Reactivity of Co-ordinated Ligands. Part XXIII.[1] Preparation of some Cyclic Ketones using Tricarbonyliron Complexes in the Presence of Aluminium Trichloride

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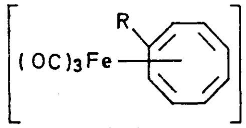
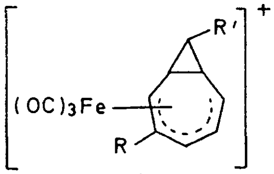
The reaction of tricarbonyl(η-cyclo-octatetraene)iron with anyhdrous aluminium trichloride in benzene gives tricarbonyl(2—4-η,8-σ-9-oxobicyclo[3.2.2]nona-2,6-dien-8-yl)iron which has been previously obtained from the direct reaction of barbaralone with enneacarbonyldi-iron. Treatment of this complex with carbon monoxide under moderate pressures and temperatures (100 atm, 120 °C) yields barbaralone in 95% yield. Extension of this reaction to other co-ordinated diene systems, *e.g.* tricarbonyl(η-cyclo-octatriene)-, tricarbonyl(1-σ,4—6-η-cyclo-octenediyl)-, and tricarbonyl(η-norbornadiene)-iron, provides a convenient method of production of other cyclic ketones.

OLEFIN complexes of tricarbonyliron are known to be reactive towards electrophilic reagents. Furthermore, in some cases where electrophilic substitution may not be conveniently carried out on the free olefin, the tricarbonyliron unit is known to provide a stabilising influence. In a previous part of this series[2] some electrophilic addition and substitution reactions of tricarbonyl(η-cyclo-octatetraene)iron were reported. The acetylation of (I; R = H) under the usual Friedel–Crafts conditions was found to produce two complexes: the cationic bicyclic derivative (II; R = H, R′ = COMe) and the neutral derivative (I; R = COMe). The relative yields of these two complexes appeared to be dependent on the amount of anhydrous aluminium trichloride used in the reaction. In reactions employing acetylium tetrafluoroborate as the electrophile only salt (II; R = H, R′ = COMe) was the product. This effect of the aluminium trichloride concentration on the course of the reaction has also been noted in similar reactions of tricarbonyl(η-cycloheptatriene)iron with MeCOCl–$AlCl_3$ which are known to produce both a cation $[(C_7H_8COMe)Fe(CO)_3]^+$ and the neutral acetyl derivative $[(C_7H_7COMe)Fe(CO)_3]$. In this paper we report details of some recent studies of this $AlCl_3$ effect which have led to the discovery of a new convenient route to several cyclic ketone derivatives. A brief report of some aspects of this work has been made.[3]


(I)


(II)

RESULTS AND DISCUSSION

The reaction of tricarbonyl(η-cyclo-octatetraene)iron, (I; R = H), with anhydrous aluminium chloride in benzene at 10 °C in a nitrogen atmosphere gave a yellow complex in *ca.* 40% yield. This complex was identified as (III; R = H), which had previously been obtained from the reaction of barbaralone with enneacarbonyldi-iron.[4] Reactions of tricarbonyl(η-methylcyclo-octatetraene)iron (I; R = Me) under the same conditions gave the complex (III; R = Me) as the major product. The assignment of the structure of the latter was based on a comparison of its ^1H n.m.r. spectrum with that of complex (III; R = H) (Table 1).

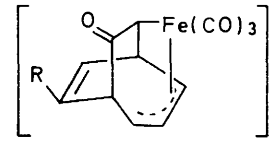
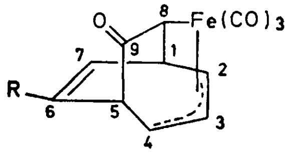

(III)

TABLE 1

^1H N.m.r. absorptions for complexes (III) (0·2M-solutions in $CDCl_3$; δ/p.p.m., *J*/Hz)



	R = H		R = Me	
		Downfield shift (p.p.m.) on addition of 0·05M-$[Eu(dpm)_3]$		Downfield shift (p.p.m.) on addition of 0·05M-$[Eu(dpm)_3]$
H_1	2·88(q), *J* 7	0·96	2·86(q), *J* 7	0·84
H_2	4·15(t), *J* 7	0·64	4·18(t), *J* 7	0·66
H_3	4·45(t), *J* 8	0·68	4·45(t), *J* 7·5	0·68
H_4	5·16(t), *J* 8	0·96	5·13(t), *J* 8	1·0
H_5	3·11(t), *J* 8	2·32	2·94(d), *J* 8	2·29
H_6	6·25(m)	0·62	0·62(s)	0·0
H_7	6·07(m)	0·40	5·74(d), *J* 7	0·48
H_8	1·96(dd), *J* 8,2	3·04	1·92(bd), *J* 8	2·66

