Chemistry of the Metal Carbonyls. Part LXXIII.[1] Tricarbonyl-iron and -ruthenium Complexes of Bicyclo[4.2.0]octa-2,4,7-trienes

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Cyclo-octatetraene complexes $[M(CO)_3(C_8H_7R)]$ (M = Fe, R = $SiMe_3$, Ph, or CPh_3; M = Ru, R = CPh_3) isomerise on heating in octane to give the corresponding tricarbonylmetal complexes of the bicyclo[4.2.0]octa-2,4,7-triene ligands. These rearrangements, especially in the case of the ruthenium compounds, are accompanied by formation of polynuclear complexes $[M^1_2(CO)_5(C_8H_7M^2Me_3)]$ (M^1 = Fe or Ru, M^2 = Si; M^1 = Ru, M^2 = Ge), $[Ru_2(CO)_6(C_8H_7CPh_3)]$, or $[Ru_3(CO)_4(C_8H_7CPh_3)_2]$. The disubstituted cyclo-octatetraene complex (IIg) $[Fe(CO)_3\{C_8H_6(SiMe_3)(CPh_3)\}]$ also isomerises to a bicyclo[4.2.0]octa-2,4,7-triene structure, a fact established by a single-crystal *X*-ray diffraction study. Crystals of (IIg) are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions a = 10.968(4), b = 11.496(4), c = 12.213(5) Å, α = 95.63(3), β = 108.56(3), γ = 91.60(3)°. The structure was solved by the heavy-atom method and refined by block-matrix least-squares to R 0.055 for 3 842 observed reflections measured by diffractometer. The crystal structure reveals the existence of a fused six- and four-membered ring system, the bridgehead bond being significantly the longest. The cyclobutene ring carries an $SiMe_3$ group on one of the bridgehead atoms and a triphenylmethyl group *trans* to this.

The hexadiene ring is folded into two planar segments; the first embraces the bridgehead bond, while the second comprises a diene system which is in turn η^4-bonded to the $Fe(CO)_3$ group. The ring system presents a convex face to the metal atom, and the pivotal atom of the CPh_3 group is coplanar with the cyclobutene ring. The $SiMe_3$ group lies *endo* to the metal.

CYCLO-OCTATETRAENE (cot) reacts with the carbonylruthenium complexes $[Ru(MMe_3)_2(CO)_4]$, $[\{Ru(MMe_3)(CO)_4\}_2]$ (M = Si or Ge), and $[Ru_3(CO)_{12}]$ to give a variety of compounds including ruthenium complexes of the unstable hydrocarbon pentalene.[2] With dodecacarbonyltriruthenium only very small quantities of $[Ru_3(CO)_8(C_8H_6)]$ are obtained.[3] Substituted cyclo-octatetraenes (C_8H_7R; R = Ph or $SiMe_3$), however, especially in reactions with $[Ru(SiMe_3)_2(CO)_4]$, more readily undergo dehydrogenative transannular ring closure thereby affording ruthenium complexes of substituted pentalenes.

We have not succeeded in isolating a pentalene complex of iron {analogous to $[Ru_3(CO)_8(C_8H_6)]$} by reaction of cyclo-octatetraene with iron carbonyls under a variety of conditions; only the well known [4,5] cot complexes of iron are obtained.

The pentalene nucleus is, however, stabilised by the presence of bulky substituents on the rings (*e.g.* Bu^t [6]). In this connection it is interesting that trimethylsilyl-substituted pentalenes form readily in reaction of trimethylsilylcyclo-octatetraene with trimethylsilylruthenium carbonyls.[7] It was possible, therefore, that

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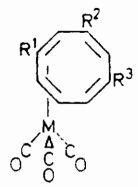
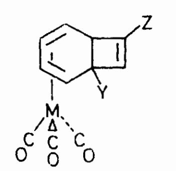
iron complexes $[Fe(CO)_3(\eta^4-C_8H_7R)]$ (R = CPh_3, Ph, $SiMe_3$, and $GeMe_3$) [8] of substituted cyclo-octatetraenes, or their ruthenium analogues prepared in the present study, would yield pentalene complexes on heating.[9]

RESULTS AND DISCUSSION

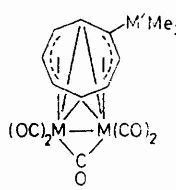
Thermolysis of the deep-red crystalline compound (Ia) in octane in a sealed tube at 150° gave a yellow oil, and a red-brown crystalline compound. The spectroscopic properties (mass, i.r., and n.m.r.) of the oil were in accord with the structure (IIa), while the red-brown crystalline compound was characterised as $[Fe_2(CO)_5(C_8H_7SiMe_3)]$ (IIIa). There was no evidence for formation of an iron–pentalene complex.



