Hydrocarbon Complexes of Iron, Ruthenium, and Osmium. Part VIII.[1] Isolation of η-(1,1,1-Tricarbonyl-1-metallainden-1-yl)tricarbonylmetal-(*M*–*M*) [M = Iron, Ruthenium, or Osmium] Complexes: Crystal and Molecular Structure of η-(1,1,1-Tricarbonyl-1-osmainden-1-yl)tricarbonylosmium(*Os*–*Os*)

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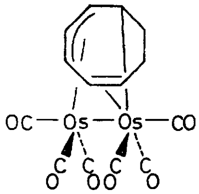
Treatment of $[Os(MMe_3)_2(CO)_4]$ (M = Si or Ge) or $[\{Os(SiMe_3)(CO)_4\}_2]$ with cyclo-octatetraene (COT) gives primarily the 1,2,3,3a,6a-η-1,4,5,6-tetrahydropentalenyl complexes $[Os(MMe_3)(CO)_2(C_8H_9)]$, with minor formation of $[Os_2(CO)_6(C_8H_{10})]$ and of complexes of unidentified dimers of COT, $[Os(CO)_2(C_{16}H_{16})]$ and $[Os(CO)_3(C_{16}H_{16})]$. The latter is also formed on heating $[Os_3(CO)_{12}]$ with COT in octane. Under u.v. irradiation a moderate yield of $[Os(CO)_3(C_8H_8)]$ is obtained from $[\{Os(SiMe_3)(CO)_4\}_2]$ and COT. Dimethyl(tetracarbonyl)osmium and cyclo-octatetraene afford a complicated mixture from which η-(1,1,1-tricarbonyl-1-osmainden-1-yl)tricarbonylosmium(*Os*-*Os*), $[Os_2(CO)_6(C_8H_6)]$, was obtained and characterised by *X*-ray diffraction. Crystals are triclinic ($P\bar{1}$) with two molecules per unit cell [a = 7.973(4), b = 10.684(4), c = 9.191(3) Å, α = 89.16(3), β = 99.28(3), γ = 91.75(3)°]. The structure was solved by conventional heavy-atom methods from 2 152 independent reflections and refined to R = 0.053 (R' = 0.064). One osmium atom has been incorporated with the eight carbon atoms of the original cyclo-octatetraene ring to form a planar osmaindenyl system. The second osmium atom is bonded to the first [Os–Os = 2.754(2) Å] and is also η^4-bonded to the four carbon atoms of the 5-membered ring, thereby achieving octahedral co-ordination.

Debromination of 1,4-dibromocyclo-octatetraene with $[Fe_2(CO)_9]$ or $[Fe(CO)_4]^{2-}$ affords benzocyclobutadiene(tricarbonyl)iron. In refluxing hydrocarbons, $[Fe_2(CO)_9]$ or $[Ru_3(CO)_{12}]$ and 1,4-dibromocyclo-octatetraene yield the metallainden-1-yl complexes $[M_2(CO)_6(C_8H_6)]$ (M = Fe or Ru).

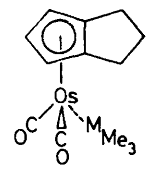
WE have shown previously that pentalene complexes of ruthenium may be obtained from reactions of the compounds $[Ru(MMe_3)_2(CO)_4]$ (M = Si or Ge) or $[\{Ru(SiMe_3)(CO)_4\}_2]$ with cyclo-octatetraene (COT).[2-4] Here we describe corresponding reactions of COT with the compounds $[Os(MMe_3)_2(CO)_4]$ (M = Si or Ge) and $[\{Os(SiMe_3)(CO)_4\}_2]$, studied to establish whether pentalene complexes of osmium would be formed by dehydrogenative ring-closure of COT in a similar manner. No pentalene complexes were isolated from these reactions, and work was as a consequence extended to the carbonyl $[OsMe_2(CO)_4]$. The latter on reaction with COT also failed to provide a route to an osmium-pentalene complex, but afforded *inter alia* a binuclear osmium compound $[Os_2(CO)_6(C_8H_6)]$, analogous to species obtained in a parallel investigation of ring-closure of 1,4-dibromocyclo-octatetraene through debromination with $[Fe_2(CO)_9]$, $[M_3(CO)_{12}]$, or $[M(CO)_4]^{2-}$ (M = Fe or Ru).

RESULTS AND DISCUSSION

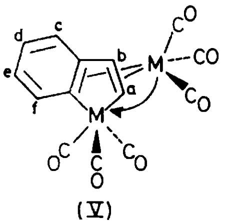
In heptane or octane under reflux, COT and the compound $[Os(SiMe_3)_2(CO)_4]$ afford a mixture of the complexes $[\{Os(SiMe_3)(\mu\text{-}SiMe_2)(CO)_3\}_2]$, $[Os_2(CO)_6(C_8H_{10})]$ (I), $[Os(SiMe_3)(CO)_2(C_8H_9)]$ (IIa), and $[Os(CO)_2(C_{16}H_{16})]$ (III).



