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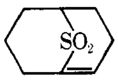

i

on the basis of stereoisomeric Diels-Alder adducts [C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95**, 1342, 6120 (1973)]. The sulfone group considerably expands the short bridge in this system, so that the *E* isomer of i would be significantly less strained than **15b**.

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Selective Trapping of Dienes by Benzylideneacetoneiron Tricarbonyl. Synthetic and Mechanistic Studies of the Reactions of 1,3,5-Cyclooctatriene and its Derivatives with Benzylideneacetoneiron Tricarbonyl

Charles R. Graham, Gary Scholes, and Maurice Brookhart*

Contribution from the William Rand Kenan, Jr., Laboratories of Chemistry, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.

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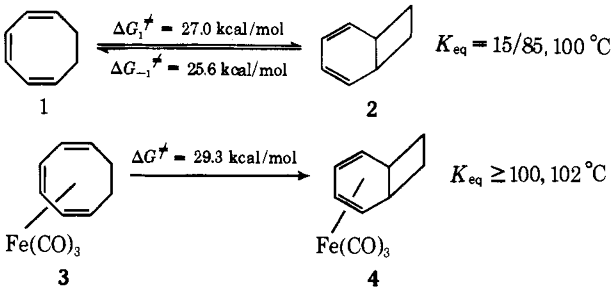
Abstract: Thermal reactions of benzylideneacetoneiron tricarbonyl (BDAFe(CO)$_3$) with cyclooctatriene (**1**), bicyclo[6.2.0]decatriene (**5b**), bicyclo[6.1.0]nonatriene (**5a**), and *syn*-9-methylbicyclo[6.1.0]nonatriene (**17**) are reported. For **1**, **5b**, and **17**, BDAFe(CO)$_3$ selectively traps the diene tautomers present in low concentrations in equilibrium with the trienes to yield bicyclo[4.2.0]octadieneiron tricarbonyl (**4**), tricyclo[4.4.0.0^{2,5}]deca-7,9-dieneiron tricarbonyl (**7**), and *syn*-8-methyltricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl (**19**), respectively, as the sole products of reaction in good yields. In the case of **5a**, the major product of reaction is tricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl (**10**) (48%) but also found are *cis*-8,9-dihydroindeneiron tricarbonyl (**14**) (21%) and *cis*^{4}-cyclononatetraeneiron tricarbonyl (**15**) (9%) from trapping by BDAFe(CO)$_3$ of thermal rearrangement products of **5a**. Low temperature oxidative cleavage of **7**, **10**, and **19** with ceric ion yields the corresponding free diene ligands, tricyclo[4.4.0.0^{2,5}]deca-7,9-diene (**6b**), tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**6a**), and *syn*-8-methyltricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**18**). Rates for the electrocyclic ring openings of the dienes to the trienes have been measured for **6b**, **6a**, and **18** and the equilibrium ratio of triene:diene tautomers has been determined to be 40 for **5b**:**6b** and estimated as 4500 for **5a**:**6a** and **17**:**18**. A kinetic study of the reaction of excess BDAFe(CO)$_3$ with **1** has revealed that the rate-limiting step is the ring closure of the triene **1** to the diene **2** and the selectivity of BDAFe(CO)$_3$ results from a kinetic selectivity for the diene relative to the triene. A study of the kinetics of the reaction of BDAFe(CO)$_3$ with 1,3-cyclohexadiene to yield cyclohexadieneiron tricarbonyl suggests a mechanism which involves dechelation of the carbonyl group of the bound enone to form a four-coordinate, 16 electron iron complex which is then trapped by cyclohexadiene.

The manner in which the stabilities and reactivities of polyolefins are modified by coordination to transition metals has received considerable attention over the past several years. One of the most interesting and synthetically useful applications in this area has been the preparation of transition metal complexes of highly reactive polyolefins which are not normally stable at ambient temperatures. For example, the iron tricarbonyl moiety has been extensively used to stabilize as iron complexes such highly reactive species as cyclobutadiene,[1] cyclopentadienone,[2] 7-norbornadienone,[3] and trimethylenemethane.[4]

A second aspect of this chemistry which has been of particular interest to us has been the modification, through binding to transition metals, of the thermal chemistry of cyclic polyolefins capable of undergoing electrocyclic ring opening and ring closing reactions. We have found that binding an iron tricarbonyl moiety to polyolefins capable of such tautomerization can have substantial effects on both the position of the tautomeric equilibrium and the rates of interconversion of the tautomers. For example, whereas *cis*^{4}-cyclononatetraene undergoes rapid ring closure to *cis*-dihydroindene ($\Delta G^{\ddagger} \sim 23$ kcal/mol)[5] at 25 °C, *cis*^{4}-cyclononatetraeneiron tricarbonyl is stable at room temperature and undergoes isomerization to *cis*-dihydroindeneiron tricarbonyl at 100 °C ($\Delta G^{\ddagger} = 28.4$ kcal/mol).[6]

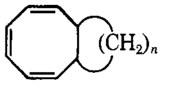
A system for which more quantitative information is available involves the tautomeric equilibrium between 1,3,5-cyclooctatriene (**1**) and bicyclo[4.2.0]octadiene (**2**).



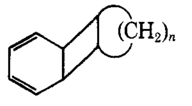
Huisgen[7] has shown that at equilibrium the triene **1** is favored over the diene **2** by a ratio of 85:15 at 100 °C.

Early reports by Stone[8] and Wilkinson[9] showed that reaction of this equilibrating system ($\mathbf{1} \rightleftharpoons \mathbf{2}$) with iron pentacarbonyl at 140 °C gave only bicyclo[4.2.0]octadieneiron tricarbonyl (**4**), while reaction at lower temperatures (80–100 °C) with $Fe_3(CO)_{12}$ gave mixtures of cyclooctatrieneiron tricarbonyl (**3**) and the diene complex **4**. Pure triene complex can be prepared by photolysis of iron pentacarbonyl in the presence of triene **1**.[10,11] We have shown that the triene complex **3** undergoes clean thermal ring closure to the bicyclic diene complex **4** at 102 °C ($\Delta G^{\ddagger} = 29.3$ kcal/mol), with an equilibrium constant for the reaction of at least 100 at 102 °C.[10] This shift in the equilibrium in the complexed systems toward the diene tautomer was ascribed to induced ring strain in the triene complex **3** due to distortion from the preferred tub conformation of **1** into an energetically unfavorable conformation in the complex **3**, in which the four carbons of the bound diene unit must be approximately coplanar.

Cotton and Deganello[12] have studied the reactions of ring-fused derivatives of cyclooctatriene, **5b–d**, with $Fe_2(CO)_9$. In each case stable iron tricarbonyl complexes of the diene tautomers **6b–d** were isolated. The reaction of **5b** with $Fe_2(CO)_9$

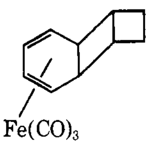


5a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$



6a, $n = 1$
b, $n = 2$
c, $n = 3$
d, $n = 4$

led not only to the tricyclic diene complex **7** in a low yield, but also to the binuclear complex **8** and other unidentified complexes.[12b,13] Isolation of complex **7** is of substantial interest in that the diene tautomer **6b** is less stable than the triene tautomer **5b**, and is present in only very low concentrations with respect to triene **5b** at equilibrium.



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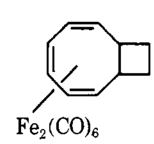

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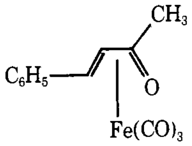
In a preliminary communication[14] we have reported the use of benzylideneacetoneiron tricarbonyl[15] (BDAFe(CO)$_3$) (**9**) as a remarkably selective reagent for trapping of the unstable diene tautomers **6a** and **6b** as iron tricarbonyl complexes. Reaction of **5b** with BDAFe(CO)$_3$ gave complex **7** in an 84% yield, whereas reaction with triene **5a** led to the tricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl complex **10** as the major product. Low temperature oxidative cleavage of the complexes **7** and **10** gave the unstable tautomers **6b** and **6a**, respectively, which then underwent thermal electrocyclic ring openings to the more stable trienes **5b** and **5a**. In a similar fashion,[16] reaction of BDAFe(CO)$_3$ with 2,4,6-cyclooctatrienone gave the bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl complex in a ca. 50% yield. The free bicyclic ketone was generated by low temperature iron cleavage, and at 0 °C underwent a rapid electrocyclic ring opening to the trienone. We now wish to report the full details concerning these as well as other trapping reactions using BDAFe(CO)$_3$. We also report the results of kinetic studies which lend insight into the mechanism and reasons for the high selectivity of these reactions.



