volumes of the species in these phases. In obtaining this expression, we have assumed that the partition functions for the rotational and internal degrees of freedom of the species are the same in both phases so that the term $R\ d(T \ln q_B)/dT$ cancels when taking the difference.

Under hypothetical standard state conditions of unit concentrations in both phases, $\Delta s(\alpha \rightarrow \beta)$ becomes the standard molar entropy of transfer $\Delta s_c^0(\alpha \rightarrow \beta)$ (the subscript c denotes standard states based on concentration) and the term $-R \ln (c_\beta/c_\alpha)$ equals zero. Thus $\Delta s_c^0(\alpha \rightarrow \beta)$ and $\Delta s'$ are identical.

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Structure and Chemistry of Bis(cyclopentadienyl)-ML$_n$ Complexes

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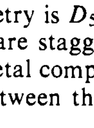
Abstract: A construction of the molecular orbitals of a bent bis(η^5-cyclopentadienyl)M fragment, Cp_2M, M = a transition metal, serves as a starting point for a general account of the electronic structure of Cp_2ML_n molecules, $n = 1-3$. The following problems are analyzed: the geometry of Cp_2ML_n as a function of the d electron configuration; bonding with π acceptor and donor ligands, emphasizing orbital interactions with conformational consequences such as olefin and carbene orientation and dithiolene bending; distortions of the Cp_2M moiety; insertion reactions of coordinated olefins; carbonyl insertion reactions; oxidative coupling; allyl and tetrahydroborate complexes; triscyclopentadienyl complexes.

The remarkably rich chemistry of bent bis(π-cyclopentadienyl) transition metal complexes[1] is the focus of this study. We proceed to formulate a model for the electronic structure of such molecules, and relate that model to the various known complex types, and the known structures. The eventual goal is an understanding of the chemistry of these molecules.

We begin by considering the valence orbitals of a bent bis(cyclopentadienyl) transition metal fragment. This is followed by a consideration of the interactions of such a fragment with additional ligands with various bonding capabilities.

The Bis(π-cyclopentadienyl) Metal, Cp_2M, Fragment

Normal bis(π-cyclopentadienyl) [bis(η^5-cyclopentadienyl), to be abbreviated throughout this paper as Cp_2] transition metal complexes such as ferrocene are highly symmetric molecules with parallel cyclopentadiene rings (**1**).



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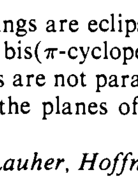

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Their symmetry is D_{5h} if the two rings are eclipsed, or D_{5d} if the rings are staggered. In bent bis(π-cyclopentadienyl) transition metal complexes the rings are not parallel, that is the angle between the normals to the planes of the cyclopentadienyl ligands is less than 180°, and there are from one to three additional ligands bound to the metal. **2** shows a schematic Cp_2ML_3 structure, for which Cp_2NbH_3 is a real example. A bent Cp_2M fragment has C_{2v} symmetry if the Cp ligands have an eclipsed geometry, and only C_s symmetry if the rings are staggered.

The bonding in the normal metallocenes has been the subject of numerous theoretical and experimental papers[2] and will be discussed here only briefly. In a D_{5d} geometry the π orbitals of two parallel $C_5H_5^-$ ligands yield three sets of approximately degenerate orbitals: a low-lying filled pair of a_{1g} and a_{2u} symmetry, a set of filled orbitals, e_{1g} and e_{1u}, and a high-lying empty set of antibonding orbitals of symmetry e_{2g} and e_{2u}. These interact with the orbitals of the metal as shown in Figure 1, which is a schematic interaction diagram of a normal Cp_2M complex. There is a strong interaction with the metal s and p orbitals and also a strong bonding interaction with the $e_{1g}(d_{xz}, d_{yz})$ set. The remaining three d orbitals of the metal, the $a_{1g}(d_{z^2})$ and the $e_{2g}(d_{x^2-y^2}, d_{xy})$ set, remain essentially nonbonding. Thus the d-level splitting is $e_{2g} \lesssim a_{1g} < e_{1g}^*$ or $(d_{x^2-y^2}, d_{xy}) \lesssim (d_{z^2}) < (d_{xz}, d_{yz})$.

Ferrocene is by far the most stable of the metallocenes, which is not surprising, because it has the ideal number of electrons for Cp_2M complexes. Considering each $C_5H_5^-$ ligand as a six-electron donor, together with the six d electrons of Fe(II), one achieves an 18-electron configuration by filling precisely the nonbonding e_{2g} and a_{1g} levels. Cobaltocene, a d^7 – 19 electron complex, and nickelocene, a d^8 – 20 electron complex, each has an excess number of elec-

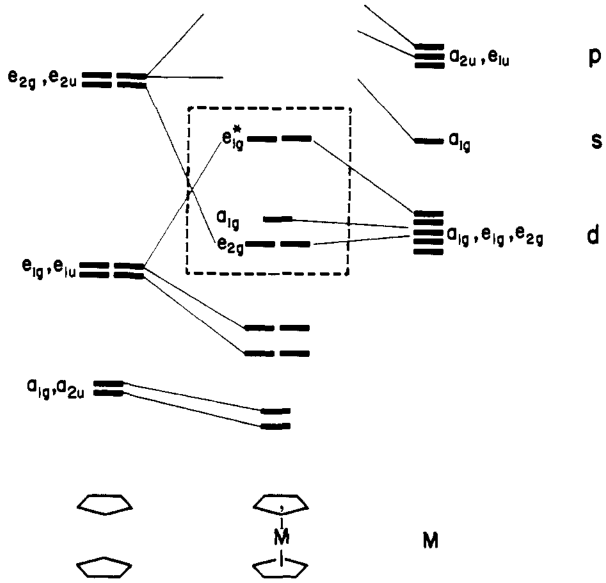


Figure 1. Interaction diagram for a D_{5d} metallocene. The frontier orbitals are in the box.

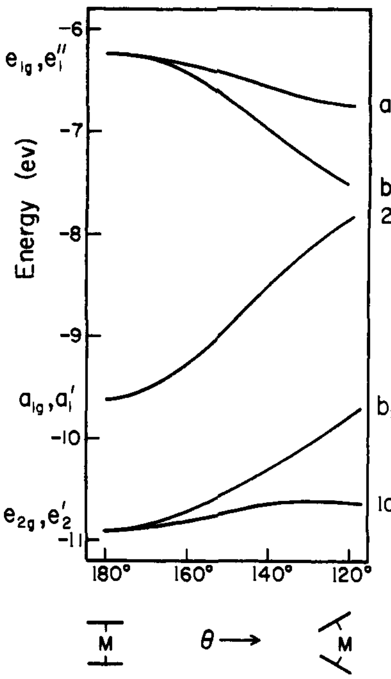
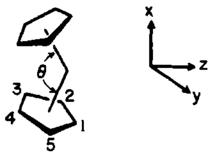


Figure 2. Cp_2M orbitals as a function of the bending angle θ. Bending is from an eclipsed D_{5d} form, but the labels at left are given for both D_{5d} and D_{5h} geometries.

trons which go into the higher lying e_{1g}* (d_{xz}, d_{yz}) orbitals. Their chemistry reflects this since both molecules are easily oxidized.[4,5] At the other extreme complexes such as vanadocene (d^3 – 15 electrons) or chromocene (d^4 – 16 electrons) are electron deficient, having fewer than 6 d electrons. In these two cases the three nonbonding orbitals are only partially filled.

One way the electron-deficient complexes can achieve the desired 18-electron configuration is to add additional ligands, which can contribute additional electrons. When additional ligands coordinate to the metal, the $C_5H_5^-$ ligands bend back. To understand the way in which the additional ligands bind we wish to examine the frontier orbitals of a bent Cp_2M fragment. This was accomplished by means of an extended Hückel calculation on a model Cp_2Ti, **3**. Computational details are given in the Appendix.



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We wish to study the variation of the energy of the Cp_2Ti orbitals as a function of θ, the angle between the normals to the Cp rings. In the motion which lowers θ from 180° the molecular symmetry changes from D_{5h} or D_{5d} to C_{2v} or C_s. To make maximum use of symmetry we bend from the eclipsed D_{5h} geometry, though we will occasionally refer to the original "unbent" Cp_2M levels in terms of the more familiar D_{5d} symmetry labels. Note also that we have redefined the coordinate system (and the d levels that go with it) as shown in **3**, with z along the twofold rotation axis. The energy of the frontier orbitals as a function of θ is shown in Figure 2.

The basic trend noted in the figure is that the orbitals descended from the e_{1g}* are stabilized with bending and those descended from a_{1g} and e_{2g} are destabilized. For the lower orbitals, $1a_1$, b_2, $2a_1$, this trend is the result of increased σ antibonding as one departs from the θ = 180° geometry. The effect is especially noticeable for the a_{1g} – $2a_1$, which was initially nonbonding by virtue of the cyclopentadienyl ligand component of that orbital lying approximately in the nodal plane of the d_{z^2}. Another contribution to the steep rise in energy of $2a_1$ with decreasing θ is its interaction with $1a_1$. In D_{5d} or D_{5h} these orbitals were of different symmetry. In C_{2v} they mix, and that mixing will be important in the sequel. As a consequence of the mixing, they repel each other. This increases the upward slope of the $2a_1$ and actually keeps the $1a_1$ approximately constant in energy. The e_{1g}* set splits, yielding the a_2* and b_1* orbitals which occur at lower energies than did the e_{1g}* set. These two orbitals have been stabilized partly because of a decrease in the overlap of the metal d's with the filled ligand orbitals (and thus less of an antibonding interaction), but more importantly in the C_{2v} geometry the d_{xy} and d_{xz} orbitals are now of proper symmetry to interact with two of the empty antibonding orbitals of the ligands. This is a net stabilizing effect and lowers the energy of these orbitals.

The composition of these frontier orbitals is of some importance in assessing their bonding capability. Accordingly Table I shows the electron distribution in the five orbitals for a typical θ = 136°, and Figure 3 illustrates the computed shapes of the three lowest orbitals, $1a_1$, b_2, and $2a_1$. The molecules of interest to us carry four or fewer d electrons, and so it is these three orbitals which will play a prime role in coordinating further ligands.