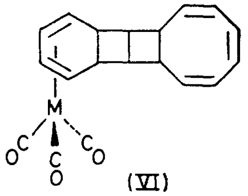
(I)



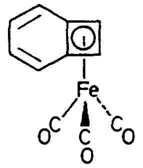
(II)
a; M = Si
b; M = Ge



(V)
a; M = Os
b; M = Ru
c; M = Fe



(VI)
a; M = Os
b; M = Fe



(VIII)

The complex $[\{Os(SiMe_3)(\mu\text{-}SiMe_2)(CO)_3\}_2]$ is a thermal decomposition product of $[Os(SiMe_3)_2(CO)_4]$ and has been previously reported.[5] Although (I) was obtained in low yield, i.r. and mass spectral data suggest that it is the osmium analogue of the known cyclo-octatrieneruthenium complex $[Ru_2(CO)_6(C_8H_{10})]$.[6] The i.r., mass, and ^1H n.m.r. spectra of the compound (IIa) are in accord with the formulation shown, the compound being a 1,2,3,3a,6a-η-1,4,5,6-tetrahydropentalenyl complex, the ruthenium analogue of which has been described.[7] Complex

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[1] Part VII, J. D. Edwards, J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Dalton*, 1976, 75.

[2] A. Brookes, J. A. K. Howard, S. A. R. Knox, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1973, 587.

[3] J. A. K. Howard, S. A. R. Knox, V. Riera, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1974, 452.

[4] S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, **7**, 321.

[5] A. Brookes, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3469.

[6] A. C. Szary, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 662.

[7] S. A. R. Knox, R. P. Phillips, and F. G. A. Stone, *J.C.S. Dalton*, 1974, 658.

TABLE 1

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

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Os(1)	0.458 71(9)	0.760 68(7)	0.822 83(8)	4.16(5)	4.49(5)	3.18(4)	−0.14(3)	0.73(3)	−0.50(3)
Os(2)	0.744 78(9)	0.831 41(6)	0.706 03(7)	3.99(4)	3.41(4)	3.14(4)	0.22(3)	0.48(3)	0.15(3)
C(1)	0.618 2(23)	0.632 3(17)	0.742 7(21)	2.9(9)	4.0(10)	4.5(10)	−1.4(7)	−0.6(8)	−0.1(8)
C(2)	0.700 1(29)	0.526 4(19)	0.813 1(23)	5.9(13)	4.4(11)	4.6(12)	−0.8(10)	0.6(10)	0.9(9)
H(2)	0.680	0.520	0.920	*					
C(3)	0.784 3(32)	0.443 0(20)	0.745 2(35)	5.5(14)	3.5(11)	10.3(21)	0.2(10)	−0.3(13)	−0.0(12)
H(3)	0.860	0.360	0.780	*					
C(4)	0.791 1(30)	0.459 1(22)	0.591 1(34)	4.6(13)	5.0(13)	10.1(21)	0.2(10)	1.0(13)	−3.0(13)
H(4)	0.870	0.400	0.550	*					
C(5)	0.722 3(32)	0.559 8(24)	0.511 2(30)	6.1(15)	6.4(14)	7.1(15)	1.0(11)	0.7(12)	−3.9(12)
H(5)	0.730	0.570	0.390	*					
C(6)	0.628 8(23)	0.647 5(20)	0.586 8(23)	2.6(10)	5.8(12)	5.2(12)	−0.9(8)	1.1(8)	−1.2(10)
C(7)	0.550 3(28)	0.755 4(20)	0.519 3(19)	6.1(13)	5.8(12)	1.6(9)	−0.7(10)	0.0(8)	−0.8(8)
H(7)	0.580	0.780	0.410	*					
C(8)	0.461 6(26)	0.823 1(21)	0.610 8(22)	3.8(11)	6.2(13)	3.6(10)	0.1(9)	0.0(8)	−1.1(9)
H(8)	0.400	0.890	0.580	*					
C(11)	0.544 0(31)	0.723 9(22)	1.023 9(25)	6.2(14)	6.7(14)	4.4(13)	−1.2(11)	2.6(11)	0.1(10)
O(11)	0.610 0(28)	0.703 2(20)	1.146 7(20)	10.4(15)	10.4(15)	4.3(10)	0.1(12)	1.2(10)	1.8(10)
C(12)	0.338 4(29)	0.911 1(24)	0.859 7(25)	4.3(12)	7.1(15)	5.2(13)	−0.8(11)	−0.1(10)	−2.1(11)
O(12)	0.267 2(28)	−0.001 1(19)	0.877 2(25)	9.4(14)	7.1(12)	10.2(15)	3.2(11)	1.8(12)	−3.4(11)
C(13)	0.265 1(29)	0.652 2(22)	0.809 1(27)	4.4(13)	5.0(13)	7.0(15)	0.2(11)	0.8(11)	−1.8(11)
O(13)	0.151 7(23)	0.584 1(19)	0.798 1(25)	4.6(10)	8.7(13)	11.6(16)	−2.0(10)	1.3(10)	−3.1(12)
C(21)	0.893 4(31)	0.810 2(19)	0.891 3(21)	7.6(15)	4.4(11)	2.5(10)	1.6(10)	−1.6(10)	−0.6(8)
O(21)	0.975 3(26)	0.797 2(20)	0.000 5(21)	7.7(12)	9.3(13)	6.3(12)	1.0(10)	−1.5(10)	0.0(10)
C(22)	0.738 0(31)	1.005 6(19)	0.733 8(20)	7.9(15)	3.8(12)	2.6(9)	0.7(10)	0.2(9)	1.24(8)
O(22)	0.721 5(28)	0.109 4(15)	0.758 3(20)	11.7(16)	4.0(10)	7.1(11)	1.3(10)	−0.8(11)	0.1(8)
C(23)	0.919 7(36)	0.841 4(22)	0.586 8(26)	7.8(17)	5.2(13)	5.1(14)	0.5(12)	−0.3(12)	0.5(10)
O(23)	1.028 4(26)	0.847 7(20)	0.514 1(20)	8.2(13)	10.1(4)	7.9(13)	−0.7(11)	5.3(11)	−0.6(11)

$B = 8\pi^2 U$. * U_H (isotropic) fixed equal to 0.063 Å^2.