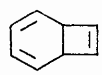
(Ia) $R^1 = SiMe_3$, $R^2 = R^3 = H$; M = Fe
(Ib) $R^1 = GeMe_3$, $R^2 = R^3 = H$; M = Fe
(Ic) $R^1 = SiMe_3$, $R^2 = R^3 = H$; M = Ru
(Id) $R^1 = R^2 = H$, $R^3 = Ph_3C$; M = Fe
(Ie) $R^1 = R^2 = H$, $R^3 = Ph_3C$; M = Ru
(If) $R^1 = R^2 = H$, $R^3 = Ph$; M = Fe
(Ig) $R^1 = SiMe_3$, $R^2 = Ph_3C$, $R^3 = H$; M = Fe



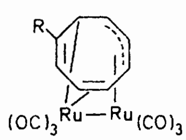
(IIa) Z = $SiMe_3$, Y = H; M = Fe
(IIb) Z = $GeMe_3$, Y = H; M = Fe
(IIc) Z = $SiMe_3$, Y = H; M = Ru
(IId) Z = Ph_3C, Y = H; M = Fe
(IIe) Z = Ph_3C, Y = H; M = Ru
(IIf) Z = Ph, Y = H; M = Fe
(IIg) Z = Ph_3C, Y = $SiMe_3$; M = Fe



(IIIa) M = Fe, M′ = Si
(IIIb) M = Ru, M′ = Si
(IIIc) M = Ru, M′ = Ge



(IV)



(Va) R = CPh_3
(Vb) R = $SiMe_3$
(Vc) R = H

Complex (IIa) contains a bicyclo[4.2.0]octa-2,4,7-triene ligand which is of interest because the bicyclic isomer (IV) of cyclo-octatetraene has only a transient existence at room temperature. The triene (IV) has recently been stabilised by co-ordination to a tricarbonyliron group but this adduct was prepared indirectly,[10] and not by thermal isomerisation of $[Fe(CO)_3(cot)]$. It appears that the rearrangement of (Ia) to (IIa), and similar isomerisations (see later), are facilitated by the presence of the co-ordinated metal–tricarbonyl group and the bulky substituents on the cyclo-octatetraene ring. It is known from other work [11] that although (IV) cannot be detected in cyclo-octatetraene, the presence of substituents (phenyl and methyl) on the bicyclic triene ring system stabilises this species relative to the cot isomers.

Complex (IIIa) is a derivative of the long-known compound $[Fe_2(CO)_5(cot)]$ [12] [$\nu(CO)_{max.}$ 2 022s, 1 992s, 1 959s, and 1 802m cm^{-1}] [4] and as such has a virtually identical i.r. spectrum in the carbonyl stretching region (*viz.* 2 022s, 1 992s, 1 960s, and 1 806m cm^{-1}).

Conversion of (Ia) into (IIa) prompted a study of the effect of heating on the related tricarbonylmetal cyclo-octatetraene complexes (Ib)—(Ig), with a view to establishing whether these reactions would provide a facile route from substituted cyclo-octatetraenes to the corresponding bicyclo-octatrienes, albeit stabilised by attachment to metal tricarbonyl groups. Compounds (Ib)—(Ig) required for study were synthesised by methods previously described,[8,13] except that (Ic) was best obtained by treating $C_8H_7{\cdot}SiMe_3$ with $[Ru(CO)_5]$ {from $[Ru_3(CO)_{12}]$ and CO} under reflux in heptane.

In the preparation of (Ie) from $[Ru(CO)_3(cot)]$ and Ph_3C^+ an interesting side-reaction was observed. Addition of $[Ph_3CBF_4]$ to $[Ru(CO)_3(cot)]$ followed by hydrolysis afforded the binuclear ruthenium complex (Va), as well as the desired compound (Ie). A complex (Vc) has been fully characterised by single-crystal *X*-ray diffraction studies,[14] and its i.r. spectrum in the carbonyl stretching region is virtually identical with that [15] of (Va), in accord with the structure suggested for the latter.

If $[Ru(CO)_3(cot)]$ is added to $[Ph_3CBF_4]$ formation of (Ie) is favoured. Probably (Va) forms by attack of the intermediate $[Ru(CO)_3(C_8H_8CPh_3)]^+$ on $[Ru(CO)_3(cot)]$ but the mechanism is unclear. Formation of (Va) is reminiscent of the ready conversion [2] of the mononuclear ruthenium compound $[Ru(SiMe_3)(CO)_2(C_8H_8SiMe_3)]$ into the binuclear species $[Ru_2(SiMe_3)_2(CO)_4(C_8H_6)]$.

