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Transits across a Cyclopentadienyl: Organic and Organometallic Haptotropic Shifts

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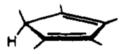
Abstract: Organic and organometallic haptotropic shifts in cyclopentadienyl compounds CpX are analyzed by studying the motion of an X^+ across the face of a $C_5H_5^-$ ring. The ligand in transit, X^+, may be H^+, CH_3^+, XH_3^+ (X = Si, Ge, Sn), $Mn(CO)_3^+$, Li^+, CuR^+, and CH_2^{2+} and CH_2, the latter serving as models for BR_2^+, AlR_2^+ and NR_2^+, PR_2^+ as well. The Cp^- offers donor orbitals of a + e symmetry. The interactions of the ligand may be dominated by an acceptor orbital of symmetry type a (H^+, CH_3^+) in which case η^1 and η^2 geometries are favored, or a set of acceptor orbitals of a + e symmetry ($Mn(CO)_3^+$, Li^+, CuR^+), the e component of which greatly stabilizes the most symmetrical η^5 coordination. The lower the energy of the e acceptor set and the better the overlap with its Cp counterpart, the more are η^2 and η^5 stabilized relative to η^1. In the case of XH_3^+ (X = C, Si, Ge, Sn) an e acceptor orbital moves to lower energy as one proceeds down the group, and this is responsible for the decreasing barrier for sigmatropic shifts in $CpXH_3$. The XH_2 case, which yields a number of interesting collapse structures, is analyzed in detail for X, a main group center.

Contrast the interaction of a cyclopentadienide anion and a proton with the interaction of the same anion and a $Mn(CO)_3^+$ fragment. Both result in stable molecules: cyclopentadiene (**1**) and η^5-$CpMn(CO)_3$ (**2**). But what a difference in the equilibrium geometries of these end products of the interaction! If we focus our attention on the cyclopentadienide site where the interacting partner settles down, then the proton chooses a position near to one carbon of the ring, but the $Mn(CO)_3^+$ fragment sits directly over the center of the ring. The ramifications of this differential are the concern of this paper. We will examine the interaction of a cyclopentadienide ($C_5H_5^-$, Cp) ion with an interacting group X, X = H^+, CH_3^+, SiR_3^+, $Mn(CO)_3^+$, CH_2^{2+}, CH_2. The result will consist of some conclusions concerning the equilibrium geometry of CpX as well as the relative energetics of the various haptotropic reactions of this species.[1,2]



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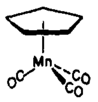

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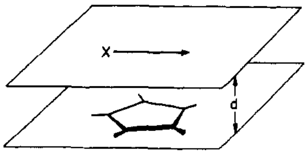
Consider the passage of the interacting group X across the face of a Cp molecule, moving as indicated in **3** in a plane parallel to the Cp ring. Let the distance d be a separation at which there is sizable interaction between the frontier orbitals of X and the Cp π system. For a surface so constrained the asymmetric unit that need be calculated consists of the shaded area in **4**, and two of the three boundaries of that area are contained in a transit along a line shown in projection in **5**. Mirror symmetry is maintained at all points. The numbers $n\eta$ shown along that line are convenient labels invoking a connection to the inorganic η^n notation[2] for denoting an approximate coordination geometry. In order to avoid confusion with structure numbers and ring carbon numbers, we have labeled the various sites along the transit line as 1η, 2η, . . . , 5η. The site labeled 1η, or some geometry near it, corresponds to η^1 or simple σ interaction, such as we have in the collapse product cyclopentadiene. The η^5 site 5η is where one better come up with maximum stabilization for X = $Mn(CO)_3^+$. The site labeled 2η positions X over the center of a bond, and obviously will describe the important transition state region for a sigmatropic shift of a system like cyclopentadiene. 3η and 4η are not so easily defined. Experimentally, slippage of Cp rings from η^5 coordination is often observed and η^3 or η^4 coordination may or may not be invoked. Somewhat arbitrarily we define 3η at the intersection of the transit line with the line joining C-2 and C-5 projected on the transit plane. The tetrahapto coordination site is most ambiguous (it could be near 3η or near 5η), and so we will not label any position as such.