Anisotropic thermal parameters are in the form: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$ with parameters given (× 10^2).

(III), colourless crystals of fairly high melting point (155 °C), showed a mass spectrum with a parent ion at *m/e* 456 and a mono-osmium isotope pattern, with peaks corresponding to loss of two carbonyl groups. The i.r. spectrum showed a pattern characteristic of a *cis*-Os(CO)$_2$ species. The ^{1}H n.m.r. spectrum was exceedingly complex, exhibiting resonances attributable to protons attached to both co-ordinated and unco-ordinated olefinic entities. No change was observed in the ^{1}H n.m.r. spectrum on varying the temperature. It is suggested that the organic ligand in (III) is a dimer of COT. Several complexes have been characterised in which various dimers of COT are co-ordinated to iron [8] or to ruthenium [9] carbonyl groups, but from the n.m.r. spectrum the ligand in (III) does not appear to correspond to any of the previously described species. In view of this it is difficult to speculate upon possible structures of (III) on the basis of the evidence available. Both (I) and (IIa) were also formed on treating [{Os(SiMe$_3$)(CO)$_4$}$_2$] with COT in octane at reflux; under u.v. irradiation, however, only [Os(CO)$_3$(1—4-η-C$_8$H$_8$)] was obtained, in moderate yield.

The compound [Os(GeMe$_3$)$_2$(CO)$_4$] and COT reacted only very slowly (2 weeks) in octane at reflux, with much decomposition, to afford a mixture of products some of which could be obtained pure by chromatography. Complex (IIb) was fully characterised, while another product (IV) was a tricarbonyl compound [Os(CO)$_3$(C$_{16}$H$_{16}$)]. As in the case of (III), the ^{1}H n.m.r. spectrum of (IV) was highly complex, and a definitive structure could not be assigned.

It would appear from the nature of the products of the reactions of [Os(MMe$_3$)$_2$(CO)$_4$] (M = Si or Ge) and [{Os(SiMe$_3$)(CO)$_4$}$_2$] with COT that hydrogen abstraction by the olefin is preferred rather than the hydrogen loss required for pentalene complex formation. The failure to obtain any pentalene derivatives, in contrast with the behaviour of the corresponding ruthenium compounds, may be due to the greater thermal stability of the transition metal-to-silicon or -germanium bonds in the former. It is known that in the formation of the pentalene compounds [Ru$_2$(MMe$_3$)$_2$(CO)$_4$(C$_8$H$_6$)] an initial reaction step involves transfer of an MMe$_3$ group from ruthenium to the C$_8$-ring.[4] It seemed worthwhile therefore to investigate the reaction of [OsMe$_2$(CO)$_4$] [10,11] with COT to establish whether the methyl group would migrate more readily. Although such a migration would require a somewhat unlikely subsequent elimination of methane for pentalene formation, insertion of COT into an osmium–carbon bond would be of interest.

The compound [OsMe$_2$(CO)$_4$] reacted only slowly with COT in octane at reflux, affording a complicated mixture of products, mostly in fairly low yield except for a binuclear osmium compound [Os$_2$(CO)$_6$(C$_8$H$_6$)] (Va). The mass spectrum of (Va) showed a strong parent ion with

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[8] G. N. Schrauzer and P. W. Glockner, *J. Amer. Chem. Soc.*, 1968, **90**, 2800.

[9] R. Goddard, A. P. Humphries, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 507, 508.

[10] F. L'Eplattenier, *Inorg. Chem.*, 1969, **8**, 965.

[11] R. D. George, S. A. R. Knox, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 972.

subsequent loss of six carbonyl groups. The presence of a C_8H_6 group was suggestive of a pentalene ligand but this possibility was eliminated by the complexity of the ^1H n.m.r. spectrum, particularly in the region τ 2.0—3.2. Moreoever, the i.r. spectrum in the carbonyl region revealed six bands (2 084s, 2 053s, 2 016s, 2 005s, 1 982s, and 1 974s cm^{-1}) suggesting a relatively unsymmetrical structure. In view of the potential interest of this complex a single crystal *X*-ray diffraction study was undertaken to establish the molecular structure. The results are illustrated in the Figure; structural parameters are in Tables 1 and 2.

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

(i) Metal–carbon bonding

Os(1)–Os(2)	2.754(2)	Os(2)–C(1)	2.37(2)
Os(1)–C(8)	2.05(2)	Os(2)–C(6)	2.35(2)
Os(1)–C(1)	2.12(2)	Os(2)–C(7)	2.26(2)
Os(1)–C(6)	3.02(2)	Os(2)–C(8)	2.28(2)
Os(1)–C(7)	3.00(2)	Os(2)–C(1,6) *	2.24(2)
		Os(2)–C(7,8) *	2.16(2)

(ii) Indenyl ring system

C(1)–C(2)	1.42(3)	C(6)–C(1)	1.45(3)
C(2)–C(3)	1.35(4)	C(2)–H(2)	1.02 †
C(3)–C(4)	1.43(4)	C(3)–H(3)	1.10
C(4)–C(5)	1.37(4)	C(4)–H(4)	1.02
C(5)–C(6)	1.46(3)	C(5)–H(5)	1.13
C(6)–C(7)	1.41(3)	C(7)–H(7)	1.09
C(7)–C(8)	1.40(3)	C(8)–H(8)	0.90

