Transition-metal Carbonyl Complexes derived from Cyclo-octa-2,4,6-trienone and Cyclohepta-2,4,6-trienone †

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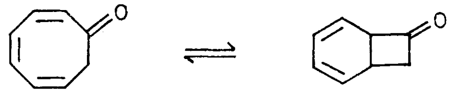
Acid-catalysed hydrolysis of methoxycyclo-octatetraene, (3), is a convenient route to cyclo-octa-2,4,6-trienone, (1). The reaction of (3) with dodecacarbonyl-*triangulo*-tri-iron affords tricarbonyl(η-methoxycyclo-octatetraene)-iron, which on acid-catalysed hydrolysis gives tricarbonyl(2—5-η-cyclo-octa-2,4,6-trienone)iron, (6); use of deuteriated acid yields (6) stereospecifically monodeuteriated in the *anti*-8-position. Treatment of (1) with (benzylideneacetone)tricarbonyliron gives the tricarbonyliron complex of bicyclo[4.2.0]octa-2,4-dien-7-one, the bicyclic valence isomer of (1). The reaction of tricarbonyl(η-cyclohepta-2,4,6-trienone)iron with diazomethane does not lead to ring expansion, but gives a pyrazoline by regiospecific 1,3-dipolar cycloaddition. Thermolysis of the pyrazoline, and its analogue prepared using [$^2H_2$]diazomethane, yields the corresponding tricarbonyliron complexes of bicyclo[5.1.0]octa-3,5-dienone.

A CONSIDERABLE amount of attention has been devoted in recent years to the study of the chemistry of metal carbonyl complexes of cyclic polyenones. Thus the relative reactivity of tricarbonylcyclohexadienoneiron and tricarbonylcycloheptadienoneiron has been compared,[1] and a number of workers have studied aspects of the chemistry of tricarbonyltroponeiron [2,3] and tricarbonyltroponechromium (tropone = cyclohepta-2,4,6-trien-1-one).[4] This paper deals with metal carbonyl derivatives of cyclo-octa-2,4,6-trienone, (1) (hereafter called cyclo-octatrienone), and with an example of a cycloaddition reaction involving tricarbonyltroponeiron.

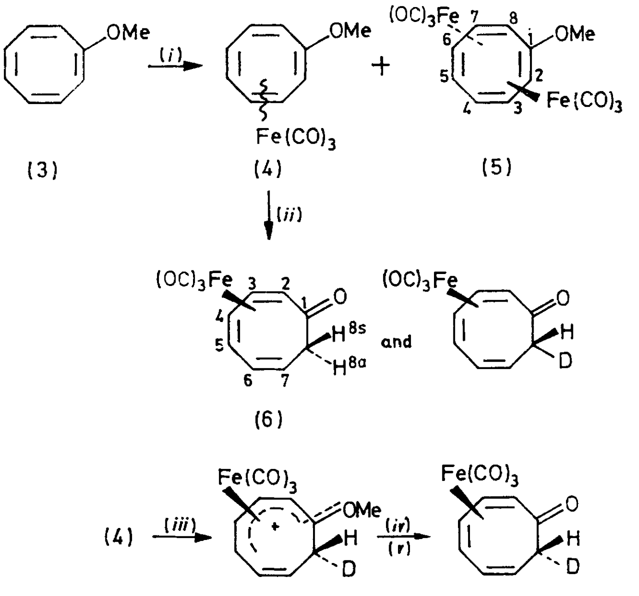
RESULTS AND DISCUSSION

Complexes derived from Cyclo-octatrienone.—Cyclo-octatrienone, (1), was first prepared by the action of di-isopropylaminolithium on cyclo-octatetraene oxide by Cope *et al.*,[5] who suggested that (1) exists in equilibrium with a small concentration of the bicyclic valence isomer, bicyclo[4.2.0]octa-2,4-dien-7-one, (2), since samples of (1) show a low-intensity carbonyl-stretching band at 1 784 cm^{-1} as well as a more intense band at 1 665 cm^{-1}, and since treatment of (1) with dienophiles (*e.g.* maleic anhydride) gives adducts derived from (2). Huisgen[6] later estimated that the equilibrium ratio of (1) : (2) was 19 : 1 at 20 °C. By the reaction of cyclo-octatrienone with dodecacarbonyl-*triangulo*-tri-iron or enneacarbonyl-di-iron, King[7] obtained a complex [$Fe(C_8H_8O)(CO)_3$] in 13% yield, which he concluded contained the ring skeleton of (1), but no attempt was made to delineate which of the π bonds of (1) are involved in bonding to the metal.



