## Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part VII.<sup>1</sup> **Complexes of Bicyclo-octatetraenyl: Crystal and Molecular Structures** of $[Ru_3(CO)_6(C_{16}H_{14})]$ and $[Fe(CO)_2(C_{16}H_{14})]$

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A minor product from the reaction of  $[Ru_3(CO)_{12}]$  with phenylcyclo-octatetraene has been identified by X-ray diffraction study as the complex  $[Ru_3(CO)_6(C_{16}H_{14})]$ , containing a bicyclo-octatetraenyl ligand attached to an  $[Ru_3(CO)_6]$  cluster. One of the C<sub>8</sub> rings has a bis- $\eta^3$ -allyl attachment to two metal atoms, with two formally bridging ' carbon atoms, one of which is also involved in bonding to the remaining ruthenium atom. The other ring is  $1,5-\eta^4$ -diene-bonded to this ruthenium atom, with the C<sub>8</sub> group in a 'tub' conformation. The complex is best obtained (80%) directly from bicyclo-octatetraenyl and [Ru<sub>3</sub>(CO)<sub>12</sub>] heated under reflux in toluene. Cleavage of bicyclo-octatetraenyl occurs on reaction with iron carbonyls, yielding known iron complexes of cyclo-octatetraene. Other products are the bicyclo-octatetraenyl complexes  $[Fe(CO)_3(C_{16}H_{14})]$  and  $[Fe(CO)_2(C_{16}H_{14})]$ . A single-crystal X-ray diffraction study of the latter reveals a central planar 1,3-diene fragment, incorporating both rings, bonded to the iron atom, while one of the rings adopts a 'tub' conformation which enables it to make a further  $\eta^2$  attachment. The co-ordination around the iron atom is distorted trigonal bipyramidal. Treatment of  $[Fe(CO)_{2}$ - $(C_{16}H_{14})$ ] with L(CO or PPh<sub>3</sub>) yields [Fe(CO)<sub>2</sub>(L)(C<sub>16</sub>H<sub>14</sub>)], containing presumably bidentate bicyclo-octatetraenyl. Reaction of bicyclo-octatetraenyl with [Os<sub>3</sub>(CO)<sub>12</sub>] gave [Os(CO)<sub>2</sub>(C<sub>16</sub>H<sub>14</sub>)] in low yield, while [{Ru- $(SiMe_3)(CO)_4$ ] afforded fluxional  $[Ru_2(SiMe_3)_2(CO)_4(C_{16}H_{14})]$ .

In the course of our studies<sup>2</sup> on carbonylruthenium complexes of pentalene and its derivatives, the reaction of phenylcyclo-octatetraene with dodecacarbonyl triruthenium was investigated. In addition to the phenylpentalene complexes<sup>3</sup> formed there were several other products, one of which was isolated in milligram quantities as deep red crystals, insufficient for definitive identification by elemental analyses, n.m.r. spectroscopy, The mass spectrum was characteristic of an etc.



 $Ru_{3}(CO)_{6}$  grouping complexed with a hydrocarbon (or hydrocarbons), and our original belief that the molecular ion was compatible with a complex of formula  $[Ru_3(CO)_6-$ (C<sub>8</sub>H<sub>6</sub>)<sub>2</sub>], containing two co-ordinated pentalene molecules, led us to initiate a single-crystal X-ray diffraction study. This revealed that the product was, in fact, a complex of bicyclo-octatetraenyl (I),<sup>4</sup> a new ligand in transition-metal chemistry, properly formulated as  $[Ru_3(CO)_6(C_{16}H_{14})]$  (II). Consequent on the determination of the unique structure of (II) the reactions of bicyclo-octatetraenyl (I) with various carbonyl-iron, -ruthenium, and -osmium complexes have been examined, with results which we describe herein.

EXPERIMENTAL

### (a) Synthetic Studies

I.r. spectra [hexane for v(CO)] were recorded by use of a Perkin-Elmer 257, and <sup>1</sup>H n.m.r. spectra with a Varian Associates HA 100 spectrometer. Mass spectra were determined with an A.E.I. MS 902 instrument operating at 70 eV (1 eV  $\approx 1.60 \times 10^{-19}$  J). All reactions were performed under nitrogen, and hydrocarbon solvents were dried by distillation from calcium hydride.

Preparation of Bicyclo-octatetraenyl.-The original method of preparation,<sup>4</sup> cobalt(III) sulphate-induced decomposition of cyclo-octatetraenyl-lithium, gives (I) in 24% yield. We have found that the hydrocarbon is formed in much greater yield (80-90%) on reaction of cyclo-octatetraenyl-lithium with cyclo-octatetraenyl bromide.

Butyl-lithium (3.54 g, 11.0 mmol) and bromocyclo-octatetraene (2.0 g, 11.0 mmol) were stirred at  $-80^{\circ}$  in diethyl ether (50 cm<sup>3</sup>) for 2 h. To the solution of cyclo-octatetraenyl-lithium so formed an ether (20 cm<sup>3</sup>) solution of bromocyclo-octatetraene (2 g, 11.0 mmol) was added

<sup>&</sup>lt;sup>1</sup> Part VI, S. A. R. Knox, B. A. Sosinsky, and F. G. A. Stone, J.C.S. Dalton, 1975, 1647. <sup>2</sup> S. A. R. Knox and F. G. A. Stone, Accounts Chem. Res.,

<sup>1974, 7, 321.</sup> 

<sup>&</sup>lt;sup>3</sup> J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 452. <sup>4</sup> A. C. Cope and D. J. Marshall, *J. Amer. Chem. Soc.*, 1953,

<sup>75, 3208.</sup> 

dropwise, and the mixture allowed to attain room temperature, then stirred for 5 h. The mixture was hydrolysed with water (20 cm<sup>3</sup>) then extracted with ether (2 × 50 cm<sup>3</sup>). The combined ether extract was washed with water (2 × 20 cm<sup>3</sup>) and dried (calcium sulphate). Evaporation of the ether, followed by recrystallisation of the residue from dichloromethane-hexane, gave yellow crystalline (I) (1.88 g, 84%) (Found: C, 93.0; H, 6.8%; *M*, 206. Calc. for  $C_{16}H_{14}$ : C, 93.2; H, 6.8%; *M*, 206), m.p. 124 °C (lit.,<sup>4</sup> 125—126 °C).

Reactions of Bicyclo-octatetraenyl.—(i) With  $[Ru_3(CO)_{12}]$ .  $[Ru_3(CO)_{12}]$  (0.5 g, 0.78 mmol) and (I) (0.8 g, 3.9 mmol) were heated in toluene (150 cm<sup>3</sup>) under reflux for 12 h. Concentration and cooling of the resulting deep red solution gave red crystalline  $[Ru_3(CO)_6(C_{16}H_{14})]$  (II) (0.42 g, 80%) (Found: C, 39.1; H, 2.3%; M, 677. Calc. for  $C_{22}H_{14}O_6Ru_3$ : C, 39.0; H, 2.1%; M, 677), m.p. 180 °C (decomp.);  $\nu(CO)_{max}$  2 040s, 2 004vs, 1 969m, 1 949m cm<sup>-1</sup>. <sup>1</sup>H N.m.r. spectrum (CDCl<sub>3</sub> solution):  $\tau$  3.7—4.4 (m, 5 H), 4.87 (d of d, 1 H), 5.02 (d of d, 1 H), 5.55 (d of d, 5 H), 5.80 (d of d, 1 H), 6.30 (m, 1 H), 6.42 (d of d, 1 H), 7.36 (d, 1 H), 7.43 (t, 1 H), and 8.33 (d, 1 H). In addition to a molecular ion, the mass spectrum had significant peaks corresponding to  $(M - nCO)^+$  (n = 1—6), and to  $C_{18}H_{15}^+$ .

