Some Reactions of Tricarbonyl(η-hexa-1,3,5-triene)iron(0)

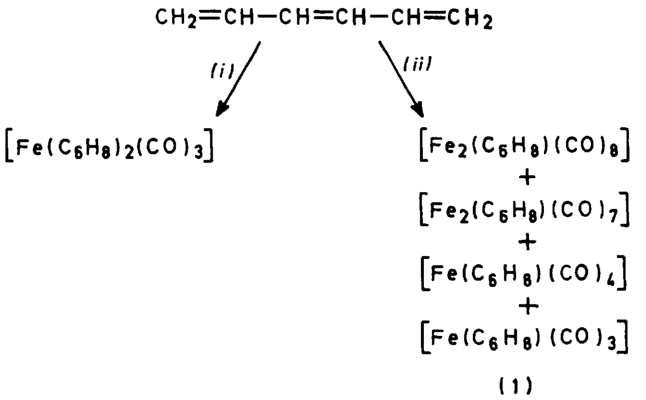
By **Brian F. G. Johnson, Jack Lewis,* David G. Parker,** and **S. Roderick Postle,** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The title complex has been prepared from the reaction of hexa-1,3,5-triene with nonacarbonyldi-iron(0), and some reactions of the unco-ordinated olefinic residue with electrophiles and with eneophiles have been studied. With boranes, tricarbonyl(3—6-η-hexa-3,5-dien-1-ol)iron(0) is obtained in moderate yields, after oxidative work-up of the intermediate borane complex, and with osmium tetraoxide in pyridine tricarbonyl(3—6-η-hexa-3,5-diene-1,2-diol)iron(0) is obtained in poor yields. With other electrophiles, no characterisable iron-containing organic compounds have been isolated. Protonation of the title complex gives tricarbonyl(2—6-η-hexadienyl)iron(0) tetrafluoroborate. Attempts to deprotonate this complex lead to the isolation of other products.

COMPLEXES of linear conjugated trienes with iron, ruthenium, and osmium are known, where two olefinic residues are bonded to the metal moiety and one is left ' free '.[1-4] Some reactions of this ' free ' carbon–carbon double bond with electrophiles have been studied in the tricarbonyl(monoterpene)iron(0) series,[3,4] and the results indicate that, with a kinetically fast electrophile, excellent yields of products deriving from attack at the unco-ordinated olefinic site are obtainable. It was decided to extend this study to observe the effect of a butadienyltricarbonyliron(0) group on an olefinic bond bearing no other substituents. To this end, tricarbonyl(η-hexa-1,3,5-triene)iron(0) (1) was prepared in order to study the reactivity of the ' free ' olefinic residue. It was hoped, further, that successful electrophilic addition to this carbon–carbon double bond, followed by oxidative cleavage of the tricarbonyliron(0) moiety, would lead to the synthesis of some preparatively useful 5,6-disubstituted hexa-1,3-dienes.

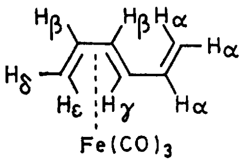
RESULTS AND DISCUSSION

Preparation of Complex (1).—Hexatriene was prepared according to the literature procedure[5] after it was discovered that acrolein and allylidenetriphenylphosphorane could not be induced to react in Wittig fashion, under a variety of conditions. The reactions of hexa-1,3,5-triene with iron carbonyls are summarised in Scheme 1.[1,6] We found that, by a modification of the reaction of nonacarbonyldi-iron(0) with hexa-1,3,5-triene where the crystalline di-iron complexes are pyrolysed to (1) by heating under reflux in benzene, an air-stable distillable liquid may be prepared in 60% yield.