The main features are the disappearance of the multiplet at δ 6·25 (H_6), the collapse of the multiplet at δ 6·07 (H_7) to a doublet at δ 5·74, and the collapse of a triplet at δ 3·11 (H_5) to a doublet at δ 2·94 p.p.m. Under the same reaction conditions tricarbonyl(η-phenylcyclo-octatetraene)iron (I; R = Ph) gave a complex mixture from which no pure complexes were isolated.

This reaction involves formal addition of one molecule of carbon monoxide but the yield was not increased by using an atmosphere of CO. When anhydrous aluminium tribromide was used the complex (III; R = H)

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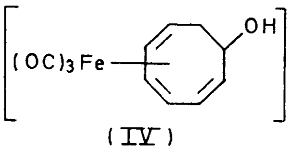
[1] Part XXII, J. Evans, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 2375.

[2] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc. (A)*, 1971, 422.

[3] V. Heil, B. F. G. Johnson, J. Lewis, and D. J. Thompson, *J.C.S. Chem. Comm.*, 1974, 270.

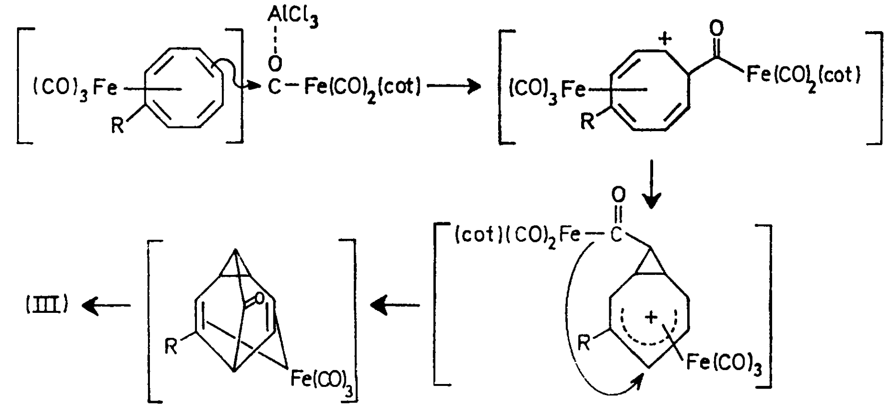
[4] A. Eisenstadt, *Tetrahedron Letters*, 1972, 2005.

was produced in 45% yield. Reaction of (I; R = H) with F_3B,OEt_2 in acetic acid gave an unstable yellow



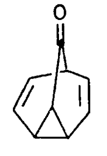
(IV)

oil which we believe to be complex (IV). The ^1H n.m.r. spectrum of this complex (see Experimental section) supports this assignment, as does the mass spectrum.



Reaction of complex (IV) with hexafluorophosphoric acid gave the bicyclic cation (II; $R = R^1 = H$), and attempted acetylation with pyridine–acetic anhydride gave (I; R = H) as the only isolable product. When complex (I; R = H) was added to a benzene solution of F_3B,OEt_2 a yellow crystalline complex precipitated out, but this material was rapidly hydrolysed to (I; R = H) and could not be identified. Complex (I) did not react with triethylaluminium or tin(IV) chloride.

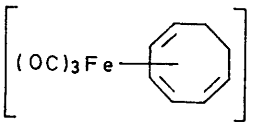
A possible mechanism for the formation of (III) from (I) is outlined in the Scheme (cot = cyclo-octatetraene). Protonation of complex (I; R = H) is known to give [5,6] the bicyclic cation (II; R = R′ = H) and protonation of (I; R = Me) yields [3] (II; R′ = H, R = Me) as the major product. The initial step in the reaction probably involves attack of aluminium trichloride at the oxygen atom of one of the CO groups. Some evidence for this was obtained from the i.r. spectrum of the gum which initially separates when complex (I; R = H) and aluminium trichloride are mixed. The gum had strong absorptions at 2 108 and 1 642 cm^{-1}, whereas the starting material absorbed at 2 050 and 1 980 cm^{-1}.