(ii) With  $[Fe_2(CO)_9]$ .  $[Fe_2(CO)_9]$  (2.2 g, 0.7 mmol) and (I) (0.5 g, 2.4 mmol) were heated under reflux in hexane  $(100 \text{ cm}^3)$  for 12 h. After removal of solvent and [Fe(CO)<sub>5</sub>] at reduced pressure, the residue was chromatographed (50 cm silica gel column). Elution with hexane gave the well-known cyclo-octatetraene complexes  $[Fe(CO)_{a}(C_{8}H_{8})]$ and  $[Fe_2(CO)_6(C_8H_8)]$ , identified by i.r. and mass spectra. Further elution with 10% dichloromethane-hexane then removed yellow crystalline [Fe(CO)<sub>2</sub>(C<sub>16</sub>H<sub>14</sub>)] (III) (120 mg, 16%) (Found: C, 67.5; H, 4.4%; M, 318. Calc. for C<sub>18</sub>H<sub>14</sub>FeO<sub>2</sub>: C, 67.9; H, 4.4%; M, 318), m.p. 112 °C;  $\nu_{max.}$  (CO): 2011s and 1967s cm<sup>-1</sup>. <sup>1</sup>H N.m.r. spectrum ( $\overline{CDCl}_3$ ) solution):  $\tau$  2.84 (d, 1 H), 3.64 (d of d, 1 H), 3.90 (m, 2 H), 4.12 (m, 4 H), 4.50 (m, 2 H), 5.87 (d of d, 1 H), 6.25 (d of d, 1 H), 8.35 (s,br, 1 H), and 8.48 (s,br, 1 H). In addition to a molecular ion, the mass spectrum had significant peaks corresponding to  $(M - nCO)^+$  (n = 1 or 2) and to  $C_{16}H_{14}^+$  and  $C_{16}H_{13}^+$ . The same solvent mixture finally eluted a small amount of a red solid, which, although not pure, gave an i.r. spectrum typical of a tricarbonyliron complex [ $\nu_{max.}(CO)$ : 2042s, 1995s, and 1 977s cm<sup>-1</sup>]; on heating in octane it gave [Fe(CO)<sub>2</sub>( $C_{16}H_{14}$ )] (III) readily, consistent with its formulation as  $[Fe(CO)_3 (C_{16}H_{14})$ ] (IV; L = CO). The mass spectrum of the solid was identical with that of (III).

Reaction of (I) with  $[Fe(CO)_5]$  (u.v. irradiation for 5 days), or  $[Fe_8(CO)_{12}]$  (toluene reflux for 1 h), gave a very similar mixture of products to that described.

(iii) With  $[Os_3(CO)_{12}]$ .  $[Os_3(CO)_{12}]$  (0.25 g, 0.28 mmol) and (I) (0.3 g, 1.5 mmol) were heated under reflux in xylene (100 cm<sup>3</sup>) for 4 days. Chromatography of the reaction mixture on silica gel yielded, on elution with 20% dichloromethane-hexane, colourless *needles* (2 mg), m.p. 159— 160 °C, characterised only by i.r.  $[v_{max}(CO): 2\ 021s$  and 1 969s cm<sup>-1</sup>] and mass spectra as  $[Os(CO)_2(C_{16}H_{14})]$ . In addition to a molecular ion (*m/e* 452), the mass spectrum showed significant peaks at *m/e* 424 (*M* - CO)<sup>+</sup> and 396 (*M* - 2CO)<sup>+</sup>, and at *m/e* 206 ( $C_{16}H_{14}$ )<sup>+</sup>, and 205 ( $C_{16}H_{13}$ )<sup>+</sup>.

(iv) With  $[{Ru(SiMe_3)(CO)_4}_2]$ .  $[{Ru(SiMe_3)(CO)_4}_2] (0.5 \text{ g}, 0.9 \text{ mmol})$  and (I) (0.9 g, 4.4 mmol) were heated in heptane (200 cm<sup>3</sup>) under reflux for 14 h. Chromatography of the

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reaction mixture, eluting with 10% dichloromethanehexane, gave orange crystalline [Ru<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>(CO)<sub>4</sub>(C<sub>16</sub>H<sub>14</sub>)] (V) (50 mg, 9%) (Found: C, 46.9; H, 4.9%; *M*, 667. Calc. for C<sub>26</sub>H<sub>32</sub>O<sub>4</sub>Ru<sub>2</sub>Si<sub>2</sub>: C, 46.8; H, 4.8%; *M*, 667), m.p. 178 °C;  $\nu_{max.}$ (CO): 2 026s, 1 988m, and 1 971s cm<sup>-1</sup>. The <sup>1</sup>H n.m.r. spectrum, which varied with temperature, is described later.

Reactions of  $[Fe(CO)_2(C_{16}H_{14})]$  (III).—(i) With PPh<sub>3</sub>. [Fe(CO)<sub>2</sub>(C<sub>16</sub>H<sub>14</sub>)] (10 mg, 0.03 mmol) and PPh<sub>3</sub> (32 mg, 0.12 mmol) were heated together in heptane (20 cm<sup>3</sup>) for 8 h. Concentration and cooling of the solution then yielded red *crystalline* [Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)(C<sub>16</sub>H<sub>14</sub>)] (IV; L = PPh<sub>3</sub>) (3 mg) (Found: C, 74.7; H, 5.3%. Calc. for C<sub>36</sub>H<sub>29</sub>FeO<sub>2</sub>P: C, 74.5; H, 5.0%), m.p. 164 °C;  $\nu_{max}$ .(CO): 1 987s and 1 936s cm<sup>-1</sup>. Insufficient material was available to allow





the recording of an n.m.r. spectrum, and the complex was too involatile to give a satisfactory mass spectrum.

(ii) With CO. After bubbling CO gas for 4 h through an octane solution (100 cm<sup>3</sup>) of  $[Fe(CO)_2(C_{16}H_{14})]$  (60 mg, 0.18 mmol) heated under reflux, chromatography afforded a small amount of  $[Fe(CO)_3(C_{16}H_{14})]$  (IV; L = CO), identified by its i.r. spectrum, on elution with hexane, and also (I).

