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Mechanism of Olefin Rearrangements Induced by Iron Carbonyls. Rearrangements in the Bicyclo[6.1.0]nonene System[1]

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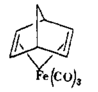
9,9-Dichlorobicyclo[6.1.0]non-4-ene (**28**) rearranged to the bicyclonon-3-ene isomer **29** and ultimately to bicyclonon-2-ene (**30**) in the presence of $Fe_2(CO)_9$. The tetracarbonyliron(0) complex of the bicyclonon-3-ene isomer (**33**) was isolated and subjected to similar reaction conditions but failed to produce the rearrangement product **30**. Furthermore, the $Fe(CO)_4$ complex corresponding to compound **30** did rearrange with the iron center intact, producing complex **33**. These results appear to suggest that two different mechanisms are operating here, one in which an iron carbonyl species is attached to the olefin throughout the rearrangement process and the other possibly not involving intermediacy of an iron carbonyl complex. The crystal and molecular structure of complex **33** was determined by single-crystal X-ray analysis and refined by full-matrix least-squares calculations to $R = 0.092$ over 1420 statistically significant reflections measured by diffractometer. Crystals are triclinic, space group $P\bar{1}$, $a = 7.094$ (4) Å, $b = 16.936$ (8) Å, $c = 6.530$ (4) Å, $\alpha = 95.49$ (5)°, $\beta = 100.16$ (5)°, $\gamma = 104.05$ (5)°, $U = 741.2$ Å^3, and $Z = 2$. The coordinated alkene occupies one equatorial site of a trigonal-bipyramidal iron coordination geometry, mean Fe–C(alkene) = 2.148 Å, Fe–C(carbonyl) = 1.794 Å. The cyclooctene ring is in a C_s chair–boat conformation.

The reaction of iron carbonyls with olefins, in which isomerization of the olefin is the predominant transformation, is one of the most extensively studied in the area of organoiron carbonyl chemistry.[3] The results of these studies have been strikingly uniform; because of this high degree of uniformity, the reaction has taken on a quality of predictability and has therefore come to be regarded as unexceptional and well understood. Indeed, only two mechanistic proposals have received serious consideration since the reaction was first observed, and the overwhelming weight of evidence has eliminated one of these as a viable possibility.[4]

In general, the reaction involves reorganization of one olefin to another in the presence of catalytic[8] amounts of an iron carbonyl (usually $Fe(CO)_5$, $Fe_2(CO)_9$, or $Fe_3(CO)_{12}$), in an inert atmosphere and inert solvent such as hexane, by use of either elevated temperature or photochemical procedures. In all cases the original σ framework of the olefin is undisturbed, so that the reaction is limited to olefin rearrangements which come about by a sequence of hydrogen shifts.

The interaction of iron carbonyls with olefins was first observed in 1930 by Reihlen and co-workers in the synthesis of butadieneiron tricarbonyl,[9] but reports of reaction of iron carbonyls with monoolefins did not appear until 1955, when Asinger and Berg described the conversion of 1-dodecene in the presence of $Fe(CO)_5$ to a mixture of the linear isomers of dodecene.[10] Similar trends have since been reported for 1-undecene,[11a–c] *n*-octenes, and *n*-hexenes,[11d] always with the result that the double bond was seen to migrate preferentially to an internal position. Manuel has observed the reaction of various hexenes in the presence of catalytic quantities of $Fe_3(CO)_{12}$, in which, when conditions of equilibrium are achieved, product ratios reflect values expected on the basis of thermodynamic stabilities of the hydrocarbons themselves.[6] Thus, at equilibrium 1-hexene produced a mixture of *cis*-2-hexene (16%), *trans*-2-hexene (58%), and 3-hexenes (25%), values calculated on the basis of thermodynamic stabilities of which were 20, 47, and 32%, respectively. Furthermore, under similar reaction conditions, both 4-methyl-1-pentene and 2-methyl-1-pentene yielded identical product mixtures composed of these hydrocarbons as well as 2-methyl-2-pentene and 4-methyl-2-pentene with ratios in excellent agreement with values based on predicted thermodynamic stabilities within this series.

Much of the work in this area has been conducted with cyclic olefins. Following their synthesis of norbornadieneiron tricarbonyl (**1**),[12] Pettit and co-workers sought other examples in which complexation of nonconjugated diene systems was possible. In attempts to prepare the analogous tricarbonyl complexes of 1,4-cyclohexadiene (**2**) and 1,5-cyclooctadiene (**3**) by heating the appropriate dienes in the presence of $Fe(CO)_5$, the conjugated cyclohexadieneiron tricarbonyl (**4**) and uncomplexed 1,3-cyclooctadiene (**5**), respectively, were obtained, the latter in essentially quantitative conversion.[13]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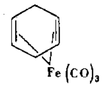
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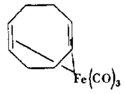
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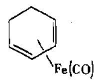
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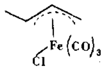
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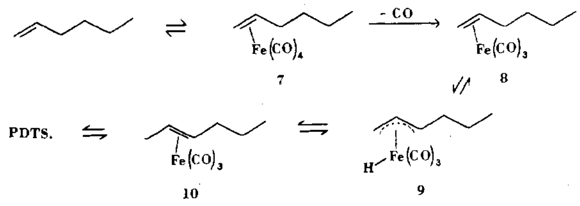
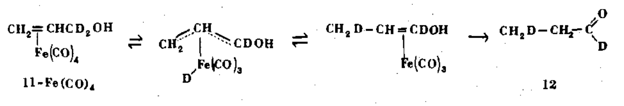
Organometallic intermediates in reactions of this kind have not been isolated, so that mechanistic proposals have been largely speculative and based primarily on implications of results as well as on analogy with similar reactions of other transition metals. Two fundamental mechanistic proposals have emerged.[4] The first of these, an addition–elimination process involving 1,2-hydrogen shifts, was based on analogy with isomerizations occurring during hydroformylation reactions catalyzed by dicobalt octacarbonyl,[14] but the evidence indicates that isomerizations in iron carbonyl-catalyzed processes take place via 1,3-hydrogen shifts. The more successful mechanistic proposal, made independently by Manuel[6] and Pettit[13,15] in 1962, was based on analogy with the reaction of butadieneiron tricarbonyl with HCl to provide π-butenyliron tricarbonyl chloride (**6**)[16] and with the existence of such complexes with other transition metals. This mechanism enjoys wide acceptance today. Scheme I illustrates the essential features of the mechanism. The reactive $Fe(CO)_4$ species[17] is generated either thermally or photochemically in the presence of the olefin (1-hexene is used here) to form a

Scheme I

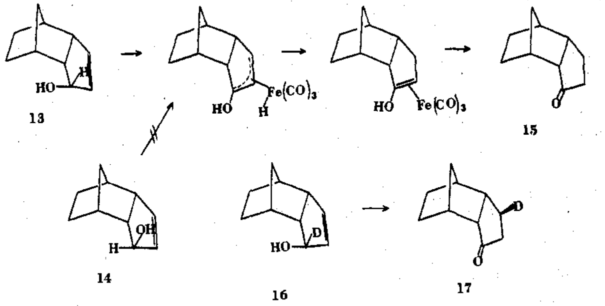


Scheme II



11-Fe(CO)₄ **12**

Scheme III

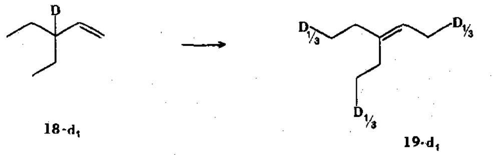


13 **14** **15** **16** **17**

monoolefiniron tetracarbonyl complex, **7**.[18] Under conditions favorable for formation of $Fe(CO)_4$, CO is lost from complex **7** to produce the coordinatively unsaturated iron tricarbonyl species **8**, which can stabilize itself by removal of a hydrogen atom from an allylic position in the complexed olefin to provide the π-allylhydridoiron tricarbonyl complex **9**. This intermediate, crucial to the mechanism from the point of view of its ability to explain observed results, ultimately gives rise to products via the rearranged iron tricarbonyl **10**, which can abstract another allylic hydrogen atom or thermally degenerate.