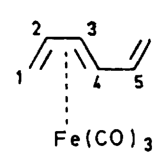


SCHEME 1 (*i*) $[Fe_3(CO)_{12}]$, reflux; (*ii*) $[Fe_2(CO)_9]$, pentane, reflux

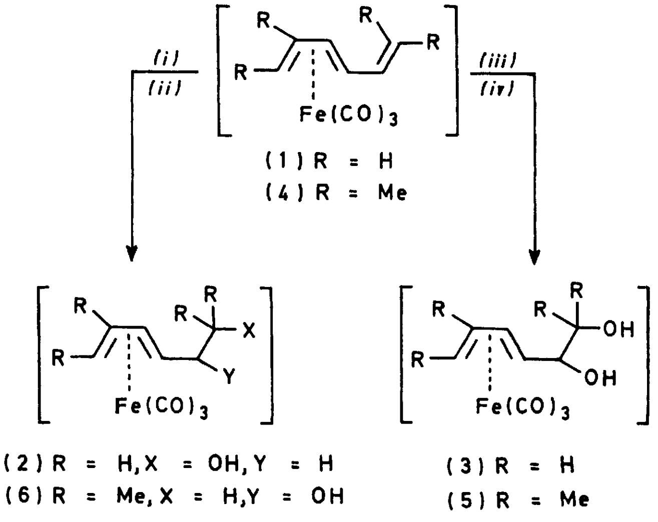
Treatment of hexa-1,3,5-triene with (benzylideneacetone)tricarbonyliron(0) in refluxing benzene furnished complex (1) in 16% yield. On the basis of its ^{1}H n.m.r. spectrum {τ(CCl_4) 4.1—5.1 (m, 5 H, $H_\alpha + H_\beta$), 8.31 (m, 2 H, $H_\gamma + H_\delta$), 9.52 [dd, $J(H_\beta H_\epsilon)$ 9.5, $J(H_\delta H_\epsilon)$ 2.4 Hz, 1 H, H_ϵ]} complex (1) was presumed to exist in the *syn* configuration (A). The ^{13}C n.m.r. spectrum was also consistent with the triene structure [δ(C^2HCl_3) 39.6 (C^1), 62.1 (C^4), 85.9 (C^2), 81.4 (C^3), 114.7 (C^6), 138.6 (C^5) in good agreement with that reported by Anderson *et al.*[7]]. The assignment of the carbon atoms was facilitated by selective off-resonance decoupling.



(A)



(B)



(1) R = H
(4) R = Me
(2) R = H, X = OH, Y = H
(6) R = Me, X = H, Y = OH
(3) R = H
(5) R = Me

SCHEME 2 (*i*) BF_3–$Na[BH_4]$–tetrahydrofuran (thf); (*ii*) $K[OH]$–water–H_2O_2; (*iii*) OsO_4–pyridine; (*iv*) $Na_2[S_2O_5]$–water

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[2] G. G. Ecke, U.S.P. 3,111,533 (*Chem. Abs.*, 1964, **60**, 3016d).

[3] D. V. Banthorpe, H. Fitton, and J. Lewis, *J.C.S. Perkin I*, 1973, 2051.

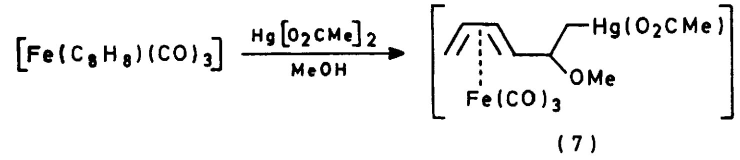
[4] G. Evans, B. F. G. Johnson, and J. Lewis, unpublished work.

[5] J. C. H. Hurd and H. Sims, *Org. Synth.*, 1961, **41**, 39.

[6] J. Xavier, M. Thiel, and E. R. Lippincott, *J. Amer. Chem. Soc.*, 1961, **83**, 2403.

[7] M. Anderson, A. D. H. Clague, L. P. Blaauw, and P. A. Couperus, *J. Organometallic Chem.*, 1973, **56**, 307.

