(the use of excess base) and the generally greater insolubility of the 1:2 adducts. Preliminary work in our laboratory indicates that the 1:1 adducts also predominate for trihaloorganotin compounds, and thus it can be stated that *in general organotin halides form predominantly 1:1 adducts in solution.* We believe that it is also significant that in addition to the formation of small concentrations of 1:2 adduct (depending of course upon the ratio of acid to base), a third equilibrium is very likely present. The most reasonable candidate for this equilibrium at present is the formation of the associated 1:1 adduct. Finally, it is significant that the equilibrium constants for the formation of the 1:1 adduct are rather severely dependent upon the size of the substituent.

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Registry No. $(CH_3)_2SnCl_2\cdot TPPO$, 68307-52-8; $(CH_3)_2SnCl_2\cdot$pyridine *N*-oxide, 39529-39-0; $(CH_3)_2SnCl_2\cdot Bz_2SO$, 22761-64-4; $(CH_3)_2SnCl_2\cdot 2$ TPPO, 20506-00-7; $(CH_3)_2SnCl_2\cdot 2$-pyridine *N*-oxide, 20572-80-9; $(CH_3)_2SnCl_2\cdot 2Bz_2SO$, 22638-29-5; $(CH_3)_2SnCl_2\cdot 2Ph_2SO$, 39529-46-9; $(CH_3)_2SnCl_2\cdot 2Me_2SO$, 19718-02-6; $(CH_3)_2SnCl_2\cdot DMA$, 108696-00-0; $(CH_3)_2SnCl_2\cdot MeCN$, 108696-01-1; $(CH_3)_2SnBr_2\cdot TPPO$, 108696-02-2; $(C_2H_5)_2SnCl_2\cdot TPPO$, 61646-57-9; $(C_3H_7)_2SnCl_2\cdot TPPO$, 108696-03-3; $(C_4H_9)_2SnCl_2\cdot TPPO$, 57220-48-1; $(C_4H_9)_2SnBr_2\cdot TPPO$, 108696-04-4; $(C_6H_5)_2SnCl_2\cdot TPPO$, 33887-61-5; $(t\text{-}C_4H_9)_2SnCl_2\cdot TPPO$, 108696-05-5; $(CH_3)_2SnCl_2$, 753-73-1; $(CH_3)_2SnBr_2$, 2767-47-7; $(C_2H_5)_2SnCl_2$, 866-55-7; $(C_3H_7)_2SnCl_2$, 867-36-7; $(C_4H_9)_2SnCl_2$, 683-18-1; $(C_4H_9)_2SnBr_2$, 996-08-7; $(t\text{-}C_4H_9)_2SnCl_2$, 19429-30-2; $(C_6H_5)_2SnCl_2$, 1135-99-5; $(CH_3)_2GeCl_2$, 1529-48-2; $(CH_3)_3SnCl$, 1066-45-1; $(C_2H_5)_3SnCl$, 994-31-0; $(C_3H_7)_3SnCl$, 2279-76-7; $(C_4H_9)_3SnCl$, 1461-22-9; $(C_6H_5)_3SnCl$, 639-58-7; $(CH_3)_3SnBr$, 1066-44-0.

Bridging Hydrides vs. Polyhydrogen Units: The Importance of Electron Count

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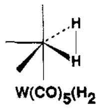
The electronic structure of $(ML_x)_yH_{n-y}$ complexes are explored where the metal and hydrogen atoms form a polynuclear cluster with *n* vertices. A special case of this type of molecule is the recently characterized class of dihydrogen complexes such as $Cr(CO)_5(H_2)$ with $n = 3$ and $y = 1$, based on the triangle. Fragments typified by $V(CO)_5^-$ and $Co(CO)_3^-$, which each contain an empty frontier orbital, are isoelectronic with H^+ and may be built into clusters which have a total of two skeletal electrons. The triangle, tetrahedron, square, trigonal bipyramid and octahedron are investigated. There is a class of complexes predicted with *n* vertices with good HOMO–LUMO gaps of the type *trans*-$(ML_x)_2H_{n-2}$ for deltahedra with $n = 5$–7, which have a total of 34 valence electrons and a planar $(n - 2)$ gon of cyclically bound hydrogen atoms. These structures are linked geometrically to a set of analogous 30-electron complexes with $(n - 2)$ bridging hydrides of which several examples have been characterized. A model that uses only one empty frontier orbital on each of the transition-metal-containing fragments, while successful in understanding the structures of many of these species, is restrictive in that it does not allow access to other geometries for the coordinated hydrogen oligomer. Inclusion of other fragment orbitals shows low-energy pathways between closed and open H_n geometries and the stability of the square over the tetrahedron for the hypothetical species $Co_2(CO)_6H_2^{2-}$.

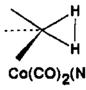
Introduction

Recently, several examples of a new class of species, namely, metal–dihydrogen complexes 1 and 2, have been synthesized.[1-15] We will write such species as $ML_n(H_2)$ to distinguish them from the conventional hydride ML_nH_2. Such (H_2) complexes have received some theoretical attention.[16-24] All of these are isoelectronic (in the broad



$W(CO)_5(H_2)$
$W(CO)_3(PR_3)_2(H_2)$*
*H-H=0.84Å

1



$Co(CO)_2(NO)(H_2)$
$Fe(CO)(NO)_2(H_2)$

2

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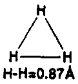
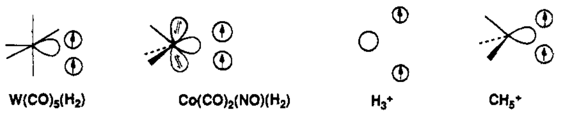
sense of the term) with the known molecule H_3^+ (**3**) in that there is one empty frontier orbital on the metal fragment analogous to the one empty in H^+. With two electrons in this collection of three orbitals, a closed three-center bonding structure is stabilized.