A large body of evidence has been accumulated which appears to support this mechanism. It has been found, for example, that isotopically labeled 3,3-dideuteriopropen-3-ol (**11**) yields 1,3-dideuteriopropanal (**12**) when treated with $Fe(CO)_5$ at elevated temperature;[19,20] the suggested mechanism is the π-allylhydridoiron tricarbonyl mechanism (Scheme II), henceforth referred to simply as the π-allyl mechanism. The reaction has been shown subsequently to be stereospecific with respect to the hydrogen atom transferred. Thus, the endo-tricyclic allyl alcohol **13**, but not its exo epimer **14**, provided the saturated ketone **15**, presumably by the pathway illustrated in Scheme III.[21] Furthermore, the site to which the hydrogen was transferred retained the exo stereochemistry required by the π-allyl mechanism (**16** → **17** in Scheme III), and deuterium-label scrambling between different systems was not observed when a mixture of **16** and unlabeled cyclohex-2-en-1-ol was treated with $Fe(CO)_5$.[22] However, the stereochemical consequences of these reactions, while lending support to the π-allyl mechanism, cannot in themselves be regarded as surprising or unusual, nor are they unambiguous or conclusive. The only possible reaction is one which takes place on the exo face of the tricyclic alcohols **13** and **16**, the endo face being sterically protected from attack by a reaction-inducing iron species, whatever its nature.

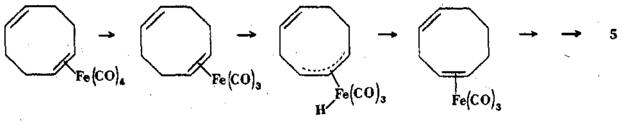
Casey and Cyr have presented persuasive arguments for hydrocarbon rearrangements which appear to take place via a π-allyl mechanism.[23] 3-Ethyl-1-pentene-*3*-d_1 (**18**) treated with catalytic amounts of $Fe_3(CO)_{12}$ at 80 °C in octane solution produced 3-ethyl-2-pentene-d_1 (**19**) in which the deuterium label was statistically distributed among the three terminal methyl groups. As in the isomerization of **16** to **17**,



18-d_1 **19**-d_1

the rearrangement was shown to be intramolecular with regard to the transferred deuterium atom; hence a mixture of **18** and an excess of 3-methyl-1-butene under reaction conditions quoted above showed no intermolecular deuterium exchange. No substantial deuterium isotope effect on reaction rate was observed, and recovered **18** at short reaction times indicated that deuterium migration had occurred about twice as fast as olefin rearrangement (to **19**), at the same time that 1,1,1-trideuterio-3-ethyl-2-pentene (**19**-d_3) was shown to scramble deuterium about 3.5 times more slowly than the **18** → **19** rearrangement. These results were interpreted in terms of the π-allyl mechanism, in which the rate of isomerization of complexed olefin is faster than decomplexation to free olefin.

Scheme IV

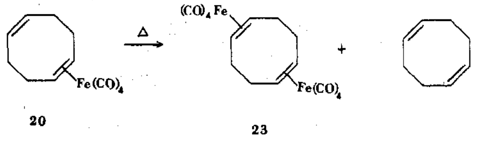


20 **21** **22**

Our own results indicate that there are problems with the π-allyl mechanism as it was originally concerned and currently viewed. They show that (1) $Fe(CO)_4$–olefin complexes, at least in the cases we will discuss, *do not* give rise to rearrangement products under conditions in which the compounds suffer thermal degradation and that (2) under conditions in which certain $Fe(CO)_4$–olefin complexes are not destroyed (decomplexation), rearrangement processes can occur which are strikingly different from cases in which the initially uncomplexed olefin is treated with iron carbonyls. We shall speculate later on what these results may imply with regard to accepted mechanisms for the rearrangement.

Pettit and Arnet, as mentioned previously, observed the rearrangement of 1,5-cyclooctadiene to its 1,3 isomer[13] in the presence of $Fe(CO)_5$ at 115 °C, the reaction proceeding quantitatively with catalytic amounts of iron carbonyl reagent. The π-allyl mechanism (Scheme IV) seemed completely plausible in its application to this transformation;[15b] the absence of 1,3-diene complex was explained on the basis of its presumed thermal instability due to strain induced in the formation of the planar diene arrangement necessary for complexation with an $Fe(CO)_3$ unit, an assumption since verified.[24]

1,5-Cyclooctadieneiron tetracarbonyl (**20**), the immediate precursor[18] of the coordinatively unsaturated monoolefiniron tricarbonyl complex **21** from which the π-allylhydridoiron complex **22** is formed in the currently accepted mechanism (see Scheme IV), has been produced as an unstable but isolable oil by irradiation of solutions of $Fe(CO)_5$ and 1,5-cyclooctadiene.[24] The complex **20** was found to decompose on standing by a disproportionation process in which 1,5-cyclooctadiene and 1,5-cyclooctadienebis(iron tetracarbonyl) (**23**) was produced. Complex **23** is a reasonably stable crystalline solid. In experiments of our own, we have subjected **23**[25] to reaction conditions expected to result in rearrangement. The complex decomposes thermally (refluxing pentane) to give only 1,5-cyclooctadiene as the initial hydrocarbon product. Continued heating eventually produces the rearranged 1,3 isomer, but its appearance is due to a subsequent reaction, probably involving catalysis by $Fe_3(CO)_{12}$, an iron carbonyl produced in substantial amounts in the initial decomposition of **23**.

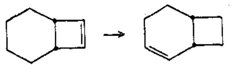


20 **23**

Prolonged irradiation of the iron pentacarbonyl–1,5-cyclooctadiene solution yielded another complex, the originally sought[13] 1,5-cyclooctadieneiron tricarbonyl (**3**), as a stable crystalline material. In none of the investigations involving 1,5-cyclooctadiene complexes was 1,3-cyclooctadiene (**5**) detected, either in its complexed or in its uncomplexed forms, suggesting that the monoolefin–iron tetracarbonyl complexes are not precursors for species responsible for rearrangement.

Results

We have been investigating rearrangements of strained olefins induced by $Fe_2(CO)_9$, specifically those of bicyclo[4.2.0]oct-7-ene (**24**), which rearranges to bicyclo[4.2.0]oct-2-ene (**25**) with a surprisingly high reaction rate,[26] and bicyclo[6.2.0]dec-9-ene (**26**), which produces a more complex mixture of hydrocarbons whose structures are currently being elucidated.[27] The unusually high reaction rate for these systems, compared with that of, for example, 1,5-cyclooctadiene, first attracted us into a more careful investigation in this area, especially in light of the strain which must be incurred in formation of the first π-allylhydridoiron tricarbonyl intermediate (**27**), in which bond angles at each of the three carbons of the allylic system approach 90°. The investigation has been extended to the bicyclo[6.1.0]nonenes as examples of systems in which the migrating double bond was not contained in the strain-providing element of the molecule, and it is these molecules which are the subject of this report.



