

Haptotropic Rearrangements of Polyene-ML_n Complexes. 2. Bicyclic Polyene-MCp, -M(CO)₃ Systems

Thomas A. Albright,^{*1a,f} Peter Hofmann,^{*1b} Roald Hoffmann,^{1c} C. Peter Lillya,^{1d} and Paul A. Dobosh^{1e}

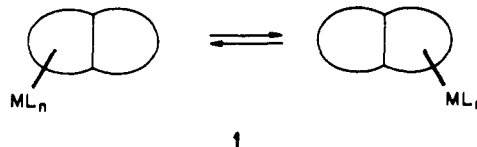
Contribution from the Departments of Chemistry, University of Houston, Houston, Texas 77004, Cornell University, Ithaca, New York 14853, University of Massachusetts, Amherst, Massachusetts 01003, Mount Holyoke College, South Hadley, Massachusetts 01075, and Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany. Received October 13, 1982

Abstract: A detailed theoretical investigation of the minimum energy pathways for shifting an ML_n group from one ring to another in a bicyclic polyene has been undertaken, where ML_n = M(CO)₃ and MCp. Specific examples that are treated in some depth include naphthalene-Cr(CO)₃, indenyl-FeCp, fluorenyl-FeCp, pentalene-FeCp cation and anion, bicycloheptatrienyl-CoCp cation and anion, and phenalenium-Cr(CO)₃ cation. A simple method is presented to analyze these rearrangements based on the topology of the interacting orbitals. This can be distilled further into an electron counting method, provided that some precautions are taken. Two patterns emerge from this study. In one class of compounds the two primary bonding interactions between the ML_n and polyene fragments are lost during a least-motion transit from one ring to another (naphthalene-Cr(CO)₃ and indenyl-FeCp are examples). A very circuitous minimum energy path is followed and a dissociative, intermolecular mechanism may operate competitively. There is some similarity between these and forbidden sigmatropic rearrangements in organic chemistry. The other common situation arises when one of the bonding interactions is retained and the other is lost along a least-motion path (pentalene-FeCp⁺ and bicyclo[3.2.0]heptatrienyl-CoCp⁺ are examples). Minimum energy pathways close to a least-motion one are found and the activation energies are lower than that in the previous case when they can be directly compared. Strategies are presented for altering the activation energies and in one case, the phenalenium-Cr(CO)₃ cation, both bonding interactions between the ML_n unit and polyene are retained when the Cr(CO)₃ group migrates from one η⁶ position to another.

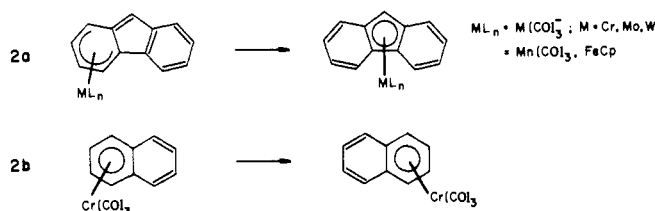
Introduction

The term haptotropic rearrangements has been coined² to cover those cases where an ML_n unit changes its connectivity (hapticity) to some ligand with multicoordinate site possibilities. In the majority of situations this ligand will be a polyene. Thus, a haptotropic rearrangement in a polyene-ML_n complex will be one where the ML_n unit migrates from one coordination site to another in a polyene. A large body of experimental information exists for processes of this type in simple cyclic polyene complexes.³ There have been some, but not many, theoretical excursions into this area.⁴ On the other hand, very little is known about the ability of an ML_n unit to migrate in a bicyclic (or multicyclic) polyene complex from one ring to another. A stylized representation of this process is given in 1. In this study we shall restrict ourselves to ML_n complexes of the M(CO)₃ and isolobal⁵ MCp categories. What caught our attention was that just such a rearrangement takes place in fluorenyl-ML_n complexes.

Nicholas, Kerber, and Stiefel⁶ first observed the reaction for



the Cr(CO)₃⁻ derivative, 2a. Further investigations were provided



by Johnson and Treichel,⁷ Ustynyuk and co-workers,⁸ as well as

(1) (a) University of Houston. (b) Universität Erlangen-Nürnberg. (c) Cornell University. (d) University of Massachusetts. (e) Mount Holyoke College. (f) Camille and Henry Dreyfus Teacher-Scholar, 1979-1984; Alfred P. Sloan Research Fellow, 1982-1984.

(2) Anh, N. T.; Elian, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 110; the first analysis of a haptotropic rearrangement was discussed in Hoffmann, R.; Hoffmann, P. *Ibid.* **1976**, *98*, 598.

(3) (a) Cotton, F. A. "Dynamic Nuclear Magnetic Resonance Spectroscopy", Jackman, L. M.; Cotton, F. A., Ed.; Academic Press: New York, 1975, Chapter 10. (b) Fallor, J. W. *Adv. Organomet. Chem.* **1977**, *16*, 211. (c) Deganello, G. "Transition Metal Complexes of Cyclic Polyolefins" Academic Press: New York, 1979. (d) Fedorov, L. A. *Russ. Chem. Rev.*, **1973**, *42*, 678.

(4) (a) Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159. (b) Hoffmann, P.; Albright, T. A. *Angew. Chem.* **1980**, *92*, 747; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 728. (c) Albright, T. A.; Hoffmann, R.; Tse, Y.-C.; D'Ottavio, T. *J. Am. Chem. Soc.* **1979**, *101*, 3812. (d) Albright, T. A.; Geiger, W. E., Jr.; Moraczewski, J.; Tulyathan, B. *Ibid.* **1981**, *103*, 4787. (e) Herndon, W. C. *Ibid.* **1980**, *102*, 1538. (f) Su, C.-C. *Ibid.* **1971**, *93*, 5653. (g) Hoffmann, P. *Z. Naturforsch.* **1976**, *31b*, 1019. (h) Schmitt, G.; Keim, W.; Lfeischhauer, J.; Walbergs, U. *J. Organomet. Chem.* **1978**, *152*, 315. (i) Mingos, D. M. P.; Nurse, C. R. *J. Organomet. Chem.* **1980**, *184*, 281. (j) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 31. (k) Karel, K. J.; Albright, T. A.; Brookhart, M. *Organometallics* **1982**, *1*, 419. (l) Mealli, C.; Midollini, S.; Moneti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95.

(5) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.

(6) Nicholas, K. M.; Kerber, R. C.; Stiefel, E. I. *Inorg. Chem.* **1971**, *10*, 1519.

(7) (a) Johnson, J. W.; Treichel, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, *16*, 749. (b) Johnson, J. W.; Treichel, P. M. *J. Am. Chem. Soc.* **1977**, *99*, 1427. (c) Treichel, P. M.; Johnson, J. W. *Inorg. Chem.* **1977**, *16*, 749. (d) Treichel, P. M.; Fivizzani, K. P.; Haller, K. J. *Organometallics* **1982**, *1*, 931.

(8) (a) Thoma, T.; Pleshakov, V. G.; Prostavok, N. S.; Ustynyuk, Yu. A.; Nesmeyanov, A. N.; Ustynyuk, N. A. *J. Organomet. Chem.* **1980**, *192*, 359. (b) Ustynyuk, N. A.; Lokshin, B. V.; Oprunenko, Yu. F.; Roznyatovskiy, V. A.; Luzikov, Yu. N.; Ustynyuk, Yu. A. *Ibid.* **1980**, *202*, 279. (c) Nesmeyanov, A. N.; Ustynyuk, N. A.; Novikova, L. N.; Rybina, T. N.; Ustynyuk, Yu. A.; Oprunenko, Yu. F.; Trifonova, O. I. *Ibid.* **1980**, *184*, 63. (d) Nesmeyanov, A. N.; Markarova, L. G.; Ustynyuk, N. A.; Andrae, S.; Andrianov, V. G.; Struchkov, Yu. T.; Ustynyuk, Yu. A.; Malyugina, S. G. *Ibid.* **1978**, *159*, 189. (e) Nesmeyanov, A. N.; Ustynyuk, N. A.; Markarova, L. G.; Andrae, S.; Ustynyuk, Yu. A.; Novikova, L. N.; Luzikov, Yu. N. *Ibid.* **1978**, *154*, 45. (f) Ustynyuk, N. A.; Ustynyuk, Yu. A.; Nesmeyanov, A. N. *Dokl. Akad. Nauk SSSR* **1980**, 509. (g) Nesmeyanov, A. N.; Ustynyuk, N. A.; Novikova, L. N.; Andrianov, V. G.; Struchkov, Yu. T.; Ustynyuk, Yu. A.; Oprunenko, Yu. F.; Luzikov, Yu. N. *J. Organomet. Chem.* **1982**, *226*, 239. (h) Oprunenko, Yu. F.; Luzikov, Yu. N.; Ustynyuk, Yu. A.; Ustynyuk, N. A. *Ibid.* **1982**, *231*, 137. (i) Yezernitskaya, M. G.; Lokshin, B. V.; Zdanovich, V. I.; Lobanova, I. A.; Kolobova, N. E. *Ibid.* **1982**, *234*, 329. (j) Nesmeyanov, A. N.; Oprunenko, Yu. F.; Ustynyuk, N. A.; Lokshin, B. V.; Ustynyuk, Yu. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 1942. (k) Nesmeyanov, A. N.; Ustynyuk, N. A.; Thoma, T.; Prostavok, N. S.; Soldaatenkov, A. T.; Pleshakov, V. G.; Urga, K.; Ustynyuk, Yu. A.; Trifonova, O. I.; Oprunenko, Yu. F. *J. Organomet. Chem.* **1982**, *231*, 5.

several other groups.^{9,10} Slipping the ML_n unit from the six-membered ring to the five-membered one also has been demonstrated for the indenyl system.^{8e,9a} These haptotropic rearrangements require substantial activation energies. A similar situation exists for the degenerate reaction in **2b** unless the reaction is carried out in the presence of a coordinating solvent.^{6,11} Apparently *intermolecular* exchange can readily occur and, in fact, arene exchange in naphthalene-Cr(CO)₃ is more facile than that in other arene-Cr(CO)₃ complexes.¹² There have been brief reports¹³⁻¹⁵ of a few other haptotropic rearrangements in bicyclic systems, but not much else is experimentally known about this interesting type of fluxional process.

It is our intention to show how a simple theoretical strategy can be used to analyze these reactions. This strategy will predict whether the barriers for a least-motion pathway are of low, medium, or high activation energy *relative* to a completely dissociative, intermolecular mechanism. Extended Hückel molecular orbital calculations¹⁶ were also used to construct detailed potential energy surfaces for these haptotropic rearrangements. Despite the fact that this computational technique is relatively unsophisticated, we believe that the qualitative results and trends are reliable.

General Theoretical Strategy

A natural way to investigate haptotropic rearrangements of the type given by **1** concentrates on how the bonding between the ML_n unit and bicyclic polyene evolves as a function of the reaction path. The strongest bonding interactions will originate from the π orbitals of the polyene and the valence, metal-centered orbitals of the ML_n fragment. The "basis-sets" of M(CO)₃ and MCp levels are presented in Figure 1. They can be derived, for example, from the removal of three *fac* carbonyls in M(CO)₆ and CpM(CO)₃, **3a**, yielding the requisite fragments given by **3b**. What

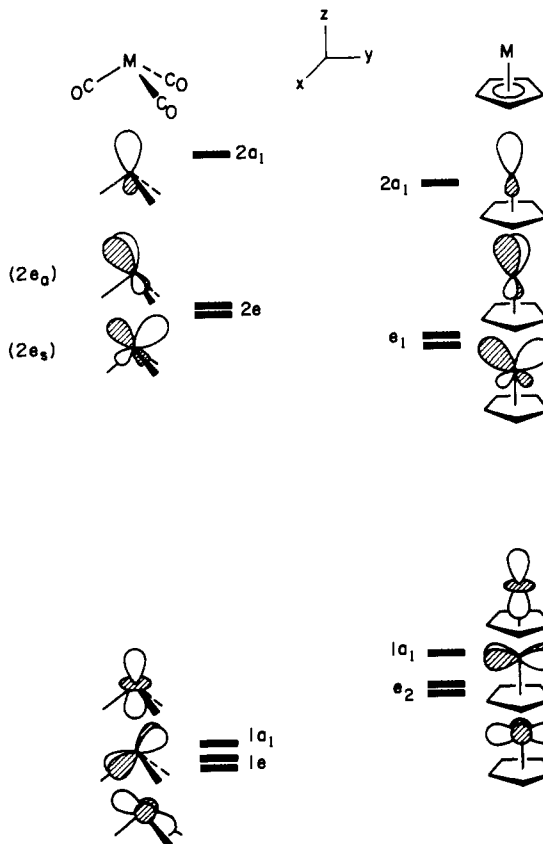
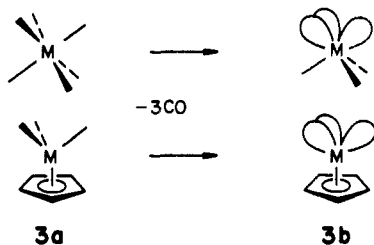
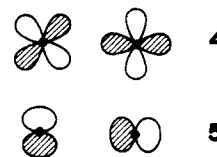


Figure 1. The valence orbitals of M(CO)₃ (left) and MCp (right) fragments.

happens to the metal-centered orbitals when the carbonyls are removed from **3a** has been treated in detail elsewhere.^{5,17} We shall only present the important details here. The "t_{2g}" set in **3a**



happens to the metal-centered orbitals when the carbonyls are removed from **3a** has been treated in detail elsewhere.^{5,17} We shall only present the important details here. The "t_{2g}" set in **3a**

(9) (a) White, C.; Thompson, J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654. (b) Fairhurst, G.; White, C. *Ibid.* **1979**, 1531. (c) Helling, J. F.; Hendrickson, W. A. *J. Organomet. Chem.* **1977**, 141, 99.

(10) Cecon, A.; Gambaro, A.; Agostini, G.; Venzo, A. *J. Organomet. Chem.* **1981**, 217, 79.

(11) (a) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1977**, 110, 1555. (b) Deubzer, B.; Fischer, E. O.; Fritz, H. P.; Kreiter, C. G.; Kriebitzsch, N.; Simmons, H. D.; Willeford, B. R. *Ibid.* **1967**, 100, 3084. (c) Greenwood, J. M.; Veening, H.; Willeford, B. R. *Ibid.* **1974**, 38, 345. (d) Deubzer, B. Ph.D. Dissertation, Technische Hochschule München, 1966. (e) Öfele, K., personal communications. (f) Deubzer, B.; Fritz, H. P.; Kreiter, C. G.; Öfele, K. *J. Organomet. Chem.* **1967**, 7, 289. (g) Coletta, F.; Gambaro, A.; Rigatti, G.; Venzo, A. *Spectros. Lett.* **1977**, 10, 971. (h) Kundig, E. P.; Timms, P. L. *J. Chem. Soc., Dalton Trans.* **1980**, 991.

(12) See, for example, Mahaffy, C. A. L.; Pauson, P. L. *J. Chem. Res. Synop.* **1979**, 126; (*M*) **1979**, 1752 and references therein.

(13) Magon, M.; Schröder, G. *Liebigs Ann. Chem.* **1978**, 1379.

