Ir–P, and Ir–H distances of 1.85, 2.24, and 1.70 Å, respectively, with Cp(center)–Ir–P and P–Ir–H angles of 120° and cis H–Ir–H angles of 60° with all three hydrides lying in a plane perpendicular to the Cp(center)–Ir–P plane. All the organic molecules and ligands have standard bond lengths and angles.[27] The parameters for Os and Ir are given in Table IV.

Note Added in Proof. In order to verify that the difference in C–H and M–H distances were not influencing the difference between organic and inorganic hydrides we have carried out calculations on SiH_4 and SiH_5^+ (Si–H = 1.40 Å). The results are very similar to the CH_4 and CH_5^+ cases, respectively.

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Fused and Linked Deltahedral Clusters in the Chemistry of the Group 13 Elements

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Abstract: The electronic requirements associated with the linking and fusion via vertex, edge, and face of main group deltahedra are examined by using molecular orbital and tight-binding ideas. The focus is on the chemistry of borides and gallides. For the vertex-linked case it is shown how the traditional ideas of a mixture of multicentered intradeltahedral bonding and localized interdeltahedral bonding naturally fall out of an energy band model. The electron-counting rules for fusion turn out to be considerably more complex than those previously developed for their transition-metal analogues. Especially the interactions between orbitals on atoms not formally included in the fusion process need to be considered. As a result the electron-counting rules are often dependent upon the identity of the deltahedron itself and whether is of the closo, nido, or arachno type. The rules are used to organize the structures of a number of solid-state borides and gallides. A new rule is discovered concerning the electron count per group 13 atom found in extended solid-state structures. It appears that no deltahedral units are found in solids where the number of electrons per deltahedral boron or gallium atom exceeds 3.5. In all materials where the electron count is higher, structures containing six-membered rings or other open structures are found. The result is very different from that found in molecular boranes, where no such restriction occurs. The difference is attributed to the greater structural versatility of the solid-state. Some of the electronic reasons behind the difference between boron and gallium structural chemistry are explored.

Introduction

Chemists have had a long-standing interest in the structures and reactivity of atomic clusters, both as in small molecules and as the building blocks of infinite solids.[1,2] The discovery of the correct way to count electrons[3] and the development of the isolobal analogy[4] provided dramatic advances in our understanding of these systems and provoked several studies[5-8] of why such schemes work. Today we have sets of rules which are capable of giving the electron counts favored for polyhedra and especially deltahedra of various types.[9] Much of the attention in this field has centered around transition-metal-based polyhedral molecules, and the recent topological electron-counting schemes of Mingos[5b,c] and Teo[7] are largely concerned with molecules containing elements from this part of the periodic table. We will see, however, that these rules do not work in general when applied to fused boron or gallium deltahedra, the topic of this paper.

In extended solid-state arrays the clusters will be joined together to build up the structure. **1**–**4** show some one-dimensional examples of the different ways in which the solid may be assembled. **1** contains *linked* polyhedra but in **2**–**4** the polyhedra are *fused* together. In the latter, although the octahedron is clearly visible, the repeating unit of the structure is a smaller fragment: B_3, B_4, and B_5 for face, edge and vertex sharing, respectively. In two and three dimensions these building blocks may be linked or fused in turn to give an enormous variety of structures. The majority of the known examples contain frameworks made up of main-group atoms. That of CaB_6[10] contains B_6 vertex-linked octahedra (**5**) and that of KGa_3,[11] Ga_8 dodecahedra (**6**) linked via gallium atom

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