(iii) Carbonyl groups

Os(1)–C(11)	1.90(2)	Os(2)–C(21)	1.92(2)
C(11)–O(11)	1.19(3)	C(21)–O(21)	1.12(3)
Os(1)–C(12)	1.96(2)	Os(2)–C(22)	1.89(2)
C(12)–O(12)	1.14(5)	C(22)–O(21)	1.15(3)
Os(1)–C(13)	1.89(2)	Os(2)–C(23)	1.91(3)
C(13)–O(13)	1.14(3)	C(23)–O(23)	1.18(4)

(*b*) Angles

(i) Metal–carbon bonding

C(1)–Os(1)–C(8)	77.2(8)	C(6)–Os(2)–C(1)	35.9(7)
C(11)–Os(1)–C(12)	95.9(8)	C(7)–Os(2)–C(8)	35.9(8)
C(11)–Os(1)–C(13)	96.1(9)	C(1,6)–Os(2)–C(7,8) *	54.7
C(13)–Os(1)–C(12)	95.2(9)	C(21)–Os(2)–C(22)	91.7(8)
C(1)–Os(1)–C(11)	93.4(9)	C(21)–Os(2)–C(23)	96.2(10)
C(1)–Os(1)–C(12)	164.0(9)	C(22)–Os(2)–C(23)	95.3(10)
C(1)–Os(1)–C(13)	96.4(9)	Os(1)–Os(2)–C(1,6) *	58.4
C(8)–Os(1)–C(11)	158.0(9)	Os(1)–Os(2)–C(7,8) *	58.9
C(8)–Os(1)–C(12)	89.1(9)	C(21)–Os(2)–C(1,6) *	102.1
C(8)–Os(1)–C(13)	104.7(9)	C(22)–Os(2)–C(1,6) *	153.1
Os(2)–Os(1)–C(1)	56.4(5)	C(23)–Os(2)–C(1,6) *	105.9
Os(2)–Os(1)–C(8)	54.4(5)	C(21)–Os(2)–C(7,8) *	149.7
		C(22)–Os(2)–C(7,8) *	103.1
		C(23)–Os(2)–C(7,8) *	108.5

(ii) Indenyl ring system

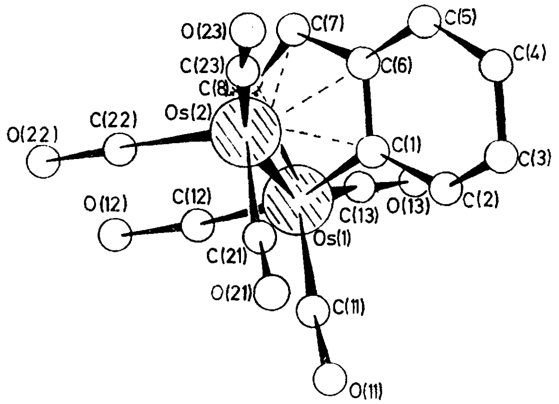
Os(1)–C(1)–C(6)	114.3(13)	C(4)–C(5)–C(6)	117(2)
Os(1)–C(1)–C(2)	129.8(15)	C(5)–C(6)–C(7)	124(2)
Os(1)–C(1)–Os(2)	75.5(6)	C(5)–C(6)–C(1)	121(2)
C(1)–C(2)–C(3)	124(2)	C(7)–C(6)–C(1)	114(2)
C(2)–C(3)–C(4)	119(2)	C(6)–C(7)–C(8)	114(2)
C(3)–C(4)–C(5)	122(2)	C(7)–C(8)–Os(1)	119(1)

(iii) Carbonyl groups

Os(1)–C(11)–O(11)	175(2)	Os(2)–C(21)–O(21)	178(2)
Os(1)–C(12)–O(12)	178(2)	Os(2)–C(22)–O(22)	173(2)
Os(1)–C(13)–O(13)	177(2)	Os(2)–C(23)–O(23)	179(2)
Os(2)–Os(1)–C(11)	103.8(8)	Os(1)–Os(2)–C(21)	93.2(7)
Os(2)–Os(1)–C(12)	108.7(7)	Os(1)–Os(2)–C(22)	98.3(7)
Os(2)–Os(1)–C(13)	146.6(8)	Os(1)–Os(2)–C(23)	163.2(7)

* C(*n*,*m*) is the midpoint of the line joining atom C(*n*) to C(*m*). † C–H Bond lengths have no e.s.d.'s because the H atom co-ordinates were not refined.

It is at once apparent that one of the osmium atoms has been incorporated into a metallacyclic system and that, as suspected, there is no pentalene moiety present.