(14) Müller, J. P.; Gosser, P.; Elian, M. *Angew. Chem. Int. Ed. Engl.* **1969**, 8, 374.

(15) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142.

(16) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, 36, 2179, 3489; **1962**, 37, 2872; Hoffmann, R. *Ibid.* **1963**, 39, 1397.

(17) (a) Lauher, J.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, 98, 3219. (b) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *Ibid.* **1977**, 99, 7546. (c) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, 14, 1058. (d) Burdett, J. K. *Ibid.* **1975**, 14, 375; *J. Chem. Soc., Faraday Trans. 2* **1974**, 70, 1599. (e) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, 98, 50.

For any d⁶-d¹⁰ complex, and those will be the ones that we shall deal with here, the 1a₁ + 1e triad or the 1a₁ + e₂ triad will be filled. At higher energy are three more orbitals. 2e and e₁ are primarily metal xz and yz (see the coordinate system at the top of Figure 1) antibonding with respect to carbonyl σ for M(CO)₃ or the Cp 2π set for MCp. Furthermore, metal x and y mixes into these orbitals in a way which hybridizes them out toward the polyene. The s and a subscripts utilized for the members of 2e in Figure 1 refer to whether the orbital is symmetric or antisymmetric with respect to the yz plane. An important facet in this analysis is that 2e and e₁, represented by a top view in **5**, are of π symmetry with respect to a coordinated polyene. Finally, the 2a₁ orbital of M(CO)₃ and MCp is comprised mainly of metal s and z character. It too is hybridized out toward the polyene. An alternative way¹⁸ to construct these orbitals is to take symmetry adapted linear combinations of the three localized hybrid orbitals in **3b** which point toward the missing carbonyls. This directly yields the 2a₁ + 2e set of M(CO)₃ and 2a₁ + e₁ set of MCp.

It is clear that the hybridization and π (or σ) symmetry make the 2a₁ + 2e and 2a₁ + e₁ triads the predominate source of bonding to the π orbitals of a bicyclic polyene. If that overlap between the ML_n triad and the π orbitals of a polyene is retained during a haptotropic rearrangement, then the reaction should proceed with a low activation energy. On the other hand, if overlap is lost,

(18) (a) Hoffmann, R. *Science* **1981**, 211, 995. (b) Albright, T. A. *Tetrahedron* **1982**, 38, 1339.

then a high energy of activation would be encountered for the reaction path and an alternative path will be preferred. Now there are two simplifications that can be made. Firstly, the $2a_1$ orbital can always find a bonding partner. In any polyene the lowest occupied molecular orbital has no nodes and, therefore, $2a_1$ can always interact with it. In fact, $2a_1$ will normally interact with this orbital to a greater extent at the ground state geometry than it will with any other polyene π orbital. Thus, to a first approximation $2a_1$ does not energetically differentiate reaction paths and can be disregarded in our analysis. We are left then with $2e$ and e_1 of $M(\text{CO})_3$ and MCp , respectively. If they are empty, in a d^6 complex, for example, then they will seek strongest bonding interactions with the two highest occupied orbitals of the bicyclic polyene. When the metal is d^8 , one member of $2e$ or e_1 is filled and the other formally empty. Therefore, the dominant bonding interactions will originate from the highest occupied and lowest unoccupied orbitals of the polyene. The second simplification is based on the close electronic resemblance between the $M(\text{CO})_3$ and MCp fragments. Both have the same number, symmetry type, radial extension, and approximate energy of their valence orbitals. The two fragments are said to be isolobal.⁵ Because of this similarity, it is expected that there will be little difference between them in the reaction paths and activation energies for haptotropic reactions. We shall see that this is generally true. Careful inspection of Figure 1 shows that $1e$ and $2e$ of $M(\text{CO})_3$ are tilted^{17b} with respect to the xz plane, whereas e_1 and e_2 are not. The tilting of $M(\text{CO})_3$ will only serve to make specific orientations of $M(\text{CO})_3$ favored over others.^{17b} It does not in any other way complicate the analysis.

The strategy described here is very close to one of the ways sigmatropic rearrangements in organic chemistry can be analyzed.¹⁹ The major difference is that for sigmatropic reactions the orbital corresponding to $2a_1$ is the only one utilized. Here two orbitals, $2e$ or e_1 , with π rather than σ symmetry are employed and $2a_1$ is disregarded. In the next sections we shall show how this method works for least-motion paths and provide detailed potential surfaces which were constructed at the extended Hückel level. The computational and geometrical details for the calculations are given in the Appendix.

Naphthalene-Cr(CO)₃

Before we discuss the haptotropic rearrangement, **2b**, for naphthalene-Cr(CO)₃, the bonding between naphthalene and Cr(CO)₃ in the ground state, η^6 , geometry shall be developed in some detail as an illustrative example. An interaction diagram for the molecule is presented in Figure 2. This is a d^6 complex so $1a_1 + 1e$ are filled for Cr(CO)₃ on the right side of Figure 2 and $2a_1 + 2e$ are empty. On the left side are displayed the filled π orbitals of naphthalene. They have been labeled with s and a subscript according to whether the orbital is symmetric or antisymmetric to the mirror plane of the complex (the yz plane). The $3\pi_s$ level of naphthalene is stabilized greatly by $2e_s$, giving the molecular orbital labeled $3\pi_s + 2e_s$ in Figure 2. Something more complicated happens with $2\pi_s$ and $1\pi_a$. Both are stabilized by $2e_a$. What evolves is a typical three orbital pattern. The molecular orbital labeled $1\pi_a + 2e_a$ contains $1\pi_a$ and $2\pi_a$ bonding with respect to $2e_a$. The next level, labeled $2\pi_a + 2e_a$, is predominantly $2\pi_a$ bonding with respect to $2e_a$. Furthermore, some $1\pi_a$ is also mixed into this level in an antibonding fashion to $2e_a$. The highest molecular orbital, not shown in Figure 2, is mainly $2e_a$ antibonding with respect to $1\pi_a$ and $2\pi_a$. Important to the analysis is that naphthalene $2\pi_a$ is stabilized much more than $1\pi_a$ is by Cr(CO)₃ $2e_a$. $2\pi_a$ lies at higher energy and, therefore, is closer in energy to $2e_a$. The $2\pi_s$ and $1\pi_s$ levels of naphthalene are stabilized by $2a_1$ on Cr(CO)₃. Here the interaction to $1\pi_s$ is slightly larger at the η^6 geometry. The reason behind this is

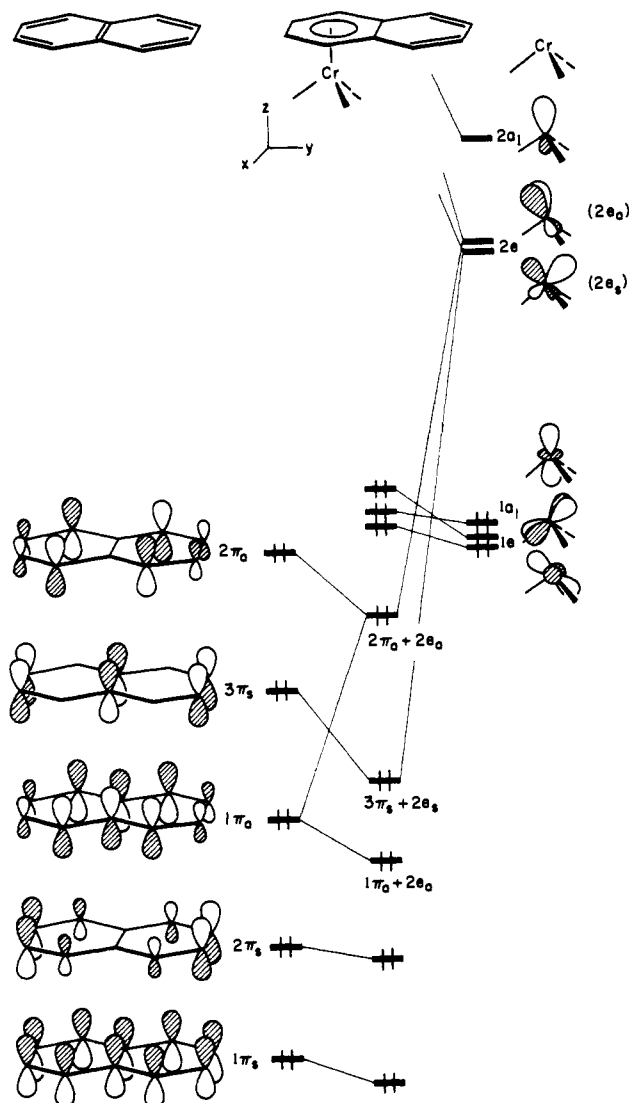
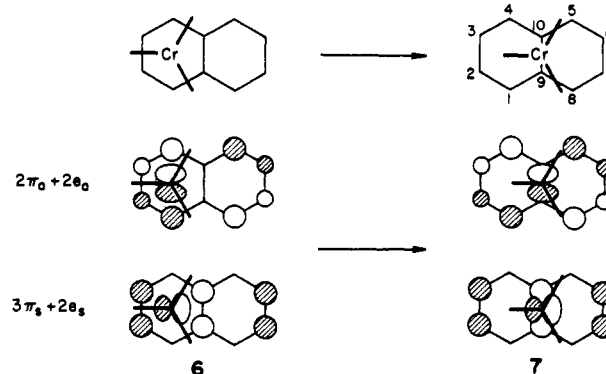


Figure 2. Orbital interaction diagram for η^6 -naphthalene-Cr(CO)₃.

that the overlap of $1\pi_s$ with $2a_1$ (0.199) is larger than that between $2\pi_s$ and $2a_1$ (0.131).

In terms of an analysis of haptotropic rearrangements it is the interaction of the two LUMO's of Cr(CO)₃, $2e_s$ and $2e_a$, with the two HOMO's of naphthalene, $3\pi_s$ and $2\pi_a$, that are the dominant bonding ones. These are shown from a bottom view in **6** at the ground state, η^6 geometry. The transition state for



a least motion path will be one where the Cr(CO)₃ group lies approximately over the bisection of C₉-C₁₀ in naphthalene. We shall call this the central- η^7 geometry. What happens is indicated in **7**. The orbitals of both fragments are drawn with the same phase relationship as they started with in **6**. At the transition state the bonding of Cr(CO)₃ $2e_a$ with the naphthalene atomic p orbitals

(19) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim, 1970; pp 114-140; Nguyen, T. A. "Les regles de Woodward-Hoffmann"; German translation, Verlag Chemie: Weinheim, 1972; pp 59-112; Fleming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976; pp 98-103; Fukui, K. *Acc. Chem. Res.* 1971, 4, 57.

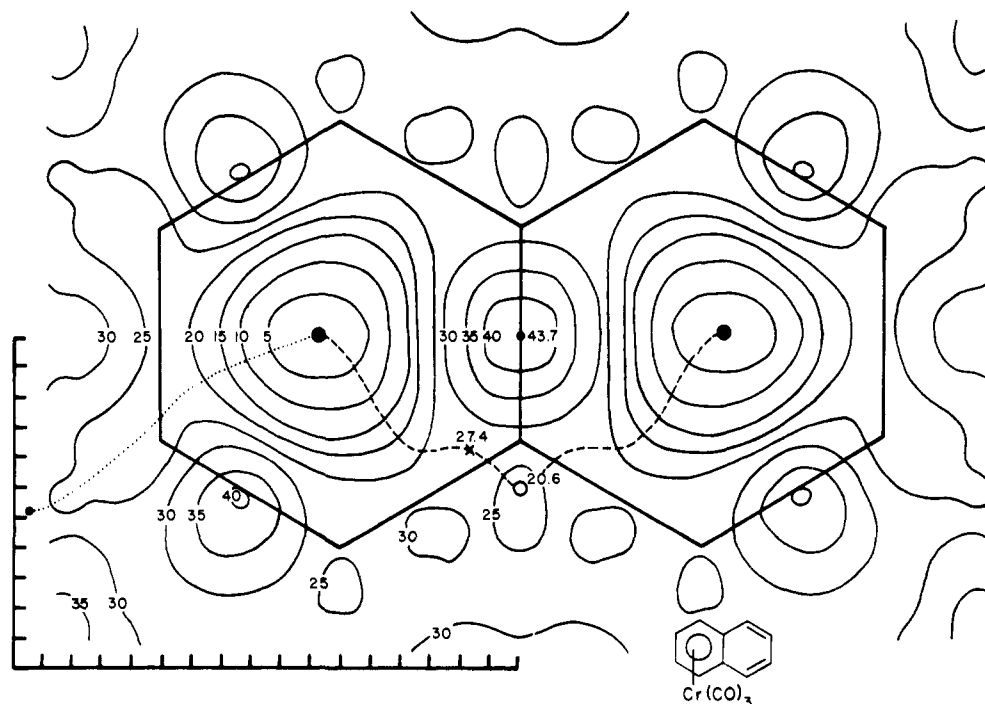
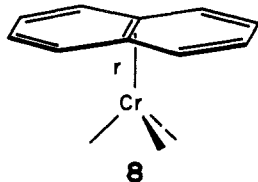


Figure 3. Potential energy surface for shifting the $\text{Cr}(\text{CO})_3$ group in naphthalene- $\text{Cr}(\text{CO})_3$. The distance scale at the lower left is plotted in 0.2 Å intervals and energy contours are in kcal/mol. Ground-state minima are indicated by solid circles, local minima by open circles, and transition states by crosses. The energies relative to the ground state for these points are given. Reaction paths are shown as dashed lines. The distance of the $\text{Cr}(\text{CO})_3$ group to the naphthalene plane was held constant at 1.73 Å.

at C_1 and C_4 in $2\pi_a$ is canceled by the antibonding between $2e_a$ to C_5 and C_8 . In other words, all overlap between $2e_a$ and $2\pi_a$ is lost at the transition state. The same occurs between $3\pi_s$ and $2e_s$ in 7. Putting this another way, at the central- η^2 geometry $2\pi_a$ has δ symmetry with respect to the orbitals of $\text{Cr}(\text{CO})_3$. The local symmetry of $3\pi_s$ is of σ type, or δ if the bonding of $1e_s$ on $\text{Cr}(\text{CO})_3$ to C_2 , C_3 , C_6 , and C_7 is strong. Since the $\text{Cr}(\text{CO})_3$ $2e$ set is of π symmetry, the two dominant bonding interactions between naphthalene and $\text{Cr}(\text{CO})_3$ are lost during the least-motion transit. This is precisely what happens in a symmetry-forbidden sigmatropic rearrangement.¹⁹ A nonleast-motion or dissociative mechanism will be more favorable.