(iii) With H<sub>2</sub>. Bubbling hydrogen for 15 min through an octane (30 cm<sup>3</sup>) solution of  $[Fe(CO)_2(C_{16}H_{14})]$  (100 mg, 0.3 mmol) heated under reflux, followed by chromatography, gave on elution with hexane four complexes in very low yield. Each had an i.r. spectrum typical of dicarbonyliron species. Sufficient of the first and second of these complexes to be eluted was produced to allow their mass spectroscopic identification:  $[Fe(CO)_2(C_{16}H_{18})]$  (Found: M, 322. Calc. for  $C_{18}H_{18}O_2Fe: M, 322$ )  $[\nu_{max}(CO): 2 002s and 1 953s cm<sup>-1</sup>]; [Fe(CO)_2(C_{16}H_{16})]$  (Found: M, 320. Calc. for  $C_{18}H_{16}O_2Fe: M, 320$ )  $[\nu_{max}(CO) 2 008s and 1 965s cm<sup>-1</sup>].$ 

(b) X-Ray Data Collection and Structure Determination

(i)  $[\operatorname{Ru}_{3}(\operatorname{CO})_{6}(\operatorname{C}_{16}\operatorname{H}_{14})]$  (II).—The crystal of (II) chosen for intensity measurements (0.10 × 0.10 × 0.28 mm) was mounted on a Syntex  $P2_{1}$  four-circle diffractometer according to methods described earlier.<sup>5</sup> Of the total (3 639) reflections for  $3.7^{\circ} < 20 < 50^{\circ}$ , 2 630 were deemed observed according to the criterion  $I > 2.5\sigma(I)$ , and only these were used in the solution and refinement of the structure.

Crystal Data.— $C_{22}H_{14}O_6Ru_3$ , (II), M = 677.6, mono-

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clinic, a = 8.936(3), b = 16.221(3), c = 15.944(3) Å,  $\beta = 118.54(2)^{\circ}$ ,  $D_{\rm c} = 2.22$  g cm<sup>-3</sup>, Z = 4,  $D_{\rm m} = 2.18$  g cm<sup>-3</sup>, F(000) = 1 304. Space group  $P2_1/c$ . Mo- $K_{\alpha}$  X-radiation (graphite monochromator),  $\lambda = 0.710$  69 Å;  $\mu(\text{Mo-}K_{\alpha}) = 21.94$  cm<sup>-1</sup>.

(ii) [Fe(CO)<sub>2</sub>( $C_{16}H_{14}$ )] (III).—The crystal of (III) chosen for intensity measurements was  $0.09 \times 0.25 \times 0.27$  mm, and was treated exactly as (II). Of the total 1 190 reflections, 994 were considered observed.

Crystal Data.—C<sub>18</sub>H<sub>14</sub>O<sub>2</sub>Fe, (III), M = 317.8, Orthorhombic, a = 6.822(2), b = 12.582(4), c = 16.931(5) Å,  $D_c = 1.46$  g cm<sup>-3</sup>, Z = 4,  $D_m = 1.42$  g cm<sup>-3</sup>, F(000) = 656. Space group  $P2_12_12_1$ .  $\mu(Mo-K_{\alpha}) = 10.63$  cm<sup>-1</sup>.

Solution and Refinement of Structures .-- Both structures were solved by conventional heavy-atom methods and refined by block-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. Weights were applied according to the schemes w = x. y for (II), and  $w = 1/(\sigma_F)^2$  for (III), where  $\sigma_F$  is the estimated standard deviation of the observed structure factor based on counting statistics; and x = 1 for  $\sin \theta \ge b$ , and  $x = \sin \theta/b$  for  $\sin\theta < b$ , while y = 1 for  $F_0 \leq c$ , and  $y = c/F_0$  for  $F_0 > c$ , with two parameters b = 0.2, c = 60.0. These schemes gave satisfactory weight analyses following the final cycles of refinement, showing maximum shift-to-error ratios of 0.9 for (II) and 0.2 for (III). Hydrogen atoms were incorporated at positions estimated from the electron density difference maps, and were refined isotropically. The refinement converged to R 0.052 (R' 0.059) for (II) and R 0.044 (R' 0.038) for (III).

Final electron-density difference syntheses showed no peaks >0.8 or <-1.1 eÅ<sup>-3</sup> for (II) and none >0.7 or <-0.8 eÅ<sup>-3</sup> for (III), with general background levels very much less than this. No absorption corrections were applied, and the atomic scattering factors were those of ref. 6 for non-hydrogen atoms, and of ref. 7 for hydrogen. All computational work was carried out at the University of London Computing Centre with the 'X-Ray' system of programmes.<sup>8</sup> Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21559 (17 pp., 1 microfiche).\*

#### RESULTS AND DISCUSSION

The X-ray analysis (Tables 1 and 2) of  $[Ru_3(CO)_6 (C_{16}H_{14})$ ] (II) establishes that the molecule has the overall structure shown in Figure 1, in which a bicyclooctatetraenyl ligand is attached to an  $Ru_3(CO)_6$  cluster. Within the  $Ru_3(CO)_6$  unit, three of the carbonyl groups are related essentially equatorially, and three axially, to the plane of the Ru<sub>3</sub> triangle, which is made up of non-equivalent bonds [Ru(1)-Ru(2) 2.99, Ru(2)-Ru(3) 2.80, Ru(1)-Ru(3) 2.89 Å]. The ring C(1)-(8) is coordinated in a manner reminiscent of that in [Fe<sub>2</sub>(CO)<sub>5</sub>- $(C_8H_8)$ ],<sup>9</sup> *i.e.* via two  $\eta^3$ -allyl groupings and two ' bridging ' carbon atoms. While it is formally possible, however, to regard C(4), C(5), C(6) and C(2), C(1), C(8) as  $\eta^3$ -allyl units bonded to Ru(1) and Ru(2) respectively [the mean Ru–C(allyl) distance is 2.23 Å], with C(3) and C(7) functioning as 'bridging' carbons involved in a

\* For details, see Notice to Authors No. 7, in J.C.S. Dalton, 1975, Index issue.

<sup>5</sup> A. Modinos and P. Woodward, J.C.S. Dalton, 1974, 2065.

#### TABLE 1

Atomic positional (fractional co-ordinates) and thermal \* parameters for (II), with estimated standard deviations in parentheses

