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Cycloheptatriene and Fulvene $Cr(CO)_3$ Complexes

Thomas A. Albright and *Roald Hoffmann**

Department of Chemistry, Cornell University, Ithaca, New York 14853, U.S.A., and

Peter Hofmann

Institut für Organische Chemie, Universität Erlangen-Nürnberg,
D-8520 Erlangen, Federal Republic of Germany

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1,6-Methano[10]annulene-$Cr(CO)_3$ and several related complexes adopt an anomalous orientation of the $Cr(CO)_3$ unit with respect to the polyene, compared to all other hexatriene-$Cr(CO)_3$ complexes. A theoretical analysis of this problem shows that these conformational preferences are closely related to the cycloheptatriene-norcaradiene valence tautomerism. Several strategies for influencing the barrier to internal rotation in these complexes are presented. An analysis of the conformational preference, rotational barrier, and bending of the exocyclic methylene group in fulvene-$Cr(CO)_3$ is also discussed. This is extended to the analogous benzyl-$Cr(CO)_3$ and cyclobutadiene-carbinyl-$Fe(CO)_3$ cations. Finally, the orientations of these complexes are contrasted to those containing two more electrons.

Cycloheptatrien- und Fulven-$Cr(CO)_3$-Komplexe

Im Tricarbonylchrom(0)-Komplex von 1,6-Methano[10]annulen und in einigen verwandten Komplexen nimmt die $Cr(CO)_3$-Einheit verglichen mit allen anderen Hexatrien-$Cr(CO)_3$-Systemen eine anomale Orientierung relativ zum Polyen ein. Eine theoretische Analyse dieses Problems zeigt, daß diese Vorzugskonformation eng mit der Cycloheptatrien-Norcaradien-Valenztautomerie zusammenhängt. Mögliche Wege, die Rotationsbarriere in derartigen Komplexen zu beeinflussen, werden aufgezeigt. Vorzugskonformation, Rotationsbarriere und Abknicken der exocyclischen Methylengruppe in Tricarbonyl(η^6-fulven)chrom(0) werden diskutiert und die Analyse wird auf die analogen Benzyl-$Cr(CO)_3$- und Cyclobutadiencarbinyl-$Fe(CO)_3$-Kationen ausgedehnt. Die Konformation dieser Komplexe wird solchen gegenübergestellt, die zwei Elektronen mehr enthalten.

In the vast majority of hexatriene-ML_3 complexes a single conformation **1** is chosen [1]. The unique carbonyl or other substituent of the ML_3 fragment is positioned over the "open" side of the polyene ribbon. There is a substantial barrier, $\approx 11-12$ kcal/mole [2],

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[2] [2a] *M. Djazayeri*, *C. G. Kreiter*, *H. M. Kurz*, *M. Lang*, and *S. Özkar*, Z. Naturforsch., Teil B **31**, 1238 (1976). – [2b] *C. G. Kreiter*, *M. Lang*, and *H. Strack*, Chem. Ber. **108**, 1502 (1975). – [2c] *C. G. Kreiter* and *S. Özkar*, Z. Naturforsch., Teil B **32**, 408 (1977).

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to a rotation about the metal-triene axis. Both the equilibrium conformation and the magnitude of the rotational barrier are well understood from a theoretical perspective[3]. In fact, almost any acyclic polyene-ML_3 complex chooses its equilibrium position so that the unique carbonyl lies over the "open" face of the acyclic polyene[4].

There exist several striking exceptions to this geometrical generalization and they form one of the foci of this investigation. While one cycloheptatriene-$Cr(CO)_3$ complex (**2**)[1a] has the expected conformation, three others (**3**[5], **4**[6], and **5**[7]) assume an anomalous geometry, with the unique carbonyl under the "closed" side of the polyene. While one might seize upon the extra bridge in the bicyclic compounds **3**–**5** as indicative of a steric explanation, we suspected that an electronic effect was at work. Furthermore, because of the folding in the uncomplexed bridges of these compounds, there might well be more steric interaction between the two carbonyls in **3** and **4** with the methylene groups in the observed conformation than in the normal one. We were reinforced in this feeling by the observation that an $Fe(CO)_3$ complex (**6**), closely related to **3**, has a structure[5] that is normal for butadiene-$Fe(CO)_3$ compounds[4]. Complexes **3**–**6** are prepared[8] from 1,6-methano[10]annulene and its related polyenes[9] as elegantly synthesized by the *Vogel* group[10]. It should be noted, parenthetically, that a mass of physical data has indicated that 1,6-methano[10]annulene contains a delocalized 10 π-electron system[11]. **3** and **4** have been described[5–8] as "homoaromatic"[12] while **5** still contains a delocalized 10 π-electron system even though we have drawn it in a similar fashion to **3** and **4**. We

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

[4] For a review of these structures, see ref.[3].

