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Fluxionality in (Cycloheptatriene)iron Tricarbonyl Complexes

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^1H NMR spin saturation transfer experiments were undertaken to measure the barrier for 1,3 iron shifts in (cycloheptatriene)iron tricarbonyl (CHT = cycloheptatriene) complexes. Values of $\Delta G^\ddagger$ were determined for CHT (22.3 kcal/mol), 7-phenyl-7-(carbomethoxy)cycloheptatriene (23.9), 7-methyl-7-(carbomethoxy)cycloheptatriene (23.3 and 23.6 for the two isomers), and (8-phenylheptafulvene)iron tricarbonyl (20.0). These together with the barriers for (oxepine)-, (azepine)-, and (tropone)iron tricarbonyl are not consistent with a transition state for the 1,3 iron shift which resembles a (norcaradiene)iron tricarbonyl species. Extended Hückel molecular orbital calculations were undertaken to probe the geometry and electronic structure of the species in which the iron is at the midpoint of migration. It is found that a "modified" η^2 geometry for this "way-point" is preferred with the $Fe(CO)_3$ shifted toward the interior of the CHT ring. An electrocyclic ring closure from η^2 to a (noncaradiene)iron tricarbonyl complex is shown to be symmetry forbidden. This "modified" η^2 geometry can account for the variations of the activation energies with respect to electronic perturbations at C_7. In general, it is found that electron-donating groups at C_7 decrease the activation energy for 1,3 iron shifts and electron-withdrawing groups increase it relative to $(CHT)Fe(CO)_3$.

Several recent reviews[2] have focused on the facile thermal rearrangements observed in cyclic polyene and polyenyl transition-metal complexes. For those examples in which the metal is π bound to a fragment of a fully conjugated π system, the most commonly observed rearrangement pathway involves simultaneous 1,2 metal shifts and π-bond migrations. Evidence has been presented for the operation of 1,2 metal shifts in the degenerate rearrangements of such diverse systems as $(\eta^1\text{-}C_5H_5)ML_n$ (M = Fe, Re, Mo, Pd, Pt, etc.),[3] $(\eta^1\text{-}C_7H_7)Re(CO)_5$,[4] $(\eta^3\text{-}C_7H_7)ML_n$ (M = Co, Mo, Fe),[5] $(\eta^4\text{-}C_6R_6)RhL_n$,[6] $(\eta^4\text{-}C_8H_8)ML_n$ (M = Fe, Ru, Os),[7] $(\eta^5\text{-}C_7H_7)ML_n$ (M = Mn, Re, Ru),[8] and $(\eta^6\text{-}C_8H_4Me_4)M(CO)_3$ (M = Cr, Mo, W).[9] In sharp contrast to the tetramethylcyclooctatetraene complexes, it has been shown that the mechanism of rearrangement for the parent complexes $(\eta^6\text{-}C_8H_8)M(CO)_3$ (M

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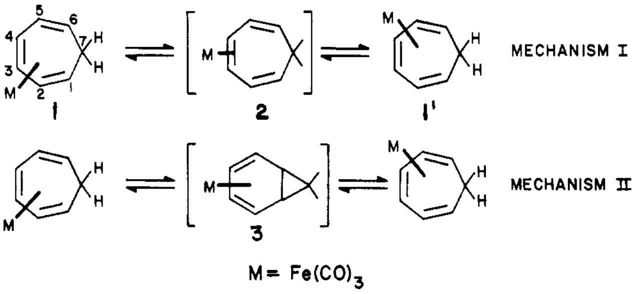
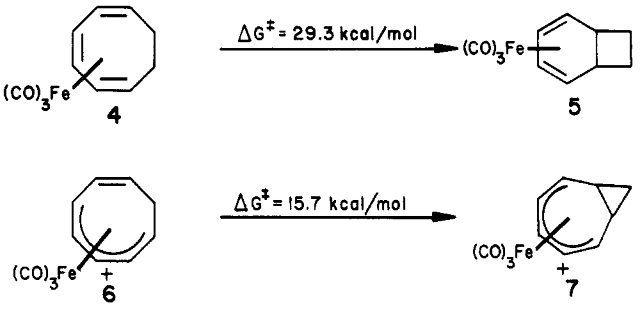
= Cr, Mo, W) occurs predominantly by 1,3 metal shifts, with only 10–30% of the rearrangements occurring by 1,2 metal shifts.[10] Observations of 1,3 metal shifts in fully conjugated cyclic polyene or polyenyl metal complexes are presently limited to these cyclooctatetraene examples, although there are a few fluxional systems for which the mechanism of rearrangement has not yet been determined: $(\eta^2\text{-}C_6R_6)NiL_2$,[11] $(\eta^4\text{-}C_8H_8)Co(\eta^5\text{-}C_8H_9)$,[12] and $(\eta^3\text{-}C_9H_9)Nb(\eta^5\text{-}C_5H_5)_2$.[13] The rearrangements in fully conjugated polyenes are in general relatively facile. However, in some cases, e.g., $(\eta^4\text{-}C_6R_6)Ru(\eta^6\text{-}C_6R_6)$,[14] $(\eta^4\text{-}C_6R_6)Rh(\eta^5\text{-}C_5R_5)$,[6,15] and $(\eta^2\text{-}C_8H_8)Mn(CO)_2(\eta^5\text{-}C_5H_5)$,[16] the barriers are apparently quite high.

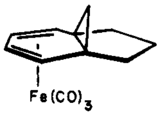
In conjugated acyclic systems or in cyclic systems where the conjugated π system has been interrupted by a $\text{+}CH_2\text{+}_n$ group, products of simple 1,2 metal shifts are not observed since such shifts do not lead to degenerate isomerization but to species clearly quite high in energy relative to the ground state of the complex. Although *simple* 1,2 metal shifts are energetically inaccessible, complexes of this type can undergo degenerate 1,3 metal shifts either through the formation of a coordinately unsaturated intermediate or by 1,2 metal migration with simultaneous eletrocyclic ring closure to form bicyclic intermediates. These two mechanisms are illustrated below for one of the simplest compounds in this class, (cycloheptatriene)iron tricarbonyl (1).



These reaction pathways really represent two *extremes* in mechanism. A more precise question which might be asked is what pathway does the metal traverse in moving from one side to the other and to what extent does bonding between C_1 and C_6 develop during metal migration in **3**? A case distinct intermediate intervene? A case between these extremes could be envisioned in which no (norcaradiene)iron tricarbonyl intermediate (with a full C_1–C_6 bond) is formed, but substantial C_1–C_6 bonding develops in a concerted 1,3 shift of metal across the ring. An even more subtle question is the nature of the bonding of $Fe(CO)_3$ to the cycloheptatriene ring in **2**. Is this η^2 with bonding to C_3 and C_4 only or is it energetically more favorable for the $Fe(CO)_3$ to be located at some point with substantial bonding also to C_2 and C_5?

The ^1H NMR of **1** showed no line broadening up to 100 °C,[17] implying that the free energy of activation, $\Delta G^{\ddagger}$, for degenerate 1,3 iron shift in **1** must be greater than 21 kcal mol^{-1}. Although the line-broadening technique had not been successful in observing fluxional behavior in **1**, the fundamental nature of this isomerization justified a reinvestigation of this system using techniques designed to detect slower rates of rearrangement. The Hoffman–Forsén NMR technique of spin saturation transfer (SST)[18,19] was selected. Even with the limited thermal stability of **1**, it was estimated that a 1,3 iron shift with a free energy of activation as high as 26 kcal mol^{-1} might be observable by using SST. Results obtained recently in our laboratory, as well as information published by others, led us to believe that $\Delta G^{\ddagger}$ for a 1,3 iron shift in **1** might be low enough to permit detection by SST. For example, the isomerization of (cyclooctatriene)iron tricarbonyl (**4**) to (bicyclo[4.2.0]octadiene)iron tricarbonyl (**5**) occurs with $\Delta G^{\ddagger}$ = 29.3 kcal mol^{-1}.[20] An even lower barrier, $\Delta G^{\ddagger}$ = 15.7 kcal mol^{-1}, is found for the conversion of the cationic cyclooctatrienyliron tricarbonyl (**6**) to bicyclo[5.1.0]octadienyliron tricarbonyl (**7**).[21] In both examples, 1,2 metal shifts occur with simultaneous electrocyclic ring closure, analogous to the norcaradiene-intermediate pathway (mechanism II), proposed for a possible 1,3 iron shift in **1**. Although there is no evidence for the existence of (norcaradiene)iron tricarbonyl, a stable iron tricarbonyl complex of tricyclo[4.3.1.0^{1,6}]deca-2,4-diene has been isolated, **8**; a crystal structure of the compound confirms its characterization as an iron tricarbonyl complexed norcaradiene derivative.[22]





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Analogies for the 1,3 iron shift pathway involving an unsaturated intermediate, **2** (mechanism I), were less numerous. It was postulated that the compounds $(\eta^6\text{-}C_8H_8M(CO)_3$ (M = Cr, Mo, W) rearrange via such a mechanism, with $\Delta G^{\ddagger}$'s sufficiently small to determine using ^1H NMR line-broadening techniques at −20 to +50

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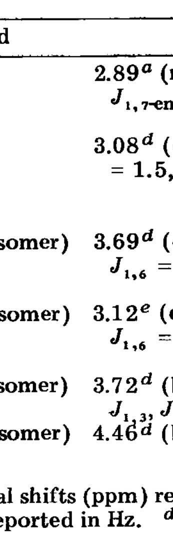
°C.[10] An acyclic system, (1-*p*-tolyl-6-phenylhexa-1,3,5-triene)iron tricarbonyl (**9**), is constrained to isomerize via a coordinatively unsaturated intermediate and exhibits a high barrier ($\Delta G^{\ddagger}$ = 33 kcal mol^{-1}) to rearrangement.[23]



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Although our initial goal was to detect and measure the rate of 1,3 iron shift in **1**, we were also interested in determining the mechanism of this process. There are numerous cycloheptatriene derivatives, particularly C_7-substituted systems, which exhibit a cycloheptatriene (CHT) $\rightleftharpoons$ norcaradiene (NCD) dynamic equilibrium with CHT:NCD ratios spanning many orders of magnitude.[24] It was felt that such dramatic substituent effects in the free ligand system could be used to advantage as a mechanistic probe. If the geometry of the transition state for 1,3 iron shift approximates that of a norcaradiene system, **3**, then substituents that stabilize the NCD form should accelerate the rate of 1,3 iron shift and a reasonable correlation between K_{eq} for NCD/CHT with the rate of metal migration might be expected. (In the extreme, **3** may become the ground-state structure.) Alternatively, if the transition state for iron migration resembled that of the coordinatively unsaturated η^2 complex **2**, then substituents at the remote C_7—particularly of the electron-withdrawing tyye which stabilize the NCD form[24,25]—would probably have little effect on the groundstate–transition state energy difference.