The position of the substituents R^1, R^2, and R^3 in complexes of type (Ia)—(If) may be deduced from ^1H n.m.r. studies,[8,13] and it is of significance that the electron-releasing $SiMe_3$ and $GeMe_3$ groups are bonded to the η^4-C_4 tricarbonylmetal systems, as indicated, whereas the CPh_3 and Ph substituents are on carbon atoms not attached to iron or ruthenium atoms.

We did not succeed in isolating complex (IIb) by heating (Ib) in octane. Moreover, under similar conditions (Ic) gave exclusively (IIIb), rather than the bicyclo[4.2.0]octa-2,4,7-triene complex (IIc). The compound (IIIb) absorbs carbon monoxide (70°/10 atm, in acetone) to give (Vb), but the latter on warming reverts to (IIIb). In contrast, (Va) did not readily decarbonylate. The complex (IIIc) was formed directly from $[Ru_3(CO)_{12}]$ and $C_8H_7{\cdot}GeMe_3$. Both (IIIb) and (IIIc) had i.r. spectra in the carbonyl stretching region virtually identical with

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[9] M. Cooke, J. A. K. Howard, C. R. Russ, F. G. A. Stone, and P. Woodward, *J. Organometallic Chem.*, 1974, **78**, C43.
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TABLE 1