Our picture of the three low-lying frontier orbitals is very similar to that reported by Brintzinger and Bartell[6a] for the same system. All three orbitals have significant extent in the yz plane. The b_2 orbital is chiefly d_{yz} in character. The two a_1 orbitals each contain some contribution from the s and p_z orbitals in addition to $d_{x^2-y^2}$ and d_{z^2} contributions. The $1a_1$ orbital is directed strongly along the y axis. The orbital can be described as similar to a d_{y^2} orbital. Note again that the orbitals are defined with respect to the coordinate system shown in **3**. Orbital $2a_1$ is the highest of the three orbitals and is hybridized nicely along the z axis away from the $C_5H_5^-$ ligands. The importance of these three orbitals has been emphasized by other authors who have considered the molecular orbitals of the bent Cp_2M fragment.[6-11] Different workers have constructed differing hybrids of these orbitals, occasionally leading to seemingly contradictory re-

Table I. Electron Distribution in Cp_2Ti Frontier Orbitals, $\theta = 136°$

	Composition, %	
Orbital	Cp_2 ligands	Metal[a]
a_2	69	31 xy
b_1	57	43 xz
$2a_1$	21	33 z^2, 27 x^2-y^2, 11 s, 8 z
b_2	34	64 yz, 2 y
$1a_1$	18	51 x^2-y^2, 30 z^2, 1 s

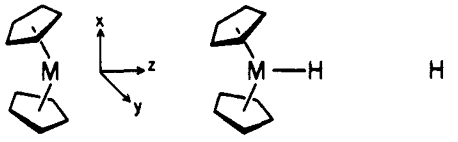
[a] Metal orbitals are defined with respect to the coordinate system in **3**.

sults, but all have noted the presence of three valence molecular orbitals lying in the yz plane available for bonding with additional ligands.

A beautiful series of investigations utilizing crystallography, electron paramagnetic resonance, and photoelectron spectroscopy by Green,[9] Green,[9,11] Prout,[9] Dahl[10] and their coworkers has secured for us an understanding of the orbital structure of Cp_2ML_n compounds. The experimental studies basically have confirmed the Alcock model[8] as extended by Green, Green, and Prout.[9] We will refer to the experimental evidence as we discuss each molecular type. In the present context, though the Cp_2M fragment is not an observable molecule, the orbital structure which we derive is consistent with the experimental information gleaned from the above cited studies. Our construction of these orbitals is not to be considered novel, but has been given in some detail as it forms the starting point for our attack on the structure and chemistry of these molecules.

Interactions with σ Bonding Ligands

The simplest examples of bent $M(C_5H_5)_2$ complexes are monohydrides of the type Cp_2MH in which the metal atom has two $C_5H_5^-$ ligands and one hydride ligand. The hydride ligand is the simplest type of ligand to consider since it can only bond in a σ fashion. Examples of this type of complex are Cp_2ReH[12] and Cp_2FeH^+.[4] The most symmetrical and presumably sterically most favorable structure for a Cp_2MH molecule is one in which the H^- ligand is located on the z axis, **4**. In this geometry the H^- ligand overlaps very well with the fragment orbital $2a_1$, overlaps somewhat with $1a_1$, and not at all with the b_2 orbital. We thus have a strong bonding interaction between the $2a_1$ orbital and the σ orbital of the H^- ligand. The b_1 orbital is unaffected and the $1a_1$ orbital is slightly destabilized. The b_2 and $1a_1$ orbitals can accommodate four electrons, so d^4 complexes of this type should be favored, as exemplified by Cp_2ReH and Cp_2FeH^+.



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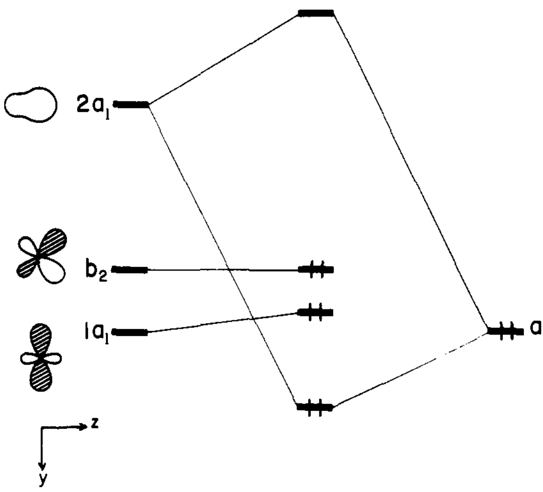


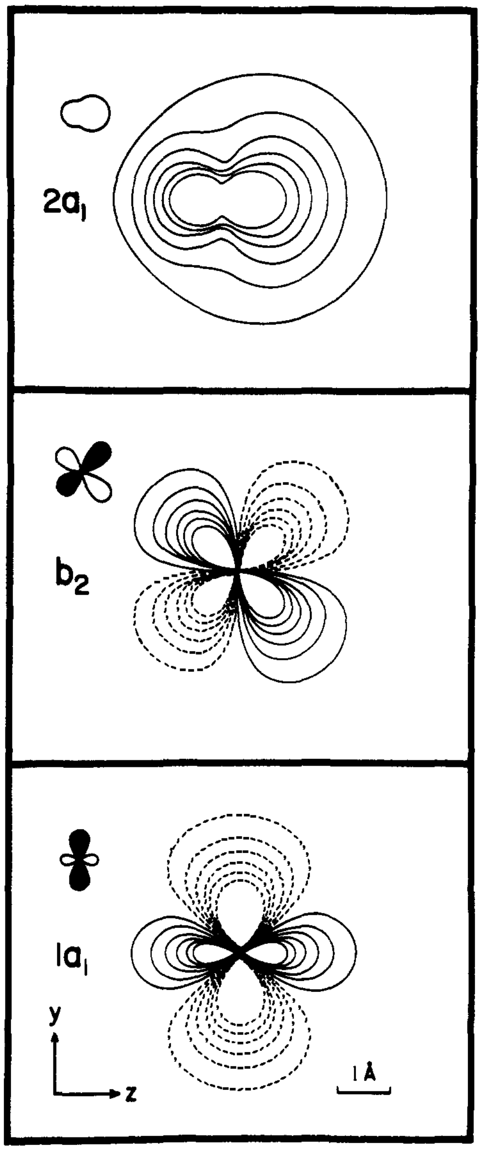
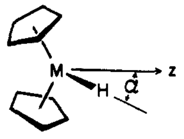


Figure 3. Contour diagram, in the yz plane, of the three important Cp_2M orbitals, computed at $\theta = 136°$. From top to bottom: $2a_1$, b_2, $1a_1$. Solid line = positive and dashed line = negative contour of the wave function. The contours are at intervals of 0.02.

The above analysis assumed the most symmetrical structure, one which has the H^- ligand along the z axis. At this geometry there is excellent overlap with the $2a_1$ orbital, but this orbital is the highest in energy of the three available valence orbitals. One might expect that a different geometry, **5**, in which the H^- is off the twofold axis but still in the yz



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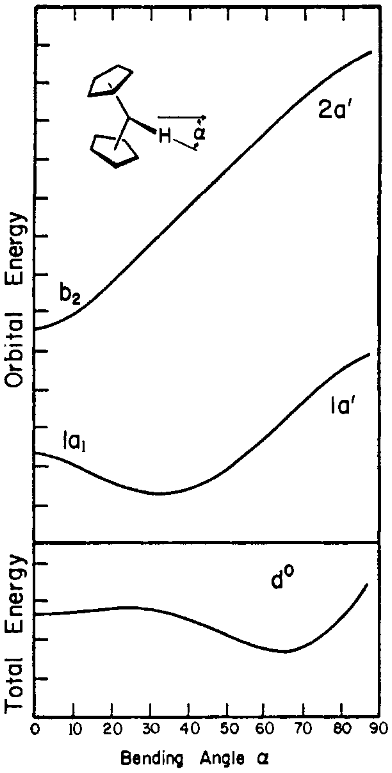


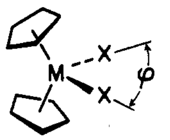
Figure 4. Bottom: total energy computed for Cp_2TiH^+ as a function of α. Top; variation in energy of the two low-lying empty orbitals of Cp_2TiH^+ as a function of α. Energy scale markings are 0.2 eV apart.

plane, having good overlap with $1a_1$ and/or b_2, both closer in energy to the donor orbital of H^- than $2a_1$, could lead to greater stabilization than in the symmetrical position.

We have performed a calculation for the mythical d^0 complex Cp_2TiH^+ (Ti-H 1.60 Å), varying the angle α from 0 to 90°. Figure 4 plots the change in the total energy vs. the angle α. Also shown are the energies of the two nonbonding orbitals which are now both of a′ symmetry since the molecular symmetry has been reduced to C_s. For a d^0 complex the energy minimum is calculated to come at about 65°. At this angle overlap is reasonably good with all three orbitals, and we have the best possible bonding interaction. If we have d electrons, they must go into the a′ orbitals. The lower a′ orbital has an energy minimum at about 35°, thus a d^1, d^3, or low-spin d^2 complex would also be expected to be stable with $\alpha > 0°$. The higher a′ orbital increases sharply in energy with increasing α. Cp_2MH complexes which are d^4 or high-spin d^2 would tend to have the symmetrical structure as previously assumed.

The only hydride complexes of the type Cp_2MH which have definitely been characterized are d^4 complexes, as exemplified by Cp_2ReH and Cp_2FeH^+. Examples of other similar complexes include high-spin d^2 complexes such as Cp_2VCl[13] which would also be expected to have a symmetrical structure. A number of d^1 titanium complexes, Cp_2TiR (R = aryl or alkyl), are known.[14] These complexes are predicted to have an unsymmetrical structure with the R group off the axis. With very large R groups, steric repulsions between the R group and the $C_5H_5^-$ ligands may force the molecule into the symmetrical and sterically more favorable conformation.

With two σ bonding ligands two of the three low-lying orbitals of the bent Cp_2M fragment will be used. There are a great number of complexes of this type including the simplest dihydrides, Cp_2MoH_2 and $Cp_2ReH_2^+$, but there are also molecules with a variety of ligands including halides and alkyl groups.[4] The molecular structures of about 20 of these complexes have been determined.[15] They all generally have the same geometry, **6**, in which the most interesting variable is the angle φ between the two X ligands. The angle φ seems to depend primarily on the number of d electrons the metal possesses. This result can easily be explained by an examination of the interaction of the fragment molecular orbitals with two σ donor ligands. The two ligands will interact with the b_2 orbital and some combination of the two a_1 orbitals. This will result in a MO scheme as shown in **7**.