Atom	x	У	z	$10^2 U/{ m \AA^2}$
Ru(1)	0.448 17(10)	0.049 86(5)	0.147 96(6)	
Ru(2)	0.220 96(10)	$0.165\ 12(5)$	0.18181(6)	
Ru(3)	0.498 35(9)	0.090 27(5)	0.335 87(5)	
cum	0.6317(15)	-0.0247(8)	0.2047(8)	
	0.7366(13)	-0.0729(6)	0.2377(7)	
C(102)	0.2990(14)	-0.0391(7)	0 1169(8)	
O(102)	0.2000(12)	-0.0948(6)	0.0916(7)	
C(21)	0.0541(14)	-0.0320(0) 0.0821(7)	0 1606(8)	
0(21)	-0.0475(13)	0.0366(6)	0.1458(8)	
C(99)	0.1180/13)	0.2330(7)	0.2328(8)	
O(22)	0.0533(13)	0.2550(1)	0.2645(8)	
C(21)	0.0000(10)	0.2741(0)	0.2149(8)	
0(21)	0.3302(14) 0.2478(14)	0.0707(6)	0.31.99(7)	
C(31)	0.3470(14)	-0.0797(0)	0.3122(1)	
O(32)	0.3303(14)	0.1232(7) 0.1444(6)	0.3347(8)	
C(0,2)	0.2814(12) 0.9610(14)	0.1444(0)	0.1000(8)	
	0.2010(14) 0.1649(15)	0.2015(8)	0.1009(8)	
C(2)	0.1042(10) 0.9919(14)	0.2004(7)	0.0304(0)	
	0.2210(14) 0.2669(15)	0.1201(8)	0.0229(8)	
	0.5002(15)	0.1070(8)	0.0000(0)	
C(0)	0.0002(10) 0.6177(10)	0.1270(0) 0.1574(7)	0.0032(8)	
	0.0177(13)	0.1074(7)	0.1094(0)	
C(1)	0.0024(11)	0.1907(0)	0.2100(7)	
U(0)	0.4124(14)	0.2009(7)	0.1002(0)	5 9/99)
П(1) П(0)	0.209(17)	0.311(0)	0.099(9)	0.0(00)
11(2)	0.000(10)	0.001(0)	0.003(3)	£.0(32) 6.1(41)
11(3)	0.147(10) 0.949(17)	0.031(3)	-0.000(10)	6 5 (41)
II(4)	0.342(17)	0.070(9)	0.043(11)	2 2 (29)
П(0) П(6)	0.012(10) 0.761(19)	0.110(7)	0.052(6) 0.199(5)	0.0(32)
II(0)	0.701(10)	0.109(9)	0.162(0) 0.918(6)	0.0(17)
	0.439(11)	0.292(0)	0.210(0)	0.0(22)
C(9)	0.0047(11)	0.1669(0)	0.3152(7) 0.3562(7)	
	0.0411(12) 0.9700(12)	0.1049(0)	0.3303(7)	
C(11)	0.8790(13)	0.0800(9)	0.3978(8)	
C(12)	0.7042(13) 0.7090(14)	0.0343(8)	0.4105(7)	
C(13)	0.7020(14) 0.7720(15)	0.0049(7)	0.4014(7)	
C(14)	0.7739(10)	0.1407(8)	0.000(8)	
C(10)	0.7390(14)	0.2127(0)	0.4924(8)	
U(10)	0.0205(14)	0.2184(7)	0.3878(7)	50(24)
H(10)	0.900(10)	0.182(8)	0.352(9)	<b>0.0(34)</b>
$H(\Pi)$	0.979(15)	0.060(7)	0.421(8)	3.3(28)
H(12)	0.751(14)	-0.018(8)	0.408(8)	3.0(32)
H(13)	0.089(12)	0.018(11)	0.011(0)	1.7(22)
$r_1(14)$	0.839(13)	0.130(0)	V.093(8)	2.6(27)
H(10)	0.778(23)	0.267(12)	0.519(13)	9.8(61)
H(16)	0.529(13)	0.244(6)	0.368(7)	2.5(26)

<sup>\*</sup>  $B = 8\pi^2 U$ . Otherwise anisotropic thermal parameters in the form  $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{32}c^{*2}l^2 + 2U_{12}-a^{*b^*hk} + 2U_{13}a^{*}c^{*hl} + 2U_{23}b^{*}c^{*kl}]$ , with parameters  $(\times 10^2)$ :

Atom	$U_{11}$	$U_{22}$	$U_{aa}$	$U_{12}$	$U_{13}$	$U_{*}$
Ru(1)	3.34(7)	3.47(8)	3.12(7)	-0.08(3)	1.97(4)	-0.53(3)
Ru(2)	2.70(7)	2.91(7)	3.69(7)	0.28(3)	1.63(4)	0.39(3)
Ru(3)	2.67(7)	2.94(7)	2.59(7)	-0.15(3)	1.48(4)	0.04(3)
C(101)	4.9(6)	4.8(7)	3.8(6)	0.4(6)	2.8(5)	0.5(5)
O(101)	7.3(6)	6.1(6)	6.4(6)	2.9(5)	4.0(5)	1.0(5)
C(102)	4.3(6)	3.4(7)	5.0(7)	-0.9(5)	2.5(5)	-1.1(5)
O(102)	6.6(6)	5.3(6)	7.1(6)	-1.9(5)	3.0(5)	-1.2(5)
C(21)	<b>3.8(6</b> )	3.7(6)	4.9(6)	0.2(5)	2.6(5)	0.1(5)
O(21)	6.9(6)	5.9(6)	9.2(8)	-3.9(5)	3.6(6)	-1.6(5)
C(22)	3.7(6)	3.3(6)	5.6(7)	-0.7(5)	2.5(5)	-0.4(5)
O(22)	9.0(7)	5.0(6)	9.3(7)	1.5(5)	7.3(6)	0.7(5)
C(31)	4.6(6)	3.7(7)	<b>3.9(6</b> )	-1.4(5)	2.6(5)	-1.1(5)
O(31)	10.4(8)	4.5(6)	7.8(7)	-3.0(5)	6.1(6)	-1.6(5)
C(32)	5.0(6)	3.3(6)	3.8(6)	-0.3(5)	2.5(5)	-0.1(5)
O(32)	7.0(6)	7.7(7)	6.5(6)	1.0(5)	5.7(5)	0.1(5)
C(1)	4.7(6)	3.5(6)	4.6(7)	1.3(5)	2.8(5)	2.1(5)
C(2)	3.9(6)	4.7(7)	3.3(6)	1.3(5)	1.2(5)	1.6(5)
C(3)	3.6(6)	4.4(7)	3.2(6)	-0.1(5)	1.0(5)	0.5(5)
C(4)	5.3(7)	5.6(8)	2.5(5)	0.4(5)	2.1(5)	-0.1(5)
C(5)	4.3(6)	5.8(8)	4.1(6)	-0.0(5)	3.2(5)	0.4(5)
C(6)	4.0(6)	5.0(7)	3.7(6)	-0.4(5)	3.0(5)	0.0(5)
C(7)	2.6(4)	3.5(6)	3.2(5)	-0.7(4)	1.7(4)	1.2(4)
C(8)	5.1(6)	1.4(5)	4.0(6)	0.3(4)	2.7(5)	-0.3(5)
C(9)	2.3(4)	3.1(6)	3.9(5)	-0.2(4)	1.5(4)	-0.5(4)

TABLE 1 (Continued)								
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$		
C(10)	2.5(5)	6.7(8)	3.2(5)	-1.6(5)	2.1(4)	-1.6(5)		
C(11)	<b>1.8(5</b> )	7.5(9)	4.4(6)	0.7(5)	0.9(5)	0.2(6)		
C(12)	3.3(5)	4.1(7)	2.8(5)	0.3(5)	1.0(4)	0.8(5)		
C(13)	4.3(6)	4.1(7)	2.9(5)	0.4(5)	1.5(5)	1.1(5)		
C(14)	4.4(6)	6.4(8)	1.9(5)	-0.6(5)	1.3(5)	0.2(5)		
C(15)	4.4(6)	5.8(8)	3.0(6)	-1.3(5)	1.9(5)	-1.7(5)		
C(16)	3.8(6)	3.2(6)	3.3(5)	-0.8(5)	2.1(5)	-0.6(4)		

multicentre interaction with Ru(1) and Ru(2) [Ru(1)-C(3) 2.40, Ru(2)-C(3) 2.61, Ru(1)-C(7) 2.60, Ru(2)-C(7) 2.79 Å], the metal-carbon and carbon-carbon distances indicate that delocalisation is extensive. This description, therefore, though useful, is obviously somewhat artificial. This is emphasised by the unique character of atom C(7), which is effectively bonded to all three ruthenium atoms [Ru(3)–C(7) 2.79 Å].