Atomic positional and thermal parameters, with estimated standard deviations in parentheses, for (IIg)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	0.02 319(8)	0.05 066(6)	0.28 709(6)	6.36(6)	5.16(4)	5.01(5)	1.21(4)	2.54(4)	0.37(3)
(*a*) Bicyclo-octatrienyl ring									
C(1)	0.0836(5)	−0.1087(4)	0.3388(5)	6.5(4)	4.8(3)	6.3(4)	2.3(3)	2.8(3)	2.0(3)
C(2)	0.1589(6)	−0.0158(5)	0.4202(4)	7.1(4)	6.6(4)	4.5(3)	2.4(3)	2.1(3)	1.3(3)
C(3)	0.2259(5)	0.0638(4)	0.3751(4)	6.5(4)	5.0(3)	4.0(3)	0.6(3)	1.6(3)	−0.2(2)
C(4)	0.2962(5)	0.0197(4)	0.2895(4)	5.3(4)	4.1(3)	3.8(3)	0.3(3)	1.6(3)	−0.2(2)
C(5)	0.3897(5)	−0.0768(4)	0.3249(4)	4.6(4)	4.4(3)	4.1(3)	−0.1(3)	1.4(3)	−0.0(2)
C(6)	0.3194(5)	−0.1581(4)	0.2419(4)	4.9(3)	4.2(3)	3.6(3)	0.4(3)	2.1(2)	0.2(2)
C(7)	0.2083(5)	−0.0795(4)	0.1973(4)	4.6(4)	3.7(3)	3.6(3)	0.3(2)	1.2(2)	−0.4(2)
C(8)	0.0849(5)	−0.1078(4)	0.2231(4)	5.3(4)	4.1(3)	4.9(3)	1.0(3)	2.0(3)	0.2(2)
(*b*) Carbonyl groups									
C(11)	−0.1402(7)	0.0017(5)	0.2458(5)	6.2(5)	6.5(4)	7.4(4)	1.6(4)	2.8(4)	1.4(3)
O(11)	−0.2475(5)	−0.0304(4)	0.2177(4)	6.8(4)	10.6(4)	12.8(4)	0.2(3)	3.2(3)	2.9(3)
C(12)	−0.0029(6)	0.1764(5)	0.3696(4)	8.1(5)	6.4(4)	6.3(4)	2.1(4)	3.1(4)	0.3(3)
O(12)	−0.0215(5)	0.2594(4)	0.4204(4)	11.9(4)	8.1(3)	11.4(4)	2.0(3)	5.8(3)	−2.7(3)
C(13)	0.0201(6)	0.1116(5)	0.1567(5)	5.7(4)	5.7(4)	5.8(4)	1.3(3)	1.5(3)	0.5(3)
O(13)	0.0171(5)	0.1466(4)	0.0725(4)	10.6(4)	10.7(3)	5.7(3)	1.3(3)	2.5(3)	3.2(4)
(*c*) Triphenylmethyl ligand									
C(61)	0.3350(5)	−0.2896(4)	0.2112(4)	4.4(3)	3.8(3)	4.2(3)	0.0(2)	1.6(2)	−0.0(2)
C(611)	0.4697(5)	−0.3212(4)	0.2838(4)	4.6(4)	3.7(3)	4.3(3)	0.4(3)	1.4(3)	−0.4(2)
C(612)	0.5774(6)	−0.2573(5)	0.2778(5)	4.6(4)	5.3(4)	6.4(4)	0.3(3)	1.9(3)	0.6(3)
C(613)	0.7007(6)	−0.2852(5)	0.3392(5)	4.0(4)	6.1(4)	8.0(4)	−0.2(3)	1.7(3)	−0.2(3)
C(614)	0.7200(6)	−0.3775(5)	0.4064(5)	5.4(5)	6.4(4)	5.9(4)	1.5(3)	1.0(3)	−0.3(3)
C(615)	0.6156(7)	−0.4417(5)	0.4103(5)	6.1(5)	6.0(4)	5.3(4)	1.6(3)	1.5(3)	0.8(3)
C(616)	0.4921(6)	−0.4140(4)	0.3505(4)	5.5(4)	4.5(3)	5.0(3)	0.3(3)	1.7(3)	0.1(3)
C(621)	0.3258(5)	−0.3203(4)	0.0829(4)	4.1(4)	4.8(3)	3.9(3)	0.0(3)	1.1(3)	−0.4(2)
C(622)	0.3059(6)	−0.2410(5)	0.0030(5)	8.1(5)	6.0(4)	5.9(4)	1.5(4)	3.7(3)	0.4(3)
C(623)	0.3003(7)	−0.2737(6)	−0.1121(5)	11.3(6)	8.2(5)	4.9(4)	2.8(4)	4.1(4)	1.1(3)
C(624)	0.3162(7)	−0.3885(6)	−0.1472(5)	7.4(5)	9.6(5)	4.8(4)	0.4(4)	3.2(4)	−1.1(4)
C(625)	0.3381(6)	−0.4688(5)	−0.0681(6)	6.9(5)	7.3(4)	6.2(4)	0.9(4)	2.1(4)	−2.1(3)
C(626)	0.3421(6)	−0.4355(5)	0.0459(5)	6.6(5)	5.7(4)	5.3(3)	0.9(3)	1.7(3)	−0.9(3)
C(631)	0.2258(5)	−0.3546(4)	0.2397(4)	4.3(4)	4.1(3)	5.0(3)	0.4(3)	1.5(3)	−0.1(2)
C(632)	0.2255(6)	−0.3478(4)	0.3535(5)	5.7(4)	4.2(3)	5.4(4)	0.7(3)	2.5(3)	0.4(3)
C(633)	0.1281(6)	−0.4027(5)	0.3828(5)	6.8(5)	5.6(3)	7.6(4)	1.6(3)	4.1(4)	1.7(3)
C(634)	0.0264(7)	−0.4636(6)	0.2979(7)	7.3(5)	8.9(5)	11.2(7)	−1.7(4)	4.9(5)	0.1(5)
C(635)	0.0250(8)	−0.4679(7)	0.1856(7)	7.3(6)	14.2(7)	8.9(6)	−5.1(5)	2.8(5)	−2.0(5)
C(636)	0.1220(6)	−0.4159(6)	0.1559(6)	5.2(5)	11.2(5)	6.4(4)	−2.2(4)	2.0(4)	−1.5(4)
(*d*) Trimethylsilyl ligand									
Si	0.37 796(18)	0.14 313(13)	0.23 989(13)	8.04(14)	4.94(9)	5.63(9)	−1.26(9)	2.14(9)	−0.05(7)
C(101)	0.3914(8)	0.0966(6)	0.0933(5)	17.4(8)	10.5(5)	6.4(4)	−5.9(5)	6.8(5)	−1.1(4)
C(102)	0.5440(7)	0.1716(6)	0.3507(5)	7.8(5)	11.0(5)	7.7(5)	−4.8(4)	0.6(4)	0.7(4)
C(103)	0.2959(8)	0.2858(5)	0.2391(8)	13.7(8)	3.9(4)	19.3(9)	1.0(4)	6.1(7)	2.6(4)

(*e*) Hydrogen atoms, numbered according to the carbon atom to which each is attached; in every case U is invariant and isotropic (U 0.1013)

Atom	x	y	z	Atom	x	y	z
H(1)	0.069	−0.192	0.369	H(622)	0.294	−0.151	0.030
H(2)	0.199	−0.030	0.511	H(623)	0.283	−0.209	−0.173
H(3)	0.299	0.131	0.423	H(624)	0.312	−0.410	−0.236
H(5)	0.481	−0.080	0.395	H(625)	0.352	−0.558	−0.095
H(7)	0.168	−0.073	0.105	H(626)	0.358	−0.500	0.107
H(8)	0.046	−0.176	0.153	H(632)	0.303	−0.298	0.421
H(612)	0.564	−0.186	0.225	H(633)	0.132	−0.398	0.473
H(613)	0.783	−0.234	0.335	H(634)	−0.050	−0.507	0.320
H(614)	0.816	−0.398	0.455	H(635)	−0.055	−0.514	0.118
H(615)	0.629	−0.515	0.461	H(636)	0.117	−0.423	0.066
H(616)	0.411	−0.466	0.356				