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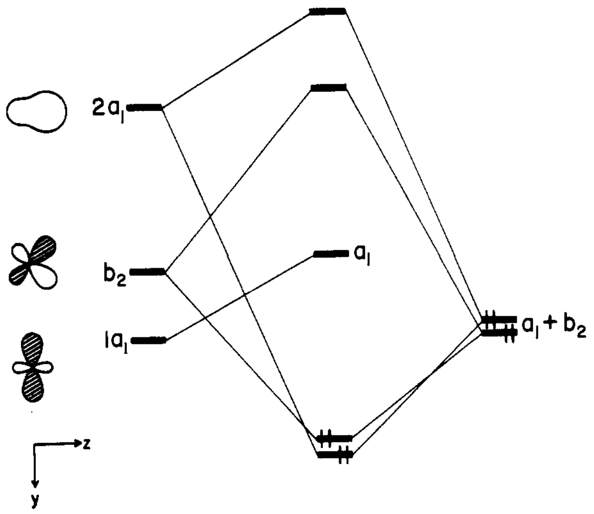

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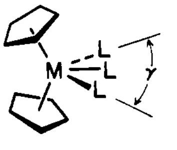
The composition and energy of the resultant nonbonding a_1 orbital is quite sensitive to the angle φ, as noted in another molecular orbital study.[10b] A calculation was performed on the model compound Cp_2TiH_2 (θ = 142°; Ti-H, 1.60 Å; other parameters as before). Figure 5 plots the variation of the total energy of the molecule and of the empty nonbonding a_1 orbital vs. the angle φ. In this d^0 complex the a_1 orbital is empty and there is a very shallow minimum with $\varphi \approx 110°$. The energy of the a_1 orbital has a sharper minimum at $\varphi = 75°$. By combining the two curves we thus find a $\varphi \approx 110°$ minimum for a d^0 complex, $\varphi \approx 85°$ for d^1, and $\varphi \approx 78°$ for a d^2 molecule. At 78° the hydride ligands lie approximately in the nodes of the $1a_1$ orbital (see Figure 3), and thus the resultant nonbonding a_1 orbital is primarily derived from orbital $1a_1$. At the greater angles there is reasonably good overlap with both a_1 fragment orbitals, and the resultant nonbonding orbital is consequently at higher energies. In short the angle φ decreases as we add d electrons.

Structures of the Cp_2MX_2 complexes have been summarized by Prout and co-workers,[15] who also present a qualitative explanation for the geometries which is similar to our description. They report that the angles experimentally determined for d^0 complexes are in the range 94-97°; d^1, 85-88°; d^2, 76-82°. The trend is in agreement with what we see in our model dihydride calculations. A molecule that can be compared directly is a d^2 system, Cp_2MoD_2, for which a neutron diffraction study yields a DMoD angle of 83.2°.[15]

That the nonbonding electron in d^1 complexes resides in an a_1 orbital made up mainly of d_{y^2} with a small admixture of $d_{x^2-z^2}$ has been clearly demonstrated in a lovely single crystal EPR study of Cp_2VS_5 and $(\eta^5\text{-}C_5H_4CH_3)_2VCl_2$ by Petersen and Dahl.[10a] A molecular orbital and photoelectron spectroscopic study by these authors and Lichtenberger and Fenske[10b] of these and related Cp_2TiL_2 complexes is in excellent agreement with the EPR results. Our calculations give much the same shape of the a_1 orbital.

There are relatively few examples of bent Cp_2M complexes with three additional ligands, Cp_2MX_3,[1,4] **8**. All examples are of necessity d^0 since all three valence orbitals of the fragment are used to bond the three σ ligands. The best examples of this type of complex are the trihydrides, Cp_2TaH_3 for example. All three hydrides lie in the *yz* plane. The angle γ between the two outer hydride ligands will be larger than the similar angle in the dihydride case considered previously. This will be due to the necessity of achieving good orbital overlap with the $1a_1$ orbital, as well as the resolving of the steric requirements of the H ligands. In a model calculation on $Cp_2TiH_3^-$ (Ti–H = 1.60 Å, θ = 142°) we calculate an energy minimum at γ = 129°. A recent crystallographic analysis of Cp_2NbH_3 finds γ = 122 (5)° and a central Nb–H bond somewhat longer than the outer ones.[16]



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The reader should note that the qualitative theoretical analysis presented here has to a significant degree been anticipated in the very nice work of Green, Jackson, and Higginson.[11] In their photoelectron studies these authors demonstrate most clearly the presence of two nonbonding orbitals with ionization potentials between 6 and 7 eV for Cp_2MX compounds, one nonbonding MO for Cp_2MX_2, and none for Cp_2MH_3. In addition to the previously cited MO calculations for Cp_2ML_2 species by Petersen, Lichtenberger, Fenske, and Dahl[10b] we mention here other calculations by Chien,[17a] Bakalik and Hayes,[17b] and Stewart and Porte.[17c]

Bonding with π-Acceptor Ligands. Carbon Monoxide and Dinitrogen

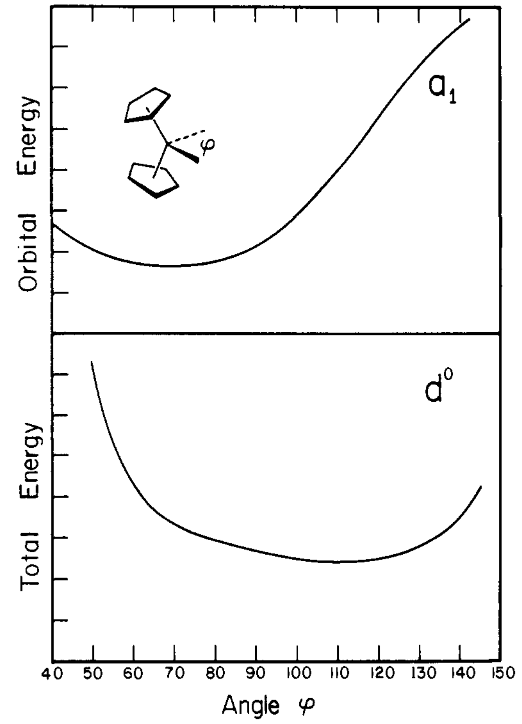
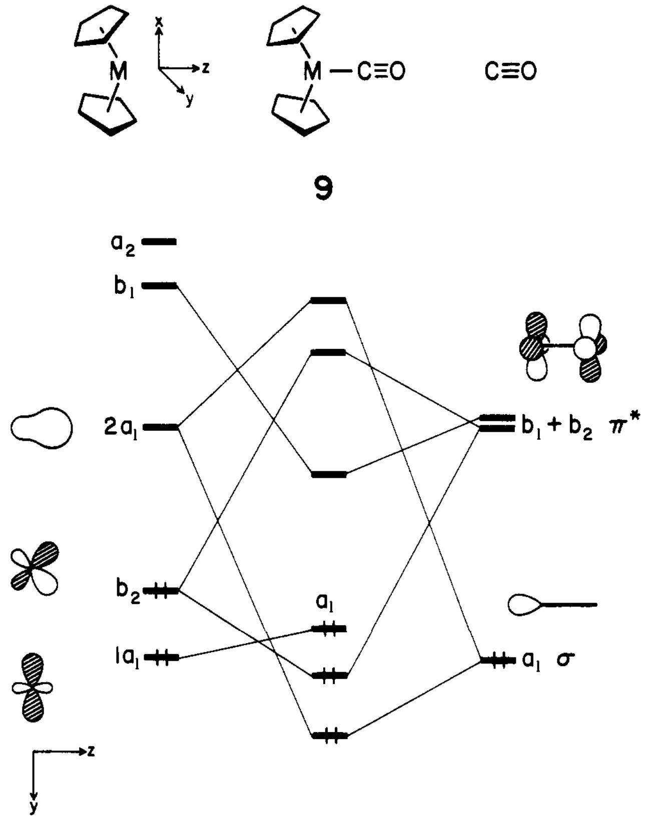


Figure 5. Bottom: total energy computed for $CpTiH_2$ as a function of φ. Top: variation in energy of the low-lying empty orbital of Cp_2TiH_2 as a function of φ. Energy scale markings are 0.2 eV apart.

Up to this point we have considered only ligands which interact with the metal primarily through σ-donor orbitals. There are, however, bent Cp_2M complexes with carbon monoxide or dinitrogen as additional ligands. These two ligands are π acceptors and can form π bonds with the metal. Consider a model Cp_2MoCO, **9**. The molecular geometry can be idealized as C_{2v}. The a_1 σ-donor orbital of the CO ligand interacts in a bonding way with metal fragment orbital $2a_1$ to form a strong σ bond, as shown in the interaction diagram **9**. The two CO π^* ligand orbitals which can accept electron density from appropriate metal orbitals are of symmetry b_2 and b_1. The b_2 π^* orbital lies in the *yz* plane interacting strongly with the fragment b_2 orbital. The fragment $1a_1$ orbital is affected only slightly. The remaining CO π^* orbital of b_1 symmetry is stabilized somewhat by the higher, empty, b_1 orbital of the Cp_2M fragment. This stabilization of an unoccupied orbital is unimportant in the Cp_2MoCO case under discussion, but will become significant in the sequel. The molybdenum CO complex is d^4, having both the nonbonding a_1 orbital and the π^* stabilized b_2 orbital filled.