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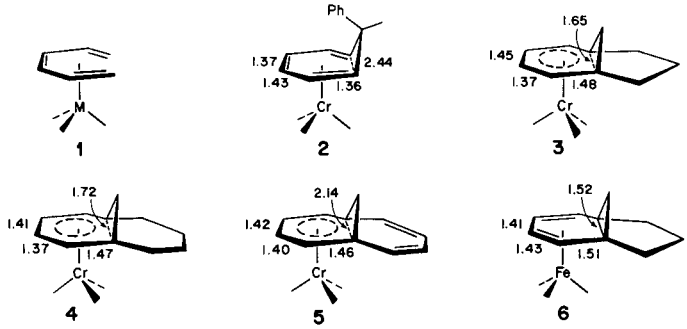
[11] [11a] X-ray: *M. Dobler* and *J. D. Dunitz,* Helv. Chim. Acta **48**, 1429 (1965). – [11b] ^1H NMR: *H. Günther,* Z. Naturforsch., Teil B **20**, 948 (1965). – [11c] ^{13}C NMR: *H. Günther, H. Schmickler, W. Bremser, F. A. Straube,* and *E. Vogel,* Angew. Chem. **85**, 585 (1973); Angew. Chem., Int. Ed. Engl. **12**, 570 (1973). – [11d] UV: *H.-R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel,* and *J. P. Weber,* Helv. Chim. Acta **49**, 2017 (1966). – [11e] P. E. Spectroscopy: *R. Boschi, W. Schmidt,* and *J.-C. Gfeller,* Tetrahedron Lett. **1972**, 4107; *C. Batich, E. Heilbronner,* and *E. Vogel,* Helv. Chim. Acta **57**, 2288 (1974). – [11f] ESR: *F. Gerson, E. Heilbronner, W. A. Böll,* and *E. Vogel,* ibid **48**, 1494 (1965); *F. Gerson, K. Müllen,* and *E. Vogel,* ibid **54**, 2731 (1971); *K. Müllen,* ibid **57**, 2399 (1974); *F. Gerson, K. Müllen,* and *C. Wydler,* ibid **59**, 1371 (1976). – [11g] Enthalpy of formation: *W. Bremser, R. Hagen, E. Heilbronner,* and *E. Vogel,* ibid **52**, 418 (1969). – [11h] Dipole moments: *W. Bremser, H. T. Grunder, E. Heilbronner,* and *E. Vogel,* ibid **50**, 84 (1967).

[12] [12a] *S. Winstein,* Q. Rev., Chem. Soc. **23**, 141 (1969). – [12b] *W. J. Hehre,* J. Am. Chem. Soc. **95**, 5807 (1973); **96**, 5207 (1974). – [12c] *R. C. Haddon,* ibid **97**, 3608 (1975); Aust. J. Chem. **30**, 1 (1977). – [12d] *W. L. Jorgensen,* J. Am. Chem. Soc. **98**, 6784 (1976).

shall see that the degree of bonding between C_1 and C_6 in **2–5** plays an important factor in determining the conformations observed.



The second focus of our study is another triene-$Cr(CO)_3$ complex, now of different topology, namely fulvene-$Cr(CO)_3$. This compound has its most stable conformation given by **7**[13] while the opposite conformation (**8**) is found for an analogous cyclopentadienone-$Fe(CO)_3$ complex[14] which has two more electrons. We are interested in the equilibrium geometries, barriers to internal rotation, and the relationship of **7** to ferrocenyl carbonium ions (**9**)[15]. This analysis will also be extended to 16 and 18 electron complexes of the benzyl and cyclobutadiene-carbinyl systems.

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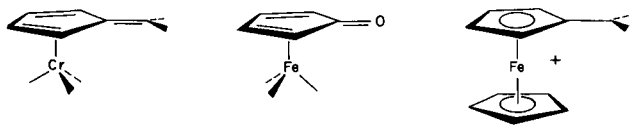
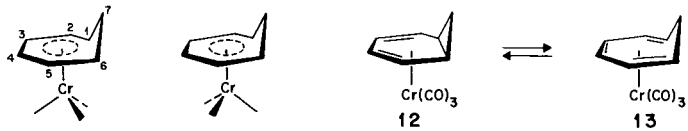


7 8 9

Cycloheptatriene vs. Norcaradiene-Chromium-Tricarbonyls

When an extended Hückel calculation (parameters are listed in the Appendix) is carried out on a hexatriene-$Cr(CO)_3$ complex, a barrier of 10.4 kcal/mole favoring the "staggered" conformation **1** is obtained[3]. However, when a similar calculation is carried out on a bridged cycloheptatriene-norcaradiene-$Cr(CO)_3$ with geometrical parameters identical to those found in the seven-membered ring of **4**[6], then the "eclipsed" form (**10**) is favored over the staggered (**11**) by 5.6 kcal/mole. Thus the calculations mirror the observed solid state geometries. The problem is to explain why the change in equilibrium orientation occurs. We will show that if the polyene system is closer to the norcaradiene extreme (**12**) then the eclipsed structure (**10**) will be at lower energy. At the cycloheptatriene end of the valence isomerism (**13**) the staggered geometry (**11**) will be preferred.



