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Conformational Preferences of Substituted Cyclopentadienyl and Heterocyclopentadienyl Complexes

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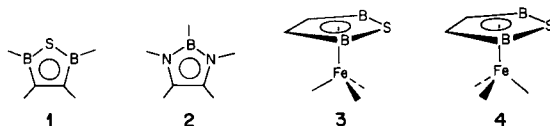
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Molecular orbital calculations indicate substantial barriers to internal rotation in thiadiborolene- $\text{Fe}(\text{CO})_3$ and diazaborolene- $\text{Cr}(\text{CO})_3$ complexes. The equilibrium geometry of the two molecules should also differ. A fragment analysis explains these results and leads to a general analysis of rotational barriers in heterocyclopentadienyl and substituted cyclopentadienyl- ML_3 and $-\text{ML}_2$ complexes. In the latter an interesting "slipping" from η^5 toward η^2 coordination is predicted.

Über die konformative Präferenz in substituierten Cyclopentadienyl- und Heterocyclopentadienyl-Komplexen

MO-Berechnungen ergeben erhebliche Barrieren für die internen Rotationen in Thiadiborolen- $\text{Fe}(\text{CO})_3$ - und Diazaborolen- $\text{Cr}(\text{CO})_3$ -Komplexen. Die Gleichgewichtsgeometrien der zwei Moleküle sollten verschieden sein. Eine MO-Fragmentanalyse erklärt diese Ergebnisse und führt darüberhinaus zu einer ganz allgemeinen Analyse der Rotationsbarrieren in Heterocyclopentadienyl- und substituierten Cyclopentadienyl- ML_3 - und $-\text{ML}_2$ -Komplexen. Für letztere wird ein gleitender Übergang von η^5 - nach η^2 -Koordination vorhergesagt.

The present report outlines an investigation of the conformational preferences of heterocyclopentadienyl- and substituted cyclopentadienyl- $\text{M}(\text{CO})_2$ and $\text{M}(\text{CO})_3$ complexes. Much of the discussion will be focused upon 2,1,3-thiadiborolene¹⁾ (1) and 1,3,2-diazaborolene²⁾ (2), because these systems are being actively studied in several laboratories. The principles illustrated by these specific molecules will be applicable to a wide range of organometallic compounds.



- ¹⁾ ^{1a)} W. Siebert, G. Augustin, R. Full, C. Krüger, and Y.-H. Tsay, *Angew. Chem.* **87**, 286 (1975); *Angew. Chem., Int. Ed. Engl.* **14**, 286 (1975). — ^{1b)} W. Siebert, R. Full, C. Krüger, and Y.-H. Tsay, *Z. Naturforsch., Teil B* **31**, 203 (1976). — ^{1c)} W. Siebert, R. Full, Th. Renk, and A. Ospici, *Z. Anorg. Allg. Chem.* **418**, 273 (1975). — ^{1d)} B. Asgarouladi, R. Full, K.-J. Schaper, and W. Siebert, *Chem. Ber.* **107**, 34 (1974). — ^{1e)} W. Siebert, Th. Renk, K. Kinberger, M. Bochmann, and C. Krüger, *Angew. Chem.* **88**, 850 (1976); *Angew. Chem., Int. Ed. Engl.* **15**, 779 (1976). — ^{1f)} W. Siebert, R. Full, J. Edwin, K. Kinberger, and C. Krüger, *J. Organomet. Chem.* **131**, 1 (1977). — ^{1g)} W. Siebert and W. Rothermel, *Angew. Chem.* **89**, 346 (1977); *Angew. Chem., Int. Ed. Engl.* **16**, 333 (1977).
²⁾ G. Schmid and J. Schulze, *Angew. Chem.* **89**, 258 (1977); *Angew. Chem., Int. Ed. Engl.* **14**, 249 (1977).

X-ray structures of analogous $\text{Fe}(\text{CO})_3$ complexes of **1** have shown that the conformation given by **3** is preferred over that in **4**^{4a, f)} in the crystal. In order to understand the origin of this conformational preference as well as that of the $\text{Ni}(\text{CO})_2$ complex of **1** and the $\text{Cr}(\text{CO})_3$ and $\text{Fe}(\text{CO})_2$ complexes of **2** we shall begin with a discussion of the orbitals of the $\text{M}(\text{CO})_3$ and $\text{M}(\text{CO})_2$ fragments. These metal fragment orbitals will then be interacted with the π levels of **1** and **2** in the two extreme orientations. The preferred conformation will be the one which maximizes two-electron stabilizing interactions and minimizes four-electron destabilizing interactions between the fragments. We shall also discuss a general approach towards modifying the height of a rotational barrier in a cyclopentadienyl- $\text{M}(\text{CO})_3$ complex by sequential substitution of heteroatoms for carbons in the polyene. Finally slipping the $\text{M}(\text{CO})_2$ fragments across the face of **1** and **2** is investigated. Our work draws on a previous analysis of rotational barriers in polyene and cyclopolyene- ML_3 complexes³⁾, and is related to a detailed study of carborane- ML_2 equilibrium orientations and deformations by *D. M. P. Mingos*⁴⁾.

Throughout this paper we need to describe conformations such as **3** or **4**. We will use the words "staggered" and "eclipsed" in the following special sense. The "staggered" conformation has a unique cyclopentadienyl or heterocyclopentadienyl atom strictly *trans* to one carbonyl group of the $\text{M}(\text{CO})_3$ fragment, while "eclipsed" corresponds to a 60° rotation of the $\text{M}(\text{CO})_3$ group relative to the Cp-ring. In this conformation one carbonyl group eclipses the unique Cp-atom. Thus we will call conformation **3** staggered and **4** eclipsed. The notation is arbitrary but some descriptor is needed.