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These orbitals are clearly seen in the photoelectron spectrum of the molecule, an analysis of which[11] contains an interaction diagram very similar to our **9**. The orbitals of Cp_2MCO have been examined by Brintzinger, Lohr, and Wong.[6b]

In the case of N_2 one could think about the alternatives of "end on" (**10**) and "edge on" (**11**) coordination. The bonding in the former would be expected to be quite similar

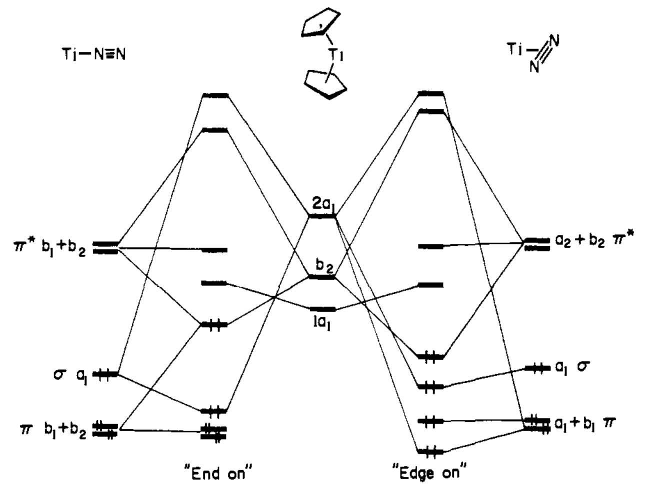
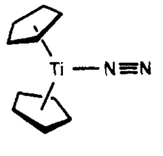


Figure 6. Interaction diagram for "end on" (left) and "edge on" (right) Cp_2TiN_2.



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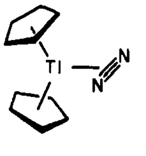

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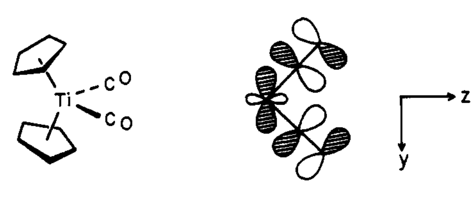
to that described for the monocarbonyl complexes. The N_2 complexes presumably should be less stable, since the N_2 should not be as good as a σ donor nor a π acceptor as CO.

The "edge on" geometry has not yet been observed,[18] so it is interesting to consider the theoretical conditions which might make this coordination possible. The optimum electronic configuration turns out to be d^2. Figure 6 compares interaction diagrams for "end on" and "edge on" N_2 coordination in a model Cp_2TiN_2. The π^* orbitals of the "edge on" complex are of symmetries a_2 and b_2, while the π's are of symmetries a_1 and b_1. There is a σ donation from a combination of the a_1 π orbital and the highest lying N_2 σ orbital. The strength of this combined σ donation is somewhat less than that found in the "end on" isomer. The b_2 π^* orbital stabilizes the fragment b_2 orbital. In the "end on" isomer the stabilization of the b_2 orbital by π^* was offset somewhat by a destabilization due to the b_2 π orbital. In the "edge on" isomer the π and π^* orbitals are of different symmetries and there is no destabilization. The overall energies of the two isomers thus appear to be similar, for a d^2 case.

Quite apart from the specific case of Cp_2TiN_2 one may conclude in general that if "edge on" N_2 complexes are to be found they should be looked for in d^2 systems. The normal "end on" isomer has two π^* orbitals which can accept electrons from filled metal orbitals. The "edge on" isomer has only one π-bonding acceptor orbital; the other π^* can only form a δ bond. Most N_2 complexes are with metals which have at least four d electrons, favoring the "end on" isomer. In Cp_2TiN_2, or another d^2 system, only one pair of d electrons is available for back donation—the main advantage of the "end on" isomer is removed. This d configuration will not guarantee the existence of "edge on" bonding, but will provide an opportunity for it.

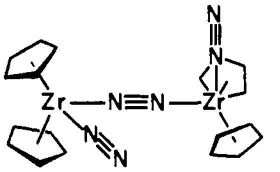
In addition to the monocarbonyl complexes there is a d^2 dicarbonyl complex, $Cp_2Ti(CO)_2$ (**12**). The two carbonyl ligands will form two σ bonds using metal fragment orbitals $2a_1$ and b_2. The $1a_1$ orbital is now of the proper symmetry to be well stabilized by a combination of π^* orbitals of both



12

carbonyls. This is shown in **12**. In $Cp_2Ti(CO)_2$ this stabilized a_1 orbital is occupied.[19a] Remarkably a dicarbonyl with two more electrons exists, $Cp_2W(CO)_2$.[19b] We will return to a discussion of this molecule later.

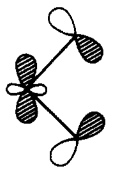
An interesting compound recently investigated by Bercaw is $((\eta^5\text{-}C_5Me_5)_2Zr)_2(N_2)_3$,[18b] which has the structure shown below. This falls then into the general category of d^2



Cp_2MX_2 structures at each end, with the additional feature of a bridging N_2 group. An interesting aspect of the solid state structure of the molecule[18b] is that the dihedral angle N_2—$ZrN{\equiv}NZr$—N_2 is 87°. If the bridging N_2 were to use its π^*-acceptor orbitals to interact, one with the filled a_1 of one Zr, the other with the corresponding electron pair on the other Zr, one would expect a torsion angle of 90°.

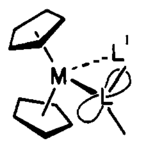
Bonding with π-Donor and π-Acceptor Ligands and Conformational Barriers

π bonding of course can be either stabilizing, if the ligand carries low-lying acceptor orbitals, or destabilizing, if the ligand brings with it relatively high-lying donor orbitals. In $Cp_2M(CO)_2$ complexes the a_1 orbital is stabilized by interaction with the carbonyls, as was indicated by **12**. In d^2 Cp_2MX_2, where X = halogen, OR, SR, or NR_2, one would expect π antibonding with the X lone pairs, as shown below:

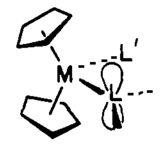


The effect should manifest itself in a lengthening of the MX bond as the a_1 orbital is occupied. The trend has been noted by Prout and co-workers[15] (Mo-Cl is 2.39 in $Cp_2MoCl_2^+$, d^1, vs. 2.47 Å in Cp_2MoCl_2, d^2) and by Petersen and Dahl[10a] (Ti-Cl is 2.36 in $(C_5H_4CH_3)_2TiCl_2$, d^0, vs. 2.40 in $(C_5H_4CH_3)_2VCl_2$, d^1). Petersen, Lichtenberger, Fenske, and Dahl[10b] have identified the π antibonding as responsible for this trend.

There is another consequence of π bonding and the specific shape of the nonbonding a_1 orbital in these compounds. This is the predicted occurrence of conformational preferences and barriers to rotation around the M-L bond in Cp_2MLL' compounds when L carries a "single-faced" π donor or acceptor system. Consider the extreme conformations of a model $Cp_2M(LR_2)L'$ system, **13a** and **13b**. In **13a** the ligand π-type orbital eclipses the a_1 orbital; in **13b** it is twisted 90° away from eclipsing. It is clear that for a d^0 system, empty a_1, a donor L with its π orbital filled should choose **13a**. For a d^2 system, a_1 filled, an acceptor L, its π orbital empty, should also prefer **13a**, while a π donor L will



13a



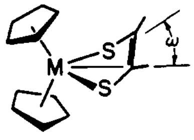
13b

try to avoid the four-electron destabilizing interaction with a_1 by going to **13b.**

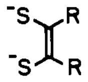
Experimental information on this point is scarce. There is a crystal structure of $Cp_2Mo(OH)NH_2CH_3^+$, d^2, but the location of the hydroxide hydrogen is not available.[15] Structures of $Cp_2Ti(SPh)_2$, d^0, and $Cp_2V(SPh)_2$, d^1, have been determined.[10] The SPh^- ligand carries two lone pairs, but its π-donor character should be set by the higher energy one of these, the p type lone pair orthogonal to the MSPh plane. In both structures the geometry is such that the S-M-S-C(Ph) dihedral angle is approximately 65°. Another interesting structure, related both to the conformational preferences discussed in this section and in the previous one for a bridging N_2 complex, is that of $(Cp_2NbCl)_2O^{2+}$. The dihedral angle between the two Cl-Nb-O planes is 72.5°, and has been interpreted by Prout and coworkers[15] in π-bonding terms similar to those discussed here. In a crystal structure of $Cp_2VBr(TCNE)$, the TCNE molecule is σ bonded through a nitrogen and orients itself so that its better π-acceptor system conjugates with the formally occupied $1a_1$.[19c] A d^2 complex with a donor substituent, $Cp_2VN(SiMe_3)_2$, has been synthesized, but its structure, is to our knowledge not available.[19d]

A recent synthesis of a simple carbene complex $Cp_2Ta(CH_3)CH_2$ is of considerable interest.[20] The question arises whether the methylene prefers an orientation analogous to **13a** ($L' = CH_3$, $L = C$) or **13b.** A carbene ligand is a two-electron donor and has one ideal acceptor orbital orthogonal to the MCH_2 plane. The equilibrium conformation of these Ta(III) d^2 complexes is set by the interaction of this carbene acceptor orbital with the filled nonbonding $1a_1$ orbital of the Cp_2TaL_2 framework. Conformation **13a** should be preferred, and this is observed in a crystallographic study.[20a] The experimental barrier to methylene rotation is too high to observe in an NMR experiment.[20a] In a model compound $Cp_2Ti(CH_3)CH_2^-$ we calculate a difference in energy of 1.2 eV between **13a** and **13b.** The importance of the carbene structure is that while in the other conformational equilibria referred to above the preferred geometry could have been set by the steric constraints of the system, in the carbene case the conformation which is electronically favored and experimentally found is the sterically less likely one.

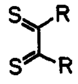
Cp_2M(dithiolene) complexes present another interesting conformational problem. Structures are available for several benzene-1,2-dithiolene, toluene-3,4-dithiolene, and ethylene-1,2-dithiolene complexes of Ti, Mo, and W.[21] One interesting feature of these structures is the degree of folding around the SS axis, as shown in **14.** The bending angle ω is less than 10° in the Mo and W complexes, but 46° in the two Ti compounds. In all molecules the SMS angle is 82-83°, a value typical for d^2 complexes. If the dithiolene ligand were viewed in its reduced form as $S_2C_2R_2^{2-}$, **15a,** the metal oxidation states would be formally Ti(IV), d^0, and Mo(IV) or W(IV), d^2. If the dithiolene were neutral, **15b,** we would have Ti(II), d^2, and Mo(II), d^4.