In this paper, we describe an SST ^{1}H NMR investigation of the rates of 1,3 shifts in variously substituted (CHT)-$Fe(CO)_3$ systems and the mechanistic implications of these results. A preliminary account of this work has appeared.[26] Mann reported a parallel study of the parent cycloheptatriene–$Fe(CO)_3$ system using ^{13}C SST experiments.[27] We have also investigated the way-point[28] of metal migration in **1**, by molecular orbital calculations of the extended Hückel type.[29] This forms part of a continuing study on the electronic requirements of fluxionality in (polyene)ML_n complexes.[30]

Table I. ^{1}H NMR Data for (Cycloheptatriene)iron Tricarbonyl and Its Derivatives

compd	H_1	$H_{2,3}$	H_4	H_5	H_6	other
1	2.89^a (m^b, $J_{1,7\text{-exo}}$ = 4.3,^{c} $J_{1,7\text{-endo}}$ = 4.3)	4.66 (m, 2)	2.72 (m, $J_{4,5}$ = 7.9, $J_{1,6}$ = 0.9 or 1.4)	5.68 (ddd, $J_{5,6}$ = 10.6, $J_{5,7X}$ = 2.6, $J_{5,7N}$ = 1.9)	5.03 (m, $J_{6,7X}$ = 3.5, $J_{6,7N}$ = 4.2)	2.12 (exo, m), 1.89 (endo, m, $J_{7X,7N}$ = 22)
11	3.08^d (ddd, $J_{1,2}$ = 7.9, $J_{1,3}$ = 1.5, $J_{1,6}$ = 2.2)	4.76 (H_2 ddd), 4.93 (H_3, ddd), $J_{2,3}$ = 4.7, $J_{2,4}$ = 1.5, $J_{3,4}$ = 7.3	2.77 (tt, $J_{4,5}$ = 7.4, $J_{4,6}$ = 1.6)	6.07 (dd, $J_{5,6}$ = 11)	5.89 (ddd)	3.59 (s, 3, COOMe), 7.32 (m, 5 , Ph)
13 (major isomer)	3.69^d (dt, $J_{1,2}$ = 8, $J_{1,6}$ = 2)	5.03 (m, 2)	2.79 (tt, $J_{3,4}$ = $J_{4,5}$ = 7.5, $J_{2,4}$ = $J_{4,6}$ = 1.1)	5.80 (dd, $J_{5,6}$ = 11)	5.51 (ddd)	3.60 (s, 3, COOMe), 1.45 (s, 3, Me)
13 (minor isomer)	3.12^e (dt, $J_{1,2}$ = 7, $J_{1,6}$ = 2)	5.50 (m, 2)	3.18 (m)	5.90 (dd, $J_{4,5}$ = 8, $J_{5,6}$ = 11)	5.04 (ddd, $J_{4,6}$ = 1)	3.61 (s, 3, COOMe), 1.26 (s, 3, Me)
19 (major isomer)	3.72^d (b d, $J_{1,2}$ = 7, $J_{1,3}$, $J_{1,6}$, $J_{1,4}$ ≈ 2)		2.81 (m)	5.73 (ddd, $J_{4,5}$ = 8, $J_{5,6}$ = 11, $J_{5,7}$ = 2)	6.19 (b d, $J_{4,6}$ ≈ 2)	6.65 (b s, H_7), 7.35 (m, 5, Ph)
19 (minor isomer)	4.46^d (b d, $J_{1,2}$ = 6)		2.81 (m)	5.66 (m, 2)		6.53 (s, H_7), 7.35 (m, 5, Ph)

[a] Chemical shifts (ppm) referenced to internal C_6D_5H (δ 7.27). [b] Abbreviations: s, singlet; t, triplet; m, complex multiplet; b s, broad singlet; b d, broad doublet. [c] Coupling constants reported in Hz. [d] Chemical shifts (ppm) referenced to internal CHD_2-C_6D_5 (δ 2.31). [e] Chemical shifts (ppm) referenced to internal CHD_2NO_2 (δ 4.29).

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(28) By "way-point" we mean that geometry in which the iron is at the midpoint of migration between the two degenerate η^4 structures and lying in the plane bisecting C_7 and the C_3–C_4 bond. At this way-point, the position of the iron with respect to the ring may then lie anywhere between the extremes of a strictly η^2 structure and a (NCD)$Fe(CO)_3$ geometry.

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Table II. Spin Saturation Transfer Data for 1,3 Iron Shifts in (Cycloheptatriene)iron Tricarbonyl and Its Derivatives

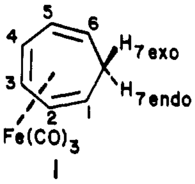
compd	t, °C	M(0)/M(∞)	T_1, s	10^2k, s	$\Delta G^{\ddagger}$, kcal mol^{-1}	$\Delta G^{\ddagger}$ (av)
1	61	1.27	14.5	1.90	22.2	
	75	1.80	17.5	4.55	22.4	
	86	2.52	10.7	14.2	22.5	
	90	4.50	10.7	32.7	22.1	22.3
11	80	1.12	7.7	1.56	23.6	
	80	1.13	7.6	1.71	23.5	
	95	1.20	7.9	2.53	24.3	
	95	1.10	3.4	2.94	24.2	
	105	1.36	4.1	8.77	24.0	23.9
13 (major isomer)	85	1.20	(6.8)	2.94	23.5	
	89	1.33	6.8	4.85	23.4	
	98	1.46	5.8	7.93	23.7	
	108	1.79	(5.0)	15.8	23.8	23.6
13 (minor isomer)	77	1.17	(6.7)	2.48	23.1	
	86	1.27	(7.1)	3.86	23.4	
	92	1.58	7.4	7.78	23.3	23.3
19	37	1.24	3.6	6.67	19.8	
	47	1.72	4.1	17.6	19.8	
	53	2.18	(4.4)	26.8	19.9	
	60	2.90	(4.6)	41.3	20.0	
	63	3.80	(4.7)	59.6	20.0	
	67	4.15	4.8	65.6	20.2	
	73	7.2	(4.8)	129	20.1	20.0

Results and Discussion

^1H NMR samples intended for use in SST experiments were carefully purified and rigorously degassed to avoid the presence of paramagnetic impurities, this ensuring the maximum values for ^1H spin–lattice relaxation times, T_1, and M(0)/M(∞). (See Experimental Section for details.) Prior to SST experiments, extensive ^1H decoupling experiments were performed on each complex to verify chemical shift assignments (See Table I). In general, it was found that by saturating H_1 and measuring the effect on the signal intensity of H_6, we could avoid potential interference by both nuclear Overhauser effects and decoupler noise. In many cases, the signal for H_5 served as an internal integration standard.

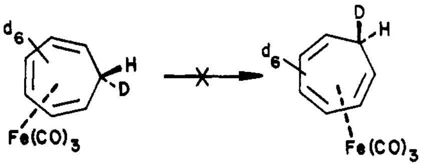
(Cycloheptatriene)iron Tricarbonyl (1). (Cycloheptatriene)iron tricarbonyl was prepared as previously described[31a] and then purified by chromatography and distillation. A 100-mg sample in toluene-d_8 (0.3 mL) was carefully degassed by several freeze–pump–thaw cycles before being sealed under vacuum in a 5-mm NMR tube.

The spin saturation transfer experiments for 1 were performed at several temperatures between 60 and 90 °C. At 90 °C a dramatic decrease (78%) was measured in the integrated intensity of the signal due to H_6 when H_1 was saturated. Correspondingly smaller decreases were observed at lower temperatures. The decrease in signal intensity upon irradiation of H_1 is selective for H_6; no other signal in the ^1H NMR spectrum is measurably affected by the saturation of H_1. Similarly, irradiation of H_6 causes a decrease only in the area of the signal due to H_1.



1

These results clearly demonstrate that *net* 1,3 iron shifts are occcurring in 1. The selective and reciprocal nature of the averaging process ($H_1 \rightleftarrows H_6$, $H_2 \rightleftarrows H_5$, $H_3 \rightleftarrows H_4$) rules out mechanisms involving 1,3 or 1,5 hydride shifts though metal hydride intermediates. Similarly, all *inter* molecular exchange mechanisms involving dissociation of the complex can be eliminated since there is no scrambling of the exo and endo substituents observed in (cycloheptatriene-d_7(*exo*-7-*h*))iron tricarbonyl (10) even after several days at 72 °C.[31]



10

The rate of 1,3 iron shift in 1 is given by eq 1, where k

$$k = (1/T_{1A})[(M(0)/M(\infty)) - 1] \qquad (1)$$

is the rate constant for exchange in a two-site, equal population system, A $\rightleftharpoons$ B.[18] T_{1A} is the spin–lattice relaxation time of the nucleus at site A, and M(0) is the normal equilibrium magnetization of the nucleus at site A after the nucleus is saturated at site B. Experimentally, M(0)/M(∞) is determined by comparing the signal areas for nucleus A with and without saturation of nucleus B. T_{1A} can be conveniently measured by the fast inversion-recovery method.[32] Values of M(0)/M(∞) and T_1 determined for H_6 are given in Table II. Also included are the rate constants, k, and the free energies of activation, ΔG^{*}. Recently, Mann reported the results of a ^{13}C SST experiment in which a ΔG^{*} of 23 kcal mol^{-1} was obtained for a 1,3 iron hift in 1 at 94 °C.[27] This value agrees well with our results obtained by ^1H SST, $\Delta G^{*} = 22.3$ kcal mol^{-1}, and demonstrates that SST exeriments need not be limited to the ^1H nucleus.[19]

In order to probe further the mechanism of 1,3 iron shift in cycloheptatriene complexes, we synthesized several derivatives of 1 in an attempt, as discussed above, to discriminate between the pathways involving a norcaradiene intermediate (mechanism II) and that involving a coordinatively unsaturated intermediate (mechanism I). Ligands were chosen on the basis of their NCD:CHT iso-

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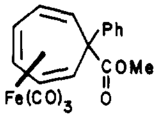
(31) (a) Brookhart, M.; Karel, K. J.; Nance, L. E. *J. Organomet. Chem.* **1977**, *140*, 203. (b) Karel, K. J.; Brookhart, M. unpublished results.