The molecular structure of $[Os_2(CO)_6(C_8H_6)]$ (Va)

TABLE 3

(*a*) Equations of some least-squares planes: distances (Å) of the relevant atoms from these planes are given in square brackets

(i) Five-membered ring

Plane I: Os(1), C(1), C(6), C(7), C(8)

$$6.0590x + 5.9380y + 1.5980z = 8.6411$$

[Os(1), −0.030; C(1), 0.049; C(6), −0.048; C(7), 0.011; C(8), 0.018]

(*ii*) Six-membered ring

Plane II: C(1), C(2), C(3), C(4), C(5), C(6)

$$6.3959x + 5.5794y + 1.0291z = 8.2492$$

[C(1), 0.0; C(2), 0.003; C(3), 0.005; C(4), −0.017; C(5), 0.019; C(6), −0.011]

(iii) Plane III: C(1)—C(8)

$$6.3433x + 5.6596y + 1.0863z = 8.2929$$

[Os(1), −0.184, C(1), 0.016; C(2), 0.011; C(3), −0.002; C(4), −0.032; C(5), 0.012; C(6), −0.002; C(7), 0.040; C(8), −0.044]

(*b*) Angles (°) between least-squares planes

I—II 175.6°

The nine atoms of the bicyclic system are substantially coplanar (Table 3), while the C–C bond lengths (Table 2) suggest extensive delocalisation within the five-membered ring, with perhaps alternate long and short bonds in the six-membered ring. This delocalisation is caused by a typical diene π-interaction between the four carbon atoms of the five-membered ring and the second osmium atom. The two osmium atoms are 2.754(2) Å apart; indeed, the whole geometry of this part of the molecule is closely similar to that already reported[12] for the compound obtained by reaction of 2,3-dimethylbuta-1,3-diene with dodecacarbonyltriosmium.[13] The Os–Os bond length is shorter than those observed in many

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[12] R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 1963, 380.

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cluster compounds[14-16] including $[Os_3(CO)_{12}]$ itself[17] (2.88 Å), but closely similar to that in the acetato-bridged compound $[Os_2(CO)_6(MeCO_2)_2]$ [2.731(6) Å].[18] Both osmium atoms can be regarded as octahedrally coordinated, and the structure allows rationalisation of 18-electron configurations.

There are, however, significant distortions of the simple bonding picture given above. First, the mean plane through the carbon atoms C(1)–(8) leaves Os(1) 0.18 Å below the plane as seen in the Figure. Secondly, the Os–C interactions are unsymmetrical: Os(1)–C(1), the σ-bond to the ring C-atom is longer than Os(1)–C(8), the σ-bond to the 'terminal' C-atom; and Os(2)–C(1,6), the π-bond to the C_6 ring, is longer than Os(2)–C(7,8) (Table 2).* Thirdly, the carbonyl groups all tend to bend away from the Os–Os bond to make all Os–Os–C angles $>90°$. The mean $Os–C_{carbonyl}$ bond length of 1.91 Å is, however, within the expected range.[19]

Thus, the main product (*ca.* 20% yield) of the thermal reaction (no reaction occurs under u.v. irradiation) of $[OsMe_2(CO)_4]$ with COT is a complex in which a carbon–carbon bond of the olefin has been broken and two hydrogen atoms lost. In view of the complexity of the reaction it would be unrealistic to speculate upon the mode of formation of (Va), though one pathway to such complexes has been established (see below).

The complex ^1H n.m.r. spectrum of (Va) can be rationalised on the basis of the crystallographically determined structure. Six non-equivalent proton signals are discernible at τ 2.86d and 2.46d ($J = 4.5$ Hz, H_a and H_b), 2.28d and 2.10d (H_c and H_f), and at 3.08m and 2.72m ($J_{ef} \sim J_{cd}$ 8.5 Hz, H_d and H_e). The iron analogue (Vc) of the osmium compound (Va) has been reported,[20-22] and the ^1H n.m.r. spectrum[20] is very similar.

Minor products of the reaction of $[OsMe_2(CO)_4]$ with COT were complexes formulated as (VIa) $[Os(CO)_3(C_{16}H_{16})]$ and (VII) $[Os_2(CO)_6(C_8H_8)]$. Compound (VIa) had a ^1H n.m.r. spectrum [τ 4.4(6 H), 4.7(2 H), 6.4(4 H), 7.4(2 H), and 8.0(2 H)] virtually identical with that previously reported[8] for the iron complex (VIb), involving a COT dimer. Complex (VII) is identified by its i.r. spectrum, which is of similar pattern to that of $[Ru_2(CO)_6(C_8H_8)]$,[23] and by its mass spectrum.

Dehalogenation of hydrocarbons by iron carbonyls is well known, and was used in the classic synthesis of tricarbonyl(cyclobutadiene) iron.[24] It seemed worthwhile, therefore, to study corresponding reactions of dibromocyclo-octatetraene with a view to pentalene complex formation. Although 1,5-dibromocyclo-octatetraene is obviously the most suitable precursor of such a complex, *via* elimination of bromine as metal bromide with concomitant trans-annular ring closure, this dibromide has not been reported as being readily available.[25,26] However, a synthesis of 1,4-dibromocyclo-octatetraene has been mentioned[26] and, therefore, some reactions of this isomer with iron or ruthenium carbonyls and their anions were studied.

We have discovered that 1,4-dibromocyclo-octatetraene undergoes ring-closure readily, but specifically to give benzocyclobutadiene complexes, and species derived from these latter. On stirring enneacarbonyldi-iron with 1,4-dibromocyclo-octatetraene in hexane or tetrahydrofuran at room temperature, the known[24,27-29] complex benzocyclobutadiene(tricarbonyl)iron (VIII) is formed. Higher yields are obtained by treating 1,4-dibromocyclo-octatetraene with a solution of disodium tetracarbonylferrate. A different mode of reaction occurs when 1,4-dibromocyclo-octatetraene and enneacarbonyldi-iron are heated under reflux in heptane or octane. Under these conditions complex (Vc) is formed. It has been recently shown[22] that (VIII) is converted into (Vc) by heating the former with $[Fe_3(CO)_{12}]$ in hydrocarbon solvents at 120 °C. It is likely, therefore, that (Vc) forms from $[Fe_2(CO)_9]$ and $C_8H_6Br_2$ in heptane or octane reflux *via* complex (VIII); indeed traces of the latter were observed.