$\text{M}(\text{CO})_3$ and $\text{M}(\text{CO})_2$ Fragments

The important valence orbitals of an $\text{M}(\text{CO})_3$ ⁵⁾ and $\text{M}(\text{CO})_2$ ^{4, 5c, 6)} group have been derived in detail elsewhere. We shall briefly reiterate the important features. The orbitals for these fragments are schematically shown in Figure 1.

In the $\text{M}(\text{CO})_3$ fragment there are three levels of low energy, $1e + 1a_1$, which bear an obvious resemblance to the t_{2g} set of an octahedral $\text{M}(\text{CO})_6$ molecule. The $1a_1$ is primarily z^2 ⁷⁾ with carbonyl π^* mixing in a bonding fashion. The $1e$ set is mainly $x^2 - y^2$ and xy . However, these orbitals are "tilted" by mixing xz and yz into them so as to keep maximal bonding with the carbonyl π^* combination. Alternatively, this tilting can be directly related to the composition of the t_{2g} set of an octahedral ML_6 molecule with the coordinate system chosen so that the z axis lies along one of the three-fold axes of the octahedron^{3, 5d, 8)}. The $2e$ set is xz and yz with again some xy and $x^2 - y^2$ mixed in. These orbitals are tilted so that they have maximal antibonding with the carbonyl σ sets and, therefore, lie higher

³⁾ *T. A. Albright, P. Hoffmann, and R. Hoffmann, J. Am. Chem. Soc.* **99**, 7546 (1977).

^{4a)} *D. M. P. Mingos, J. Chem. Soc., Dalton Trans.* **1977**, 602. — ^{4b)} *D. M. P. Mingos, M. I. Forsyth, and A. J. Welch, J. Chem. Soc., Chem. Commun.* **1977**, 605.

⁵⁾ ^{5a)} *M. Elian and R. Hoffmann, Inorg. Chem.* **14**, 1058 (1975). — ^{5b)} *M. Elian, M. M. L. Chen, D. M. P. Mingos, and R. Hoffmann, ibid.* **15**, 1148 (1976). — ^{5c)} *T. H. Whitesides, D. L. Lichtenberger, and R. A. Budnik, ibid.* **14**, 68 (1975). — ^{5d)} *D. L. Lichtenberger and R. F. Fenske, J. Am. Chem. Soc.* **98**, 50 (1976). — ^{5e)} *J. K. Burdett, J. Chem. Soc., Faraday Trans. 2* **70**, 1599 (1974).

⁶⁾ *P. Hoffmann, Angew. Chem.* **89**, 551 (1977); *Angew. Chem., Int. Ed. Engl.* **16**, 536 (1977).

⁷⁾ Throughout this paper we shall use the simplified notation z^2 , xy , xz , yz , and $x^2 - y^2$ for the n d orbitals and x , y and z for the $n + 1$ p orbitals.

⁸⁾ See, for example, *L. E. Orgel, An Introduction to Transition-metal Chemistry*, p. 174, John Wiley, New York, N. Y. 1960.

in energy than $1e$. Furthermore, they are hybridized away from the $M(CO)_3$ group by mixing metal x and y in a bonding fashion to carbonyl σ . Finally, at still higher energy is $2a_1$. This orbital consists of z^2 , z , and s at the metal. The origin of its hybridization has been discussed elsewhere^{5a, b)}.

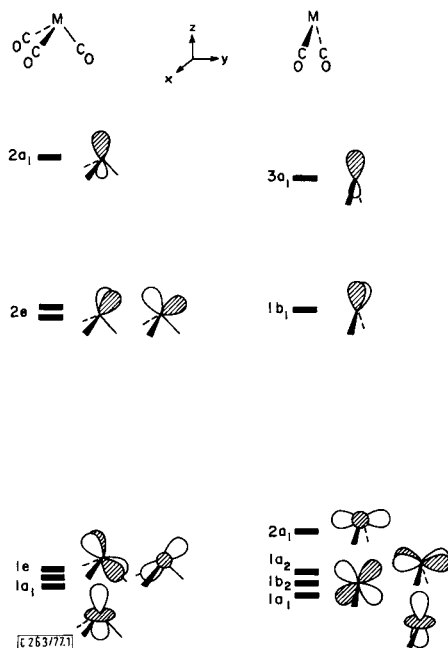
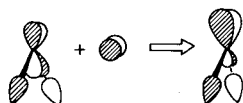


Fig. 1. The important valence orbitals of $M(CO)_3$ and $M(CO)_2$ fragments

The orbitals of an $M(CO)_2$ group bear some resemblance to those of an $M(CO)_3$. At low energy $1a_1$ (primarily z^2), $1b_2$ (yz), and $1a_2$ (xy) interact in a bonding manner to carbonyl π^* . At somewhat higher energy $2a_1$ (primarily $x^2 - y^2$) is destabilized slightly by antibonding with carbonyl σ . In some respects it can be thought of as originating from the symmetric component (with respect to the yz plane) of $2e$, $2e_g$. At higher energy is $1b_1$. This orbital consists of xz interacting in an out-of-phase manner with carbonyl σ ; however, metal x is also mixed in in a bonding fashion.



Therefore $1b_1$ is hybridized away from the $M(CO)_2$ group towards the incoming set of polyene orbitals. $1b_1$ bears an obvious resemblance to $2e_g$ (the antisymmetric component with respect to the yz plane). Finally, at still higher energy is $3a_1$. This is a mixture of z^2 , s , and z which is completely analogous to $2a_1$ in $M(CO)_3$.