14



15a



15b

The folding in the Ti complexes is easily understood from either extreme viewpoint. If one has the dithiolene as **15a,** i.e., Ti(IV), the acceptor a_1 orbital will wish to interact with the donor orbital of the ligand. This is the HOMO of **15a,** a π orbital of b_1 symmetry if $\omega = 0$. There can be no stabilizing interaction unless the dithiolene ligand folds. If we were to start from a Ti(II), d^2, formulation with the dithiolene neutral as in **15b,** then the Cp_2Ti donor orbital would seek out an interaction with the same $S_2C_2R_2$ orbital, now acting as an acceptor. Again an out-of-plane deformation of the dithiolene is required. One can equally well reason out why the dithiolene ligand is not folded much in the Mo or W complexes. For an anionic ligand, d^2, the acceptor orbital of the Cp_2Mo fragment is b_1^* (see the fragment orbitals in Figure 2). This is just the right symmetry to match the $S_2C_2R_2^{2-}$ donor orbital in C_{2v} symmetry.

Distortions of the Cp_2M Moiety

In the preceding discussion of σ and π bonding we have considered the Cp_2M fragment as a rigid partner, presenting a certain set of orbitals for bonding. But of course any bonding situation is symbiotic; the electronic demands of the ligands in Cp_2ML_n can change the geometry of the Cp_2M fragment.

The CpMCp angle θ (see **3**) is an obvious variable that can respond to the electronic nature of L. The analysis focuses on the change in energy and shape of the Cp_2M fragment orbitals with θ. This was shown in Figure 2. Note that the b_2 and $2a_1$ orbitals both rise in energy with increasing bending, decreasing θ. Their hybridization also changes in such a way that they extend further away from the metal and toward the ligands with decreasing θ. This is especially pronounced for the $2a_1$. Reasoning from the usual perturbation theoretic basis that an interaction between two orbitals is greater the greater the overlap and the smaller the energy gap between the two orbitals, we conclude that the better the π-acceptor character of L, the smaller the angle θ. The σ character of the ligand L is involved in interaction with the $2a_1$. The overlap and energy gap criteria operate in opposite directions in this case. At lower θ there is more directionality in the $2a_1$, but it is also further removed in energy from the level of an interacting ligand orbital. If it is the energy factor that dominates, then one would conclude that a ligand which is a better σ donor (i.e., has a more high-lying orbital) will favor a larger θ. That both good π acceptance and poor σ donation on the part of the ligand L would favor increased bending meshes with the reasoning cited in the introductory section that electron deficiency in Cp_2M is associated with bending. Good σ and π donation by the ligands alleviates that electron donation and should increase θ.

The available structures[22] cover a range of θ values from 148° in Cp_2MoD_2 to 126° in Cp_2ZrI_2, but unfortunately we do not see a clear sequence in σ donation or π acceptance that would allow us to test our predictions. Steric effects loom large in the determination of the equilibrium structures, as the extreme examples quoted above clearly indicate. Another geometrical distortion of the Cp_2M fragment will be discussed in the next section.

Complexes with One π-Bonding Ligand and One σ-Bonding Ligand

There are several bent Cp_2M complexes which have one π acceptor, such as CO as a ligand, and in addition one σ-bonding ligand. Examples are $Cp_2Nb(CO)H$[23] and $Cp_2V(CO)I$.[24] These complexes can only have C_s symme-

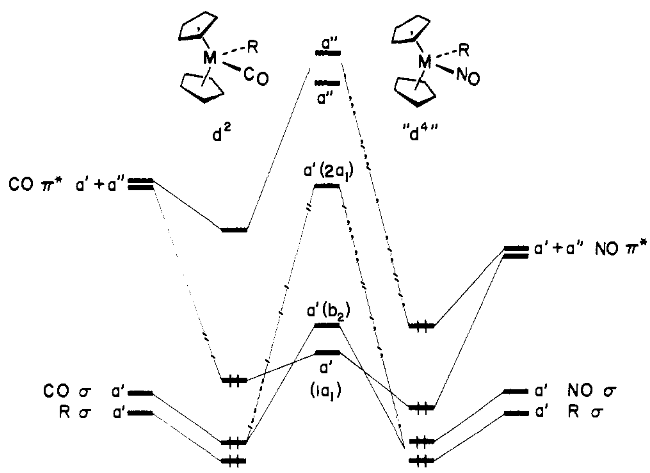
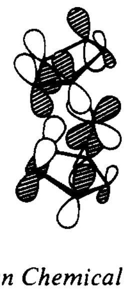


Figure 7. Interaction diagram for $Cp_2M(CO)R$ (left) and $Cp_2M(NO)R$ (right). The indicated orbital occupations correspond to M = V or Nb (left) and M = Mo (right).

try, but the bonding is similar to those cases already discussed. There will be two σ bonds, one with the purely σ-bonding ligand and one with the CO or other acceptor ligand, Figure 7, left. The CO in-plane a′ π^* orbital stabilizes the remaining metal fragment a′ orbital. With only one orbital available we again expect complexes with two or fewer d electrons to form.

Similar to these CO compounds are some interesting nitrosyl complexes of molybdenum, $Cp_2Mo(NO)R$ (R = alkyl).[25,26] The molecular structures of two of these species have been determined.[26] Each has a linear M-N-O bond and each has cyclopentadienyl ligands which are bonded to the metal atom in a grossly unsymmetrical manner. Those carbon atoms on the "back side" of the molecule away from the NO ligand are about 0.3 Å further from the molybdenum atom than are the other ring carbons. This unsymmetric bonding to the $C_5H_5^-$ ligands is highly unusual, but can be readily explained.

If the normal rules for electron counting are followed, the complexes $Cp_2Mo(NO)R$ are 20 electron complexes. The interaction diagram shown in Figure 7, right, shows how this is possible. The bonding in the NO complex is quite similar to that in the CO complexes except for the fact that the π^* orbitals of the NO molecule occur at much lower energies. This means that the Mo-NO π bond is stronger, but more importantly there is now a low-lying occupied a″ orbital. This orbital is a combination of the two highest lying valence orbitals of Cp_2M and the nitrosyl π^*. In the discussion in the first section we noted that the two highest valence orbitals of the Cp_2M fragment (a_2^* and b_1^*, descended from e_{1g}^*) were metal-cyclopentadienyl antibonding, and in the bent geometry mixed with still higher cyclopentadienyl orbitals. That mixing has the interesting effect that the bonding between the metal atoms and the rings is no longer symmetrical for these two orbitals. The two carbon atoms on the back side of the molecule, C_3 and C_4, are antibonding with respect to the metal atom while C_1, C_2, and C_5 are nonbonding or bonding. A schematic representation of one of the orbitals under discussion, b_1^*, is shown below to illustrate its shape.



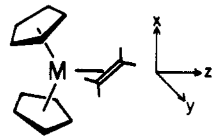
In the $Cp_2Mo(NO)R$ molecule we for the first time make use of the a_2^* and b_1^* orbitals. In the reduced C_s symmetry, both are a″, and both mix with one nitrosyl π^* to give an occupied orbital. The equivalent partial occupation of a_2^* and b_1^* is responsible for the unsymmetrical Cp-M bonding. It should be noted that the HOMO a″ is all on the NO and the Cp rings and has almost no metal contribution. The 18-electron formalism can be restored by assigning the electrons to the formally NO^+ ligand and making it a linear NO^- for the sake of our electron bookkeeping. Nevertheless, these molybdenum nitrosyl complexes are examples of molecules with excessive numbers of electrons which consequently have electrons in orbitals of at least partial antibonding character. The result is a highly unsymmetrical or distorted geometry.

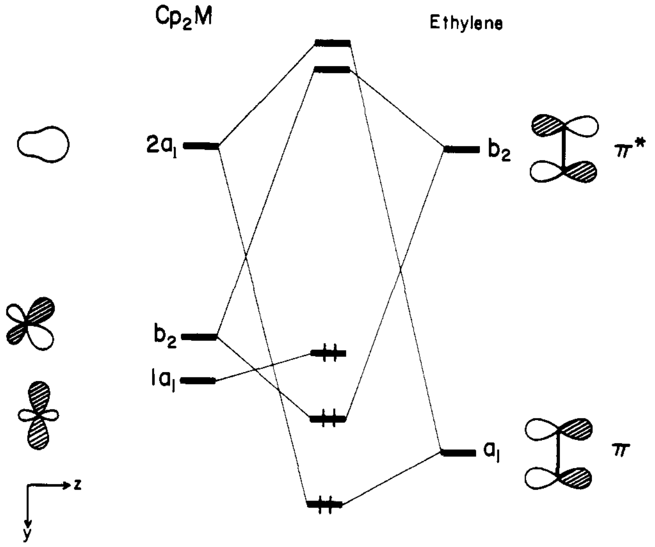
We believe that a distortion similar to the one analyzed above may occur in the structure of the formally 20-electron $Cp_2W(CO)_2$.[19a] Indeed extended Hückel calculations by Brintzinger, Lohr, and Wong[6b] on $Cp_2Mo(CO)_2$ explicitly study this effect. Another way in which this complex can escape the occupation of a high-lying orbital is by the formation of a carbon-carbon bond between the two carbonyl groups. This would be essentially an oxidative coupling, a reaction type to be discussed below.

Olefin Complexes

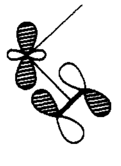
Olefin bis(cyclopentadienyl) complexes are known for several of the early transition metals and have been postulated as intermediates in many important reactions. The simple ethylene complexes $Cp_2M(C_2H_4)$ (**16**) are known for molybdenum and tungsten.[19c,27] These complexes are somewhat similar to the "edge on" dinitrogen case we have previously discussed. The filled π orbital of ethylene can act as a donor orbital, interacting strongly with the fragment $2a_1$ orbital. The empty olefin π^* orbital is of b_2 symmetry and stabilizes the metal b_2. This back-bonding appears to be particularly good in this case since we have a relatively high-energy metal donor b_2 orbital, hybridized toward the ligand and thus also having excellent overlap with the olefin π^* orbital. The remaining fragment orbital, the $1a_1$, remains essentially nonbonding. The Mo and W complexes are d^4 with the two low-lying d's, the b_2 and $1a_1$, filled.