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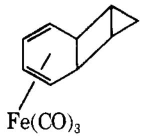
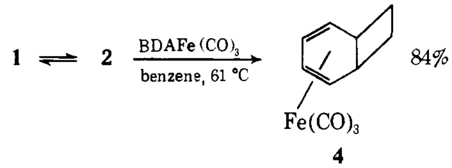


10

Results and Discussion

Formation of Complexes. At equilibrium, 1,3,5-cyclooctatriene (**1**) is favored over the bicyclo[4.2.0]octa-2,4-diene tautomer, **2**, at 100 °C by a ratio of 85:15.[7] Reactions of this equilibrating pair of tautomers with iron carbonyl reagents at various temperatures yields either the diene complex **4** or mixtures of **4** and the triene complex **3**.[8,9] In contrast, reaction of cyclooctatriene with BDAFe(CO)$_3$ in benzene at 61 °C for 48 h gives only complex **4**, in an 84% yield. None of the triene complex **4** was detected in the product.



Cotton[12b] has reported that reaction of bicyclo[6.2.0]decatriene (**5b**) gave tricyclo[4.4.0.0^{2,5}]deca-7,9-dieneiron tricarbonyl (**7**) in a low yield, plus several other complexes. Product **7** is the complex of the unstable diene tautomer **6b**, which at equilibrium is present in low concentrations with respect to the triene **5b**. An x-ray determination of the structure of **7** showed that the stereochemistry of ring fusion about the central cyclobutane ring was anti rather than syn.[17] Reaction of triene **5b** with BDAFe(CO)$_3$ in benzene at 65 °C for 48 h yields cleanly complex **7** in an 82% yield, with no other complexes detected. The product was shown by ^{1}H NMR to be identical with the complex isolated by Cotton.[12b] Further proof of the structure of the product lies in the fact that low temperature oxidative cleavage of the complex yields the free

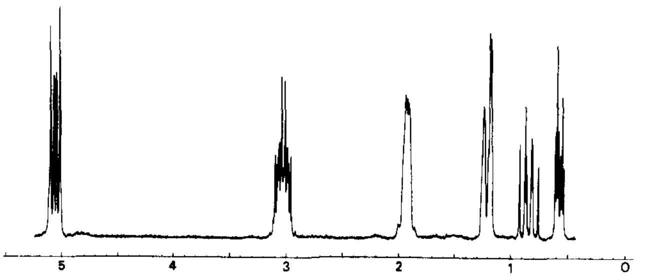
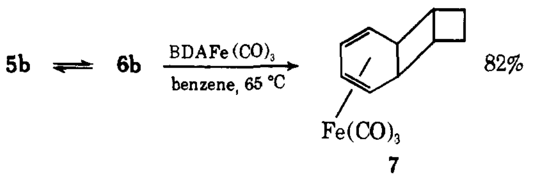


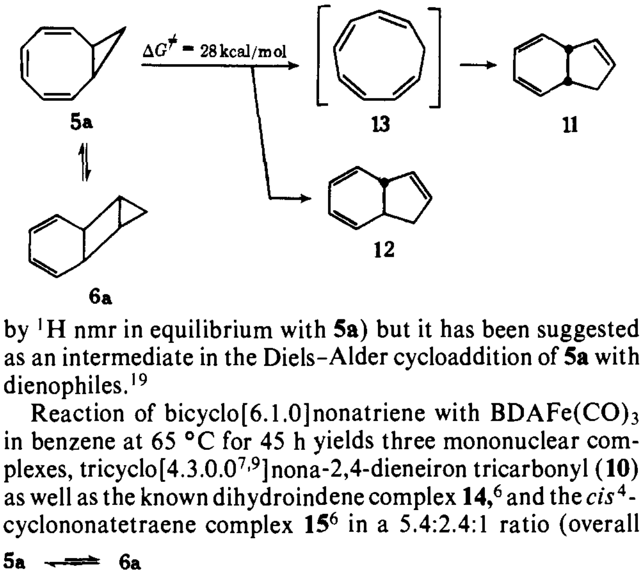
Figure 1. The 100-MHz ^1H NMR spectrum of tricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl (**10**) in benzene-d_6.

diene, **6b**, which, upon warming at 45 °C, isomerizes to the starting triene **5b** (see below).



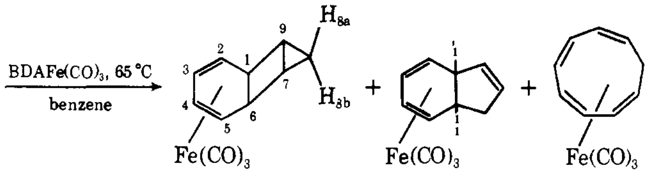
7

cis-Bicyclo[6.1.0]nonatriene (**5a**) is known to thermally rearrange at 90 °C to *cis*- and *trans*-8,9-dihydroindenes (**11** and **12**) in a 9:1 ratio.[18] The isomerization to *cis*-dihydroindene ($\Delta G^{\ddagger} = 28$ kcal/mol) is thought to proceed through the unstable *cis*^{4}-cyclononatetraene **13**.[18] No direct observation of the diene tautomer **6a** has been made (it cannot be detected by ^1H nmr in equilibrium with **5a**) but it has been suggested as an intermediate in the Diels-Alder cycloaddition of **5a** with dienophiles.[19]



Reaction of bicyclo[6.1.0]nonatriene with BDAFe(CO)$_3$ in benzene at 65 °C for 45 h yields three mononuclear complexes, tricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl (**10**) as well as the known dihydroindene complex **14**,[6] and the *cis*^{4}-cyclononatetraene complex **15**[6] in a 5.4:2.4:1 ratio (overall yield 78%). The complexes are apparently formed by trapping the polyolefins **6a**, **11**, and **13**, respectively, which are generated in the isomerization of the triene **5a**.

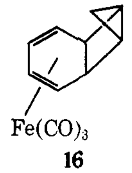
5a ⇌ **6a**



10 **14** **15**

The tricyclic diene complex **10** was isolated by medium-pressure liquid chromatography as a yellow oil, showing infrared absorptions at 2042 and 1968 cm^{-1} (br), typical of diene iron tricarbonyl complexes. The structure of **10** was unambiguously established by examination of the 100-MHz ^1H NMR spectrum (C$_6$D$_6$), illustrated in Figure 1, which displayed signals at δ 0.59 (dt, H_{8a}), 0.76–0.96 (m, H_{8b}), 1.14–1.30 (m, H_7, H_9), 1.84–2.02 (m, H_1, H_6), 2.90–3.12 (m, H_2, H_5), 5.05 (m, H_3, H_4). Assignments were verified by extensive decoupling experiments, which together with computer-simulated spectra resulted in the determination of the following coupling constants: $J_{8a,8b} = 4.6$, $J_{8a,7} = J_{8a,9} = 1.35$, $J_{8b,7} = J_{8b,9} = 5.85$, $J_{2,3} = J_{4,5} = 6.5$, $J_{3,4} = 4.2$, $J_{3,5} = J_{2,4} = 1.6$ Hz. The coupling constants $J_{6,7} = J_{1,9}$ were determined to be less than 1.5 Hz.[20] The measured coupling constants $J_{2,3} = J_{4,5}$, $J_{3,4}$ and $J_{2,4} = J_{3,5}$ and H_2–H_5 chemical shifts are in close agreement with those of other cyclohexadieneiron tricarbonyl derivatives[16b,22] while the observed couplings $J_{8a,8b}$, $J_{8a,7} = J_{8a,9}$, $J_{8b,7} = J_{8b,9}$ are in close accord with those of other bicyclo[2.1.0]pentane derivatives.[21]

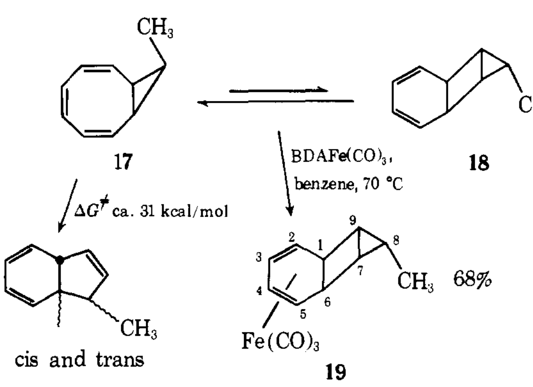
One question to be raised is the stereochemistry of the two rings fused to the central cyclobutane ring. Available data suggest that the ring fusion is anti as illustrated in **10** and not syn as in **16**. First there is the strong analogy between complex **10** and complex **7**, for which the crystal structure clearly indicates anti ring fusion.[17] Secondly, the very small $J_{1,9} = J_{6,7}$ coupling suggests anti stereochemistry. The H_1, H_9 (H_6, H_7) dihedral angle in **10** is ca. 90 °C with an expected $J_{1,9}$ ($J_{6,7}$) of less than 0.5 Hz[21] which is consistent with the spectrum,[20] while the analogous dihedral angle for the syn complex should be ca. 0 °C with an expected $J_{1,9}$ ($J_{6,7}$) of ca. 4 Hz,[21] much larger than observed. This coupling constant argument is given additional weight from the observation that the analogous coupling $J_{1,2} = J_{5,6}$ in the diene complex **7** is small and the stereochemistry has been established as anti by x-ray crystallography.[17]



16

The proton decoupled ^{13}C NMR spectrum (C$_6$D$_6$) is consistent with the proposed structure and shows resonances at 21.5 (C_8), 24.0 (C_7, C_9), 43.4 (C_1, C_6), 66.4 (C_2, C_5), 86.8 (C_3, C_4), and 212.8 ppm (carbonyls) downfield from Me$_4$Si. These assignments were made by analogy with those of the bicyclo[4.2.0]octadiene complex **4**.[16b] Further structural proof was obtained by oxidative cleavage of the complex **10** at −30 °C to yield the diene tautomer **6a**, which, upon warming, is converted quantitatively to the starting triene **5a** (see below).