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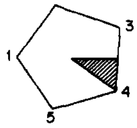

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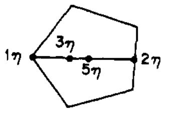

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The analysis will consist of an inspection of interaction diagrams for the orbitals of Cp and X, as the ligand X and its position along the transit are varied. The qualitative arguments based on symmetry and overlap are supported by extended Hückel calculations whose details are given in the Appendix. The reader should be aware that this is an approximate method

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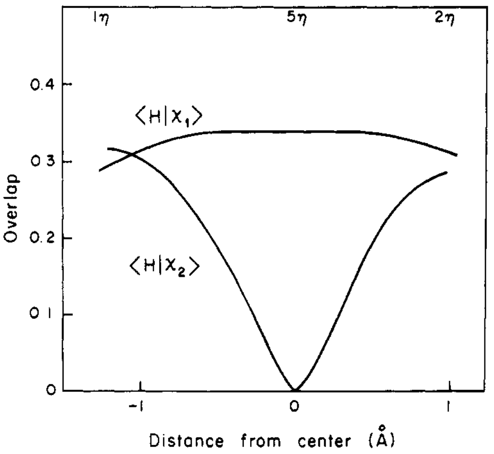
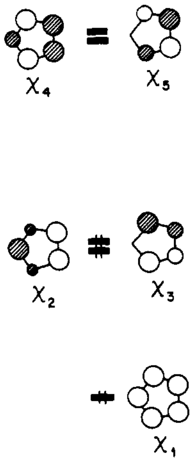


Figure 1. Overlaps between a H 1s orbital and the two lower cyclopentadienyl π orbitals that it interacts with. For $\langle H|\chi_2\rangle$ the absolute value of the overlap is plotted.

with well-documented deficiencies, and that the conclusions drawn therefrom should be considered as qualitative ones.

We begin with the well-known π orbitals of $C_5H_5^-$ shown in **6**.[3] For an X group passing above Cp the crucial features of



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these orbitals are their nodal characteristics: no angular nodes in the lowest nondegenerate orbital χ_1, one angular node in the next pair χ_2 and χ_3, the highest occupied molecular orbitals (HOMO) of the molecule, and two nodes in the higher lying, unoccupied set, χ_4 and χ_5. The degenerate orbitals are so chosen as to be symmetric (χ_2, χ_4) or antisymmetric (χ_3, χ_5) with respect to the mirror plane maintained in the transit.

CpH. When X is H^+, the orbital it bears is obviously symmetric with respect to the mirror plane. The chemically significant two-electron bonding interactions will be between that empty 1s orbital and the occupied orbitals of Cp. Of course, it is a formality that we partition the system as $C_5H_5^-$ and X^+; the analysis could just as well have been carried through with a pair of radicals, or even $C_5H_5^+$ and X^-. The position of the hydrogen in the mirror plane limits its interaction in general to χ_1 and χ_2 of Cp, and in the special site 5η just to χ_1. The important interactions are summarized in **7**.

Counting the number of interactions alone, one would decide against the 5η site. A doubt might linger that the overlap of the H 1s orbital with χ_1 could be significantly larger in the 5η position than elsewhere. We are working here within the usual framework of a one-electron perturbation theory, where the energy of interaction between two orbitals is expected to go as

$$\Delta E = |H_{ij}|^2/(E_i - E_j)$$

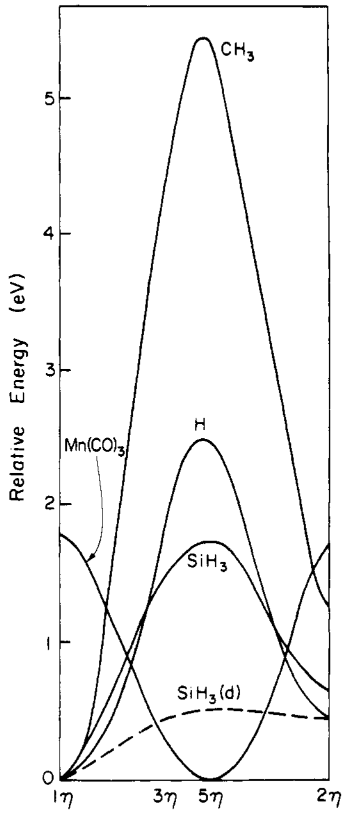
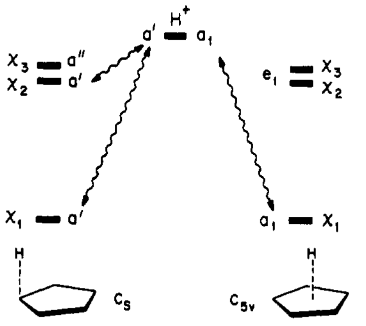