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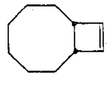

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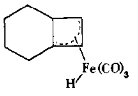

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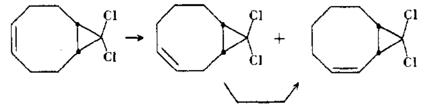
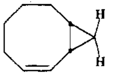
9,9-Dichlorobicyclo[6.1.0]non-4-ene (**28**) rearranged rapidly in the presence of $Fe_2(CO)_9$ in refluxing hexane to a mixture of the isomeric 3-ene (**29**) and 2-ene (**30**). Very short reaction times (ca. 5 min, the time required for complete disappearance of starting material **28**) provided **29** as the major product with **30** as a contaminant; very long reaction times (e.g., 40 h), on the other hand, produced mainly 9,9-dichlorobicyclo[6.1.0]non-2-ene (**30**). That **29** gave rise to **30** was demonstrated by reacting independently synthesized bicyclonon-3-ene (**29**) and subjecting this pure material to the conditions described above and again obtaining **30** as the major product contaminated only by small amounts of **29**. The ultimate reaction product, **30**, was shown to be completely stable under these reaction conditions. It was found that refluxing pentane and $Fe_2(CO)_9$ was sufficient to effect rearrangement of **28**. The reaction sequence was identical for the corresponding hydrocarbon bicyclo[6.1.0]non-4-ene, in which rearrangement to the 3- and 2-ene isomers was demonstrated. The present study was conducted with the chlorinated analogues because of greater ease of synthesis of starting materials, more convenient reaction rates, and greater stability of isolated iron carbonyl complexes when chlorine atoms were present in the molecule.



28 29 30



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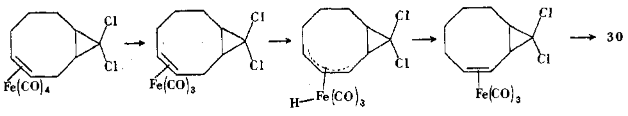
The formation of products **29** and **30** and the conversion of **29** to **30** was expected on the basis of earlier results of a study by Gardner and co-workers in which the hydrocarbon **31** was shown to be the most stable isomer among bicyclo[6.1.0]nonenes under potassium *tert*-butoxide-induced equilibrium conditions.[28] As mentioned previously, we were able to duplicate Gardner's results using $Fe_2(CO)_9$ and hydrocarbons corresponding to the dichlorobicyclic compounds **28**–**30**.

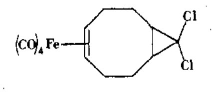
Obvious parallels exist between our results with regard to the **28** → **29** → **30** rearrangements and that observed by Pettit[13] and Koerner von Gustorf[24] for 1,5-cyclooctadiene to 1,3-cyclooctadiene. In the case of our experiments, we saw advantage in the fact that we could isolate all uncomplexed intermediates whereas in the previous case, 1,4-cyclooctadiene had apparently not been observed,[29] and we could therefore develop insights not previously possible.

Scheme V



33 35

The synthesis of the monoolefin complex **32** was attempted after the method of Koerner von Gustorf[24] by irradiation of iron pentacarbonyl–benzene solutions containing **28**, since this complex was the assumed precursor for the reaction in the way that the π-allyl mechanism is usually viewed. No **32** could be detected. Instead a stable yellow crystalline complex was obtained which proved to be the iron tetracarbonyl complex of rearranged olefin **29** on the basis of the elemental analysis, spectral characteristics, and production of **29** when the complex was oxidatively degraded with $Ce(NH_4)_2(NO_3)_6$ in acetone.



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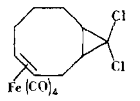

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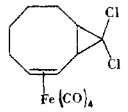

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Complex **33**, as a potential precursor to π-allyl complex **35** required by the accepted mechanism, should be thermally unstable and ultimately give rise to the rearrangement product **30**, as shown in Scheme V. Hexane solutions of **33** were heated and monitored periodically by infrared spectroscopy until iron–carbonyl absorptions due to complex **33** were essentially gone, a process which occupied about 3 h. Infrared spectra of the residue after removal of solvent showed the presence of **29** largely uncontaminated with **30**.[30] When the reaction was repeated with $Fe_2(CO)_9$ present, decomposition of **33** to **29** was rapid relative to rearrangement of **29** to **30**, but here rearrangement did occur. Whatever the mechanism for rearrangement of **29** to **30**, complex **33** is not part of it, and by implication the mechanism shown in Scheme V cannot feature the intermediacy of **33**.

The iron tetracarbonyl complex **34** of the ultimate rearrangement product was synthesized in a similar procedure by irradiation of iron pentacarbonyl–benzene solutions of the bicyclononene **30**. This complex is a crystalline solid which is not particularly sensitive to air but decomposes in solution, so that purification was impossible. The complex was identified from its infrared spectrum as an iron tetracarbonyl complex and as a complex of **30** because $Ce(NH_4)_2(NO_3)_6$ decomposition in acetone provided only 9,9-dichlorobicyclo[6.1.0]non-2-ene (**30**).

By careful dissolution of complex **34** in acetone below 30 °C, cooling to −5 °C, and allowing the solution to stand for several hours, a large amount of a crystalline material was obtained which proved to be identical in every respect, including $Ce(NH_4)_2(NO_3)_6$ decomposition to **29**, with the stable tetracarbonyl complex **33**. This is a remarkable result; it represents the first demonstration of contrathermodynamic rearrangement of an olefin by iron carbonyl involvement. Clearly such an occurrence must be due to the presence of iron complexed to the olefin throughout the rearrangement sequence, since under other conditions the thermodynamic product is the bicyclononene **30**.

We have determined the crystal and molecular structure of tetracarbonyl-η^2-{9,9-dichlorobicyclo[6.1.0]non-3-ene}iron(0) (**33**), which we regard as central to arguments and results we

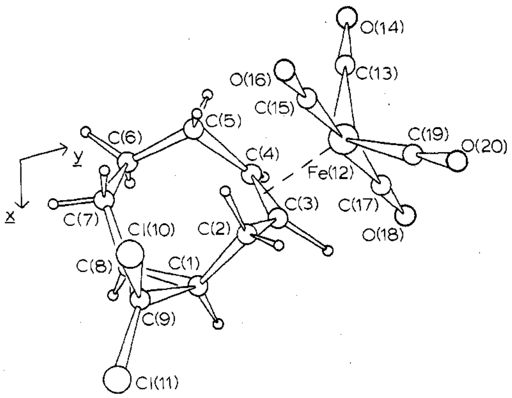


Figure 1.

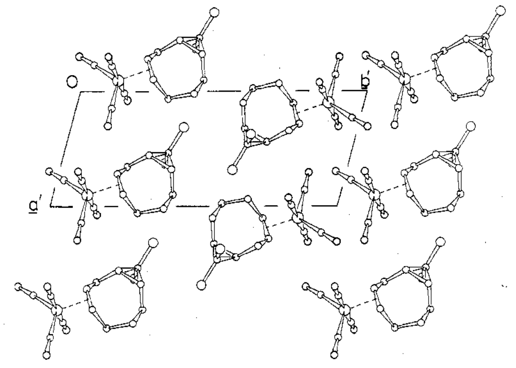


Figure 2.

present in this work. The crystals contain discrete, monomeric ($C_9H_{12}Cl_2$)Fe(CO)$_4$ molecules. A view of the molecular structure is shown in Figure 1, together with the atom numbering scheme. Intramolecular distances and angles are given in Table I. Figure 2 shows the arrangement of these complex molecules in the crystal. Intermolecular separations ≤3.50 Å between the nonhydrogen atoms, listed in Table II correspond to normal van der Waals type interactions.