3

4 shows the local relationships between some of the known examples with not only H_3^+ but also the mass spectrometer molecule CH_5^+.

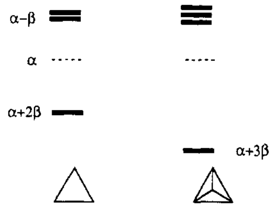


4

Notice that each cyclic three-center system is associated with one pair of electrons. This is in accord with simple theoretical ideas[25,26] which indicate stability for closed three-center bonding for two electrons but open arrangements for three and four electrons. The purpose of this paper is to explore some of the electronic requirements for stabilizing polyhedral hydrogen-containing molecules in general by extending these simple arguments to view the stability of the tetrahedron, octahedron, and pentagonal bipyramid, in which hydrogen atoms alone will populate some of the vertices. The details of the computations are given in the Appendix. We will see how the molecules that are generated are related to known hydrogen-containing species. Clusters of hydrogen atoms H_n^+ up to quite large n, have been known from mass spectrometer studies for many years,[27] and so the stability of such systems is in principle established. Theoretical studies on some of these have been carried out[28] to investigate their geometry and stability. H_5^+ for example is predicted to have a spiropentahydrogen geometry.

The Tetrahedron

The level structure for the triangle and the tetrahedron are shown in **5** in terms of the parameters of simple Hückel theory.[29]



5

Both units possess a single bonding level with a degenerate set of antibonding levels. The stability of the triangle for two electrons (H_3^+) is understandable from the level diagram and as we have noted provides a rationale for the stability of some of these metal dihydrogen complexes. For the tetrahedron a gap exists for the configuration appropriate for H_4^{2+}, and species with three or four electrons are expected to be Jahn–Teller unstable.

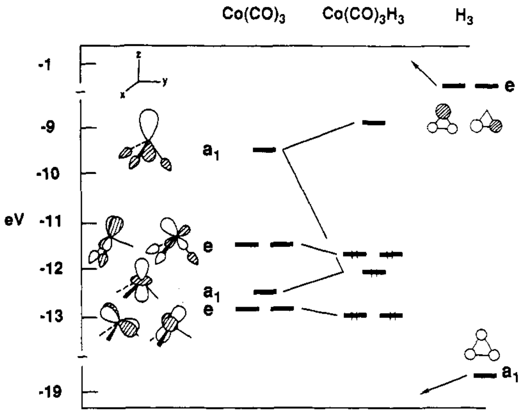
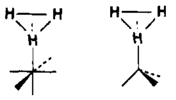


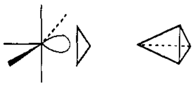
Figure 1. Assembly of the molecular orbital diagram for Co(CO)$_3$(H$_3$) from those of fragments.

If $W(CO)_5(H_2)$ and $Co(CO)_2(NO)(H_2)$ are isoelectronic with H_3^+, then the molecules $V(CO)_5(H_3)$ and $Co(CO)_3(H_3)$ (**6**) are two hypothetical species which are isoelectronic with H_4^{2+} by using the ideas of the isolobal analogy.



6

This relies on the presence of a single empty potent orbital on the metal fragment which may replace the single empty 1s orbital of H^+. In other words in this description $Co(CO)_3^-$ and $V(CO)_5^-$ are isolobal with H^+. **7** and **8** show an approximate way to view these structures, which emphasizes this relationship to the H_4^{2+} tetrahedron.



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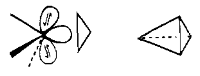
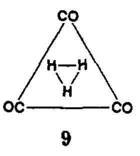


8

The analogy relies upon the lone-pair nature of two of the frontier orbitals in **8** and the potency of the third. This could be a good way to view this system. On geometrical grounds, the H_3 triangle, with its short intermolecular connections, is set up to overlap much more strongly with the one fragment frontier orbital of a_1 symmetry pointing along the figure axis than any of the others. Figure 1 shows the results of molecular orbital calculations on $Co(CO)_3(H_3)$, assembled from $Co(CO)_3$ and H_3 units, which confirm this rather simple picture. Notice the good HOMO–LUMO gap at 2.8 eV. The most stable conformation is calculated to be that where the coordination of the metal is roughly octahedral (as in **9**), i.e., where the planes of carbon and hydrogen atoms are staggered.



9

An alternative way to regard this structure of course is by visualizing an H_3^+ unit as a simple two-electron donor ligand to give an 18-electron count at the metal. In this case **8** would be isoelectronic

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(29) If every vertex of a graph is connected to every other, a complete graph results. The eigenvalue spectra of such graphs are very simple in this case. For the n-vertex structure using the isomorphism between graph theory and Hückel theory, there is a single bonding orbital and a collection of $n - 1$ exactly degenerate antibonding orbitals.

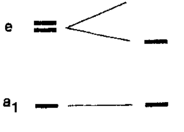
with many other saturated tetrahedral complexes.

There is a small amount of stabilization of the metal e set forming the HOMO by the unoccupied e pair of H_3^+ and also some destabilization of the occupied $Co(CO)_3$ a_1 orbital. The two lone pairs in **8** may be associated with the occupied e pair largely located on the metal in Figure 1. The fact that these energy changes on compound formation are small allows such a description. In this sense the picture is very similar indeed to that of the coordination of H_2 described elsewhere[16] and illustrated in **4** where this time a three- rather than four-orbital bonding picture is a good one.