In contrast to the unsubstituted triene, **5a**, *syn*-9-methylbicyclo[6.1.0]nonatriene (**17**) rearranges to *cis*- and *trans*-8,9-dihydroindenes only at much higher temperatures ($\Delta G^{\ddagger} = 31$ kcal/mol).[23] However, it is expected that the rate of interconversion of the triene tautomer **17** with the tricyclic diene tautomer **18** would be little affected by the 9-methyl substituent. Therefore, one would expect that at 70 °C, the major thermal reaction of triene **17** would be equilibration with the

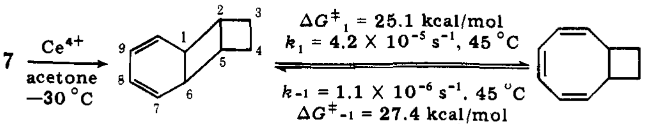


energetically disfavored tricyclic diene **18**. Indeed, reaction of triene **17** with BDAFe(CO)$_3$ in benzene at 70 °C for 45 h yields the yellow crystalline *syn*-8-methyltricyclo[4.3.0.0^{7,9}]-nona-2,4-dieneiron tricarbonyl complex **19** (mp 87-89 °C) as the sole detectable product (68% yield).

Complex **19** shows typical infrared absorptions at 2042 and 1968 cm^{-1} (br) and displays resonances in the ^{1}H NMR spectrum (C$_6$D$_6$) at δ 0.88-1.26 (m, H$_7$, H$_8$, H$_9$, and CH$_3$), 1.84-2.02 (br s, H$_1$, H$_6$), 2.90-3.16 (m, H$_2$, H$_5$), and 5.07 (dd, H$_3$, H$_4$). Aside from the complex resonance from the methyl and cyclopropane protons, the NMR spectrum of **18** is virtually identical with that displayed by the tricyclic diene complex **10**, indicating a similar structure for complex **19**. In addition, the broadened singlet at δ 1.84-2.02 is characteristic of anti ring fusion about the central cyclobutane ring, as was discussed previously for the other tricyclic diene complexes (**7** and **10**). The ^{13}C NMR spectrum (C$_6$D$_6$) is consistent with the proposed structure and exhibits resonances at δ 7.5 (CH$_3$), 24.1 (C$_8$), 27.4 (C$_7$, C$_9$), 37.6 (C$_1$, C$_6$), 65.6 (C$_2$, C$_5$), 85.9 (C$_3$, C$_4$), and 212.0 ppm (carbonyls) downfield from Me$_4$Si. In a fashion analogous to complexes **7** and **10**, the tricyclic complex was cleaved with ceric ion at −30 °C to yield the free tricyclic diene **18**, which rearranged upon warming to the triene **17** (see below).

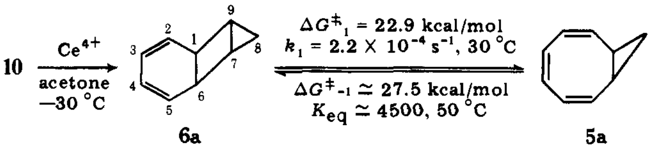
Generation and Thermal Rearrangements of the Dienes. The reaction of cyclooctatriene derivatives with BDAFe(CO)$_3$ yields not only complexes of the diene tautomers, but low temperature cerium(IV) cleavage of the complexes can also lead to the isolation and spectroscopic observation of the unstable diene tautomers as well. Upon warming, the rates of electrocyclic ring opening of the dienes may be measured. By comparing these values with the rates for ring closure, the value of the equilibrium ratio of tautomers may be estimated. Therefore, the use of BDAFe(CO)$_3$ as a trapping reagent not only allows isolation of the unstable tautomers, but also yields quantitative information regarding the relative stabilities of the diene and triene isomers.

For example, the tricyclic diene complex **7** was cleaved at −30 °C in acetone with ceric ammonium nitrate to give the colorless tricyclo[4.4.0.0^{2,5}]deca-7,9-diene (**2b**) in an 84% yield. The 100-MHz ^{1}H NMR spectrum (CS$_2$) of diene **6b** exhibited signals at δ 2.0-2.6 (m, H$_3$, H$_4$), 2.8-3.0 (m, H$_2$, H$_5$), 3.12 (br s, H$_1$, H$_6$), and 5.30-5.70 (m, H$_7$, H$_8$, H$_9$, H$_{10}$). The broad singlet at δ 3.12 (H$_1$ and H$_6$) indicated that the ring fusion about the central cyclobutane remained anti through the cleavage reaction. The proton decoupled ^{13}C NMR spectrum (CS$_2$, −20 °C) showed resonances at 29.4 (C$_3$, C$_4$), 40.3 (C$_2$, C$_5$ or C$_1$, C$_6$), 50.2 (C$_1$, C$_6$ or C$_2$, C$_5$), 121.6 (C$_7$, C$_{10}$ or C$_8$, C$_9$), and 126.3 ppm (C$_8$, C$_9$ or C$_7$, C$_{10}$) downfield from Me$_4$Si.



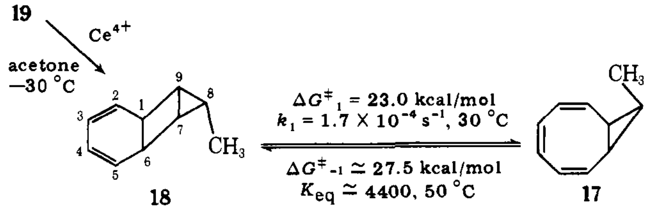
Upon warming at 45 °C, diene **6b** underwent a clean first-order thermal electrocyclic ring opening in essentially quantitative yield to triene **5b**, $k_1 = 4.2 \times 10^{-5}\ \mathrm{s}^{-1}$, $\Delta G_1{}^{\ddagger} = 25.1$ kcal/mol. The equilibrium ratio of **5b**:**6b** at 45 °C was determined using ^{13}C FT NMR by two methods. In the first, the gated decoupling method was employed, in which the broad band proton decoupler was gated on only during data acquisition in order to avoid possible NOE effects. In addition, long pulse delay times (1 min) were used to allow for complete relaxation of all ^{13}C nuclei. The second method employed the paramagnetic relaxation reagent Cr(acac)$_3$ (0.03 M) to reduce all carbon T_1's to similar values and to eliminate NOE effects.[24] Both methods gave the same values for ^{13}C integrals, from which a value of 40 for the equilibrium ratio of **5b** to **6b** was obtained ($\Delta G = 2.3$ kcal/mol, 45 °C). From this, the rate constant for ring closure, k_{-1}, could be calculated as $1.1 \times 10^{-6}\ \mathrm{s}^{-1}$, $\Delta G^{\ddagger} = 27.4$ kcal/mol, at 45 °C. It is of interest to note that at 45 °C, the unstable tautomer **6b** is selectively trapped by BDAFe(CO)$_3$, even though it is present in low concentration.

In a similar manner, cleavage of the tricyclic diene complex **10** at −30 °C in acetone with ceric ammonium nitrate, followed by vacuum distillation at −30 °C, gave pure tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**6a**). The diene **6a** exhibits ^{1}H NMR signals at δ 0.27-0.53 (m, H$_{8a}$, H$_{8b}$), 1.65-1.79 (m, H$_7$, H$_9$), 2.47-2.59 (br s, H$_1$, H$_6$), and 5.37-5.83 (m, H$_2$, H$_3$, H$_4$, H$_5$). The doublet with additional fine structure at δ 1.65-1.79 is assigned to the cyclopropyl bridgehead protons H$_7$ and H$_9$, and shows a coupling of 5.9 Hz to H$_8$, typical of bicyclo[2.1.0]pentane derivatives.[21] The broad singlet at δ 2.47-2.59 due to H$_1$ and H$_6$ clearly indicates anti ring fusion, as has been previously described.