(1) (2)

We find that (1) is more readily obtained by the acid-catalysed hydrolysis of the readily available[8] methoxycyclo-octatetraene, (3). Reaction of (3) with [$Fe_3(CO)_{12}$] gave the expected complex (4) ‡ in good yield, as well as a small amount of the bis(tricarbonyliron) complex, (5). Acid-catalysed hydrolysis of (4) gave in essentially quantitative yield the complex [$Fe(C_8H_8O)(CO)_3$] previously obtained by King. When the hydrolysis of (4) was repeated using deuteriated acid, the ketone complex obtained was specifically deuteriated both in a positional and in a stereochemical sense. This can be seen by comparing the ^1H n.m.r. spectra of the deuteriated and undeuteriated complex (Figure 1). These spectra also



(3) (4) (5) (6) (4) (7) (8)

SCHEME (*i*), [$Fe_3(CO)_{12}$]; (*ii*), H_3O^+ or D_3O^+; (*iii*), D_3O^+; (*iv*), $+D_2O$; (*v*), $-MeOD$

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† No reprints available.

‡ Stereochemically non-rigid (see L. A. Paquette, *Tetrahedron*, 1975, **31**, 2855; in particular, p. 2875).

[1] R. J. H. Cowles, B. F. G. Johnson, J. Lewis, and A. W. Parkin, *J.C.S. Dalton*, 1972, 1768.

[2] A. Eisenstadt and S. Winstein, *Tetrahedron Letters*, 1971, 613.

[3] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

[4] P. L. Pauson and K. H. Todd, *J. Chem. Soc.* (*C*), 1970, 2315.

[5] A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, 1951, **73**, 4158; A. C. Cope, S. F. Schaeren, and E. R. Trumbull, *ibid.*, 1954, **76**, 1096.

[6] R. Huisgen, *Chem. Soc. Special Publ.*, 1964, **19**, 3.

[7] R. B. King, *Inorg. Chem.*, 1963, **2**, 807.

[8] J. Gasteiger, G. E. Gream, R. Huisgen, W. E. Konz, and U. Schnegg, *Chem. Ber.*, 1971, **104**, 2412.

allow the 2—5-η structures (6) and (8) to be assigned to the complexed ketones, rather than the alternative 4—7-η structures (9) and (10). Thus the doublet at δ 2.97 p.p.m. and the doublet of doublets (apparent triplet) at δ 3.36 p.p.m. are the same in the deuteriated and undeuteriated ketone complex; these signals can therefore be assigned to the outer complexed diene protons H^2 and H^5 respectively. In the alternative structures (9) and (10) the outer complexed diene protons would be H^4 and H^7. Both of these protons would be expected to give rise to doublet of doublets in the deuteriated compound (10): H^4 through coupling to H^3 and H^5, and H^7 through