The requirements for a strong conformational preference in a polyene $M(\text{CO})_3$ or $M(\text{CO})_2$ molecule are clear. The major interactions between the polyene π orbitals and the metal carbonyl fragment occur from the $2e$ set in $M(\text{CO})_3$ and $1b_1$ in $M(\text{CO})_2$. Any significant change in overlap between these fragment orbitals and the π levels of the polyene with respect to rotation between the fragments will create a barrier. Also for a d^6-d^{10} $M(\text{CO})_3$ or $M(\text{CO})_2$ fragment the most favorable orientation will minimize repulsions between $1e$ of $M(\text{CO})_3$ and $1b_2$ in $M(\text{CO})_2$ with the filled π orbitals of the polyene. $2a_1$ and $1a_2$ in $M(\text{CO})_2$ have δ symmetry, and therefore will not match, in symmetry, any filled π orbital. Finally, $1a_1$ and $2a_1$ in $M(\text{CO})_3$ along with $1a_1$ and $3a_1$ in $M(\text{CO})_2$ are cylindrically symmetric. Consequently, they also give rise to no conformational preference.

$M(\text{CO})_3$ Complexes of Thiadiborolene and Diazaborolene

Our extended Hückel calculations give the staggered conformation of tricarbonyl-(2,1,3-thiadiborolene)iron (**3**) more stable than the eclipsed form **4** by 8.2 kcal/mole. On the other hand, the eclipsed geometry **5** of tricarbonyl(1,3,2-diazaborolene)chromium is 12.3 kcal/mole more stable than the staggered conformer **6**. The parameters of the calculation are specified in the Appendix. To understand these computed preferences let's look at what happens to the z coefficients of the π orbitals in going from the parent cyclopentadienyl system to **1** or **2**. The perturbation encountered when the carbon atoms in a

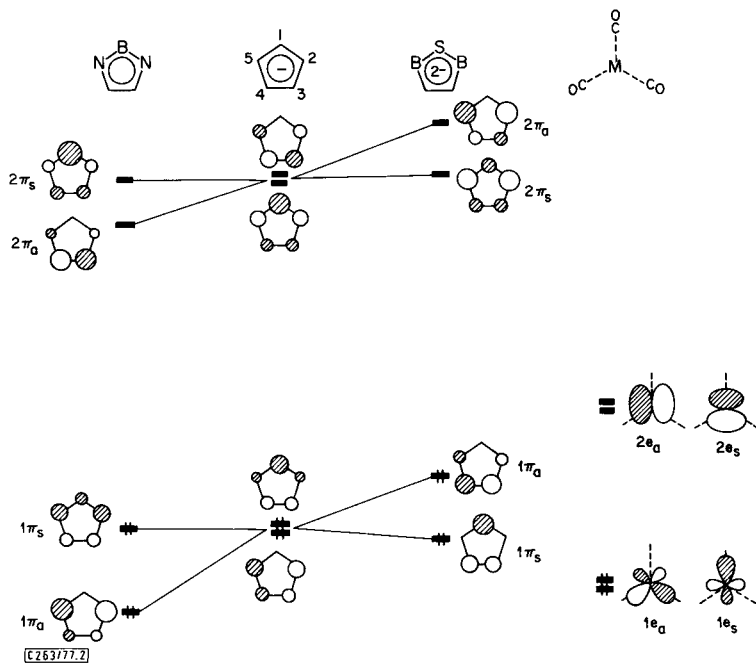
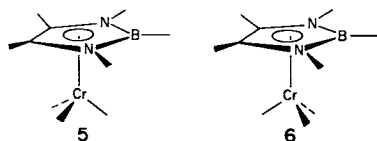


Fig. 2. The nodal properties and approximate energies of diazaborolene (left) and thiadiborolene (right). At far right are shown the $1e$ and $2e$ levels of an $M(\text{CO})_3$ fragment

cyclic polyene are replaced by heteroatoms has been discussed in detail in several texts⁹⁾. In simple terms, when the heteroatom is more electronegative than carbon, then the z coefficient of the heteroatoms is increased in the π levels and decreased in π^* . Exactly the reverse occurs when the heteroatom is less electronegative than carbon. The relative magnitudes of the coefficients and approximate energies for the π orbitals in **1** and **2** are shown in Figure 2. On the right side of Figure 2 is a sketch of a top view of the $1e$ and $2e$ orbitals in an $M(CO)_3$ fragment. Note, for example, that in $1\pi_a$ for thiadiborolene the coefficients at positions 3 and 4 increase while those at 2 and 5 decrease, relative to the cyclopentadienyl system. The reverse occurs in $1\pi_a$ for diazaborolene¹⁰⁾.



We shall now interact these polyene π orbitals with the orbitals of an $M(CO)_3$ group in either the staggered or eclipsed conformations. Table 1 lists the group overlaps between these orbitals. Irrespective of conformation, the overlap between 1π and $2e$ is always much larger than that between 2π and $1e$. The energy gap between 1π and $2e$ is also much smaller, so that the major interaction in the molecules occurs between these pairs of fragment orbitals. In tricarbonyl(cyclopentadienyl)iron cation there is a small overlap difference between $2e_s$ and $1\pi_s$ in going from the staggered to eclipsed geometries; however, this is precisely cancelled by the $2e_a-1\pi_a$ combination. The other overlaps are essentially invariant with respect to rotation. Therefore, our calculations give essentially no barrier to rotation for this complex — 0.002 kcal/mole. This is consistent with the fact that there seems to be no preferred conformation in the structures of cyclopentadienyl- ML_3 complexes¹¹⁾, and indeed on symmetry grounds alone the fifteen-fold barrier would be expected to be small.