(32) Canet, D.; Levy, G. C. *J. Magn. Reson.* **1975**, *18*, 199.

mer ratios and for compatibility of the substituent groups with iron carbonyl reagents. Results obtained for several systems are presented below.

(7-Phenyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl (11). In contrast to cycloheptatriene, for which the CHT:NCD ratio is estimated to be at least 200:1,[33] the ratio of 7-phenyl-7-(carbomethoxy)cycloheptatriene (12) to the corresponding norcaradiene isomer is 1:1.65 at 32.5 °C in $CDCl_3$.[34] Although (benzylideneacetone)iron tricarbonyl ((BDA)$Fe(CO)_3$) has been shown to be a very selective diene trapping agent for species containing a cyclohexadiene ring,[35] the only product isolated from the reaction of 12 with (BDA)$Fe(CO)_3$ was a (cycloheptatriene)iron tricarbonyl derivative, (7-phenyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl (11), of unknown stereochemistry at C_7. Photolysis of 12 in benzene with $Fe(CO)_5$ also gave 11.

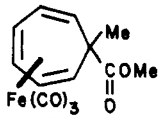


11

The failure to isolate a norcaradiene complex of 12 using (BDA)$Fe(CO)_3$ is interesting and likely indicates that the (NCD)$Fe(CO)_3$ complex is neither thermodynamically nor kinetically stable with respect to the (CHT)$Fe(CO)_3$ form. (BDA)$Fe(CO)_3$ has been shown to react selectively with the diene tautomers of cyclooctatriene, bicyclo[6.2.0]decatriene, bicyclo[6.1.0]nonatriene, and cyclooctatrienone, for which K_{eq} = [triene]/[diene] = 5.6, 40, 4500, and 140, respectively.[35,36] This dramatic stabilization of the complexed diene tautomer probably arises from the relief of steric strain in the complexed triene upon the ring closure.[35,36] Similar relief of strain in the complexed cycloheptatriene system will be much less upon ring closure to a norcaradiene complex due to the less strained nature of the cycloheptatriene complex. (Free cycloheptatriene is more planar than the tub-shaped cyclooctatriene derivatives.)

Spin saturation transfer experiments were performed in the same manner for 11 as for 1. However, preparation of the ^1H NMR sample was modified to allow in vacuo filtration of the dissolved complex directly into a 5-mm NMR tube immediately prior to the final freeze–pump–thaw degassing cycles and vacuum sealing. (See Experimental Section.) As before, H_1 was saturated while the changes in signal intensity of H_6 were observed. The results of the SST experiments are presented in Table II. Between 80 and 105 °C, spin saturation transfer was observed in 11, indicating that 1,3 iron shifts are occurring in this species as well. However, ΔG^*_{av} = 23.9 kcal mol^{-1}, a 1.6 kcal mol^{-1} *increase* over that calculated for 1. An increase in ΔG^* is opposite to the trend expected for a norcaradiene-like transition state and is suggestive of a mechanism involving a coordinatively unsaturated iron tricarbonyl intermediate (mechanism I). An alternative but less attractive explanation is that if the large phenyl group were to be exo at C_7, then increased steric interactions with the ring may develop in a NCD-like transition state and retard the rate of 1,3 iron shift. Other ligands with relatively high NCD:CHT ratios and substituents smaller than a phenyl group were sought to probe the effect of the size of the substituent at C_7 on the rate of 1,3 iron shift in (cycloheptatriene)iron tricarbonyl complexes.

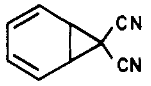
(7-Methyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl (13). One such ligand is 7-methyl-7-(carbomethoxy)cycloheptatriene, for which CHT:NCD is 1:20 at −120 °C in $CHFCl_2/CDCl_3$ (4:1).[37] Photolysis of this ligand with $Fe(CO)_5$ in benzene gave three products which were separated by medium-pressure liquid chromatography. The first two yellow bands were identified as the *endo*- and *exo*-methyl isomers of (7-methyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl (13); the third, red band gave one isomer of a binuclear complex, (7-methyl-7-(carbomethoxy)cycloheptatriene)diiron hexacarbonyl. Although it would be advantageous to know the stereochemistry at C_7 in these and other (cycloheptatriene)iron tricarbonyl complexes, no simple way of obtaining that information has been found.



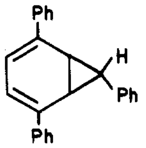
13

Spin saturation transfer experiments on the major isomer of 13 in toluene-d_8 were performed by saturating H_1 and observing the change in signal intensity for H_6. For the minor isomer of 13, a nonaromatic solvent, octane-d_{18}, was chosen to provide adequate separation of the H_6 resonance from those of H_2 and H_3. In the SST experiments on this isomer, H_6 was saturated and the integral of the overlapping multiplets H_1 and H_4 measured by using the methyl resonance of the carbomethoxy groups as an integration standard. The results of these SST experiments are presented in Table II.

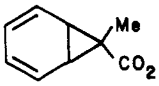
The free energies of activation for 1,3 iron shifts in these two isomers, ΔG^* = 23.6 and 23.2 kcal mol^{-1}, are more than 1.0 kcal mol^{-1} higher than that measured for the unsubstituted complex 1. This result is not consistent with the mechanism involving a norcaradiene complex intermediate; however, this mechanism could not be convincingly ruled out until systems with very high NCD:CHT ratios were studied. Among those norcaradienes selected for study were 7,7-dicyanonorcaradiene (14),[38] 2,5,7-triphenylnorcaradiene (15),[39] 7-methyl-7-norcaradienecarboxylic acid (16),[37] 3,4-dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene (17),[40] and 2,5-disubstituted derivatives of 7-



14



15



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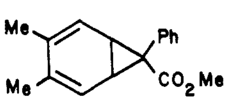

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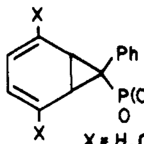

18 X = H, Cl, OH

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[33] Warner, P. M.; Lu, S.-L. *J. Am. Chem. Soc.* **1980**, *102*, 331 and references therein.

[34] Hall, G. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 2203.

[35] Graham, C. R.; Scholes, G.; Brookhart, M. *J. Am. Chem. Soc.* **1977**, *99*, 1180.

[36] Brookhart, M.; Koszalka, G. W.; Nelson, G. O.; Scholes, G.; Watson, R. A. *J. Am. Chem. Soc.* **1976**, *98*, 8155.

[37] Klarner, F. G.; Yaslak, S.; Wette, M. *Chem. Ber.* **1977**, *110*, 107.

[38] Ciganek, E. *J. Am. Chem. Soc.* **1967**, *89*, 1454.

[39] (a) Jutz, C.; Voitenleitner, F. *Chem. Ber.* **1964**, *97*, 29. (b) Mukai, T.; Kubota, H.; Toda, T. *Tetrahedron Lett.* **1967**, 3581.

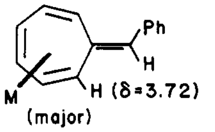
[40] The synthesis of this compound is analogous to that for 12,[41] except that *o*-xylene was used as the solvent in the photolytic decomposition of methyl phenyldiazoacetate.[42]

[41] Ciganek, E. *J. Org. Chem.* **1970**, *35*, 862.

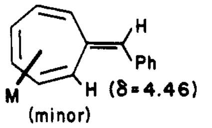
phenyl-7-(dimethoxooxophosphoric)norcaradienes (**18**).[43] No iron carbonyl complexes of **14**, **16**, or **18** were isolated from the reactions of the ligands with $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, or $(BDA)Fe(CO)_3$. Presumably, the cyano, carboxylic acid, and phosphorio functionalities preclude reaction of the iron carbonyl reagents with the diene unit. Reaction of $Fe_3(CO)_{12}$ or $Fe(CO)_5$ with **15** gave several products, including (2,5,7-triphenylcycloheptatriene)iron tricarbonyl. In SST experiments with this complex, observed T_1's were short (1.5–3.0 s) and no more than a 10% decrease in the signal area for H_6 could be measured upon saturation of H_1, even at 105 °C. No reliable ΔG^{*} values could be calculated from this experiment. Only small amounts of the expected cycloheptatriene complex were obtained from the reaction of **17** with $Fe(CO)_5$ or $Fe_3(CO)_{12}$. Low yields and difficulties encountered in separating the desired complex from the large number of other unidentified products precluded the use of this complex in SST experiments.

(8-Phenylheptafulvene)iron Tricarbonyl (19). Although the results obtained for the 7-carbomethoxy-substituted systems provide evidence supporting mechanism I, it was felt that additional insight into the mechanism of iron migration could be obtained by examining a substituted system where the activation energy is predicted to be substantially *raised* if a norcaradiene-like transition state (mechanism II) is involved. (8-Phenylheptafulvene)iron tricarbonyl, generously supplied by Dr. Patrick McArdle, is such a system. Operation of mechanism II would require formation of a very highly strained methylene cyclopropane-like transition state, and on this basis the activation energy would be predicted to increase substantially.