It is important in (H_2) complexes to discourage extensive mixing of the $\sigma^*(H_2)$ orbital into the occupied metal-located orbitals.[16,19–22] Otherwise H–H fission will occur with formation of the dihydride. One way this may be achieved is to ensure the presence of good π-acceptors coordinated to the metal. Best of all we can replace the CO ligand by the stronger π-acceptor NO. In several complexes this leads[16] to a stronger computed $M-(H_2)$ bond. In complexes containing cyclic H_3 a similar problem obviously exists. This may be overcome by analogously avoiding excessive admixture of the antibonding e pair of orbitals of the H_3 fragment into the metal-centered orbitals. In a similar way we suggest that the stability of **8** may be enhanced by replacing a CO by NO (and therefore Co by Fe), a result supported by a computations. On a more general note, perhaps the best way to completely remove the destabilizing effect of mixing with the $\sigma^*(H_2)$ orbital is to ensure that there are no electrons in these π-donor metal-located orbitals. Is it possible perhaps to make (H_2) compounds with early-transition-metal systems?

The analogy between the energy levels of H_n units and those of the π systems of conjugated hydrocarbons is a useful one.[25] Thus notice that the molecule also has close similarities to a cobalt carbonyl cyclopropenium complex. This species may in turn be viewed either as a complex of $Co(CO)_3^-$ with a cyclopropenium cation or as a nido-trigonal bipyramid isoelectronic with tetrahedrane or $Co_4(CO)_{12}$ by using Wade's rules and Hoffmann's isolobal analogy.

We can investigate the distortion of the H_3 complex as shown in **10**, which leads eventually to a species containing a hydride and a dihydrogen molecule. **11** shows the energy level changes from the results of a computation. Clearly the higher energy e set has split into two. One component has been stabilized as a result of interaction with the σ^* orbital of the incipiently bound (H_2) molecule. The other component of the occupied e pair is considerably destabilized as the distortion proceeds since it becomes a M–H σ^* orbital. A simple way of describing the structure is as shown in **12**. Our extened Hückel calculations will not accurately give us the energetics of such a distortion, but with two fewer electrons than in $Co(CO)_3(H_3)$ the distortion may be envisaged as a Jahn–Teller one. In this case a species isoelectronic with $Mn(CO)_3H(H_2)$ is produced with a vacant coordination site into which points an empty orbital. Coordination of another H_2 is now possible, and indeed the pseudooctahedral 18-electron species $Cr(CO)_4(H_2)_2$ is known.[12]



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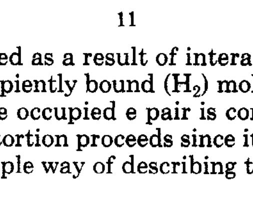

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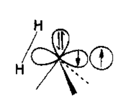
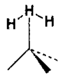


12

A more important distortion is toward an open H_3 unit, **13**. **14** shows a molecular orbital diagram for such a species. There is extensive mixing of Ψ_2 of the H_3 unit into occupied metal-centered orbitals as a direct result of the small energy separation between the two. This level is a nonbonding orbital, and because of its nodal properties its population via this route stabilizes the metal–(H_3) complex without weakening the H–H linkages, in contrast to the similar process involving higher energy orbitals described above for cyclic (H_3) or (H_2) complexes. Notice that one component of the ML_3 fragment e set has been considerably stabilized as a result. Our simple one-electron calculations show an energy difference of about 35 kcal/mol for the open and closed forms of $Co(CO)_3(H_3)$. The open form is of lower energy. From the nature of the computations this difference is certainly not a reliable estimate even as to the sign since bonds have been broken. All we can say from our calculations is that the two isomers are probably close in energy.



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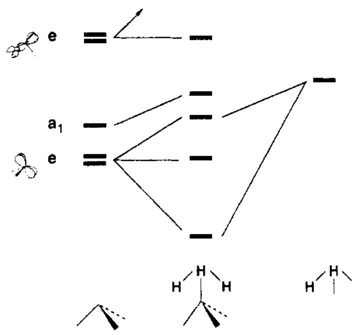
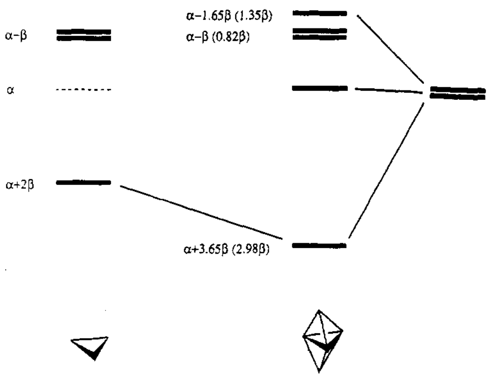


14

We may ask why the simple model concerning these polyhedral molecules shown in **7** and **8** is not good enough to view these species in general. It is just that an approach which only uses the a_1 orbital of the fragment is too much of a simplification. Although it allows a rationale for the stability of the polyhedral species, other geometries naturally involve other available frontier fragment orbitals.

The Trigonal Bipyramid

The energy levels of a trigonal bipyramid may be generated from those of a planar H_3 unit and H_2 as in **15**. The diagram differs from those of **5** in that it contains a single nonbonding orbital. The trigonal bipyramid could then be stable for two or four electrons (H_5^{3+} and H_5^+, respectively). We note that high quality calculations for H_5^+ indicate[14] that a distorted form of the spiro structure **16** is most stable.