The C(1)—(8) ring is fairly symmetrically bent about the line  $C(3) \cdots C(7)$  and, to a lesser extent, about the lines  $C(3) \cdots C(5)$  and  $C(6) \cdots C(8)$ , so as to present a convex face to the metal-atom cluster. The dihedral angle between the two allyl moieties is 103°.

The other cyclo-octatetraene ring adopts a 'tub' conformation and is linked via C(9), on one of the folds of the ring, to the pivotal atom C(7) of the first ring. This second ring is bonded to Ru(3) via double bonds C(9)-C(16) and C(12)-C(13) of length 1.42 Å. The atoms C(10)-C(11) and C(14)-C(15) are two unco-ordinated double bonds of length 1.35 Å. The lines joining C(9) to C(12) and C(13) to C(16) divide the ring into three coplanar sections, for which the dihedral angles are 123 and 126°, respectively. Likewise, the groups of atoms C(10), C(9), C(16), C(15), and C(11), C(12), C(13), C(14)

### TABLE 2

Bond lengths (Å) and angles (°) for (II)

(a) Distances

(a) Distances			
Ru(1)-Ru(2)	2.992(1)	C(1) - C(2)	1.39(1)
$Ru(2) \rightarrow Ru(3)$	2.800(1)	C(2) - C(3)	1.45(2)
Ru(1) - Ru(3)	2.885(1)	C(3) - C(4)	1.45(2)
Ru(1) - C(101)	1.89(1)	C(4) - C(5)	1.38(2)
C(101) - O(101)	1.14(1)	C(5) - C(6)	1.43(1)
Ru(1) - C(102)	1.86(1)	C(6) - C(7)	1.44(2)
C(102) - O(102)	1.14(1)	C(7) - C(8)	1.46(1)
Ru(2) - C(21)	1.91(1)	C(8) - C(1)	1.40(1)
C(21) - O(21)	1.11(2)	C(7) - C(9)	1.47(1)
Ru(2) - C(22)	1.84(1)	C(9) - C(10)	1.50(1)
C(22) - O(22)	1.15(2)	C(10) - C(11)	1.33(2)
Ru(3) - C(31)	1.87(1)	C(11) - C(12)	1.48(2)
C(31) - O(31)	1.13(1)	C(12) - C(13)	1.43(2)
Ru(3) - C(32)	1.93(1)	C(13) - C(14)	1.46(2)
C(32) - O(32)	1.12(2)	C(14) - C(15)	1.32(2)
Ru(1) - C(3)	2.39(1)	C(15) - C(16)	1.49(1)
Ru(1) - C(4)	2.19(1)	C(16) - C(9)	1.41(2)
Ru(1) - C(5)	2.25(1)	C(1) - H(1)	0.84(15)
Ru(1) - C(6)	2.26(1)	C(2) - H(2)	0.92(12)
Ru(1) - C(7)	2.60(1)	C(3) - H(3)	0.83(13)
Ru(2)-C(1)	2.23(1)	C(4) - H(4)	0.91(16)
Ru(2) - C(2)	2.19(1)	C(5) - H(5)	0.80(15)
Ru(2) - C(3)	2.61(1)	C(6) - H(6)	1.15(8)
Ru(2) - C(7)	2.79(1)	C(8) - H(8)	0.73(10)
Ru(2) - C(8)	2.24(1)	C(10-H(10))	1.10(15)
Ru(3) - C(7)	2.78(1)	C(11) - H(11)	0.86(12)
Ru(3) - C(9)	2.28(1)	C(12) - H(12)	0.85(13)
Ru(3) - C(12)	2.21(1)	C(13) - H(13)	0.93(11)
Ru(3) - C(13)	2.20(1)	C(14) - H(14)	0.82(10)
Ru(3) - C(16)	2.31(1)	C(15) - H(15)	0.96(18)
Ru(3) - C(9, 16) *	2.18(1)	C(16) - H(16)	0.83(11)
Ru(3)-C(12,13) *	2.03(1)		

\* C(n,m) is the midpoint of the line joining C(n) to C(m).

TABLE 2 (Continued)

(b) Angles

Ru(1) - Ru(2) - Ru(3)	59.6(1)
$\mathbf{Ru}(2) - \mathbf{Ru}(3) - \mathbf{Ru}(1)$	63 5ÌÚ
$D_{11}(2) = D_{11}(1) = D_{11}(2)$	FC 0(1)
$\operatorname{Ku}(3)$ - $\operatorname{Ku}(1)$ - $\operatorname{Ku}(2)$	90.9(1)
Ru(1)-C(101)-O(101)	176(1)
$\mathbf{B}_{11}(1) = \mathbf{C}(109) = \mathbf{O}(109)$	174(1)
T(1) = O(102) = O(102)	
Ru(2) - C(21) - O(21)	177(1)
Ru(2) - C(22) - O(22)	179(1)
$B_{11}(3) = C(31) = O(31)$	179(1)
$D_{1}(0) = O(01) = O(01)$	1/2(1)
Ru(3) - C(32) - O(32)	169(1)
C(101) - Ru(1) - C(102)	89.9(5)
$C(101) = R_{11}(1) = R_{11}(2)$	145 5(4)
C(101) $Ru(1)$ $Ru(2)$	110.0(1)
C(101) - Ru(1) - Ru(3)	88.8(4)
C(102) - Ru(1) - Ru(2)	93.9(4)
C(102) - Ru(1) - Ru(3)	100 8(4)
O(102) $Ru(1)$ $Ru(3)$	100.0(1)
C(21) - Ru(2) - C(22)	89.3(6)
C(21)-Ru(2)-Ru(1)	93.9(4)
C(21) = Bu(2) = Bu(3)	08 0(3)
C(21) Ru(2) Ru(3)	30.0(3)
C(22) = Ru(2) = Ru(1)	100.4(3)
C(22)-Ru(2)-Ru(3)	106.8(3)
C(31) - Bu(3) - C(32)	90.8(5)
$C(21) = P_{11}(2) = P_{11}(1)$	77 9(4)
C(31) = Ku(3) = Ku(1)	11.4(4)
C(31) - Ru(3) - Ru(2)	95.0(3)
C(32)-Ru(3)-Ru(1)	134.1(3)
C(32) - Bu(3) - Bu(2)	73 9(3)
C(1) - C(2) - C(2)	199/1
C(1) - C(2) - C(3)	120(1)
C(2) - C(3) - C(4)	129(1)
C(3) - C(4) - C(5)	130(1)
C(4) - C(5) - C(6)	197(1)
$C(\pm)$ $C(0)$ $C(0)$	120(1)
C(0) - C(0) - C(1)	132(1)
C(6) - C(7) - C(8)	129(1)
C(7) - C(8) - C(1)	133(1)
C(8) = C(1) = C(2)	195(1)
C(0) C(1) C(2)	114(1)
C(6) - C(7) - C(9)	114(1)
C(8) - C(7) - C(9)	116(1)
C(7) - C(9) - C(10)	120(1)
C(7) = C(0) = C(16)	199/1
C(1) - C(3) - C(10)	123(1)
C(9) - C(10) - C(11)	120(1)
C(10)-C(11)-C(12)	121(1)
C(11) - C(12) - C(13)	120(1)
C(12) = C(12) = C(14)	100(1)
U(12) = U(13) = U(14)	122(1)
C(13) - C(14) - C(15)	120(1)
C(14) - C(15) - C(16)	121(I)
C(15) - C(16) - C(0)	199/1
C(10) = C(10) = C(0)	122(1)
U(10) - U(9) - U(10)	117(1)
C(12,13)- $Ru(3)$ - $C(9,16)$	84(1)
	• • •

are coplanar within +0.02 Å. Such a conformation is unprecedented for a cyclo-octatetraene ring co-ordinated to a metal atom of the iron triad; known modes of coordination are typified by [Ru(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>)]<sup>10</sup> and  $[Os(CO)_{3}(C_{8}H_{8})].^{11}$ 