In tricarbonyl(2,1,3-thiadiborolene)iron the overlap between $1\pi_s$ and $2e_s$ is approximately the same in both conformations. However, because of the polarization in $1\pi_a$, its interaction with $2e_a$ is more favorable for the staggered conformer — compare **7** with **8**. The differential in the $1e + 2\pi$ combinations approximately cancel each other in the two geometries. Note that the overlap between $1e$ and 1π favors the staggered geometry. Since this interaction involves two pairs of orbitals which are filled, the conformation

⁹⁾ E. Heilbronner and H. Bock, *Das HMO-Modell und seine Anwendung*, pp. 132–167, Verlag Chemie, Weinheim 1968; F. C. Goodrich, *A Primer of Quantum Chemistry*, pp. 106–110, John Wiley, New York, N. Y. 1972; L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, pp. 43–47, W. A. Benjamin, New York 1966; N. D. Epiotis, W. R. Cherry, F. Bernardi, and W. J. Hehre, *J. Am. Chem. Soc.* **98**, 4361 (1976).

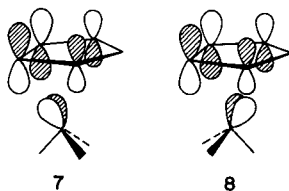
¹⁰⁾ For a description of the bonding in diazaborolenes, see J. Kroner, H. Nöth, and K. Niedenzu, *J. Organomet. Chem.* **71**, 165 (1974).

¹¹⁾ ^{11a)} A. F. Brendt and R. E. Marsh, *Acta Crystallogr.* **16**, 118 (1963); — ^{11b)} M. E. Gress and R. A. Jacobsen, *Inorg. Chem.* **12**, 1746 (1973); — ^{11c)} C. Barbeau and R. J. Dubey, *Can J. Chem.* **51**, 3684 (1973); **52**, 1140 (1974); C. Barbeau, K. S. Dichmann, and L. Ricard, *ibid.* **51**, 3027 (1973); — ^{11d)} B. Müller and J. Krause, *J. Organomet. Chem.* **44**, 141 (1973); — ^{11e)} T. L. Khotyanova, S. I. Kuznetsov, E. V. Bryukhova, and Yu. V. Makarov, *ibid.* **88**, 351 (1975); — ^{11f)} W. Harrison and J. Trotter, *J. Chem. Soc., Dalton Trans.* **1972**, 678.

Table 1. Group Overlaps Between the Valence Orbitals of the $M(\text{CO})_3$ and Cyclopentadienyl Fragments

Compound	$\langle 2e_s 1\pi_s \rangle$	$\langle 2e_a 1\pi_a \rangle$	$\langle 1e_s 2\pi_s \rangle$	$\langle 1e_a 2\pi_a \rangle$	$\langle 1e_s 1\pi_s \rangle$	$\langle 1e_a 1\pi_a \rangle$
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3^+$						
Stag.	0.279	0.281	0.097	0.097	0.078	0.078
Eclip.	0.281	0.279	0.097	0.097	0.078	0.078
$\text{SB}_2\text{C}_2\text{H}_4\text{Fe}(\text{CO})_3$						
Stag.	0.239	0.265	0.006	0.048	0.032	0.040
Eclip.	0.233	0.245	0.099	0.007	0.093	0.079
$\text{BN}_2\text{C}_2\text{H}_5\text{Cr}(\text{CO})_3$						
Stag.	0.254	0.227	0.060	0.074	0.100	0.080
Eclip.	0.274	0.235	0.127	0.118	0.035	0.050

which shows the largest interaction will be the least stable (when two orbitals interact, the antibonding combination is destabilized more than the bonding one is stabilized; this closed shell-closed shell repulsion is the molecular orbital equivalent of steric repulsion¹²⁾). Therefore it is the larger $2e_a-1\pi_a$ interaction and repulsions between 1π and $1e$ which make the staggered form **3** more stable than the eclipsed **4**. The situation is even more evident for tricarbonyl(1,3,2-diazaborolene)chromium. Because of the polarization in the π orbitals, there is greater overlap of $2e$ with 1π and $1e$ with 2π in the eclipsed geometry. There is, additionally, less repulsion between $1e$ and 1π in this conformation. Therefore all of these factors work in concert to make a large barrier in going from **5** to **6**.



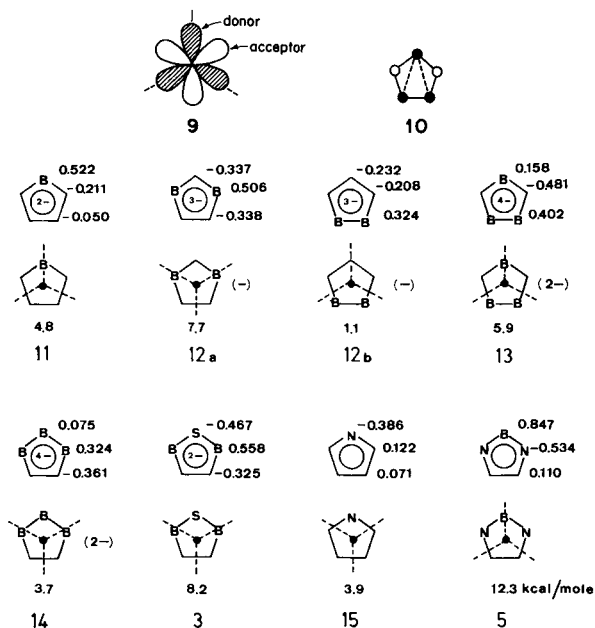
We can look at these barrier problems in a simpler, but perhaps less rigorous manner. Consider a d^6 $M(\text{CO})_3$ fragment such as $\text{Cr}(\text{CO})_3$ or $\text{Fe}(\text{CO})_3^+$. The $1e$ set is filled and corresponds to "lone pairs" which will orient themselves to regions of low electron density on the polyene. The $2e$ orbitals form an acceptor set which seeks out regions of high electron density in the coordinated ligand. A top view of the combined angular properties of these orbitals is given by **9**. $1a_1$ and $2a_1$ are mixed in as well to give the equivalent of three localized donor and three localized acceptor orbitals.