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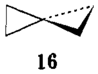
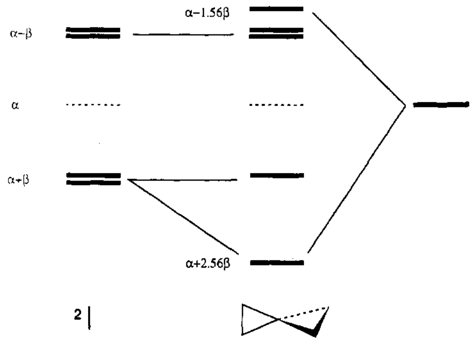


16

17 shows the generation of an orbital diagram for the D_{2d} (undistorted) spiro arrangement. Since the coordination numbers in the two structures are different, there is a problem in relating them energetically. A common solution[26] in such cases is to set the second moment, $\mu_2 = \sum_i \epsilon_i^2$, equal in the two cases. The $\{\epsilon_i\}$ are the energy levels of the molecule. Thus the energy levels in parentheses in **15** are adjusted to have the same μ_2 as those in **17**. As can be seen for H_5^+, the spiropentahydrogen geometry has a lower stabilization energy (7.12β) than the trigonal bipyramid (5.96β) but the converse is true for H_5^{3+} (5.12β and 5.96β, respectively).



17

Drawing the analogy between a $Co(CO)_3^-$ unit and H^+, the species of $Co_2(CO)_6H_3^-$ (**18**) is isoelectronic with H_5^{3+}.

18

It is interesting to investigate its electronic structure. Figure 2 shows the construction of a molecular orbital diagram for **18**, which contains an H_3 triangle with close H–H distances, from that of $Co_2(CO)_6$ and H_3. The M_2L_6 dimer itself has been studied[30] by Summerville and Hoffmann, and the $M_2L_6H_3$ and $M_2L_4H_4$ structures containing bridging hydrides have been studied by Dedieu, Albright, and Hoffmann.[31] They also studied the $M_2L_6H_5$ species, but here their concern lay in designing a molecule which combined both M–H bonding and H···H nonbonding distances. (The species $H_5Fe_2(CO)_6^{3+}$ was a suggestion, although they also felt that the molecule with four more electrons was a possibility. We return to this point below.) Here in the systems we shall study we deliberately wish to let the hydrogen atoms come together. Our calculations for 34-electron $Co_2(CO)_6(H_3)^-$ containing an H_3 triangle with an H–H distance of 0.87 Å (and an M–H distance of 1.755 Å) show a significant stabilization of the conformation actually shown in **18**, in contrast to the small structural preferences for $Co_2(CO)_6$ itself. Dedieu et al.[31] found a similar conformational stabilization for the (known) $M_2L_6H_3$ complex with bridging hydrides and four electrons less. (Examples include the 30-electron molecule[32] $Os_2(PMe_2Ph)_6H_3^+$.) The orbital picture for **18** in Figure 2 is very similar to that for the one depicted for $Co(CO)_3H_3$ in Figure 1. The symmetric e′ pair arising from the metal–metal interaction is stabilized by overlap with the H_3^+ e′ levels, and there is some destabilization of the occupied symmetric combination of metal a_1 orbitals. The largest interaction is between the a_1' level of the H_3 moiety and the corresponding in-phase combination of unoccupied a_1 $Co(CO)_3$ frontier orbitals. **19** shows an approximate way to describe the structure which highlights the analogy with H_5^{3+} and with **8**. This is a rather striking example of the use of the fragment formalism and the isolobal analogy. Notice the good HOMO–LUMO gap in Figure 2 at this electron count, computed to be 2.3 eV. The e′ species metal fragment levels are a little depressed on formation of the complex but basically remain as lone pair orbitals in accord with the description in **19**. Again in this geometry the tightness of the H_3 triangle keeps the interaction with the metal a_1 orbital high but that with the metal e orbitals low.

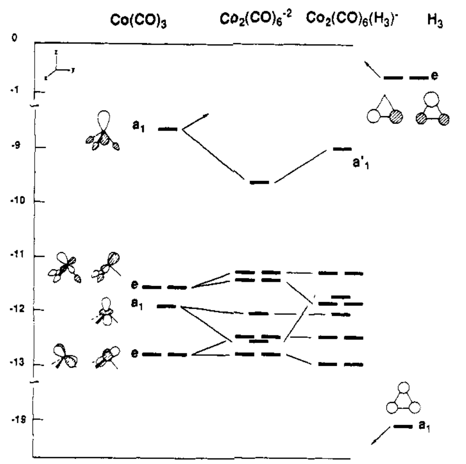
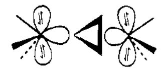
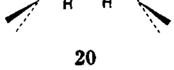


Figure 2. Assembly of the molecular orbital diagram for $Co_2(CO)_6(H_3)^-$ from those of fragments.