The formation of (II) from the reaction of phenylcyclo-octatetraene with  $[Ru_3(CO)_{12}]$  is surprising, even in view of the fact that the carbonyl is known<sup>12</sup> to be capable of inducing carbon-carbon bond cleavage and formation. We cannot discount the possibility that the complex arose from some (I) impurity in the phenylcyclo-octatetraene, which was prepared <sup>13</sup> from phenyl-

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<sup>13</sup> A. C. Cope and M. R. Kinter, J. Amer. Chem. Soc., 1951, 73, 3424.

lithium and cyclo-octatetraene. Cyclo-octatetraenyllithium is an intermediate in this synthesis and is known<sup>4</sup> to yield (I) on decomposing. The complex (II) is, in fact, readily (*ca.* 80%) prepared by treating  $[\operatorname{Ru}_3(\operatorname{CO})_{12}]$  with (I) when heated under reflux in toluene. Crystals thus obtained showed the same X-ray diffraction properties as the original specimen. Sufficient of (II) was formed by this route to allow the



FIGURE 1 Molecular structure of [Ru<sub>3</sub>(CO)<sub>6</sub>(C<sub>16</sub>H<sub>14</sub>)] (II)

recording of a <sup>1</sup>H n.m.r. spectrum, which revealed fourteen signals between  $\tau$  3.5 and 8.5 (see Experimental section).

Complex (II) is unreactive; treatment with hydrogen, carbon monoxide, iodine, cyclopentadiene, or cyclooctatetraene resulted in little or no reaction even after extended periods under vigorous conditions.

Reaction of  $[Ru_3(CO)_{12}]$  with (I) for a shorter time (4 h) than that (12 h) which leads to (II) predominantly, resulted in the detection of four other products, formed in very low yield, one of which was isolated as an orange powder [v(CO) 2 037m, 2 014s, 1 972m, and 1 960m cm<sup>-1</sup>] which had a mass spectrum identical with that of (II). Insufficient was obtained to permit further characterisation. The i.r. spectra of the other products indicated their nature as  $Ru(CO)_2$ ,  $Ru(CO)_3$ , and  $Ru_2(CO)_6$  complexes of (I).

With iron carbonyls, under various conditions, (I) yields a very similar mixture of products. Two of these are the known <sup>14</sup> complexes of cyclo-octatetraene  $[Fe(CO)_3(C_8H_8)]$  and  $[Fe_2(CO)_6(C_8H_8)]$ , indicative of a cleavage of (I), which was used free of cyclo-octatetraene impurity. The remaining two products have been identified as complexes of (I), and are evidently closely related in that each gives the same mass spectrum, with an ion of highest mass corresponding to  $[Fe(CO)_2-(C_{16}H_{14})]^+$ . The major (16%) yellow crystalline product has an i.r. spectrum typical of a dicarbonyl  $[\nu(CO) 2 011s \text{ and } 1967s \text{ cm}^{-1}]$  and analyses confirm the formulation as  $[Fe(CO)_2(C_{16}H_{14})]$  (III). The i.r. spectrum of the other, low yield, species is characteristic of a tricarbonyliron complex  $[\nu(CO) 2 042s, 1995s, \text{ and } 1967s, \text{ m}^{-1}]$ 

I 977s cm<sup>-1</sup>]. Moreover, it can be shown that heating this tricarbonyl in octane yields the dicarbonyl (III) cleanly, and that, conversely, treating (III) with carbon monoxide generates the tricarbonyl. It seems reasonable, therefore, to formulate the tricarbonyl (IV) as  $[Fe(CO)_3(C_{16}H_{14})]$  in which (I), on the basis of the 'eighteen-electron rule', functions as a bidentate ligand. It can, likewise, be anticipated that in (III) the ligand (I) acts as a terdentate chelate. The <sup>1</sup>H n.m.r. spectrum (see Experimental section) of (III), however, could not be unambiguously interpreted in terms of any particular molecular structure and recourse to X-ray crystallography was undertaken.

The crystal structure determination of  $[Fe(CO)_2-(C_{16}H_{14})]$  (II) shows (Figure 2, Tables 3 and 4) that the central bonding feature is a  $1,3-\eta^4$ -diene attachment to the iron atom of carbon atoms C(2), C(1), C(11), and C(21), encompassing both rings. The two pivotal carbon atoms C(1) and C(11) are significantly closer to the iron atom (at 2.05 Å) than are C(2) and C(21) (at 2.12 Å), while extensive delocalisation is evident in the carbon-carbon distances within the diene fragment (1.42—1.44 Å).

One of the  $C_8$  rings adopts a 'tub' conformation and is thereby able to make a further  $\eta^2$ -attachment to the iron atom via the double bond C(5)-C(6), of length 1.40 Å; the Fe-C distances are equal (2.17 Å). The co-ordination sphere of the iron is completed by two carbonyl groups, giving a distorted trigonal bipyramidal arrangement of bonds; Fe-C(102) and Fe-C(1,2) must



FIGURE 2 Molecular structure of  $[Fe(CO)_2(C_{16}H_{14})]$  (III)

be regarded as the axial ligands, and Fe-C(101), Fe-C(5,6), Fe-C(11,21) as the equatorial. The 'tub' ring retains two unco-ordinated double bonds, C(3)-C(4) and C(7)-C(8), while the other ring retains three: C(31)-C(41), C(51)-C(61), and C(71)-C(81), of mean length 1.32 Å.

The lines joining C(1) to C(6) and C(2) to C(5) divide the 'tub' ring C(1)-(8) into three substantially coplanar sections, for which the dihedral angles are 121 and 127°, respectively. The central 'diene' C(2), C(1), C(11), C(21) section of the molecule is planar, as also are the groups of atoms: C(4)-(7); C(1)-(3), C(8); C(21), C(31), C(41), C(51); C(41), C(51), C(61), C(71); <sup>14</sup> T. A. Manuel and F. G. A. Stone, J. Amer. Chem. Soc., 1960, 82, 366.