The donor functions eclipse the projection of the $M(\text{CO})_3$ bonds onto the plane of a polyene and the acceptors lie in a staggered position.

When a heteroatom is substituted into a cyclopentadienyl ring, charge will build up or decrease in the various positions. The most stable conformation is then achieved by matching regions of high and low electron density in the cyclopentadienyl system with the donor and acceptor functions on $M(\text{CO})_3$ in **9**. The way to provide the maximum orientational preference in a perturbed cyclopentadienyl fragment is by changing the electronegativity

¹²⁾ R. Hoffmann, *Acc. Chem. Res.* **4**, 1 (1971); K. Müller, *Helv. Chim. Acta* **53**, 1112 (1970); L. Salem, *J. Am. Chem. Soc.* **90**, 543 (1968).

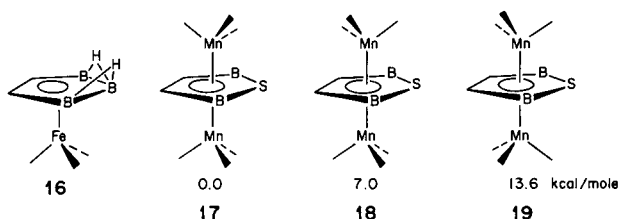
of the atoms marked by either the closed circles in **10** or the open ones, but not both in the same direction, i. e. not both more electronegative or both electropositive. Examples of these principles in action are given below.



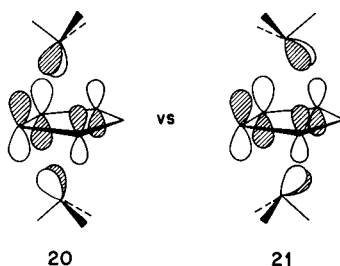
The most stable conformation, the rotational barrier, and the π charge distribution are shown for each structure. The total π charge in each five-membered ring was adjusted so that it served as a six-electron ligand to an $\text{Fe}(\text{CO})_3^{2+}$ metal fragment. This is just a formalism which facilitates intercomparison of the various structures. The π charges in the above structures were converted relative to the cyclopentadienyl anion (which would then have a π charge of zero on each carbon). Notice that in **12a** and **13**, which correspond to the substitution pattern in **10**, the calculated barriers are larger than that for the mono-substituted system **11**. However, the barrier in **14** drops since two open and one closed site are being perturbed in the same direction. In **5** and, to a lesser degree, **3**, the perturbation in the π orbitals is enhanced by changing the electronegativity of both the open and one of the closed circles in an opposite sense. Therefore, the barrier increases. There is a rough, linear correlation between the barrier height and the difference in charges between the open and closed circles in **10**. As the difference becomes larger, our calculated barriers increase. Note also that all of the preferred conformations correspond to our arguments concerning the orientation of the donor and acceptor orbitals of the $\text{Fe}(\text{CO})_3^{2+}$ unit. The available structural information for an analog of **15**¹³⁾ is in accord with our prediction of the most stable conformation.

¹³⁾ ^{13a)} G. Huttner and O. S. Mills, Chem. Ber. **105**, 301 (1972). — ^{13b)} Thiophene complexes also have this orientation; M. F. Bailey and L. F. Dahl, Inorg. Chem. **4**, 1306 (1965); Y. Dusausoy, J. Protas, and R. Guillard, Acta Crystallogr. Sect. B **29**, 726 (1973); J. A. D. Jeffreys and C. Metters, J. Chem. Soc., Dalton Trans. **1977**, 1624.

The reader is cautioned not to accept the barrier heights as being quantitatively correct. They are calculated with idealized geometries within the extended Hückel formalism, a method with well-known limitations; however, this method is known to reproduce angular deformations with qualitative acceptability. The actual barriers may differ somewhat from those calculated, but the relative ordering with substitution pattern should be reliable.



A compound analogous to **14** is the carborane complex **16**. We calculate a barrier of 3.9 kcal/mole for this molecule with the most stable orientation of the $\text{Fe}(\text{CO})_3$ group as shown in **16**. This is in good agreement with the conformation found in the X-ray structure¹⁴. Both the size of the barrier and the orientation agree with that found for **14**. This analysis can be extended to more complex systems. For example, the relative stability of the various conformers in (2,1,3-thiadiborolene)-bis(tricarbonylmanganese) follows that found in **3** versus **4**. The barrier for rotating one of the $\text{Mn}(\text{CO})_3$ groups is quite close to that in thia-diborolene- $\text{Fe}(\text{CO})_3$. The major factor again in favoring **17** over **19** is set by the interaction of $1\pi_a$ with the out-of-phase combination of the $2e_a$ components. The overlap in **20** is clearly larger than that in **21**. Our calculations are in agreement with the X-ray structure¹⁵ in that **17** is the most stable conformation.