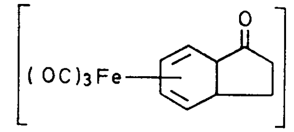
(V)

Reaction of (III; R = H) with carbon monoxide under moderate temperature and pressure liberates barbaralone, (V), in high yield and thus provides a convenient preparative route of this ketone from the readily available complex (I; R = H). The analytical and spectroscopic properties of this ketone are as described elsewhere.[7]

When tricarbonyl(η-cyclo-octatriene)iron, (VI), was treated with anhydrous aluminium trichloride under similar conditions the major product was (VII). The structure of the complex was assigned mainly on its spectroscopic properties. The mass spectrum and analytical data suggested the molecular formula, $C_{12}H_{10}O_4Fe$, and the i.r. and ^1H n.m.r. spectra indicated the presence of a 1,3-diene tricarbonyliron unit. The band at 1 745 cm^{-1} in the i.r. was assigned to a five-membered ring ketone, and the complex readily formed a 2,4-dinitrophenylhydrazone derivative. Assignment



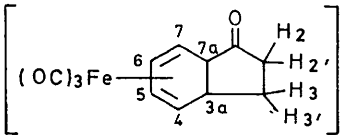
(VI)



(VII)

Table 2

^1H N.m.r. absorption for complex (VII) (0·2M-solution in $CDCl_3$; δ/p.p.m., J/Hz)



		Shift (p.p.m.) on addition of 0·05M-$[Eu(fod)_3]$
H_2	2·40 (ddd), J 16, 8, 4	1·80
$H_{2'}$	2·64(m)	1·80
H_3	1·90(m)	0·80
$H_{3'}$	1·60(m)	0·60
H_{3a}	3·06(dd), J 10, 4	0·73
H_4	3·14(m)	0·46
$H_{5,6}$	5·64(t), J 4	0·34
H_7	3·14(m)	1·0
H_{7a}	2·90(dd), J 10, 5	1·77

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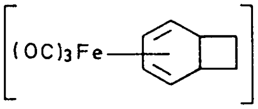
[5] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4821.

[6] M. Brookhart, E. R. Davis, and D. L. Harris, *J. Amer. Chem. Soc.*, 1972, **94**, 7853.

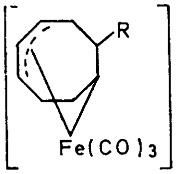
[7] W. Von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 1967, **23**, 3943.

of the signals in the ^1H n.m.r. spectrum was aided by the use of a europium shift reagent (Table 2). Further evidence for the structure of the ketone came from degradation experiments. Treatment of complex (VII) with silver picolinate under mild conditions removed the $Fe(CO)_3$ group to give a crude product which was dehydrogenated with 10% palladium on charcoal to give a high yield of indan-1-one, which was identified by comparison with an authentic sample. The mechanism of formation of this complex is not obvious, but the bicyclic complex (VIII) does not react under these conditions.

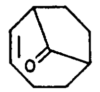


(VIII)

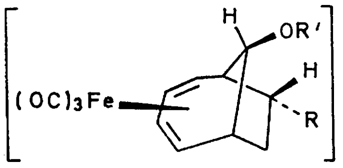
Reaction of tricarbonyl(1-σ,4—6-η-cyclo-octenediyl)-iron, (IX; R = H),[8] with aluminium trichloride gave two major products. The first, obtained in *ca.* 20% yield, was identified as the bicyclic ketone (X).[8] This compound could be obtained in much higher yield (85%) by reaction of complex (IX; R = H) with carbon monoxide under moderate pressure (100 atm). The other product, obtained in *ca.* 25% yield as a colourless crystalline product, was identified as the complex (XI; R = R′ = H). The mass spectrum and analytical data indicated the formula $C_{12}H_{12}O_4Fe$, and the i.r. and ^1H n.m.r. spectra (Table 3) indicated the presence of a 1,3-diene tricarbonyliron system. The ^1H n.m.r. spectrum also indicated the presence of a secondary hydroxyl group which was readily acetylated to give the monoacetate (XI; R = H, R′ = CO·Me). The ^1H n.m.r. spectrum of the acetate was very similar to that of (XI; R = R′ = H) except that the signal at δ 3·20 (H_9) had moved downfield to δ 4·20, the signal due to the hydroxyl group had disappeared, and a new three-proton singlet (O·CO·Me) at δ 1·92 p.p.m. had appeared. The assignment of the signals in the ^1H n.m.r. spectrum was aided by the use of a europium shift reagent (Table 3). The signal due to H_9 was a sharp singlet and hence the hydroxyl group must be pointing away from the diene system [*cf.* the related compound (XII) in which the related proton appears as a doublet of triplets (*J* 12, 6 Hz)].[9]