Figure 2. Computed total energies for H^+, CH_3^+, SiH_3^+, and $Mn(CO)_3^+$ moving across the face of a cyclopentadienyl. For SiH_3^+ two curves are shown, one without 3d orbitals, the other with 3d orbitals included with parameters described in the Appendix. All curves are referred to an arbitrary zero of energy at the 1η site.



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and H_{ij} is in some way related to the overlap.[4] Figure 1 plots the group overlaps between χ_1, χ_2 and a hydrogen 1s orbital passing in a plane 1.11 Å above the Cp ring plane. Not only is the 5η site disfavored on both overlap and energy (see **7**) grounds, but it is also clear that 1η and 2η or their environs are the favored points on the transit. This is confirmed in Figure 2 which shows the computed total energy of the CpH system. The lowest energy is at 1η, which were it allowed further degrees of freedom would certainly collapse to cyclopentadiene. The next higher energy point is 2η, indicating in another way the well-known fact that hydrogen migration in cyclopentadiene occurs by a symmetry-allowed [1,5] sigmatropic shift.[5-7] The observed activation energy for the rearrangement is 24.3 kcal/mol.[6c] The calculated difference in energy between 1η and 2η is ~10 kcal/mol, considerably smaller. However, we have not allowed the other geometrical parameters in the two structures to relax, and this geometrical relaxation (as well as a better computational method than ours) is necessary to obtain a reasonable theoretical estimate for the activation energy.[7]

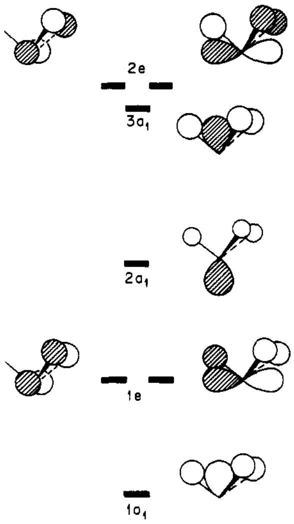
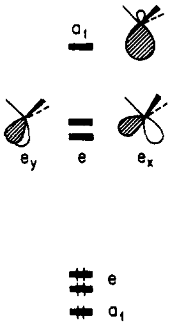


Figure 3. The molecular orbitals of a methyl group.

CpMn(CO)$_3$. The valence orbitals of a d^6 Mn(CO)$_3$$^+$ fragment are well known.[8-11] As shown in **8**, they consist of a trio of filled orbitals, the remnant of the octahedral t_{2g} set. Above these are three acceptor orbitals, of a_1 + e symmetry, beautifully hybridized to provide maximum interaction with other ligands. When the Mn(CO)$_3$$^+$ is positioned at 5η, the a_1 + e acceptor set is perfectly set up to mix with all three Cp orbitals. As the Mn(CO)$_3$$^+$ moves away from 5η toward either 1η or 2η, the net overlap suffers, especially that of e_x with χ_2. This has the energetic consequences shown in Figure 2. The Mn(CO)$_3$$^+$ fragment prefers 5η, as it should. It is difficult to point to any definitive experimental information to test whether a distortion from 5η toward 1η is easier than toward 2η. Our calculations do not indicate a large energy differential between the two deformation modes.



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CpXH$_3$. We next consider the motion of an XH$_3$ group, X = C or Si, across the face of a Cp ring. The motivation here is the knowledge that migration of a methyl group is more difficult than that of a hydrogen atom ($\Delta G^{\ddagger}$ in 1,1-dimethylcyclopentadiene = 41.8 kcal/mol[12]), but that the activation energy for other group 4 migrating centers[13] is considerably lower ($\Delta G^{\ddagger}$ = 15.2 kcal/mol for Si(CH$_3$)$_3$,[13a] 13.3 kcal/mol for Ge(CH$_3$)$_3$,[13b] 6.6 kcal/mol for Sn(CH$_3$)$_3$[13b]).