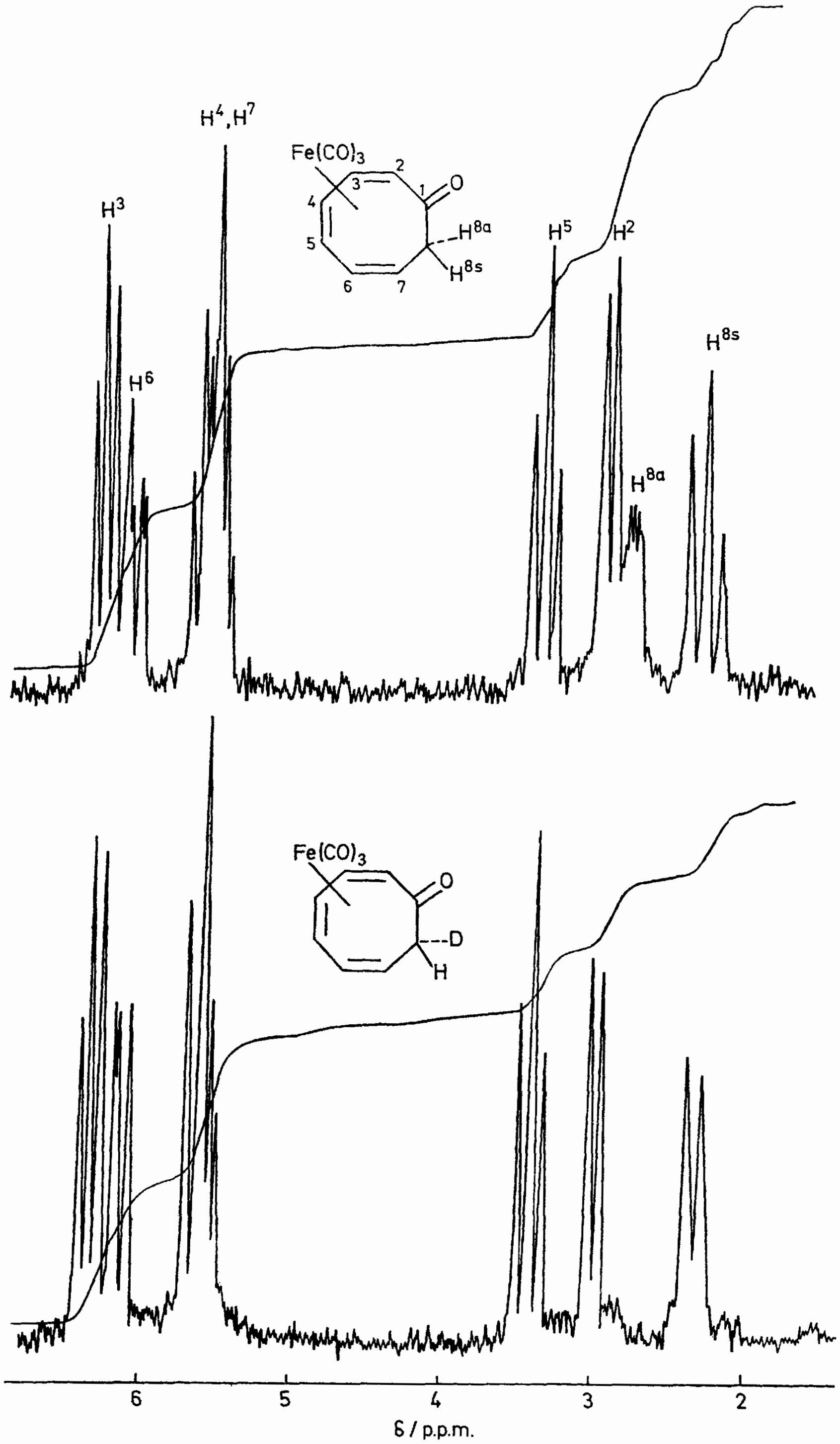


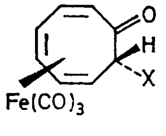
FIGURE 1 ^{1}H N.m.r. spectrum of tricarbonyl(2—5-η-cyclo-octa-2,4,6-trienone)iron

^1H N.m.r. data (100 MHz, $CDCl_3$, $SiMe_4$ internal standard) and infrared carbonyl bands (cyclohexane) for the metal carbonyl complexes

Complex	Protons	Chemical shift, δ/p.p.m.	Intensity	ν(CO)/cm⁻¹
(4)	OCH_3	3.54 (s)	3	2 050, 1 988, 1 974
	H^2—H^8	4.45—6.80 (m)	7	
(5)	H^4, H^5, H^8	2.55—3.60 (m)	3	2 043, 1 983, 1 978
	OCH_3	3.70 (s)	3	
	H^3	4.20 (d)	1	
	H^2	5.25 (dd), *J* 8.5, 1.5 Hz	1	
	H^6, H^7	5.40—5.62 (m)	2	
(6)	H^{8s}	2.30 (ddd), *J* 10.0, 10.0, 2.0 Hz	1	2 063, 2 006, 1 985, 1 673
	H^{8a}	2.85 (m)	1	
	H^2	2.97 (d), *J* 6.5 Hz	1	
	H^5	3.37 (dd), *J* 7.5, 7.5 Hz	1	
	H^4, H^7	5.42—5.75 (m)	2	
	H^6	6.10 (ddd), *J* 9.0, 7.5, 2.0 Hz	1	
	H^3	6.25 (dd), *J* 6.5, 6.5 Hz	1	
(8)	H^8	2.32 (d), *J* 9.5 Hz	1	2 061, 2 005, 1 985, 1 670
	H^2	2.96 (d), *J* 6.5 Hz	1	
	H^5	3.36 (dd), *J* 7.5, 7.5 Hz	1	
	H^4, H^7	5.42—5.70 (m)	2	
	H^6	6.10 (dd), *J* 9.0, 7.5 Hz	1	
	H^3	6.24 (dd), *J* 6.5, 6.5	1	
(11)	H^8	2.15 (dt), *J* 17.0, 3.5	1	2 051, 1 984, 1 980, 1 785
	H^1, H^6, H^8	2.55—3.2 (m)	3	
	H^2, H^5	3.45 (m)	2	
	H^3, H^4	5.46 (dd), *J* 5.0, 5.0 Hz	1	
		5.75 (dd), *J* 5.0, 5.0 Hz	1	
(14)	H^8	2.40 (dd), *J* 12.0, 8.5 Hz	1	1 989, 1 954, 1 925, 1 687
	H^8	3.55 (m)	1	
	H^2—H^7	5.35—6.00 (m)	6	
(16) *	H^1	2.57 (ddd), all *J ca.* 10 Hz	1	2 067, 2 008, 1 998, 1 650
	H^3	3.16 (dt), *J* 7.5, 1.0 Hz	1	
	H^6	3.42 (dd), *J* 7.5, 4.0 Hz	1	
	H^{10x}	4.0 (ddd), *J* 18.0, 10.5, 2.0 Hz	1	
	H^{10n}	4.75 (dd), *J* 18.0, 10.5 Hz	1	
	H^4, H^5, H^7	5.40—5.90 (m)	3	
(17) *	H^1	2.56 (d), *J* 10.0 Hz	1	2 066, 2 008, 1 998, 1 651
	H^3	3.16 (d), *J* 7.5 Hz	1	
	H^6	3.40 (dd), *J* 7.5, 4.0 Hz	1	
	H^4, H^5, H^7	5.40—5.90 (m)	3	
(21)	H^8	1.00 (m)	1	2 060, 2 001, 1 986, 1 652
	H^8	1.25 (m)	1	
	H^1	1.55 (m)	1	
	H^7	2.01 (m)	1	
	H^3	3.12 (d), *J* 7.5 Hz	1	
	H^6	3.61 (dd), *J* 7.5, 7.5 Hz	1	
	H^4, H^5	5.46 (m)	1	
		5.80 (m)	1	
(22)	H^1	1.56 (d), *J* 7.5 Hz	1	2 060, 2 001, 1 987, 1 652
	H^7	2.00 (dd), *J* 7.5, 7.5 Hz	1	
	H^3	3.11 (d), *J* 7.5 Hz	1	
	H^6	3.62 (dd), *J* 7.5, 7.5 Hz	1	
	H^4, H^5	5.46 (m)	1	
		5.81 (m)	1	