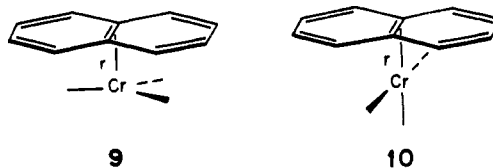
Figure 3 shows a potential energy surface for shifting the $\text{Cr}(\text{CO})_3$ group relative to the naphthalene ring. The distance scale at the lower left of Figure 3 is plotted in 0.2 Å intervals. The energy contours are given in kcal/mol relative to the two equivalent ground state geometries, symbolized by solid circles. The distance between the naphthalene ring and $\text{Cr}(\text{CO})_3$ was initially held constant at 1.73 Å for the construction of this surface. As indicated in Figure 3, it requires 44 kcal/mol to attain the central- η^2 geometry. This is approximately equal to the computed binding energy of $\text{Cr}(\text{CO})_3$ to naphthalene (47 kcal/mol). The calculated minimum energy path is shown by the dashed line. A transition state, indicated by a cross, and a local minimum, shown by an open circle, are computed to be 27 and 21 kcal/mol, respectively, less stable than the ground state. The nonleast-motion path is definitely favored over a least-motion alternative. Next the distance of $\text{Cr}(\text{CO})_3$ to the naphthalene ring, r in 8, was



optimized along with the relative orientation of $\text{Cr}(\text{CO})_3$ at the four critical points of the potential surface. The optimum value of r at the ground state geometry was computed to be 1.73 Å which is identical with the average value found from X-ray structural determinations of naphthalene- $\text{Cr}(\text{CO})_3$ and derivatives.²⁰ The

optimized value of r at the central- η^2 geometry is much longer—2.11 Å. Its energy relative to the ground state is reduced to 35 kcal/mol. However, the intermediate (given by the open circle in Figure 3) and the transition state are still found to be at lower energies. The optimized values of r were 1.86 and 1.96 Å at relative energies that remain at 27 and 21 kcal/mol, relative to the optimized ground state structure, for the transition state and intermediate, respectively. Öfele and co-workers^{11d,e} have measured the activation energy for this rearrangement in 2,3-dimethylnaphthalene- $\text{Cr}(\text{CO})_3$. The reaction carried out in decane proceeds by first-order kinetics with $\Delta H^\ddagger = 30$ kcal/mol. For reasons that will be dealt with later, we believe this to be the activation energy for the intramolecular path, and our calculations are in excellent agreement with it.

Various distortions of the naphthalene ring from planarity were also investigated at these four points. In all cases optimum structures were found for keeping the ring planar. Finally, to ensure that the central η^2 structure was definitely not on the lowest energy path for the haptotropic shift, we also considered two distortions of the $\text{Cr}(\text{CO})_3$ unit. The CO groups in one were bent up toward a trigonal geometry as in 9 while r was allowed to vary

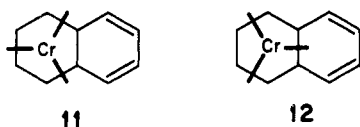


(20) (a) Kunz, V.; Nowacki *Helv. Chim. Acta* **1967**, *50*, 1052. (b) Carter, O. L.; McPhail, A. T.; Sim, G. A. *J. Chem. Soc. A* **1968**, 1866. (c) Dötz, K. H.; Dietz, R.; vonImhof, A.; Lorenz, H.; Hüttner, G. *Chem. Ber.* **1976**, *109*, 2033. (d) Dietz, R.; Dötz, K. H.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59. (e) Cais, M.; Kaftory, M.; Kohn, D. H.; Tatarsky, D. *J. Organomet. Chem.* **1979**, *184*, 103. (f) Kaftory, M. *Acta Crystallogr.* **1980**, *B36*, 2971. (g) Hanic, F.; Mills, O. S. *J. Organomet. Chem.* **1968**, *11*, 151. (h) Muir, K. W.; Ferguson, G.; Sim, G. A. *J. Chem. Soc. B* **1968**, *11*, 151. (i) Guss, J. M.; Mason, R. *J. Chem. Soc., Dalton Trans.* **1973**, 1834. (j) Deuschl, H.; Hoppe, W. *Acta Crystallogr.* **1964**, *17*, 800. (k) Lal De, R.; Von Seyerl, J.; Zsolnai, L.; Hüttner, G. *J. Organomet. Chem.* **1979**, *175*, 185. (l) Shakir, R.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D., submitted for publication. (m) Hall, J. W., Jr.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 264.

independently. Secondly, the CO groups were bent towards a square-planar environment, **10**, and r was varied. In both cases these motions are found to be destabilizing. Thus, with extensive geometrical optimization the nonleast-motion path is still definitely favored over a least-motion one.

Notice in Figure 3 that shifting the $\text{Cr}(\text{CO})_3$ group in a direction away from the uncomplexed portion of the naphthalene ring is of lower energy than moving $\text{Cr}(\text{CO})_3$ toward it. Only 25 kcal/mol is required to attain an η^2 geometry where $\text{Cr}(\text{CO})_3$ is complexed to the C_2 - C_3 bond (see the numbering system in 7). The dotted line in Figure 3 illustrates one such dissociative pathway. We shall not present the details of arene exchange here.²¹ It is sufficient to say that an external (solvent) ligand is predicted to attack Cr at an η^2 geometry like this with little or no additional activation energy. Therefore, our calculations predict that in the presence of a coordinating solvent (e.g., ethers) an *intermolecular* exchange mechanism is more favorable than the intramolecular, nonleast-motion one. The available experimental data support this.¹¹ The value of 30 kcal/mol for ΔH^\ddagger in 2,3-dimethylnaphthalene- $\text{Cr}(\text{CO})_3$ found by Öfele and co-workers represents, we feel, that for the intramolecular mechanism. First of all, decane is certainly a noncoordinating solvent. Furthermore, naphthalene- $\text{Cr}(\text{CO})_3$ has been shown to undergo arene exchange with much greater facility than benzene- $\text{Cr}(\text{CO})_3$.¹² This is also evident from our calculations on the two systems.^{21,22} However, ΔH^\ddagger for arene exchange in benzene- $\text{Cr}(\text{CO})_3$ was experimentally found to be 29.6 kcal/mol,²³ which means that the *intermolecular* path for naphthalene- $\text{Cr}(\text{CO})_3$ must be significantly lower than this. In this connection we also note that the low potential for dissociation to η^2 in naphthalene- $\text{Cr}(\text{CO})_3$ may have a bearing on why this compound is a more efficient catalyst²⁴ than benzene analogues for the hydrogenation of butadienes.

There are several other pieces of experimental information which can be compared to our calculations. The conformation of all naphthalene- $\text{Cr}(\text{CO})_3$ derivatives is that shown by **11** rather



than **12**.²⁰ Our calculations also reveal that **11** is the most stable conformation. The electronic reasons behind this have been presented elsewhere.²⁰ More importantly, we calculate that the ground-state geometry is not exactly at η^6 . That is, the projection of the Cr atom onto the plane of naphthalene is not at the center of the complexed ring. Careful inspection of Figure 3 shows this; the ground state is shifted 0.12 Å away from η^6 toward the C_2 - C_3 bond. This is also the direction and is in the range of magnitudes²⁰ that are experimentally found for complexes of this sort. The origin of this distortion is easily traced from Figure 3. There is a very high potential region around the central- η^2 position for the reasons given before. That is not counterbalanced by an equally high energy for moving the $\text{Cr}(\text{CO})_3$ group to an η^2 geometry in the opposite direction, over the C_2 - C_3 bond. Here there is still some overlap between $2e_a$ of $\text{Cr}(\text{CO})_3$ and naphthalene $2\pi_a$ (see Figure 2). Therefore, the ground-state geometry is shifted away from C_9 - C_{10} toward C_2 - C_3 . Finally, the binding energy of benzene

(21) Albright, T. A., to be published. For a review of the arene exchange mechanism, see Muettterties, E. L.; Bleeke, J. R.; Sievert, A. C. *J. Organomet. Chem.* **1979**, *178*, 197; Muettterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499.

(22) The activation energy for benzene- $\text{Cr}(\text{CO})_3$ is ~ 30 kcal/mol, whereas in naphthalene- $\text{Cr}(\text{CO})_3$ it is ~ 25 kcal/mol.

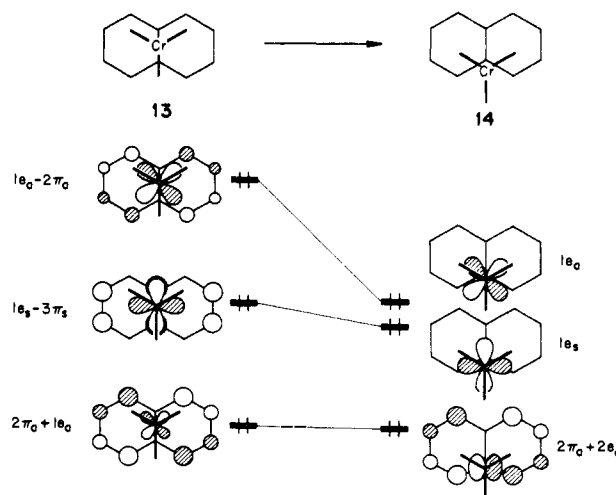
(23) Zimmerman, C. L.; Shaner, S. L.; Roth, S. A.; Willeford, B. R. *J. Chem. Res. Synop.* **1980**, 108; (*M*) **1980**, 1289.

(24) (a) Gandolfi, O.; Cais, M. *J. Organomet. Chem.* **1977**, *125*, 141; Eden, Y.; Fraenkel, D.; Cais, M.; Halevi, E. A. *Isr. J. Chem.* **1976-7**, *15*, 223. (b) It would be interesting to see if this is a general phenomenon for other types of arene- $\text{Cr}(\text{CO})_3$ catalyzed reactions; see, for example, Faron, M. F. "Organometallic Reactions and Synthesis"; Vol. 6; Becker, E. I.; Tsutsui, M., Ed.; Plenum Press: New York, 1977; pp 222-285; Garnett, J. L. *Catal. Rev.-Sci. Eng.* **1971**, *5*, 229.

to $\text{Cr}(\text{CO})_3$ has been measured at 42.5 ± 3 kcal/mol by Connor and co-workers.²⁵ The calculated value of 47 kcal/mol is fortuitously close to it and no reliance should be placed on the quantitative values at this level of theory. The important point is that the extended Hückel calculations are providing an adequate potential for the binding of naphthalene to $\text{Cr}(\text{CO})_3$ and the instability of the central- η^2 geometry is not an artifact of the method.

A full potential energy surface for naphthalene-MnCp was also constructed. It is quantitatively almost the same as that in Figure 3 for the $\text{Cr}(\text{CO})_3$ complex. An intermediate and transition state were found at the approximately same positions with energies relative to the ground state of 19 and 24 kcal/mol, respectively. There again is a very high potential energy region around the central- η^2 geometry. The relative energy for this point was calculated to be 42 kcal/mol. So changing the $\text{Cr}(\text{CO})_3$ fragment for the isolobal MnCp one does not cause any substantial change for the haptotropic rearrangement; a nonleast-motion path with a relatively high activation energy is predicted. Nothing is known experimentally about this complex. Solodovnikov and co-workers^{26a} have shown that facile rearrangement from one ring to the other does *not* occur from the ESR spectra of 17-electron naphthalene- FeCp^{2+} complexes. That is in agreement with our analysis. Figure 2 shows that the one electron removed from naphthalene- $\text{Cr}(\text{CO})_3$, and this will be the same for the MnCp complexes, comes from a metal-centered " t_{2g} -like" orbital. That orbital does not figure heavily in the origin of the activation barrier. A series of 19-electron naphthalene- FeCp complexes have also been observed^{26b} by low-temperature ESR studies. Near -120°C the anisotropic spectrum was transformed into an isotropic one. It was suggested^{26b} that this was due to the onset of a rapid haptotropic shift from one ring to the other. We doubt that this is the cause of the spectral transformation since two-electron reduction of the two separate isomers of 2,3-dimethylnaphthalene- $\text{Cr}(\text{CO})_3$ followed by reoxidation only regenerates the starting isomers.²⁷ Therefore, this rearrangement is demonstrably slow for the 20-electron species and we can see nothing special as to why the 19-electron FeCp derivatives should be any different.

Before turning to other bicyclic polyene complexes, it is instructive to analyze in greater depth why the intermediate in this haptotropic rearrangement is more stable than the central- η^2 species. A somewhat simplified picture of the electronic changes that occur is given in **13** and **14**. Not only do the two HOMO's



(25) (a) Adedji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M. L.; Paz-Andrade, I. M.; Skinner, H. A. *J. Organomet. Chem.* **1975**, *97*, 221. (b) Brown, D. L. S.; Connor, J. A.; Demain, C. P.; Zafarani-Moattar, M. T. **1977**, *142*, 321. (c) Connor, J. A. *Top. Curr. Chem.* **1977**, *71*, 71.

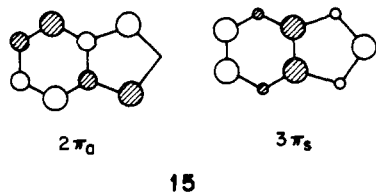
(26) (a) Solodovnikov, S. P.; Nesmeyanov, A. N.; Vol'kenau, N. A.; Kotova, L. S. *J. Organomet. Chem.* **1980**, *201*, C45. (b) Solodovnikov, S. P.; Nesmeyanov, A. N.; Vol'kenau, N. A.; Kotova, L. S. *Ibid.* **1980**, *201*, 447.

(27) Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951.

of naphthalene lose stabilization from $2e$ at the central- η^2 geometry, but they also become entangled with the filled $1e + 1a_1$ triad. For example, at 13 $2\pi_a$, $3\pi_s$, and $1e$ are of δ symmetry. They combine to form bonding (illustrated for one component by $2\pi_a + 1e_a$) and antibonding ($1e_s - 3\pi_s$ and $1e_a - 2\pi_a$) molecular orbitals. These four electron-two orbital interactions are repulsive.²⁸ Furthermore, not shown in **13** is the fact that $3\pi_s$ and the filled $1a_1$ also overlap substantially (recall that $3\pi_s$ is of local σ symmetry) and repel each other at the central- η^2 geometry. Slipping the $\text{Cr}(\text{CO})_3$ to the intermediate structure, **14**, removes the repulsion between these metal "lone-pairs" and the HOMO's of naphthalene. In particular, the $1e_a - 2\pi_a$ and $1e_s - 3\pi_s$ levels are stabilized. An important point is also that $2\pi_a + 1e_a$ in **13** does not rise in energy to a nonbonding $2\pi_a$ orbital. As $\text{Cr}(\text{CO})_3$ is shifted toward **14**, overlap between $2\pi_a$ and $2e_a$ is turned on. The resultant level is labeled in **14** as $2\pi_a + 2e_a$. The calculations indicate that there is strong bonding of Cr to C_1 , C_8 (see $2\pi_a + 2e_a$ in **14**) and to C_9 via the $2a_1$ orbital of $\text{Cr}(\text{CO})_3$. There is not much interaction between Cr and C_{10} .²⁹ This is an η^3 -allyl type of intermediate and a low-lying unoccupied orbital primarily of $2e_s$ character emerges. Thus, the intermediate is essentially a 16 electron η^3 -allyl- $\text{Cr}(\text{CO})_3$ anion with a heptatrienyl cation fused to the allyl portion. We shall see that intermediates of this sort will be a pervasive feature in symmetry forbidden haptotropic rearrangements.