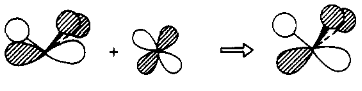
The familiar orbitals of a methyl group[14] are shown in Figure 3. Those of another XH$_3$ group (X = Si, Ge, Sn, Pb) will differ from these in a number of well-understood ways. First there will be an effect of the decreasing electronegativity of X as one proceeds down the group.[14] This will shift levels in energy; for instance, the crucial LUMO of an XH$_3$$^+$ group, the 2a_1 orbital, will be at higher energy for Si than for C. A second effect of electronegativity will be to cause shifts in electron density within the orbitals. An important orbital in the subsequent discussion will turn out to be the hyperconjugating X-H σ^* combination 2e. As one progresses down the group this will become more localized on the X atom. A second effect, not independent of the first one, is that of the weaker and longer X-H bonds. This will decrease the energy of the 2e as one moves down the group. A third effect is that of hypothetical participation in bonding of d orbitals on Si, Ge, Sn, Pb. This is a problem of long standing.[15] These orbitals (3d for Si, 4d for Ge, etc.) are clearly there, but we have no way of knowing if they are sufficiently contracted and at sufficiently low energy to play a significant acceptor role. If they do get involved then among them is a pair of the same symmetry as the 2e set, *xz* and *yz*. The 2e set will be further stabilized by interaction with d orbitals.

Figure 2 shows a very sharp curve for the motion of a CH$_3$$^+$ (pyramidal) across the face of a Cp ring. The methyl axis was kept perpendicular to the Cp plane throughout the transit. The general behavior of the curve parallels that for H$^+$, but both the higher energy of the 5η position and the 1η − 2η difference are increased for the methyl case. A fragment molecular orbital analysis[16] shows that the essential pattern is set by the methyl LUMO 2a_1, playing the same role as the hydrogen 1s orbital discussed earlier. This was to be expected. That the energy changes more sharply along the transit for CH$_3$$^+$ compared to H$^+$ may be traced to four-electron destabilizing interaction between 1a_1 and 1e and various Cp σ and π orbitals. These are greater in 5η than 1η or 2η, and of course do not have an analogue in the H$^+$ case.

An SiH$_3$$^+$ group shows a much softer energy curve for transit across a Cp face. The calculation which led to the curve shown in Figure 2 did not include 3d orbitals on Si. The relative destabilization of 5η is much less in the silyl case compared to methyl, and is even lower than for a migrating hydrogen. The 1η − 2η difference, which should be related to the activation energy for the allowed 1,5-sigmatropic shift, is lower for silyl than for methyl. This is in accord with the experimental data quoted above. However, the SiH$_3$ 1η − 2η difference is greater than for H, which is not in accord with experimental findings, at least for Si(CH$_3$)$_3$.[13a] CNDO/2 and MINDO/2 calculations by Shchembelov and Ustynyuk,[7a] which allow for geometrical relaxation, order the H, CH$_3$, and SiH$_3$ activation energies correctly.

In the SiH$_3$ case the major factor shaping the curve is once again the 2a_1 orbital, which favors 1η and 2η sites. The same repulsive terms which we mentioned in the methyl case are also present here. But there is a new factor at work in the silyl case, and it is responsible for the lowered energy of the 5η geometry. The fragment molecular orbital analysis shows that the 2e orbitals in the SiH$_3$$^+$ fragment interact much more strongly than the corresponding levels in CH$_3$$^+$. They do so both because they are lower in energy and they overlap better; such are the consequences of the electronegativity and bond length effects mentioned above as one progresses down the group. The more the 2e orbitals interact, the more is 5η stabilized. Whatever stabilization occurs at 5η is also "remembered", at least in part, at the 2η site. There one member of the 2e set has the correct pseudo-symmetry to interact with χ_3.