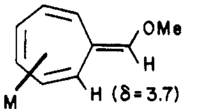
(8-Phenylheptafulvene)iron tricarbonyl exists in solution as a 4:3 mixture of two isomers—**19a** and **19b**. Comparison of the chemical shifts of H_1 in these two isomers and those in (8-methoxyheptafulvene)iron tricarbonyl (**20**)[44] suggests that the major isomer **19a** contains the phenyl group trans to the bound diene unit. In performing the SST experiments on **19**, it is necessary to saturate a signal from one isomer and monitor the decrease in intensity for a signal from the other isomer. Therefore, H_1 of the minor isomer **19b** was saturated while the signal intensity for the peak due to H_6 of the major isomer, **19a**, was measured. The results of the SST experiments are summarized in Table II. These data apply to the conversion of **19b** to **19a**; however, since K_{eq} is close to 1, rates and activation energies for the conversion of **19a** to **19b** will be quite simliar. The free energy of activation of 20 kcal mol^{-1} for **19** is more than 2 kcal mol^{-1} *less* than that for 1,3 iron shift in unsubstituted **1**. The change in activation energy is again *opposite* to that expected for the norcaradiene mechanism and adds strong support for mechanism I.



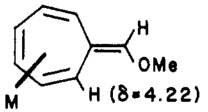
(major)
19a



(minor)
19b



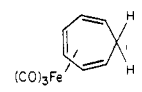
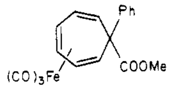
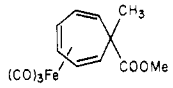
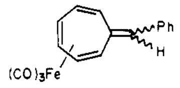
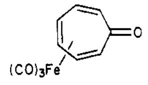
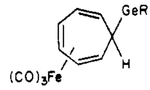
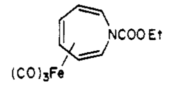
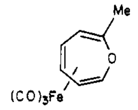
20a



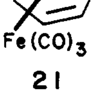
20b

M = $Fe(CO)_3$

Table III. Fluxional Cycloheptatriene–$Fe(CO)_3$ Systems

complex	$\Delta G^{\ddagger}$, kcal mol^{-1}
 **1**	22.3
 **11**	23.9
 **13**	23.3 (minor isomer)
	23.6 (major isomer)
 **19**	20.0
 **21**	>25[45-47]
	17.0 (R = CH_3)[48]
	17.4 (R = Ph)
	15.5[49]
	15.8[50]

Instructive trends emerge when the results of the studies reported here are compared with the previously determined activation energies for 1,3 iron shift in seven-membered cyclic triene complexes. A comprehensive list of systems is given in Table III. Contrast the free energy of activation of (8-phenylheptafulvene)iron tricarbonyl (20 kcal mol^{-1}) with that of (tropone)iron tricarbonyl (**21**) (>25 kcal mol^{-1}). This lower limit is based on the observations of Eisenstadt[45] and Hunt,[46] who found that **21** can be deuterium-labeled preferentially at C_6 with no observable



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(42) Ciganek, E. *J. Am. Chem. Soc.* **1971**, *93*, 2207.

(43) Scherer, H.; Hartmann, A.; Regitz, M.; Tunggal, B. D.; Günther, H. *Chem. Ber.* **1972**, *105*, 3357.

(44) Goldschmidt, Z.; Bakal, Y. *J. Organomet. Chem.* **1979**, *179*, 197.

(45) Eisenstadt, A.; Guss, J.; Mason, R. *J. Organomet. Chem.* **1973**, *80*, 245.

(46) Hunt, D. F.; Farrant, G. C.; Rodeheaver, R. T. *J. Organomet. Chem.* **1972**, *38*, 349.

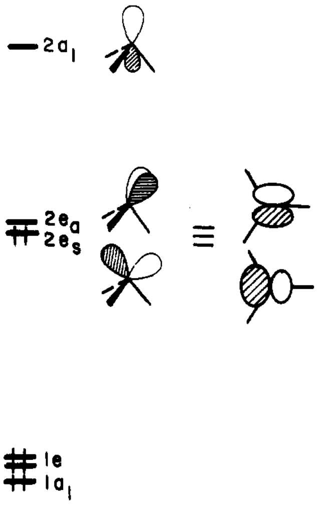
(47) Goldschmidt, Z.; Bakal, Y. *Tetrahedron Lett.* **1976**, 1229.

(48) (a) Li Shing Man, L. K. K.; Takats, J. *J. Organomet. Chem.* **1976**, *117*, C104. (b) The stereochemistry of $[(7\text{-}exo\text{-}GeMe_3C_7H_7)Fe(CO)_3]$ was determined by X-ray crystallography and reported at the Second Joint Meeting of the Chemical Institute of Canada–The American Chemical Society, Montreal, May 29–June 2, 1977 (Inorganic Section C, No. 90).

scrambling to C_1 at 25 °C. Goldschmidt has also observed that an optically active (tropone)iron tricarbonyl complex can be observed at 25 °C (1,3 iron shift would racemize the complex). The steric constraints are quite similar in these complexes; thus, differing electronic effects of the $>C{=}CHC_6H_5$ and $>C{=}O$ groups must be responsible for the substantial differences in $\Delta G^{\ddagger}$'s with the strongly π-electron-withdrawing carbonyl function *increasing* the activation energy for 1,3 iron migration.

A similar trend can be noted for other complexes. In the azepine and oxepine[49,50] complexes the lone pairs on oxygen and nitrogen atoms at the 7-positions serve as strong π donors and accordingly the activation energies are substantially diminished with respect to the parent system, 1. Among those complexes which have saturated carbon atoms at position 7, the 7-*exo*-GeR_3 substituted systems studied by Takats[48] have unusually low activation energies for metal shift compared to 1. This is consistent with the fact that the weak carbon–germanium σ bond can serve as an excellent π donor via a hyperconjugative mechanism. Last, the complexes containing the electron-withdrawing 7-carbomethoxy groups exhibit activation energies slightly higher than the parent system in line with the trend that electron-withdrawing groups at the 7-position increase the activation energy for iron migration while electron-donating groups decrease the activation energy.

Theoretical Calculations. We have carried out a series of molecular orbital calculations at the extended Hückel level on $(CHT)Fe(CO)_3$, 1. Computational details are given in the Experimental Section. Our primary concerns are the electronic and geometric nature of the way-point for a 1,3 shift. We also would like to know why the (norcaradiene)iron tricarbonyl path (mechanism II) appears to be energetically unfavorable. Finally, a simple model will be provided for rationalizing the data of Table III, namely, that electron donors at C_7 accelerate the reaction. Let us begin with the orbitals of an $Fe(CO)_3$ group, shown in 22. Full details have been given elsewhere.[51] The lower three orbitals, $1e + 1a_1$, strongly resemble the octahedral t_{2g} set. At very high energy is $2a_1$, an empty hybrid orbital which is pointed toward the CHT ligand. At moderate energy lies the 2e set. $2e_s$ and $2e_a$ (the s and a subscripts refer to whether the orbital is symmetric or antisymmetric with respect to the plane of the paper) are identifiable with octahedral e_g. In addition they are hybridized away from the carbonyls, toward CHT. The 2e set is half-filled and is the source of greatest interaction with the π orbitals of CHT. Therefore, maximal bonding between CHT and $Fe(CO)_3$ will occur when one member of 2e interacts with the HOMO of CHT and the other interacts with the LUMO of CHT. Top views of $2e_a$ and $2e_s$ are also illustrated in 22. At the ground-state, η^4, geometry, 23, the HOMO of CHT interacts with $2e_a$ as shown in 24. The LUMO of CHT finds a strong interaction with $2e_s$, 25. We have illustrated the CHT ligand as being planar in 23. In fact the structures of related complexes[52] show C_1–C_4 to be roughly planar with C_5–C_7 bent out of the plane, away from the Fe. (Tropone)-[53] and (azepine)iron tricarbonyl[54] and no doubt the other complexes in Table III also have this geometrical arrangement. This means that the magnitudes of the atomic p coefficients in the CHT portion of 24 and 25 may be somewhat altered. However, the relative phases will be the same as that shown. The bonding situation in 23 is then very reminiscent to that in (butadiene)iron tricarbonyl[51b]. As far as the local symmetry around Fe is concerned, 24 resembles the bonding interaction of $2e_a$ with the HOMO of butadiene and 25 is $2e_s$ bonding with LUMO of butadiene. Let us turn now to the η^2 way-point.



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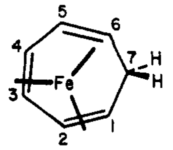
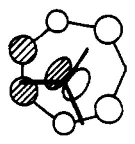
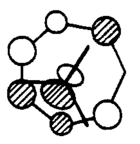


23



24



25

Figure 1 shows a full interaction diagram for $Fe(CO)_3$ with CHT at an "ideal" η^2 geometry where the projection of the iron bisects the C_3–C_4 bond (see 23). The valence orbitals of $Fe(CO)_3$ are again displayed on the right side of this figure. The HOMO and LUMO π orbitals of CHT are given on the left along with the next lower filled orbital, $2\pi_a$. The lowest occupied π orbital, $1\pi_s$, which contains no nodal planes along the polyene ribbon is not shown in the figure. The LUMO of CHT, $2\pi_a$, interacts with $2e_a$ giving $3a''$. However, the HOMO of CHT, $2\pi_s$, lies approximately on the nodal plane of $2e_s$. Thus, the interaction between these two fragment orbitals is close to zero so that molecular orbitals $3a'$ and $4a'$ are essentially in character identical with the respective fragment orbitals, $2\pi_s$ and $2e_s$. The low-lying $4a'$ is empty and serves to remind us that at this geometry the molecule is an unsaturated 16-electron complex. Consider now that a per-

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26

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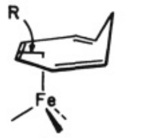
turbation is introduced at C_7, symbolized by **26**. This could be a high-lying occupied level of the (CHT)GeR_3 derivatives, the π system of tropone or heptafulvene, or a lone pair in oxepin and azepin complexes. $2\pi_a$ is uneffected; the perturbation is symmetric with respect to the mirror plane in **26** while $2\pi_a$ is antisymmetric. $2\pi_s$ will be raised or lowered in energy, depending upon the perturbation, but that orbital is noninteracting in our "ideal" η^2 complex. In other words, the perturbation does not result in any stabilization or destabilization in the complex. A similar argument can be constructed for an electron-withdrawing substituent at C_7, symbolized by **27** (for example, the CO π^* orbital of a carboethoxy group). A small stabilization of $2\pi_a$ would occur translating into a small stabilization of the η^2 way-point.[55] Clearly these predictions are at variance with the experimental results in Table III. As we shall see, if a modification of the geometry occurs so that $2e_s$ interacts with $2\pi_s$ in a more significant way, this will lead us out of the dilemma.