Indenyl and Fluorenyl-ML_n Compounds

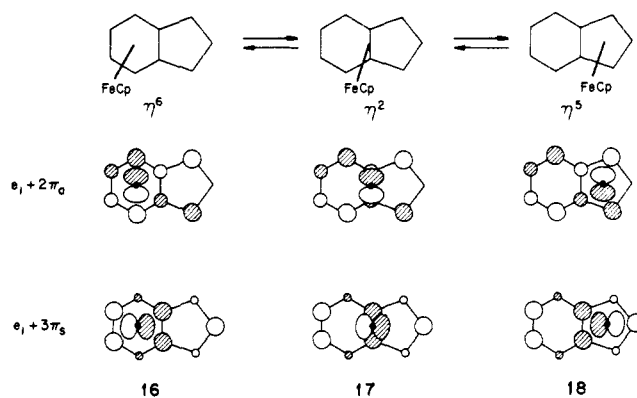
As mentioned in the Introduction, an appreciable body of experimental information exists for haptotropic rearrangements in fluorenyl-ML_n complexes, **2a**, and indenyl analogues.⁶⁻¹⁰ The indenyl anion is isoelectronic and topologically equivalent to the π system of naphthalene; the fluorenyl anion is equivalent to the anthracene or phenanthrene ligands. One, therefore, should expect that there is a closely related picture of haptotropic interconversions between the η^6 and η^5 isomers in **2a** compared to the situation which we have just discussed for naphthalene-ML_n. The reader should note that we are using the η^6 terminology for mnemonic purposes only. Here the ML_n unit is coordinated to the six-membered ring portion of the ligand. Whether the coordination number is η^6 or η^5 is a difficult question particularly for the fluorenyl case.^{7b,d} The truth probably lies somewhere between these two idealized representations,^{7d} but what is different in the fluorenyl and indenyl systems is that the two isomers are expected to have different thermodynamic stability. A theoretical analysis must address this issue as well as the least-motion vs. nonleast-motion pathways for interconversion. We shall start with the simpler and more symmetrical indenyl systems first, using indenyl-FeCp as our model compound. Conceptually the molecule can be partitioned into an indenyl anion bound to FeCp⁺, which is isoelectronic to MnCp and isolobal to $\text{Cr}(\text{CO})_3$. The e_1 set (see Figure 1) of FeCp⁺ is then empty and the strongest bonding interactions will occur between it and the two HOMO's of the indenyl anion, shown from a top view in **15**. The reader should



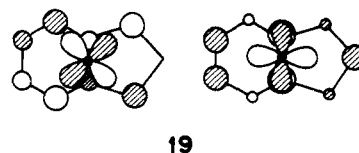
15

be aware that there are no ambiguities introduced by the exact way the two fragments are partitioned. For example, one could have chosen FeCp⁻ where one component of e_1 is filled and the other empty. The indenyl⁺ fragment is now one where $2\pi_a$ is

empty and $3\pi_s$ is filled. Therefore, the HOMO and LUMO of FeCp⁻ interact with the HOMO and LUMO of indenyl⁺. What is important is that in the composite picture $2\pi_a$ and $3\pi_s$ are stabilized by e_1 at the η^6 and η^5 geometries. This is shown in **16** and **18**. A least motion path from η^6 to η^5 passes through a



central- η^2 structure where, as can be seen in **17**, the overlap of e_1 to $3\pi_s$ and $2\pi_a$ is lost. The situation here is clearly analogous to the naphthalene- $\text{Cr}(\text{CO})_3$ case. Due to the inequivalence of the two rings this does not happen exactly underneath the central C-C bond; the overlap is lost at a point which is displaced slightly inside the six-membered ring. Notice that the phase of e_1 in **16** and **17** has been reversed on going to **18**. Had that not been done, **18** would have evolved into the two unoccupied levels where e_1 is antibonding with respect to $3\pi_s$ and $2\pi_a$. This is just another way of pointing to the fact that overlap is lost near **17**. Now there is not an actual occupied/unoccupied orbital crossing going from η^6 to η^5 . Near central- η^2 the stabilization of $3\pi_s$ and $2\pi_a$ by e_1 is replaced by repulsions from e_2 and $1a_1$ of the FeCp unit (see Figure 1). A Walsh diagram shows that especially two filled molecular levels, the antibonding combinations of $2\pi_a$ and $3\pi_s$ with e_2 , rise to high energy near the central- η^2 geometry. This is shown in **19**. Additionally, $1a_1$ is also destabilized by $3\pi_s$ at this ge-



19

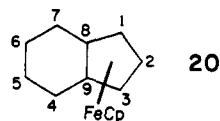
ometry. Therefore, the loss of the two principal bonding interactions and destabilization of the filled metal "t_{2g}" triad by filled π indenyl orbitals will conspire to make the least-motion pathway energetically inaccessible. Just as in naphthalene- $\text{Cr}(\text{CO})_3$, a nonleast-motion pathway and/or an intermolecular mechanism are viable alternatives.

The computed energy surface for indenyl-FeCp is presented in Figure 4. The distance between the iron atom and indenyl plane, r (see **8**), was held constant at 1.59 Å. The orientation of the FeCp unit was also fixed. This is justified by the extremely low rotational barriers of metallocenes, as determined by experimental and theoretical studies,³⁰ and was confirmed to be the case here as well by calculating different rotamers at relevant points of the surface. What is evident from Figure 4 is that it requires a prohibitive 77 kcal/mol for the least motion shift going from the η^5 to η^6 isomer. This is in the neighborhood of dissociation energies for Fe-Cp bonds.²⁵ The η^5 geometry is about 19 kcal/mol more stable than η^6 . This stability difference stems mainly from a larger overlap between e_1 with $2\pi_a$ at the η^5 position. The overlap $\langle e_1 | 2\pi_a \rangle$ at η^5 was computed to be 0.234, whereas at the optimum η^6 structure it was 0.107. The larger coefficients at C_1 and C_3 in **20**, as well as the antibonding of e_1 to the atomic orbitals at C_8 and C_9 in $2\pi_a$ at an η^6 geometry (see $e_1 + 2\pi_a$ in **16**), are at the heart of this overlap difference. The $e_1 + 3\pi_s$

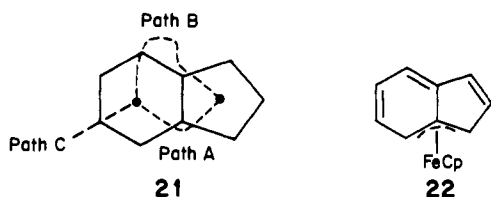
(28) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1; Müller, K. *Helv. Chim. Acta* **1970**, *53*, 1112; Salem, L. *J. Am. Chem. Soc.* **1968**, *90*, 543.

(29) Although the distance of Cr to C_{10} is not much different than that to C_1 and C_8 , the Cr-C overlap population is much smaller to C_{10} (0.001) than it is to C_1 or C_8 (0.095). That conformation of the $\text{Cr}(\text{CO})_3$ group shown in **14** is 9.5 kcal/mol more stable at $r = 1.73$ Å than the one where the $\text{Cr}(\text{CO})_3$ group has been rotated by 60°.

(30) See, for example, Bagus, P.; Walgren, U. I.; Almlöf, J. *J. Chem. Phys.* **1976**, *64*, 2324. A full listing may be found in ref 17b.



interaction also slightly favors the η^5 isomer. The computed overlaps were 0.252 and 0.208 at η^5 and η^6 , respectively. Figure 4 shows that there are two nonleast-motion pathways for the haptotropic shift of FeCp. Path A in **21** requires 35 kcal/mol



to go from the η^6 minimum to an η^3 type of intermediate, **22** (the barrier from η^5 to **22** is 41 kcal/mol). This pathway is analogous to the intramolecular one in naphthalene-Cr(CO)₃ and must compete with dissociative paths, one of which is illustrated in Figure 4 and leads to an η^1 intermediate, represented by an open circle (path C in **21**). Finally, a second minimum energy pathway appears on the surface. Path B in **21** initially follows an exit channel for dissociation to an η^1 isomer like path C, but our calculations show that there is a shallow valley which leads to the η^3 intermediate, **22**. Path B may well be an artifact of our computational method and may disappear at a more sophisticated level. What is causing it is a region of high energy for shifting the FeCp unit under the C₄-C₉ (see **20**) bond. These regions of high potential energy for positioning ML_n over a C-C bond at the perimeter of polyene rings are a common feature and are primarily due to repulsions between the "t_{2g}" ML_n set and high-lying σ levels of the polyene.

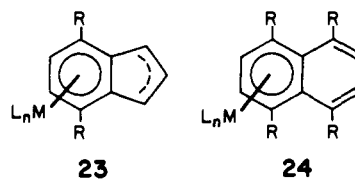
Of critical significance is the behavior of the Fe-indenyl plane distance, r . The optimized values at the η^5 and η^6 minima were found to be 1.62 and 1.64 Å, respectively. The values of r were 1.71 and 1.90 Å for the η^3 -intermediate, **22**, and the transition state leading from η^6 to **22** (on path A). Energetically this amounts to a relative preference of 23 kcal/mol for η^5 compared to η^6 . The η^3 -intermediate was found to be 16 kcal/mol less stable than η^6 and it requires 23 kcal/mol to attain the transition state geometry (from η^6 on path A).

As a further check to ascertain that the origin of these barriers was due to the loss of overlap between FpCp and the π orbitals of indenyl, we also constructed a potential energy surface analogous to the one in Figure 4 where all overlap between Fe and the σ system of indenyl was neglected. It is nearly identical with the full extended Hückel surface (Figure 4). The important point is that a very high region of potential energy is encountered for a least-motion shift requiring 71 kcal/mol relative to the optimum η^5 structure. The η^5 isomer was found to be 23 kcal/mol more stable than η^6 within this approximation. These findings corroborate the simple topological analysis presented in **16-18**. A nonleast-motion pathway very similar to path A in **21** with an intermediate analogous to **22** is found.

Definitive experimental evidence for haptotropic shifts is scarce for indenyl-ML_n systems. Deprotonation of η^6 -indene-Cr(CO)₃ directly leads to η^5 -indenyl-Cr(CO)₃ without the observation of an η^6 species.^{8e} An η^6 -indenyl-RhCp²⁺ and -IrCp²⁺ isomer can be observed^{9a} by NMR. They rearrange slowly and irreversibly to the η^5 forms at room temperature. Both observations are in accord with our theoretical studies. There are two X-ray structures of indenyl-ML₃ complexes.³¹ Both are of the η^5 isomer and show minor slippage of the ML₃ unit away from the central carbon-carbon bond. Our calculations also show a 0.08 Å displacement from η^5 in this direction. The reasons for this distortion are

identical with that presented for naphthalene-Cr(CO)₃ in the previous section.

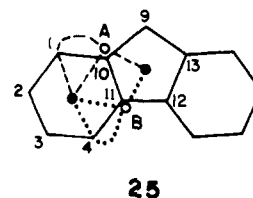
Of obvious interest would be the generation of a neutral η^6 -indenyl-ML_n complex at low temperature. The kinetics of the rearrangement could then be measured in a noncoordinating solvent. A nonleast-motion path could be inferred by a number of strategies in this as well as the naphthalene-Cr(CO)₃ system. The placement of bulky groups at C₄ and C₇ in **23** (R = Ph or



t-Bu) or the analogous positions in **24** should slow the rearrangement rate. The ML_n group must migrate quite close to the bulky substituent via path A or B in **21** and the minimum energy path in naphthalene-Cr(CO)₃. A way to accelerate either reaction would be to stabilize the coordinatively unsaturated η^3 -intermediate. Utilizing strong electron donating groups for R in **23** and **24** should accomplish this task.

It should be mentioned that MNDO calculations³² have been carried out on indenyl-BeH and -BeCl. The BeH⁺ and BeCl⁺ fragments were used as models for transition metal d⁶-ML₃ and MCp moieties. Least-motion pathways were predicted, in contrast to our findings. This may be due to the fact that for groups like BeX⁺ the dominant interaction with a π system occurs via the sp-type hybrid of a₁ symmetry which corresponds to our 2a₁ in M(CO)₃ or MCp (see Figure 1). For main group fragments this orbital lies at a lower energy than the p-type e set which is analogous to our e₁ or 2e. Furthermore, there is no "t_{2g}-like" triad to destabilize 2 π_a and 3 π_s at the central- η^2 way point for a BeX substituted compound.

A potential energy surface was also constructed for fluorenyl-FeCp. It is almost identical in its general features with that presented in Figure 4 for the indenyl system. Here the two isomers are at more comparable energies. The η^6 isomer was calculated to be 7 kcal/mol less stable than η^5 . Although we will not dwell on this point, the stability difference can again be determined by overlap considerations. As in the case of indenyl-FeCp, a direct path which interconverts η^5 and η^6 isomers is energetically impossible. An energy maximum of 63 kcal/mol relative to the ground state would be encountered. There are four nonleast-motion paths which can be followed. An idealized representation is shown in **25**. There are two basic pathways which are related



to path A and path B for the indenyl system in **21**. Since there is no longer a mirror plane which bisects the central C-C bond, shifting FeCp in the direction over C₁₀ by the dashed lines in **25** is energetically different from that given by the dotted lines which requires FeCp to move in the direction of C₁₁. Starting from η^5 it requires 25 kcal/mol to reach the η^3 intermediate, labeled A in **25**. The activation energy for the path leading to the other η^3 intermediate, labeled B, requires 36 kcal/mol. The difference here can be traced to the relative stabilities of the η^3 intermediates. Intermediates A and B are 21 and 32 kcal/mol, respectively, less stable than the η^5 ground state. Both intermediates are stabilized primarily via the interaction of one component of e₁ from the FeCp fragment with the HOMO of fluorenyl anion. This is clearly analogous to the naphthalene (see 2 π_a + 2e_a in **14**) and indenyl

(31) Honan, M. B.; Atwood, J. L.; Bernal, I.; Herrmann, W. A. *J. Organomet. Chem.* **1979**, *179*, 403; Shakir, R.; Atwood, J. L. *Acta Crystallogr.* **1981**, *B37*, 1656.

(32) Dewar, M. J. S.; Rzepa, H. S. *Inorg. Chem.* **1979**, *18*, 602.