We now return to the effect of d orbitals on Si. As we said above, it is difficult to estimate the extent to which 3d orbitals on Si are involved. We can, however, get an idea of the effect of these orbitals by including them in the calculations with parameters (exponent and H_{ii}) which allow them to mix strongly with other orbitals. When we do this, the most important effect is that the 2e orbitals are stabilized as a result of p-d mixing which relieves their antibonding character and, most important for the rearrangement surface, hybridizes the p orbitals so that they point away from the silyl hydrogens and toward the Cp ring. This is shown below for one member of the 2e set. The result is an increased stabilizing interaction between



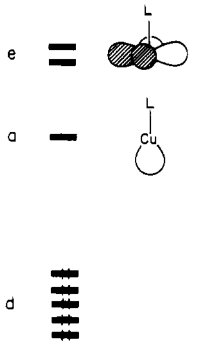
2e and the degenerate Cp orbital, maximized in the 5η geometry. The energy of 5η decreases relative to 2η. With d orbitals contracted and low in energy we can get the energies of the two alternative transition states to be comparable. The 3d parameters that it takes to do this are not realistic ones, in our opinion.[17] However, the trend is clear.

The conclusion of the previous discussion comparing CH_3^+ and SiH_3^+ is that an important role is played by the hyperconjugating 2e orbitals of the XH_3^+ group. This set of levels is expected to play a more important role as one moves down group 4, with all three factors enumerated (electronegativity decrease, bond length increase, increasing d participation) probably playing a role. It is not inconceivable to us that by the time one gets to Sn or Pb not much energy will separate 1η, 2η, and 5η sites. As indirect evidence for this supposition one might cite the lowered sigmatropic shift activation energies given above,[13] the existence of η^5 Cp_2Sn and Cp_2Pb in the vapor phase,[18] mixed η^5 and η^4 coordination for Cp_2Pb in the solid phase,[19] and a slightly slipped η^5 geometry for CpSnX in the solid.[20]

One is tempted to summarize the XH_3^+ trend as one moves down the group, 2e interacting more and more, by saying that XH_3^+ is beginning to resemble $Mn(CO)_3^+$, the $2a_1$ and 2e orbitals of XH_3^+ taking the place of the empty e + a_1 orbitals of the transition metal carbonyl fragment. This is not quite right, for in XH_3^+ the 2e always stays above $2a_1$, whereas in $Mn(CO)_3^+$ the e orbital is always lower.

In some ways the XH_3^+ trend is more an approach to Li^+, BeX^+, or CuL^+ than to $M(CO)_3^+$. We have not discussed the Li^+ case here, but the analysis is obvious. In addition to the Li^+ 2s orbital, playing a role analogous to an H^+ 1s or the XH_3^+ $2a_1$, there is a set of relatively low-lying 2p orbitals. One combination of these, p_x, p_y, is of e symmetry and has the limiting appearance of the 2e set of XH_3^+. The geometry of CpLi is not definitely known, but calculations[21a-d] predict an η^5 structure. That is also the gas-phase structure of CpTl[21e] and CpIn.[21f]

CpCuL, L = phosphine, molecules are well-characterized molecules with an η^5 geometry.[22] We have not carried out any calculations on this system, but the orbitals of a CuL^+ group are easily constructed, **9**. In addition to a filled d band there is a hybrid orbital pointing toward the Cp ring and two p orbitals above it. The availability of an a + e acceptor set favors the η^5 coordination. The electronic structure of a BeX^+ (X = halide) fragment is similar, of course with the d orbitals omitted. CpBeX possess an η^5 geometry.[23a] However, our picture of the electronic structure of these compounds cannot be complete, for subtle quantitative factors obviously influence whether an η^5 ground-state geometry is achieved. CpHgX (X = halide) species, which should electronically resemble $CpCuPR_3$, are not η^5 but η^1, and rearrange readily by sequential 1,2 shifts.[23b]



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In concluding this discussion of group 4 $CpXH_3$ systems, we note two matters. First these molecules exhibit interesting distortion in their ground-state geometries; namely, that with X ≠ C the carbon ring is sometimes nonplanar.[24] There must be a low barrier to out-of-plane deformations of the Cp ring. This was not considered in our studies, which assumed a planar carbon ring. A second point is that in addition to other theoretical considerations on sigmatropic shifts in cyclopentadiene and related organometallic systems[25] there is in the literature a very interesting correlation of photoelectron spectroscopy, theory, and the kinetic parameters of sigmatropic rearrangements. Cradock, Ebsworth, and co-workers[26] correlate the fluxionality of the molecules with the extent of mixing of the lowest diene π with the Si-C bonding orbital. The same mixing influences the splitting between the π levels. The approach is in a sense complementary to ours, for whereas we focus on the transition state, these workers seek correlations between ground-state properties and ease of sigmatropic rearrangement.