* 60-MHz Spectrum.

coupling to H^6 and H^8. The highest-field resonance in (6) is that due to H^{8s} (H^8 which is *syn* * to the metal carbonyl group), due to coupling with H^{8a} and H^7. In (8) this signal has become a broad doublet, since H^{8a} is now replaced by D. The conclusion that it is H^{8a} which is replaced by D is based on the assumption that attack of D^+ on the enol ether double bond of methoxycyclo-octatetraene occurs from the less-hindered side [the side *anti* to the $Fe(CO)_3$ group, Scheme]. In this mechanism the positive charge developing at C^1 in the transition state can be stabilised by the electron-rich metal centre.



(9) X = H

(10) X = D

Such stereospecific attack from the *anti* side is also observed in the protonation of tricarbonylcyclo-octatetraeneiron in concentrated acid.[9], † The remaining proton assignments are listed in the Table.

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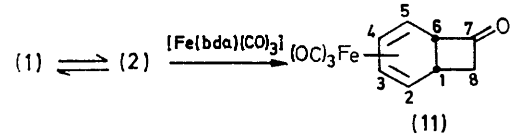
* Most workers refer to protons which are on the same or opposite side of the ring as the metal carbonyl group as being *endo* or *exo*, respectively. This nomenclature gives rise to confusion in describing metal complexes of bicyclic olefins. The terms *syn* and *anti* seem preferable, although as an alternative the terms M-*endo* or M-*exo* may be employed (implying *endo* or *exo* with regard to the metal respectively).

† This of course refers to the stereochemistry of the final bicyclic product; the stereochemistry of the initial product of H^+ addition at low temperatures may be different.

[9] M. Brookhart and E. R. Davis, *Tetrahedron Letters*, 1971, 4349 and refs. therein.

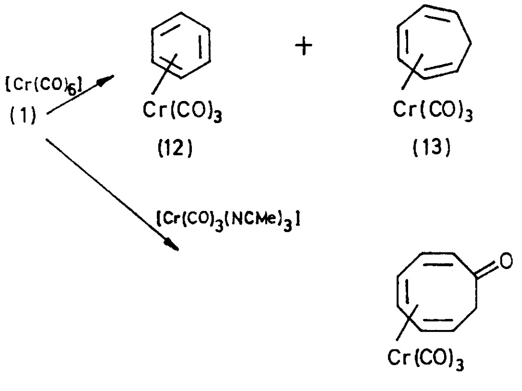
The formation of (6) rather than (9), both in the reaction described by King,[7] and in the hydrolysis of (4), suggests that (6) is thermodynamically more stable than (9). In the hydrolysis of (4), protonation is expected to occur as shown in the Scheme to give a dienyl cation (7) which derives additional stability from delocalisation of the positive charge on to the ether oxygen atom. Nucleophilic attack of water at C^1 would then be expected to give rise to ketone (6) or (8), rather than (9) or (10). It may be noted that the bis(tricarbonyliron) complex (5) is stable under these hydrolysis conditions: the enol ether double bond here is not free to be protonated under mild conditions.

When cyclo-octatrienone was heated with (benzylideneacetone)tricarbonyliron,[10] [Fe(bda)(CO)$_3$], at 75 °C the bicyclic complex (11) was obtained in 59% yield.*



(11)

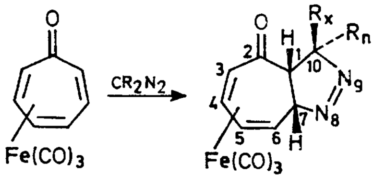
The structure of this complex follows from its ^{1}H n.m.r. spectrum, which showed only two protons in the low-field region, each as a doublet of doublets (apparent triplet), readily assignable to the inner complexed diene protons H^3 and H^4. Its i.r. spectrum showed, in addition to the metal carbonyl bands, a strong cyclobutanone carbonyl-stretching band at 1 785 cm^{-1}. The formation of (11) in this reaction thus represents another example[11] of the remarkable ability of [Fe(bda)(CO)$_3$] to selectively trap the cyclohexadiene valence isomer in a cyclohexadiene–hexatriene electrocyclic equilibrium situation.