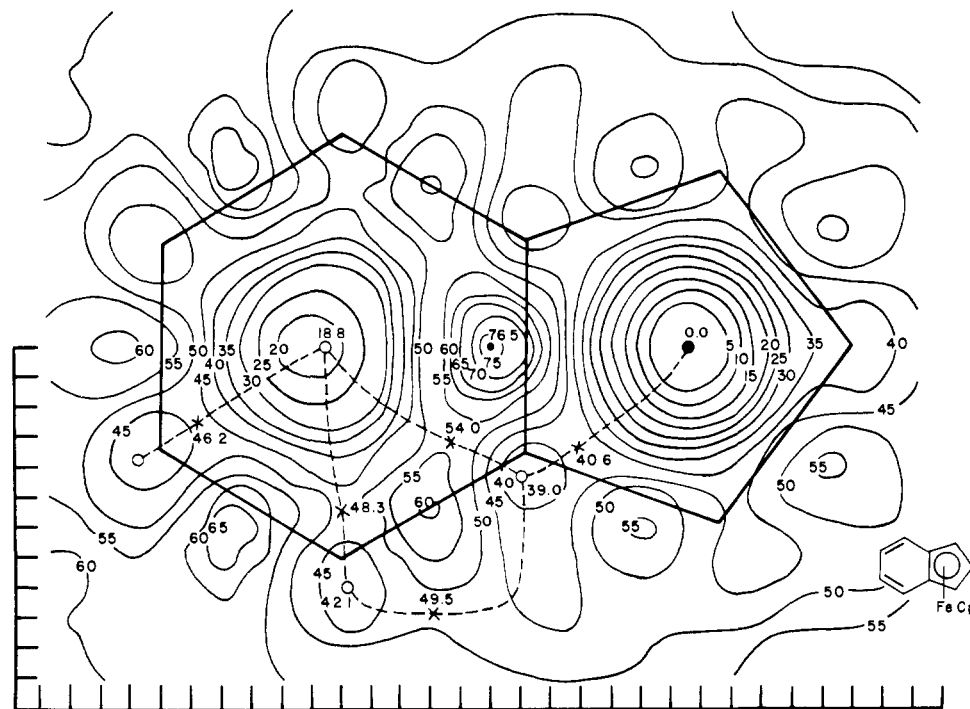
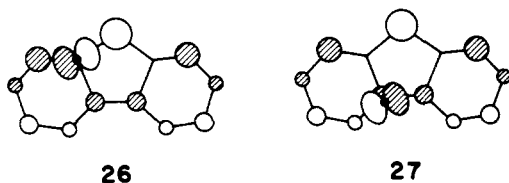
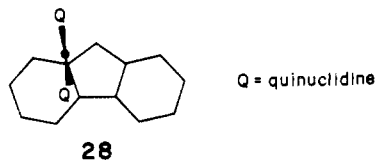


Figure 4. Potential energy surface for indenyl-FeCp. The details displayed are the same as in Figure 3 with a constant Fe-indenyl distance of 1.59 Å.

systems. A top view of the interaction for A and B is shown in **26** and **27**, respectively. The coefficients in the HOMO of



fluorenyl anion are larger at C_9 and C_1 than those at C_{12} and C_4 and, therefore, **26** is more stabilizing for intermediate A than **27** is for intermediate B. Remarkably, there exists some, albeit indirect, evidence for the energetic viability of intermediate A. The structure³³ of fluorenyllithium bisquinuclidine, **28**, is quite



close to the η^3 -intermediate A. As pointed out by Stucky and coworkers,³³ bonding from the fluorenyl anion HOMO to the empty lithium cation p orbital, perpendicular to the LiQ_2 plane, is of crucial importance. This is topologically equivalent to the interaction described in **26**. Referring back to **25**, there are two branches from each η^3 intermediate which lead to the η^6 isomer. As in the indenyl system there is not much energetic differentiation between the corresponding activation energies. The values range from 38 to 44 kcal/mol relative to the η^5 ground state.

The structure³⁴ of η^5 -fluorenyl- $Cr(CO)_2NO$ shows a nearly planar fluorenyl ring. The $Cr(CO)_2NO$ group is slightly displaced from η^5 toward C_9 (see **25** for the numbering system employed). Our calculations on η^5 -fluorenyl-FeCp also give a 0.03 Å displacement in this direction. Structures of η^6 -fluorenyl-FeCp and - $Mn(CO)_3$ have also been obtained.^{7b,d} There is a marked slippage of ML_n in both cases toward C_3 . The value from our calculations

was 0.26 Å. This is exactly in the direction of a dissociative exit channel. The fluorenyl ligand was again found to be not much distorted from planarity. η^6 -fluorenyl- $Mn(CO)_3$ rearranges slowly and irreversibly in refluxing hexane to the η^5 isomer.^{7c} However, η^6 -fluorenyl-FeCp^{7b} and η^6 -9-(triphenylphosphonium)fluorenyl- $Cr(CO)_3$ ³⁵ do not. It is not clear whether this is a kinetic or thermodynamic effect. Ustynuk and co-workers^{8f} have shown that minor substitutions can appreciably alter the equilibrium population of η^6 and η^5 isomers in the $Cr(CO)_3^-$ system. Our calculations also point to a substantial barrier that must be surmounted for the interconversion to take place. It may well be that decomposition of these thermally sensitive complexes obscures the issue. The isomerization reaction has been studied for fluorenyl- $Cr(CO)_3^-$ in some depth.^{6,8,10} The kinetics are complicated here by solvent effects. First of all, solvent reorganization has been shown to be energetically important.^{8b,10} An equilibrium between contact and solvent separated ion pairs^{8b} is a further worry, but most importantly, the isomerizations are carried out using coordinating solvents (e.g., THF, Me_2SO). Just as for naphthalene- $Cr(CO)_3$, intermolecular exchange will be a competitive process.³⁶ The large negative values of ΔS^\ddagger measured^{8b,10} for the isomerization are in fact similar to those observed²³ for arene exchange in benzene- $Cr(CO)_3$ and its derivatives. Perhaps competition experiments can shed some light on this possibility.

Pentalene-FeCp Cation and Anion

The previous haptotropic rearrangements were similar because they were cases where $d^6 ML_3$ or MCp fragments transversed the faces of topologically equivalent π systems. The least-motion paths for these examples were clearly symmetry forbidden in that both dominant interactions between the π system and ML_n fragment were lost at some point along the transit. But there is another pattern that we have also commonly found. Here one frontier orbital interaction is lost and the other is retained. A least-motion path relative to dissociation for this case should be more favorable than that for the totally symmetry forbidden ones of naphthalene, indenyl, and fluorenyl- ML_n . That is not to say that the least-

(33) Brooks, J. J.; Rhine, W.; Stucky, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 7339.

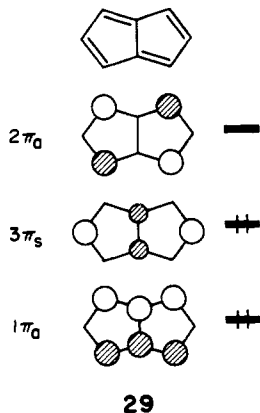
(34) Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P. E.; Alt, H. G. *J. Organomet. Chem.* **1979**, *165*, 65.

(35) Holy, N., private communication.

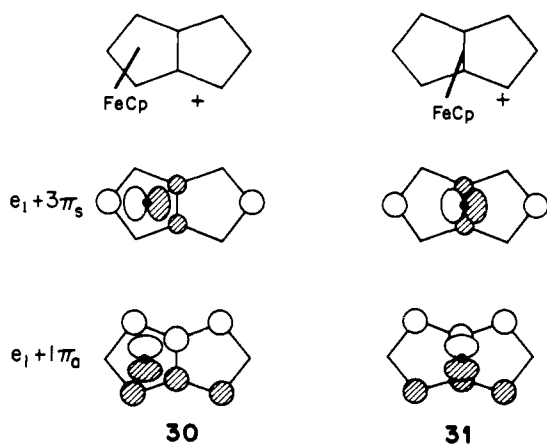
(36) For example, to attain an η^1 or close to an η^2 geometry which will be intercepted by solvent molecules requires 4 kcal/mol less energy than the intramolecular path for going from η^6 to η^2 .

motion transit will be the minimum energy reaction path for the haptotropic rearrangement, but such a path will not require the ML_n unit to completely avoid passage under the fused carbon-carbon bond of the bicyclic system which does occur in the totally symmetry forbidden cases.

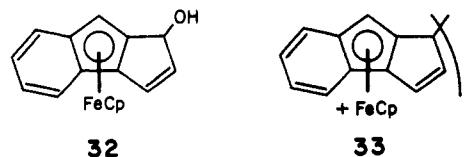
Pentalene-FeCp cation and anion nicely illustrate these points. Let us start with the cationic system. One way to portion the two interacting fragments would be to choose neutral pentalene and $FeCp^+$. The two highest occupied and lowest unoccupied π orbitals of pentalene are shown in **29**. Notice that $2\pi_a$ which is topo-



logically analogous to the filled $2\pi_a$ of naphthalene and indenyl anion is now empty. Since $FeCp^+$ is d^6 , e_1 is empty and will stabilize the two HOMO's, $3\pi_s$ and $1\pi_a$, in pentalene. These two frontier interactions at η^5 and the central- η^2 positions are displayed in **30** and **31**, respectively. The $e_1 + 3\pi_s$ combination loses overlap



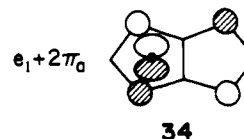
at central- η^2 while that in $e_1 + 1\pi_a$ is retained. Here again the stabilization of $3\pi_s$ by e_1 is replaced by repulsions from $1a_1$ and $x^2 - y^2$ of the e_1 set along a least-motion path. However, the $e_1 + 1\pi_a$ level remains at an essentially constant energy. Figure 5 presents the energy surface which was constructed so that the distance of Fe to the pentalene, r , was held constant at 1.69 Å. No local minima appear on the potential surface during the haptotropic shift in contrast to that found for naphthalene- $Cr(CO)_3$ and indenyl- $FeCp$ (see Figures 3 and 4). The transition state, indicated by a cross in Figure 5, has the $FeCp$ positioned under the fused carbon-carbon bond and shifted 0.6 Å away from the midpoint. The activation energy for this nonleast-motion path is 10 kcal/mol lower than what would be required for a least-motion path. Recall that in naphthalene- $Cr(CO)_3$, this difference is 23 kcal/mol. Allowing r to vary at these three points only very slightly changes their relative energies. The optimum values of r at the ground state, central- η^2 , and transition state were calculated to be 1.58, 1.82, and 1.82 Å, respectively. The ground state is predicted to have the $FeCp$ unit almost at the barycenter of the ring in contrast to η^5 -indenyl- $FeCp$ as discussed previously. Pentalene- $FeCp^+$ as well as isoelectronic examples are not known. A potential precursor to a benzo derivative, **32**, when treated with HBF_4/CH_3COOH underwent a dimerization reaction yielding



33.³⁷ The preparation of the isolobal pentalene and 1-methylpentalene- $Mn(CO)_3^+$ has been reported,³⁸ but no further details about the compounds have appeared. We shall return to a discussion of the electronic structure in pentalene- $FeCp^+$, but we note here that it closely resembles an allyl cation fused to ferrocene. The stability of ferrocenyl carbenium ions is well-known^{39,40} and we see no reason why a similar stabilization should not be found here.⁴¹

The features of the pentalene- $FeCp^+$ surface can best be compared to the complex with two more electrons. The potential energy surface for pentalene- $FeCp^-$ is displayed in Figure 6. There are many radical differences here in comparison to the pentalene- $FeCp^+$ surface in Figure 5. Firstly, the energy required to attain the central- η^2 structure has almost doubled (79 kcal/mol). The minimum energy path now swings widely away from under the central C-C bond. An η^3 intermediate is found and the activation energy is 10 kcal/mol larger than that for pentalene- $FeCp^+$. The ground state is shifted 0.21 Å from η^5 , in a direction away from central- η^2 . Several derivatives of this complex have been prepared,^{42,43} but nothing is known about their structure or propensity to undergo a haptotropic rearrangement.

A frontier orbital analysis immediately points to the difference between the pentalene- $FeCp$ cation and anion. In the cation we divided the molecule into neutral pentalene and $FeCp^+$ fragments. In the anionic complex a heuristically useful approach would be to divide the molecule into an $FeCp^+$ again and pentalene²⁻ fragments. The two empty e_1 orbitals of $FeCp^+$ will stabilize $3\pi_s$ and now $2\pi_a$, see **29**, of pentalene²⁻. The frontier interaction $e_1 + 1\pi_a$ in pentalene- $FeCp^+$ has been replaced by $e_1 + 2\pi_a$, shown in **34**, for pentalene- $FeCp^-$. The interaction in **34** will be lost on



going to the central- η^2 geometry along with $e_1 + 3\pi_s$ in **30**. Therefore, both frontier interactions are now lost. Note that the filled $2\pi_a$ and $3\pi_s$ levels of pentalene²⁻ are topologically equivalent to the $2\pi_a$ and $3\pi_s$ HOMO's of indenyl anion and naphthalene. A complete MO analysis of the shift would start with one component of e_1 , $1\pi_a$, and $2\pi_a$. The lowest molecular orbital will be primarily $1\pi_a$ with some e_1 mixed in a bonding fashion, **35**. Furthermore, $2\pi_a$ mixes into this orbital in a bonding way with respect to e_1 . The resultant orbital is given by **36**. The next molecular level is primarily $2\pi_a$, bonding to e_1 , **37**. Now $1\pi_a$ mixes into **37** in an antibonding fashion to e_1 . The resultant orbital, **38**, is heavily concentrated on the two carbons which are connected to the coordinated cyclopentadienyl portion. Let us take each orbital in turn to evaluate what occurs when the $FeCp$ unit shifts from η^5 to the central- η^2 position. The overlap between $1\pi_a$ and

(37) Cais, M.; Modiano, A.; Raveh, A. *J. Am. Chem. Soc.* **1965**, *87*, 5607.

(38) Cais, M.; Modiano, A.; Tirosh, N.; Eisenstadt, A.; 8th International Conference on Coordination Chemistry, Vienna, Sept 7-11, 1963; Abstracts of Papers, pp 229-232, as reported in ref 39; Cais, M. "The Chemistry of Alkenes"; Patai, S., Ed.; Interscience: New York, 1964; pp 380-2.

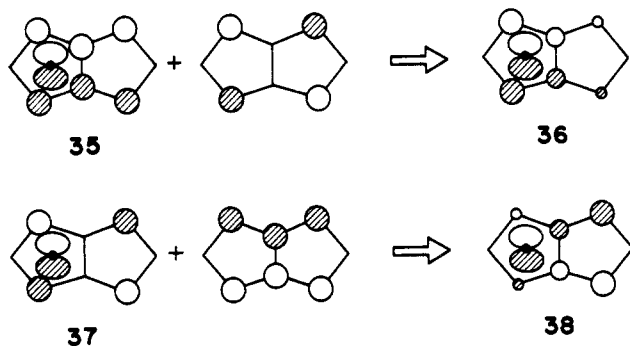
(39) Kerber, R. C.; Ehntholt, D. *J. Synthesis* **1970**, 449.

(40) For reviews, see Cais, M. *Organomet. Chem. Rev.* **1966**, *1*, 435; Haynes, L.; Pettit, R. In "Carbonium Ions"; Olah, G.; Schleyer, P. v. R., Ed.; Vol. 5, Wiley: New York, 1975.

(41) Other interesting precursors are known: Schlögl, K.; Scholm, R. *Monatsh. Chem.* **1978**, *109*, 1227; Lehner, H.; Schlögl, K. *Ibid.* **1970**, *101*, 1970; **1971**, *102*, 277; Le Plouzennec, M.; Dabard, R. *J. Organomet. Chem.* **1977**, *133*, 359. Several pentalene metal dimer and trimer complexes are known: Knox, S. A. R.; Stone, F. G. A. *Acc. Chem. Res.* **1974**, *7*, 321.

(42) Katz, T. J.; Rosenberger, M. *J. Am. Chem. Soc.* **1963**, *85*, 2030; Katz, T. J.; Mrwoca, J. *J. Ibid.* **1967**, *89*, 1105.