Reaction of 1,4-dibromocyclo-octatetraene with dodecacarbonyltriruthenium in hexane affords complex (Vb). This compound is presumably formed from benzocyclobutadiene(tricarbonyl)ruthenium as an intermediate, but the latter was not detected nor could it be isolated from reactions of the anion $[Ru(CO)_4]^{2-}$ with 1,4-dibromocyclo-octatetraene.

EXPERIMENTAL

(a) *Synthetic Studies.*—I.r. spectra (measured in hexane for ν_{CO}) were recorded using a Perkin-Elmer 257 instrument, and ^1H n.m.r. spectra with Varian Associates T60 and HA100 spectrometers. Mass spectra were determined with

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* This asymmetry does not, of course, arise in the butadiene compound $[Os_2(CO)_6(C_6H_8)]$. The bond lengths determined by O. S. Mills and B. W. Shaw (personal communication) are as follows: Os–Os = 2.744(2), Os–C(chain) σ = 2.10(4) mean, Os–C(chain) π = 2.22(4) mean, Os–C(carbonyl) = 1.83(5) mean, C–O(carbonyl) = 1.19(6) Å mean. Further details of this structure determination may be obtained from B. W. Shaw, Ph.D. Thesis, University of Manchester, 1963.

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an AEI MS902 instrument operating at 70 eV.† All reactions were performed under a nitrogen atmosphere using hydrocarbon solvents dried by distillation from calcium hydride. The complexes $[\mathrm{Os(MMe_3)_2(CO)_4}]$, (M = Si or Ge),[30] $[\{\mathrm{Os(SiMe_3)(CO)_4}\}_2]$,[30] and $[\mathrm{OsMe_2(CO)_4}]$ [10,11] were prepared by published methods.

Since no details [26] have been given for the preparation of 1,4-dibromocyclo-octatetraene a procedure was devised as follows. Bromine (8.0 g, 50 mmol) in methylene chloride (30 cm^3) was slowly added (1 h) to a stirred solution of bromocyclo-octatetraene [31] (9.1 g, 50 mmol) in methylene chloride (70 cm^3) at −80 °C. After addition was complete, the mixture was stirred (1 h). Potassium t-butoxide (8.0 g, 70 mmol) was then added (4 h) in small portions, the temperature being held between −60 and −80 °C. The mixture was then stirred overnight at −60 to −10 °C. The dark brown solution so formed was poured into iced-water (75 cm^3) to which glacial acetic acid (1.5 cm^3) had been added. The liquid phases were separated and diethyl ether (75 cm^3) was added to the organic material which was washed with aqueous sodium hydrogencarbonate (5% solution) and then water. After the solution had been dried ($\mathrm{Na_2SO_4}$), solvent was removed under reduced pressure, and distillation (0.01 Torr) gave at 40 °C unchanged bromocyclo-octatetraene (0.5 g) and at 65 °C 1,4-dibromocyclo-octatetraene (10.0 g, 77%) (Found: C, 37.6; H, 2.4%; *M*, 260. $\mathrm{C_8H_6Br_2}$ requires C, 36.9; H, 2.30%; *M*, 260), ^{1}H n.m.r. ($\mathrm{CDCl_3}$) τ 3.7 m.

Reactions of Cyclo-octatetraene.—(i) *With* $[\mathrm{Os(SiMe_3)_2(CO)_4}]$. Reaction between $[\mathrm{Os(SiMe_3)_2(CO)_4}]$ (600 mg, 1.33 mmol) and COT (600 mg, 5.8 mmol) in heptane at reflux (4 days) gave after chromatography on Florisil and elution with hexane: $[\{\mathrm{Os(SiMe_3)(\mu\text{-}SiMe_2)(CO)_3}\}_2]$ (49 mg, 10%), identified by its i.r. spectrum; $[\mathrm{Os_2(CO)_6(C_8H_{10})}]$ (I) (22 mg, 5%), the i.r. and mass spectra $[(M - n\mathrm{CO})^+$, n = 0—6] being of similar pattern to the ruthenium analogue; [6] and $[\mathrm{Os(SiMe_3)(CO)_2(C_8H_9)}]$ (IIa) (261 mg, 46%), a pale yellow *oil* purified by distillation (50 °C/10^{-2} Torr) (Found: C, 35.5; H, 4.4%; *M*, 426. $\mathrm{C_{13}H_{18}O_2OsSi}$ requires C, 36.6; H, 4.2%; *M*, 426), ν_{CO}(max), 2 002s and 1 943 s cm^{-1}; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 4.93 (d, 2 H, J = 1.5 Hz), 5.15 (t, 1 H, J = 1.5 Hz), 7.60 (m, 6 H), and 9.62 (s, 9 H). Elution of the column with hexane–dichloromethane (7 : 3) gave colourless *crystals* of $[\mathrm{Os(CO)_2(C_{16}H_{16})}]$ (III), m.p. 154—156 °C (Found: C, 47.6; H, 3.3%; *M*, 456. $\mathrm{C_{18}H_{16}O_2Os}$ requires: C, 47.4; H, 3.5%; *M*, 456), ν_{CO}(max) 2 009s and 1 950s; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 3.59 (m, 1 H), 4.33 (m, 4 H), 4.71 (m, 2 H), 5.48 (m, 1 H), and 6.35—8.24 (m, 8 H).