(12) (13) (14)

King reported[7] that he was unable to obtain a tricarbonylchromium or tricarbonyltungsten complex from cyclo-octatrienone. We found that the reaction of (1) with hexacarbonylchromium in refluxing dibutyl ether gave (benzene)tricarbonylchromium, (12) (4%), and tricarbonyl(cycloheptatriene)chromium, (13) (11%). The formation of (12) is not surprising, since Cope and his co-workers[5] report that (1) on heating gives benzene and ketene, apparently *via* a $\pi2 + \pi2$ cycloreversion of the bicyclic ketone (2). Any benzene so formed would give rise to (12). The formation of (13) is more difficult to rationalise. Although the overall reaction involves a simple decarbonylation of (1) or (2), and a species such as $[Cr(CO)_5]$ would have a high affinity for carbon monoxide, it is difficult to write a satisfactory mechanism for such a conversion. The chromium complex (14) was, however, obtained readily under mild conditions from (1) using tri(acetonitrile)tricarbonylchromium.

Reaction of Tricarbonyltroponeiron with Diazomethane.—Another possible approach to cyclo-octatrienone metal carbonyl complexes would be by a one-carbon-ring expansion of cycloheptatrienone (tropone) metal carbonyl complexes. In order to investigate this possibility tricarbonyltroponeiron (15) was treated with excess of diazomethane in diethyl ether. A crystalline adduct was obtained on 83% yield.† Two minor, more polar (thin-layer chromatography), products were also present, but these could not be obtained pure; however tricarbonylcyclo-octatrienoneiron was shown to be absent by t.l.c. The ^{1}H n.m.r. spectrum of the cycloadduct is shown in Figure 2. The low-field multiplet at δ 5.90—5.40 p.p.m., due to three protons, can be assigned to the inner complexed diene protons H^4 and H^5, and H^7, the proton adjacent to the N=N linkage, since the latter type of proton is expected to resonate at such a low field.[13] The assignment of the remaining, well spread, one-proton multiplets could be made by comparison with the spectrum of the adduct obtained from (15) and [^{2}H$_2$]diazomethane (Figure 2). Thus the AB pattern, J_{AB} 18.0 Hz, with the A part further split by 10.5 Hz, and the B part further split by two couplings of 10.5 and 2.0 Hz, is due to the methylene protons H^{10}. The 10.5-Hz splitting arises from H^1, which itself gives rise to the highest-field multiplet (a ddd with all J *ca.* 10 Hz) at δ 2.54 p.p.m. This was confirmed by spin-decoupling experiments, since irradiation of the H^1 signal gave rise to an almost



(15) (16) R = H
(17) R = D

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* *Note added at proof:* This reaction has also recently been reported by M. Brookhart, G. O. Nelson, G. Scholes, and R. A. Watson, *J.C.S. Chem. Comm.*, 1976, 195.

† The reaction of (15) with diazomethane and substituted diazomethanes has recently been independently described by Franck-Neumann and Martina.[12] Their results are in complete agreement with our findings, where overlap exists.

[10] J. A. S. Howell, B. F. G. Johnson, P. L. Josty, and J. Lewis, *J. Organometallic Chem.*, 1972, **39**, 329.

[11] G. Scholes, C. R. Graham, and M. Brookhart, *J. Amer. Chem. Soc.*, 1974, **96**, 5665.

[12] M. Franck-Neumann and D. Martina, *Tetrahedron Letters*, 1975, 1759.

[13] See, for example, G. C. Overberger, N. Weinshenker, and J.-P. Anselme, *J. Amer. Chem. Soc.*, 1965, **87**, 4119.

clean AB quartet for the methylene protons H^{10x} and H^{10n}. In the deuteriated adduct (17), the H^1 resonance appeared as a broad doublet, *J ca.* 10 Hz, since the couplings with the methylene protons H^{10x} and H^{10n} have been removed, and only the coupling with H^7 remains. This latter coupling could be removed by irradiating at *ca.* δ 5.5 p.p.m. The doublet of doublets at δ 3.42 p.p.m. can be assigned to the outer co-ordinated diene proton H^6, while the doublet (with further splitting) at δ 3.12 p.p.m. is due to H^3. It is interesting to note that the further small splitting of this doublet must arise from long-range coupling, apparently with H^5 and H^1. Also the small 2.0-Hz splitting of one of the H^{10} signals must arise from long-range coupling to H^7, since this splitting was removed by irradiation at *ca.* δ 5.5 p.p.m. Molecular models reveal that a W arrangement of the type which