(43) Volz, H.; Kowarsch, H. *J. Organomet. Chem.* **1977**, *136*, C27.



e_1 actually increases on going to the central- η^2 position; however, all overlap between e_1 and $2\pi_a$ is lost by symmetry. Therefore, molecular level **36** remains essentially at constant energy on shifting to the central- η^2 geometry. The loss of bonding between $2\pi_a$ and e_1 in **36** is compensated by an increase in the bonding between $1\pi_a$ and e_1 . The energy of **38** will rise dramatically for the same reasons. In pentalene- $FeCp^+$ **38** is the LUMO, so that the only frontier interaction which is destabilized is $e_1 + 3\pi_s$, illustrated in **30** and **31**. The addition of two electrons for pentalene- $FeCp^-$ fills **38** and the least-motion path becomes strongly forbidden.

Potential energy surfaces were also constructed for pentalene- $Mn(CO)_3$ cation and anion. They are very similar to their isolobal counterparts in Figures 5 and 6. The activation energy associated with the cation amounts to 32 kcal/mol. It is shifted only 0.25 Å away from the midpoint of the central C-C bond. The activation energy for the anion was computed to be 39 kcal/mol. The position of the transition state and η^3 intermediate were very close to those in Figure 6.

Bicyclo[3.2.0]heptatrienyl-CoCp Cation and Anion

A third pattern that is conceivable in haptotropic rearrangements is one where the ML_n unit slips to a coordination number which exceeds the 18-electron rule. The bicyclo[3.2.0]heptatrienyl-CoCp anion is such an example. At the η^4 geometry, **39**,



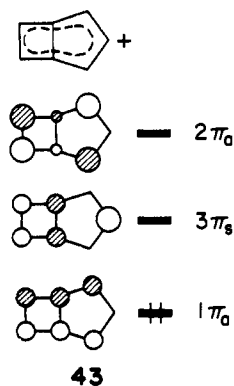
the compound is a saturated, eighteen electron complex with an allyl anion fused to the coordinated cyclobutadiene ligand. The isolobal $Fe(CO)_3$ compound has been prepared and is stable.⁴⁴ An η^5 complex, **40**, would be a 20-electron species. Like nickelocene, there is the possibility of a triplet ground state or distortion to a lower coordination number on the singlet manifold. There is then a substantial thermodynamic difference between the isomers, as well as a kinetic barrier for the haptotropic rearrangement. What makes this system theoretically interesting is that it can be compared to compounds with two electrons less, i.e., **41** and **42**. Here the η^4 and η^5 isomers are of the saturated, 18-



electron type. As in pentalene- $FeCp$, it will make a tremendous difference whether the compound is cationic or anionic.

We start our topological analysis with the cationic, **41** and **42**, system. The relevant π orbitals of bicyclo[3.2.0]heptatrienyl cation are displayed in **43**. A neutral CoCp fragment is d^8 . It contains two more electrons than the formal way we have treated the other ML_n fragments. Those two electrons (see Figure 1) will fill one

component of the e_1 set. The dominant interactions at **41** or **42** will then come from the union of e_1 with the HOMO, $1\pi_a$, and LUMO, $3\pi_s$, in **43**. It is easy to see that a least motion path from



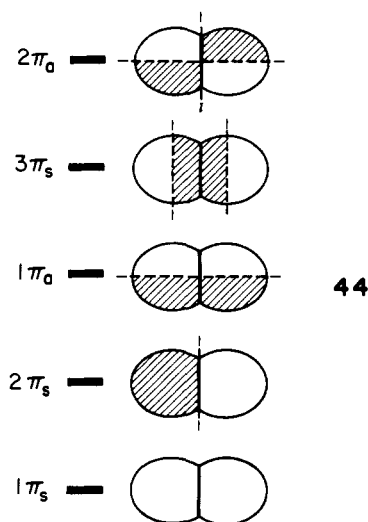
η^4 to η^5 preserves the overlap in $e_1 + 1\pi_a$. The $e_1 + 3\pi_s$ interaction is lost at some point in the transit. This is precisely analogous to the pentalene- $FeCp^+$ rearrangement which was presented in the preceding section. A potential energy surface is shown in Figure 7. The distance of Co to the bicycloheptatrienyl ligand, r , was held constant at 1.69 Å. The η^5 and η^4 isomers are very close in energy. The η^4 isomer actually becomes decidedly more stable than η^5 by 10 kcal/mol when r is allowed to vary. The optimum values of r were 1.48 Å at η^4 and 1.50 Å at η^5 . Higher level SCF calculations should be utilized to examine this question. The energy difference between η^4 and η^5 should be small. More importantly, allowing r to vary shifts the transition state slightly closer in Figure 7 toward a least-motion path to a point only 0.4 Å off from the mirror plane. The activation energy of 32 kcal/mol ($r = 1.62$ Å) relative to the ground-state η^4 geometry is only slightly lower than that calculated along the least-motion pathway (33 kcal/mol, $r = 1.69$ Å). In other words, the CoCp unit crosses an "activated ridge" that includes the central- η^2 point rather than a geometrically well-defined transition state.

The addition of two electrons causes the haptotropic rearrangement for bicyclo[3.2.0]heptatrienyl-CoCp⁻ to be significantly different. In orbital terms we can formally assign the extra two electrons to the heptatrienyl ligand. Therefore, the CoCp e_1 set will interact with the HOMO, $3\pi_s$ in **43**, and LUMO, $2\pi_a$. Both interactions are now lost during a least-motion transit. The implications of this are evident from the potential surface which is presented in Figure 8. The CoCp unit swings widely away from a least-motion path. Furthermore, a singlet 20-electron complex is not predicted to be stable. An η^3 geometry, 31 kcal/mol above the ground-state η^4 structure, is found to be the only local minimum. As mentioned previously, the $Fe(CO)_3$ analogue of this anion has been prepared and its ¹H NMR spectrum at room temperature is consistent with a static η^4 structure.⁴⁴

Generalizations and Extensions

Readers will have noticed that $1\pi_a$, $3\pi_s$, and $2\pi_a$ for the naphthalene, indenyl, pentalene, and bicyclo[3.2.0]heptatrienyl ligands are topologically equivalent. In general, the nodal structure of bicyclic polyenes corresponds to that given in **44**. When the two fused rings are of different sizes the vertical nodes in **44** may shift slightly but that will not alter their symmetry properties. Two patterns have emerged from the preceding examples. When the ML_n $2e$ or e_1 sets (Figure 1) find dominant interactions with $2\pi_a$ and $3\pi_s$ in **44** then both primary bonding combinations are lost in a least-motion transit. We shall describe this situation as a "forbidden" one based on the analogous type of sigmatropic rearrangement in organic chemistry. A strikingly circuitous intramolecular or dissociative path is predicted to occur. Notice here that when the ML_n species is d^6 , the bicyclic polyene represented by **44** will possess 10 π electrons. A d^8 ML_n fragment will find one interaction with the LUMO of the bicyclic polyene. For the reaction to be of this forbidden type, the π levels through $3\pi_s$ in **44** must be filled; in other words, the bicyclic polyene must have 8 π electrons. The alternative pattern which we shall call

(44) Bamberg, J. T.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, 99, 3173.



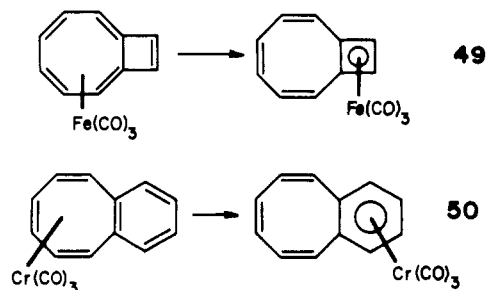
“partially allowed” is one where the ML_n , $2e$ or e_1 set combines with $3\pi_s$ and $1\pi_a$. The interaction to $3\pi_s$ is lost and that to $1\pi_a$ is retained along the least-motion transit. Moderate activation energies are predicted for minimum energy reaction paths that are geometrically close to the least-motion transit. In this case a d^6 ML_n unit would require an 8 π electron bicyclic polyene to be bound to it. Likewise, a 6 π electron ligand would be utilized with a d^8 ML_n complex. A fully “allowed” rearrangement would require that the ML_n unit forms its dominant interactions with $1\pi_a$ and $2\pi_s$ in **44**. That is probably an unreasonable situation. An 18-electron complex would be one where the ML_n unit is positioned under the fused carbon-carbon bond and coordinated simultaneously to both rings. One can see from **44** that the largest overlap of ML_n , $2e$ or e_1 to $2\pi_s$ and $1\pi_a$ would also occur at this geometry. However, the circumference of two fused rings would be too large to match effectively the radial extent of the ML_n valence orbitals. Shortly, we shall see an alternative way to create a fully allowed haptotropic rearrangement from one ring to another in a polycyclic polyene.

It is clear from the preceding discussion that there is an electron counting method to determine whether a haptotropic rearrangement will be of the forbidden or partially allowed types in bicyclic polyene- ML_3 or MCp complexes. In fact, this can be generalized to include any polyene- ML_n ($ML_n = ML_3, MCp$) system where the haptotropic rearrangement involves the ML_n unit *passing under a C-C bond*. Scheme I illustrates the three possibilities in a stylized fashion.

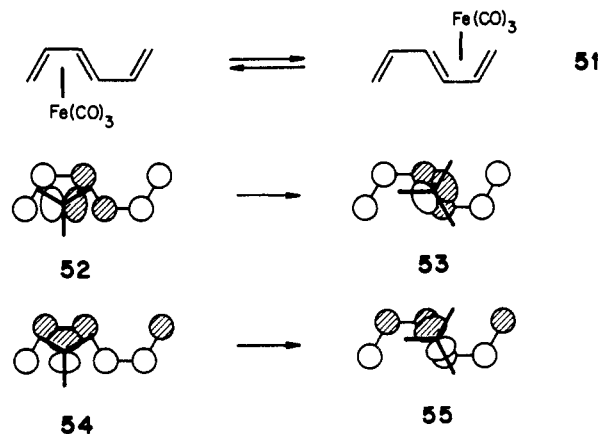
The patterns which we have extensively studied for bicyclic polyenes in **45** are also found in **46** and **47**. The total number of electrons to be counted is the sum of π electrons from the polyene plus the number of electrons supplied by the MCp or ML_3 unit, $n - 6$, where n is the number of d electrons formally assigned to the metal (counting Cp as an anionic, six-electron donor). When this sum equals $4q + 2$, where $q = 2, 3, \dots$, then the rearrangement path shown by the arrow in **45-47** is of the forbidden type. On the other hand, if the sum equals $4q$, then it will be partially allowed. Some reactions of type **45** that we have not covered are illustrated by **48-50**. In **48** the butadiene ligand contributes 6 π

**48**

electrons and the metal is d^8 so the total number of electrons is 8 which is of the $4q$, partially allowed class. The shift given in **49** has actually been observed.¹³ The total number of electrons is 12 so the rearrangement is partially allowed. The rearrangement in **50** is also of the 12-electron type. An η^4 -1,2,5,6-dibenzocyclooctatetraene- $Cr(CO)_4$ complex loses CO upon heating and rearranges to an η^6 complex where the $Cr(CO)_3$ is coordinated to one of the benzenoid rings.^{14,45} **50** is an obvious relative for



the shifting portion of the rearrangement. We know of no examples where a shift of type **46** has been found. There is one example of **47** that has been extensively studied. Derivatives of hexatriene- $Fe(CO)_3$ have been shown to undergo the rearrangement indicated in **51**.⁴⁶ The value of ΔG^\ddagger is approximately



33 kcal/mol for the reaction.^{46a} This is a d^8 complex and with the 6 π electrons of hexatriene an 8-electron, $4q$ system is predicted. In the $Fe(CO)_3$ fragment one member of $2e$ (Figure 1) is empty. It will interact most strongly with the HOMO of hexatriene, as shown in **52**. That bonding combination is lost, see **53**, on going to a “central- η^2 ” geometry. The other component of $2e$ on $Fe(CO)_3$ is filled. Therefore, its strongest bonding combination will be derived from the LUMO of hexatriene. Overlap between the two fragments in this molecular orbital is retained on going from **54** to **55**. A rearrangement analogous to **51** of η^6 -*cis,trans,cis*-decapentaene- $Cr(CO)_3$ would be interesting to study since it is of the 10 electron, forbidden type.

There are two cautionary notes that must be applied to the electron counting method of analysis. First, the fusion of a benzo group, etc., on the polyene ligand may alter the relative stabilities of the minima but they will not significantly change the reaction paths or prohibitions for a least-motion transit. That was shown in some detail by a comparison of the indenyl and fluorenyl- $FeCp$ systems. Likewise, the addition of an extra vinyl group to the hexatriene ligand in **51** will not create an additional constraint. Therefore, it is important to count only those polyene electrons that are directly involved in the haptotropic rearrangement. Secondly, the analysis requires that the ML_n unit will move across an internal C-C bond. The electron counting method will not

(45) Yet another 12-electron system is heptalene- $Cr(CO)_3$; see Vogel, E.; Königshofen, H.; Wassen, J.; Müllen, K.; Oth, J. M. *Angew. Chem.* **1974**, *86*, 777; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 732. No coalescence of the ring protons was observed at room temperature in the 1H NMR which would indicate a shift of the $Cr(CO)_3$ group from one ring to another. This implies that ΔG^\ddagger must be greater than 15 kcal/mol.

(46) (a) Whitlock, H. W.; Chuah, Y. N. *J. Am. Chem. Soc.* **1965**, *87*, 3605; Whitlock, H. W.; Reich, C.; Woessner, W. D. *Ibid.* **1971**, *93*, 2483; Whitlock, H. W.; Chuah, Y. N. *Inorg. Chem.* **1965**, *7*, 425. (b) Banthorpe, D. V.; Fitton, H.; Lewis, J. J. *Chem. Soc., Dalton Trans.* **1973**, 2051; Brodie, A. M.; Johnson, B. F. G.; Lewis, J. *Ibid.* **1973**, 1997. (c) El-Awady, A. A. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2185.

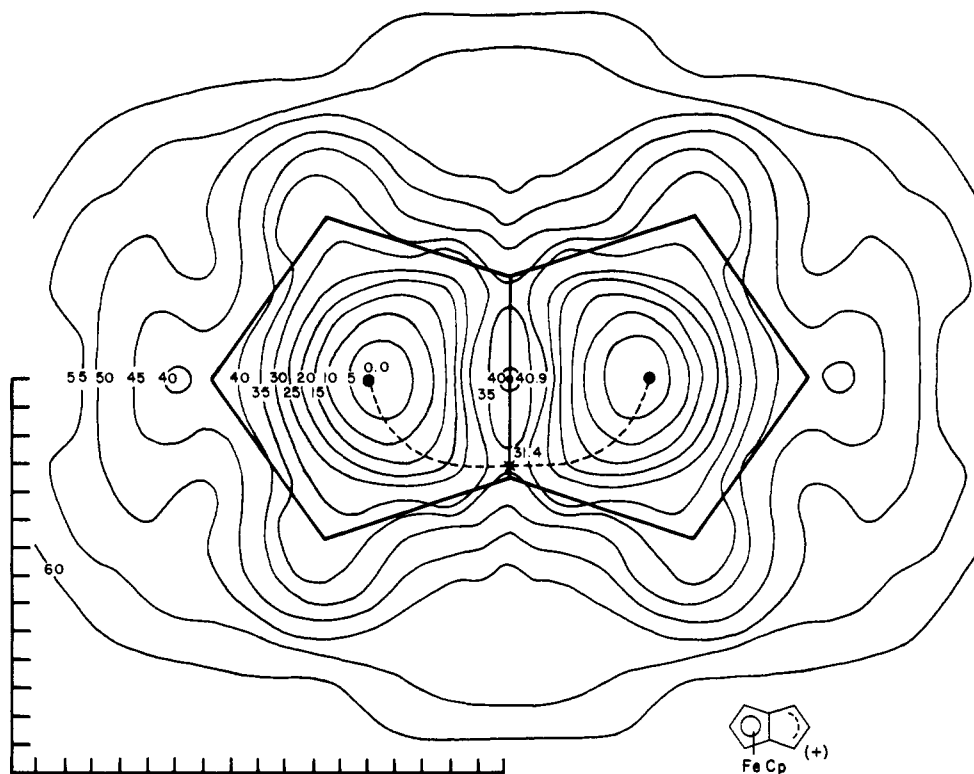


Figure 5. Potential energy surface for pentalene- $FeCp^+$. The details for the illustration of the surface may be found in Figure 3. The Fe-pentalene distance was fixed at 1.69 Å.