Anisotropic thermal parameters in the form: $\exp[-2\pi^2\{U_{11}a^{*2}h^2 + U_{22}b^{*}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl\}]$

that[16] of $[Ru_2(CO)_5(cot)]$. Prolonged heating of (IIIb) afforded low yields (<10%) of the pentalene complexes $[Ru_3(CO)_8(C_8H_5SiMe_3)]$ (two isomers).[7]

Complexes (Id)—(If) were similar in behaviour to (Ia) in isomerising to (IId), (IIe), and (IIf), respectively, on heating in octane. Rearrangement of (Ie) to (IIe) was accompanied by formation of (Va), and a cluster compound $[Ru_3(CO)_4(C_8H_7CPh_3)_2]$ (VI). The latter is presumed to be a derivative of $[Ru_3(CO)_4(C_8H_8)_2]$.[5,15]

The ^1H n.m.r. spectra of the complexes (II) (Y = H; Z = $SiMe_3$, $GeMe_3$, CPh_3, and Ph) are in accord with the bicyclo-octatriene structures suggested. Thus the spectrum of (IIa) showed four resonances of intensity 1 : 2 : 2 : 2 at τ 3.55s, 4.7dd, 6.9m, and 7.1m, and a signal due to the trimethylsilyl group (τ 9.7 p.p.m.). The singlet at 3.55 (1 H) is characteristic[17] of a proton attached to a carbon atom of the double bond of a cyclobutene ring. Moreover, the spectrum of the $Fe(CO)_3$ adduct of (IV) shows[10] such a singlet (2 H) at τ 3.78.

16 M. I. Bruce, M. Cooke, and M. Green, *J. Organometallic Chem.*, 1968, **13**, 227.

17 R. Huisgen, W. E. Konz, and G. E. Gream, *J. Amer. Chem. Soc.*, 1970, **92**, 4105.

In these complexes the substituents occupy a position on a carbon atom of the unco-ordinated double bond of the cyclobutene ring.

During the course of the study, complex (IIg) was prepared in which there are two substituents on the bicyclic ring system. The n.m.r. spectrum did not provide conclusive evidence for the positions of the $SiMe_3$ and CPh_3

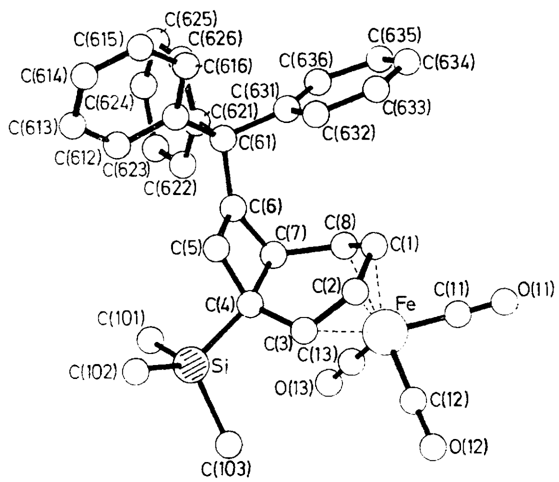

FIGURE 1 Molecular structure of (IIg)

groups. For this reason, and also because it was important to place this new type of organometallic compound on an unequivocal structural foundation, an *X*-ray diffraction study was undertaken.

The molecular structure of [(IIg), excluding H atoms]

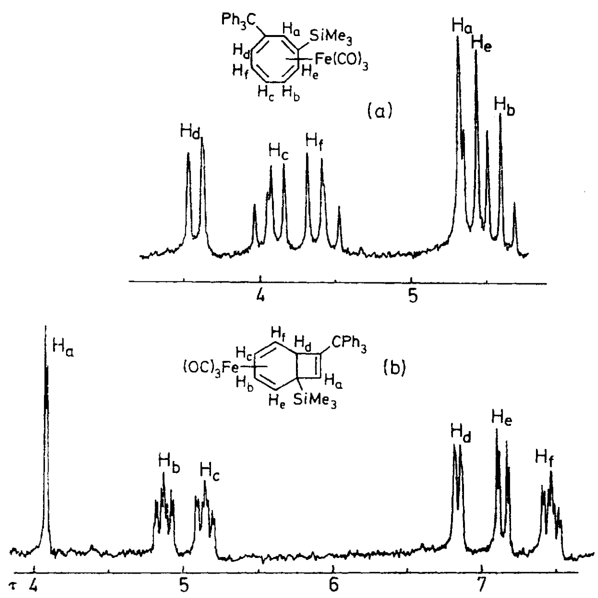

FIGURE 2 ^{1}H n.m.r. spectra (100 MHz, $CDCl_3$) of complexes (a) (Ig) and (b) (IIg)