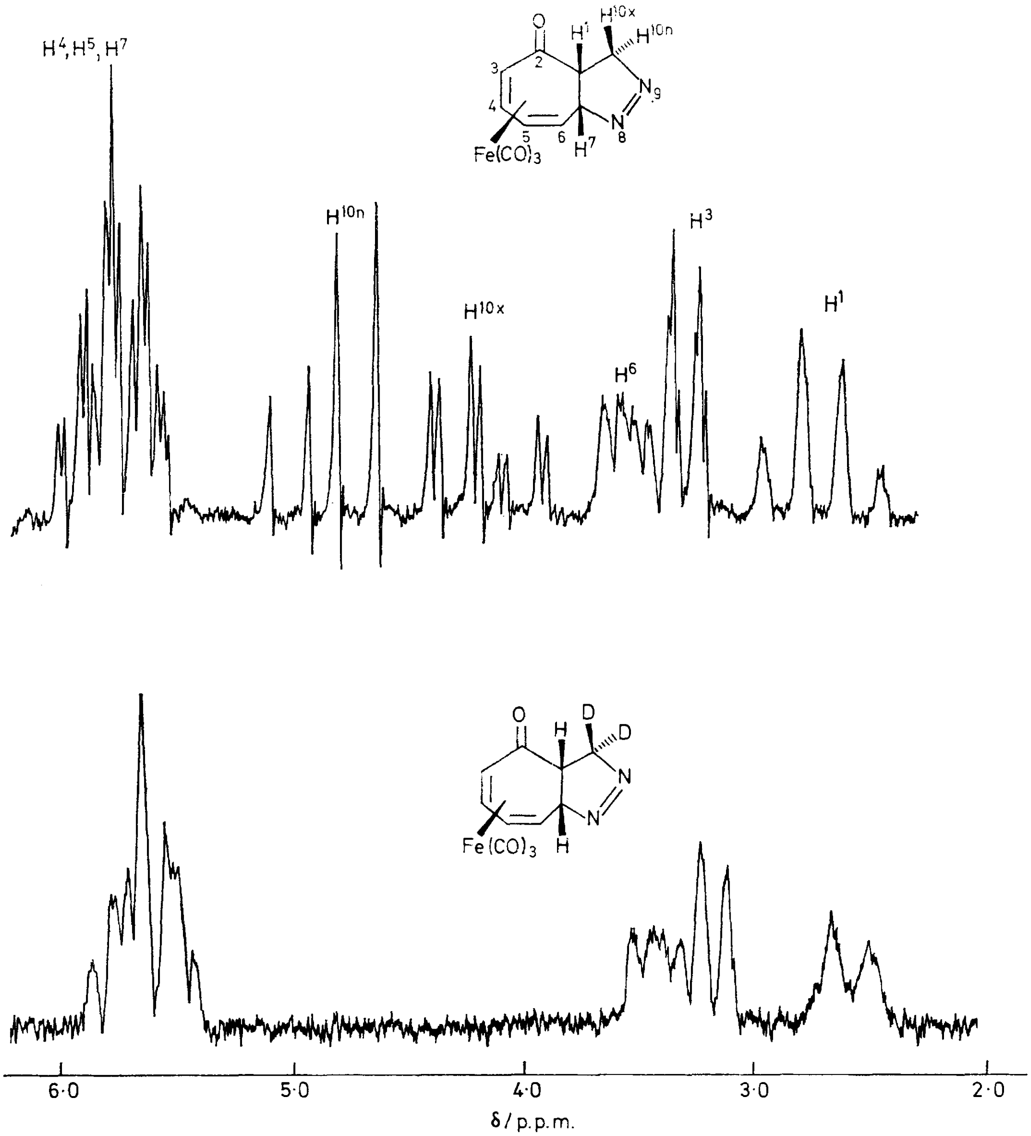
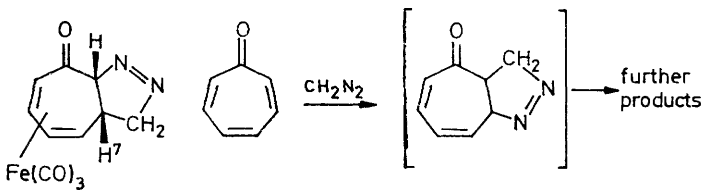


FIGURE 2 ^{1}H N.m.r. spectrum of tricarbonyl(3—6-η-8,9-diazabicyclo[5.3.0]deca-3,5,8-trien-2-one)iron

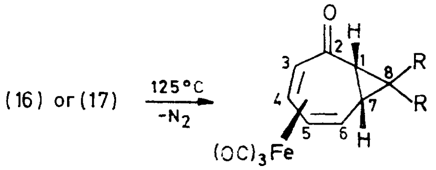


(18) (19) (20)

favours long-range coupling over four σ bonds[14] exists between H^7 and H^{10x}, the proton at the latter position having the *exo* configuration. The H^{10x} resonance is therefore that at δ 4.0 p.p.m., and the H^{10n} resonance is at δ 4.75 p.p.m.

The alternative structure (18) for the cycloadduct can be dismissed since the highest-field resonance in (18) would have to be that due to H^7. In the deuteriated analogue of (18) this resonance should be more complex than the observed doublet, since coupling to H^1 and H^6 should occur.

The addition of diazomethane to (15) thus occurs regiospecifically, to give an adduct (16) having the same regiochemistry as the adduct (20), postulated to be an intermediate in the reaction of tropone (19) with diazomethane.[15] In the latter reaction, the adduct (20) could not be isolated, but apparently underwent formal dehydrogenation (loss of H^1 and H^7), followed by tautomerism and methylation by diazomethane. Loss of nitrogen from (20) to give bicyclo[5.1.0]octa-3,5-dienone (2,3-homotropone) was another reaction path.[15] Co-ordination of tropone to the tricarbonyliron group thus serves to stabilise the cycloadduct, and leads to a cleaner reaction with fewer products. Furthermore, the small amount of attack at the carbonyl-carbon atom of tropone observed[15] [which gave rise to cyclo-octatrienone, (1)] is also suppressed in the complex (15).