16





These ethylene complexes have one nonbonding orbital, the $1a_1$, and thus can be readily protonated to form the species $Cp_2M(C_2H_4)H^+$ (M = Mo and W).[27] These complexes are analogous to the neutral niobium and tantalum hydrides, $Cp_2M(C_2H_4)H$ (M = Nb and Ta).[23,27] The molecular structure of a similar ethyl complex $Cp_2Nb(C_2H_4)(C_2H_5)$ has been published.[28] The symmetry in these complexes is at most C_s. All three of the key fragment orbitals are of a' symmetry. The olefin and the hydride or alkyl donor orbitals will have bonding interactions with two of these a' orbitals. The olefin π^* will stabilize the remaining a' orbital, the one which was $1a_1$ in C_{2v} symmetry, as shown in **17**.



17

In the above analysis we have assumed that the ethylene molecule lies in the yz plane. Guggenberger and co-workers[28] have pointed out, however, that there is no compelling steric reason forcing this planar geometry over an upright geometry. With the $C_5H_5^-$ ligands bent back there is adequate room for either isomeric arrangement. In the $Cp_2Nb(C_2H_4)(C_2H_5)$ structure the ethylene ligand does indeed lie exactly in the yz plane. This preference for the planar geometry is also attested to by NMR studies which show the ethylene to be nonfluctional, while the $C_5H_5^-$ ligands are fluctional at room temperature.

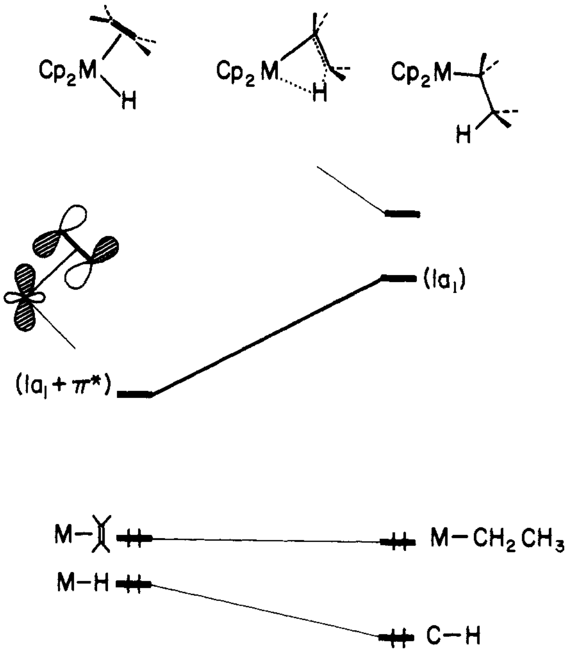
An examination of the fragment orbitals shows an obvious electronic reason for the planar arrangement. The molecules have C_s symmetry in both the planar and upright geometries. The donating function of the ethylene is in both cases from the filled π orbital of a' symmetry. The back-bonding, metal to ligand, must be into the π^* orbital which would be a' if the ethylene is planar, in the yz plane, and a'' if the ethylene were upright. The most available Cp_2M donor orbital is of a' symmetry, giving the stabilizing interaction already shown in **17**. Donor orbitals of a'' symmetry are not so readily available, so that the in-plane positioning of the ethylene in $Cp_2Nb(C_2H_4)(C_2H_5)$ is favored.

A similar analysis can be made for the C_{2v} d^4 complex $Cp_2Mo(C_2H_4)$. A planar ethylene π^* would interact with the metal's filled b_2 orbital, while an upright ethylene π^* would interact with an empty b_1 orbital. Our calculations on the model complex $Cp_2Ti(C_2H_4)^{2-}$ show that the planar isomer is about 2.2 eV more stable than the upright isomer. The lower energy results primarily from the stabilization of the b_2 orbital by the ethylene π^*. This point has also been noted by Green, Jackson, and Higginson.[11] A substituted ethylene would of course have an additional steric reason for favoring the planar geometry.

Insertion Reactions of Coordinated Olefins

The Nb ethylene hydride complex is an unusual molecule in a number of respects. Very few compounds which have coordinated olefin ligands cis to a hydride ligand are stable. Indeed other similar complexes are known to insert the olefin into the hydride metal bond readily. Schwartz has developed extensively the "hydrozirconation" reaction which involves the reaction of Cp_2ZrClH with olefins.[29] Immediate olefin insertion occurs. The so-called "soluble" Ziegler-Natta catalysts for olefin polymerization are based on alkyls of the Cp_2Ti system.[30] Colomer and Corriu have reported reactions which reduce and isomerize various olefins with Cp_2TiH as the proposed intermediate.[31]

Why then are the Nb and similar d^2 complexes such as $Cp_2Mo(C_2H_4)H^+$ relatively stable? The answer can be seen by considering the electronic structure of the $Cp_2Nb(C_2H_4)H$ and the supposed product of an insertion, which would be an ethyl complex, $Cp_2Nb(C_2H_5)$. The ethylene complex has been considered above, while the ethyl compound will be essentially similar to the monohydride case **4**. A correlation of the various orbitals involved in the insertion reaction is shown in **18**. The hydride and ethylene ligands are pictured moving toward each other, forming a new C-H bond, while simultaneously the olefin-metal bond is converted to the new metal-alkyl bond and the metal-hydride bond is broken. Throughout the reaction path C_s symmetry is maintained. This means that all the orbitals involved are of a' symmetry, and no level crossings occur.



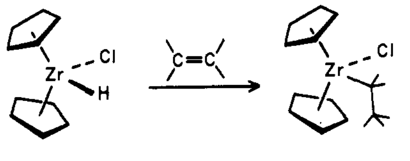
18

The crucial dependence of the activation energy of the insertion reaction on the number of d electrons may be understood with the help of **18**. With a d^0 complex, a species such as $Cp_2Ti(C_2H_4)H^+$, the two lowest levels in **18** would be occupied. The insertion would proceed rapidly, driven by the energy gain on transforming Ti-H and Ti-(C_2H_4) bonds into Ti-C_2H_5 and C-H bonds. This may be the mechanism of action of the "soluble" Ziegler-Natta catalysts. Some workers have hypothesized that the reactive intermediates are cationic alkyls,[32] Cp_2TiR^+, which are also d^0 complexes. An olefin might coordinate to the Ti atom, insert into the alkyl bond forming a new d^0 alkyl complex, then could coordinate another olefin which would also insert, and so forth, leading to an eventual polymer. Note in this connection our previous conclusions on the possible departure from C_{2v} symmetry of d^0 Cp_2ML complexes. A motion of L to the side, coupled with the availability of acceptor orbitals in Cp_2ML, would facilitate the entrance of another ligand.

The d^2 complexes are quite different, a consequence of the variation in energy of the one filled d orbital. In the olefin hydride complex this orbital, marked by the heavier line in **18**, has been stabilized by the ethylene π^*, as illustrated earlier in **17**. In the ethyl complex this orbital is somewhat destabilized by the alkyl σ bond formation. In model calculations this orbital is destabilized by some 1.2 eV, meaning that insertion for a d^2 complex would be about 50 kcal/mol less favorable than for a d^0 case. The insertion can be forced in the d^2 cases by adding an additional ligand which can coordinate to the ethyl complex, but there is certainly no evidence reported for a polymerization reaction.

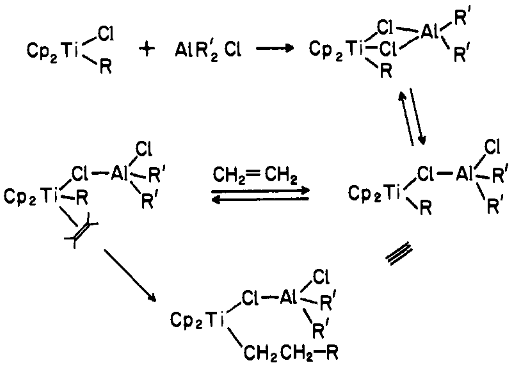
In between these two extremes would be a d^1 complex. The only direct experimental evidence on such a system is the study by Colomer and Corriu[31] who find that a Ti(III) hydride, d^1, will partially reduce, but also isomerize, olefins. The isomerization of olefins implies that the insertion must be reversible, perhaps an indication that a d^1 case is truly intermediate. We note here several other quantum mechanical calculations on possible models for Ziegler-Natta catalytic systems.[33]

The "hydrozirconation" reactions, exemplified by **19**, involve the reactions of olefins with Cp_2ZrClH to give insertion products.[29] The coordination number is one greater than in the previously discussed examples, but the essentials of the olefin insertion remain the same. The Cp_2ZrClH molecule has one open coordination site to coordinate an olefin. It is a d^0 complex, so there is no stability added to the olefin-metal bond due to donation into the empty π^* orbital. Upon coordination the olefin will be in close proximity to the hydride ligand, and thus the insertion can take place readily, driven again by the energy gained from forming the new C-H bond.



19

A second possible intermediate for the polymerization reactions of the "soluble" Ziegler-Natta catalysts involves a Ti(IV) species similar to the Zr compound just discussed. The intermediate illustrated in the reaction sequence **20** contains an aluminum alkyl residue which results from the initial addition of an aluminum alkyl to $Cp_2Ti(R)Cl$, R = alkyl.[30] The key point in this mechanism is that the olefin can only react with a coordinatively unsaturated species. Thus the $Al(Cl)_2R_2^-$ group must be monodentate when the olefin initially coordinates. This is important to realize because some of the intermediates previously hypothesized have been coordinately saturated, 18-electron complexes.[30] These catalysts are complicated and almost certainly the reactive intermediates are quite variable. We can say, however, that the best candidate for a polymerization catalyst of this type would be a coordinatively unsaturated d^0 complex.



20

In addition to the olefin insertion reactions already discussed there is a second class of insertion reactions which is fundamentally different. The hydride Cp_2ReH is an 18-electron complex without any low-lying empty orbitals, as was illustrated in **4**. One would not expect this hydride to coordinate an additional electron-donating ligand. It has been observed, however, that the complex readily reacts with dimethylacetylene dicarboxylate to give the vinyl insertion product.[34] Similar reactions are also known for Cp_2MoH_2, also an 18-electron species, which reacts with a variety of olefins and acetylenes to give insertion products.[35] The particular olefins and acetylenes which react have electron-accepting substituents.