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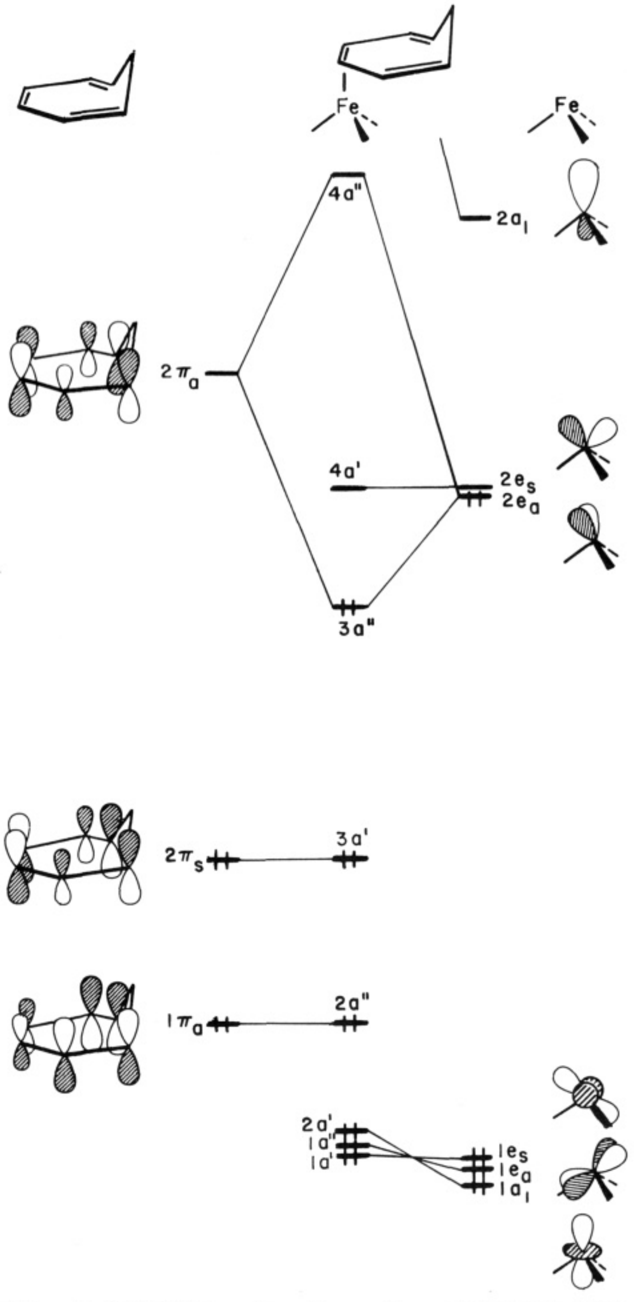

Figure 1. Orbital interaction diagram for an (η^2-CHT)$Fe(CO)_3$.

An attractive way to do this is to allow the $Fe(CO)_3$ group to move toward the interior of the CHT ring, as in **28** or **29**. Here R is the distance between the projection of Fe on the CHT ring and the C_3–C_4 bisector. Figure 2 shows how the overlap between $2e_s$ and $2\pi_s$ along with $2e_a$ and $2\pi_a$ vary as a function of *R*. Figure 3 plots the energies of the molecular orbitals and total energy of **28**. The most drastic change with increasing R occurs between $2e_s$ and $2\pi_s$. That overlap, as seen in Figure 2, increases sharply. The bonding combination, 3a′–**30**, is then lowered in energy and the empty, antibonding combination, 4a′, is pushed up. The total energy we calculate, therefore, drops as *R* is increased. An optimum value of *R* for **28** was found at 0.38 Å. It can be seen from Figure 2 that the optimum overlap of $2e_s$ with $2\pi_s$ actually comes when $R = 1.15$ Å. That is approximately on the bisector of C_2–C_5 (see **28**) and not far from an η^6 geometry. There are two factors that stop the $Fe(CO)_3$ group from slipping any further. First of all, the other primary bonding interaction, $2e_a$ with $2\pi_a$–3a″ shown in **31**, loses overlap a little beyond the optimum structure. This is due to the nodal plane close to C_2–C_5. At η^6, $2e_a$ is almost on the nodal plane of $2\pi_a$ and the overlap drops nearly to zero (see Figure 2). The second reason lies in the fact that as *R* increases the overlap between $2e_a$ and $1\pi_a$, a lower π orbital of CHT increases. This is indicated by the dashed line in Figure 2. Referring back to the orbital interaction of Figure 1, in a formal sense $2e_a$ and $1\pi_a$ are filled; $2\pi_a$ is empty. Therefore, as *R* is increased, a 2-electron, 2-orbital stabilization ($2e_a$ with $2\pi_a$) is replaced by a 4-electron, 2-orbital destabilization ($2e_a$ with $1\pi_a$). 3a″ then rises (see Figure 3) as *R* is increased. The energetic balance of 3a″ with 3a′ gives the minimum with the $Fe(CO)_3$ group slipped toward the interior of the CHT ring. At η^6 this repulsion between the filled $2e_a$ and $1\pi_a$ is the molecular orbital consequence of a 20-electron complex.

There are two further points to be considered before we turn to (norcaradiene)iron tricarbonyl complex. A series of calculations was carried out on varying *R* together with folding along the $C_2 \cdots C_5$ axis, as in **32**. We find that for

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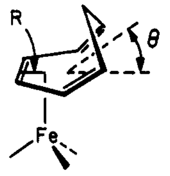
[55] (a) These perturbations on the η^4 ground state geometry, **23**, will not be as strongly felt, since the CHT is folded in the manner previously described. However, a donor of type **26** will push $2\pi_s$ up in energy, closer to $2e_s$; therefore, **24** becomes more stabilized. An electron acceptor of type **26** would do the opposite. Here again, one would predict that (heptafulvene), (oxepine), or (azepine)iron tricarbonyl complexes would undergo 1,3 shifts less readily, since the η^4 ground state is stabilized. (b) An electron acceptor of type **27** would stabilize **25** at η^4 so that both the ground state and η^2 way-point are stabilized, leading to little change in the activation energy.



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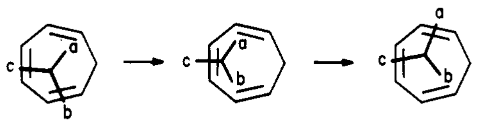
all values of R, θ is at an optimum at 0°, although excursions away from this are quite soft. The reason behind this lies in **30**. The bonding between C_1 and C_2 (C_6 and C_5) inhibits the folding process. Secondly, at the optimum value of R, the $Fe(CO)_3$ group prefers to be oriented as in **28** rather than **29**. The calculated energy difference is small—1.1 kcal mol^{-1}. In **31**, the $2e_a$ is tilted over the symmetry-unique carbonyl.[51a] In $2\pi_a$ the coefficients are larger at C_3 and C_4 compared to C_2 and C_5. Therefore, the overlap between $2e_a$ with $2\pi_a$ is greater in **28** compared with that in **29** (notice that the nodal plane near C_2 and C_5 also will diminish the overlap between $2e_a$ and $2\pi_a$ in **29**). At the η^4 ground state the three carbonyls are different, labeled a–c in **33**. For a 1,3 shift to **33'** by way of



33 34 33'

34, we then would predict that carbonyl a exchanges with b, but a and b do not exchange with c. If the conformation of the way-point was that given by **29** and the $Fe(CO)_3$ group rotates with respect to CHT in a counterclockwise fashion to attain this orientation, then continuing this rotational sense to **33'** results in the exchange of a with c. If the rotation was carried out in a clockwise fashion, then b exchanges with c. It is difficult to see why there should be much of a difference in the sense of rotation to **29** since approximately the same reorientational motion is required. Likewise since there is a mirror plane of symmetry in **29**, collapse to **33'** should be equally facile in both rotational modes. Either or both of these conditions create exchange between all three carbonyls. The rotational barriers in (η^4-polyene)iron tricarbonyl are in the 9–10 kcal/mol range.[51a] This will exchange the carbonyls at a far lower activation energy than any of the 1,3 shifts reported in Table III.