(21) R = H
(22) R = D

When tricarbonyltroponechromium was treated with diazomethane in diethyl ether no reaction (apart from some decomposition) was observed. In particular, no new coloured (complexed) products, *e.g.* tricarbonyl(cyclo-octatrienone)chromium (14), could be detected. Co-ordination of tropone to a metal thus lowers the reactivity of the carbonyl group towards attack by diazomethane.

Thermolysis of adducts (16) and (17) readily gave the complexes (21) and (22) in excellent yield. The considerable simplification of the ^1H n.m.r. spectrum of the deuteriated complex (22) allows the coupling constants for most of the remaining protons to be extracted (Table). This synthesis of (bicyclo[5.1.0]octa-3,5-dienone)tricarbonyliron, (21), is a useful complement to the existing synthesis[16] starting with tricarbonyl(cyclo-octatetraene)iron, and, as has been shown by Franck-Neumann and Martina,[12] can be extended to other 8-substituted derivatives of (21).

EXPERIMENTAL

^1H N.m.r. spectra were recorded on Varian HA100 or Perkin-Elmer R12B or R25A spectrometers. Analyses were by the Microanalytical Section of this department. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer. All reactions involving metal complexes were carried out in an atmosphere of nitrogen.

*Reaction of Methoxycyclo-octatetraene with Dodecacarbonyl-*triangulo*-tri-iron.*—A solution of methoxycyclo-octatetraene[8] (1.0 g, 7.5 mmol) in octane (10 cm^3) was heated under reflux with $[Fe_3(CO)_{12}]$ (2.5 g, 4.0 mmol) for 2 h. The mixture was applied directly to a column of alumina (500 g). Elution with light petroleum gave initially a yellow solution, which on concentration to *ca.* 20 cm^3 gave *trans*-μ-(1—4-η : 5—8-η-1-methoxycyclo-octatetraene)-bis(tricarbonyliron), (5), as yellow crystals (210 mg, 10%), m.p. 132—133 °C (Found: C, 43.7; H, 2.6. $C_{15}H_{10}Fe_2O_7$ requires C, 43.5; H, 2.4%). This was closely followed by a red band, which on elution and evaporation afforded tricarbonyl(η-methoxycyclo-octatetraene)iron, (4), as a red low-melting solid (1.61 g, 79%). Sublimation (40 °C, 0.1 mmHg)* gave red-orange plates, m.p. 40—42 °C (Found: C, 52.7; H, 3.8. $C_{12}H_{10}FeO_4$ requires C, 52.6; H, 3.6%).

Tricarbonyl(η-cyclo-octatrienone)iron, (6).—A solution of complex (4) (460 mg) in tetrahydrofuran (thf) (10 cm^3) was treated with aqueous sulphuric acid (1 : 1) (3 cm^3). The colour changed rapidly from red to light orange. The mixture was stirred at room temperature for 10 min, diluted with water, and the complex (6) was isolated as an orange solid (380 mg, 90%) by extraction with light petroleum. Recrystallisation from light petroleum gave yellow needles, m.p. 103—104 °C (lit.,[9] 103 °C). The deuteriated analogue, (8), was prepared in a similar manner, except that D_2SO_4–D_2O (1 : 1) was used in the hydrolysis.

Cyclo-octatrienone, (1).—A solution of methoxycyclo-octatetraene (2.0 g) in thf (20 cm^3) was treated with aqueous sulphuric acid (1 : 1) (5 cm^3) and kept at room temperature for 30 min. The solution was diluted with water, and the ketone (1) was isolated by diethyl ether extraction as a pale yellow oil (1.7 g, 94%). The ^1H n.m.r. spectrum of this material was identical with the spectrum recorded[17] for (1) prepared according to Cope.[5]

(2—5-η-*Bicyclo*[4.2.0]*octa*-2,4-*dien*-7-*one*)*tricarbonyliron,* (11).—Cyclo-octatrienone (400 mg, 3.3 mmol) and (benzylideneacetone)tricarbonyliron (1.2 g, 4.2 mmol) in benzene (25 cm^3) were stirred at 70 °C for 68 h. Complex (11) was obtained by preparative t.l.c. (silica gel, CH_2Cl_2) from the fast-running yellow band as a pale yellow solid (510 mg, 59%), m.p. 67—68 °C (light petroleum) (Found: C, 50.5; H, 3.4. $C_{11}H_8FeO_4$ requires C, 50.8; H, 3.1%). A slower-running broad yellow band was shown by n.m.r. and t.l.c. analysis to consist mainly of benzylideneacetone and cyclo-octatrienone.