10 11 12 13

There are two ways to come to this conclusion. First we will consider the equilibrium preference of butadiene-$Cr(CO)_3$ and hexatriene-$Cr(CO)_3$ as models for **12** and **13**. The hexatriene-$Cr(CO)_3$ complex has been analyzed previously[3] and its conformational preference for the staggered geometry, **1** or **11**, is well understood. The butadiene-$Cr(CO)_3$ species has not been studied, but we can reach the required conclusion from a consideration of the well-known butadiene-$Fe(CO)_3$ system.

Figure 1 shows an interaction diagram for butadiene-$Fe(CO)_3$ in its most stable, staggered, geometry. At left are the orbitals of an iron-tricarbonyl group[3,16]. There is a lower set of three orbitals descended from t_{2g} of an octahedral complex and an upper set of acceptor levels, $2a_1$ and 2e, pointing away from the carbonyls and toward the incoming ligand. At right are the well-known π orbitals of a butadiene. The major interactions of the two fragments are between π_2 and $2e_a$ and π_3 with $2e_s$. The latter interaction is also the one which determines the equilibrium geometry[3].

The essential symmetric interactions in the staggered geometry are emphasized in **14** at left below. Rotation by 60° into the eclipsed form (**15**) turns on an interaction between $1e_s$ and π_3. This stabilizes that level derived from $1e_s$, φ_1. However, $1e_s$ mixes into

[16] [16a] *M. Elian* and *R. Hoffmann*, Inorg. Chem. **14**, 1058 (1975). – [16b] *M. Elian, M. M. L. Chen, D. M. P. Mingos,* and *R. Hoffmann*, ibid **15**, 1148 (1976). – [16c] *T. H. Whitesides, D. L. Lichtenberger,* and *R. A. Budnik*, ibid **14**, 68 (1975). – [16d] *D. L. Lichtenberger* and *R. F. Fenske*, J. Am. Chem. Soc. **98**, 50 (1976). – [16e] *J. K. Burdett*, J. Chem. Soc., Faraday Trans. 2 **70**, 1599 (1974).

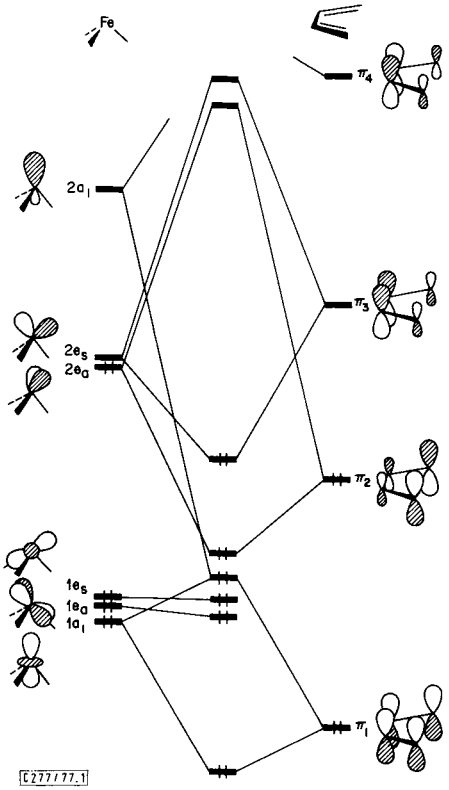
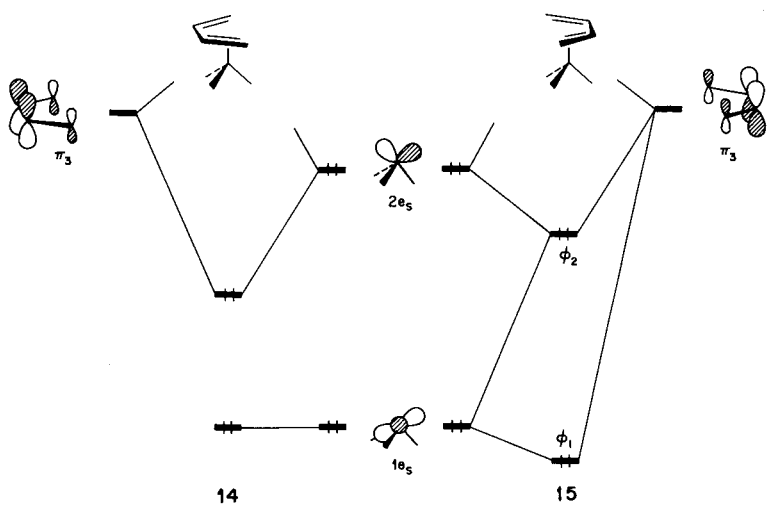