(ii) *With* $[\{\mathrm{Os(SiMe_3)(CO)_4}\}_2]$. (a) *Thermally*. A solution of $[\{\mathrm{Os(SiMe_3)(CO)_4}\}_2]$ (300 mg, 0.40 mmol) and COT (310 mg, 2.98 mmol) in octane (150 cm^3) was heated under reflux for 26 h. Chromatography on Florisil, eluting with hexane, gave in order $[\mathrm{Os(SiMe_3)(CO)_2(C_8H_9)}]$ (IIa) (211 mg, 62%) and $[\mathrm{Os_2(CO)_6(C_8H_{10})}]$ (I) (10 mg, 4%), each identified by its i.r. spectra.

(b) *Photochemically*. U.v. irradiation of a sealed Pyrex tube containing a hexane (30 cm^3) solution of $[\{\mathrm{Os(SiMe_3)(CO)_4}\}_2]$ (200 mg, 0.27 mmol) and COT (315 mg, 3.03 mmol) for 3 weeks, followed by chromatography on Florisil, gave the known [32] $[\mathrm{Os(CO)_3(C_8H_8)}]$ (47 mg, 23%), identified by its i.r., mass $\{(M - n\mathrm{CO})^+$, n = 0—3$\}$, and ^{1}H n.m.r. (singlet at τ 4.8) spectra.

(iii) *With* $[\mathrm{Os(GeMe_3)_2(CO)_4}]$. Reaction between $[\mathrm{Os(GeMe_3)_2(CO)_4}]$ (400 mg, 0.74 mmol) and COT (730 mg, 7.02 mmol) proceeded slowly in refluxing octane to afford a mixture of products, mostly in low yield. Chromatography allowed isolation of $[\mathrm{Os(GeMe_3)(CO)_2(C_8H_9)}]$ (IIb) (189 mg, 54%) as a pale yellow *oil* (Found: C, 33.2; H, 3.7%; *M*, 472. $\mathrm{C_{13}H_{18}GeO_2Os}$ requires C, 33.1; H, 3.8%; *M*, 472), ν_{CO}(max) 1 999s and 1 941s cm^{-1}; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 4.96 (d, 2 H, J = 1.5 Hz, 5.12 (t, 1 H, J = 1.5 Hz), 7.60 (m, 6 H), and 9.55 (s, 9 H).

(iv) *With* $[\mathrm{OsMe_2(CO)_4}]$. The compound $[\mathrm{OsMe_2(CO)_4}]$ (800 mg, 2.4 mmol) and COT (920 mg, 8.85 mmol) were heated under reflux (84 h) in octane. Chromatography on Florisil afforded in order of elution with hexane: (a) $[\mathrm{Os(CO)_3(C_{16}H_{16})}]$ (X) (63 mg, 5%), colourless *crystals*, m.p. 122—123 °C [Found: C, 47.3; H, 3.6%; *M*, 484. $\mathrm{C_{19}H_{16}O_3Os}$ requires C, 47.1; H, 3.3%; *M*, 484], ν_{CO}(max), 2 067s, 1 991s, and 1 985 cm^{-1}; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 4.45 (m, 6 H), 4.70 (m, 2 H), 6.41 (m, 4 H), 7.38 (m, 2 H), and 8.02 (m, 2 H). (b) A species tentatively formulated as $[\mathrm{Os(CO)_3(C_8H_7Me)}]$ (8 mg, 1%) on the basis of its i.r. and mass spectra. (c) $[\mathrm{Os_2(CO)_6(C_8H_6)}]$ (Va) (168 mg, 21%), yellow *crystals*, m.p. 89—91 °C [Found: C, 25.9; H, 1.3%; *M*, 652. $\mathrm{C_{14}H_6O_6Os_2}$ requires C, 25.8; H, 0.9%; *M*, 652], ν_{CO}(max) 2 084r, 2 053s, 2 016s, 2 005s, 1 982s, and 1 974s cm^{-1}; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 2.10 (d, 1 H), 2.28 (d, 1 H), 2.46 (d, 1 H, J = 4.5 Hz), 2.86 (d, 1 H, J = 4.5 Hz), 2.72 (m, 1 H, J = 8.5 Hz) and 3.08 (m, 1 H, J = 8.5 Hz). (d) $[\mathrm{Os_2(CO)_6(C_8H_8)}]$ (VII) (15 mg, 2%) identified only by i.r. spectroscopy as being similar to its ruthenium analogue. (e) An unidentified blue solid (14 mg).

Reactions of 1,4-*Dibromocyclo-octatetraene*.—(i) *With* $[\mathrm{Fe_2(CO)_9}]$. The carbonyl (14 g, 38 mmol) and $\mathrm{C_8H_6Br_2}$ (0.5 g, 1.9 mmol) were stirred in tetrahydrofuran (30 cm^3) for 17 h. After removal of volatile material, chromatography on alumina, eluting with hexane, gave unchanged $\mathrm{C_8H_6Br_2}$ (200 mg, 40%) and $[\mathrm{Fe(CO)_3(C_8H_6)}]$ (VIII) (100 mg, 22%), an orange oil identified by its mass spectrum and from its [27] i.r. [ν_{CO}(max) 2 047s and 1 978vs cm^{-1}] and ^{1}H n.m.r. [($\mathrm{CDCl_3}$) τ 2.95 (m, 4 H) and 5.82 (s, 2 H)] spectra.