The coordination geometry at the iron atom is distorted trigonal bipyramidal with two carbonyl groups and the midpoint of the C(3)–C(4) bond defining the equatorial plane while the remaining two carbonyl groups occupy axial sites. The very similar distances from the olefinic C(3) and C(4) atoms to the axial carbonyl carbon atoms C(15) and C(17) (2.743 (16)–2.810 (17) Å) demonstrate that the axial C–Fe–C line approximately bisects the C(3)–C(4) bond. This arrangement and the associated Fe–C distances are in good accord with those found for all previously characterized (alkene)Fe(CO)$_4$ complexes.[31-39]

None of the individual Fe–C(carbonyl) distances in the present study departs significantly from their mean (1.794 Å) which lies close to the 1.799–1.810 Å range for the corresponding means in the recent accurately determined iron tetracarbonyl complexes of *cis*-2,3-dicarbomethoxymethylenecyclopropane,[36] acenaphthylene,[37] 3-methylene-*exo*-4-vinyldihydrofuran-2(3*H*)-one,[38] and diphenylfulvene.[39] (The relatively large esd's obtained in the present study obscure any small differences which might exist between axial and equatorial Fe–C(carbonyl) bond lengths.) In these four accurately determined structures[36-39] the alkene mid-point–Fe–equatorial C (carbonyl) angles are approximately equal (Δ range 2.2–3.9°) and the mean Fe–C(alkene) distance at 2.148 Å found in the present study is thus in very good agreement with those from these other structural studies but a larger difference (Δ 10.2°) occurs between the corresponding equatorial angles. We ascribe the larger difference found here to crystal packing effects since there is no obvious intracomplex steric or electronic factor which could be responsible.

Table I. Interatomic Distances (Å) and Angles (deg)

(a) Distances

C(1)–C(2)	1.512 (15)	Fe(12)–C(3)	2.150 (11)
C(1)–C(8)	1.525 (15)	Fe(12)–C(4)	2.146 (10)
C(1)–C(9)	1.494 (15)	Fe(12)–M[a]	2.026 (11)
C(2)–C(3)	1.483 (16)	Fe(12)–C(13)	1.805 (12)
C(3)–C(4)	1.427 (16)	Fe(12)–C(15)	1.765 (13)
C(4)–C(5)	1.541 (15)	Fe(12)–C(17)	1.792 (13)
C(5)–C(6)	1.561 (15)	Fe(12)–C(19)	1.814 (13)
C(6)–C(7)	1.528 (17)	C(13)–O(14)	1.136 (16)
C(7)–C(8)	1.522 (16)	C(15)–O(16)	1.197 (16)
C(8)–C(9)	1.491 (16)	C(17)–O(18)	1.162 (16)
C(9)–Cl(10)	1.744 (11)	C(19)–O(20)	1.126 (16)
C(9)–Cl(11)	1.764 (11)		

(b) Angles

C(2)–C(1)–C(8)	121.9 (9)	C(3)–Fe(12)–C(15)	90.3 (5)
C(2)–C(1)–C(9)	123.5 (10)	C(3)–Fe(12)–C(17)	87.7 (5)
C(8)–C(1)–C(9)	59.2 (7)	C(3)–Fe(12)–C(19)	107.9 (5)
C(1)–C(2)–C(3)	106.5 (9)	C(4)–Fe(12)–C(13)	97.6 (5)
C(2)–C(3)–C(4)	123.8 (10)	C(4)–Fe(12)–C(15)	91.3 (5)
C(2)–C(3)–Fe(12)	123.2 (8)	C(4)–Fe(12)–C(17)	88.5 (5)
C(3)–C(4)–C(5)	123.5 (10)	C(4)–Fe(12)–C(19)	146.6 (5)
C(5)–C(4)–Fe(12)	115.7 (7)	C(13)–Fe(12)–C(15)	90.2 (6)
C(4)–C(5)–C(6)	113.6 (9)	C(13)–Fe(12)–C(17)	92.8 (6)
C(5)–C(6)–C(7)	114.7 (10)	C(13)–Fe(12)–C(19)	115.8 (6)
C(6)–C(7)–C(8)	115.0 (9)	C(13)–Fe(12)–M	117.0 (6)
C(1)–C(8)–C(7)	122.8 (9)	C(15)–Fe(12)–C(17)	177.0 (6)
C(1)–C(8)–C(9)	59.4 (7)	C(15)–Fe(12)–C(19)	88.7 (6)
C(7)–C(8)–C(9)	121.2 (10)	C(15)–Fe(12)–M	90.9 (6)
C(1)–C(9)–C(8)	61.5 (7)	C(17)–Fe(12)–C(19)	89.8 (6)
C(1)–C(9)–Cl(10)	119.9 (8)	C(17)–Fe(12)–M	88.0 (6)
C(1)–C(9)–Cl(11)	117.7 (7)	C(19)–Fe(12)–M	127.2 (6)
C(8)–C(9)–Cl(10)	121.2 (8)	Fe(12)–C(13)–O(14)	179.4 (12)
C(8)–C(9)–Cl(11)	117.8 (8)	Fe(12)–C(15)–O(16)	175.6 (11)
Cl(10)–C(9)–Cl(11)	110.9 (6)	Fe(12)–C(17)–O(18)	178.8 (11)
C(3)–Fe(12)–C(4)	38.8 (4)	Fe(12)–C(19)–O(20)	176.5 (12)
C(3)–Fe(12)–C(13)	136.4 (5)		

(c) Some Intramolecular Distances

C(3)···C(15)	2.790 (16)	C(4)···C(15)	2.810 (17)
C(3)···C(17)	2.743 (16)	C(4)···C(17)	2.759 (16)

[a] M is the midpoint of the C(3)–C(4) bond and has fractional coordinates 0.1925 (15), 0.7750 (6), 0.1838 (18).

Table II. Intermolecular Distances ≤3.50 Å between the Nonhydrogen Atoms[a]

O(16)···O(18$^{\mathrm{I}}$)	3.08	C(15)···O(20$^{\mathrm{II}}$)	3.32
O(16)···O(20$^{\mathrm{II}}$)	3.16	O(14)···O(18$^{\mathrm{VI}}$)	3.33
O(16)···C(17$^{\mathrm{I}}$)	3.19	C(15)···O(18$^{\mathrm{I}}$)	3.34
O(20)···O(18$^{\mathrm{I}}$)	3.24	C(19)···O(18$^{\mathrm{I}}$)	3.34
O(14)···O(18$^{\mathrm{III}}$)	3.24	O(16)···C(13$^{\mathrm{I}}$)	3.36
O(18)···O(14$^{\mathrm{IV}}$)	3.24	O(16)···O(14$^{\mathrm{I}}$)	3.36
O(20)···O(20$^{\mathrm{V}}$)	3.26	O(16)···C(2$^{\mathrm{III}}$)	3.50
C(19)···O(20$^{\mathrm{V}}$)	3.30	C(2)···O(16$^{\mathrm{IV}}$)	3.50

[a] Roman numeral superscripts refer to the following transformations of the coordinates of Table IV: I, x, y, $1 + z$; II, $-x$, $2 - y$, $1 - z$; III, $-1 + x$, y, z; IV, $1 + x$, y, z; V, $1 - x$, $2 - y$, $1 - z$; VI, $-x$, $2 - y$, $-z$,