The conversion of an (η^2-CHT)$Fe(CO)_3$ at any value of R to the norcaradiene form is symmetry forbidden. Figure 4 shows the essential details of an orbital correlation diagram for disrotatory ring closure. The three orbitals between 3a″ and $1\pi_s$ (derived from $1a_1$ and 1e) transform as an equivalent set on $Fe(CO)_3$ in the norcaradiene complex. The orbital crossing comes fairly early on the potential surface. When R = 1.64 Å (see **28**), a value typical for (butadiene)iron tricarbonyl complexes,[51a] the $C_1 \cdots C_6$ distance is 2.44 Å for the CHT complex and the crossing occurs when the $C_1 \cdots C_6$ distance is 2.05 Å (the $C_1 \cdots C_6$ in **8** is 1.52 Å[22]). We have not tried to calculate a reaction path from the (η^4-CHT)$Fe(CO)_3$ ground state to the norcaradiene form. That would be geometrically very complicated. But there still should be a significant barrier to get to the norcaradiene structure. Not much motion is required to bring the $Fe(CO)_3$ onto the mirror plane passing from C_7 to the C_3–C_4 bisector. Recall that the barrier of **4** to **5** is quite large. We also have not tried to optimize the norcaradiene form, but there appear to be several electronic problems which should destabilize it. These are tied to the high-lying, filled Walsh set of σ orbitals[56] in the cyclopropane portion of the molecule, **35** and **36**. **35** (represented by 3a′ on the right of Figure 4) and

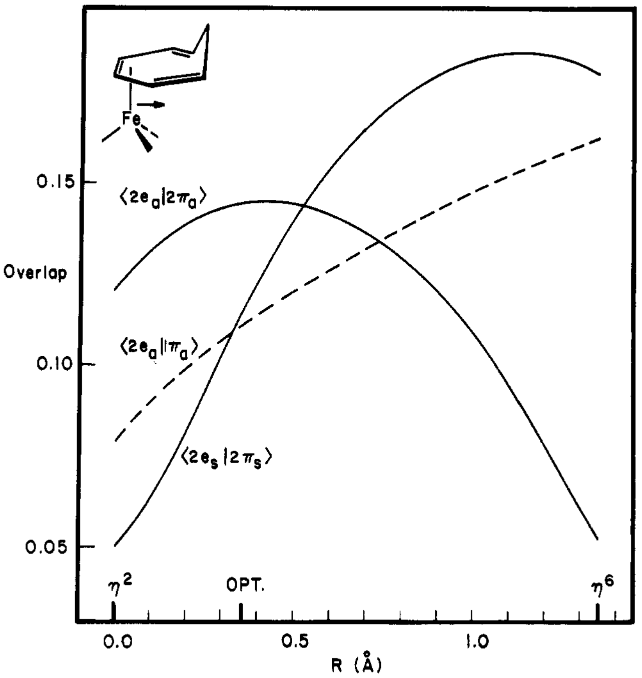


Figure 2. Overlap between the 2e set and valence π orbitals of $(CHT)Fe(CO)_3$. R is defined in **28**.

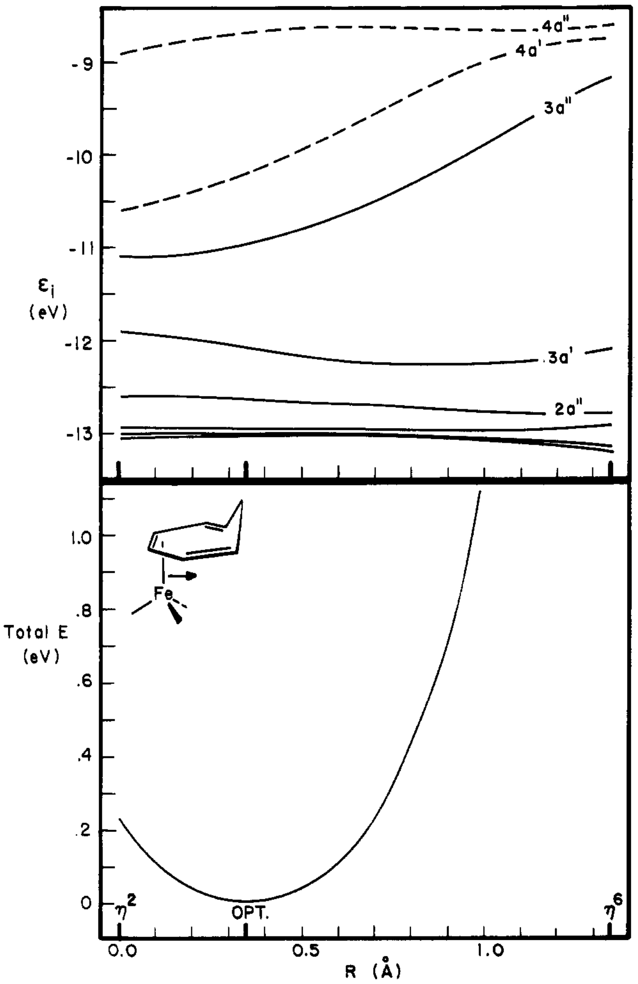
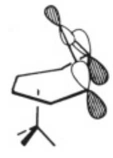


Figure 3. Top: variation of the orbital energies in $(CHT)Fe(CO)_3$ as a function of R, defined in **28**. The dashed lines represent empty orbitals. The orbital labeling scheme follows that in Figure 1. Bottom: variation of the calculated total energy as a function of R.



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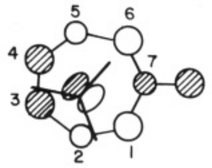
36 destabilize 1a″ and 2a′ of (norcaradiene)iron tricarbonyl. This is then consistent with our previous conclusion that there are both kinetic and thermodynamic problems in attaining this structure.

We are then left with the conclusion that the 1,3 shift proceeds via an "open" CHT structure with the $Fe(CO)_3$ moved toward the interior of the CHT ring.[57] A strong π donor of type **26** will push the energy of $2\pi_s$ up closer to $2e_s$ and consequently its interaction with $2e_s$ will become stronger. Therefore, the activation energy for the 1,3 shift is expected to be lowered. An alternative way to view this is by looking at what happens in the η^4 geometry for **24**. When a π donor of type **26** is incorporated, it will enter out-of-phase with respect to the coefficients at C_1 and C_6. This is shown in **37**, for a heptafulvene system. An additional node is brought into that orbital between C_7 and C_1 (C_6). There is then some antibonding introduced between the p orbital at C_7 and $2e_a$. That should cause the $Fe(CO)_3$ group to move back, toward the C_3–C_4 bond and way-point of the 1,3 shift. An ultimate π donor would put a carbanion at C_7 giving $C_7H_7Fe(CO)_3^-$. The filled p orbital at C_7 pushes $2\pi_s$ up in energy, becoming degenerate with $2\pi_a$. **38** is the resultant orbital. The $Fe(CO)_3$ is pushed back to an η^3 geometry in the ground state, and the η^4 structure becomes the transition state for ring whizzing.[5e] The substitution of π acceptors at C_7 of type **26** will be incorporated in-phase with respect to the coefficients at C_1–C_6. **39** shows the situation for (tropone)iron tricarbonyl. The $Fe(CO)_3$ should be shifted toward C_7 away from the way-point of the 1,3 shift. Therefore, the barrier should and does increase with respect to the heptafulvene complexes. An additional geometrical feature that one can see from **39** is that the C_7 portion should be less pushed out of the coordination plane of C_1–C_2–C_3–C_4. This appears to be the case.[53] An extreme situation would put an empty p orbital at C_7, giving **40**. The distortion toward C_7 is large, C_7 becomes coplanar with C_1–C_4, and a η^5 geometry is observed for $C_7H_7Fe(CO)_3^+$.[58] The η^4 structure again becomes the transition state for ring whizzing. Note that there must be a point where the C_7 position becomes such a good acceptor that the $Fe(CO)_3$ group may migrate around the ring now in a counterclockwise fashion as opposed to the clockwise motion in (tropone)iron tricarbonyl etc.



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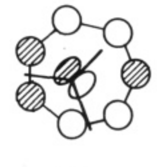

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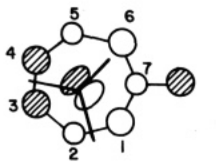

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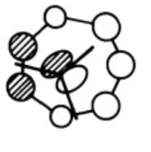

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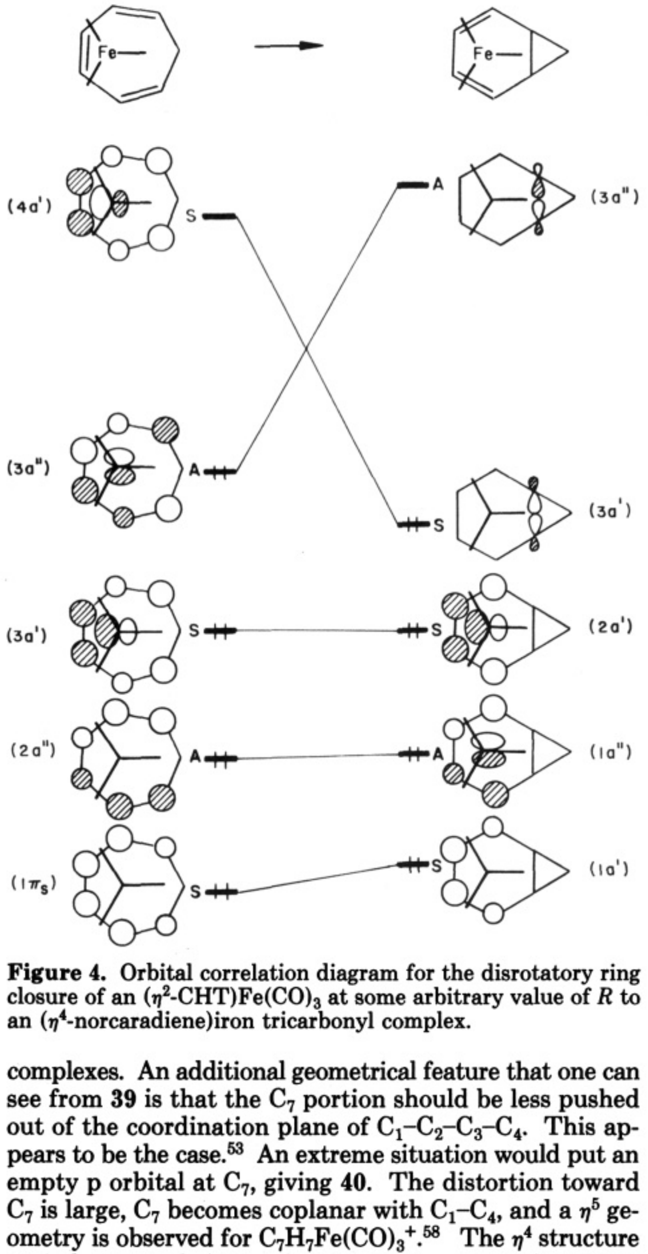

Figure 4. Orbital correlation diagram for the disrotatory ring closure of an (η^2-CHT)$Fe(CO)_3$ at some arbitrary value of R to an (η^4-norcaradiene)iron tricarbonyl complex.