19

As with the mononuclear $Co(CO)_3(H_3)$ complex itself, we can investigate the effect of opening up the H_3 unit as in **20** by lengthening one H–H distance but keeping constant the other H–H and M–H distances. **21** shows how the orbitals change during the distortion for the $Co_2(CO)_6H_3^+$ species. The situation is very similar indeed to that of **14** where one component of the frontier e orbital pair is stabilized by Ψ_2 of the H_3 unit. We calculate an energy difference of about 10 kcal/mol for the distortion



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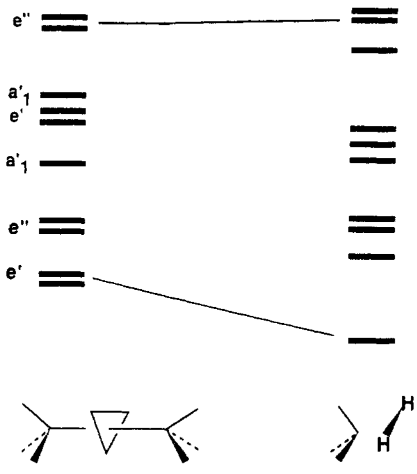
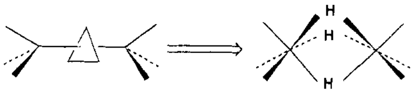


21

of the triangle (H–H–H angle = 60°) to an open unit (H–H–H angle = 100°). As before this number is not very reliable, but it does indicate that the D_{3h} and "slipped" geometries are close in energy.

The behavior of the orbital picture as the H–H distance increased (**22**) is interesting. It will lead to a connection



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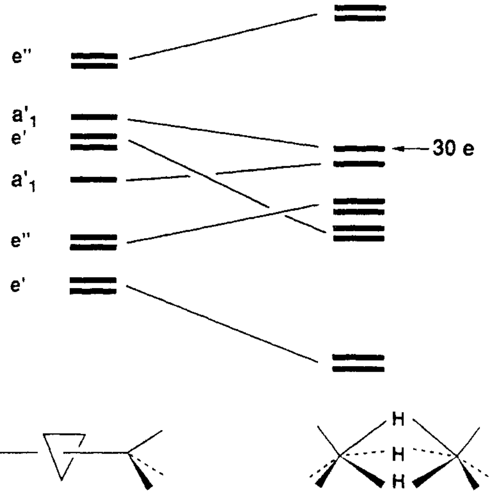
with characterized species since the distortion eventually converts the polyhedral structure to the conventional bridged one. **23** shows the results of some calculations that



23

used a constant M–H distance. The e′ pair of orbitals, largely located on the hydrogen atoms and symmetric with respect to the two metal atoms, drop in energy as the antibonding interaction between them decreases and eventually cross the symmetric metal e′ pair. This metal set of levels now become M–H antibonding and rise in energy. There is therefore an avoided crossing associated with this orbital quartet. An exactly analogous result occurs in the oxidative addition of H_2 to a d^8 square-planar metal complex. As the M–M distance decreases, the e″ levels, antisymmetric with respect to the metals go up in energy since they are M–M antibonding and the corresponding a_1' M–M bonding combination analogously drops in energy. A reasonable energy gap is now generated with four electrons less. The hydrogen atoms are now of course best described as bridging hydrides. In accord with these ideas, a structure with this geometry and electron count is found, inter alia, for the molecules[33,34] $H_3Ru_2(PMe_3)_6^+BF_4^-$ and $H_3Fe_2[MeC(CH_2PPh_2)_3]_2^+PF_6^-$. Although our calculations will not give accurate distances for the process in **22**, the computed minimum in this slice through the potential energy surface changes from M–M = 2.8 Å for the molecule with 34 electrons to 2.4 Å for the 30-electron case. (In $H_3Ir_2(C_5Me_5)_2^+BF_4^-$ the distance[35] is 2.458 Å.)

We noted above that the H_5 unit could perhaps be stable with only a single charge if the nonbonding orbital at $E = \alpha$ is occupied. The analogous orbital in Figure 2 is the a_1' level at around 9 eV arising from the in-phase overlap of the fragment frontier a_1 orbitals. Since this is separated rather a long way energetically from the rest of the orbitals, we doubt that there will be a stable molecule with this electron count. (Not shown on the diagram but close to this orbital are some CO π^* orbitals. Their presence also means that population of this orbital is unlikely.)

Substitution of CO by NO but keeping the electron count constant leads to some changes in the level ordering. Just as in the case of $M(CO)_3(H_2)$ described elsewhere[16] and mentioned above for $M(CO)_3(H_3)$, incorporation of nitrosyl reduces both the destabilization of the occupied metal a_1 orbitals and the stabilization of occupied metal e′ orbitals associated with back-donation into the corresponding unoccupied H_3^+ orbitals. The bond overlap populations for some of these species are shown in **24**.

Overlap Population for H-H:

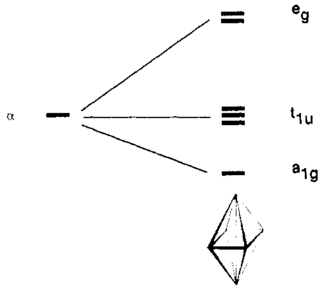
$Co(CO)_3H_3$	$Co_2(CO)_6H_3^-$	$Co_2(CO)_4(NO)_2H_3^+$	$Co_2(CO)_6H_4$
0.2961	0.2574	0.2570	0.2061

24

Replacement of a single CO by a better π-acceptor (NO) results in a small decrease in the strength of the H–H bond. There is an added bonus too. With the stronger π-acceptor the energy gap between the degenerate (e′) HOMO and the next occupied level is reduced. We calculate a shift from 0.59 to 0.36 eV on going from $[Co(CO)_3]_2(H_3)^-$ to $[Co(CO)_2(NO)]_2(H_3)^+$. This indicates an increase in the tendency for reduction of the 30-electron compound to give the species that we predict will be of the polyhedral type.