(IX)



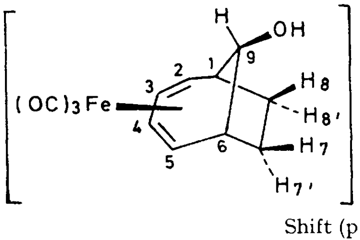
(X)



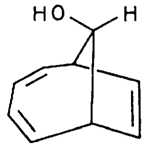
(XI)

TABLE 3

^1H N.m.r. absorptions for complex (XI) (0·2M-solutions in $CDCl_3$; δ/p.p.m., *J*/Hz)



		Shift (p.p.m.) on addition of 0·03M-[Eu(fod)$_3$]
$H_{1,6}$	2·28(m)	0·80
$H_{2,5}$	3·56(m)	0·20
$H_{3,4}$	5·10(dd), *J* 6, 4	0·10
$H_{7,8}$	1·80(dd), *J* 10, 4	0·65
$H_{7',8'}$	1·10(d), *J* 10	0·30
H_9	3·20(s)	1·6
OH	1·50(s)	



(XII)

Tricarbonyl(1-σ,4—6-η-2-deuteriocyclo-octenediyl)iron (IX; R = D)[8] gave the monodeuteriated product (XI; R = D, R′ = H) when treated with aluminium trichloride. The ^1H n.m.r. spectrum of (XI; R = D, R′ = H) was very similar to that of compound (XI; R = R′ = H) except that the two-proton doublet at δ 1·10 now only integrated for one proton and the doublet of doublets at δ 1·80 p.p.m. had become a complex multiplet. If the deuterium is *exo* to the $Fe(CO)_3$ group in the starting material,[10] then it seems reasonable to assume it will be *exo* in the product and hence the stereochemistry of complex (XI) is as shown.

The reaction of tricarbonyl(η-norbornadiene)iron, (XIII), with aluminium trichloride and acetyl chloride has been briefly mentioned and gives an unknown ketonic complex.[11] When (XIII) was stirred with anhydrous aluminium trichloride in benzene at room temperature in a nitrogen atmosphere two products were obtained. The ratio of the products varied slightly from run to run and in an atmosphere of carbon monoxide essentially one product resulted, but the overall yield remained constant at *ca.* 35%. The major product (XIV) in all cases was isolated as colourless

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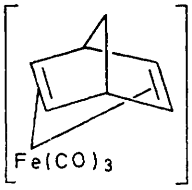
[8] A. J. Deeming, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2093.

[9] T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Schechter, *J. Amer. Chem. Soc.*, 1972, **94**, 5366.

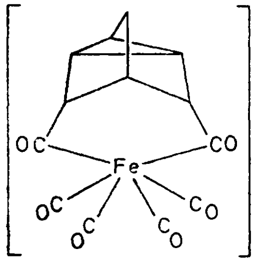
[10] F. A. Cotton, M. D. LaPrade, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4626.

[11] R. E. Graf and C. P. Lillya, *J.C.S. Chem. Comm.*, 1973, 271.

crystals which decomposed above 40 °C with the evolution of carbon monoxide to give the other reaction product (XV). Complex (XV) was obtained as colourless crystals which were purified by sublimation (0·1 mmHg, 20 °C). The mass spectrum and analytical data indicated the molecular formula $C_{12}H_8O_5Fe$. The i.r. spectrum had bands at 2 096, 2 035, 2 018, and 2 014 cm^{-1}, assigned to four terminal Fe–CO groups, and a band at 1 712 cm^{-1} assigned to an acyl carbonyl group. The ^1H n.m.r. spectrum was assigned with the aid of a europium shift reagent (Table 4). Further proof for the structure of complex (XV) came from its synthesis from quadricyclene (XVI) and enneacarbonyl-di-iron. The i.r. spectrum of complex (XIV) indicated the presence of four terminal Fe–CO groups and in addition had a strong band at 1 660 cm^{-1}, which was assigned to the two acyl carbonyl groups. The ^1H n.m.r. spectrum of complex (XIV) (Table 5) is in complete agreement with the proposed structure. The related rhodium complexes (XVII) and (XVIII) had bands at 1 750 and 1 680 cm^{-1}, respectively, which were assigned to the acyl carbonyl groups.[12]