The tricyclic diene **6a** undergoes a rapid first-order thermal electrocyclic ring opening at 30 °C to the starting triene **5a**, $k_1 = 2.2 \times 10^{-4}\ \mathrm{s}^{-1}$, $\Delta G^{\ddagger} = 22.9$ kcal/mol. The rate of ring closure of bicyclo[6.1.0]nonatriene cannot be easily measured; however, it can be estimated with a reasonable degree of accuracy based on the following information. Triene **5a** undergoes isomerization to 8,9-dihydroindenes with a free energy of activation of 28 kcal/mol.[18] Reaction of **5a** with maleic anhydride gives Diels-Alder adducts of *cis*-8,9-dihydroindene and the tricyclic diene **6a**.[19] This implies that ring closure must be competitive with the irreversible isomerization to dihydroindene and sets an upper limit of ca. 28 kcal/mol on the free energy of activation of ring closure of **5a** to **6a**. Secondly, it is important to note that known free energies of activation for the closure of cyclooctatriene derivatives are remarkably similar; for example, unsubstituted 1,3,5-cyclooctatriene[7] (26.9 kcal/mol, 45 °C), bicyclo[6.2.0]decatriene (27.4 kcal/mol, 45 °C, see above), and cyclooctatetraene[7] (27.7 kcal/mol, 45 °C). Based on this information, it is reasonable to expect that $\Delta G^{\ddagger}$ for closure of **5a** should exceed that of cyclooctatriene and probably lies between the value of 27.4 kcal/mol for **5b** and 27.7 kcal/mol for cyclooctatetraene, at approximately 27.5 kcal/mol. Using this estimated $\Delta G^{\ddagger}{}_{-1}$ for closure of **5a** and the measured $\Delta G^{\ddagger}{}_1$ for opening of **6a** of 22.9 kcal/mol, a ΔG for the equilibrium can be estimated as 4.6 kcal/mol, indicating an equilibrium ratio of **5a**:**6a** of ca. 4500 at 50 °C. Again, the remarkable selectivity of BDAFe(CO)$_3$ is demonstrated by the fact that the unstable tautomer **6a** is efficiently trapped, even though it is in only a 0.02% concentration relative to the triene **5a**.

Cleavage of the methyl substituted diene complex **19** in acetone at −30 °C with ceric ammonium nitrate yields *syn*-8-methyltricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**18**), which dis-



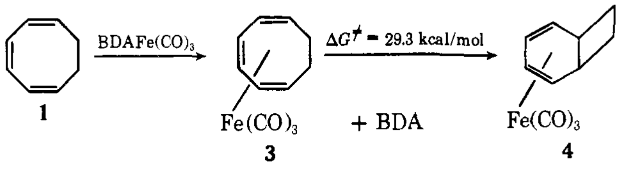
plays ^{1}H NMR signals ($CDCl_3$) at δ 0.58 (sextet, H_8, $J = 5.9$ Hz), 1.13 (d, CH_3, $J = 5.9$ Hz), 1.68 (br d, H_7, H_9, $J = 5.8$ Hz), 2.52 (br s, H_1, H_6), and 5.43-5.96 (m, H_2, H_3, H_4, H_5). Proton decoupling experiments confirmed the assignments and established $J_{8,CH_3} = 5.9$ and $J_{7,8} = J_{9,8} = 5.8$ Hz, which are typical values for bicyclo[2.1.0]pentane derivatives.[21] The broadened singlet at δ 2.52 indicates that the stereochemistry of ring fusion is anti, as previously described. The ^{13}C NMR spectrum ($CDCl_3$, −34 °C) is consistent with the structure and shows resonances at 7.1 (CH_3), 10.9 (C_8), 25.6 ($C_{7,9}$ or $C_{1,6}$), 30.6 (C_1, C_6, or C_7, C_9), 121.6 (C_2, C_5 or C_3, C_4), and 127.3 ppm (C_3, C_4 or C_2, C_5) downfield from Me_4Si.

The tricyclic diene **18** undergoes a first-order thermal electrocyclic ring opening to triene **17** at 30 °C at a rate very similar to the ring opening of the tricyclic diene **6a**, $k_1 = 1.7 \times 10^{-4}$ s^{-1}, $\Delta G^{\ddagger} = 23.0$ kcal/mol. Assuming that the free energy of activation for ring closure of **17** is the same as that of **5a** ($\Delta G^{\ddagger}$ ca. 27.5 kcal/mol), the equilibrium ratio of **17** to **18** is estimated to be ca. 4400 at 45 °C.

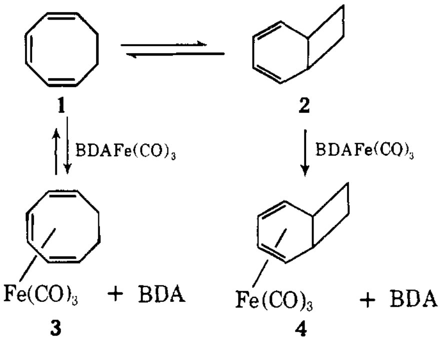
Kinetics and Mechanism of Complex Formation. BDA-Fe(CO)$_3$ and 1,3,5-Cyclooctatriene. Since the reaction of BDAFe(CO)$_3$ and cyclooctatriene derivatives surprisingly yields not triene complexes but only complexes of the tautomeric dienes, a kinetic study was undertaken to determine the mechanism and reason for the remarkable selectivity of the reaction. Preliminary data suggested to us that the mechanism involved efficient trapping of the diene tautomers by BDA-Fe(CO)$_3$, since in the case of bicyclo[6.2.0]decatriene (**5b**), the qualitative rate of formation of diene complex approximated the rate of ring closure of the free triene to the diene tautomer, **6b**. Furthermore, it is important to note that reaction of BDAFe(CO)$_3$ with bicyclo[6.1.0]nonatriene (**5a**) yields iron tricarbonyl complexes of the triene's thermal rearrangement products, *cis*-8,9-dihydroindene and *cis*^{4}-cyclononatetraene,[18] as well as the diene tautomer, **6a**. Reaction of BDAFe(CO)$_3$ with *syn*-9-methylbicyclo[6.1.0]nonatriene, on the other hand, gives no complexes other than that of its diene tautomer, **18**, in agreement with its known higher barrier to thermal isomerization.[23] These results support the postulate that the product complexes are formed by trapping of the thermal rearrangement products, rather than by direct reaction of the trienes with BDAFe(CO)$_3$.

To clarify the mechanistic aspects of these reactions, a detailed study of the reaction of cyclooctatriene (**1**) with BDAFe(CO)$_3$ to form bicyclo[4.2.0]octadieneiron tricarbonyl (**4**) was undertaken. Four plausible mechanisms for this reaction were considered.

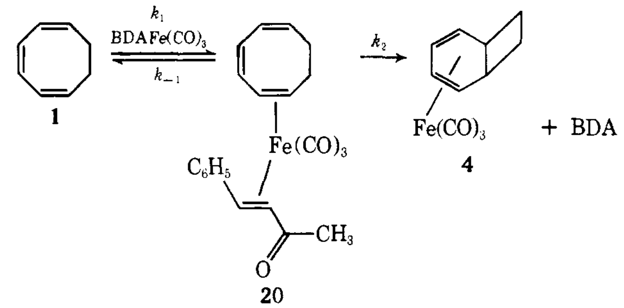
1. BDAFe(CO)$_3$ reacts with the triene to form the triene-Fe(CO)$_3$ complex **3**, which is followed by ring closure of **3** to the diene complex **4**.



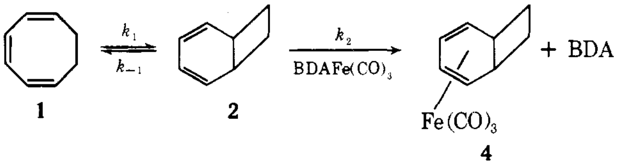
2. BDAFe(CO)$_3$ reacts with the triene to form the triene complex **3** but is thermodynamically unstable with respect to BDAFe(CO)$_3$ and reacts rapidly with the free benzylideneacetone (BDA) to return to BDAFe(CO)$_3$. Thus, the triene complex never builds up in any appreciable concentration. BDAFe(CO)$_3$ then eventually reacts with free bicyclic diene **2** as it is formed from triene to give the diene complex **4** as the stable product. (Such a mechanism involves a *thermodynamic*, not a kinetic, selectivity of BDAFe(CO)$_3$ for the diene relative to the triene tautomer.)