Fig. 1. Interaction diagram for (butadiene)tricarbonyliron

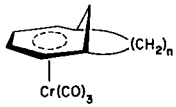


the $2e_s + \pi_3$ combination, φ_2, in an out-of-phase manner, destabilizing this orbital. The destabilization in φ_2 is larger than the stabilization in φ_1. There is also a smaller overlap between $2e_s$ and π_3 in **15** which again creates a preference for butadiene-$Fe(CO)_3$ in conformation **14**. For this case the $1e_a$ and $2e_a$ interactions with π_2 and π_4 are approximately independent of conformation. A straight-forward adaptation of this analysis has been applied to hexatriene-$Cr(CO)_3$ [3].

The interesting point is that with two electrons less in this system, e.g. butadiene-$Cr(CO)_3$, φ_2 is now empty and we expect **15** to be more stable than **14** because φ_1 now dominates the conformational preference. Extended Hückel calculations give butadiene-$Fe(CO)_3$ in conformation **14** 7.2 kcal/mole more stable than **15**. However, in the 2+ cation (isoelectronic with the $Cr(CO)_3$ complex), **15** is more stable than **14** by 7.6 kcal/mole.

We have thus reached the desired conclusion – the 16 electron butadiene-$Cr(CO)_3$ complex prefers the opposite conformation to that favored by the 18 electron hexatriene-$Cr(CO)_3$. We infer that a system that is balanced between the norcaradiene and cycloheptatriene extremes, as the complexes in question are [17], will take on the staggered conformation **11** if it is closer to the cycloheptatriene end and the eclipsed, **10**, near the norcaradiene end of the valence tautomerism. Complex **2** is clearly a cycloheptatriene type. The other molecules which exhibit the "anomalous" geometry have a variable but consistently shorter C_1-C_6 separation and a degree of bond alternation consistent with approach toward the norcaradiene extreme as one progresses from **5** to **4** to **3**.

An interesting corollary to this discussion is that as the C_1-C_6 distance is made to decrease, for instance by application of a "Klammer effect" by shortening the bridging methylene chain in **16**, the barrier to internal rotation is expected to decrease to a minimum and then increase again as the eclipsed conformation becomes more stable.



16

17

18 **19**

a) X = CH_2
b) X = NH
c) X = O

The strong tendency of 1,6-ethano[10]annulene or similar compounds with a two carbon bridge to favor the propellane side [18], may be reflected in a larger rotational barrier for $Cr(CO)_3$ complexes of **17** compared to that for **3**–**5**. Also, the substitution

[17] For experimental studies on the ligands see: [17a] References [8], [9b] and [11c]. – [17b] *R. Bianchi, G. Morosi, A. Mugnoli,* and *M. Simonetta,* Acta Crystallogr., Sect. B **29**, 1196 (1973); *C. M. Grammaccioli* and *M. Simonetta,* ibid **28**, 2231 (1972); *M. Simonetta,* Acc. Chem. Res. **7**, 345 (1974).

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of electron withdrawing groups at C_7 has been shown to stabilize the norcaradiene valence tautomer[19,20].

This may, in turn, lower the barrier in **11** or reverse the orientation to **10** for the $Cr(CO)_3$ complexes. Experimental studies on these points will be undertaken. It is also known[21] that the equilibrium is shifted more towards the bicyclic tautomer **19** in the order: **19c** > **b** > **a**. Therefore, we might expect that the barriers of $Cr(CO)_3$ complexes of **18** might decrease in going from **18a** to **c**. However, azepine-$M(CO)_3$ complexes have approximately the same barriers as their cycloheptatriene-$M(CO)_3$ counterparts[2c]. We shall comment more on this problem shortly.

The second way to view the energetic preference of **10** over **11** is to examine directly the interaction of the orbitals of the polyene with those of $Cr(CO)_3$, as shown in Figure 2. $1\pi_s$, $2\pi_a$, and $3\pi_s$ correspond to π_1, π_2, and π_3, respectively of butadiene. The $1\pi_a$ and $2\pi_s$ levels are more heavily weighted on the C_1, C_6, and C_7 portions and correspond to the high-lying Walsh orbitals of cyclopropane[22]. In going from the eclipsed conformation **10** (the one shown in Figure 2) to **11** the interaction between $1e_s$ and $2\pi_s$ is turned on. This is a 4 electron- 2 orbital destabilization (3a′ goes up in energy more than 2a′ goes down). Also note that as the C_1-C_6 bond distance decreases, the overlap between $1e_s$ and $2\pi_s$ becomes larger, and hence, there is more repulsive destabilization. There is also less overlap between $1e_s$ and $3\pi_s$ in the staggered conformation and this also creates a preference of **10** over **11**. From our extended Hückel calculations the largest contributor to the rotational barrier is 3a″. This orbital is the antibonding combination between $1e_a$ and $1\pi_a$. Upon rotation to the staggered conformation, $1e_a$ interacts now more with $2\pi_a$ and since the energy difference between $1e_a$ and $2\pi_a$ is less than that for $1e_a$ and $1\pi_a$, 3a″ rises in energy. As we go from cycloheptatriene to oxepin, the coefficients