The Octahedron

The energy levels of the H_6 octahedron are shown in **25**. There are three nonbonding orbitals in this geometry and a single bonding one. We may therefore envisage stability for this unit for electron counts corresponding to the species H_6^{4+} and perhaps the quartet state at H_6^+. Figure



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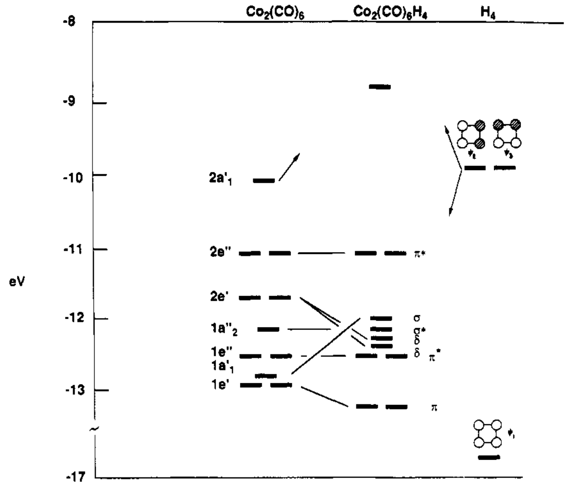
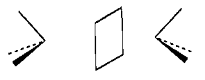


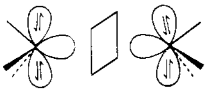
Figure 3. Assembly of the molecular orbital diagram for $Co_2(CO)_6(H_4)$ from those of fragments.

3 shows the assembly of a computed orbital diagram for the species $Co_2(CO)_6(H_4)$ (**26**). We use the δ label to



26

describe a skewed π-type interaction. Extending the ideas of the previous sections we could describe this as in **27**, a



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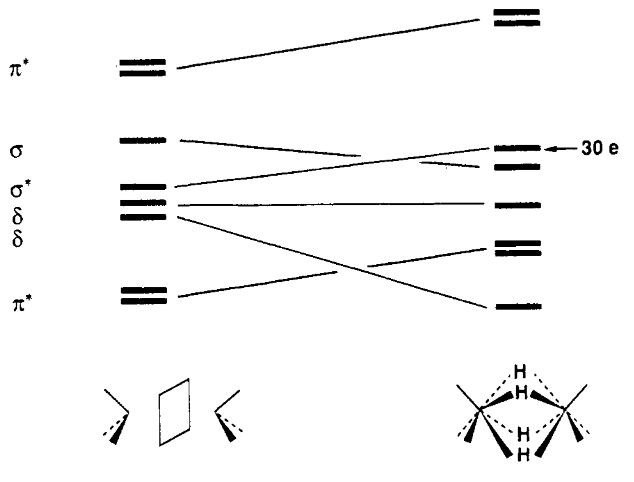
molecule isoelectronic with H_6^{4+}. The energy is not very sensitive to the conformation of the terminal ligands. The levels at $E = \alpha$ in **25** are not degenerate in this molecule. One of them is a metal-located orbital, and the others are nonbonding hydrogen orbitals. The former orbital lies at about 9 eV just as in the trigonal-bipyramidal analogue and molecules whose electron count is such as to populate it will probably not therefore be stable. Shown in **28** is the result of distorting the molecule as in **29**. The result is similar to the one we showed above in **23** for the molecule with three hydrogen atoms. A gap opens up at 30 electrons, just four electrons less than for the polyhydrogen system. An example of a species with this electron count and four bridging hydrogen atoms is[36] $H_4[Re(PEt_2Ph)_2H_2]_2$, although this molecule is not based on an M_2L_6 framework.



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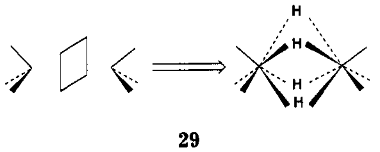
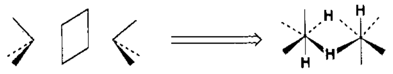


29

We can now return to the result of Dedieu et al.,[31] who concluded that an $M_2L_6H_5$ species with five bridging hydrogen atoms could be stable for the d^4 configuration, in the 30-electron molecule $Fe_2L_6H_5^{3+}$ and perhaps too in the d^6 dimer with four more electrons. The orbital diagrams for all of these trans $M_2L_6H_n$ species are similar. Indeed it appears that as long as the polyhedral molecule is stable when isoelectronic with $H_n^{(n-2)+}$, i.e., when only the lowest, totally symmetric orbital of the skeleton is doubly occupied, then the bridging hydride is stable for 30 electrons and the polyhydrogen molecule stable for 34 electrons. From the level diagram of ref 31 such a species has a small HOMO–LUMO gap and could distort in this way. We would suggest that Dedieu et al.'s d^6 dimer should be of the polyhydrogen type. This is an interesting result. Addition of electrons to molecules usually leads to breakup of the molecule. Such is the case for example in the series $P_4 \rightarrow B_4H_{10} \rightarrow P_4R_4 \rightarrow PCl_3$ which involves a change from 20 to 26 electrons. Here however, addition of electrons leads to creation of the polyhedral species.

It is of interest to investigate how the molecule **26** might distort if the HOMO was only half full, with an electron count of 32 electrons. A Jahn–Teller distortion would remove the degeneracy of the HOMO, the e′ set of orbitals. **30** shows one possible route which indeed leads to the observed structure[37] of the 32-electron $Os_2(PMe_2Ph)_6H_4$. **31** shows the results of two calculations, the first is appropriate for the distortion **30** which keeps the M–M distance constant and the second shows the effect of decreasing the M–M distance at the end of the coordinate. The destabilization of the M–M antibonding orbital which results is apparent and leads to the opening of a nice gap at 32 electrons.