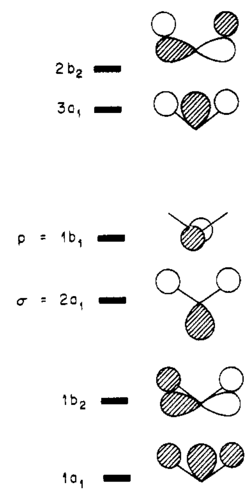
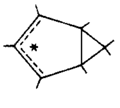


Figure 4. The molecular orbitals of a methylene group.

$CpXL_2$. Let us begin with a model CH_2^{2+} or CH_2 group passing across the cyclopentadienyl face. The organic ligand and its charge may seem unusual until one examines the possible "collapse products" of such a transit. These might be **10–12. 10** as a cation is the well-characterized bicyclo[3.1.0]hexenyl system, **11** the less well-known but still realistic bicyclo[2.1.1] cation or anion, and **12** a possible transition state geometry for a degenerate sigmatropic rearrangement of **10,** or a cation or anion in its own right. Isoelectronic with $CpCH_2^-$ would be $CpNH_2$ which in turn is related to $CpPF_2$, whose fluxionality is established.[27] Isoelectronic with $CpCH_2^+$ would be $CpBH_2$, to which a number of other group 3 cyclopentadienyls ($CpXR_2$, X = Al, Ga, In) are related.[28,29]

* = + or −



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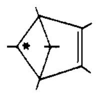

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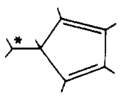

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The orbitals of a methylene group are well known[14] and are shown schematically in Figure 4. The critical orbitals in our discussion will be the directed hybrid $2a_1$ and the 2p orbital orthogonal to the CH_2 plane, $1b_1$. In the context of a general discussion of methylenes these have been called σ and p, respectively.[30] σ and p are both empty if the fragment is CH_2^{2+}, and σ is filled while p remains empty for a CH_2 fragment.

It is further important to distinguish two orientations of the methylene plane relative to the Cp vertical mirror plane. We shall refer to "in-plane" geometries, when the CH_2 lies in the vertical symmetry plane of the cyclopentadienyl (**13**) and

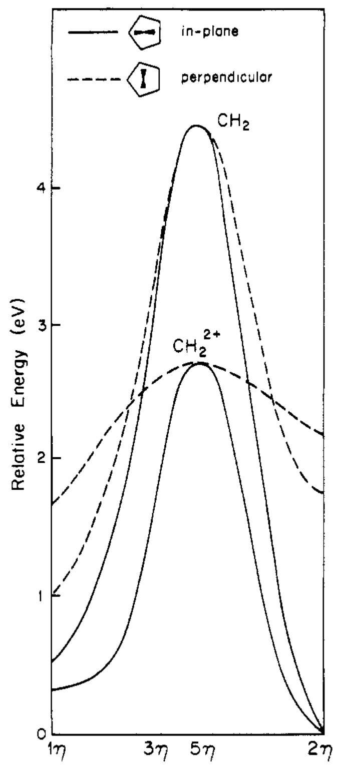
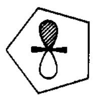


Figure 5. Computed total energies for CH_2^{2+} and CH_2 transits across the face of a Cp^-. Solid line = in-plane orientation; dashed line = perpendicular orientation. The arbitrary energy zero is chosen at the most stable 2η, in-plane, geometry of both CH_2^{2+} and CH_2.

"perpendicular", when these planes are mutually orthogonal (**14**).



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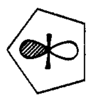