$\text{M}(\text{CO})_2$ Complexes of Thiadiborolene and Diazaborolene

To simplify our discussion we will refer to the two possible orientations of an $\text{M}(\text{CO})_2$ group on a cyclopentadienyl ring as the in-plane (**22**) and perpendicular (**23**) conformations. An interaction diagram for dicarbonyl(cyclopentadienyl)cobalt is given in Figure 3 for

¹⁴ J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.* **12**, 2266 (1973). An account of the bonding in **16** from *ab initio* calculations has recently been given by D. R. Armstrong and R. H. Findlay, *Inorg. Chim. Acta* **21**, 55 (1977)

¹⁵ W. Siebert and K. Kinberger, *Angew. Chem.* **88**, 451 (1976); *Angew. Chem., Int. Ed. Engl.* **15**, 434 (1976); W. Siebert, private communication.



the perpendicular conformation. There is a strong bonding interaction between 1π and the $1b_1, 1b_2$ set, giving $1a''$ and $2a'$. Both $1a_2$ and $2a_1$ have δ symmetry and can interact with the 2π levels. However, our calculations suggest that they also interact with high-lying σ levels in an antibonding fashion, so that $2a''$ and $4a'$ are not shifted much in energy

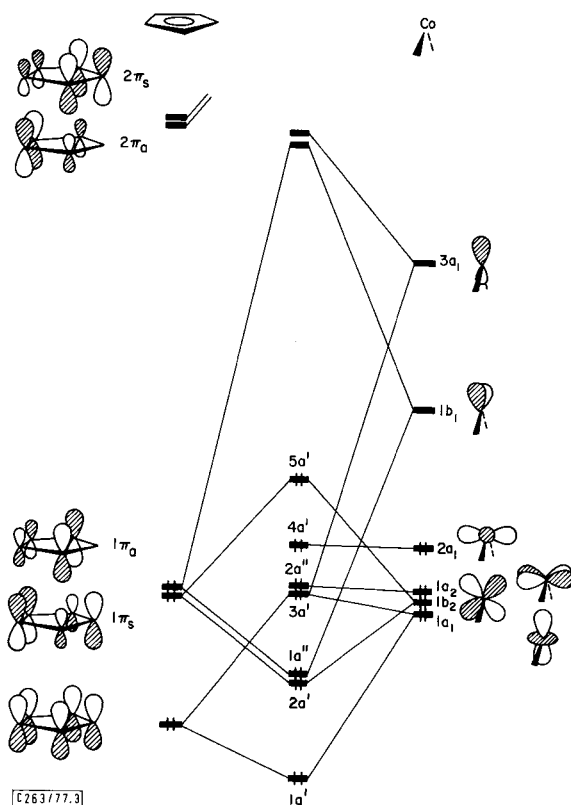
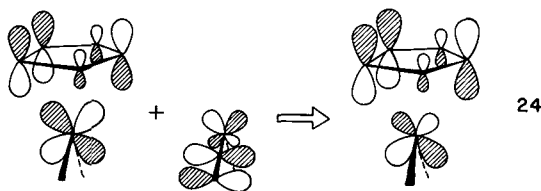


Fig. 3. Interaction diagram for cyclopentadienyl- $\text{Co}(\text{CO})_2$

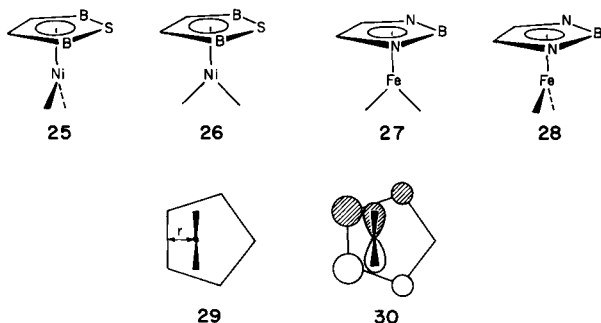
from their parent fragment orbitals. The HOMO for this system is the antibonding combination of $1\pi_s$ and $1b_2$. The reason why $5a'$ does not become greatly destabilized in energy is that another b_2 level on the $\text{Co}(\text{CO})_2$ fragment interacts in $5a'$ to reduce the antibonding. This fragment orbital is comprised mainly of carbonyl π^* with yz and y on the metal. It mixes into $5a$ as indicated by **24**.



Therefore, the net interaction of $1b_2$ and its counterpart with $1\pi_s$ is either slightly antibonding or nonbonding. It is the interaction of $1b_1$ with $1\pi_a$ in our calculations which provides the dominant interaction between the Cp ring and the ML_2 fragment. We shall return to this point shortly.

Upon rotation to the in-plane conformation (**22**) $1b_1$ will now interact with $1\pi_s$ and $1b_2$ with $1\pi_a$. $1\pi_s$ and $1\pi_a$ are degenerate and the overlap between the $1b_2$ - $1b_1$ pair with 1π is the same, irrespective of conformation. Thus, there is essentially no barrier of rotation in dicarbonyl(cyclopentadienyl)cobalt (0.001 kcal/mole)¹⁶⁾. On the other hand, in constructing the molecular orbitals for the $Ni(CO)_2$ complex of thiadiborolene¹⁶⁾ or the $Fe(CO)_2$ complex of diazaborolene, we recall that the energy of $1\pi_a$ is increased in **1** or decreased in **2** relative to the cyclopentadienyl system (see Fig. 2). The energy difference between $1b_1$ and $1\pi_a$ is less than that between $1b_1$ and $1\pi_s$, therefore **25** (where $1b_1$ interacts with $1\pi_a$) should be favored over **26**.

We calculate that **25** is more stable than **26** by 8.3 kcal/mole. Because of the polarization in the π levels, we also find that the overlap between $1b_1$ with $1\pi_a$ in **25** is larger than that between $1b_1$ and $1\pi_s$ in **26** (0.221 versus 0.204, respectively). Similarly, $1\pi_a$ in diazaborolene is lower in energy than $1\pi_s$; therefore, **27** is more stable than **28**. The calculated barrier was 3.1 kcal/mole. Again there is an overlap difference between $1b_1$ and the 1π set which favors **27**.