Treatment of (1) with diborane (generated *in situ*) gave, after oxidative work-up, tricarbonyl(3—6-η-hexa-3,5-dien-1-ol)iron(0) (2) in a reproducible yield of 42% (Scheme 2). Complex (1) was recovered in *ca.* 35% yield. Treatment of (1) with the sterically hindered 9-borabicyclo[3.3.1]nonane resulted in the isolation of (2) in only 15% yield, again after oxidative work-up. Complex (1) was recovered only in 20% yield. It may be conjectured that, with the kinetically slower borane, a greater percentage of attack is occurring at iron as opposed to the ' free ' olefin.

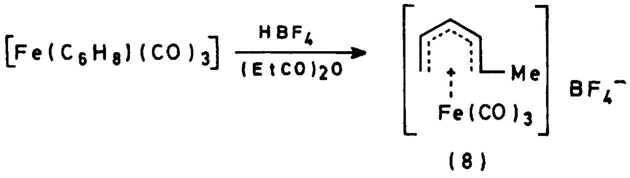


SCHEME 3

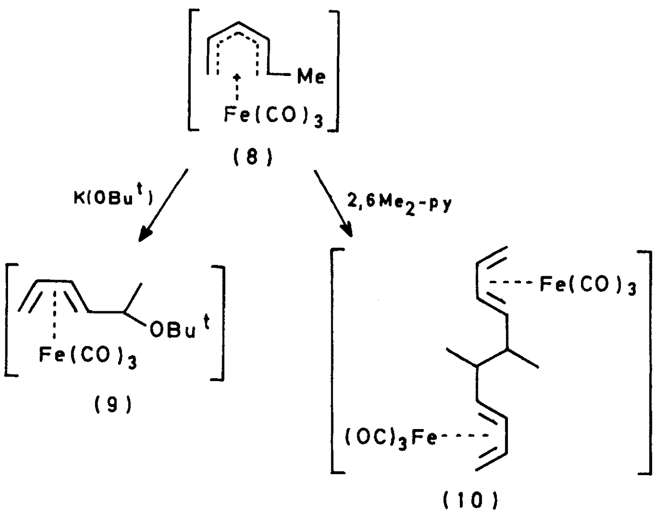
Complex (1) was recovered quantitatively after treatment with the Simmons–Smith reagent (Zn–Cu–CH_2I_2). {The related tricarbonyl(η-cycloheptatriene)iron(0) is reported to undergo cyclopropane formation with this reagent, to give (bicyclo[5.1.0]octa-1,3-diene)tricarbonyliron(0) in 20% yield.[8]} With osmium tetraoxide complex (1) furnished tricarbonyl(3—6-η-hexa-3,5-diene-1,2-diol)iron(0) (3) in, reproducibly, 10% yield (Scheme 2). No starting material was ever recovered. By way of comparison, the 2,6-dimethylocta-2,4,6-triene complex (4) is converted into diol (5) in 69% yield on treatment wth OsO_4 under exactly analogous conditions, and yields alcohol (6) in 63% on hydroboration[3,4] (Scheme 2).

It appears that the two methyl groups conjoining the ' free ' olefinic residue in complex (4) increase considerably the nucleophilicity of this group relative to the comparable olefinic residue in (1), thus furnishing a much higher yield of product deriving from attack at this centre rather than at iron. The view that the ' free ' olefinic and iron centres in complex (1) have not very different nucleophilicities was substantiated by the reactions of (1) with less kinetically rapid electrophiles. Treatment of (1) with methanolic sulphuric acid gave no organic products containing an iron carbonyl moiety. Treatment of (1) under Vilsmier conditions ($POCl_3$–Me_2NCHO, 10 °C) gave, on work-up, only polymeric materials not containing iron. With methanolic mercury(II) acetate, complex (1) furnished a 4.5% yield of yellow crystalline material believed to be the mercury(II) adduct (7) (Scheme 3). Conditions were not found under which complex (1) would undergo a Diels–Alder reaction. It was recovered unchanged after treatment with freshy distilled cyclopentadiene, tetraphenylcyclopentadienone in hexane, or 2-ethoxybutadiene in hexane, all under reflux.