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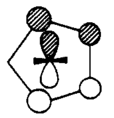
The results of extended Hückel calculations on the four transits, CH_2 and CH_2^{2+}, in-plane and perpendicular, are shown in Figure 5. Let us analyze the shape of these curves, beginning with the $CpCH_2^+$ case. The CH_2^{2+} fragment has two important acceptor orbitals, σ and p. Interaction with σ is no different from the H^+ or XH_3^+ cases, and leads to an energy factor greatly favoring 1η and 2η. This sets the main feature of the energy curve along the transit coordinate. However, superimposed on this one has the effect of the acceptor function p, which depending on its orientation can mix with one or the other member of the degenerate Cp e_1 set. These interactions, shown in **15** and **16,** are maximal (and equal to each other) at 5η. They are *not* equal when the CH_2 moves away from 5η. Detailed calculations show that the symmetric function, derived from **16** and corresponding to a "perpendicular" methylene, always has a smaller overlap than the antisymmetric function. This is responsible for the steady destabilization of the perpendicular transit, relative to the in-plane one, that may be seen in Figure 5. The difference in overlap may be appreciated from a drawing of the interactions at 2η, shown in **17** and **18.** In **17** there is clearly retained a substantial overlap, while in **18** the "local" overlap with p orbitals at C_3 and C_4 is zero, and only the smaller long-distance overlap with C_1, C_2, and C_5 remains.



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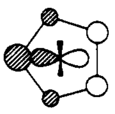

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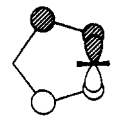

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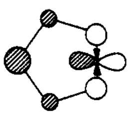

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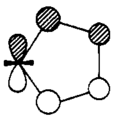

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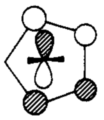
An intriguing feature of the calculations is that for the more stable in-plane CH_2 orientation the 2η site is at lower energy than 1η. This is a direct consequence of the better overlap in **17** than **19,** and is consistent with the stability of the collapse product, the bicyclo[3.1.0]hexyl cation. It is also consistent with the observed geometry of $CpAl(CH_3)_2$,[29] a molecule related to the hypothetical $CpBH_2$ which is isoelectronic to $CpCH_2^+$. CNDO/2 and ab initio SCF-MO calculations by Haaland and co-workers[29,31] on $CpAlR_2$ also prefer such a geometry and, as we would also infer, find substantial barriers to twisting the AlR_2 group by 90°.

The 1η site models a transition state for the degenerate sigmatropic rearrangement of the bicyclo[3.1.0]hexenyl cation. This [1,4] sigmatropic shift should proceed with inversion at the migrating carbon,[5] a prediction that has been experimentally confirmed.[32] The required geometry is the one we have called in-plane. Ab initio calculations by Hehre[33] put this conformation of a cyclopentadienyl carbinyl 9–12 kcal/mol below an alternative in which the CH_2 group is twisted by 90°, which would be modelled by our perpendicular geometry.

An interesting problem is the absence in the calculation of any low-energy region around 3η, which might be an indication of a collapse to **11,** a molecule for which a perfectly reasonable valence structure may be drawn. Indeed one can draw a correlation diagram interrelating the 3η site orbitals with the orbitals of **11.** There is no level crossing along the way. It appears that the reason why the existence of a collapse channel leading to **11** is not indicated by the energy curve is that such a collapse requires great geometrical deformations. There are signs of incipient bonding in the overlap populations, but not in the energy.

We next turn to the $CpCH_2^-$ systems, formally constructed from the interaction of Cp^- with a neutral CH_2. While a singlet methylene would have the σ orbital doubly occupied, we cannot assume that this is so in $CpCH_2^-$. As was mentioned above, both σ and p interact with the Cp orbitals, and the interaction of σ is much the stronger. Thus while σ may be below p in an isolated methylene, in $CpCH_2^-$ the antibonding combinations represented schematically by $\sigma-\lambda\chi(Cp)$ and $p-\lambda'\chi(Cp)$ order themselves in such a way that the latter, shown in **20** or **21,** is at lower energy. This is the orbital occupied by the two additional electrons as one goes from $CpCH_2^+$ to $CpCH_2^-$. Recall that the maximum overlap of p with the appropriate symmetry Cp orbital, whether one is in the in-plane or the perpendicular geometry, is at the 5η site. This is then the site of maximum antibonding in $CpCH_2^-$, with the result that relative to $CpCH_2^+$ all curves become sharper. Figure 5 clearly shows this.