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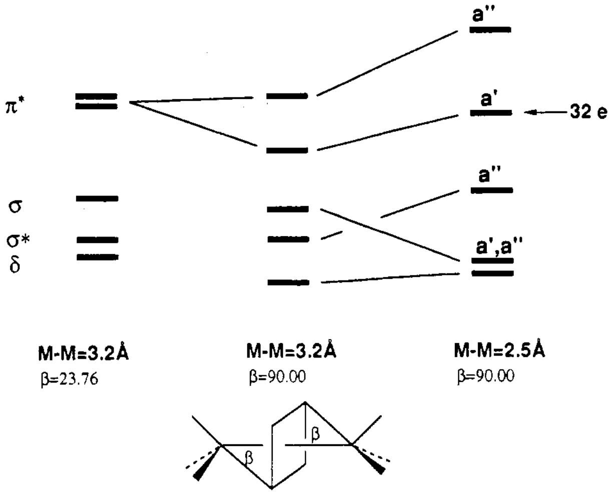

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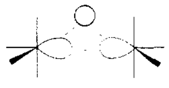
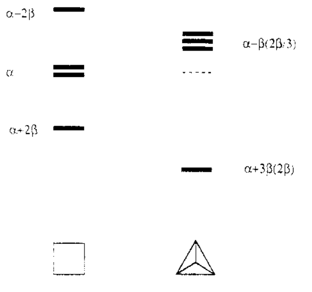
Units with Adjacent Metal Atoms

So far we have not considered polyhedra where the metal atoms are located on adjacent sites. Here we are interested in seeing how the simple picture described above will change if the frontier orbitals of two close metal atom fragments interact with each other. Certainly in a trimeric complex $H(ML_x)_3$ such as the known species $HRu_3(CO)_{10}CoMe$[38] the orbital picture will be such that the geometry of the complex will be described by Wade's rules if the hydrogen atom is considered to donate one electron to skeletal bonding. In other words we must consider the electronic structure of the metal framework as being assembled from the three frontier orbitals of each fragment and not just one. However, in the known series of molecules[39] typified by $[Cr(CO)_5]_2H^-$ the two metal atoms and the hydrogen atom form a triangle in several examples, in accord with the view of this species as being isoelectronic with H_3^+. This is shown schematically in **32**. Computational studies, however,[40] show a rather soft motion linking the open and closed forms.



32

The four-atom unit allows investigation of the structure of $(ML_x)_2H_2$ systems. Here we examine the structure of molecules based on the square and the tetrahedron. The levels of these moieties are shown in **33**. In parentheses we show the levels of the tetrahedron obtained by requiring that the second moments of the two energy level patterns are the same. Notice that for one pair of electrons the energies of the two geometries are equal (4β) if the second moments are equalized but that the tetrahedron wins out if they are not. More detailed quantitative comment would require very accurate ab initio calculations that are not well-developed for molecules of this type.



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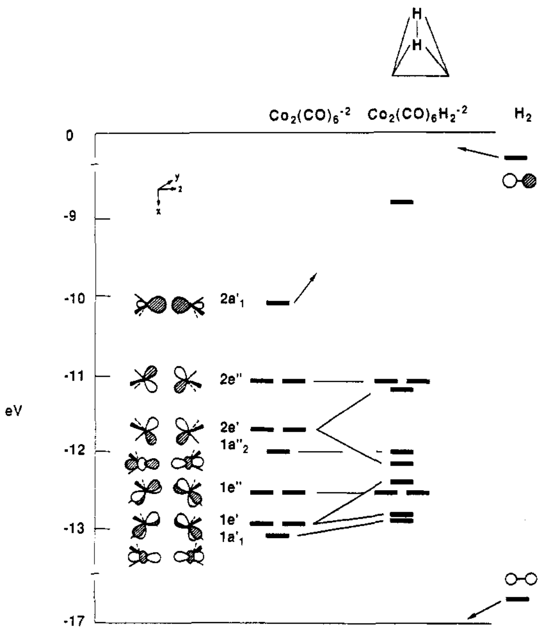


Figure 4. Assembly of the molecular orbital diagram for tetrahedral $Co_2(CO)_6(H_2)$ from those of fragments.

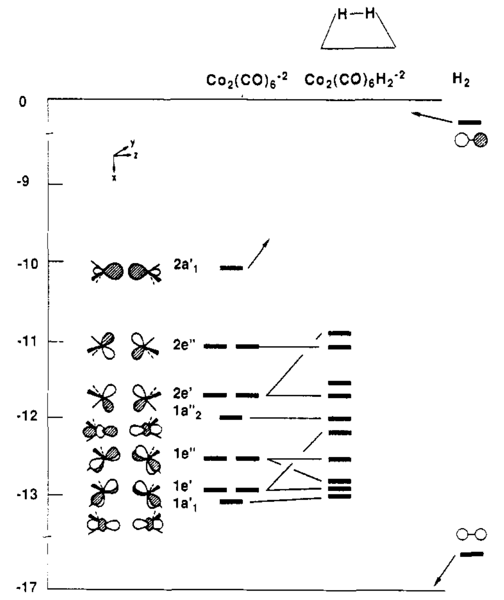
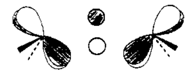


Figure 5. Assembly of the molecular orbital diagram for square $Co_2(CO)_6(H_2)$ from those of fragments.