3. BDAFe(CO)$_3$ reacts with the triene to form an intermediate complex **20** involving both BDA and triene (dihapto coordinated),[25,26] followed by a metal-assisted ring closure of the bound triene and loss of BDA to give the product diene complex, **4**.



4. The triene undergoes ring closure to the diene tautomer, which is trapped by BDAFe(CO)$_3$ to yield the diene complex **4**. (This mechanism suggests that the triene does not react with BDAFe(CO)$_3$, but that the selectivity is a kinetic selectivity of BDAFe(CO)$_3$ for the diene relative to the triene.)



The first two of the possibilities, mechanisms 1 and 2, can be readily eliminated. We have previously measured the rate of ring closure of triene complex **3** to diene complex **4** and find at 102 °C, $k = 7 \times 10^{-5}$ s^{-1}, $\Delta G^{\ddagger} = 29.3$ kcal/mol.[10] Extrapolation of this rate to 60 °C yields a value for the rate constant of ca. 5×10^{-7} s^{-1} ($t_{1/2}$ ca. 385 h) which is far too small to account for a half-life of product formation of ca. 10 h at 60 °C (see below) as required by mechanism 1. The second mechanism requires that triene complex react rapidly with free BDA under the reaction conditions to yield BDAFe(CO)$_3$. This is found not to be the case. Treatment of cyclooctatrieneiron tricarbonyl with 1 equiv of BDA at 60 °C for 3.3 h results in no reaction of triene complex and production of no BDAFe(CO)$_3$ (<2%).

To distinguish between mechanisms 3 and 4, a kinetic study must be performed. For mechanism 3, the rate of product formation should clearly depend on BDAFe(CO)$_3$ concentration, regardless of whether the formation of **20** or the conversion of **20** to product is rate determining.

For mechanism 4 various kinetic expressions may apply, depending on the relative magnitudes of k_1, k_{-1}, and k_2. Applying the steady-state approximation to the diene **2**, the reaction should obey the following rate law:

$$\text{rate} = \frac{k_1k_2[\text{BDAFe(CO)}_3][\text{triene}]}{k_{-1} + k_2[\text{BDAFe(CO)}_3]} \qquad (1)$$

If, as we suspected on the basis of earlier qualitative data, the trapping of the diene is efficient relative to ring closure, then

Table I. Kinetics of Reaction of BDAFe(CO)$_3$ with 1,3,5-Cyclooctatriene in Benzene at 60.0 °C

BDAFe(CO)$_3$:triene ratio	[BDAFe(CO)$_3$], M	First-order rate constant k_{obsd} (× 10^5), s^{-1}
22.4	0.101	1.9 ± 0.2[a,b]
44.8	0.202	2.0 ± 0.1[a,b]

[a] First order in 1,3,5-cyclooctatriene. [b] Rate determined by gas chromatography.

Table II. Kinetics of Reaction of BDAFe(CO)$_3$ with 1,3-Cyclohexadiene in Benzene

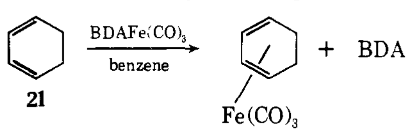
BDAFe(CO)$_3$: diene ratio	[BDAFe(CO)$_3$], M	Temp, °C	First-order rate constant k_{obsd} (× 10^4), s^{-1}
1:10.9	0.0139	50.0	6.8 ± 0.4[a,b]
1:20.5	0.0144	50.0	6.6 ± 0.5[a,b]
1:22.0	0.0144	50.0	7.0 ± 0.4[a,b]
1:39.7	0.0134	50.0	6.1 ± 0.4[a,b]
20.6:3	0.0857	30.0	5.6 ± 0.7[c,d]
19.1:1	0.0834	30.0	3.3 ± 0.4[c,d]
40.9:1	0.171	30.0	8.1 ± 0.7[c,d]

[a] First order in BDAFe(CO)$_3$. [b] Rate determined by infrared spectroscopy. [c] First order in 1,3-cyclohexadiene. [d] Low temperature workup; rate determined by gas chromatography.

at high BDAFe(CO)$_3$ concentrations, k_2[BDAFe(CO)$_3$] should be greater than k_{-1} and eq 1 simplifies such that rate = k_1[triene]; that is, the rate-determining step is ring closure of the triene, and the rate of formation of product will be independent of the concentration of BDAFe(CO)$_3$ (in contrast to mechanism 3). To test this possibility, we investigated the kinetics of the reaction between triene **1** and BDAFe(CO)$_3$ under conditions which employed a large excess of BDAFe(CO)$_3$ relative to triene **1**. Results are summarized in Table I.

The rate was monitored by following the appearance of the bicyclo[4.2.0]octadieneiron tricarbonyl complex, **4**, relative to an internal standard (hexadecane), using gas chromatography. The results show that under these conditions, the rate of the reaction has a first-order dependence on triene **1** and has no dependence on BDAFe(CO)$_3$, since doubling the BDAFe(CO)$_3$ concentration has no effect on the rate. Furthermore, the average first-order rate constant measured for the reaction (k_{obsd} = 1.95 × 10^{-5} s^{-1}, 60 °C, $\Delta G^{\ddagger}$ = 26.8 kcal/mol) matches very closely that for the ring closure of the triene **1** to diene **2** ($k_1 \sim 1.6 \times 10^{-5}$ s^{-1}, 60 °C, $\Delta G^{\ddagger}$ = 26.9 kcal/mol) estimated from the data of Huisgen.[7] These results are in clear agreement with the diene-trapping reaction, mechanism 4. The fact that the rate is independent of BDAFe(CO)$_3$ rules out mechanism 3, while the identity of the measured rate constant with that of the known k_1 for ring closure of the triene confirms mechanism 4. Thus, under conditions of excess BDAFe(CO)$_3$, diene trapping is rapid and the rate-determining step is ring closure of the triene to the diene tautomer.

The Kinetics of Reaction of BDAFe(CO)$_3$ with 1,3-Cyclohexadiene. To better understand the reaction between the bicyclic and tricyclic dienes and BDAFe(CO)$_3$, we have carried out kinetic studies of the reaction of BDAFe(CO)$_3$ with 1,3-cyclohexadiene, which serves as a model for the diene tautomers. Preliminary examination of this reaction revealed that 1,3-cyclohexadiene (**21**) reacts with BDAFe(CO)$_3$ to give cyclohexadieneiron tricarbonyl (**22**) in quantitative yield. The rate of this reaction is, in general, substantially faster than those of BDAFe(CO)$_3$ with cyclooctatrienes, due to lack of the requirement of ring closure which is rate limiting in the case of the trienes. Kinetic measurements were performed under conditions of both excess cyclohexadiene and excess BDAFe(CO)$_3$. Results are summarized in Table II.

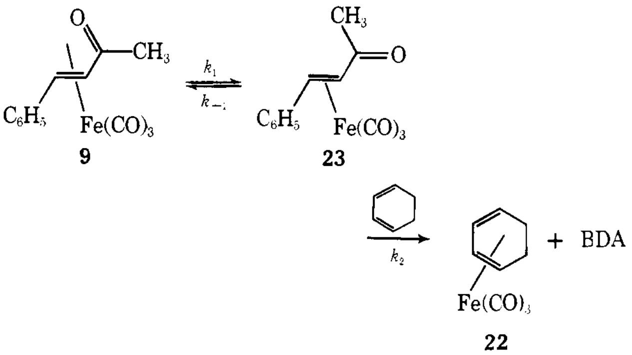


21 **22**

Under conditions of excess cyclohexadiene, the rate is conveniently monitored by FT infrared spectroscopy by measuring the disappearance of the 2066-cm^{-1} band of BDAFe(CO)$_3$ and the appearance of the 2043-cm^{-1} band of cyclohexadieneiron tricarbonyl (**22**). Both bands are very sharp and overlap of the bands is minimal. Excellent plots, first order in BDAFe(CO)$_3$, were obtained through at least 3 half-lives.[27] As seen in Table II, the rate constant k_{obsd} is independent of cyclohexadiene concentration under these conditions. Therefore at high diene concentrations the kinetics follow the simple first-order expression, rate = k_{obsd}[BDAFe(CO)$_3$].