Experimental Section

Proton magnetic resonance spectra were recorded at 100 MHz by using a Varian XL-100 FT-NMR spectrometer; ^{13}C NMR spectra were recorded at 25.2 MHz. Probe temperatures were measured by the use of an ethylene glycol sample. Infrared spectra were recorded on a Beckman spectrophotometer (IR 4250), using polystyrene film as a standard. A Buchi capillary apparatus was used to determine melting points (uncorrected).

Manipulations of all iron carbonyl compounds were conducted under an atmosphere of dry, oxygen-free nitrogen. All ^1H NMR samples used in the SST experiments or in the determination of spin relaxation times, T_1, were carefully prepared and sealed in vacuo on an all Teflon stopcock greaseless vacuum line equipped with an oil diffusion pump capable of reaching 10^{-6} torr. Deu-

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(56) (a) A recent report has totally confirmed these expectations: Grimme, W.; Köser, H. G. *J. Am. Chem. Soc.* **1981**, *103*, 5919. Both (*exo*-norcaradiene)- and (*endo*-norcaradiene)iron tricarbonyl were prepared by alternative methods. Both rearrange irreversibly to (CHT)$Fe(CO)_3$ which means that the latter is thermodynamically more stable. Furthermore the first-order rate constant for isomerization is approximately 10^8 slower than that for the 1,3 shift. In other words, there is a significant barrier for isomerization to (norcaradiene)iron tricarbonyl and this must be larger than that for the direct 1,3 pathway. (b) For a description of these orbitals, see: Jorgenson, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals", Academic Press: New York, 1973; pp 19–23, 254.

(57) We consider an (η^4-1,2,5,6-CHT)$Fe(CO)_3$ structure to be an unlikely intermediate or transition state for the 1,3 shift. At this geometry, $2e_s$ would interact only with $1\pi_s$, and $2e_s$ can interact, by symmetry, only with an unoccupied orbital *higher* in energy than $2\pi_s$ (see Figure 1).

(58) There are no X-ray structures of $C_7H_7Fe(CO)_3^+$ that we are aware of, but the spectra of these complexes[8] are consistent only with an η^5 geometry.

terated solvents were stored in Teflon stopcock equipped ampules which contained 4A molecular sieves.

Photolyses were performed in an immersion well using a 450-W medium-pressure Hanovia lamp. The medium-pressure liquid chromatography (MPLC) system was assembled from parts purchased from Altex. Assembly and operating instructions were supplied by Dr. A. Meyers of Colorado State University.

The following compounds were prepared according to published procedures: (benzylideneacetone)iron tricarbonyl,[35] (cycloheptatriene)iron tricarbonyl,[31a] 7-phenyl-7-(carbomethoxy)-cycloheptatriene,[42] 2,5,7-triphenylnorcaradiene,[39] 7,7-dicyanonorcaradiene,[38] 7-*exo*-(dimethoxooxophosphorio)-7-phenylnorcaradiene,[43] 7-methyl-7-norcaradienecarboxylic acid,[37] and 7-methyl-7-(carbomethoxy)cycloheptatriene.[37]

(Cycloheptatriene)iron Tricarbonyl SST Sample Preparation. (Cycloheptatriene)iron tricarbonyl was prepared by the photolysis of cycloheptatriene and $Fe(CO)_5$ in benzene, as described by Brookhart.[31a] After filtration and removal of the benzene and excess $Fe(CO)_5$ at reduced pressure, the photolysis mixture was chromatographed (activity III Al_2O_3, 2 × 30 cm) by using degassed hexane as eluant. The yellow oil obtained from the first band was further purified by distillation under vacuum. A 100-mg sample was distilled directly into a 5-mm NMR tube which had been sealed to a Teflon stopcock adapter; toluene-d_8 (0.3 mL) was then distilled into the liquid nitrogen cooled NMR tube. Samples were degassed by several freeze–pump–thaw cycles and sealed under vacuum.

(7-Phenyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl. A solution of the ligand, 7-phenyl-7-(carbomethoxy)cycloheptatriene ⇄ 7-phenyl-7-(carbomethoxy)norcaradiene (650 mg), and (benzylideneacetone)iron tricarbonyl (600 mg) in degassed benzene (180 mL) was stirred at 52–53 °C for 72 h. No evidence was found in the ^1H NMR spectrum for the formation of either a (cycloheptatriene)- or (norcaradiene)iron tricarbonyl complex. The reaction mixture was then cooled, filtered, degassed, and heated at reflux for 24 h, after which the solution was cooled and filtered. Following removal of the solvent, the residue was chromatographed (Florisil, 2 × 15 cm) by using degassed benzene as eluant. The first pale yellow band contained unreacted ligand; the second band, slightly darker, contained (7-phenyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl (300 mg, ~40%): mp 110–112 °C; IR (cyclohexane) 2050, 1995, 1980, 1742, cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 52.5, 57.7, and 67.0 (C_1, C_4, C_7), 53.4 (OCH_3), 85.1 and 94.7 (C_2, C_3), 125.5, 126.7, 127.1, 128.7, 128.7, 130.8, and 144.8 (C_5, C_6, phenyl), 172.2 (*C*(O)OMe), 209.5 (FeC≡O). See Table I for a summary of ^1H NMR data. Anal. Calcd for $C_{17}H_{18}O_5Fe$: C, 59.04; H, 3.85. Found: C, 59.05; H, 3.62.

(7-Phenyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl can also be made by photolyzing the ligand (1.0 g) with $Fe(CO)_5$ (4 mL) in degassed benzene (150 mL) for 22 h. The product isolated is identical with that obtained from the reaction of the ligand and (BDA)iron tricarbonyl (BDA = benzlideneacetone). This complex can be crystallized and isolated as yellow needles from ether/pentane at −20 °C.

Preparation of (7-Phenyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl for Spin Saturation Transfer. Solid samples such as this complex were prepared for spin saturation transfer experiments using NMR tube assemblies in which a 10-mm coarse glass frit was sealed between the 5-mm NMR tube and the Teflon stopcock adapter. In this way, samples could be dissolved, filtered, and sealed in vacuo.

After being recrystallized from ether/pentane, 100 mg of the complex was placed in one of the glass frit modified NMR tube assemblies and dried under vacuum. Solvent (toluene-d_8) was distilled in by cooling the glass above the glass frit with liquid nitrogen. When the apparatus was allowed to warm up and the toluene melted, some of the complex dissolved and was filtered through the frit. More complex could be washed down into the NMR tube by distilling the solvent into the space above the frit and then, as the glass above the frit warmed up, allowing the pressure differential to force the solvent and dissolved complex through the frit. When the solution coming through the frit was no longer colored, the sample was degassed by several freeze–pump–thaw cycles and then sealed under vacuum.

(7-Methyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl. A degassed solution of 7-methyl-7-(carbomethoxy)norcaradiene (0.2 g) and $Fe(CO)_5$ (2 mL) in benzene (150 mL) was photolyzed for 8–12 h, at which time the solution had turned from pale yellow to red. After the photolysis mixture was filtered quickly through a pad of Celite and alumina, the solvent was removed on a rotary evaporator. The oily red residue was chromatographed by MPLC using hexane as eluant. The first yellow band containing the major isomer of the complex (7-methyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl (0.15 g, ~40%) was isolated as a yellow oil: IR (cyclohexane) 2050, 1970, 1740 cm^{-1}. ^{13}C NMR (toluene-d_8) δ 31.4 (CH_3), 48.2 (C_7), 52.3 (OCH_3), 55.0 and 67.2 (C_1, C_4), 85.7 and 95.6 (C_2, C_3), 128.6 and 130.0 (C_5, C_6), 174.7 (COMe), 210.9 (FeCO). See Table I for a summary of ^1H NMR data. Anal. Calcd for $C_{13}H_{12}O_5Fe$: C, 51.34; H, 3.98. Found: C, 52.04; H, 4.32. A second yellow band was eluted with hexane/benzene (2:1) and characterized as the other isomer of (7-methyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl (~0.08 g, 21%), in which the relative endo and exo positions of the methyl and carbomethoxy groups at C_m have been reversed: IR (cyclohexane) 2049, 1993, 1983, 1750 cm^{-1}. See Table I for a summary of ^1H NMR data. Anal. Calcd for $C_{13}H_{12}O_5Fe$: C, 51.34; H, 3.98. Found: C, 53.07; H, 4.02. The last fraction contained a red complex whose ^1H NMR and IR spectra were consistent with its formulation as a binuclear complex, (7-methyl-7-(carbomethoxy)cycloheptatriene)diiron hexacarbonyl (~0.05 g, 11%): IR (cyclohexane) 2059, 2047, 2022, 1993, 1976, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (3 H, CH_3), 2.40 (2 H, H_1 and H_6), 3.63 (3 H, COOMe), 4.39 (2 H, H_2 and H_5), 5.13 (2 H, H_3 and H_4).

Preparation of (7-Methyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl for Spin Saturation Transfer Experiments. These complexes are nonvolatile oils and were prepared in a manner similar to that described for solid samples such as (7-phenyl-7-(carbomethoxy)cycloheptatriene)iron tricarbonyl. After chromatography (MPLC), the sample (~100 mg) was dissolved in a small amount of degassed pentane and transferred to a small Schlenk tube. The bulk of the solvent was first removed in a stream of nitrogen, and then the Schlenk tube was placed on a vacuum line to remove the residual solvent. After several hours or overnight on a high vacuum line, the appropriate solvent was distilled into the Schlenk tube. The dissolved complex was then pipetted under nitrogen into an NMR tube assembly in which a 10-mm coarse glass frit had been sealed between the NMR tube and the Teflon stopcock adapter. The sample was filtered through the glass frit, degassed by several freeze–pump–thaw cycles, and sealed under vacuum.