In another experiment $[\mathrm{Fe_2(CO)_9}]$ (8.0 g, 21.6 mmol) and $\mathrm{C_8H_6Br_2}$ (1.0 g, 3.8 mmol) were heated under reflux (20 h) in heptane. Chromatography gave (VIII) (120 mg, 13%) and red crystals of (Va) (360 mg, 25%) (Found: C, 44.2; H, 2.5%; *M*, 382. $\mathrm{C_{14}H_6O_6Fe_2}$ requires C, 43.9; H, 1.56%; *M*, 382), ν_{CO}(max) 2 072m, 2 037s, 2 005s, and 1 995sh cm^{-1}; ^{1}H n.m.r. ($\mathrm{CDCl_3}$): τ 3.36d and 2.90d (J_{ab} 5.8 Hz, $\mathrm{H_a}$ and $\mathrm{H_b}$), 2.34d and 2.20d ($\mathrm{H_c}$ and $\mathrm{H_f}$), 3.03m and 2.71m ($J_{\mathrm{cd}} \simeq J_{\mathrm{ef}} \sim 8.5$ Hz, $\mathrm{H_d}$ and $\mathrm{H_e}$).[20]

(ii) *With* $[\mathrm{Fe(CO)_4}]^{2-}$. A solution of the anion {from 1.9 mmol $[\mathrm{Fe_2(CO)_9}]$ and 1% sodium amalgam} in tetrahydrofuran (20 cm^3) was treated with $\mathrm{C_8H_6Br_2}$ (1 g, 3.8 mmol) in the same solvent (10 cm^3). The mixture was stirred (1 h), decanted from the amalgam, and chromatographed on alumina; elution with hexane giving (VIII) (560 mg, 64%), identified as above.[27]

(iii) *With* $[\mathrm{Ru_3(CO)_{12}}]$. The carbonyl (0.5 g, 0.78 mmol) and $\mathrm{C_8H_6Br_2}$ (0.6 g, 2.3 mmol) were heated under reflux in hexane (30 cm^3) for 22 h. Chromatography of the products on alumina afforded pale yellow *crystals* of $[\mathrm{Ru_2(CO)_6(C_8H_6)}]$ (Vb) (65 mg, 18%), m.p. 91—92.5 °C (Found: C,

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† 1 eV ≈ 1.60 × 10^{-19} J.

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36.2; H, 1.5%; *M*, 473. $C_{14}H_6O_2Ru_2$ requires C, 35.5; H, 1.3%; *M*, 473), ν_{CO}(max) 2 084m, 2 056vs, 2 016vs, and 1 997s cm^{-1}.

X-*Ray Data Collection*.—Crystals of (Va) grow as large irregular yellow prisms on slow sublimation (10^{-2} Torr, 25 °C). One crystal was cut to a conveniently small size for data collection because of the high linear absorption coefficient (dimensions *ca.* 0.12 × 0.20 × 0.15 mm). Diffracted intensities were recorded for $2.9° < 2\theta < 50°$ on a Syntex $P2_1$ four circle diffractometer according to methods described earlier.[33] Of the total 2 802 recorded independent intensities, 2 152 satisfied the criterion $I \geqslant 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. The intensities were corrected for the effects of *X*-ray absorption, and all computation was carried out with the '*X*-Ray System' of programs [34] available on the CDC 7600 Computer at the London Computing Centre.

Crystal Data. $C_{14}H_6O_6Os_2$, $M = 650.6$. Triclinic, $a = 7.973(4)$, $b = 10.684(4)$, $c = 9.191(3)$Å, $\alpha = 89.16(3)$, $\beta = 99.28(3)$, $\gamma = 91.75(3)°$, $U = 772.3(5)$ Å^3; D_m(flotation) = 2.75, $Z = 2$, $D_c = 2.81$ g cm^{-3}, $F(000) = 580$. Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å; μ(Mo-K_α) = 175 cm^{-1}. Space group $P\bar{1}$ (No. 2).

Solution and Refinement of the Structure.—The two osmium atoms were located from a Patterson synthesis, and all remaining atoms (including hydrogen) by successive electron density difference syntheses. The structure was refined by full-matrix least-squares, with anisotropic thermal parameters for all non-hydrogen atoms. For the hydrogen atoms the positional and thermal parameters were kept invariant ($U_{iso} = 0.063$ Å^2). The refinement converged at *R* 0.053 (*R'* 0.064) with a mean shift/error ratio in the last two cycles of 0.02. A weighting scheme of the form $1/w = x.y$, where $x = 1$ if $\sin\theta > b$, $x = b/\sin\theta$ if $\sin\theta \leqslant b$, and $y = 1$ if $F < a$, $y = F/a$ if $F \geqslant a$ ($a = 65.0$, $b = 0.25$), gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.6 or < −1.0 e Å^{-3} except in the neighbourhood of the Os atom, where peaks *ca.* 3.5 e Å^{-3} were found. These can probably be ascribed to inadequate absorption corrections arising from the difficulty of characterising adequately the geometry of a cut fragment of crystal. Scattering factors were from ref. 35 for carbon and oxygen, ref. 36 for hydrogen, and ref. 37 for osmium, where also corrections for the effects of anomalous dispersion were applied (Os: $\Delta f' = -1.816$, $\Delta f'' = 7.605$). Atomic positional and thermal parameters are in Table 1, interatomic distances and angles in Table 2, and some least-squares planes in Table 3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21654 (10 pp., 1 microfiche).*

We thank the S.R.C. for support and for research studentships (P. J. H. and R. P. P.).

[5/1511 *Received*, 30*th July*, 1975]

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

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