A Transition-metal Carbonyl Complex of Pentalene

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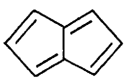
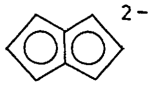
Summary Reaction of *cis*-$Ru(CO)_4(GeMe_3)_2$ with cyclooctatetraene affords the pentalene complex $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$, the structure of which has been determined by *X*-ray crystallography.

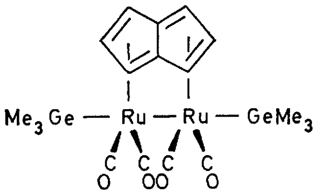
Pentalene has been of interest for many years and is predicted to have a singlet ground state (I).[1] Although various derivatives are known, attempts to synthesise pentalene itself have so far been unsuccessful. Significantly, 1-methylpentalene[2] and 1,3-dimethylpentalene[3] are very unstable, each being detected spectroscopically only at −196°. In contrast, the dianion (II),[4] a ten π-electron aromatic system, has a well established existence and is known[5] to form transition-metal complexes. The possibility of eight π-electron pentalene being stabilised as a ligand analogously to *inter alia* cyclobutadiene[6] or trimethylenemethane[7] has been partially realised by isolation[8] of the species 1-dimethylaminopentalene and 1-phenylpentalene complexed with $Fe_2(CO)_5$, formed by reaction of the appropriate dihydropentalene with $Fe(CO)_5$. Herein we report the first metal carbonyl complex of pentalene itself, obtained *via* dehydrogenative ring closure of cyclo-octatetraene.



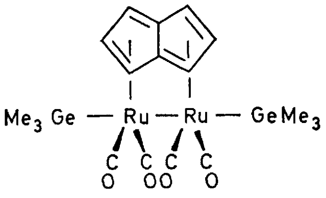
(I)



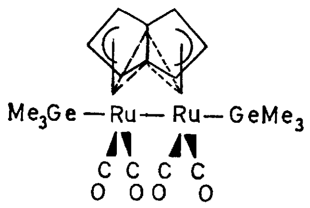
(II)



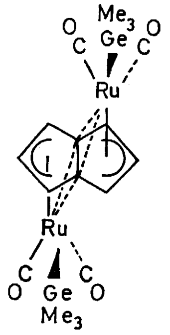
(IIIa)



(IIIb)



(IV)



(V)

In refluxing octane or heptane *cis*-$Ru(CO)_4(GeMe_3)_2$[9] and cyclo-octatetraene afford several complexes, one of which is a pale yellow solid (11%) m.p. 235° (decomp.), formulated as $Ru_2(CO)_4(C_8H_6)(GeMe_3)_2$ from elemental analyses and the mass {M^+ at m/e 652}, n.m.r. {τ, 4·24 (2H, t, J_{HH} 2·5 Hz), 6·50 (4H, d, J_{HH} 2·5 Hz), and 9·40 (18H, s)} and i.r. {ν_{CO} 2029s, 2023w,sh, 1995w, and 1977s cm^{-1}} spectra.

These data are consistent with either the fluxional 8π electron molecular structure (III), which involves movement of the metal-containing unit relative to the pentalene ligand, or the isoelectronic static structure (IV), or a structure (V) analogous to the nickel complex *trans*-$[Ni(\pi\text{-}C_3H_5)]_2$-$C_8H_6$.[5c] A single-crystal *X*-ray diffraction study has established that in the solid state the structure is most nearly represented by (IV).

Crystals (from hexane) are monoclinic ($P2_1$) with four molecules in a unit cell of dimensions a = 9·39; b = 25·55; c = 10·98 Å; β = 96·9° (*i.e.* the asymmetric unit comprises two crystallographically distinct molecules). The structure was solved by direct methods from data collected on a Syntex $P2_1$ 4-circle diffractometer to 2θ = 50° (Mo-K_α radiation); current R 0·083.

The overall structure is as in Figure 1; a section showing the relation between the pentalene species and the metal atom chain is in Figure 2. The metal sequence (Ge–Ru = 2·49; Ru–Ru = 3·05 Å) is significantly non-linear (Ge–Ru–Ru = 171°) but is symmetrically related to the pentalene so that the Ru–Ge bond is directed away from the molecular centre. The pentalene is likewise non-planar, with the two planar five-membered rings hinged to one another at an angle of 173°, again away from the molecular centre. The whole molecule has approximate mirror symmetry about the plane perpendicular to, and through the midpoint of, the Ru–Ru bond; *i.e.* the $GeMe_3$ groups take up an eclipsed configuration. The Ge–Me and Ru–C–O distances are all normal.

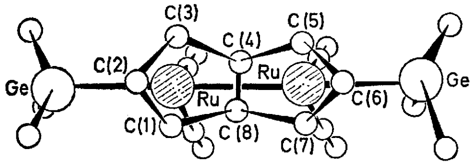


FIGURE 1

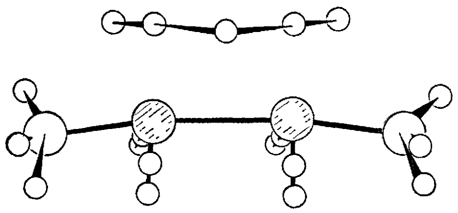


FIGURE 2

There are two sets of ring-carbon–ruthenium distances. C(1)—(3), and C(5)—(7) are on average 2·21 Å from their nearest Ru atom, while C(4) and C(8) are equidistant (2·53 Å) from each Ru atom. Thus atoms C(1)—(3) and C(5)—(7) can be simplistically regarded as being components of inter-annular π-allyl units bonded to their respective Ru atoms, while C(4) and C(8) and the two Ru atoms are involved in a four-electron multicentre interaction, as proposed for the cyclo-octatetraene complex $Fe_2(CO)_5C_8H_8$).[10]

Ring closures of cyclo-octatetraene and cyclo-octadienes to yield bicyclo[3,3,0]-transition metal derivatives are known[11] but the mechanisms of such reactions are as yet obscure. We have established that the pentalene complex described herein is formed *via* a cyclo-octatetraene complex $Ru(CO)_2(C_8H_8)(GeMe_3)_2$ (whose fluxional behaviour is under investigation), isolable when *cis*-$Ru(CO)_4(GeMe_3)_2$ and C_8H_8 react slowly in hexane at reflux.

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