These reactions may be rationalized by considering the olefin or acetylene ligands acting not as donors but as acceptors toward a donor Cp_2ML_n. The basicity of the bis(cyclopentadienyl) compounds is attested to by their chemical properties[4] and the low magnitude of their first ionization potential (6-6.5 eV).[11] The acceptor orbital of the olefin has a node between the carbons, so that the metal should interact asymmetrically, with one of the carbon atoms. The proposed mechanism, **21**, involves the formation of a Lewis acid-base complex with build-up of positive charge at the metal and negative charge at the uncomplexed carbon terminus. This facilitates a proton migration from the metal to the vinyl ligand, thus completing the so-called insertion reaction. Evidence for such a reaction mechanism has been found for the Cp_2MoH_2 system for which kinetic evidence indicates that Lewis acid-base adducts are formed.[35]

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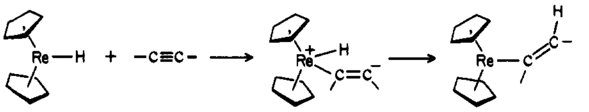
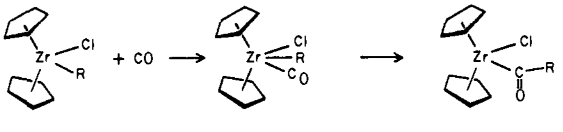


Carbonyl Insertion Reactions

As an extension of their hydrozirconation reaction, Schwartz and co-workers[29] have observed that the Zr(IV) alkyl complexes which they prepared by olefin insertion reactions will readily react with CO to give CO insertion into the metal alkyl bond. This formation of acyl derivatives from olefins and CO is similar to the reactions which take place in the cobalt hydroformylation process. Similar CO insertions have been observed for a number of Ti(IV) and Zr(IV) dialkyls also.[36]



These insertion reactions are easily understood. The dialkyl complexes are d^0 with one low-lying empty orbital, the $1a_1$ in **7**. The complex will thus readily react with a good σ donor with the direction of ligand attack expected to be along the y axis of the molecule. The resulting complex, also d^0, has three σ-bonding ligands. Significantly there is now no possibility for the normal π back-bonding into the CO π^* orbitals which one finds in nearly all known CO complexes. The angle between the alkyl group and the CO ligand is predicted to be less than 90°, meaning that there is substantial overlap between the CO π^* and the alkyl σ-donor orbital. The insertion or migration reaction should thus readily take place. In principle there is no symmetry restriction since all involved orbitals are of a′ symmetry in the C_s point group. The resulting acyl compound is more stable than the CO complex because of the added energy due to the C-C bond. There also seems to be a supplemental stabilization due to an interaction of the acyl oxygen with the one empty orbital on the metal. This is indicated by the

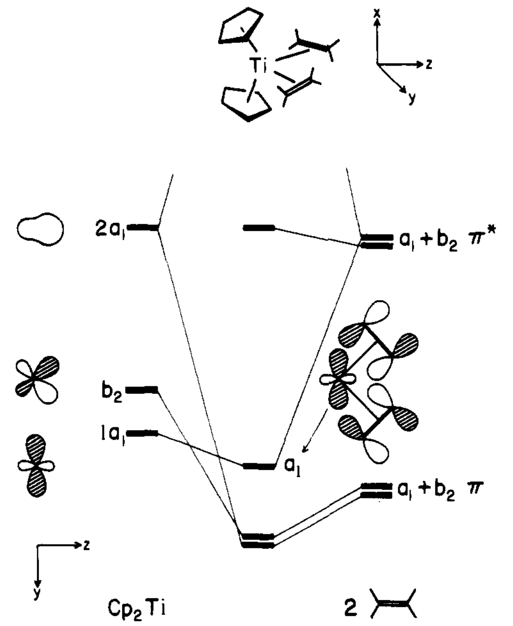
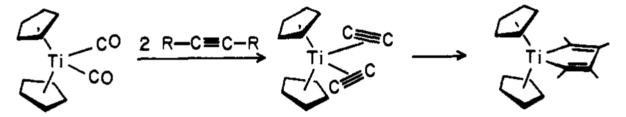


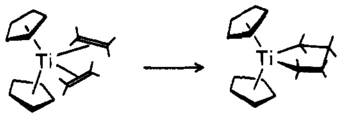
Figure 8. Interaction diagram for $Cp_2Ti(C_2H_4)_2$. The orbitals are sketched in the yz plane.

anomalous infrared stretching frequencies found for acyl derivatives,[35] but has not been confirmed by structural studies.

Oxidative Coupling Reactions

When $Ti(C_5H_5)_2(CO)_2$ is reacted with diphenylacetylene, an unusual "titanacyclopentadiene" complex is formed.[37] A similar coupling step, **22** → **23**, has been suggested for an olefin analogue.[38] These reactions fall in the general category of oxidative coupling reactions. Some very unusual reactions which occur when $Ti(C_5H_5)_2(C_6H_5)_2$ is thermally decomposed are also thought to involve a coupling reaction.[39]





22 **23**

The coupling reaction can be reversible. McDermott and Whitesides prepared the "titanacyclopentane complex", **23**, and found that the thermal decomposition of the compound yielded ethylene.[38] In Figure 8 is shown an interaction diagram for $Cp_2Ti(C_2H_4)_2$, which is a Ti(II) d^2 complex. The primary metal acceptor orbitals are the b_2 and the $2a_1$ while the remaining orbital, the $1a_1$, is ideally situated for a back-bonding interaction with one combination of the π^* orbitals of the ethylene ligands. The molecular orbital scheme for the coupled product of the reaction, **23**, is similar to that for the dihydride case discussed earlier in **7**. A correlation diagram for the elementary step of the oxidative coupling, **22** → **23**, is shown in Figure 9. The reaction is symmetry allowed,[40] proceeding from a d^2 Ti(II) complex to a d^0 Ti(IV) complex with simultaneous formation of the new CC bond. It appears from the qualitative features of the orbital scheme that the metallocycle should indeed be more stable.

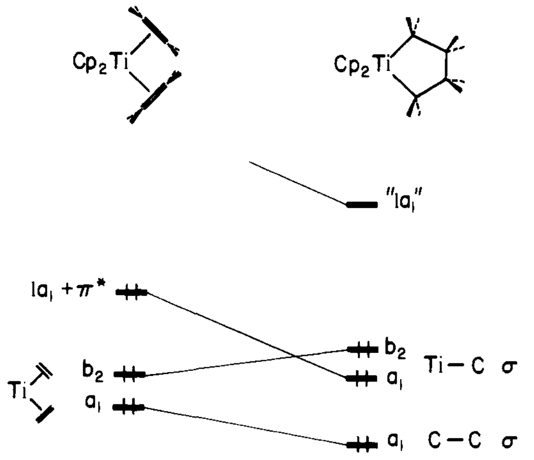
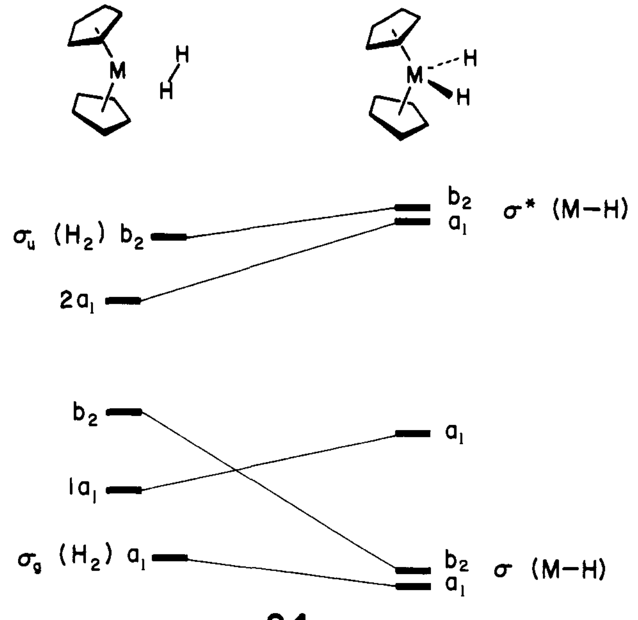


Figure 9. Correlation diagram for the oxidative coupling of two ethylenes coordinated to Cp_2Ti.

Note that the reversal of the coupling reaction for an analogue of **23** with two more electrons, for instance a d^2 Mo complex, would not be expected since it would lead to a 20-electron species with occupied antibonding orbitals.

It is perhaps appropriate here to discuss the carbene analogy which has played a certain role in discussions of the reactivity of Cp_2M fragments. The analogy was first made by Volpin and co-workers[37a] for Cp_2Ti and was made explicit by the calculations of Brintzinger and Bartell.[6] In the broad sense that a carbene is characterized by at least one high-lying filled orbital and at least one low-lying unfilled orbital the assignment of carbenoid character to Cp_2Ti is certainly correct. But perhaps the analogy is more direct for the d^4 system Cp_2Mo, as illustrated by the following considerations.

Let us construct a correlation diagram for an analogue of a typical carbene reaction, insertion into a σ bond. This reaction is of course an oxidative addition. More specifically we consider the least motion C_{2v} interaction of Cp_2M and H_2, obtaining the interaction diagram **24** shown below.