as revealed by the crystallographic study (Tables 1 and 2) is shown in Figure 1, which also gives the (arbitrary) atom numbering sequence used in the analysis. The ring system is non-planar, and presents a convex face to the iron atom; it is η^4-bonded thereto *via* atoms C(3), C(2), C(1), and C(8) which themselves form a coplanar diene moiety. The C–C bond distances (Table 2) show substantial delocalisation in this part of the hexadiene ring. The ring is folded about the line C(3) $\cdots$ C(8) into two planar segments with a dihedral angle of 142°. The second segment C(3)–(8) embraces the two bridgehead atoms C(4) and C(7), along the line of which there is another fold (dihedral angle 117°) to the cyclobutene ring. The bonds around the bridgehead atoms are tetrahedrally oriented and have a mean bond length of 1.54_6 Å. Amongst this group, however, the bridgehead

TABLE 2

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

(*a*) Distances			
Fe–C(11)	1.795(7)	C(3)–C(4)	1.541(8)
C(11)–O(11)	1.153(9)	C(4)–C(5)	1.532(7)
Fe–C(12)	1.763(6)	C(5)–C(6)	1.330(6)
C(12)–O(12)	1.146(8)	C(6)–C(7)	1.529(7)
Fe–C(13)	1.793(6)	C(7)–C(8)	1.518(8)
C(13)–O(13)	1.131(8)	C(8)–C(1)	1.419(8)
Mean Fe–C	1.772	C(4)–C(7)	1.579(6)
Mean C–O	1.143	Si–C(4)	1.905(5)
Fe–C(3)	2.133(5)	Si–C(101)	1.871(7)
Fe–C(2)	2.052(5)	Si–C(102)	1.888(6)
Fe–C(1)	2.055(5)	Si–C(103)	1.892(7)
Fe–C(8)	2.124(5)	C(6)–C(61)	1.549(6)
C(1)–C(2)	1.424(7)	Mean C(61)–Ph	1.540
C(2)–C(3)	1.415(9)	Mean C–C(Ph)	1.381
(*b*) Angles			
C(11)–Fe–C(12)	91.6(3)	C(8)–C(7)–C(6)	116.9(4)
C(12)–Fe–C(13)	100.1(3)	C(3)–C(4)–Si	113.1(3)
C(13)–Fe–C(11)	98.4(3)	C(5)–C(4)–Si	109.6(4)
Fe–C(11)–O(11)	179.4(6)	C(4)–Si–C(101)	110.1(3)
Fe–C(12)–O(12)	178.0(5)	C(4)–Si–C(102)	106.0(3)
Fe–C(13)–O(13)	177.8(5)	C(4)–Si–C(103)	113.7(3)
C(1)–C(2)–C(3)	115.7(5)	C(101)–Si–C(102)	109.9(4)
C(2)–C(3)–C(4)	120.7(4)	C(101)–Si–C(103)	110.5(4)
C(3)–C(4)–C(5)	117.3(4)	C(102)–Si–C(103)	106.5(3)
C(4)–C(5)–C(6)	95.0(4)	C(5)–C(6)–C(61)	133.2(4)
C(5)–C(6)–C(7)	94.2(4)	C(7)–C(6)–C(61)	132.2(4)
C(6)–C(7)–C(8)	116.9(4)	C(6)–C(61)–C(611)	109.1(3)
C(7)–C(8)–C(1)	121.5(4)	C(6)–C(61)–C(621)	112.9(3)
C(8)–C(1)–C(2)	115.4(5)	C(6)–C(61)–C(631)	104.8(4)
C(3)–C(4)–C(7)	109.4(4)	C(611)–C(61)–C(621)	106.1(3)
C(5)–C(4)–C(7)	84.8(3)	C(611)–C(61)–C(631)	112.8(3)
C(6)–C(7)–C(4)	85.7(3)	C(621)–C(61)–C(631)	111.3(2)
C(8)–C(7)–C(4)	111.5(4)	Mean C–C–C(Ph)	120.0
C(3)–C(4)–C(5)	117.3(4)		

bond C(4)–C(7) is significantly the longest (1.58_0 Å). Atom C(4) carries a terminal $SiMe_3$ group *endo* to the iron atom (C–Si 1.90_5 Å).

The cyclobutene ring is planar and carries a triphenylmethyl group on C(6). As expected, the pivotal atom of the Ph_3C group [C(61)] is coplanar with the ring, and the bond C(5)–C(6) is a normal double bond (1.33_1 Å). The geometries of the Ph_3C and Me_3Si groups are normal, and for this reason details of bond lengths and angles in the phenyl groups have been omitted from Table 2.