The reaction was studied using a large excess of BDAFe(CO)$_3$ relative to cyclohexadiene. Since the presence of a large excess of BDAFe(CO)$_3$ precluded use of infrared spectroscopy for kinetic measurements, the rate was followed using gas chromatography, by monitoring the appearance of the cyclohexadiene complex relative to an internal standard, tetradecane. The increased rate under these reaction conditions also necessitated using lower reaction temperatures and a low temperature workup procedure for each point. The method of analysis resulted in considerable error and the rate constants reported in Table II for these experiments are substantially less accurate than those determined by FT IR spectroscopy. Nevertheless, the data did reveal that under these conditions, the rate was first order in cyclohexadiene and the observed first-order rate constant was roughly proportional to the concentration of BDAFe(CO)$_3$. Thus, under these conditions of excess BDAFe(CO)$_3$, the observed rate constant is a pseudo-first-order constant and the reaction is first order in both BDAFe(CO)$_3$ (as expected from the earlier results) and cyclohexadiene, where rate = k[BDAFe(CO)$_3$] [diene] and k_{obsd} = k[BDAFe(CO)$_3$].

The simplest and most reasonable mechanism which accounts for these results is shown below:



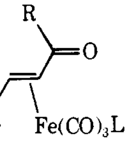
9 **23** **22**

The first-order dependence on only BDAFe(CO)$_3$ at high diene concentrations, yet overall second-order kinetics at low diene concentrations, suggests that an intermediate is formed reversibly which may be trapped by diene. The most reasonable structure we can envision for the intermediate is the 16 electron unsaturated intermediate **23**, which is formed by dechelation of the carbonyl group from BDAFe(CO)$_3$. Applying the steady-state approximation to **23**, the following rate law is obtained:

$$\text{rate} = \frac{k_1 k_2[\text{BDAFe(CO)}_3][\text{diene}]}{k_{-1} + k_2[\text{diene}]} \qquad (2)$$

At high diene concentrations, k_2[diene] > k_{-1} and eq 2 reduces to rate = k_1[BDAFe(CO)$_3$], where the rate-determining step is dechelation and formation of **23.** This is in agreement with the experimental results obtained at high diene concentrations where $k_{obsd} = k_1 = 6.6 \times 10^{-4}$ s^{-1}, 50 °C. At low diene concentrations, return to BDAFe(CO)$_3$ is rapid (k_{-1} > k_2[diene]) and the rate expression reduces to (k_1k_2/k_{-1})·[BDAFe(CO)$_3$][diene], where the observed pseudo-first-order rate constant is (k_1k_2/k_{-1}) [BDAFe(CO)$_3$] (entries 5-7 in Table II).

Several previously reported results have relevance to the proposed intermediate **23** and the proposition that the carbonyl group of the bound enone initially dechelates in preference to the carbon-carbon double bond. Dixneuf[28] and Cardaci[29] have both observed that reactions of substituted enoneiron tricarbonyl complexes with various donor ligands, such as P(OCH$_3$)$_3$,[28] P(CH$_3$)$_2$C$_6$H$_5$,[28] P(C$_6$H$_5$)$_3$,[29a] As(C$_6$H$_5$)$_3$,[29a] and Sb(C$_6$H$_5$)$_3$,[29] give complexes of the structure **24,** often under mild conditions. Formation of such complexes indicates that the carbonyl group of the bound enone is more weakly coordinated than the carbon-carbon double bond and supports the proposed carbonyl dechelation as the first step in reaction of BDAFe(CO)$_3$ with cyclohexadiene. Such a dechelation and formation of intermediates analogous to **23** may also account for formation of complexes of general structure **24.**[30]

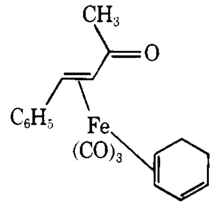


R = H, CH$_3$, C$_6$H$_5$

L = P(OCH$_3$)$_3$, P(CH$_3$)$_2$(C$_6$H$_5$), P(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$, Sb(C$_6$H$_5$)$_3$

24

An additional comment on the proposed mechanism is necessary. For kinetic arguments, we have treated the second-order step (k_2) in the proposed mechanism as a single step. However, it seems likely that this step proceeds by trapping the coordinatively unsaturated species **23** with cyclohexadiene to give an intermediate such as **25.** Dissociation of BDA from **25** and chelation of the second double bond of cyclohexadiene then results in product formation. This type of intermediate for displacement of BDA by dienes is analogous to that suggested for diene exchange in dieneiron tricarbonyl derivatives studied by Cais.[31]



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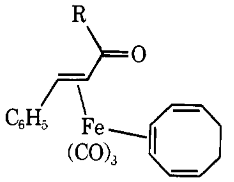
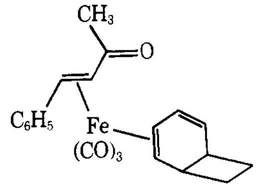
The reason for the high selectivity of BDAFe(CO)$_3$ for diene tautomers of cyclooctatriene derivatives remains to be addressed. The fact that mechanism 4 applies indicates a kinetic selectivity of BDAFe(CO)$_3$ for the diene relative to the triene tautomers. In addition, the mechanism of the reaction of BDAFe(CO)$_3$ with the diene tautomers (which all include planar 1,3-cyclohexadiene moieties) should be similar to that with cyclohexadiene. We feel that the slow rate of reaction of the triene tautomers is due to the nonplanar tub conformations of the triene derivatives. Assuming that formation of η^4-triene complexes would occur in a similar manner to that of cyclohexadiene complex, then a dihapto-bound intermediate, **26,** analogous to **25,** would be formed.[25] For such a species to form η^4-triene complexes, dissociation of BDA must occur *in addition to* distortion of the tub-shaped bound triene to a relatively planar conformation, in order to coordinate a second double bond to iron. The diene tautomers, however, require no such distortion by virtue of their planar cyclohexadiene moieties. Thus, it seems likely that the activation energy required for conversion of **26** to η^4-triene complexes would be considerably higher than the corresponding barrier for conversion of the analogous η^2-diene complexes **27** to η^4-diene complexes. Such an increased activation barrier for the conversion of the η^2-triene species to η^4-triene complexes could then account for the much lower rate of reaction of BDAFe(CO)$_3$ with cyclooctatrienes relative to the diene tautomers and the resulting high selectivity displayed in the reactions.



26



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Experimental Section

General. All materials were handled under an atmosphere of dried, oxygen-free nitrogen gas. Solvents were distilled prior to use. Melting points were uncorrected. ^{1}H NMR spectra were routinely recorded on a JEOL C-60HL spectrometer, whereas ^{1}H decoupled and ^{13}C NMR spectra were recorded on a Varian XL-100 FT NMR spectrometer. All ^{13}C chemical shifts are reported in parts per million downfield from internal Me$_4$Si. Routine infrared spectra were recorded on a Perkin-Elmer 421 spectrophotometer; quantitative measurements for kinetic studies were taken using matched CaF$_2$ cells (0.1 mm) with a Digilab FTS-14 FT infrared spectrophotometer. A Haake constant temperature bath was used for all kinetic experiments. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Analytical gas chromatography was performed on a Hewlett-Packard 5750 research chromatograph using a flame ionization detector, helium as a carrier gas, and aluminum columns (6 ft × 0.25 in.) packed with a 3% loading of silicon gum rubber UC-W98 on Chromosorb W (60-80 mesh).

The difficult preparative separation of complexes was achieved with a modified medium-pressure liquid chromatography system, comprised of a short scrubber column (15 × 250 mm) and a main column (15 × 1000 mm, Altex), each packed with silica gel (0.032-0.063 mm). The pressure source (60-80 psi) for the system was a cylinder of helium gas which was connected to metal solvent reservoirs.

Preparation of Benzylideneacetoneiron Tricarbonyl (BDAFe(CO)$_3$). Benzylideneacetone (BDA, 4.0 g, 27 mmol) and Fe(CO)$_5$ (10 ml, 75 mmol) were photolyzed in degassed benzene (150 ml) for 8 h using a 450-W Hanovia medium-pressure mercury arc lamp. The dark red solution was filtered, concentrated under reduced pressure, and then heated in degassed benzene for several hours at 60 °C to convert any BDAFe(CO)$_4$ to BDAFe(CO)$_3$. The solution was refiltered, concentrated, and then chromatographed under nitrogen on a silica gel column (2.8 × 30 cm) with degassed 5% ethyl acetate in benzene. The solution was concentrated to give dark red crystals (mp 88-89 °C, 60% overall yield), identical with that reported by Lewis.[15]

Reaction of BDAFe(CO)$_3$ and 1,3,5-Cyclooctatriene (1). A mixture of BDAFe(CO)$_3$ (3.58 g, 12.5 mmol) and 1,3,5-cyclooctatriene (0.84 g, 7.9 mmol) was heated under nitrogen at 61 ± 5 °C for 48 h in 150 ml of degassed benzene. The mixture was filtered, concentrated, and chromatographed on activity II basic alumina (2.5 × 28 cm) with hexane. The first yellow band was collected and, after solvent evaporation, yielded a yellow oil which was confirmed by ^{1}H NMR to be bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl[8,9,32] (1.61 g, 83% yield).