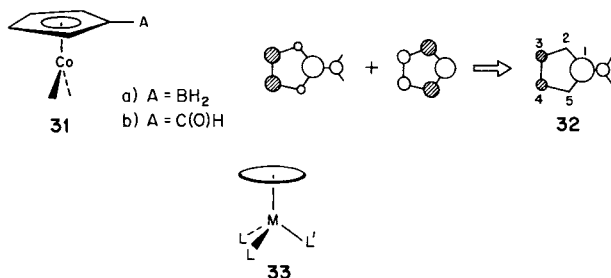


¹⁶⁾ This is consistent with the variety of conformations found for cyclopentadienyl- ML_2 complexes and the large thermal motion in the plane of the cyclopentadienyl ring; see *M. J. Bennett, J. L. Pratt, and R. M. Tuggle*, *Inorg. Chem.* **13**, 2408 (1974); *L. J. Guggenberger and R. Cramer*, *J. Am. Chem. Soc.* **94**, 3779 (1972); *V. W. Day, B. R. Stults, and K. J. Reimer*, *ibid.* **96**, 1227 (1974); *K. J. Reimer and A. Shaver*, *Inorg. Chem.* **14**, 2707 (1975); *J. A. Ibers, J. Organomet. Chem.* **73**, 389 (1974); *F. Glockling, A. McGregor, M. L. Schneider, and H. M. M. Shearer*, *J. Inorg. Nucl. Chem.* **32**, 3101 (1970); *G. Evard, R. Thomas, B. R. Davis, and I. Bernal*, *J. Organomet. Chem.* **124**, 59 (1977); *P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward*, *Angew. Chem.* **89**, 671 (1977); *Angew. Chem., Int. Ed.* **16**, 648 (1977).

These calculations refer to an $M(\text{CO})_2$ group in a pentahapto (η^5) position (approximately equal distances to all of the atoms in the ring). However, since the major bonding interaction in **25** is between $1b_1$ and $1\pi_a$ and because the z orbital coefficients are polarized toward the two carbons in $1\pi_a$ (see Fig. 2), our calculations show that the $\text{Ni}(\text{CO})_2$ unit in **25** slips back towards the dihapto (η^2) geometry as in **29**. This increases the overlap of $1b_1$ with $1\pi_a$ as shown in **30**. Our calculations place the optimum distance of the projection of the nickel atom on the thiadiborolene ring to the midpoint of the carbon-carbon bond, r , at 0.2 Å.

It is possible that the extended Hückel method overemphasizes this slipping motion by polarizing $1\pi_a$ too much in the direction of **30**; however, we do feel that the tendency of the $\text{Ni}(\text{CO})_2$ unit to move towards the η^2 geometry is a realistic proposition for the perpendicular conformation. The isoelectronic dicarbonyl(cyclopentadienyl)cobalt and (cyclopentadienyl)bis(phosphine)cobalt both find deep minima in the η^5 geometry for the two distinct conformations. Of course, this slipping motion will not be favored for the in-plane orientation of dicarbonyl(2,1,3-thiadiborolene)nickel, since the overlap of $1b_1$ with $1\pi_a$ is now zero. However, $1b_1$ does interact strongly with $1\pi_s$, which by Fig. 2 still favors approximately the η^5 geometry. The optimized value of r for **26** was 1.5 Å which roughly lies on the bisector of the two boron atoms. The energy difference between the two optimized orientations now is increased to 19.5 kcal/mole. The slipping motion was also investigated for **27** and **28**. Since the electron density in $1\pi_a$ for **2** is not increased at the two carbons, we would not expect a movement to the η^2 geometry. The calculations agree with this notion. We do find that **27** moves back slightly from the η^5 position (0.2 Å). Taking this result (**28** favors the η^5 geometry), the overall barrier of rotation for dicarbonyl(1,3,2-diazaborolene)iron is now 5.1 kcal/mole.

The nmr data for a number of acceptor-substituted cyclopentadienyl- RhL_2 complexes have been interpreted in terms of restricted rotation around the $\text{Rh}-\text{Cp}$ bond¹⁷). An X-ray structure for 1,5-cyclooctadiene(methoxycarbonylcyclopentadienyl)rhodium shows a perpendicular orientation of the RhL_2 group¹⁷). We have carried out calculations on two $\text{Co}(\text{CO})_2$ models of these systems (**31**). The perpendicular conformations for **31a** and **31b** were found to be more stable than the in-plane ones by 2.9 and 5.8 kcal/mole,



respectively. This is again set by the energy difference in the formerly degenerate 1π set. A π acceptor lowers the energy of $1\pi_s$ and leaves $1\pi_a$ unaffected. Therefore, the energy difference between $1b_1$ and $1\pi_a$ is less than that between $1b_1$ and $1\pi_s$, and the perpendicular

¹⁷) M. Arthurs, S. M. Nelson, and M. G. B. Drew, J. Chem. Soc., Dalton Trans. **1977**, 779.

conformation is preferred. The X-ray structure of the rhodium complex also shows a small slipping motion of the RhL_2 unit towards the substituted cyclopentadienyl carbon. The origin of this movement can be traced as follows. A π acceptor not only lowers the energy of $1\pi_s$, but also mixes $2\pi_s$ into $1\pi_s$ ¹⁸). The result of this polarization is to increase the z coefficient at C_1 while diminishing those at C_2 through C_5 . The antibonding between $1b_2$ and $1\pi_s$ in the HOMO, $5a'$ (refer back to Fig. 3), is lost by moving away from the η^5 position. Furthermore, $3a_1$ on the $\text{Co}(\text{CO})_2$ fragment can now mix into this level in-phase with z at C_1 if the $\text{Co}(\text{CO})_2$ unit is shifted towards the substituted carbon. This is moderated to a large extent by the interaction of $1b_1$ with $1\pi_a$ which favors η^5 . Our calculations on **31** do mimic the features described above. However, lower levels and the interaction of $1b_1$ with $1\pi_a$ still make the total energy rise when the $\text{Co}(\text{CO})_2$ unit is moved from the η^5 geometry. Another complex where this slipping motion is seen is in the triphenylphosphonium-cyclopentadienyl adduct of tetrakis(methoxycarbonyl)-palladiacyclopentadiene¹⁹). Here the distortion is most likely to be due to close contacts between the phosphonium phenyl rings and the methyl carboxylate groups.