Knowing the molecular structure of complex (IIg), double-resonance experiments allowed assignment of the n.m.r. spectrum (Figure 2).

EXPERIMENTAL

^{1}H N.m.r. spectra were recorded on Varian HA 100 and T60 spectrometers and mass spectra with an AEI MS902 instrument operating at 70 eV.* I.r. spectra were measured

* 1eV $\approx 1.60 \times 10^{-19}$J.

TABLE 3

Analytical and physical data for the complexes [a]

Compound	Colour	M.p.(θ_c/°C)	Yield(%)	C	H	M [b]
(Ic)	Yellow	55°	27	46.2 (46.4)	4.4 (4.4)	362 (362)
(Ie)	Orange	130	35	67.6 (67.8)	4.1 (4.1)	532 (532)
(IIa)	Yellow	oil	13	53.9 (53.2)	5.6 (5.1)	316 (316)
(IId)	Yellow	174	76	74.2 (74.1)	4.7 (4.6)	486 (486)
(IIe)	White	175	20	68.0 (67.8)	4.2 (4.1)	532 (532)
(IIf)	Yellow	110	22	63.8 (63.8)	4.1 (4.7)	320 (320)
(IIg)	Yellow	164	64	70.8 (71.0)	5.4 (5.4)	558 (558)
(IIIa)	Red-brown	162	62	45.5 (44.9)	3.8 (3.8)	428 (428)
(IIIb)	Yellow	187	49	37.5 (37.1)	3.3 (3.1)	520 (520)
(IIIc)	Yellow	185	75	34.4 (34.7)	2.9 (2.9)	566 (566)
(Va)	Yellow	189	30	55.4 (55.3)	3.3 (3.1)	718 (718)
(VI)	Salmon red	$>$280 [c]	23	63.1 (62.9)	4.2 (4.0)	—

[a] Calc. values in parentheses. [b] Mass spectrometry. [c] Decomp.

on a Perkin-Elmer 257 spectrophotometer. Solvents were dried and distilled under nitrogen, and all operations were conducted under dry oxygen-free nitrogen.

Analytical and physical data for new compounds are summarised in Table 3, and i.r. and n.m.r. measurements are given in Table 4. The complexes $[Fe(CO)_3(\eta^4\text{-}C_8H_7SiMe_3)]$,[8] $[Fe(CO)_3(\eta^4\text{-}C_8H_7GeMe_3)]$,[8] $[Fe(CO)_3(\eta^4\text{-}C_8H_7CPh_3)]$,[13] $[Fe(CO)_3(\eta^4\text{-}C_8H_7Ph)]$,[13] and $[Fe(CO)_3\{\eta^4\text{-}C_8H_6(SiMe_3)(CPh_3)\}]$ [8] were prepared as previously described. The compound $[Ru(CO)_3(\eta^4\text{-}C_8H_7CPh_3)]$ (Ie) was obtained in a similar manner to its iron analogue (Id).[13]

Reaction of Pentacarbonylruthenium with Trimethylsilylcyclo-octatetraene.—Dodecacarbonyltriruthenium (0.5 g, 0.782 mmol) in heptane (50 cm^3) was treated with carbon monoxide (90 atm, 200 °C, 48 h) to give a solution of pentacarbonylruthenium [18] which was then heated under reflux with $C_8H_7SiMe_3$ (1.0 g, 5.7 mmol) for 30 min. Removal of solvent, chromatography in hexane on alumina, with final purification by sublimation, gave (0.22 g, 27%) yellow *crystals* of $[Ru(CO)_3(\eta^4\text{-}C_8H_7SiMe_3)]$ (Ic).

Thermal Rearrangement of Tricarbonyl(cyclo-octatetraene)-metal Complexes.—The following experiment is representative of those studied involving the conversion of complexes of type (I) into type (II). Complex $[Fe(CO)_3(C_8H_7SiMe_3)]$ (Ia) (0.5 g, 1.58 mmol) in octane (2 cm^3) was sealed in a Carius tube and heated at 150° for 20 h. Filtration and crystallisation from ether–hexane afforded red-brown *crystals* of $[Fe_2(CO)_5(C_8H_7SiMe_3)]$ (IIIa) (0.21 g, 62%). Chromatography of the solution after filtration gave $[Fe(CO)_3(C_8H_7SiMe_3)]$ (IIa) (0.65 g, 13%), yellow oil (b.p. 50°/10^{-1} Torr).