Torsion angles defining the conformation of the olefin are given in Table III. The cyclooctene ring adopts a chair–boat conformation in which the C_s axis passes through C(2) and C(6). This form is related to the lowest energy chair–boat cyclooctane conformation[40] by placing the olefinic bond and the cyclopropyl ring junction at the symmetry-related smallest torsion angles in the cyclooctane ring. Coordination of the C(3)–C(4) olefinic bond by the iron atom results in significant lengthening from the normal isolated double bond value of 1.337 (6) Å[41] to 1.427 (16) Å, a distance which lies close to the mean of 1.409 Å in the other four accurately determined structures cited above. The dihedral angle between the C(2)–C(5) and Fe, C(3), C(4) least-squares planes at 112.9° is strikingly similar to that of 111.2° between the cyclopropyl C(1), C(2), C(7), C(8) and C(1), C(8), C(9) least-squares

Table III. Torsion Angles[a]– (deg) in the Coordinated Olefin

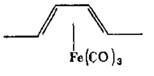
C(8)-C(1)-C(2)-C(3)	−86.5 (10)	C(2)-C(3)-C(4)-C(5)	8.8 (11)
C(9)-C(1)-C(2)-C(3)	−158.3 (10)	C(3)-C(4)-C(5)-C(6)	−81.0 (10)
C(2)-C(1)-C(8)-C(7)	−3.1 (11)	C(4)-C(5)-C(6)-C(7)	85.9 (10)
C(2)-C(1)-C(8)-C(9)	−112.7 (13)	C(5)-C(6)-C(7)-C(8)	−86.7 (10)
C(9)-C(1)-C(8)-C(7)	109.6 (9)	C(6)-C(7)-C(8)-C(1)	77.2 (10)
C(2)-C(1)-C(9)-C(8)	110.0 (9)	C(6)-C(7)-C(8)-C(9)	148.7 (10)
C(2)-C(1)-C(9)-Cl(10)	−1.5 (9)	C(7)-C(8)-C(9)-C(1)	−112.2 (9)
C(2)-C(1)-C(9)-Cl(11)	−141.7 (9)	C(7)-C(8)-C(9)-Cl(10)	−2.7 (9)
C(8)-C(1)-C(9)-Cl(10)	−111.5 (11)	C(7)-C(8)-C(9)-Cl(11)	139.6 (9)
C(8)-C(1)-C(9)-Cl(11)	108.3 (11)	C(1)-C(8)-C(9)-Cl(10)	109.5 (11)
C(1)-C(2)-C(3)-C(4)	84.2 (11)	C(1)-C(8)-C(9)-Cl(11)	−108.2 (11)

[a] The torsion angle A-B-C-D is defined as positive if, when viewed along the B-C bond, atom A must be rotated clockwise to eclipse atom D.

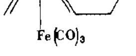
planes. Although H(3) and H(4) are both displaced (Δ 0.09 and 0.20 Å) to the opposite side of the C(2), C(3), C(4) and C(3), C(4), C(5) planes, respectively, from the iron atom, their positions are not established with sufficient certainty to permit the unequivocal conclusion to be drawn that the geometry at C(3) and C(4) truly represents departure from trigonal bonding rather than a tilting of the trigonal-bipyramid C(15)-Fe-C(17) axis away from the C(2) and C(5) cis methylene groups to relieve steric overcrowding. More definitive information on this point may be derived from the recent structural studies on the *cis*-2,3-dicarbomethoxymethylenecyclopropane[36] and 3-methylene-*exo*-4-vinyldihydrofuran-2(3*H*)-one[38] complexes where significant departures from trigonal bonding at trisubstituted olefinic carbon atoms are quite evident, and this situation presumably extends to the disubstituted C(3) and C(4) atoms in the present complex.

Discussion and Conclusion

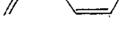
Our results, and those of Koerner von Gustorf,[24] show conclusively that whatever the actual pathway responsible for rearrangement of olefins induced by iron carbonyls, the sequence does not begin with the previously assumed[18] monoolefin–iron tetracarbonyl complex. More intriguing to us, however, is the observation that **34** provides **33** under conditions where decomplexation apparently does not occur, for this result can have far-reaching implications. As we have already pointed out, the normal outcome of interaction between iron carbonyls and olefins is production of a mixture of olefins which reflects their relative thermodynamic stabilities, much the same result as that obtained in olefin reorganizations which follow ionic pathways. The rearrangement of **34** to **33**, then, represents a contrathermodynamic process insofar as the olefins alone are concerned. This result is clearly different from the ordinary one, in which olefins are treated with iron carbonyls and in which reaction intermediates involving some sort of iron carbonyl–olefin interaction have not been isolated. Such intermediates have been assumed to exist by inference based on a variety of careful studies by previous workers. Our results are reminiscent of those obtained in which the rearranging olefin is part of a diene system and in which the final product is a dieneiron tricarbonyl complex. It is well-known that the least substituted diene forms the most stable iron tricarbonyl complex, and the stability of the complex, rather than that of the uncomplexed olefin, is the guiding factor which determines the product. For example, it has been shown that the more substituted olefiniron tricarbonyl **36** is *less* stable than isomeric **37** when these complexes are formed from the nonconjugated diene **38**.[43] These results underscore the fact that the most stable olefin does not necessarily, and does not usually, form the most stable organoiron complex. In this context, the **34** → **33** rearrangement should not be surprising, in fact it should be expected. It is conceivable that the two separate reaction conditions (olefin and iron carbonyl on one hand, monolefiniron tetracarbonyl such as **33** on the other) give rise to different reaction pathways. Since it is likely that the iron moiety is attached to the olefin's π system throughout the rearrangement of **34** to **33**, without additional evidence to the contrary it would seem that this result could be accounted for satisfactorily by the π-allyl mechanism, in which carbon monoxide is lost by **34** in an initial step to be reclaimed after rearrangement through the π-allylhydridoiron tricarbonyl intermediate had occurred. If such a scenario applies here, however, it seems unlikely that it can apply to the rearrangement in which the iron carbonyl is not initially attached to the rearranging olefin, since the type of olefin obtained in this case is different from the one obtained in the case just discussed.



36



37



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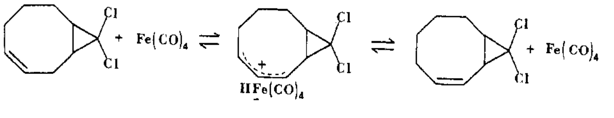
Scheme VI



29 **39** **30**

An alternative mechanism, which might account for the differences discussed above as well as for the fact that rearrangements of olefins when treated with iron carbonyls (e.g. **29** → **30**) parallel rearrangements for which a cationic mechanism has been established, is indicated in Scheme VI and is offered as a speculative proposal, without proof at this time. In this mechanistic possibility, $Fe(CO)_4$ (or possibly $Fe_2(CO)_8$), generated thermally from $Fe_2(CO)_9$, interacts with **29** by abstraction of a allylic hydride ion to produce the ion pair **39**, which ultimately provides the final product **30** and regenerates $Fe(CO)_4$ (or $Fe_2(CO)_8$); the iron tetracarbonyl eventually produces trimeric $Fe_3(CO)_{12}$, a material appearing in large quantities in the course of these reactions.

In addition to the attractive feature that no iron carbonyl–olefin coordination is required, there are other requirements of such a scheme that appear to be supported by observations. The $HFe(CO)_4$ anion is a very stable species in the absence of air,[42] hence it should be relatively easily formed in an ion-pair situation such as **39**. Furthermore, in this rearrangement sequence, reaction would be expected to proceed in the direction of the most stable cation, to ultimately provide the most stable olefin or to produce a mixture of olefins which reflects their relative stabilities.