Protonation of Complex (1).—It was proposed that the *anti* isomer of complex (1) might be preparable by a protonation–deprotonation sequence from (1). The cationic complex (8) was prepared in 74% yield as shown in Scheme 4. The reactions of complex (8) with a wide variety of nucleophiles, to yield 5-substituted hexa-1,3-diene complexes, have been described.[9] Triethylamine added to (8) to give a quaternary ammonium salt,* rather than reacting by proton abstraction.[10] Treatment of complex (8) with basic alumina yields complex (1).[7] However, attempts by us to deprotonate complex (8) were unsuccessful. Treatment of complex (8) with 1,8-diaminonaphthalene in acetone gave only polymeric material. With potassium t-butoxide in thf, complex (8) underwent addition to give tricarbonyl(3—6-η-2-t-butoxyhexa-3,5-diene)iron(0) (9) in 35% yield (Scheme 5). No hexatriene complexes were detected. Treatment of complex (8) with 2,6-dimethylpyridine gave the dimeric complex (10) in 45% yield. This complex had been prepared previously from (8) by reaction with alkali-metal hydroxides in methanol–acetone or with



SCHEME 4



SCHEME 5

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* It has recently been reported that pyrolysis of this ammonium salt affords complex (1) in near-quantitative yield.[11]

[8] D. L. Reger and A. Gabrielli, *J. Amer. Chem. Soc.*, 1975, **96**, 4421.

[9] J. E. Mahler, D. H. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 3959.

[10] P. McArdle and H. Sherlock, *J. Organometallic Chem.*, 1973, **52**, C29.

[11] P. McArdle and H. Sherlock, *J.C.S. Chem. Comm.*, 1976, 537.

zinc in thf.[9] Efforts to prepare the *syn* isomer of (1) from complex (8) were thus abandoned.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian CFT-20 instrument operating at 79.5 MHz, ^{13}C n.m.r. spectra on a Varian XL-100-15 instrument operating at 25.2 MHz. The solvent in each case was $CDCl_3$. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Tetrahydrofuran (thf) was redistilled from sodium diphenylketyl prior to use. Reactions were performed under an atmosphere of nitrogen.

Tricarbonyl(η-*hexa*-1,3,5-*triene*)*iron*(0) (1).—Nonacarbonyldi-iron(0) (72 g, 0.2 mol) and hexatriene (5.4 g, 0.067 mol) were heated under reflux in pentane (120 cm^3) for 2.5 h. The cooled filtrate, stored at 0 °C, gave a crop of green-brown crystals (8.9 g). Concentration of the mother liquors gave a further crop (2.1 g). The crystals were heated briefly in refluxing benzene (100 cm^3), and the solvent was removed under reduced pressure to give a green oil. This was combined with the filtrate (see above), taken up in pentane, filtered under a slight vacuum through a 10 cm column of neutral alumina (removing the green colour), and distilled to give a fraction, b.p. 53—54 °C (0.8 mmHg) [lit.,[1] 48 °C (0.05 mmHg)],* of *tricarbonyl*(η-*hexa*-1,3,5-*triene*)*iron*(0) (8.60 g, 60%) as a red liquid of minty odour; i.r. bands in pentane at 2 050, 1 990, and 1 975 cm^{-1} (as in ref. 1).