X-Ray Crystallographic Investigation.—The crystal of (IIg) chosen for intensity measurements (0.64 × 0.15 × 0.30 mm) was mounted on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[19] Of the total (4 967) reflections for $3.7° < 2\theta < 50°$, only 3 842 having $I > 2.5\sigma(I)$ were considered observed and used in the solution and refinement of the structure.

Crystal Data.—$C_{33}H_{30}FeO_3Si$, $M = 560.7$, Triclinic, $a = 10.968(4)$, $b = 11.496(4)$, $c = 12.213(5)$ Å, $\alpha = 95.63(3)$, $\beta = 108.56(3)$, $\gamma = 91.60(3)°$, $U = 1\,450.0$ Å^3, $D_c = 1.29$, $Z = 2$, $D_m = 1.28$ g cm^3, $F(000) = 584$. Space group $P\bar{1}$. Mo-K_α-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 6.09 cm^{-1}.

Solution and Refinement of the Structure.—The structure was solved by conventional heavy-atom methods and refined by block-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. For the final cycles the parameters for the carbon atoms of the triphenylmethyl group were kept invariant and a full-matrix refinement was used. Weights were applied according to the scheme: $1/w = (\sigma_F)^2$. Hydrogen atoms were incorporated at calculated positions (except for those of the $SiMe_3$ groups, which were not included); neither thermal nor positional parameters were refined. The refinement converged to R 0.055 (R' 0.068). Final electron-density difference syntheses showed no peaks >0.5 or < -0.5 eÅ^{-3}. Corrections for Lorentz, polarisation, and absorption effects were made and the atomic scattering factors were those of ref. 20 for

TABLE 4

I.r.[a] and ^1H n.m.r. data for the complexes

Compound	ν_{CO}/cm^{-1}	Chemical shift (τ) [b]
(Ic)	2 066s, 2 006s, 1 990s	[c]4.2 (3 H, m), 4.76 (2 H, t), 5.52 (2 H, d), 9.81 (9 H, s)
(Ie)	2 067s, 2 007s, 1 997s	2.8 (15 H, m), 4.45 (2 H, d), 4.95 (4 H, m), 5.45 (1 H, t)
(IIa)	2 044s, 1 979s, 1 972s	[c]3.55 (1 H, s), 4.77 (2 H, dd), 6.9 (2 H, m), 7.1 (2 H, m), 9.7 (9 H, s)
(IId)	2 045s, 1 979s, 1 973s	2.8 (15 H, m), 4.0 (1 H, s), 4.70 (1 H, m), 5.1 (1 H, m), 6.74 (2 H, m), 6.98 (1 H, t), 7.3 (1 H, m)
(IIe)	2 059s, 1 993s, 1 987s	2.8 (15 H, m), 3.93 (1 H, s), 4.55 (1 H, m), 4.92 (1 H, m), 6.71 (1 H, m), 6.81 (1 H, dd), 7.08 (1 H, dd), 7.26 (1 H, m)
(IIf)	2 047s, 1 980s, 1 975s	[c]2.78 (5 H, s), 3.72 (1 H, s), 4.68 (2 H, m), 6.70 (3 H, m), 6.96 (1 H, t)
(IIg)	2 041s, 1 973vs,br	2.8 (15 H, m), 4.11 (1 H, d), 4.88 (1 H, m), 5.14 (1 H, m), 6.88 (1 H, d), 7.17 (1 H, dd), 7.46 (1 H, m), 10.08 (9 H, s)
(IIIa)	2 022s, 1 992s, 1 960s, 1 806m	5.7 (7 H, m), 9.98 (9 H, s)
(IIIb)	2 036m, 2 009s, 1 970s, 1 823m	4.86 (1 H, t), 5.40 (6 H, m), 9.87 (9 H, s),
(IIIc)	2 048m, 2 009s, 1 970s, 1 823m.	4.8 (1 H, dd), 5.5 (6 H, m), 9.73 (9 H, s)
(Va)	2 072s, 2 049s, 2 005s, 1 995m, 1 981m, 1 975w	2.75 (15 H, m), 3.96 (1 H, d), 5.81 (2 H, m), 6.12 (1 H, m), 6.43 (2 H, m), 8.03 (1 H, m)
(Vb)	2 073s, 2 040s, 2 006s, 2 001sh, 1 984s, 1 978sh	
(VI)	2 004vs, 1 961m, 1 929s	2.8 (30 H, m), 4.73 (14 H, s)

[a] Measured in hexane. [b] Measured in $CDCl_3$ unless otherwise stated. [c] Measured in CS_2.

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non-hydrogen, and of ref. 21 for hydrogen atoms. Computational work was mainly carried out at the University of London Computing Centre with the ' *X*-Ray ' system of programmes.[22] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21 526 (23 pp., 1 microfiche).*

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

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