We have mentioned previously that our analysis is related to that given by *D. M. P. Mingos* and coworkers⁴⁾ for the orientational preference and distortions in metallocarboranes²⁰). The similarity follows from the close relationship between the orbitals of a carborane fragment and those of cyclopentadienyl.

The slipping motion will not be a likely one for 18-electron, substituted cyclopentadienyl- $\text{M}(\text{CO})_3$ complexes. In $\text{M}(\text{CO})_3$ $2e_s$ and $2e_a$ are degenerate in energy and have the same hybridization (mixing of p into mainly d orbitals). This differs from the $\text{M}(\text{CO})_2$ group where $1b_1$ and $1b_2$ are not only at different energy, but also $1b_1$ is hybridized away from the carbonyls towards the incoming polyene. One could in principle generate slippage by preparing substituted cyclopentadienyl- $\text{ML}_2\text{L}'$ complexes. By making L' in **33** a stronger σ donor than L , $2e_s$ will lie higher in energy than $2e_a$ or, conversely, $2e_a$ will lie higher than $2e_s$ when L' is a weaker σ donor. By splitting the degeneracy of both the π orbitals and $2e$ set, some distortion away from the η^5 geometry may be observed.

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Appendix

All calculations were of the extended Hückel type²¹). The H_{ii} 's for Cr, Fe, and Co were taken from previous work³⁾. Those for Mn were obtained by a charge iterative calculation on

¹⁸⁾ This polarization phenomenon has been developed in some detail for substituted olefins and benzenes; see *L. Libit* and *R. Hoffmann*, *J. Am. Chem. Soc.* **96**, 1370 (1974).

¹⁹⁾ *C. G. Pierpont*, *H. H. Downs*, *K. Ithoh*, *H. Nishiyama*, and *I. Ishii*, *J. Organomet. Chem.* **124**, 93 (1976).

²⁰⁾ ^{20a)} *L. F. Warren* and *M. F. Hawthorne*, *J. Am. Chem. Soc.* **90**, 4823 (1968). — ^{20b)} *R. M. Wing*, *ibid.* **89**, 5599 (1967); **90**, 4828 (1968). — ^{20c)} *M. F. Hawthorne* and *K. P. Callahan*, *Adv. Organomet. Chem.* **14**, 145 (1976). — ^{20d)} *P. A. Wegner*, *Inorg. Chem.* **14**, 212 (1975). — ^{20e)} *H. M. Colquhoun*, *T. J. Greenhough*, and *M. G. H. Wallbridge*, *J. Chem. Soc., Chem. Commun.* **1976**, 1019. — ^{20f)} *W. E. Carroll*, *M. Green*, *F. G. A. Stone*, and *A. J. Welch*, *J. Chem. Soc., Dalton Trans.* **1975**, 2263. — ^{20g)} *A. J. Welch*, *ibid.* **1975**, 1473.

²¹⁾ *R. Hoffmann*, *J. Chem. Phys.* **39**, 1397 (1963); *R. Hoffmann* and *W. N. Lipscomb*, *ibid.* **36**, 3179, 3489 (1962); **37**, 2872 (1962).

$C_5H_5Mn(CO)_3$. The metal orbital exponents for the 3d functions²²⁾ and 4s,4p atomic orbitals²³⁾ were taken from published work. These are given in Table 2. The geometry used for **3**¹⁾, **16**¹⁴⁾,

Table 2. Parameters Used in Extended Hückel Calculations

Orbital	H_{ii} (eV)	ζ_1	ζ_2	$C_1^{a)}$	$C_2^{a)}$
Cr	3d	-11.22	4.95	1.60	0.4876
	4s	-8.66	1.70		
	4p	-5.24	1.70		
Mn	3d	-11.59	5.15	1.90	0.5320
	4s	-8.63	1.80		
	4p	-5.06	1.80		
Fe	3d	-12.70	5.35	1.80	0.5366
	4s	-9.17	1.90		
	4p	-5.37	1.90		
Co	3d	-12.11	5.55	2.10	0.6060
	4s	-8.54	2.00		
	4p	-4.76	2.00		
Ni	3d	-12.99	5.75	2.00	0.5683
	4s	-8.86	2.10		
	4p	-4.90	2.10		
B	2s	-15.20	1.30		
	2p	-8.20	1.30		
C	2s	-21.40	1.625		
	2p	-11.40	1.625		
N	2s	-26.00	1.95		
	2p	-13.40	1.95		
O	2s	-32.30	2.275		
	2p	-14.80	2.275		
S	2s	-20.00	2.122		
	2p	-11.00	1.827		
H	1s	-13.60	1.30		

^{a)} Coefficients in the double zeta expansion.

and **17**¹⁵⁾ were taken from the X-ray structures. The geometry used for the diazaborolene was taken from the structure of a related compound¹⁰⁾. The metal to polyene ring distance for **5**, **25**, and **27** was chosen as 1.73, 1.77 and 1.73 Å, respectively. The Fe-C, Cr-C, and Ni-C bond distances were 1.78, 1.84 and 1.81 Å, respectively, with the C-O bond length always set at 1.14 Å. All $M(CO)_3$ and $M(CO)_2$ units had idealized C-M-C angles of 90°.

²²⁾ J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, J. Chem. Phys. **36**, 1057 (1962).

²³⁾ R. H. Summerville and R. Hoffmann, J. Am. Chem. Soc. **98**, 7240 (1976).