Reaction of (1) *with Hexacarbonylchromium.*—A solution of (1) (1.0 g, 8.3 mmol) in dibutyl ether (20 cm^3) was heated under reflux with $[Cr(CO)_6]$ (2.0 g, 9.1 mmol) for 40 h while

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[14] L. M. Jackman and S. Steinhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon Press, Oxford, 1969, p. 334.

[15] L. J. Luskus and K. N. Houk, *Tetrahedron Letters*, 1972, 1925.

[16] J. D. Holmes and R. Pettit, *J. Amer. Chem. Soc.*, 1963, **85**, 2531; for experimental details see L. A. Paquette and O. Cox, *ibid.*, 1967, **89**, 5633.

[17] C. Ganter, S. M. Pokras, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1966, **88**, 4235.

the $[Cr(CO)_6]$ was continuously returned to the flask with the aid of a mechanical scraper placed in the reflux condenser. The dark mixture was filtered through Celite and the filtrate was evaporated to dryness under reduced pressure to give a reddish solid (450 mg). T.l.c. analysis [silica gel, CH_2Cl_2–light petroleum (1 : 9)] showed a fast-running red spot followed by a yellow spot. Preparative t.l.c. gave tricarbonyl-(η-cycloheptatriene)chromium (13) (210 mg, 11%) from the red band; the n.m.r. spectrum was identical with that of an authentic sample.[18] The yellow band afforded (η-benzene)-tricarbonylchromium (12) (80 mg, 4%) as yellow crystals, m.p. 161—163 °C (lit.,[19] 162—163 °C), n.m.r. δ 5.30(s) p.p.m.; on standing at room temperature the n.m.r. sample decomposed to liberate free benzene, δ 7.3(s) p.p.m.

Tricarbonyl(η-*cyclo-octa*-2,4,6-*trienone*)*chromium*, (14).—Hexacarbonylchromium (2.0 g, 9.1 mmol) was heated under reflux in acetonitrile (50 cm^3) for 24 h. Removal of the acetonitrile *in vacuo* gave bright yellow $[Cr(CO)_3(NCMe)_3]$, and to this was added (1) (1.6 g, 10.3 mmol) in anhydrous thf (50 cm^3), and the mixture was heated under reflux for 2 h. The product was adsorbed on to silica gel (20 g), and placed on to a column of silica gel (150 g). Elution with diethyl ether–light petroleum (1 : 5) gave unchanged (1) (1.1 g). Diethyl ether and diethyl ether–methanol (19 : 1) eluted a red band, which on evaporation gave complex (14) as red crystals (900 mg, 26%), m.p. 128—130 °C (decomp.) (benzene–light petroleum) (Found: C, 51.3; H, 3.5. $C_{11}H_8CrO_4$ requires C, 51.6; H, 3.1%); *M* (mass spectrum) 256.

Reaction of Tricarbonyl(η-*cyclohepta*-2,4,6-*trienone*)*iron*, (15), *with Diazomethane*.—A solution of (15) (660 mg, 2.7 mmol) in diethyl ether (10 cm^3) was treated with excess of diazomethane (*ca.* 18 mmol) in diethyl ether (40 cm^3) and kept in the refrigerator for 60 h. The mixture was filtered through Celite to remove decomposition products, and the filtrate was concentrated and subjected to preparative t.l.c [silica gel, $MeCO_2Et$–CH_2Cl_2 (1 : 9)] to give *tricarbonyl*(3—6-η-8,9-*diazabicyclo*[5.3.0]*deca*-3,5,8-*trien*-2-*one*)*iron*, (16), as a yellow solid (640 mg, 83%), which crystallised from benzene–light petroleum as plates, m.p. 130—137 °C (decomp., gas evolution) (Found: C, 46.2; H, 2.95; N, 9.8. $C_{11}H_8FeN_2O_4$ requires C, 45.8; H, 2.8; N, 9.7%). Two slower-running yellow bands were also present, but no pure material could be isolated from these. The reaction was repeated using (15) (360 mg) and excess of $[^2H_2]$diazomethane.[20] Preparative t.l.c. as before gave unchanged (15) (120 mg), followed by the deuteriated adduct (17) (210 mg).

(*Bicyclo*[5.1.0]*octa*-3,5-*dien*-2-*one*)*tricarbonyliron*, (21).—A solution of the adduct (15) (120 mg) in toluene (5 cm^3) was heated at 125 °C until gas evolution ceased (15 min). Evaporation of the toluene under reduced pressure gave (21) as a crystalline solid (100 mg, 91%), which crystallised from benzene–light petroleum as yellow needles, m.p. 132—133 °C (lit.,[16] 131—132.5 °C). The deuteriated ketone (22) was prepared in a similar manner from (17).

Attempted Reaction of Diazomethane with Tricarbonyl(η-*cyclohepta*-2,4,6-*trienone*)*chromium*.—A solution of the complex (250 mg, 1 mmol) in diethyl ether (50 cm^3) containing excess of diazomethane (*ca.* 10 mmol) was kept in the refrigerator for 65 h. Some insoluble decomposition product was present, but t.l.c. analysis of the solution showed starting material as the only coloured spot.

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