We are not prepared to suggest that such a mechanism as is shown in Scheme VI is a general one, indeed we do not believe that it is. We believe that the divergent results discussed above are due to the operation of different mechanisms, however, and offer the mechanism of Scheme VI as a possibility for consideration. The π-allylhydridoiron tricarbonyl mechanism has two major advantages, wide acceptance and versatility in explaining a large portion of the observations having been made in this area of investigation. We believe a second mechanism must exist and present the ion-pair mechanism as one we regard as reasonable, which adequately explains the results at hand and which has no less a foundation in fact than does the older mechanism. Perhaps the mechanism of Scheme VI will not survive experimental scrutiny; our efforts continue to be directed toward determination of its validity.

Experimental Section

General Information. All chemicals were used as obtained commercially, unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Nuclear magnetic resonance spectra were obtained with a Varian T-60 NMR spectrometer, and gas chromatographic analyses were conducted on a Hewlett-Packard 5720A gas chromatograph. Melting and boiling points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

9,9-Dichlorobicyclo[6.1.0]non-4-ene (28). 1,5-Cyclooctadiene (54 g) and 65 g of chloroform were cooled to 10 °C. The solution was agitated vigorously by mechanical stirring while 100 mL of 50% aqueous NaOH solution was added. The mixture was again cooled to 10 °C and 1.5 g of benzyltriethylammonium chloride was added. External cooling was removed and the temperature gradually rose to 45 °C, where it was maintained by careful positioning of the cooling bath. When the temperature began to drop spontaneously, external cooling was removed and vigorous stirring was continued for 2 h. Workup included pouring the reaction mixture into water, extracting the mixture with ethyl ether, washing the ether extracts with water, drying them over $MgSO_4$, removing the ether with the aid of a rotary evaporator, and distilling the residue. 1,5-Cyclooctadiene (20.3 g) distilled first, followed by 40.7 g of **28** (bp 110–113 °C (13 mmHg)), a yield of 68% based on converted cyclooctadiene: IR (thin film) 3018, 2940, 2890, 1482, 1445, 1435, 1205, 1175, 1104, 1014, 964, 826, 779, and 715 cm^{-1}; NMR ($CDCl_3$) δ 5.55 (symmetrical broad triplet, 2 H), 2.7–1.4 (complex band, 10 H).

9,9-Dichlorobicyclo[6.1.0]non-3-ene (29) was prepared in an identical manner, using 3.0 g of 1,4-cyclooctadiene,[44] 3.6 g of chloroform, 6 mL of 50% NaOH solution, and 0.1 g of benzyltriethylammonium chloride: bp 110–112 °C (13 mmHg); IR (thin film) 3020, 2935, 2862, 1460, 1444, 1175, 1100, 1030, 889, 860, 834, 810, 744, 711, and 670 cm^{-1}; NMR ($CDCl_3$) δ 5.65 (complex narrow absorption, 2 H), 2.8–1.1 (complex band, 10 H).

9,9-Dichlorobicyclo[6.1.0]non-2-ene (30) was prepared from 54 g of 1,3-cyclooctadiene, 65 g of chloroform, 100 mL of 50% aqueous NaOH solution, and 1.5 g of benzyltriethylammonium chloride, using the procedure described for **28** above. Product **30** was obtained in 72% yield based on converted cyclooctadiene: bp 106–110 °C (10 mmHg); IR (thin film) 3025, 3005, 2930, 2860, 1455, 1223, 1176, 1090, 830, 814, 775, 770, 742, and 671 cm^{-1}; NMR ($CDCl_3$) δ 6.1 (complex absorption, 1 H), 5.5 and 5.3 (broadened singlets, 1 H), 2.7–1.0 (complex band, 10 H).

Tetracarbonyl{η^2-(9,9-dichlorobicyclo[6.1.0]non-3-ene)}iron(0) (33). A solution of 10 g of 9,9-dichlorobicyclo[6.1.0]non-4-ene (**28**) in 545 mL of anhydrous reagent-grade benzene was deoxygenated by passage of N_2 through the solution for 30 min and then 10 g of $Fe(CO)_5$ was added, and the resulting solution was irradiated with a 450-W Hanovia medium-pressure lamp equipped with a Pyrex filter, while a N_2 atmosphere was maintained. Irradiation was continued for 7 h and interrupted only for periodic removal of $Fe_2(CO)_9$ from the lamp's immersion well surface. The mixture was filtered and the benzene removed at reduced pressure below 35 °C. The oily residue was cooled to −5 °C, and the yellow crystalline material obtained in this way was collected by suction filtration. The product was recrystallized from acetone (for best results, deoxygenated by passage of N_2 through the solution, and never exceeding 30–35 °C during purification, finally cooling the filtered acetone solution to −5 °C) to produce bright yellow platelets, mp 84.5–85.5 °C dec. Anal. Calcd for $C_9H_{12}Cl_2Fe(CO)_4$: C, 43.49; H, 3.37; Cl, 19.75. Found: C, 43.59; H, 3.51; Cl, 19.64. IR (hexane) 2079, 1995 (plus shoulder), and 1970 cm^{-1}.

Decomposition of a small amount of the complex was accomplished by dissolving it in acetone and adding an excess of the oxidizing agent $Ce(NH_4)_2(NO_3)_6$, stirring the mixture until CO production ceased, and then pouring the mixture into water, extracting the product with ether, washing the ether extracts with water, drying them with $MgSO_4$, and evaporating the solvent at reduced pressure. The product was identified as essentially pure 9,9-dichlorobicyclo[6.1.0]non-3-ene (**29**) by comparison of its IR and NMR spectra with those of authentic material (see above).

Single-Crystal X-ray Analysis of Tetracarbonyl{η^2-(9,9-dichlorobicyclo[6.1.0]non-3-ene)}iron(0) (33). Crystal Data. $C_{13}H_{12}Cl_2FeO_4$, mol wt = 35.0, triclinic, $a = 7.094$ (4) Å, $b = 16.936$ (8) Å, $c = 6.530$ (4) Å, $\alpha = 95.49$ (5)°, $\beta = 100.16$ (5)°, $\gamma = 104.05$ (5)°, $U = 741.2$ Å^3. d_{measd}(flotation) = 1.59 g cm^{-3}, $A = 2$, $d_{calcd} = 1.608$ g cm^{-3}, $F(000) = 364$. Cu Kα radiation, λ 1.5418 Å, μ(Cu Kα) = 117.2 cm^{-1}, space group $P\bar{1}(C_1{}^1)$ or $P1(C_i{}^1)$ (shown to be the latter by structure solution and refinement).

Crystallographic Measurements. Preliminary unit-cell dimensions were obtained from oscillation and Weissenberg photographs taken with Cu Kα radiation and from precession photographs taken with Mo Kα (λ 0.7107 Å) radiation. Attempts to cut larger crystals into approximately equidimensional fragments failed owing to the ready cleavage of the crystals and so it proved necessary to employ a plate-like crystal for the collection of intensity data. Accordingly, a crystal of dimensions ca. 0.08 × 0.60 × 0.60 mm was oriented on an Enraf-Nonius CAD 3 automated diffractometer (Ni-filtered Cu Kα radiation; 3° takeoff angle), and accurate unit-cell parameters were derived by least-squares treatment of the θ, χ, and ϕ angles for 40 high-order reflections widely separated in reciprocal space. Intensities to θ 67° were measured by the θ–2θ scanning technique with scan widths $(1.20 + 0.50 \tan \theta)°$; background counts were recorded at each end of the scan range for times equal to half the duration of the scan. Instrument and crystal stability were monitored throughout by remeasuring the intensity of the $\bar{1}1\bar{1}$ reflection; no significant variation was noted. From a total of 2820 measurements those unique 1420 reflections for which $I > 2.0\sigma(I)$ [$\sigma^2(I)$ = scan count + total background count] were corrected for the usual Lorentz and polarization effects and used in the structure analysis and refinement. Absorption corrections, determined from the ϕ dependence of the $00\bar{3}$ reflection measured at $\chi = 90°$, were also applied to these data.