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For M = Ti, low spin, the reaction is a forbidden one. Of course, if the driving force for a reaction exists, and the least-motion pathway is symmetry forbidden, then one must not doubt that the reaction partners will find a way, albeit nonleast motion, to carry through the reaction. This is what

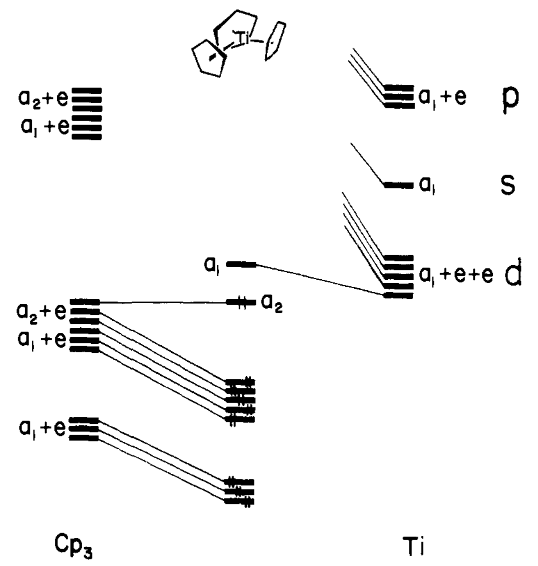


Figure 10. Interaction diagram for C_{3v} Cp_3Ti^+.

happens in the case of methylene,[41a] and was noted for Cp_2Ti by Brintzinger and Bartell.[6]

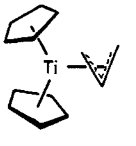
For M = Mo or W, with $1a_1$ and b_2 filled in the Cp_2M fragment, the least-motion cycloaddition is symmetry allowed. The carbene analogy for Cp_2Mo and Cp_2W was carefully delineated by Thomas,[18c] who reported the specific addition to H_2. Green and co-workers have found that the photolysis of Cp_2WH_2 leads to insertion of Cp_2W into the C–H bond of benzene and the methyl CH bond of *p*-xylene and mesitylene.[42] While neither of these studies directly established the intermediacy of Cp_2Mo or Cp_2W, the indirect evidence for these fragments and their subsequent insertion into σ bonds is good. It may be worth noting that a bent Cp_2Mo is not like an ordinary carbene, but that its HOMO (b_2) is a p- or π-type orbital and its LUMO ($2a_1$) is a σ-type orbital. This makes it more like a p^2 carbene,[41b] **25**, a fairly unusual type in methylene chemistry.

25

For a much more detailed analysis of Cp_2M insertion reactions, including a proper accounting of the spin factors omitted by us, the reader is referred to the elegant study of Brintzinger, Lohr, and Wong.[6b]

Allyl and Tetrahydroborate Complexes

There are several examples of bis(cyclopentadienyl) π-allyl complexes including $Cp_2Ti(C_3H_5)$,[43a] a d^1 complex, and



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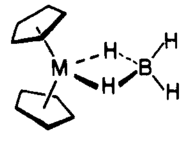

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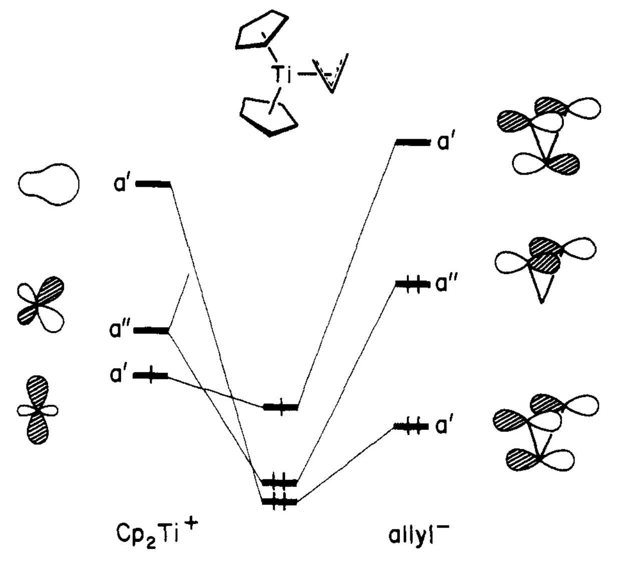
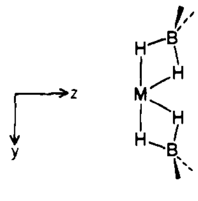
$Cp_2Nb(C_3H_5)$,[43b] a d^2 complex. The orbitals of the allyl anion are well-known, appearing at right in the interaction diagram shown below. The complexes have C_s symmetry. The lowest filled allyl orbital overlaps well with the higher a′ fragment orbital, forming a σ-bonding interaction. The a″ ligand orbital donates well into the fragment a″. The lower fragment a′ orbital and the empty allyl antibonding π orbital are of the same symmetry and have the same nodal surface, meaning there can be significant back-bonding from the metal to the allyl ligand. A similar interaction diagram has been given by Green, Jackson, and Higginson, who assigned the photoelectron spectrum of $Cp_2Nb(C_3H_5)$.[11]



Analogous to the π-allyl species are complexes of the tetrahydroborate anion, Cp_2TiBH_4 and Cp_2NbBH_4, **27**.[44a] The symmetry of these compounds is C_{2v}. The BH_4^- ligand has two donor orbitals, a_1 and b_2 in symmetry, which are similar to the two donor orbitals of the allyl ligand.[45] An interesting compound of as yet unknown structure is $Cp_2Zr(BH_4)_2$.[44b] Were the borohydrides arranged as in **28a**, then one of the four donor orbitals of the two BH_4^-, the b_2 combination shown in **28b**, would not have the proper pseudosymmetry to interact with the Cp_2Zr fragment. This MO is antibonding between the two borohydrides, a factor which should count against this conformation. Alternatives are **28c** and **28d**. In model calculations the former suffers from close steric contacts with the Cp rings. The latter is of lower energy, but there is no precedent for monodentate BH_4^- coordination. We do not consider the calculations overly reliable because of the steric complications and the fact that a complete potential energy surface was not explored. A structure determination would be of great interest.



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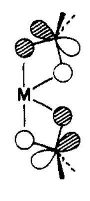

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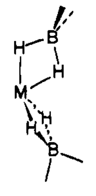
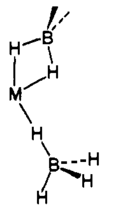


28c



28d

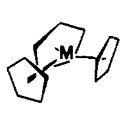
The Triscyclopentadienyl Complexes

The preceding discussions have covered the bis(cyclopentadienyl)metal fragment and its complexes in considerable detail. Before concluding we wish to briefly discuss a tris(cyclopentadienyl)(transition metal) fragment. The triscyclopentadienyls are quite common for the lanthanides and actinides, for which many complexes of the types Cp_3M (**29**), Cp_3MX (**30**), and Cp_3MB (**31**) (X = halogen, B = base) are known.[46] There appear to be a few examples within the transition metal series, including reported yttrium complexes[47] and perhaps Cp_4Zr.

Table II. Extended Hückel Parameters

Orbital	H_{ii}, eV	ζ^a
H 1s	−13.60	1.300
C 2s	−21.40	1.625
C 2p	−11.40	1.625
Ti 4s	−8.97	1.075
Ti 4p	−5.44	0.675
Ti 3d	−10.81	4.550 (0.4206), 1.40 (0.7839)

[a] Slater exponent. For the Ti 3d function two are given, followed in parentheses by the coefficient in the expansion of that orbital.



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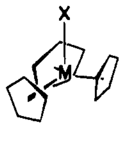

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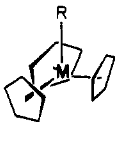

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The structure of $Zr(C_5H_5)_4$ has been reported by Kulishov et al.,[48] who conclude that there are three η^5-$C_5H_5^-$ ligands and one η^1-$C_5H_5^-$ ligand. Some doubt has been raised concerning the correctness of this structure.[49] The molecules Cp_4M (M = Ti, Zr or Hf) are all known to be fluctional with all four rings equivalent on an NMR time scale.[50,51] The structure of the Ti complex shows that it has two η^5-$C_5H_5^-$ ligands and two η^1-$C_5H_5^-$ ligands in the crystalline state.[49] Although the authors of the fluctional studies do not propose it, a viable intermediate for the interchange of the ligands would be a molecule with three η^5-$C_5H_5^-$ rings.

The geometry of a hypothetical Cp_3Ti^+ fragment is shown in Figure 10 which also shows a molecular orbital scheme for the C_{3v} fragment. Three $C_5H_5^-$ ligands can potentially donate six electrons each for a total of 18 electrons in all. It happens, however, that one of the donor orbitals resulting from the $C_5H_5^-$ ligands is of a_2 symmetry. Since there is no a_2 metal orbital in the C_{3v} point group, this molecular orbital cannot serve as a donor orbital.[52,53] Thus the three ligands donate 16 electrons to the metal leaving one orbital on the metal fragment empty. The lone remaining orbital is of a_1 symmetry and is mainly d_{z^2} with only a little p_z and s character (63% d_{z^2}, 3% s, 0.7% p_z). With one available metal orbital d^2 complexes of the type Cp_3M are theoretically possible. In the complexes Cp_3MR and Cp_3MB this one lone a_1 orbital will be used to form the σ bond to the alkyl group or the base.[54] It should be noted that there are no high-lying filled orbitals suitable for π back-bonding into π-acceptor ligand orbitals. Thus complexes such as Cp_3MCO would not be stable.

The bulk of the Cp_3M complexes are within the lanthanide and actinide series.[46] These metals have f orbitals, and there is an f orbital of the required a_2 symmetry in C_{3v}.[53,55] It is not possible to assess the importance of ligand donation into the f orbitals, but at least this one symmetry restriction is removed. The scarcity of Cp_3M complexes within the transition metal series may be due to steric considerations and the relatively poor overlaps between the appropriate orbitals. The lanthanides and actinides have larger radii, which may alleviate the steric problems, and in addition possess f orbitals.

Acknowledgment. Conversations with L. J. Guggenberger and F. N. Tebbe formed the stimulus to the initiation of our studies. We are most grateful to L. F. Dahl, R. Bau, and J. E. Bercaw for kindly supplying us with information prior to publication, and to R. Weber for the drawings. Our research was generously supported by the National Science Foundation and by the Advanced Research Projects Agency through the Materials Science Center at Cornell University.

Appendix

The calculations were of the extended Hückel type.[56] A charge iterative calculation was carried out on $(C_5H_5)_2Ti$ in the geometry shown in **3**: Ti–C, 2.32 Å; C–C, 1.39 Å, C–H, 1.1 Å; θ = angle between normals to rings = 136°. The basis set used for Ti consisted of single Slater orbitals for the 4s and 4p functions, and a 3d function taken as a contracted linear combination of two Slater-type functions. The various exponents were taken from the work of Richardson et al.[57] A quadratic charge dependence was assumed for the H_{ii} of titanium.[58] The H_{ii} for carbon and hydrogen were kept fixed. The orbital parameters along with the final self-consistent H_{ii} values are summarized in Table II. All other calculations in the paper used these parameters.

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