Reaction of BDAFe(CO)$_3$ and *cis*-Bicyclo[6.2.0]deca-2,4-triene (5b). BDAFe(CO)$_3$ (4.0 g, 14 mmol) and *cis*-cyclo[6.2.0]decatriene[33] (2.2 g, 17 mmol) were heated at 65 °C for 48 h under nitrogen in 150 ml of degassed benzene. The dark red solution was concentrated under reduced pressure and chromatographed on neutral activity II alumina with hexane. The yellow band was collected, and after concentration and removal of remaining triene by vacuum, the product was recrystallized at −78 °C from pentane to yield pale yellow crystals (3.6 g, 82% yield), identical by ^{1}H NMR with complex **7** as reported by Cotton.[12b]

Reaction of $BDAFe(CO)_3$ and *cis*-Bicyclo[6.1.0]nonatriene (5a). A mixture of $BDAFe(CO)_3$ (13.0 g, 45.7 mmol) and triene **5a**[33] (1.50 g, 12.7 mmol) was heated in 300 ml of degassed benzene at 65 ± 5 °C for 45 h. The reaction was constantly purged of oxygen by bubbling nitrogen through the solution. after cooling, the mixture was then filtered, concentrated, and chromatographed on a column (2.5 × 30 cm) of activity II alumina with degassed hexane. The first band was a yellow oil, 2.55 g, composed of the tricyclic diene complex, **10,** the dihydroindene complex, **14,** and the cyclononatetraene complex, **15,** in a 5.4:2.4:1 ratio (78% overall yield). Separation of the complexes was achieved with hexane on a medium-pressure liquid chromatography column (15 × 1000 mm) of silica gel at 70 psi. The tricyclic diene complex, **10,** which eluted first as a yellow oil, was identified by its ^{1}H NMR spectrum (C_6D_6, 100 MHz): δ 0.59 (dt, H_{8a}), 0.76–0.96 (m, H_{8b}), 1.14–1.30 (m, H_7, H_9), 1.84–2.02 (m, H_1, H_6), 2.90–3.12 (m, H_2, H_5), 5.05 (dd, H_3, H_4); $J_{2,3} = J_{4,5} = 6.5$, $J_{2,4} = J_{3,5} = 1.6$, $J_{3,4} = 4.2$, $J_{8a,7} = J_{8a,9} = 5.85$, $J_{8b,7} = J_{8b,9} = 1.35$, $J_{8a,8b} = 4.6$ Hz; ^{13}C NMR (C_6D_6) 21.5 (C_8), 24.0 (C_7, C_9), 43.4 (C_1, C_6), 66.4 (C_2, C_5), 86.8 (C_3, C_4), 212.8 ppm (carbonyls); IR (C_6H_6 solution) 2042, 1968 cm^{-1} ($MC{\equiv}O$). Anal. ($C_{12}H_{10}O_3Fe$) C, H, Fe. The dihydroindene complex **14** and the cyclononatetraene complex **15** eluted later and were identified by their ^{1}H NMR spectra.[6]

Reaction of $BDAFe(CO)_3$ and *syn*-9-Methylbicyclo[6.1.0]nonatriene (17). $BDAFe(CO)_3$ (2.8 g, 9.8 mmol) and *syn*-9-methylbicyclo[6.1.0]nonatriene[33] (0.83 g, 6.3 mmol) were heated under nitrogen in 300 ml of refluxing benzene for 39.5 h. After cooling, the reaction mixture was filtered, concentrated under reduced pressure, and chromatographed on a column (2.5 × 30 cm) of activity II alumina with hexane. The yellow band which emerged was collected, concentrated, and recrystallized from pentane at −20 °C to give the yellow crystalline *syn*-8-methyltricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl complex **19** (68% overall yield): mp 87–89 °C; IR (C_6H_6 solution) 2042, 1968 cm^{-1} (br) ($MC{\equiv}O$); ^{1}H NMR (100 MHz, C_6D_6) δ 0.88–1.26 (m, H_7, H_8, H_9, CH_3), 1.84–2.02 (br s, H_1, H_6), 2.90–3.16 (m, H_2, H_5), 5.07 (dd, H_3, H_4); ^{13}C NMR (C_6D_6) 7.5 (CH_3), 24.1 (C_8), 27.4 (C_7, C_9), 37.6 (C_1, C_6), 65.6 (C_2, C_5), 85.9 (C_3, C_4), and 212.0 ppm (carbonyls). Anal. ($C_{13}H_{12}O_3Fe$) C, H, Fe.

Preparation and Thermal Rearrangement of Tricyclo[4.4.0.0^{2,5}]deca-7,9-diene (6b). Ceric ammonium nitrate (2.0 g, 3.7 mmol) was added over a 15-min period to a solution of tricyclic diene complex **7** (0.40 g, 1.5 mmol) in 10 ml of degassed acetone at −30 °C. After 20 additional min of stirring, a saturated salt solution at 0 °C was added, and the mixture was extracted three times with cold pentane. The extracts were washed until colorless with cold brine, and then dried and concentrated at −20 °C. The colorless oil was then bulb-to-bulb distilled under high vacuum at −20 °C to yield 0.16 g (84% yield) of the tricyclic diene **6b:** ^{1}H NMR (CS_2) δ 2.0–2.6 (m, H_3, H_4), 2.8–3.0 (m, H_2, H_5), 3.12 (br s, H_1, H_6), 5.3–5.7 (m, H_7, H_8, H_9, H_{10}); ^{13}C NMR (CS_2, −20 °C) 29.4 (C_3, C_4), 40.3 (C_2, C_5 or C_1, C_6), 50.2 (C_1, C_6 or C_2, C_5), 121.6 (C_7, C_{10} or C_8, C_9), 126.3 ppm (C_8, C_9 or C_7, C_{10}).

At 45 °C, the tricyclic diene **6b** cleanly underwent a thermal rearrangement to the triene **5b.** The rate of the isomerization was determined by monitoring ^{1}H NMR integrals of resonances of both tautomers. Using standard kinetic analysis, the first-order rate constant k_1 was calculated to be 4.2×10^{-5} s^{-1} at 45 °C ($\Delta G^{\ddagger} = 25.1$ kcal/mol).

The equilibrium constant for the tautomerization was determined to be 40 by ^{13}C NMR. In the first method using gated decoupling, the ^{1}H decoupler frequency was gated on only during data acquisition to avoid NOE effects, and long pulse delay times (60 s) were employed. In the second method, the paramagnetic relaxation reagent tris(acetylacetonato)chromium(III)[24] (0.03 M) was added to the mixture of equilibrating tautomers to reduce the values of ^{13}C T_1 relaxation times. Using the two methods, the ^{13}C NMR resonances were recorded, cut out, and weighed, and the values obtained for the relative integrals were 38.5 and 41.6, respectively, which corresponds to K_{eq}. From the average value of K_{eq}, 40, the rate of ring closure, k_{-1}, is calculated to be 1.1×10^{-6} s^{-1} at 45 °C ($\Delta G^{\ddagger} = 27.4$ kcal/mol) from the relationship $k_{-1} = k_1/K_{eq}$.

Preparation and Thermal Rearrangement of Tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (6a). Ceric ammonium nitrate (624 mg, 1.14 mmol) was added over a 25-min period to a solution of complex **10** (120 mg, 0.465 mmol) in 10 ml of degassed acetone at −30 °C. The mixture was extracted (3 × 10 ml) with isopentane at −30 °C, and the combined extracts were washed with aqueous NaCl solution at −30 °C. The colorless solution was dried over $MgSO_4$, concentrated under reduced pressure, and vacuum distilled at −30 °C to give 28 mg (51% yield) of the tricyclic diene **6a:** ^{1}H NMR ($CDCl_3$) δ 0.27–0.53 (m, H_{8a}, H_{8b}), 1.65–1.79 (m, H_7, H_9), 2.47–2.59 (br s, H_1, H_6), 5.37–5.83 (m, H_2, H_3, H_4, H_5).

At 30 °C, the tricyclic diene **6a** underwent a clean thermal isomerization in $CDCl_3$ to the bicyclic triene **5a.** The rate of the isomerization was determined by monitoring the resonances of the diene **6a** at δ 0.27–0.53 (H_{8a}, H_{8b}) and the triene **5a** at δ −0.13 (H_9, syn). Standard kinetic analysis yielded the first-order rate constant k_1 for the ring opening of **6a** to **5a**, $k_1 = 2.2 \times 10^{-4}$ s^{-1} at 30 °C ($\Delta G^{\ddagger} = 22.9$ kcal/mol).