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[19] For experimental studies regarding this topic, see: [19a] *E. Vogel*, Angew. Chem. **74**, 829 (1962); Angew. Chem., Int. Ed. Engl. **2**, 1 (1963). – [19b] *G. Maier*, Angew. Chem. **79**, 446 (1967); Angew. Chem., Int. Ed. Engl. **6**, 402 (1967). – [19c] *H. Günther*, *W. Peters*, and *R. Wehner*, Chem. Ber. **106**, 3683 (1973); *M. Gorlitz* and *H. Günther*, Tetrahedron **25**, 4467 (1969); *H. Günther*, *B. D. Tunggal*, *M. Regitz*, *H. Scherer*, and *T. Keller*, Angew. Chem. **83**, 585 (1971); Angew. Chem., Int. Ed. Engl. **10**, 563 (1971); *H. Günther* and *T. Keller*, Chem. Ber. **103**, 323 (1970); *H. Scherer*, *A. Hartmann*, *M. Regitz*, *B. D. Tunggal*, and *H. Günther*, ibid **105**, 3357 (1972); *R. Wehner* and *H. Günther*, J. Am. Chem. Soc. **97**, 923 (1975). – [19d] *E. Ciganek*, ibid **87**, 652, 1149 (1965); **89**, 1454 (1967); **93**, 2207 (1971); *H. J. Keich*, *E. Ciganek*, and *J. D. Roberts*, ibid **92**, 5166 (1970). – [19e] *J. B. Lambert*, *L. J. Durham*, *P. Lepoutere*, and *J. D. Roberts*, ibid **87**, 3896 (1965); *G. E. Hall* and *J. D. Roberts*, ibid **92**, 5166 (1970). – [19f] *G. Maas* and *M. Regitz*, Chem. Ber. **109**, 2039 (1976). – [19g] *W. Betz* and *J. Daub*, ibid **107**, 2097 (1974); *W. Betz*, *J. Daub*, and *K. M. Rapp*, Liebigs Ann. Chem. **1974**, 2098. – [19h] *F.-G. Klärner*, Tetrahedron Lett. **1974**, 19; *F.-G. Klärner*, *S. Yaslak*, and *M. Wette*, Chem. Ber. **110**, 107 (1977). – [19i] *G. Mukherjee-Müller*, *T. Winkler*, *J. Zsindley*, and *H. Schmid*, Helv. Chim. Acta **59**, 1763 (1976). – [19j] *H. Dürr* and *H. Kober*, Chem. Ber. **106**, 1565 (1973). – [19k] *T. Tsuji*, *S. Teratake*, and *H. Tanida*, Bull. Chem. Soc. Jpn. **42**, 2033 (1969).

[20] For the theoretical work see: [20a] *R. Hoffmann*, Tetrahedron Lett. **1970**, 2907. – [20b] *H. Günther*, ibid **1970**, 5173. – [20c] *R. Hoffmann* and *W.-D. Stohrer*, J. Am. Chem. Soc. **93**, 6941 (1971).

[21] [21a] *W.-D. Stohrer*, Chem. Ber. **106**, 970 (1973). – [21b] *L. A. Paquette*, Angew. Chem. **83**, 11 (1971); Angew. Chem., Int. Ed. Engl. **10**, 11 (1971); *H. Günther*, *J. B. Pawliczek*, *B. D. Tunggal*, *H. Prinzbach*, and *R. H. Levin*, Chem. Ber. **106**, 984 (1973); *H. Prinzbach*, *H. Babsch*, *H. Fritz*, and *P. Hug*, Tetrahedron Lett. **1977**, 1355. – [21c] *E. Vogel* and *H. Günther*, Angew. Chem. **79**, 429 (1967); Angew. Chem., Int. Ed. Engl. **6**, 385 (1967); *E. Vogel*, *D. Beermann*, *E. Balci*, and *H.-J. Altenbach*, Tetrahedron Lett. **1976**, 1167.

[22] A description of these orbitals may be found in *W. L. Jorgensen* and *L. Salem*, The Organic Chemist's Book of Orbitals, p. 19–23, 154, Academic Press, New York, N. Y. 1973.

at C_7 increase, relative to those at C_1 and C_6 for $1\pi_a$, $2\pi_s$, and $2\pi_a$ since oxygen is more electronegative than carbon. These levels will also decrease in energy. Therefore, the destabilization with $1e_s$ and $1e_a$ decreases although the tendency for the uncomplexed ligand to distort towards the bicyclic form **19** increases. This balance may be responsible for the small difference between cycloheptatriene and azepine complexes.