Figures 4 and 5 show the assembly of molecular orbital diagrams for the square and tetrahedral variants of the hypothetical species $(Co(CO)_3)_2H_2$ from the dinuclear metal complex. They are very easy to follow. In both geometries there is a large destabilization of the unoccupied a_1 orbital of the dimer by the σ-bonding orbital of the H_2 unit. In both geometries however, there is considerable orbital movement associated with occupied metal orbitals, so that the model analogous to **20**, where all of these metal-located electrons are regarded as lone pairs, is not at all applicable. In the tetrahedron notice that one component of both occupied symmetric $Co(CO)_3$ e combinations has been destabilized on interaction with H_2 in an exactly analogous fashion to that in $Co(CO)_3(H_3)$. There is only one significant stabilzation of one of the other components of these levels in this geometry because of the poor overlap shown in **34**. In the square one component of each of the four sets of e orbitals may interact with the levels of H_2. Overlap with each is good, and so in contrast to the tetrahedron there are two stabilizing and two destabilizing interactions. This situation overall is less destabilizing than in the tetrahedron. We calculate that the square is more stable than the tetrahedron by around 70 kcal/mol. This is in spite of the fact that the totally symmetric orbital, constructed from the in-phase overlap of the empty metal a_1 frontier orbitals and the hydrogen



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1s orbitals, is calculated to be lower in energy for the tetrahedron than for the square. Thus it is the energetic preferences of the occupied d block which control the geometry. The direct analogy with the orbitals of the H_5 cluster is lost.

The Stability of H_n Fragments

There has been some recent interest[41] in exploring the reasons underlying the stability of the symmetrical structures for cyclic conjugated hydrocarbons. For example, the D_{6h} structure of benzene, long the organic chemists prototypic "aromatic" molecule is predicted via a second-order Jahn–Teller effect to be unstable with respect to the structure with bond alternation. It is only the structural preferences of the σ framework which prevent the distortion occurring. (See ref 42 for a discussion of a similar balance in polyacetylene, polyacene, graphite, and related systems.) By way of contrast, for the isoelectronic molecules cyclic N_6 or H_6, theoretical results[41] suggest the opposite. In both cases the cyclic system is predicted to be unstable with respect to three separate N_2 or H_2 molecules, respectively. In H_6 there is of course no underlying framework of different symmetry to resist the deformation. The magnitude of the distortion away from such symmetric geometries has been identified in valence bond language[41] with the strength of the bond in the resulting diatomic. Clearly the strength of the linkage in H_2 and N_2 molecules is enormous and should favor the diatomic rather than the cyclic structure. This is also true of the polyhedral structures. Since we have focused on the structures of systems with a total of two skeletal bonding electrons, the bond order between each H–H contact will rapidly decrease as the cluster size increases. At some stage the strength of metal–hydrogen bonding will not be sufficient to stabilize the cluster relative to free or coordinated H_2 molecules. The balance between intrafragment forces of this type and the role of metal–hydrogen bonding requires orbital methods more exact than the ones we have used here. Whether stable complexes of transition-metal fragments with cyclic or polyhedral H_n molecules can be isolated needs to be seen. However, we do note that for triangular H_3 a soft distortion coordinate that involves the shortening of one H–H distance and the lengthening of the other two will lead to a facile transformation between the species $Cr(CO)_4(H_2)_2$ and $Cr(CO)_4(H_3)H$ which we have described elsewhere.[16] On the othe hand the HOMO–LUMO gap in H_3^+ is the largest possible for a two connected cyclic system (3β) which should encourage stability of the symmetric structure. There is no evidence for a soft stretching mode in Oka's experiments[43] on free H_3^+.

Thus in conclusion, the idea that polyhedral systems give rise to a good HOMO–LUMO gap if isoelectronic to their $H_n^{(n-2)+}$ analogues appears to be a good way to view the complexes of this paper. However, their stability relative to other isomers does not seem to be so readily predictable. In many cases slippage of an H_2 or H_3 unit can occur to involve other orbitals on the metal fragment.

Acknowledgment. This research was supported by NSF DMR841475.

Appendix

The computations were of the extended Hückel type with the geometrical and electronic parameters as used in our previous study.[16] The distortions we investigated employed constnt metal–hydrogen (1.755 Å) and H–H (0.870 Å in H_3 and 1.00 Å for H_4 complexes) distances, but the metal–metal distances had to vary (from 3.36 to 2.50 Å in $Co_2(CO)_6(H_3)$, for example) in the motions which converted polyhedral species into those with bridging hydrides for example. Numerical results from calculations that involve the making and breaking of bonds are not at all reliable with use of our computational method, but association of stability with the presence of energy gaps for particular electron counts is probably quite good.

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Synthesis of Bis(η^6-2,6-dimethylpyridine)metal (Ti, V, Mo) by Metal Vapor Deposition. Spectral Properties of Bis(η^6-2,6-dimethylpyridine)metal (Cr, Ti, V, Mo, Cr^+)

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The syntheses of bis(2,6-dimethylpyridine)metal sandwich compounds by metal atom–ligand cocondensation and solution-state redox reactions have been investigated. The new sandwich compounds bis(2,6-dimethylpyridine)metal (Ti, V, Mo, Cr^+) have been obtained. The IR, NMR/ESR, and UV–vis spectra of bis(2,6-dimethylpyridine)metal (Cr, Ti, V, Mo, Cr^+) are reported and used to compare π-bonding properties of η^6-benzene with those of η^6-(ortho-disubstituted)pyridine.

Introduction

In the course of investigating the interactions of transition metals with small unsaturated or aromatic organic molecules,[2] we noticed a lack of information about bis(heteroaromatic)metal sandwich compounds. While fer-

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