Preparation and Thermal Rearrangement of *syn*-8-Methyltricyclo[4.3.0.0^{7,9}]nona-2,4-diene (18). Ceric ammonium nitrate (1.59 g, 2.9 mmol) was added over a 25-min period to a solution of the methyl tricyclic diene complex **19** (0.137 g, 1.16 mmol) in 10 ml of degassed acetone at −30 °C. The mixture was extracted with isopentane (3 × 10 ml) and washed with saturated aqueous NaCl solution at −30 °C. The solution was dried with $MgSO_4$, concentrated, and vacuum distilled at −30 °C to give a colorless oil, the tricyclic diene **18:** ^{1}H NMR ($CDCl_3$) δ 0.58 (sextet, H_8), 1.13 (d, CH_3), 1.68 (br d, H_7, H_9), 2.52 (br s, H_1, H_6), 5.43–5.96 (m, H_2, H_3, H_4, H_5), $J_{8,CH_3} = 5.9$, $J_{8,7} = J_{8,9} = 5.8$ Hz; ^{13}C NMR ($CDCl_3$, −34 °C) 7.1 (CH_3), 10.9 (C_8), 25.6 (C_7, C_9 or C_1, C_6), 30.6 (C_1, C_6 or C_7, C_9), 121.6 (C_2, C_5 or C_3, C_4), 127.3 ppm (C_3, C_4 or C_2, C_5).

At 30 °C the tricyclic diene **18** in $CDCl_3$ underwent a clean thermal isomerization to the triene **17**. The rate of the isomerization was monitored, by integration of ^{1}H NMR resonances, by the disappearance of the bridgehead protons (H_1 and H_6) of the diene **18,** and the growth of the vinyl region of both tautomers (**17** and **18**). Standard kinetic analysis yielded the first-order rate constant k_1 for the ring opening of **18** to **17**, $k_1 = 1.7 \times 10^{-4}$ s^{-1} at 30 °C ($\Delta G^{\ddagger} = 23.0$ kcal/mol).

Kinetics. General. Benzene was stirred with concentrated H_2SO_4, washed with distilled water and aqueous $NaHCO_3$, and dried with anhydrous $MgSO_4$. It was then distilled from sodium chips onto molecular sieves, and was degassed on a vacuum line immediately prior to preparation of samples. 1,3-Cyclohexadiene and 1,3,5-cyclooctatriene were bulb-to-bulb distilled and stored under nitrogen over molecular sieves. Benzylideneacetoneiron tricarbonyl (**9**) was purified as previously described.

Kinetics of the Reaction of 1,3,5-Cyclooctatriene (1) with Excess $BDAFe(CO)_3$. Stock solutions of both hexadecane (internal standard) in triene **1** and $BDAFe(CO)_3$ were prepared under streams of nitrogen using degassed, purified benzene. After mixing the stock solutions in various proportions, the samples were filtered into Schlenk tubes, degassed on a vacuum line over molecular sieves. and stored frozen under nitrogen until use. Each sample was then transferred to another Schlenk (fitted with a rubber septum) and heated under nitrogen to 60.0 ± 0.1 °C in a constant temperature bath. Each aliquot was removed by a syringe and chromatographed on a 40 × 12 mm column of activity II Baker alumina with degassed hexane to remove BDA and $BDAFe(CO)_3$ from the product **4.** The solvent was removed under reduced pressure, and the remaining liquid was gas chromatographed on a UC-W98 column (6 ft × 0.25 in.) at 135 °C. The rate was then determined by the appearance of the bicyclic diene complex **4** with respect to the internal standard, hexadecane. The peaks were photocopied, cut out, weighed, and the areas converted to concentrations. Standard kinetic analysis showed the reaction to be first order in cyclooctatriene (results shown in Table II).

Reaction of Cyclooctatrieneiron Tricarbonyl (3) with BDA. Cyclooctatrieneiron tricarbonyl (**3**,[11] 99 mg, 0.40 mmol) and BDA (57 mg, 0.39 mmol) were heated in degassed benzene at 60 °C for 3 h 20 min. The solution was periodically monitored by FT IR spectroscopy; no decrease of the 2043 cm^{-1} (triene complex **3**) or appearance (less than 2%) of a band at 2066 cm^{-1} ($BDAFe(CO)_3$) was noted. The solution was then concentrated and chromatographed on a column of activity II basic alumina with hexane. The yellow band which emerged was collected, concentrated, and confirmed by ^{1}H NMR to be unreacted triene complex **3.**

Kinetics of the Reaction of $BDAFe(CO)_3$ with Excess 1,3-Cyclohexadiene (21). A stock solution of $BDAFe(CO)_3$ was prepared by weighing an exact amount of complex into a 10-ml volumetric flask under a stream of nitrogen and diluting with degassed, purified benzene. The stock solution was then diluted in various proportions under nitrogen, and each sample was filtered into a Schlenk tube over molecular sieves, degassed on a vacuum line, and stored frozen under nitrogen until use. Each sample was then pipetted into another nitrogen-filled Schlenk tube, fitted with a rubber septum, and heated in a constant temperauure bath to 50.0 ± 0.1 °C. The kinetic experiment was begun when an excess of cyclohexadiene was added to the heated complex. Aliquots were removed with a syringe, quenched by injection into cold nitrogen-filled Schlenk tubes fitted with rubber septa, and frozen at −30 °C until infrared spectra were recorded. The $MC\equiv O$ stretching frequencies of both $BDAFe(CO)_3$ ($2066\ cm^{-1}$) and cyclohexadiene complex **22** ($2043\ cm^{-1}$) were monitored in duplicate scans on a Digilab FTS-14 infrared spectrophotometer. The bands were sharp and overlap was minimal; nevertheless, errors due to overlap were corrected for by obtaining spectra of standard solutions of both complexes. Concentrations were then determined from a working absorbance vs. concentration curve, and subsequent $\ln[BDAFe(CO)_3]$ vs. time plots showed good first-order kinetics through at least 3 half-lives. First-order rate constants for the reaction are shown in Table II.

Kinetics of the Reaction of 1,3-Cyclohexadiene with Excess $BDAFe(CO)_3$. Solutions of $BDAFe(CO)_3$ were prepared and degassed as described above. After heating to 30.0 ± 0.1 °C, a degassed solution of 1,3-cyclohexadiene and tetradecane (internal standard) in benzene was added by pipet, and time for the kinetic experiment was begun. Aliquots were removed by syringe, quenched by addition to a cold Schlenk tube, and stored at −30 °C until ready for workup. Each aliquot was then chromatographed on a 30 × 12 mm column of activity II Baker alumina (maintained at −5 ± 5 °C with a stream of cold nitrogen gas) with approximately 40 ml of degassed isopentane, in order to separate BDA and $BDAFe(CO)_3$ from the product complex **22**. The isopentane was partially removed by reduced pressure and finally with a stream of nitrogen; great care was exercised to avoid loss of cyclohexadiene complex. Each aliquot was then gas chromatographed on a UC-W98 column (6 ft × 0.25 in.) at 115 °C. The appearance of the cyclohexadiene complex **22** was then monitored in comparison to the constant tetradecane standard. The peaks were photocopied, cut out, and weighted, and converted to concentrations. Standard kinetic analysis showed the reaction to be first order in cyclohexadiene **21**; rate constants are shown in Table II.

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(20) The signal for H_1 and H_6 appears as a broad singlet, with a width at half-height of ca. 7 Hz. Irradiation of H_2 and H_5 sharpens H_1 and H_6 to a line with a width of ca. 3.5 Hz. Protons H_1 and H_6 are also coupled to H_3 and H_4 (ca. 1 Hz), as evidenced by sharpening of H_1 and H_6 upon irradiation of H_3 and H_4. Based on these observations, $J_{6,7} = J_{1,9}$ must be less than 1.5 Hz. It is also likely that the major remaining coupling is actually $J_{6,9} = J_{1,7}$ (ca. 1.5 Hz), in agreement with other bicyclo[2.1.0]pentane derivatives.[21]
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(25) An equally likely structure for intermediate **20** would be **26** where the iron is coordinated to the central double bond in the cyclooctatriene ring.
(26) No intermediate such as **20** can be detected by ^{1}H NMR or IR spectroscopy; if mechanism 3 applies, the relative values of k_1', k_{-1}', and k_2' must be such that the concentration of **20** does not build to an appreciable value during the course of the reaction.
(27) Each kinetic sample gave excellent first-order plots with very little deviation (less than 7%); however, the rate constants from sample to sample varied by about 10%, well outside the experimental error in determining the values of k_{obsd}. This discrepancy apparently is due to traces of water, oxygen, or other impurities which may affect the rate of formation of intermediate **23**.
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