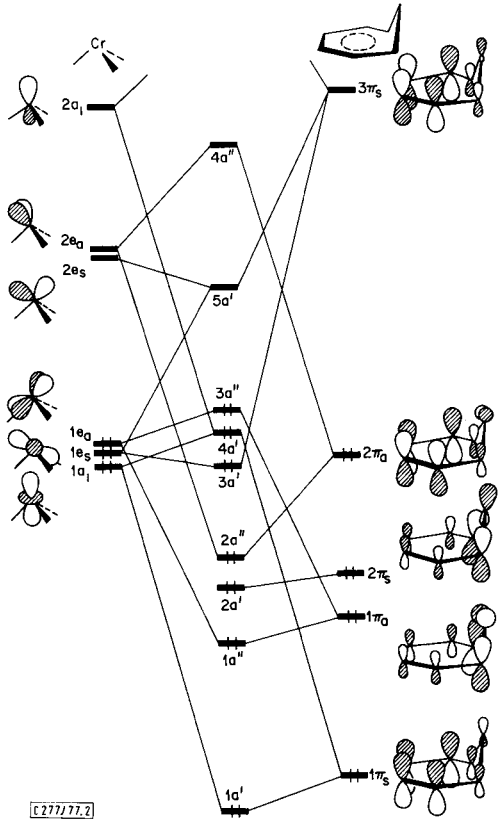
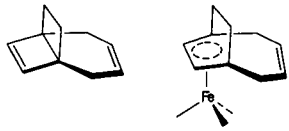


Fig. 2. Interaction diagram for tricarbonylchromium with a polyene intermediate between norcaradiene and cycloheptatriene

Putting two more electrons in the interaction diagram in Figure 2 brings us to the $Fe(CO)_3$ complex **6**. 5a′ is now filled and it is $1e_s$ mixing into this level for the eclipsed geometry which destabilizes it over the staggered one. The barrier to internal rotation for this compound would be smaller than that for butadiene-$Fe(CO)_3$. In fact adding two more electrons to our calculations still gives the eclipsed conformer more stable than the staggered one by 0.1 kcal/mole. However, the dihedral angle between the planes defined by $C_2-C_3-C_4-C_5$ and $C_1-C_2-C_5-C_6$ is clearly smaller from the X-ray structure of **3** compared to **6**[5]. Also the $Fe(CO)_3$ group is moved back towards the C_3-C_4 bond relative to the $Cr(CO)_3$ structure. Therefore, the interactions between the $C_1-C_7-C_6$ portion of the polyene and the $Fe(CO)_3$ group are diminished for **6**. It

may be possible to prepare the $Fe(CO)_3$ complex of **20**[23], which by virtue of the "Klammer effect" may present an "anomalous" eclipsed conformation **21**. We shall pursue experimental studies of this case in the future.



20 **21**

Note added in Proof: The relationship between the $M(CO)_3$ orientation and the cycloheptatriene-norcaradiene equilibrium has recently been noted by *L. A. Paquette* et al.[34].

Fulvene-$Cr(CO)_3$ and Related Complexes

In the X-ray structure of fulvene-$Cr(CO)_3$ the methylene group is bent out of the plane of the cyclopentadienyl ring and toward the metal by 30°. Our calculations give $\Theta = 21°$ for **22**; however, it costs only 0.6 kcal/mole to increase Θ to 30°. In the alternate conformation of the $Cr(CO)_3$ group (**23**) we calculate that $\Theta = 10°$. The total energy difference between the optimized structures of **22** and **23** was 9.3 kcal/mole with **22** being

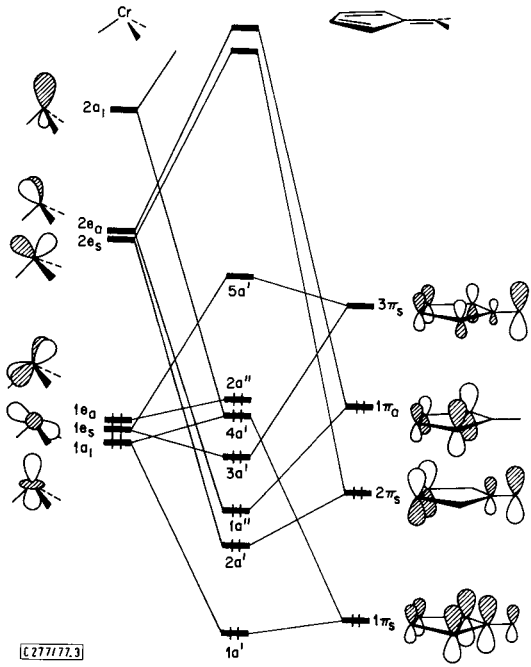
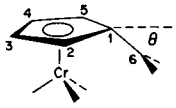