Structure Analysis. The structure was solved by direct methods by use of MULTAN and the 257 highest $|E|$ values. An E map computed with that set of phase constants which produced the second highest figure-of-merit and second lowest residual revealed clearly the positions of all the nonhydrogen atoms. Four cycles of full-matrix least-squares refinement of atomic positional and isotropic thermal parameters reduced R ($=\sum||F_o| - |F_c||/\sum|F_o|$) from its value of 0.282 for the initial structure model to 0.125. Hydrogen atom positions were computed and confirmed to coincide with regions of positive electron density in a difference Fourier synthesis which showed no usual features. Several further least-squares iterations during which the nonhydrogen atoms were allowed to assume anisotropic thermal parameters and the positions of the hydrogen atoms were also varied brought the refinement to convergence at $R = 0.092$ when no parameter shift was greater than 0.2σ. Final atomic positional and anisotropic thermal parameters for the nonhydrogen atoms are listed in Tables IV and V. Hydrogen atom positional and isotropic thermal parameters are given in Table VI.

For all structure factor calculations neutral atom scattering factors were those of Cromer and Waber for iron, carbon, chlorine, and oxygen and those of Stewart, Davidson, and Simpson for hydrogen; the scattering factors of iron and chlorine were corrected for anomalous dispersion effects. In the least-squares calculations, $\sum w\Delta^2$ ($\Delta = |F_o| - |F_c|$) was minimized with weights w assigned according to the scheme $w^{1/2} = 1$ for $|F_o| \leq 16.0$ and $w^{1/2} = 16.0/|F_o|$ for $|F_o| > 16.0$. The adequacy of this scheme was indicated by the fact that there was no systematic dependence of $\langle w\Delta^2 \rangle$ when it was analyzed in ranges of $|F_o|$. A table of observed and calculated structure factors is available.

Tetracarbonyl{η^2-(9,9-dichlorobicyclo[6.1.0]non-2-ene)}iron(0) (34). The synthetic approach followed that for photochemical conversion of **28** to the tetracarbonyliron complex **33** exactly. Thus 9,9-dichlorobicyclo[6.1.0]non-2-ene (**30**) and $Fe(CO)_5$ were irradiated in benzene solution under an atmosphere of N_2. Removal of the solvent at reduced pressure while maintaining the temperature below 30 °C and then cooling the green, oily residue at −5 °C yielded pale yellow needles, mp 75–77 °C dec, which were collected by suction filtration. All attempts at purification of this relatively unstable complex resulted in rearrangement of this complex to the more stable complex **33** (see above). Thus attempted recrystallization by dissolution in acetone

Table IV. Fractional Atomic Coordinates[a] ($\times 10^4$) for the Nonhydrogen Atoms

Atom	*x*	*y*	*z*
C(1)	4420 (14)	6988 (6)	4153 (18)
C(2)	3415 (16)	7658 (6)	4614 (19)
C(3)	2822 (15)	7945 (6)	2583 (18)
C(4)	1028 (15)	7554 (6)	1093 (17)
C(5)	−638 (16)	6862 (6)	1547 (18)
C(6)	−233 (17)	5995 (6)	1293 (19)
C(7)	1007 (16)	5801 (6)	3246 (18)
C(8)	3245 (16)	6093 (6)	3440 (18)
C(9)	4619 (15)	6347 (7)	5536 (16)
Cl(10)	3716 (4)	6362 (2)	7852 (5)
Cl(11)	6853 (4)	6046 (2)	5882 (5)
Fe(12)	986 (2)	8783 (1)	2192 (3)
C(13)	−1429 (17)	8752 (8)	685 (19)
O(14)	−2958 (13)	8729 (8)	−251 (19)
C(15)	−102 (18)	8450 (6)	4297 (22)
O(16)	−756 (13)	8270 (6)	5809 (14)
C(17)	2215 (19)	9127 (7)	139 (20)
O(18)	3035 (14)	9341 (7)	−1184 (15)
C(19)	2301 (18)	9745 (7)	3873 (23)
O(20)	3056 (15)	10362 (5)	4857 (17)

[a] Estimated standard deviations in the least significant digit(s) are given in parentheses in this and all subsequent tables.

at 25–30 °C (N_2 atmosphere) and cooling to −5 °C resulted in separation of yellow crystals of complex **33**. Furthermore, attempted chromatography of **34** on alumina resulted in rearrangement to **33**. That the product of irradiation of benzene solutions of $Fe(CO)_5$ and 9,9-dichlorobicyclo[6.1.0]non-2-ene (**30**) was indeed complex **34** was shown by $Ce(NH_4)_2(NO_3)_6$–acetone decomposition, as had been described previously in regard to complex **33**, and subsequent identification of the oxidation product as **30** was shown by comparison of spectral data with those of known samples of the bicyclic olefin **30**.

Attempted Rearrangement of Tetracarbonyl{η^2-(9,9-Dichlorobicyclo[6.1.0]non-3-ene)}iron(0) (33). The pure complex (0.5 g) was dissolved in hexane and placed in an atmosphere of N_2 and then heated to reflux. The initially yellow solution became green very quickly, indication that decomposition of the complex had begun. The decomposition was monitored by IR and NMR spectroscopy. After about 7 h of reflux, absorptions in the IR spectrum due to iron–carbonyl stretch had disappeared. Workup by filtration of the cooled reaction mixture and evaporation of solvent produced a dark green oil whose NMR and IR spectra showed 9,9-dichlorobicyclo[6.1.0]non-3-ene (**29**) to be the only organic material present.

In another experiment, 0.7 g of the complex **33**, 0.65 g of $Fe_2(CO)_9$, and 15 mL of hexane were heated to reflux in an inert atmosphere (N_2). After about 45 min, IR spectra of a sample taken from the reaction vessel showed only unrearranged **29** among uncomplexed species. After about 1.5 h, a trace of the rearrangement product **30** could be seen. IR spectra showed the presence of substantial amounts of compound **30** after 6.25 h, although it was still not the major product of the reaction.

General Procedure for Rearrangement of Olefins with $Fe_2(CO)_9$. A. Chlorinated Bicyclononenes 28, 29, and 30. In a typical experiment the olefin (0.01 mol) was dissolved in hexane (25 mL), $Fe_2(CO)_9$ (0.003 mol) was added, and the mixture was heated to reflux with magnetic stirring under N_2 atmosphere. In all cases, the reaction mixture became dark green as it approached reflux temperature due to the presence of the decomposition product $Fe_3(CO)_{12}$. Gas chromatography could be used only to monitor the disappearance of compound **28**, since we were unable to separate **29** and **30** on a variety of columns. In cases where further monitoring was necessary, infrared spectra were used. Specifically, the absorptions at 826, 779, and 715 cm^{-1} for **28**, at 810, 744, and 711 cm^{-1} for **29**, and at 830, 814, 775, 770, 742, and 671 cm^{-1} for **30** were used to detect the presence of each of these compounds.