(XIII)



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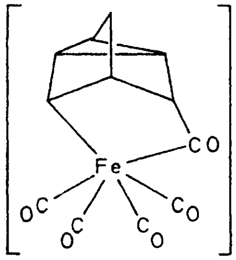
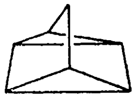
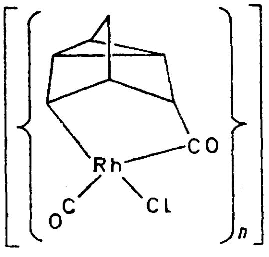


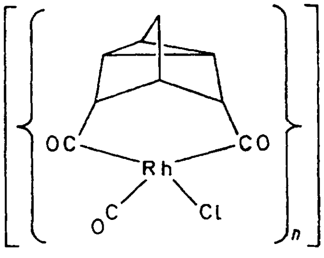
(XV)



(XVI)



(XVII)

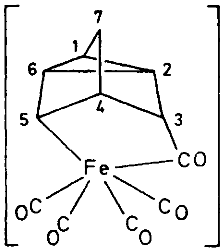


(XVIII)

Tricarbonyl(η-cyclohexa-1,3-diene)-, tricarbonyl(η-cycloheptatriene)-, and tricarbonyl(η-cyclo-octa-1,5-diene)-iron did not give CO insertion products under the reaction conditions.

TABLE 4

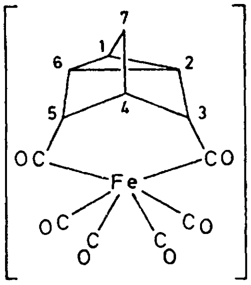
^1H N.m.r. absorptions for complex (XV) (0·2M-solutions in $CDCl_3$; δ/p.p.m., J/Hz)



		Shift (p.p.m.) on addition of 0·05M-[Eu(dpm)$_3$]
H_1	1·52(m)	0·03
H_2	1·28(dist. t), J 5	0·21
H_3	2·46(bs)	0·52
H_4	2·36(bs)	0·30
H_5	2·44(bs)	0·18
H_6	2·02(dist. t), J 5	0·17
H_7	1·54(s)	0·06

TABLE 5

^1H N.m.r. absorptions (0·2M-solutions in $CDCl_3$; δ/p.p.m., J/Hz)



		Shift (p.p.m.) on addition of 0·05M-[Eu(dpm)$_3$]
H_1	1·52(t), J 5	0·03
$H_{2,6}$	1·58(d), J 5	0·35
$H_{3,5}$	2·56(s)	0·71
H_4	2·34(s)	0·46
H_7	1·56(s)	0·03

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra (hexane solutions) were recorded using a Perkin–Elmer 257 spectrometer and ^1H n.m.r. spectra were measured with a Varian HA-100 spectrometer (trimethylsilane as internal standard). Mass spectra were determined with an A.E.I. M.S.-902 instrument.

Benzene was freshly distilled and sodium dried and anhydrous aluminium trichloride was freshly sublimed. All chromatography was carried out on preparative silica plates, and all reactions took place under pure dry nitrogen.

Reaction of the Complexes with Anhydrous Aluminium Trichloride.—(a) *Tricarbonyl*(η-*cyclo-octatetraene*)*iron*, (I; R = H). The complex (0·8 g) in benzene (10 cm^3) was

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[12] L. Cassar and J. Halpern, *Chem. Comm.*, 1970, 1082.

added dropwise to a stirred suspension of anhydrous aluminium trichloride (0·56 g) in benzene (2 cm^{3}) at 10 °C. After 3·5 h the mixture was hydrolysed [H_2O (15 cm^{3}), conc. HCl (3 drops)]. The organic phase was then separated, the aqueous phase extracted with dichloromethane (× 2), and the combined organic layers dried over magnesium sulphate. Removal of the solvent gave a yellow oil which was chromatographed (10% ethyl acetate–benzene) to give tricarbonyl(2—4-η,8-σ-9-oxobicyclo[3.2.2.]-nona-2,6-dien-8-yl)iron, (III; R = H), as colourless crystals (42%), m.p. 133 °C (lit.,[4] 132—133 °C); $\nu_{\text{max.}}$ at 2 058, 2 000, 1 922, and 1 670 cm^{-1}; *m/e* 272 (M^{+}), 244, 216, 188, 160, and 134.