Tricarbonyl(3—6-η-*hexa*-3,5-*dien*-1-*ol*)*iron*(0) (2).—To complex (1) (0.55 g, 2.5 mmol) and sodium tetrahydroborate (0.15 g, 4 mmol) in thf (10 cm^3) was added over 1.5 h $OEt_2 \cdot BF_3$ (redistilled over CaH_2) (0.38 cm^3, 3 mmol). The mixture was stirred at ambient temperature for 22 h, then treated with 10% potassium hydroxide solution (25 cm^3), followed by 27.5% hydrogen peroxide (6 cm^3). After 30 min, oxygen evolution had ceased and the mixture was separated. The aqueous layer was extracted with diethyl ether (25 cm^3), the ether portions were washed with 3% hydrochloric acid (2 × 20 cm^3) and water (25 cm^3), dried, and evaporated under reduced pressure to yield a red liquid (0.50 g). Chromatography (diethyl ether–alumina) eluted first starting material (0.176 g, 32%), and, on changing the eluant to diethyl ether–ethanol (1 : 1), a green-yellow oil (0.252 g, 42%) which could not be induced to crystallise. It was identified as *tricarbonyl*(3—6-η-*hexa*-3,5-*dien*-1-*ol*)*iron*(0) (Found: C, 45.1; H, 4.5. $C_9H_{10}FeO_4$ requires C, 45.4; H, 4.25%); i.r. bands in $CHCl_3$ at 3 360br, 2 045, 1 975, and 1 965 cm^{-1}. N.m.r. spectrum: τ 4.72 (m, 2 H), 6.30 (m, 2 H; on addition of ^2H_2O this signal became a triplet, *J* 7 Hz), 7.95—9.0 (m, 4 H), and 9.65 (dd, *J* 8.5, 2.5 Hz, 1 H).

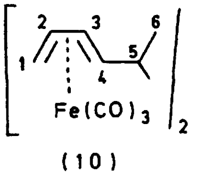
Tricarbonyl(3—6-η-*hexa*-3,5-*diene*-1,2-*diol*)*iron*(0) (3).—Osmium tetraoxide (0.1 g, 3.9 mmol) and complex (1) (0.086 g, 3.9 mmol) were stirred at ambient temperature in dry pyridine for 23 h. Water (10 cm^3) and disodium disulphite (2 g) were added, and the mixture was shaken for 24 h. It was then extracted with ethyl acetate (2 × 10 cm^3), and the extracts were washed with 3% HCl (2 × 20 cm^3) and brine (10 cm^3), dried, and evaporated under reduced pressure to give a yellowish solid (0.010 g, 10%), identified as *tricarbonyl*(3—6-η-*hexa*-3,5-*diene*-1,2-*diol*)*iron*(0). Recrystallisation from diethyl ether afforded yellowish needles, m.p. 107—108 °C (Found: C, 42.7; H, 3.8. $C_9H_{10}FeO_5$ requires C, 42.55; H, 3.95%), i.r. bands in $CHCl_3$ at 3 550br, 3 400br, 2 051, 1 983, and 1 973 cm^{-1}; the mass-spectrum showed peaks at *m/e* 226 (*M* − CO), 198 (*M* − CO)$^+$, 198 (*M* − 2CO)$^+$, and 170 (*M* − 3CO)$^+$.

Reaction of Mercury(II) *Acetate with Complex* (1).—Complex (1) (0.44 g, 2 mmol) was added dropwise to a stirred mixture of mercury(II) acetate (0.42 g, 2 mmol) and methanol [redistilled from $Mg(OMe)_2$, 3 cm^3]. After 20 min, the mixture was filtered and the filtrate was evaporated under reduced pressure to yield a brown oil (1.08 g). Chromatography (diethyl ether–alumina) gave starting material (0.128 g, 29%). Elution with diethyl ether–methanol (1 : 1) furnished a yellow solid (0.045 g). No other compounds could be eluted, even on changing to neat methanol. The solid was recrystallised from diethyl ether, m.p. 109—110 °C, i.r. bands in $CHCl_3$ at 2 048 and 1 964br cm^{-1}; n.m.r. spectra τ 4.58 (m, 2 H), 5.95 (m, 1 H), 6.62 (s, 3 H), 7.5—9.35 (m, 7 H), and 9.55 (m, 1 H). Satisfactory analytical data were not obtained. The mass spectrum showed peaks at *ca. m/e* 510, but also some small peaks up to at least *m/e* 600. Treatment of the crystalline material with sodium tetrahydroborate in methanol gave a small amount of heavy black precipitate.