Reactions of 2,5,7-Triphenylnorcaradiene. a. With (BDA)Fe(CO)$_3$. A solution of the norcaradiene (200 mg) and (BDA)$Fe(CO)_3$ (500 mg) in benzene was heated at reflux for 18 h. An ^1H NMR spectrum of the hexane-soluble product showed peaks only for the starting materials and uncomplexed BDA.

b. With Fe(CO)$_5$. A solution of the norcaradiene (300 mg) was photolyzed with $Fe(CO)_5$ in degassed benzene (150 mL). After 10 h, it was necessary to filter the solution to remove $Fe_2(CO)_9$, but no evidence of an iron tricarbonyl complex was seen in the infrared spectrum of the reaction mixture. After an additional 14 h of photolysis, the solution was very dark. The solution was filtered, and the solvent and unreacted $Fe(CO)_5$ were removed on a rotary evaporator. The residue was chromatographed (MPLC) with degassed hexane to give two yellow bands and one very broad red band. The first yellow band contained unreacted norcaradiene; the product in the second band was isolated as a yellow oil and characterized as (2,5,7-triphenylcycloheptatriene)iron tricarbonyl: IR ($CDCl_3$) 2055, 1995 (br) cm^{-1}; ^1H NMR (toluene-d_8) δ 3.58 (t, H_7, $J_{1,7} = J_{6,7} = 2$ Hz), 3.70 (dd, H_4, $J_{3,4} = 8$ Hz, $J_{4,5} = 2$ Hz), 4.20 (q, H_1, $J_{1,6} = J_{1,3} = J_{1,7} = 2$ Hz), 5.48 (dd, H_3, $J_{1,3} = 2$ Hz, $J_{3,4} = 8$ Hz), 5.83 (q, H_6, $J_{1,6} = J_{4,6} = J_{6,7} = 2$ Hz), 7.20–7.75 (m, Ph).

The red band was collected in two fractions. The first contained 1,4,7-triphenylcycloheptatriene, the iron tricarbonyl complex of that ligand, (3,6,7-triphenylcycloheptatriene)iron tricarbonyl, and minor amounts of unidentified products. The second fraction contained predominantly (3,6,7-triphenylcycloheptatriene)iron tricarbonyl: IR ($CDCl_3$) 2050, 1990 (br) cm^{-1}. ^1H NMR (toluene-d_8) δ 3.48 (dd, H_1, $J_{1,2} = 8$ Hz, $J_{1,7} = 5.5$ Hz), 3.82 (dd, H_4, $J_{2,4} = 2$ Hz, $J_{4,5} = 8.5$ Hz), 4.28 (dd, H_7, $J_{1,7} = 5.5$ Hz, $J_{5,7} = 1$ Hz), 5.30 (dd, H_2, $J_{1,2} = 8$ Hz, $J_{2,4} = 2$ Hz), 6.50 (dd, H_5, $J_{4,5} =$

8.5 Hz, $J_{5,7}$ = 1 Hz), 7.0–7.6 (m, Ph).

c. With $Fe_3(CO)_{12}$. A degassed solution of benzene (100 mL), the norcaradiene ligand (0.3 g), and $Fe_3(CO)_{12}$ (2 g) was refluxed for 8–12 h. The solution was cooled and filtered through a pad of Celite and alumina. After the solvent was removed the residue was washed with several aliquots of degassed hexane (5 mL) to separate the products from the less soluble starting materials. The hexane extracts were concentrated to ~5 mL and chromatographed (MPLC) with hexane. The first two yellow bands corresponded to 2,5,7-triphenylnorcaradiene and (2,5,7-triphenylcycloheptatriene)iron tricarbonyl. A third yellow band, although the major product in this reaction (yield, ~30%), could not be completely characterized: IR (C_6D_6) 2050, 1980 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.5–3.3 (m, 5 H), 6.3 (s, 2 H), 7.3–7.8 (m, 15 H, phenyl).

Reactions of 7,7-Dicyanonorcaradiene. Photolysis of dicyanonorcaradiene with $Fe(CO)_5$ in degassed benzene gave a dark reddish brown solution. Filtration and removal of the solvent and excess $Fe(CO)_5$ were accompanied by substantial decomposition of the reaction mixture, and no iron tricarbonyl containing complexes could be isolated. Similar results were obtained with the reaction of the norcaradiene with $Fe_3(CO)_{12}$, $Fe_2(CO)_9$, and (BDA)$Fe(CO)_3$.

Reactions of 7-*exo*-(Dimethoxooxophosphorio)-7-phenylnorcaradiene, 2,5-Dichloro-7-*exo*-(dimethoxooxophosphorio)-7-phenylnorcaradiene, and 2,5-Dimethoxy-7-*exo*-(dimethoxooxophosphorio)-7-phenylnorcaradiene. Reaction of any of these ligands with $Fe_2(CO)_9$ in ether at room temperature led to substantial decomposition of the iron reagent. When it was found that the decomposition of $Fe_2(CO)_9$ was also catalyzed by dimethyl benzoylphosphonate, no further attempts were made to prepare iron tricarbonyl complexes from these phosphate esters.

2,3-Dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene and 3,4-Dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene. These two norcaradienes were prepared by a modification of Ciganek's method for the synthesis of 7-phenyl-7-(carbomethoxy)cycloheptatriene ⇄ 7-phenyl-7-(carbomethoxy)norcaradiene.[41] A solution of methyl phenyldiazoacetate (2.0 g) in degassed *o*-xylene (150 mL) was irradiated through a Pyrex filter for 12 h. After photolysis, unreacted xylene was removed under reduced pressure and the residue chromatographed on Florisil (2 × 25 cm) using hexane/benzene (2:1). The unsymmetrical isomer (2,3-dimethyl) eluted first, followed by fractions containing increasing amounts of the symmetrical norcaradiene (3,4-dimethyl). The last fractions, obtained after ~1500 mL of solvent had been used, contained the symmetrical isomer in >90% purity. An ^{1}H NMR of the crude photolysis product revealed that these two isomers were the major products, with 2,3-dimethyl:3,4-dimethyl = 2:1. Photolyzing more concentrated solutions of the diazoacetate results in the appearance of another product, which is assumed on the basis of ^{1}H NMR to result from the reaction of a second diazoacetate molecule with the 2,3-dimethylnorcaradiene.

2,3-Dimethyl-7-phenyl-7-(carbomethoxy)norcardiene: mp 113–116 °C; ^{1}H NMR ($CDCl_3$) δ 1.74 (s, 3 H, Me), 2.32 (s, 3 H, Me), 3.35 (d, H_1, $J_{1,6}$ = 9 Hz), 3.51 (dd, H_6, $J_{1,6}$ = 9 Hz, $J_{5,6}$ = 5 Hz), 3.90 (s, 3 H, OMe), 5.86 (d, H_4, $J_{4,5}$ = 9 Hz), 6.26 (dd, H_5, $J_{4,5}$ = 9 Hz), $J_{5,6}$ = 5 Hz), 7.2–7.6 (m, 5 H, Ph). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.25; H, 7.20.

3,4-Dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene: mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 1.78 (s, 6 H, Me), 3.46 (dd, 2 H, H_1 and H_6), 3.90 (s, 3 H, OMe), 6.14 (dd (br), 2 H, H_2 and H_5), 7.3–7.5 (s, 5 H, Ph); ^{13}C ($CDCl_3$) δ 19.0 (CH_3), 27.2 (C_7), 42.4 (C_1, C_6), 52.3 (OCH_3), 126.0 (para-phenyl C), 121.6 (C_2, C_5), 126.4 (meta-phenyl C), 133.1 (ortho-phenyl C), 133.4 (ipso-phenyl-C), 134.6 (C_3, C_4), 167.7 (COOMe). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.13. Found: C, 80.49; H, 7.30.

(3,4-Dimethyl-7-phenyl-7-(carbomethoxy)cycloheptatriene)iron Tricarbonyl. 3,4-Dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene (0.1 g) was photolyzed wwith $Fe(CO)_5$ (1 mL) in degassed benzene for 12 h. After the solution was filtered, solvent and excess $Fe(CO)_5$ were removed under reduced pressure. The residue was chromatographed (MPLC) with hexane or hexane/benzene to give at least six separate bands, most of whose ^{1}H NMR spectra were too complex to permit full characteriziation of the compounds present. The fourth band contained a small amount (~50 mg) of a yellow oil with an ^{1}H spectrum suggesting the presence of the two isomers of the cycloheptatriene complex. Heating a benzene solution of the 3,4-dimethylnorcaradiene, with $Fe_3(CO)_{12}$ at reflux gave no identifiable compounds other than starting materials.

Theoretical Calculations. The calculations were carried out with the extended Hückel method.[29] The orbital H_{ii}'s and exponents were taken from previous work.[51a] The modified Wolfsberg–Helmholz formula was used.[59] The Fe–C(O), C–O, and Fe···CHT distances used were 1.78, 1.14, and 1.64 Å, respectively. The Fe–C–O and (O)–C–Fe–C(O) angles were idealized at 180 and 90°, respectively. Bond lengths and angles in the CHT portion were idealized from the structure of (7-Ph-CHT)Fe(CO)$_3$.[52a] Bond lengths and angles for the η^2 form were taken from (7-Ph-CHT)Cr(CO)$_3$.[60] The slipping distortions for **28** and **29** were done so that the Fe–C_3 (C_4) distance was kept constant at 2.10 Å.

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Registry No. 1, 36343-88-1; 11, 66526-83-8; 13 (isomer 1), 79839-89-7; 13 (isomer 2), 79896-44-9; 19 (isomer 1), 38904-35-7; 19 (isomer 2), 38855-88-8; (benzylideneacetone)iron tricarbonyl, 38333-35-6; iron pentacarbonyl, 13463-40-6; 7-phenyl-7-(carbomethoxy)norcaradiene, 32777-09-6; 7-methyl-7-(carbomethoxy)norcaradiene, 79839-51-3; (2,5,7-triphenylcycloheptatriene)iron tricarbonyl, 79839-90-0; (3,6,7-triphenylcycloheptatriene)iron tricarbonyl, 79839-91-1; 2,3-dimethyl-7-phenyl-7-(carbomethoxy)norcaradiene, 79839-52-4; 3,4-dimethyl-7-phenyl-7(carbomethoxy)norcaradiene, 79839-53-5.

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