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TABLE 3

Atomic positional (fractional co-ordinates) and thermal \* parameters, with estimated standard deviations in

				parentnese	5, 101 (.					
Atom	x	у	z 1	$0^2 U/{ m \AA^2}$	Atom	x		у	z	$10^2 U/{ m \AA^2}$
Fe	$0.092 \ 24(12)$	0.295 90(6)	0.259 57(5)		H(7)	0.548(	9) 0.5	262(4)	0.114(3)	5.4(20)
C(101)	0.8528(9)	0.3545(4)	0.2672(4)		H(8)	0.427(	9) 0.0	087(4)	0.153(3)	6.1(20)
O(101)	0.7027(7)	0.3921(4)	0.2745(4)		C(11)	0.2145	(9) 0.	1592(4)	0.3050(3)	
C(102)	0.2087(10)	0.3868(5)	0.3245(4)		C(21)	0.0440	(9) 0.1	821(5)	0.3491(4)	
O(102)	0.2783(8)	0.4455(4)	0.3683(3)		C(31)	0.0374	(10) 0.2	2103(6)	0.4353(4)	
C(1)	0.1874(10)	0.1509(4)	0.2204(3)		C(41)	0.0964	(13) 0.	1511(6)	0.4944(4)	
C(2)	-0.0007(11)	0.1001(5)	0.1897(4)		C(81)	0.1934	(14) 0.0 (15) 0.0	)480(6)	0.4905(5)	
	-0.0323(10) 0.0250(11)	0.1909(7)	0.1009(3)		C(71)	0.3003	(10) 0.0	1233(0) 1021(6)	0.4000(4)	
C(5)	0.0250(11)	0.2521(7)	0.0352(4) 0.1433(4)			0.4137	(11) 0.0	1514(5)	0.4009(4) 0.3405(4)	
C(6)	0.3070(12)	0.3052(0) 0.3475(6)	0.1433(4) 0.1722(4)		H(21)	0.935(	(11) 0.1	49(3)	0.332(2)	0.4(12)
C(7)	0.4258(12)	0.2543(6)	0.1487(4)		$\mathbf{H}(31)$	-0.031(	6) 0.5	274(4)	0.447(3)	2.5(16)
Č(8)	0.3636(11)	0.1591(6)	0.1681(4)		H(41)	0.068(9	9) 0.1	77(4)	0.545(3)	5.0(19)
H(2)	0.861(8)	0.132(4)	0.223(3)	5.6(19)	H(51)	0.368()	11) 0.0	003(4)	0.022(3)	5.7(23)
H(3)	0.927(9)	0.136(5)	0.062(4)	7.3(21)	H(61)	0.404(	-0.0	948(4)	0.459(3)	5.4(19)
H(4)	0.026(8)	0.321(4)	0.031(3)	5.7(21)	H(71)	0.610(8	B) 0.0	)89(5)	0.410(3)	<b>4.6(21</b> )
H(5)	0.073(7)	0.436(3)	0.144(3)	1.5(14)	H(81)	0.494('	7) 0.1	188(4)	0.312(3)	1.9(16)
H(6)	0.364(9)	0.412(4)	0.193(3)	3.4(19)						
* B	$= 8\pi^2 U$ . Otherw	vise anisotropie	c thermal para	neters (see	footnote	e to Table 1	), with para	meters ()	$< 10^{2}$ ):	
	Atom	Û.,	$U_{aa}$	`U.,		$U_{10}$	U.,	Ú.	, ,	
	Fe	3.45(	8) 2.98(8)	4.48	(9)	0.11(5)	-0.10(5)	-0.20	0(5)	
	C(101)	4.5(5	2.7(4)	6.7(8	5)	0.2(3)	-1.7(4)	-1.2(	(4)	
	O(101)	4.1(3	6.4(3)	11.7(8	5)	1.6(3)	-0.5(3)	0.8	(3)	
	C(102)	3.4(5)	2.8(4)	5.7(8	5)	1.1(4)	-0.7(4)	-0.4	(4)	
	O(10 <b>2</b> )	7.0(4	) 4.9(3)	8.1(4	L)	-0.5(3)	-2.4(3)	-1.5	(3)	
	C(1)	4.6(4	) 2.7(4)	3.3(4	1)	0.5(3)	0.1(4)	0.3	(3)	
	C(2)	4.0(4	3.3(4)	4.1(5	5)	-0.2(3)	0.1(4)	-0.5	(3)	
	C(3)	5.0(5	5.9(5)	5.4(8		0.6(5)	-0.2(4)	-0.60	(5)	
	C(4)	5.4(5	) 7.5(6)	4.1(6		1.2(5)	-1.2(4)	0.3	(5)	
	C(5)	5.0(0	(1) 4.0(5)	0.0(0	D) 5)	0.4(0)	-0.7(5)	1.7	(4)	
	C(0)	4.9(0	77(6)	4.0(6	2) 5)	-0.3(5)	11(4)	0.0	(4)	
	C(3)	5.4(5 4.0(5	5.4(5)	3 5(4	// L\	24(4)	0.6(4)	0.4	( <b>1</b> )	
	C(1)	3 2/4	2 2(3)	4 5(4	ן, ה	-0.1(3)	0.3(3)	0.0	(3)	
	C(21)	3.5(5	3.0(4)	5.7(8	5)	-0.6(3)	-0.3(3)	0.1	3)	
	$\tilde{C}(31)$	5.6(5	4.3(4)	4.9(6	5)	0.3(4)	1.7(4)	-1.0	(4)	
	C(41)	6.8(5	7.0(5)	3.0(4	E) ·	-2.2(5)	0.9(5)	-0.5	4)	
	C(51)	9.1(7	5.2(6)	4.7({	5)	-1.8(5)	1.2(5)	1.2	(5)	
	C(61)	9.6(7	4.1(5)	4.4(8	<b>5</b> )	0.9(5)	-1.2(5)	0.8	(4)	
	C(71)	4.8(6	5.3(5)	4.2(5	5)	1.6(4)	-0.6(4)	-0.7	(4)	
	C(81)	4.7(4)	) 3.0(4)	3.8(4	E) -	-0.1(4)	1.2(5)	-0.2	(3)	

and C(61), C(71), C(81), C(11), each of which embraces an unco-ordinated double bond. Indeed, the C<sub>8</sub> ring C(11)-(81) has an approximate mirror plane perpendicular to the double bond C(51)-C(61) and passing through its mid-point.

In the light of the molecular structure of (III) a partial assignment of the <sup>1</sup>H n.m.r. spectrum of the complex can be made. Only four of the six carbon atoms co-ordinated to iron bear a proton, and this is reflected in signals corresponding to ten olefinic protons in the range  $\tau 2.8$ —4.5 and signals due to four protons at higher fields, viz. 7 5.87 (d of d, J 2.5, 8.5 Hz; 1 H), 6.25 (d of d, J 1.0, 8.5 Hz; 1 H), 8.35 (s,br, 1 H), and 8.48 (s,br, 1 H). The latter two resonances are at shifts typical <sup>15</sup> of terminal protons of a (1,3-diene)tricarbonyliron complex, and are assigned to the protons attached to carbons C(2) and C(21), each weakly coupled to a single adjacent proton. The resonances at  $\tau$  5.87 and 6.25 are similarly in the range expected for protons attached to a co-ordinated non-conjugated double bond. Double-irradiation experiments show that, as expected, these are coupled to one another (J 8.5 Hz), and also to an adjacent olefinic proton.

