Pentalene Complexes from Cyclo-octatetraenes: Crystal Structure of $Ru_3(CO)_8(C_8H_6)$

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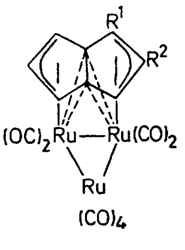
Summary Cyclo-octatetraenes R-C_8H_7 (R = H, Me, Ph) undergo transannular cyclisation on reaction with $Ru_3(CO)_{12}$ in refluxing heptane or octane to form pentalene complexes $Ru_3(CO)_8$(R-C_8H_5); the molecular structure of fluxional $Ru_3(CO)_8(C_8H_6)$ has been determined by an *X*-ray diffraction study.

We recently described[1] a transition-metal carbonyl complex of the unstable hydrocarbon pentalene, formed through dehydrogenative ring closure of cyclo-octatetraene induced by $Ru(GeMe_3)_2(CO)_4$. We have now studied reactions of cyclo-octatetraenes R-C_8H_7 (R = H, Me, Ph) with the parent carbonyl $Ru_3(CO)_{12}$, and find that these species yield pentalene complexes of a new structural type, $Ru_3(CO)_8$(R-C_8H_5).

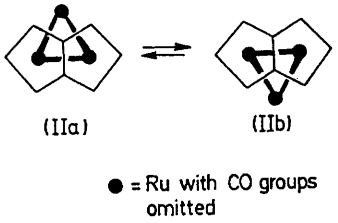
Reaction between $Ru_3(CO)_{12}$ and cyclo-octatetraene gives, in addition to the several complexes previously characterised,[2,3] two new products in low yields, one[4] of which is a complex of pentalene $Ru_3(CO)_8(C_8H_6)$ (I; $R^1 = R^2 = H$). This orange-yellow crystalline compound [m.p. 220° (decomp.); ν_{CO} (hexane) 2089m, 2029m, 2015s, 2008m, 2000w, 1987w, 1962m, 1950w, cm^{-1}] is fluxional. The ^1H n.m.r. spectra at the high-temperature limit (+60°) [τ 3·8 (2H, t, J_{HH} 2·5 Hz), 6·2 (4H, d, J_{HH} 2·5 Hz)] and low-temperature limit (−60°) [τ 3·7 (2H, t, J_{HH} 2·5 Hz), 5·4 (2H, d, J_{HH} 2·5 Hz), 6·9 (2H, d, J_{HH} 2·5 Hz)] are consistent with an oscillatory process which generates a time-averaged mirror plane of molecular symmetry. An *X*-ray diffraction study has established that in the crystal the molecular configuration is as shown (Figure), suggesting the unique oscillation (IIa) $\rightleftharpoons$ (IIb).

Crystals of $Ru_3(CO)_8(C_8H_6)$ are triclinic ($P\bar{1}$) with two molecules in a unit cell: $a = 9{\cdot}824(2)$, $b = 8{\cdot}866(2)$, $c = 12{\cdot}665(3)$ Å, $\alpha = 83{\cdot}82(2)$, $\beta = 93{\cdot}97(2)$, $\gamma = 125{\cdot}90(2)^\circ$. The structure was solved by conventional heavy-atom methods from data collected on a Syntex $P2_1$ 4-circle diffractometer to $2\theta = 50^\circ$ (Mo-K_α radiation); $R = 0{\cdot}077$.

The three ruthenium atoms (Figure) form an isosceles triangle in which the apical atom Ru(3) carries four carbonyl groups, while the atoms Ru(1) and Ru(2) each carry two carbonyl groups and are bonded to the pentalene in a manner similar to that already described[1] for $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$. The Ru(1)–Ru(3) and Ru(2)–Ru(3) distances are 2·81 Å, but the Ru(1)–Ru(2) distance, at 2·94 Å, is significantly shorter than the Ru–Ru distance (3·05 Å) found in $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$.[1] As indicated above, a most significant feature is that the plane of the metal triangle makes a 50° angle with the mean plane of the pentalene. Again the ring-carbon ruthenium distances fall into two main groups, with C(1)–(3) and C(5)–(7) at a mean distance of 2·23 Å and the junction atoms C(4) and C(8) at 2·48 Å. In each of the inter-annular π-allyl units, however, the central atom is significantly more closely bonded (2·17 Å). Within the accuracy of the determination the C–C bond lengths of the pentalene are all equivalent at 1·43 Å.



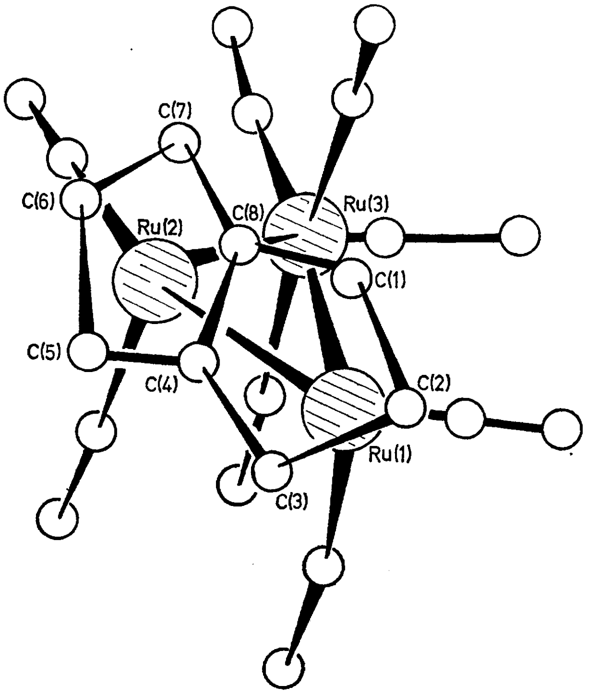
(I)



(IIa) (IIb)

(I; $R^1 = R^2 = H$) is also formed from reaction of cyclooctatetraene and $[Ru(SiMe_3)(CO)_4]_2$.[5] Both $Ru_3(CO)_{12}$ and $[Ru(SiMe_3)(CO)_4]_2$ react with methyl- or phenyl-cyclooctatetraene to give (1—7%) mixtures of isomeric 1- and 2-substituted pentalene complexes (I; R^1 = Me or Ph, R^2 = H) and (I; R^1 = H, R^2 = Me or Ph). Apparently, during dehydrogenative ring closure of cyclo-octatetraenes $R\text{-}C_8H_7$ the position of central σ-bond formation is not greatly influenced by the substituent.

An interesting situation arises in that the 2-substituted complexes (I; R^1 = H, R^2 = Me or Ph) are fluxional, while the 1-substituted isomers (I; R^1 = Me or Ph, R^2 = H) are not. The two fluxional complexes appear from their n.m.r. spectra to be undergoing a process analogous to that of (I; $R^1 = R^2 = H$); the free energy of activation is essentially independent of the 2-substituent, being 12·8 ± 0·3 kcal mol^{-1} for each complex. A process of this type is not possible for complexes of the unsymmetrical 1-substituted pentalenes, since the two components of the fluxional oscillation would be non-degenerate. Although the possibility remains of these components having an independent existence, we have at present no evidence for this form of isomerism.



FIGURE

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[2] F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.

[3] M. I. Bruce, M. Cooke, and M. Green, *J. Organometallic Chem.*, 1968, **13**, 227.

[4] The other is currently the subject of an *X*-ray diffraction study by Professor R. Bau.

[5] S.A.R. Knox and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 2559.