Tricarbonyl(2—6-η-*hexadienyl*)*iron*(0) *Tetrafluoroborate* (8).—To a solution of fluoroboric acid (40% w/v, 1.12 g) in propionic anhydride (3 cm^3) was added a solution of complex (1) (1.10 g, 5 mmol) in $(EtCO)_2O$ (2 cm^3), such that $5 \leqslant \theta_c \leqslant 10$ °C (*ca.* 30 min). The mixture was stirred for another 15 min, then diethyl ether (15 cm^3) was added, and the solution was stirred for 10 min. It was then filtered and the yellow residue was washed with much dry diethyl ether, and dried in air, giving *tricarbonyl*(2—6-η-*hexadienyl*)-*iron*(0) *tetrafluoroborate* (1.14 g, 74%), decomp. >190 °C (lit.,[9] decomp. >195 °C), i.r. bands in Nujol at 2 110 and 2 052 cm^{-1} (lit.,[9] for the $[ClO_4]^-$ salt in $MeNO_2$ at 2 120 and 2 072 cm^{-1}).

Tricarbonyl(3—6-η-2-*t-butoxyhexa*-3,5-*diene*)*iron*(0) (9).—Complex (8) (0.15 g, 1.6 mmol) was stirred with potassium t-butoxide (as the 1 : 1 complex with t-butyl alcohol; 0.30 g, 1.6 mmol) in thf (10 cm^3) for 5 min. Filtration and evaporation of the filtrate under reduced pressure gave a brown oil, purified by preparative t.l.c. (diethyl ether–silica), giving a yellow-brown oil identified as *tricarbonyl*-(3—6-η-2-*t-butoxyhexa*-3,5-*diene*)*iron*(0) (0.165 g, 35%) (Found: C, 53.25; H, 5.85. $C_{13}H_{18}FeO_4$ requires C, 53.1; H, 6.15%), i.r. bands at 2 840s, 2 041, 1 976, and 1 965 cm^{-1}; n.m.r. spectrum τ 5.12 (m, 2 H) and 6.75—9.50 [m, 16 H; including 8.33 (strong s)].

μ-(1—4-η:7—10-η-5,6-*dimethyldeca*-1,3,7,9-*tetraene*)-*bis*(*tricarbonyliron*) (10).—To a stirred solution of complex (8) (0.55 g, 1.79 mmol) in thf (5 cm^3) was added, dropwise, 2,6-dimethylpyridine (0.21 cm^3, 1.79 mmol) in thf (5 cm^3). The mixture was stirred for another 30 min, evaporated under reduced pressure, and the residue was extracted with dimethyl ether, filtered, and the filtrate evaporated to yield an oil (0.23 g) which crystallised on standing. Recrystallisation from diethyl ether afforded lemon crystals (0.180 g,



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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

45%) identified as μ-(1—4-η:7—10-η-5,6-*dimethyldeca*-1,3,7,9-*tetraene*)-*bis*(*tricarbonyliron*) (presumed to be a mixture of diastereoisomers), m.p. 108—126 °C (as lit.[9]), i.r. bands in $CHCl_3$ at 2 051, 1 987, and 1 973 cm^{-1} (lit.,[9] 2 046, 1 985, and 1 971 cm^{-1}); n.m.r. spectrum τ 4.62 (m, 2 H), 8.19 (m, 1 H), 8.6—8.9 [m, 5 H: including 8.65 (d, *J* 6 Hz)], and 9.65 (m, 1 H) (approximately as lit.[9]). Carbon-13 n.m.r.; δ 23.1 (C^6), 41.1 (C^5), 66.2 (C^4), 75.4 (C^1), 82.8 (C^3), and 87.3 (C^2) (assignments based on the selective off-resonance decoupled spectrum); mass spectrum, *m/e* 442.

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