Pentalene Complexes from Cyclo-octatrienes: Crystal Structure of η-(1,5-Bistrimethylsilyl)pentalene-1,1,2,2,3,3,3,3-octacarbonyl-*triangulo*-triruthenium, $\{Ru_3(CO)_8[C_8H_4(SiMe_3)_2]\}$

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Summary The trimethylsilyl-substituted cyclo-octa-1,3,6-trienes $C_8H_8(SiMe_3)_2$ and $C_8H_7(SiMe_3)_3$ react with $Ru_3(CO)_{12}$ to give the pentalene complexes $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$ and $Ru_3(CO)_8[C_8H_3(SiMe_3)_3]$, respectively; the molecular structure of the former has been established by an *X*-ray diffraction study.

Transition-metal complexes of the unstable hydrocarbon pentalene and its derivatives have been prepared from the anion[1] $C_8H_6{}^{2-}$, and by reactions between dihydropentalenes[2] or pentalene dimer[3] with di-ironenneacarbonyl. These syntheses depend on organic compounds already containing the relatively inaccessible bicyclic C_8 ring system of pentalene. In contrast it has been possible to obtain pentalene–ruthenium complexes by dehydrogenative transannular ring closure of cyclo-octatetraenes using carbonylruthenium compounds.[4,5] Although attempts to extend this method to cyclo-octatriene[6] failed under similar conditions to effect a similar dehydrogenation, we have found that readily prepared trimethylsilyl-substituted cyclo-octa-1,3,6-trienes do form pentalene complexes.

5,8-Bis(trimethylsilyl)cyclo-octa-1,3,6-triene (I)[7] reacts with $Ru_3(CO)_{12}$ or $[Ru(SiMe_3)(CO)_4]_2$ in heptane at reflux to give (6%) $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$ (II) [ν_{CO} (hexane), 2085s, 2026m, 2010s, 2003s, 1981w, 1953m, and 1940w cm^{-1}, m.p. 125° (decomp.)]. Its nature as a complex related to $Ru_3(CO)_8(C_8H_6)$,[5] indicated from the ^1H n.m.r. spectrum [τ 3·80 (1H, d, J_{HH} 2·5 Hz), 5·80 (1H, s), 6·93 (1H, d, J_{HH} 2·5 Hz), 7·03 (1H, s), 9·63 (9H, s), and 9·95 (9H, s)], has been confirmed by a single crystal *X*-ray diffraction study (Figure).

Crystals of $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$ are monoclinic, space group $P2_1/a$, $Z = 4$, $a = 13·298(8)$, $b = 10·793(2)$, $c = 19·812(6)$ Å, $\beta = 97·35(4)°$. The structure was solved by conventional heavy atom methods from data collected (to $2\theta = 50°$) on a Syntex $P2_1$ four-circle diffractometer with monochromatised Mo-K_α X-radiation; R 0·057. The molecular configuration (apart from the $SiMe_3$ groups) is nearly identical to that of $Ru_3(CO)_8(C_8H_6)$.[5]

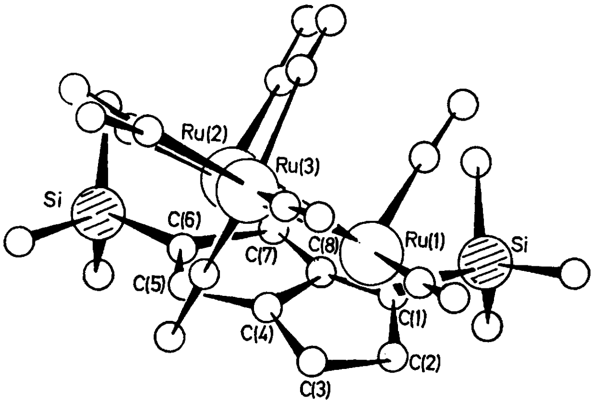
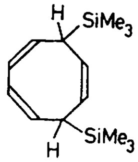
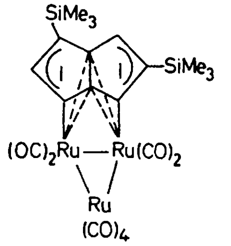


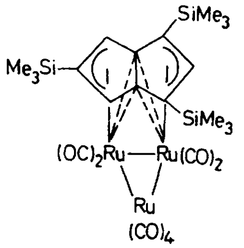
FIGURE. X-Ray structure of $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$. Ru(1)–Ru(3) = Ru(2)–Ru(3) = 2·806(1), Ru(1)–Ru(2) = 2·930(1); the ring-carbon–ruthenium distances fall into two groups: C(1)–C(3) and C(5)–C(7) at 2·23(1) Å, and C(4) and C(8) at 2·48(1) Å; mean pentalene C–C = 1·44(1) Å. The angle between the Ru_3 plane and the mean plane of the pentalene is 50°.



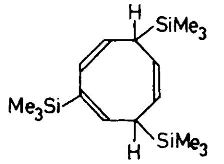
(I)



(II)



(III)



(IV)

Like $Ru_3(CO)_8$ complexes of unsymmetrical 1-substituted pentalenes,[5] (II) is not a fluxional molecule. However, a complex (III) of a symmetrically trisubstituted pentalene obtained by dehydrogenative ring closure of (IV) could be fluxional, assuming an oscillatory process similar to that invoked to account for the ^1H n.m.r. spectrum of $Ru_3(CO)_8(C_8H_6)$.[5] This proved to be the case, and compound (III) [ν_{CO} (hexane), 2087s, 2028m, 2012s, 2002s, 1984w, 1954m, and 1943w cm^{-1}, m.p. 135° (decomp.)], prepared (10%) from (IV) and $Ru_3(CO)_{12}$ showed a variable temperature (+35° to −100°) ^1H n.m.r. spectrum in accord with a free energy of activation of 9·2 ± 0·2 kcal mol^{-1} for the degenerative rearrangement. The corresponding free energy barrier for complexes $Ru_3(CO)_8(2\text{-}R\text{-}C_8H_5)$ (R = H, Me, Ph) is higher (12·8 ± 0·3 kcal mol^{-1}), perhaps indicating a weaker coordination of the trisubstituted pentalene.

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[7] Prepared by Drs. J. M. Bellama and J. B. Davison of the University of Maryland during a visit to our laboratory.