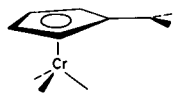
Fig. 3. Interaction diagram for tricarbonyl(fulvene)chromium

[23] *L. A. Paquette* and *R. W. Houser*, J. Am. Chem. Soc. **93**, 4522 (1971).

the most stable conformation. Even by keeping $\Theta = 0°$ for both conformations, **22** is more stable by 7.2 kcal/mole. Experimental information on the magnitude of the rotational barrier in this molecule is just becoming available. *Kreiter* has studied the 6,6-dimethyl derivative and finds that carbonyl interchange is frozen out at 183 K[24]. This probably corresponds to a barrier of 7–9 kcal/mole which is in qualitative agreement with our theoretical estimate. Adding two more electrons to this system brings us to the cyclopentadienone-$Fe(CO)_3$ complex which is more stable in the reverse orientation (**8**)[14]. The C_1-O group is now displaced away from the iron. The rotational barriers for the iron and ruthenium analogues of **8**[25] are quite similar to those found for butadiene-$Fe(CO)_3$ or $Ru(CO)_3$ complexes (9–12 kcal/mole)[3]. The source of these orientational preferences is of some interest to us, as well as the bending motions of the methylene group in **22**. We have previously discussed the bending in cyclopentadienone-$Fe(CO)_3$ elsewhere[26].

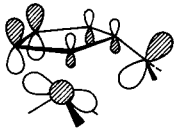


22



23

An interaction diagram for the valence orbitals of $Cr(CO)_3$ and the important π levels of fulvene is presented in Figure 3. The dominant interaction occurs between the 2e orbitals of $Cr(CO)_3$ and the $2\pi_s$ and $1\pi_a$ orbitals of fulvene, giving 2a′ and 1a″, respectively. $1e_a$ is slightly destabilized by σ levels from the fulvene (in our calculations the symmetric and antisymmetric π^* levels on fulvene, while having the correct symmetry to interact with $1e_s$ and $1e_a$, lie too high in energy to have significant interactions). The $1e_s$ function is stabilized by a bonding interaction with $3\pi_s$ to give 3a′. As the methylene group is bent down towards the chromium atom, $3\pi_s$ mixes more with $1e_s$, which stabilizes 3a′ more, as shown in **24**.



24

This is moderated by repulsive interactions between the hydrogens on the methylene group and the carbonyls, so the bending surface is quite soft. There are great similarities here to the stabilization of the isoelectronic ferrocenyl-methyl cation[15], as discussed by *Gleiter* and *Seeger*[27]. We also find that there is larger overlap between $2e_s$ and $2\pi_s$ as Θ is increased. In fulvene-$Fe(CO)_3$, 5a′, the antibonding combination of $3\pi_s$ and $1e_s$ is filled, and therefore the methylene group bends away from instead of towards the iron.

Upon rotation to **23** the overlap between $1e_s$ and $3\pi_s$ decreases, as shown below.

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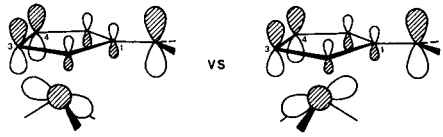
[24] *C. G. Kreiter*, personal communication.

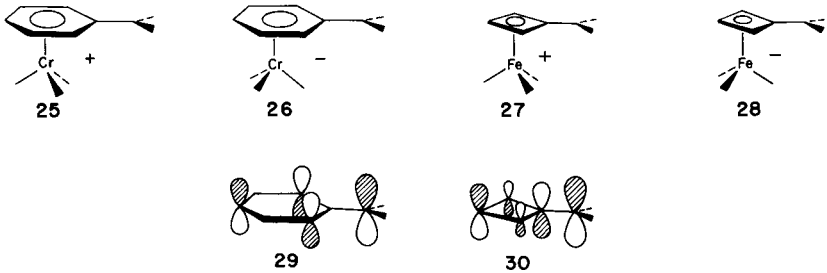
[25] *L. Kruczynski, J. L. Martin,* and *J. Takats*, J. Organomet. Chem. **80**, C9 (1974); *L. Kruczynski* and *J. Takats*, Inorg. Chem. **15**, 3140 (1976).

[26] *R. Hoffmann* and *P. Hofmann*, J. Am. Chem. Soc. **98**, 598 (1976).



Not only is there smaller overlap between $1e_s$ and the p orbitals on C_3 and C_4, but there is increased antibonding between $1e_s$ and p_z on C_1. It is this factor which sets up the energetic preference of **22** over **23**. In a fulvene-$Fe(CO)_3$ complex the methylene group should bend out of the plane of C_2-C_5. The equilibrium conformation assumed and the magnitude of the barrier will be similar to butadiene-$Fe(CO)_3$.