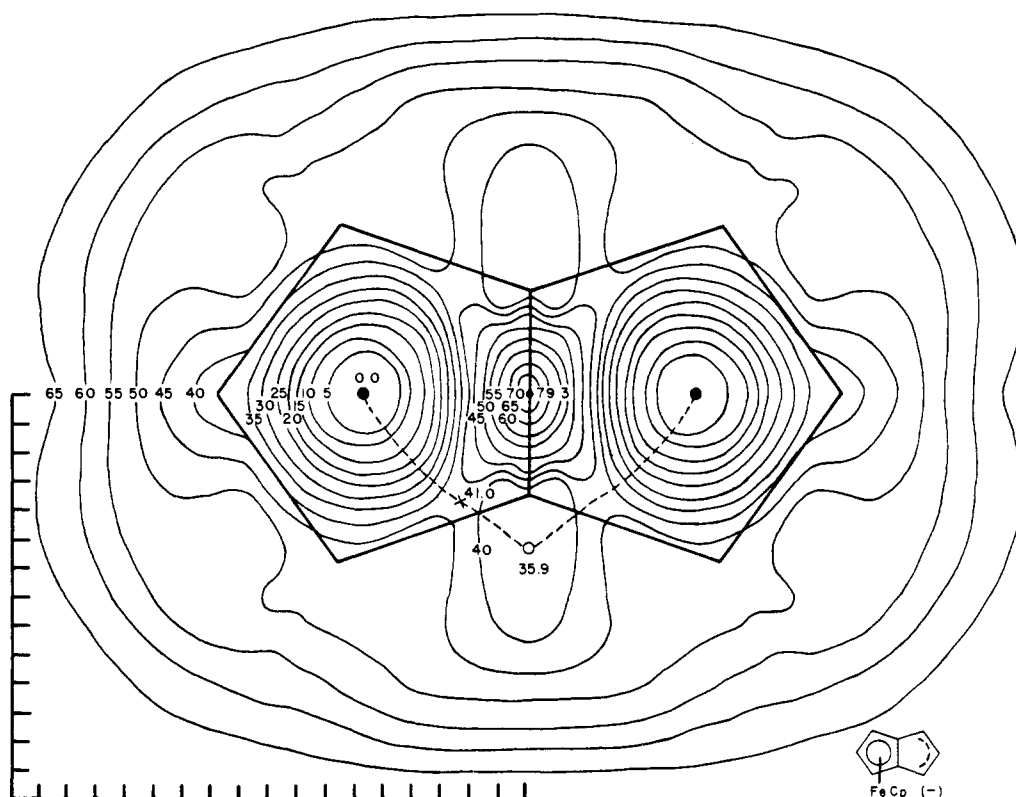


Figure 6. The potential energy surface for pentalene- $FeCp^-$. The details for the illustration may be found in Figure 3. The Fe-pentalene distance was held constant at 1.69 Å.

apply to a situation where the ML_n unit crosses a carbon atom, for example, in a polynuclear hydrocarbon. These cases can readily be handled by an explicit examination of how the overlap between the two valence ML_n orbitals and polyene π levels vary along the reaction path.

One way in which the MCp or ML_3 units retain *both* bonding interactions during a haptotropic rearrangement is created by

taking advantage of degeneracies in the polyene π levels. Ring-whizzing, wherein the ML_n unit migrates around the periphery of a fully conjugated cyclic polyene, is an example where this commonly occurs. We shall not pursue this to any extent here,^{48,47} but taking linear combinations of the two members in a degenerate

(47) Albright, T. A.; Hoffmann, R.; Dedieu, A. to be published.

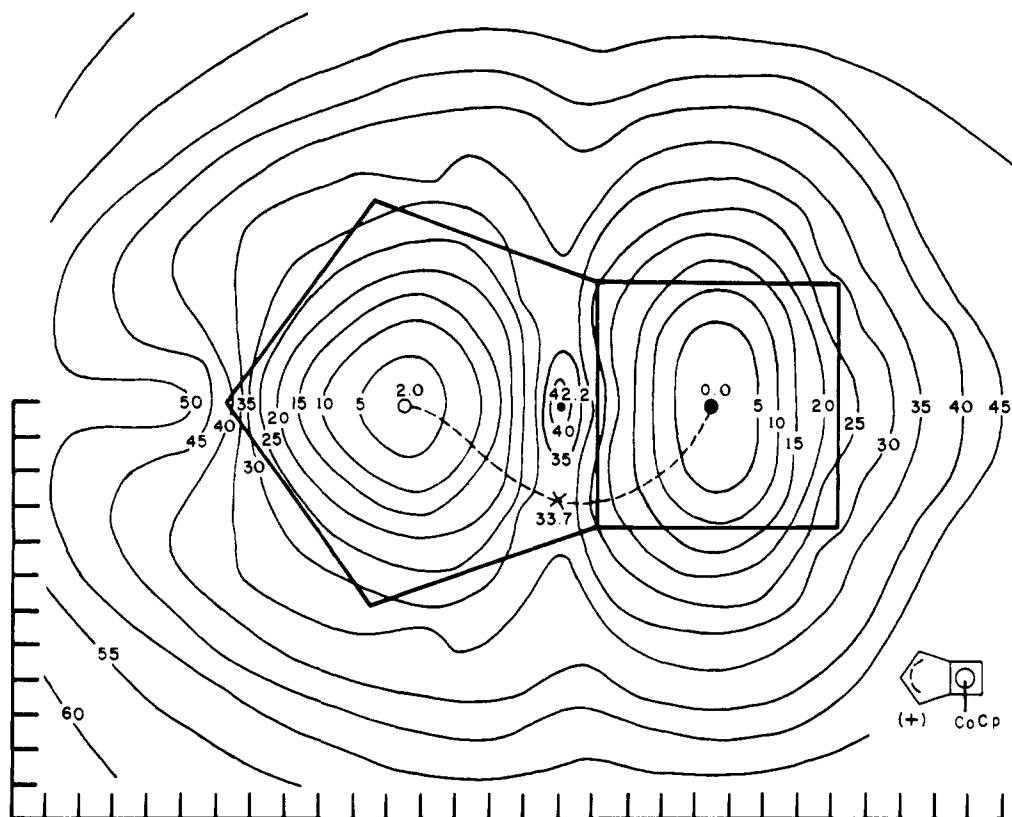
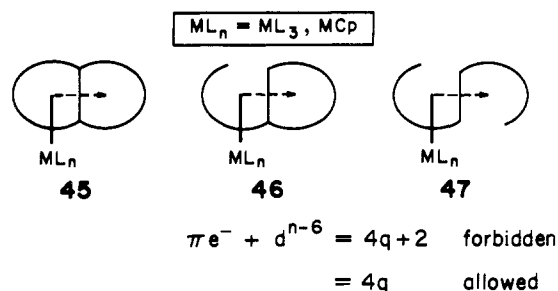


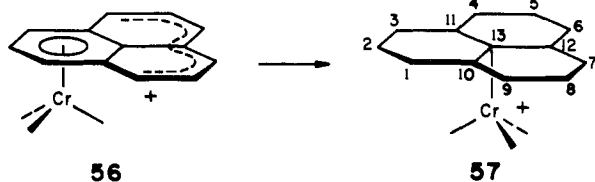
Figure 7. The potential energy surface for bicyclo[3.2.0]heptatrienyl-CoCp⁺. Details for the illustration are given in Figure 3. The Co-ligand distance was fixed at 1.69 Å.

Scheme I



π set allows the overlap between them and $2e$ (or e_1) to be retained in a continuous fashion from one ground-state structure to another. In this "fully allowed" reaction the activation energies should be and have been experimentally found to be,³ with some understandable exceptions, much lower than those we have presented here.

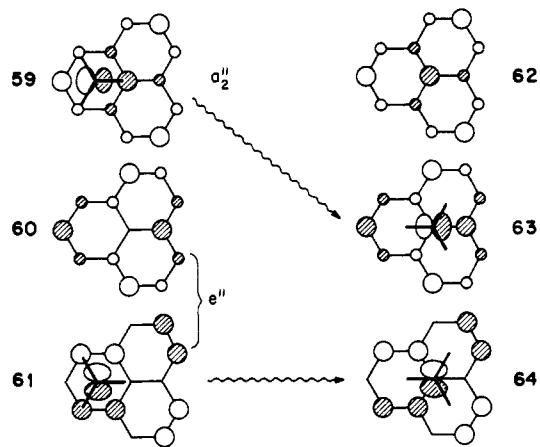
Real or accidental degeneracies can also be exploited in certain polynuclear benzenoid systems where the ML_n group migrates from one ring to another. A case in point is the experimentally unknown phenalenium-Cr(CO)₃ cation or anion⁴⁸ where Cr(CO)₃ can migrate from an η^6 ground state, **56**, to an η^4 structure **57**.



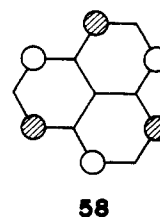
Whether the complex is a cation or anion does not make much

(48) A precursor to this compound, phenalene-Cr(CO)₃, has been prepared; see Lin, S.; Boudjouk, P. *J. Organomet. Chem.* **1980**, *187*, C11, and ref 11d. Other phenalenium complexes are known; Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1978**, 142.

Scheme II



difference; the orbital which is empty or filled is mainly localized on the phenalenium ligand. It is shown in **58**. At the η^4 geometry



58 does not interact with any of the Cr(CO)₃ valence orbitals and that interaction is also very small at η^6 . So for the moment we shall concentrate on the cationic system. The three highest occupied π levels of the phenalenium cation are of a_2'' and e'' symmetry. At the Hückel level a_2'' and e'' are accidentally degenerate. The splitting between a_2'' and e'' remains small at the extended Hückel level (0.1 eV).⁴⁹ Scheme II shows that a_2'' , **59**,

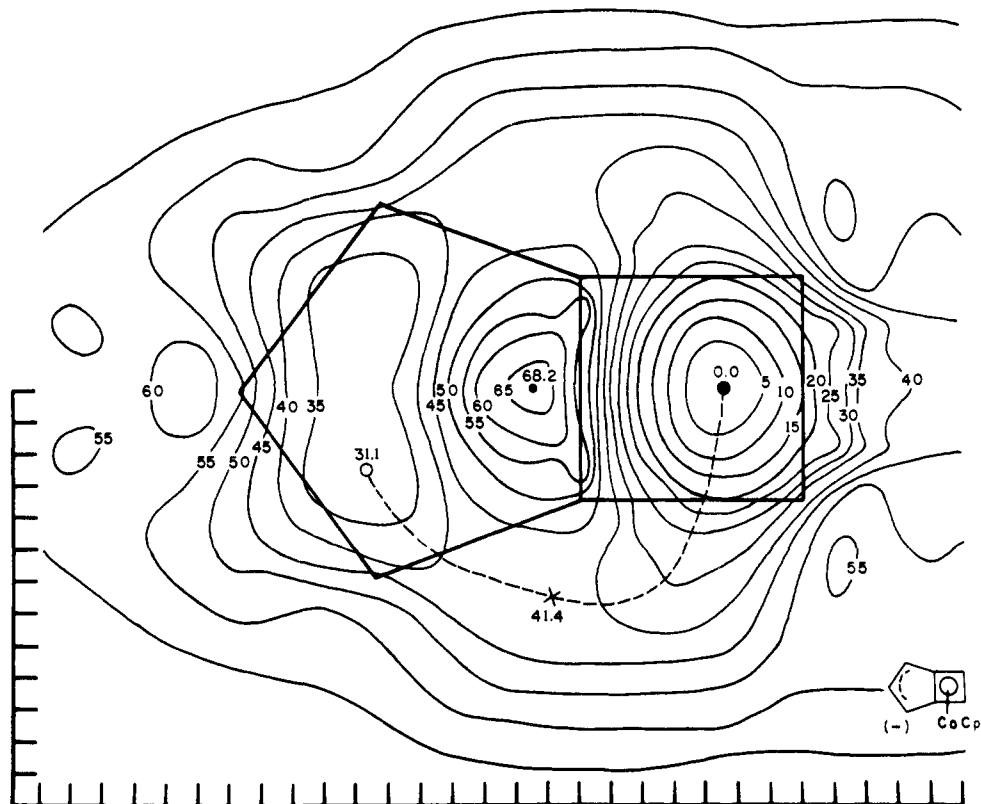
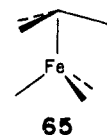


Figure 8. The potential energy surface for bicyclo[3.2.0]heptatrienyl-CoCp⁻. The value of r was identical to that used in Figure 7.

is stabilized by $2e_s$ of Cr(CO)₃ (see Figure 1) at an η^6 ground state. One component of e'' , **61**, is stabilized by $2e_a$ while the other member, **60**, remains *basically* nonbonding. Now as the Cr(CO)₃ group is shifted toward the η^4 structure, **57**, the overlap between a_2'' and $2e_s$ diminishes. However, overlap between $2e_s$ and **60** grows in, eventually yielding **63** at the η^4 geometry. The a_2'' orbital becomes "nonbonding" **62** (**62** will actually form a three-orbital interaction with the Cr(CO)₃ $2a_1$ and $1a_1$ functions). Finally, overlap is maintained going from **61** to **64**. Because a_2'' and e'' are nearly degenerate to begin with, there will be little preference from an energetic sense as to which is stabilized by the Cr(CO)₃ $2e$ set. Hence, both primary bonding interactions are retained in the haptotropic rearrangement.