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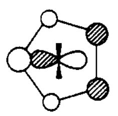

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In the in-plane conformation the overlap in question is consistently greater than in the perpendicular geometry. This was discussed above (see **17** and **18**). In $CpCH_2^-$, where the antibonding combination **20** or **21** is filled, that geometry which offers least overlap will be least destabilized. Therefore we would expect the in-plane and perpendicular alternatives for

Table I. Extended Hückel Parameters

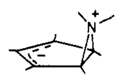
Orbital		H_{ij}, eV	Exponent[a]
H	1s	−13.60	1.300
C	2s	−21.40	1.625
	2p	−11.40	1.625
Si	3s	−17.30	1.383
	3p	−9.20	1.383
	3d	−6.00	1.383
Mn	4s	−9.75	0.970
	4p	−5.89	0.970
	3d	−11.67	5.150 (0.51391) 1.700 (0.69291)
C[b]	2s	−24.26	1.625
	2p	−9.32	1.625
C[c]	2s	−25.48	1.625
	2p	−10.48	1.625
O[d]	2s	−30.31	2.275
	2p	−11.31	2.275
H[d]	1s	−12.08	1.300

[a] Two exponents are listed for Mn, with corresponding coefficients of the double-ζ expansion in parentheses. [b] For cyclopentadienyl carbons in $CpMn(CO)_3$. [c] For carbonyl carbons in $CpMn(CO)_3$. [d] In $CpMn(CO)_3$.

$CpCH_2^-$ to lie closer to each other in energy than they do in $CpCH_2^+$, and this is also seen in Figure 5.

So far we have considered only the repulsive four-electron interactions between p and χ_2 or χ_3 of Cp. But in addition one can have attractive interactions with unfilled Cp orbitals χ_4 and χ_5. These do not mix much in our analysis, in part because they are at high energy, in part because their pseudo-symmetry (two angular nodes) does not match the pseudo symmetry of the p orbital (one angular node). We do find some of this effect in the perpendicular 1η site. Note incidentally that at 1η the perpendicular conformation for $CpCH_2^-$ is still at higher energy than the in-plane one. This is not in accord with the orbital symmetry prediction for a transition state for a [1,4] sigmatropic shift with retention, but may be the result of an incomplete geometry optimization.

The general ordering in energy of 1η and 2η, in-plane and perpendicular, conformations in $CpCH_2^-$ may not be reliably given by these calculations. Lowest in energy is the in-plane 2η geometry. For species related to $CpCH_2^-$, such as $CpNR_2$ or $CpPF_2$, this would correspond to a zwitterionic structure **22.** There is nothing wrong with this one, but perhaps the alternative **23,** which is not charge-separated, looks better. In the case of $CpPF_2$ the equilibrium geometry is η^1. This molecule is no doubt strongly pyramidal at the phosphorus, so that our trigonal CH_2 group will not be a good model for the energetics of sigmatropic shifts in this case.



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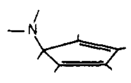

23

Other Organometallic Groups. A great deal has been learned about haptotropic rearrangements in organometallic compounds containing Cp rings and transition metal centers, from the elegant work of Cotton as well as others.[1,34] The molecules best understood experimentally, $Cp_2Fe(CO)_2$, Cp_4Ti, and Cp_3MoNO, present a fairly complicated picture theoretically because of the low symmetry of the fragment coordinated to the Cp ring. We do not wish to examine these molecules in this initial paper but will return to them in the future. For the moment we are satisfied with having achieved a basic understanding of the factors governing the potential energy surface for haptotropic shifts across a cyclopentadienyl of both organic and organometallic groups.

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Appendix

All calculations were of the extended Hückel type,[35] with a "weighted H_{ij}" formula[36] used for approximating the off-diagonal matrix elements. The parameters which we used are given in Table I. $CpMn(CO)_3$ was a special case in that we cycled to self-consistency on the charges of all the atoms, including C, O, and H. The Coulomb integrals for those atoms thus differ from the C, O, H parameters used for the other CpX calculations. However, a repetition of the $CpMn(CO)_3$ calculation with the other parameters shows no substantial differences. The Mn 3d function was taken as a linear combination of two Slater functions.[37]

In all computations the Cp ring had CC 1.418 Å, CH 1.111 Å. CH_3 and SiH_3 groups were tetrahedral: CH 1.10 Å, SiH 1.521 Å. The methyl group moved 1.54 Å, the silyl group 1.87 Å above the Cp plane. The methylene group had CH 1.111 Å, angle HCH 116°, and moved 1.54 Å above the Cp plane. The $Mn(CO)_3$ group was taken as an octahedral fragment, MnC 1.80 Å, CO 1.15 Å, which made the transit at 1.80 Å above the Cp ring.

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