(b) *Tricarbonyl*(η-*methylcyclo-octatetraene*)*iron*, (I; R = Me). Reaction of complex (I; R = Me) (0·2 g) [6] with $AlCl_3$ according to the method used above gave, after chromatography, a yellow oil (35%) which consisted of *ca.* 85% of complex (III; R = Me) as judged by ^{1}H n.m.r. spectroscopy; $\nu_{\text{max.}}$ at 2 065, 2 009, 1 992, and 1 693 cm^{-1}; *m/e* 286 (M^{+}), 258, 230, 202, 174, 148, and 134.

(c) *Tricarbonyl*(η-*cyclo-octatriene*)*iron*, (VI). Complex (VI) [13] was treated with $AlCl_3$ (0·34 g) as described above to give, after chromatography (10% ethyl acetate–benzene), tricarbonyl(4,5:6,7-η-3a,7a-dihydroindan-1-one)iron, (VII) (28%), as pale yellow *crystals*, m.p. 58—59 °C (from EtOH); $\nu_{\text{max.}}$ at 2 051, 1 984, 1 982, and 1 745 cm^{-1}; *m/e* 274 (M^{+}), 246, 228, and 190. The 2,4-*dinitrophenylhydrazone* had m.p. 175—177 °C (from MeOH) (Found: C, 48·0; H, 3·3; N, 12·3. Calc. for $C_{18}H_{14}FeN_4O_7$: C, 47·7; H, 3·1; N, 12·3%).

(d) *Tricarbonyl*(1-σ,4—6-η-*cyclo-octenediyl*)*iron*, (IX; R = H). Complex (IX; R = H) (0·5 g) [8] was treated with $AlCl_3$ (0·5 g) by the method described above to give a yellow oil which was chromatographed (10% ethyl acetate–benzene) to give two major compounds. The faster running compound was identified as bicyclo[4.2.1]non-2-en-9-one, (X) (0·06 g).[8] The slower running compound was purified by sublimation (0·1 mmHg, 70 °C) and crystallisation from pentane to give tricarbonyl(2,3:4,5-η-9-hydroxybicyclo[4.2.1]nona-2,4-diene)iron, (XI; R = R′ = H), as colourless *needles* (0·13 g), m.p. 135 °C; $\nu_{\text{max.}}$ at 2 049 and 1 980 cm^{-1}; *m/e* 276, 248, 220, and 192. Acetylation (pyridine–acetic anhydride) gave the (XI; R = H, R′ = Co·Me) as colourless *needles*, m.p. 120—122 °C (from pentane) (Found: C, 53·0; H, 4·1. Calc. for $C_{14}H_{14}FeO_5$: C, 52·8; H, 4·4%); $\nu_{\text{max.}}$ at 2 052, 1 988, 1 980, and 1 744 cm^{-1}; *m/e* 318, 290, 262, 234, and 206; δ ($CDCl_3$) 5·08 (2H, dd, *J* 6, 4 Hz, $H_{3,4}$), 4·20 (1H, s, H_9), 3·56 (2H, m, $H_{2,5}$), 2·40 (2H, m, $H_{1,6}$), 1·92 (3H, s, CO·*Me*), 1·66 (2H, dd, *J* 10, 4, $H_{7,8}$), and 1·14 (2H, d, *J* 10 Hz, $H_{7',8'}$).

(e) *Tricarbonyl*(1-σ,4—6-η-2-*deuteriocyclo-octenediyl*)*iron*, (IX; R = D). Complex (IX; R = D) (0·2 g) [8] gave the monodeuteriated (XI; R = D, R′ = H), m.p. 134 °C, *m/e* 277, 249, 221, and 193. Acetylation gave the monoacetate (XI; R = D, R′ = CO·Me), m.p. 120—122 °C, *m/e* 319, 291, 263, 235, and 206.