Under these reaction conditions **28** rearranged rapidly to **29** (about 5 min after reflux began for complete disappearance of **28**), but **29** rearranged sufficiently slowly to realize high conversions of **28** to **29** without heavy contamination from the ultimate rearrangement product **30**. Compound **30** was found to be completely stable under these reaction conditions. In cases where isolation of the rearrangement product was necessary or desirable, the reaction mixture was filtered through Celite filter-aid and passed through an alumina column with elution with hexane as necessary to remove $Fe_3(CO)_{12}$ and then the solvent was removed at reduced pressure and the residue distilled.

B. Bicyclononenes (e.g., 31). The hydrocarbons corresponding to their chlorinated analogues **28**, **29**, and **30** were subjected to reaction conditions essentially identical with those described above. The results were substantially the same, the only significant difference being that the rearrangements proceeded at a more rapid rate than for corresponding chlorinated compounds.

Thermal Degradation of Bis(tetracarbonyl)(η^2-1,5-cyclooctadiene)diiron(0) (23). The complex was prepared after a description by Koerner von Gustorf,[24] using 30 g of $Fe_2(CO)_9$, 36 g of 1,5-cyclooctadiene, and 150 mL of benzene and stirring the mixture at room temperature and in the dark until all $Fe_2(CO)_9$ had disappeared (about 24 h), under an atmosphere of N_2. Removal of solvent at reduced pressure produced the desired complex as a yellow crystalline solid in low yield. It was purified by careful recrystallization from pentane to provide fine yellow needles of mp 85–87 °C, in agreement with that reported for **23** by Koerner von Gustorf.[24]

Thermal decomposition of the complex **23** was conducted in refluxing pentane under an atmosphere of N_2, and the reaction was monitored by gas chromatography. After 10 min, the dark green color of $Fe_3(CO)_{12}$ had appeared; GC analysis after 20 min showed 1,5-cyclooctadiene as the only volatile decomposition product. 1,3-Cyclooctadiene began to appear in trace amounts after 0.5 h, and after 5 h it comprised 15–20% of the volatile products (and 1,5-

Table V. Anisotropic Temperature Factor Parameters[a] for the Nonhydrogen Atoms

Atom	$10^4 b_{11}$	$10^5 b_{22}$	$10^4 b_{33}$	$10^4 b_{12}$	$10^4 b_{13}$	$10^4 b_{23}$
C(1)	149 (20)	220 (31)	265 (30)	45 (13)	128 (40)	30 (17)
C(2)	198 (24)	232 (34)	211 (29)	39 (15)	−34 (46)	0 (17)
C(3)	189 (22)	276 (33)	232 (27)	57 (14)	137 (39)	61 (16)
C(4)	220 (20)	262 (30)	191 (26)	91 (12)	143 (37)	41 (15)
C(5)	172 (23)	291 (38)	212 (29)	30 (16)	58 (43)	17 (18)
C(6)	194 (25)	202 (33)	229 (31)	−4 (16)	−47 (47)	13 (17)
C(7)	178 (23)	231 (34)	234 (30)	25 (15)	82 (42)	12 (17)
C(8)	221 (22)	288 (36)	227 (28)	76 (14)	162 (41)	38 (17)
C(9)	160 (21)	328 (38)	153 (27)	47 (14)	31 (39)	−22 (17)
Cl(10)	245 (6)	631 (14)	206 (7)	88 (5)	155 (11)	54 (6)
Cl(11)	198 (6)	511 (11)	347 (9)	100 (4)	118 (12)	89 (5)
Fe(12)	169 (3)	229 (5)	220 (4)	42 (2)	74 (6)	24 (3)
C(13)	243 (25)	533 (50)	242 (31)	99 (18)	166 (45)	67 (21)
O(14)	183 (18)	1009 (57)	484 (36)	123 (16)	−83 (43)	112 (24)
C(15)	221 (26)	204 (36)	363 (39)	16 (16)	75 (53)	13 (20)
O(16)	314 (21)	474 (37)	288 (24)	45 (15)	218 (35)	−12 (16)
C(17)	287 (30)	312 (40)	218 (31)	48 (18)	14 (51)	−1 (19)
O(18)	311 (23)	656 (46)	306 (25)	26 (18)	215 (38)	63 (18)
C(19)	252 (27)	351 (40)	393 (41)	78 (17)	175 (55)	60 (22)
O(20)	410 (27)	211 (28)	447 (32)	−6 (15)	203 (47)	−54 (16)

[a] In the form: $B(\sin^2 \theta)/\lambda^2 = b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl$.

Table VI. Hydrogen Atom Fractional Coordinates[a] ($\times 10^3$) and Distances to Their Bonded Carbon Atoms

Atom	x	y	z	d, Å
H(1)	555 (15)	719 (6)	326 (17)	1.08 (11)
H(2A)	423 (15)	813 (6)	575 (17)	1.01 (11)
H(2B)	220 (15)	745 (6)	554 (17)	1.14 (11)
H(3)	411 (15)	855 (6)	216 (17)	1.29 (11)
H(4)	95 (15)	762 (6)	−26 (17)	0.90 (11)
H(5A)	−179 (15)	698 (6)	18 (17)	1.17 (11)
H(5B)	−72 (15)	699 (6)	313 (17)	1.06 (11)
H(6A)	11 (15)	595 (6)	4 (17)	0.89 (11)
H(6B)	−149 (15)	548 (6)	103 (17)	1.06 (11)
H(7A)	75 (14)	516 (6)	318 (16)	1.05 (11)
H(7B)	44 (15)	589 (6)	460 (17)	1.05 (11)
H(8)	370 (15)	583 (7)	244 (16)	0.91 (11)

[a] All hydrogen atoms were assigned an isotropic temperature factor, $B = 3.5$ Å^2.

cyclooctadiene the remainder) of the reaction.

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Registry No. **28**, 4729-12-8; **29**, 67254-56-2; **30**, 58189-58-5; **33**, 67271-76-5; **34**, 67271-75-4; **23**, 58569-67-8; 1,5-cyclooctadiene, 111-78-4; chloroform, 67-66-3; 1,4-cyclooctadiene, 1073-07-0; 1,3-cyclooctadiene, 1700-10-3; $Fe(CO)_5$, 13463-40-6; $Fe_2(CO)_9$, 15321-51-4.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Preliminary report of this work was made at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977.
(2) (a) University of North Carolina at Greensboro. (b) Duke University.
(3) For a relatively recent review of this area, see C. A. Tolman in "Transition Metal Hydrides", Vol. I, E. L. Muetterties, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 6.
(4) Two additional mechanistic proposals have been made recently. The first of these[5] is a somewhat more sophisticated and complex version of the π-allylhydridoiron tricarbonyl mechanism originally proposed by Manuel[6] and Pettit[13,15] involving two olefin molecules coordinated to the iron center, while the other invokes a σ-bonded iron complex as an intermediate.[7] The latter mechanism was proposed to explain results involving optically active intermediates and is regarded in the present work, rightly or wrongly, as a special case.
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(30) Infrared spectroscopy was employed as a means of monitoring the reaction because of difficulties encountered in attempts at separating isomers **29** and **30** by gas chromatography. We have subsequently experienced similar problems in separation of the corresponding hydrocarbons bicyclo[6.1.0]non-2-ene and -3-ene, as well as the analogous isomers in the bicyclo[6.2.0]decene series. Failure to detect rearrangement product **30** by infrared spectroscopy was substantiated subsequently by NMR spectroscopy.
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