With a knowledge of the molecular structure of (III), the structure of the tricarbonyliron complex [Fe(CO)<sub>3</sub>-(C<sub>16</sub>H<sub>14</sub>)] can be postulated to be (IV; L = CO), in which the 1,3-diene mode of co-ordination is retained. The conversion of (III) into (IV; L = CO) on treatment with carbon monoxide has been described previously. The transformation of (I) from a ter- into a bi-dentate ligand can also be achieved on reaction of (III) with triphenylphosphine; the red crystalline product [Fe(CO)<sub>2</sub>(PPh<sub>3</sub>)(C<sub>16</sub>H<sub>14</sub>)] is probably best described by structure (IV;  $L = PPh_3$ ). With hydrogen gas, when heated under reflux in octane, (III) gave four dicarbonyliron complexes in low yield. Two of these were identified by mass and i.r. spectra as [Fe(CO)<sub>2</sub>(C<sub>16</sub>H<sub>18</sub>)] and [Fe(CO)<sub>2</sub>(C<sub>16</sub>H<sub>16</sub>)].

Dodecacarbonyltriosmium proved relatively unreactive towards (I). Heating the two together in xylene for 4 days gave only a small amount of the colourless needle-like osmium analogue  $[Os(CO)_2(C_{16}H_{14})]$ of (III), identified by mass and i.r. spectra.

The reactions of cyclo-octatetraenes  $C_8H_7R$  (R = H,

<sup>15</sup> G. F. Emerson, J. E. Mahler, R. Kochhar, and R. Pettit, J. Org. Chem., 1964, 29, 3620.

TABLE 4

I	Bond	lengths	(Å)	and	angles	(°)	for	(III)
(a) Dista	nces							

() = = = = = = = = = = = = = = = = = =			
Fe-C(1)	2.047(6)	C(11)-C(21)	1.412(9)
Fe-C(2)	2.127(6)	C(21) - C(31)	1.502(9)
Fe-C(11)	2.061(5)	C(31)C(41)	1.311(10)
Fe-C(21)	2.111(6)	C(41)-C(51)	1.458(11)
FeC(5)	2.160(7)	C(51)-C(61)	1.304(13)
FeC(6)	2.181(8)	C(61)-C(71)	1.463(11)
Fe-C(1,2)	1.960(6)	C(71) - C(81)	1.316(9)
FeC(5.6)	2.053(6)	C(81) - C(11)	1.489(9)
Fe-C(11.12)	1.963(6)	C(2) - H(2)	1.14(5)
Fe-C(101)	1.797(6)	C(3) - H(3)	1.09(6)
Fe-C(102)	1.774(7)	C(4) - H(4)	0.98(5)
C(101) - O(101)	1,135(8)	C(5) - H(5)	0.93(4)
C(102) - O(102)	1.149(8)	C(6) - H(6)	0.96(6)
C(1) - C(2)	1.435(10)	C(7) - H(7)	1.02(6)
C(2) - C(3)	1.479(10)	C(8) - H(8)	1.03(6)
C(3) - C(4)	1.320(12)	C(21) - H(21)	0.91(4)
C(4) - C(5)	1.482(11)	$\tilde{C}(31) - H(31)$	0.94(4)
C(5) - C(6)	1.410(12)	C(41) - H(41)	0.94(5)
C(6) - C(7)	1 480(11)	C(51) - H(51)	0.93(6)
C(7) - C(8)	1 312(11)	C(61) - H(61)	0.97(5)
C(8) - C(1)	1 496(9)	C(71) - H(71)	0.97(5)
C(1) - C(11)	1 449(8)	C(81) - H(81)	0.86(5)
	1.440(0)	0(01) 11(01)	0.00(0)
(b) Angles			
Fe-C(101)-O(10	(1) 177.7(6)	C(31)-C(41)-C(51)	127.6(7)
Fe-C(102)-O(10	(2) 177.6(6)	C(41)-C(51)-C(61)	127.3(7)
C(1) - C(2) - C(3)	119.4(6)	C(51) - C(61) - C(71)	128.0(7)
C(2) - C(3) - C(4)	116.8(7)	C(61) - C(71) - C(81)	128.0(7)
C(3) - C(4) - C(5)	121.2(7)	C(71) - C(81) - C(11)	128.1(6)
C(4) - C(5) - C(6)	121.3(7)	C(81) - C(11) - C(21)	123.5(5)
C(5) - C(6) - C(7)	122.5(7)	C(101) - Fe - C(102)	95.6(3)
C(6) - C(7) - C(8)	118.6( <b>7</b> )	C(102) - Fe - C(1,2)	149.7(3)
C(7) - C(8) - C(1)	118.1(7)	C(102) - Fe - C(11, 21)	95.7(3)
C(8) - C(1) - C(2)	121.2(5)	C(102) - Fe - C(5,6)	96.0(3)
C(8) - C(1) - C(11)	118.5(6)	C(101) - Fe - C(1,2)	112.9(3)
C(2) - C(1) - C(11)	117.8(5)	C(101) - Fe - C(11.21)	113.8 <b>(</b> 3)
C(1) - C(11) - C(21)	115.6(5)	C(101) - Fe - C(5,6)	105.6(3)
C(1)-C(11)-C(81	120.7(5)	C(1,2) - Fe - C(5,6)	86.2(3)
C(11)-C(21)-C(3	(1) 125.9(5)	C(1,2)-Fe- $C(11.21)$	64.3(2)
C(21) - C(31) - C(4)	1) $126.7(7)$	C(5,6)-Fe- $C(11,21)$	137.4(3)

Me, or Ph) with the binuclear ruthenium compound  $[{Ru(SiMe_3)(CO)_4}_2]$  have been shown <sup>2</sup> to yield complexes of both the cyclo-octatetraene  $[Ru_2(SiMe_3)_2(CO)_4(C_8H_7R)]$ and of the corresponding pentalene  $[Ru_3(CO)_8(C_8H_5R)].$ Bicyclo-octatetraenyl, which can be regarded as a monosubstituted cyclo-octatetraene with  $R = C_8 H_7$ , behaves somewhat similarly with  $[{Ru(SiMe_3)(CO)_4}_2]$ . On heating under reflux in heptane, orange crystalline  $[Ru_2(SiMe_3)_2(CO)_4(C_{16}H_{14})]$  was the only product isolated. The i.r. spectrum is very similar to those of the  $C_8H_7R$ complexes previously mentioned, and the formulation (V) is probable. The <sup>1</sup>H n.m.r. spectrum (CCl<sub>3</sub>F solution) is temperature-dependent between limits of -60 and 60 °C. Little change occurs in the signals at  $\tau$  3.8-4.3 (7 H) which are attributable to protons of the unco-ordinated cyclo-octatetraene ring. The protons of the co-ordinated ring, however, which appear as a series of sharp signals between  $\tau 4.8$  and 6.2 at -60 °C, coalesce at ca. 40 °C and sharpen to another overlapping set of signals between  $\tau$  5.2—5.9 at 60 °C. While a fluxional oscillation of the co-ordinated C<sub>8</sub>H<sub>7</sub>R ring relative to the Ru<sub>2</sub> unit seems probable, the n.m.r. spectra are indecisive in determining this. The Me<sub>3</sub>Si signal at  $\tau$  9.50 is sharp throughout.

The last complex (V) provides the only example observed in this work of (I) acting as a derivative of cyclo-octatetraene; in all other cases it exhibits a unique activity as a two-ring chelate.

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