Figure 9 shows the potential energy surface for phenalenium-Cr(CO)₃⁺. The distance between Cr and the phenalenium ring, r , was held constant at 1.73 Å. Two reaction channels are present for intramolecular exchange. One is analogous to that we have discussed for naphthalene-Cr(CO)₃. It proceeds with an activation energy of 26 kcal/mol to an intermediate which is geometrically and electronically very similar to **14**. Somewhat surprising to us was that the path from the ground state, **56**, to the η^4 structure, **57**, required 31 kcal/mol and intermediate **57** was 30 kcal/mol less stable than **56**. Allowing r to vary stabilizes **57** somewhat, it becomes 25 kcal/mol less stable than **56** and the transition state requires 26 kcal/mol (where $r = 1.97$ Å). As in naphthalene-Cr(CO)₃ full optimization of the η^3 intermediate and transition state via the alternative reaction channel did not substantially change their energies relative to the optimized ground-state structure. Therefore, at our computational level the two pathways are energetically equivalent, but there are reasons to think that a direct path to the η^4 intermediate, **57**, should require less energy. We showed in Scheme II that both bonding interactions are kept on moving from **56** to **57**. What is not so apparent at first is that the overlap between the polyene π levels and the $2e$ set of Cr(CO)₃ are reduced considerably during the transit. At η^6 the overlap between a_2'' and $2e_s$ in **59** was computed to be 0.202. In **63** the

overlap between $2e_s$ and e'' is reduced to 0.099. Likewise, the $\langle 2e_a | e'' \rangle$ overlap goes from 0.200 in **61** to 0.099 in **64**. Notice that the bonding of $2e_a$ to C₁ and C₃ in **61** (see numbering system in **57**) is lost on going to **64** and there is some antibonding introduced by C₅-C₈ to $2e_a$ in this orbital. The small atomic coefficients at C₁₀ and C₁₁ in **63** and antibonding from C₇-C₉, also create lesser overlap to $2e_s$ in **63** compared to that in **59**. The bonding inherent in **63** and **64** is very reminiscent of that in trimethylenemethane-Fe(CO)₃. In fact the reasons why the conformation of the Cr(CO)₃ group with respect to the phenalenium cation shown in **57** is the most stable one is precisely identical with those in the trimethylenemethane-Fe(CO)₃ complex.^{17b} This offers a clue as to how one can stabilize the η^4 intermediate and transition state leading to it. All known trimethylenemethane-Fe(CO)₃ structures⁵⁰ have the trimethylenemethane ligand pyramidalized to an umbrella-like geometry, as shown by **65**. The amount of puckering for these complexes is



~15° and this includes an η^4 complex of heptafulvene^{50a} where two of the trimethylenemethane arms are in conjugation with a butadiene unit. The puckering does two things:^{17b} firstly, the p orbitals on the methylenes point more inward, toward the iron, and secondly, the hydrogens or substituents on the methylenes also pyramidalize in such a way as to hybridize the p orbitals toward the iron atom. Therefore, in η^4 -heptafulvene-Fe(CO)₃, six of the carbons in the ring approximately lie in one plane and C₇ (which corresponds to the central carbon of the trimethylenemethane unit) is displaced significantly from it away from the iron. Both of these features serve to increase the overlap

(49) At the ab initio level the splittings for accidentally degenerate filled levels also remain very small—Whangbo, M.-H.; Albright, T. A., unpublished calculations.

(50) (a) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1973**, *12*, 525. (b) Churchill, M. R.; Gold, K. *Ibid.* **1969**, *8*, 401. (c) Almenningen, A.; Haaland, A.; Wahl, K. *Acta. Chem. Scand.* **1969**, *23*, 1145. (d) Kuzmin, V. S.; Zolnikova, G. P.; Struchkov, Yu. T.; Kritskaya, I. I. *Zh. Strukt. Khim.* **1974**, *15*, 162. (e) Yasuda, N.; Kai, Y.; Yasuoka, N.; Kasai, N.; KaKudo, M. *J. Chem. Soc., Chem. Commun.* **1972**, 157.

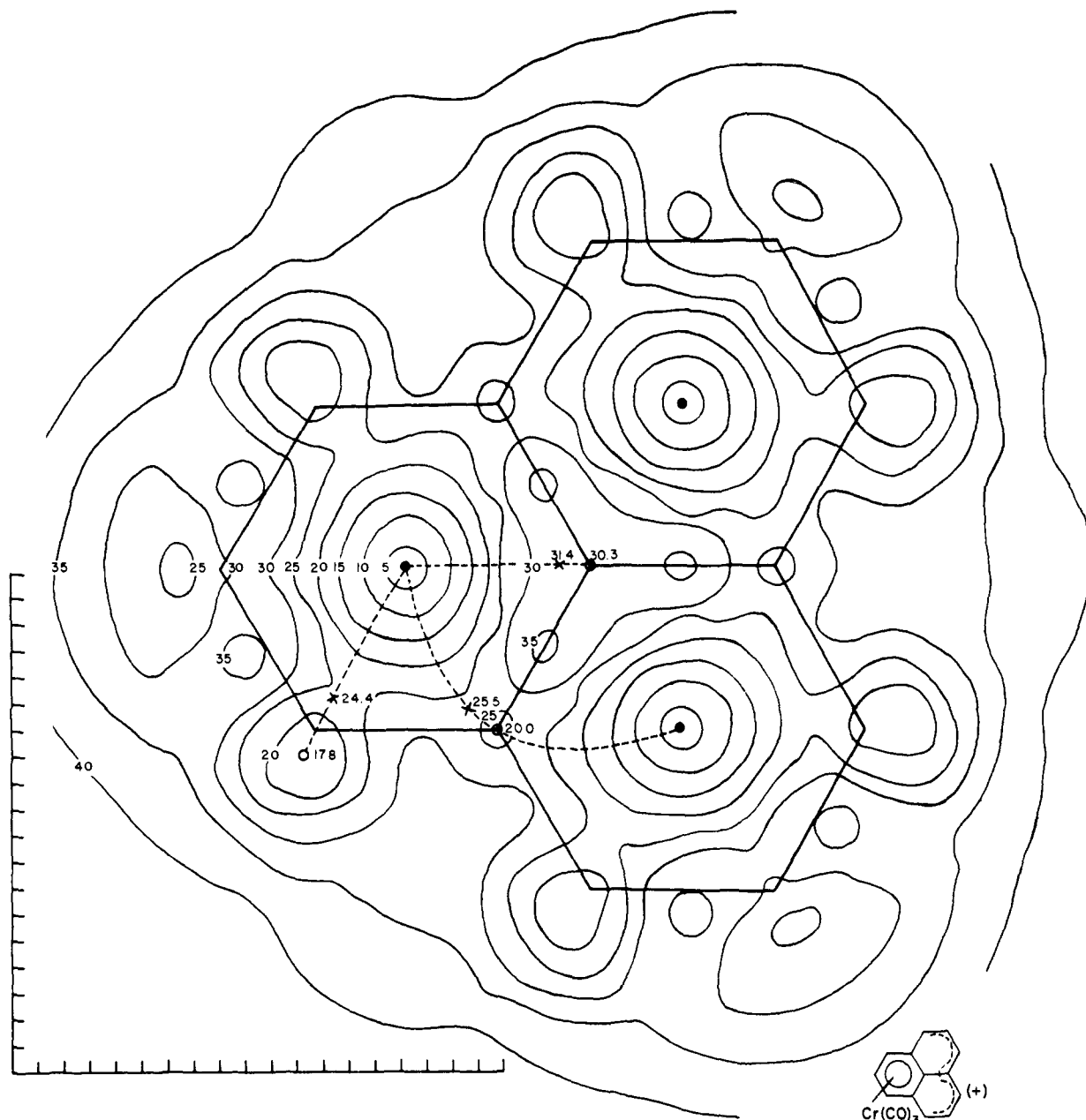
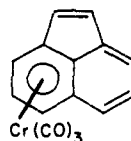


Figure 9. Potential energy surface for phenalenium- $\text{Cr}(\text{CO})_3^+$ where r was fixed at 1.73 Å.

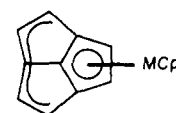
between the trimethylenemethane π levels and the $\text{Fe}(\text{CO})_3$ 2e set.^{17b} This should also stabilize **57** (and the transition state since it is geometrically quite close to the η^4 intermediate). One distortion that was tried was to move C_{13} up, out of the plane of the other 12 carbons along with an independent variation of the $\text{Cr}-\text{C}_{13}$ distance at **57**, as well as points through the transition state towards the η^6 structure. In all cases the phenalenium ring preferred to remain planar, although the surface for puckering was quite soft in the region of the transition state to the η^4 intermediate. Another motion that was tried was to move C_1-C_{12} down toward Cr with an independent variation of the $\text{Cr}-\text{C}_{13}$ distance at **57**. This also proved to be destabilizing. We think that this is an artifact of the extended Hückel method. These puckering motions interrupt π bonding in the polyenes and this must be compensated for by the increased bonding to the metal. This does not happen at our level of computation. In fact, the puckering motion was probed in trimethylenemethane- $\text{Fe}(\text{CO})_3$ and η^4 -heptafulvene- $\text{Fe}(\text{CO})_3$.⁵¹ Extended Hückel calculations for puckering angles from 0 to 8° give a very soft potential which rise sharply after that point.

Minima were found at 4° for both compounds, much smaller than the typical value of 15°. Therefore, we feel that the direct rearrangement path from **56** to **57** is most likely of lower energy than the other and that the activation energy should also be lower than that for intramolecular rearrangement in naphthalene- $\text{Cr}(\text{CO})_3$.

Surfaces were constructed for phenalenium- $\text{Cr}(\text{CO})_3$ anion as well as phenalenium-MnCp cation and anion. They are very similar to that shown in Figure 9 with the exception that exit channels via $\eta^3-\eta^1$ structures toward dissociation are energetically more accessible for the anions. This is understandable when one recalls that **58** is filled in the anionic ligand and the presence of this high-lying HOMO will stabilize η^3 and η^1 geometries. Calculations were also carried out on acenaphthalene- $\text{Cr}(\text{CO})_3$, **66**, and acepentalene-MCp, **67**. We shall not discuss these at



66



67

(51) Albright, T. A.; Hoffmann, R.; Hofmann, P., unpublished calculations.

Table I. Parameters Used in the Extended Hückel Calculations

orbital	H_{ii} , eV	ξ_1	ξ_2	C_1^a	C_2^a
Cr 3d	-11.22	4.95	1.60	0.4876	0.7205
4s	-8.66	1.70			
4p	-5.24	1.70			
Mn 3d	-11.59	5.15	1.90	0.5320	0.6490
4s	-8.63	1.80			
4p	-5.06	1.80			
Fe 3d	-12.70	5.35	1.80	0.5366	0.6678
4s	-9.17	1.90			
4p	-5.37	1.90			
Co 3d	-12.28	5.55	2.10	0.5680	0.6060
4s	-9.51	2.00			
4p	-4.78	2.00			
C 2s	-21.40	1.625			
2p	-11.40	1.625			
O 2s	-32.30	2.275			
2p	-14.80	2.275			
H 1s	-13.60	1.30			

^a Contraction coefficients used in the double- ξ expansion.

any length here. The idea in **66** is that the "extra" double bond will stabilize the η^3 intermediate and, therefore, the haptotropic rearrangement will require less energy than in naphthalene-Cr(CO)₃. In fact, calculations predict that the η^5 structure where the Cr(CO)₃ group is coordinated to the five-membered ring will be 6 kcal/mol more stable than the normal η^6 isomer. Experimentally this is not true as evidenced by the room temperature ¹³C NMR spectrum.⁵² NMR experiments have been initiated to measure the activation energies for intramolecular exchange in **66** and other derivatives of naphthalene-Cr(CO)₃.⁵² Efforts are also underway to prepare d⁶ complexes of **67**.⁵³ There are some basic differences between the π topology of acepentalene

and phenalenium. The bonding interaction analogous to **63** is not present in the acepentalene system. Accordingly, an η^4 structure is strongly avoided. There are also differences in the reaction path and associated activation energies depending upon whether the metal is d⁶ or d⁸. The complex behaves somewhat like pentalene-FeCp⁺ (Figure 5) and the d⁸ compound is analogous to pentalene-FeCp⁻ (Figure 6). A full discussion of the stability, reactivity, and potential energy surfaces will be presented elsewhere.⁵⁴

Acknowledgment. We are grateful to P. Stauffert for running the acepentalene-MCp calculations. We thank the Scientific Affairs Division of NATO (T.A.A. and P.H.), the Robert A. Welch Foundation (T.A.A.), Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie (P.H.), and the National Science Foundation (R.H.) for support of this work.

Appendix

The extended Hückel calculations¹⁶ utilized a modified version of the Wolfsberg-Helmholz formula.⁵⁵ The parameters listed in Table I were taken from previous work.^{17b} Idealized geometries for the polyenes were used with C-C = 1.41 Å and C-H = 1.09 Å. The M-Cp midpoint distance was fixed at 1.687 Å. For the M(CO)₃ groups the distances utilized were: Cr-C = 1.84 Å, Mn-C = 1.76 Å, Fe-C = 1.78 Å. All M-C-O and C-M-C angles were fixed at 180 and 90°, respectively. The C-O distance used was 1.14 Å.

Registry No. Naphthalene-Cr(CO)₃, 12110-37-1; indenyl-FeCp, 54845-16-8; pentalene-FeCp cation, 85304-57-0; pentalene-FeCp anion, 85304-58-1; bicycloheptatrienyl-CoCp cation, 85304-59-2; bicycloheptatrienyl-CoCp anion, 85304-60-5; phenalenium-Cr(CO)₃ cation, 85318-19-0; fluorenyl-FeCp, 61642-91-9.

(52) Seiglie, C.; Albright, T. A., to be published.

(53) de Meijere, A., private communications.

(54) Hofmann, P.; Stauffert, P., to be published.

(55) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.

Nuclear Spin-Spin Coupling via Nonbonded Interactions. 5. The Orientational Dependence of α -Substituent Effects on Vicinal ¹³C-¹³C Coupling Constants

M. Barfield,*^{1a} E. D. Canada, Jr.,^{1b} C. R. McDaniel, Jr.,^{1b,c} J. L. Marshall,*^{1b,d} and S. R. Walter^{1a,c}

Contribution from the Departments of Chemistry, University of Arizona, Tucson, Arizona 85721, and North Texas State University, Denton, Texas 76203. Received October 25, 1982

Abstract: To investigate the role of nonbonded interactions on vicinal ¹³C-¹³C coupling constants, a series of 2,2-dimethylcyclopropanes with ¹³C labeled substituents in the C1 position were synthesized and their NMR parameters were accurately measured. The vicinal ¹³C-¹³C coupling constants in the cis arrangement ($\phi = 0^\circ$) were found to be quite sensitive to substituent orientation. For example, the largest (3.40 Hz) and smallest (1.04 Hz) values of ³J_{CC} (0°) were found for the primary and tertiary alcohols, respectively. The ¹H chemical shifts and vicinal coupling constants were used to determine the conformations of the hydroxy group of the primary, secondary, and tertiary alcohols. The calculated INDO-FPT molecular orbital results for the Fermi contact contributions to the vicinal ¹³C-¹³C coupling constants are in good agreement with the experimental data. By means of a modified molecular orbital technique, it is demonstrated that the most important contributions to ³J_{CC} (0°) arise from the nonbonded interactions associated with the proximity and orientation of the hydrogens which are directly bonded to the coupled carbon atoms (C4 and C5). As a consequence, the larger value of ³J_{CC} (0°) occurs for the primary alcohol with two hydrogens on C4. The smaller values for the secondary alcohols depend on the H-C4 orientation. The smallest value of the cis coupling constants occurs for the tertiary alcohol which does not have any directly bonded hydrogens.

The conformational and substituent dependencies of vicinal ¹³C-¹³C coupling constants have been the subject of a number

of studies from these and other laboratories.² Recent studies have emphasized the exceedingly important role of nonbonded inter-