(f) *Tricarbonyl*(η-*norbornadiene*)*iron*, (XIII). A solution of (XIII) (1·0 g) [14] and anhydrous $AlCl_3$ (1·0 g) in benzene (10 cm^{3}) was stirred at room temperature for 16 h. Water (20 cm^{3}) was added and the mixture extracted with dichloromethane (× 3). The organic layer was dried ($MgSO_4$) and chromatographed (benzene) to give two bands. The faster running band gave (5-σ,3C′-bicyclo[2.2.1.0^{2,6}]heptane-3,5-diyl-3-carbonyl)tetracarbonyliron, (XV) (0·15 g), as colourless *crystals*, m.p. 63—65 °C (from pentane) (Found: C, 50·3; H, 2·8. Calc. for $C_{12}H_8FeO_5$: C, 50·1; H, 2·8%); $\nu_{\text{max.}}$ at 2 096, 2 035, 2 018, 2 014, and 1 712 cm^{-1}; *m/e* 288, 260, 232, 204, 176, and 148. The slower running band gave (3C′,5C′-bicyclo)[2.2.1.0^{2,6}]heptane-3,5-diyl-3,5-dicarbonyl)tetracarbonyliron, (XIV) (0·22 g), as colourless *crystals* which slowly decompose on heating above 40 °C, $\nu_{\text{max.}}$ at 2 106, 2 052, 2 044, 2 012, and 1 660 cm^{-1}.

Barbaralone (V).—A solution of complex (III; R = H) (0·8 g) in toluene (400 cm^{3}) was treated with carbon monoxide (100 atm; 120 °C) in a rocking autoclave for 8 h. Removal of the solvent and sublimation (0·01 mmHg, 30 °C) gave barbaralone, (V), as colourless crystals (96%), m.p. 52 °C (lit.,[7] 53·5 °C).

Reaction of Complex (I; R = H) *with Boron Trifluoride–Diethyl Ether* (1/1).—A solution of complex (I; R = H) (0·2 g) in chloroform (5 cm^{3}) was added dropwise to a stirred solution of F_3B,OEt_2 (1 cm^{3}) in acetic acid (2 cm^{3}). The resulting yellow solution was stirred at room temperature for 3 h and then poured into water. The organic phase was separated and the aqueous layer extracted with dichloromethane (× 2). The combined organic layers yielded a yellow oil which was chromatographed (10% ethyl acetate–benzene) to give an unstable yellow oil (0·04 g) which is probably tricarbonyl(η-7-hydroxycyclo-octa-1,3,5-triene)iron, (IV): *m/e* 262 (M^{+}), 234, 206, and 178; δ [$(CD_3)_2CO$] 5·92 (2H, m, $H_{5,6}$), 5·40 (2H, m, $H_{2,3}$), 4·08 (1H, d, *J* 6 Hz, OH), 3·68 (1H, m, H_7), 3·30 (2H, m, $H_{1,4}$), and 2·0 (2H, m, H_8).

Reaction of complex (IV) with pyridine–acetic anhydride gave (I; R = H) as the only isolable product and protonation with hexafluorophosphoric acid yielded (2-6-η-bicyclo-[5.1.0]octadienylium)tricarbonyliron hexafluorophosphate, (II; R = R′ = H).[5]

Oxidation of Complex (VII).—A solution of complex (VII) (0·2 g) and silver picolinate (1·0 g) in aqueous dimethyl sulphoxide was stirred at 40 °C for 20 min.[15] The cooled solution was extracted with pentane (× 3) and the organic phase dried over $MgSO_4$. Removal of the solvent gave a colourless oil which was dissolved in benzene (10 cm^{3}), 10% Pd–C (0·2 g) was added, and the resulting mixture heated under reflux for 16 h. Filtration and removal of the solvent gave a colourless oil which was crystallised from pentane to give indan-1-one (80%), identified by comparison with an authentic sample.

Bicyclo[4.2.1]*non-2-en-9-one*, (X).—A solution of complex (IX; R = H) (0·4 g) in benzene (20 cm^{3}) was treated with carbon monoxide (100 atm, 25 °C) in a rocking autoclave for 20 h. Removal of the solvent and chromatography on silica (benzene) gave bicyclo[4.2.1]non-2-en-9-one, (X) (80%),[8] as the only product.

Reaction of Quadricyclene with [$Fe_2(CO)_9$].—A mixture of quadricyclene (0·2 g) [16] and [$Fe_2(CO)_9$] (0·4 g) in pentane was stirred at room temperature for 4 h. Filtration and removal of the solvent gave an oil which was chromatographed (10% ethyl acetate–benzene) to give complex (XV) (15%), identical with the complex prepared from (XIII) and anhydrous $AlCl_3$.

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