An extension of this work can be developed for the complexes **25**–**28**. Experimental studies have indicated the possibility of the interaction of the metal atoms with the methylene groups in **25**[28] and **27**[29]. For **25** and **27** we calculate that the methylene groups are bent out of the plane of the polyenes and toward the metal by 11° and 17°, respectively. We again find that this is due to the interaction of $1e_s$ (see Figure 3) and the corresponding nonbonding π levels, **29** and **30**. We also find that **25** and **27** are most stable in the orientations shown above, with barriers calculated to be 6.8 and 5.6 kcal/mole, respectively.



The origin of these barriers may be understood in an analogous manner to that discussed before for fulvene-$Cr(CO)_3$. Likewise, the addition of two electrons to give **26** and **28** causes C_1 and the methylene group to move out of the polyene plane away from the metal atom[26] and the $M(CO)_3$ group to rotate by 60°. We expect the barriers of rotation and their origin to be similar to those in pentadienyl and allyl $M(CO)_3$ complexes[3]. The available experimental evidence is in accord with these conformations. A bis(cyclobutadienyl-$Fe(CO)_3$)carbinyl cation appears to have both $Fe(CO)_3$ groups oriented as in **27**, although the carbinyl carbon is not appreciably bent towards the iron atoms[30].

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[27] *R. Gleiter* and *R. Seeger*, Helv. Chim. Acta **54**, 1217 (1971). See also *G. Schmitt*, *S. Özman*, *B. Hoffmann*, and *J. Fleischhauer*, J. Organomet. Chem. **114**, 179 (1976).

[28] *J. D. Holmes*, *D. A. K. Jones*, and *R. Pettit*, J. Organomet. Chem. **4**, 324 (1965); *G. A. Olah* and *S. H. Yu*, J. Org. Chem. **41**, 1694 (1976); *D. S. Trahanovsky* and *D. K. Wells*, J. Am. Chem. Soc. **91**, 5870 (1969); also see *D. K. Wells* and *D. S. Trahanovsky*, ibid **91**, 5871 (1969); **92**, 7461 (1970); *R. S. Bly* and *R. C. Strickland*, ibid **92**, 7459 (1970); *R. S. Bly*, *K.-K. Tse*, and *R. K. Bly*, J. Organomet. Chem. **117**, 35 (1976).

[29] *J. D. Fitzpatrick*, *L. Watts*, and *R. Pettit*, Tetrahedron Lett. **1966**, 1299; *C. S. Eschbach*, *D. Seyferth*, and *P. C. Reeves*, J. Organomet. Chem. **104**, 363 (1976); see also *H. A. Brune* and *G. Horlbeck*, Z. Naturforsch., Teil B **28**, 656 (1973).

[30] *R. E. Davis*, *H. D. Simpson*, *N. Grice*, and *R. Pettit*, J. Am. Chem. Soc. **93**, 6688 (1971).

A cyclobutenonyl-$Co(CO)_3$ complex, isoelectronic to **28**, adopts the conformation shown, and the CO group is displaced away from the cobalt atom[31].

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Appendix

The calculations were carried out using the extended Hückel method[32]. The H_{ii}'s and exponents listed in Table 1 were taken from previous work[3]. The modified Wolfsberg-Helmholz formula was used throughout these calculations[26,33]. All C–C, C–H, and C–O bond lengths were idealized at 1.41, 1.09, and 1.14 Å, respectively. The M–C(O) bond distances were set at Cr 1.84 and Fe 1.78 Å. The geometrical model used for the cycloheptatriene-$Cr(CO)_3$ was taken from ref.[6]. The distance of the metal to the polyene ring for **22**, **25**, and **27** was 1.78, 1.73, and 1.64 Å, respectively. The (O)C–M–C(O) and M–C–O angles were idealized at 90° and 180°.

Table 1. Parameters Used in the Extended Hückel Calculations

Orbital		H_{ii} (eV)	ζ_1	ζ_2	C_1 [a]	C_2 [a]
Cr	3d	−11.22	4.95	1.60	0.4876	0.7205
	4s	−8.66	1.70			
	4p	−5.24	1.70			
Fe	3d	−12.70	5.35	1.80	0.5366	0.6678
	4s	−9.17	1.90			
	4p	−5.37	1.90			
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 zeta expansion.

[31] *J. Potenza, R. Johnson, D. Mastropaolo,* and *A. Efraty,* J. Organomet. Chem. **64**, C13 (1974).
[32] *R. Hoffmann,* J. Chem. Phys. **39**, 1397 (1963); *R. Hoffmann* and *W. N. Lipscomb,* ibid **36**, 3179, 3489 (1962); **37**, 2872 (1962).
[33] *J. H. Ammeter, H.-B. Bürgi, J. C. Thibeault,* and *R. Hoffmann,* J. Am. Chem. Soc. submitted for publication.
[34] *L. A. Paquette, C. C. Liao, R. L. Burson, R. E. Wingard, jr., C. N. Shih, J. Fayos,* and *J. Clardy,* J. Am. Chem. Soc. **99**, 6935 (1977).

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