Fluxional Complexes of a Valence Tautomer of a New Dimer of Cyclo-octatetraene: Crystal and Molecular Structure of $[\mathrm{Ru_2(CO)_5(C_{16}H_{16})}]$

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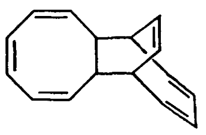
Summary Fluxional complexes $[\mathrm{Ru_2(CO)_5(C_{16}H_{16})}]$ and $[\mathrm{Ru_2(CO)_6(C_{16}H_{16})}]$ containing a valence tautomer of a new dimer of cyclo-octatetraene are described; the molecular structure of the former has been determined by *X*-ray diffraction.

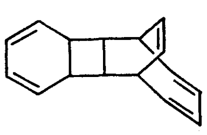
In the preceding communication[1] we reported a new dimer (II) of cyclo-octatetraene, which can be envisaged as the bicyclo-octadiene tautomer of the dimer (I) which would directly arise from Diels–Alder self-addition, were this to occur. We now describe the stabilisation of the dimer in the tautomeric form (I) in two di-ruthenium complexes.

The reaction between $[\mathrm{H_4Ru_4(CO)_{12}}]$ and cyclo-octatetraene, which affords the dimer (II), has a minor product which has been identified through an *X*-ray diffraction study as a complex $[\mathrm{Ru_2(CO)_5(C_{16}H_{16})}]$ [(III), m.p. 142—143° (decomp.); ν_{CO} (hexane) 2062s, 2004s, 1995s, 1980w, and 1940m cm^{-1}] whose molecular structure is shown in the Figure. The yellow crystals of (III) are monoclinic, space group $P2_1/n$, with 8 molecules in a unit cell of dimensions $a = 7{\cdot}010(1)$, $b = 24{\cdot}965(8)$, $c = 22{\cdot}021(7)$ Å, $\beta = 101{\cdot}03(2)°$. The structure was solved by conventional heavy-atom methods from data collected to $2\theta = 50°$ (Mo-K_α *X*-radiation). For the 4179 independent reflections $R = 0{\cdot}056$.

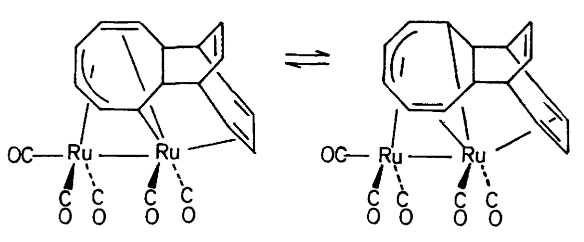
The structure determination reveals (III) to be a complex of the cyclo-octatetraene dimer in the configuration (I), with the C(3)–C(6) (substantially planar) section of the bifurcated ring lying *endo* to a metal–metal bonded $\mathrm{Ru_2(CO)_5}$ group in order to achieve η^2-bonding between C(3)–C(4) and Ru(2). The metal atoms are otherwise bonded entirely to the unbridged $\mathrm{C_8}$ ring in a manner similar to that determined[2,3] for $[\mathrm{Ru_2(CO)_6(C_8H_8)}]$ and $[\mathrm{Fe_2(CO)_6(C_8H_{10})}]$; Ru(2) is η^1-bonded to C(14) and η^2-bonded to C(9)–C(10), while Ru(1) is η^3-bonded to C(11)–C(13). Appropriate contortions of the ring systems allow all the bond lengths to lie in the expected ranges (Figure). The crystallographic asymmetric unit comprises two distinct molecules which do not differ significantly from one another. However, as the space group is centrosymmetric, each molecule is one of an enantiomorphous pair (giving 8 molecules in the unit cell).



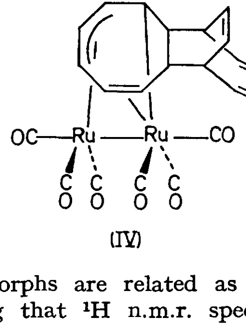
(I)



(II)



(IIIa) (IIIb)



(IV)

These enantiomorphs are related as (IIIa) and (IIIb). It is interesting that ^{1}H n.m.r. spectroscopy identifies fluxional behaviour of $[\mathrm{Ru_2(CO)_5(C_{16}H_{16})}]$ in solution consistent with a (IIIa) $\rightleftharpoons$ (IIIb) interconversion. Although the spectrum at the slow exchange limit ($-30°$) is as complex as might be anticipated for a molecule of instantaneous structure (IIIa) or (IIIb), at the fast exchange limit ($+100°$) it implies the generation of a time-averaged mirror plane of molecular symmetry [τ 4·56 (6H, m) 5·22 (2H, m) 5·75 (2H, m), 7·60 (2H, m), 8·38 (2H, m), and 8·55 (2H, d)]. This is required by the indicated process, which, within the (η^1:η^2:η^3)-bonded C_8 ring, is similar to that postulated for $[Ru_2(CO)_6(C_8H_8)]$[2] and $[Fe_2(CO)_6(C_8H_{10})]$.[3] The simultaneous interchange of η^2-bonding within the other ring represents, to our knowledge, the first example of a fluxional 1,3-shift rearrangement in a cyclic polyolefin–transition-metal complex.

The complex $[Ru_2(CO)_5(C_{16}H_{16})]$ takes up a molecule of carbon monoxide under relatively mild conditions (10 atm, 40°, acetone) to give pale yellow crystalline $[Ru_2(CO)_6(C_{16}H_{16})]$, whose i.r. spectrum [$\nu_{CO}$ (hexane) 2071s, 2035s, 2008s, 1993m, and 1977m cm^{-1}] is nearly identical to that of the cyclo-octatriene complex $[Ru_2(CO)_6(C_8H_{10})]$,[4] suggesting the structure (IV) in which a partial detachment of the olefin has occurred. Warming in hexane effects a rapid regeneration of (III). Moreover, (IV) is fluxional, undergoing an apparently identical rearrangement to (III) within the η^6-bonded ring.

It is tempting to regard both (III) and (IV) as examples of the ability[5] of carbonylmetal groups to sequester (according to their electronic requirements) particular tautomers of the bicyclo-octadiene–cyclo-octatriene system. Just how (III) is formed, however, is not clear, for treatment of either $[Ru_3(CO)_{12}]$ or $[H_4Ru_4(CO)_{12}]$ with the dimer (II) does not yield (III). The use of $[H_4Ru_4(CO)_{12}]$ as a carbonylruthenium source seems likewise unimportant, as (III) is equally well obtained from $[Ru_3(CO)_{12}]$ and cyclo-octatetraene.

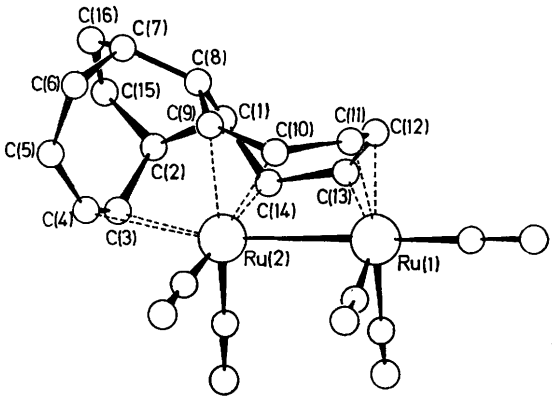


FIGURE Overall stereochemistry of the complex $[Ru_2(CO)_5(C_{16}H_{16})]$. Pertinent distances are: Ru(1)–Ru(2) = 2·891(1), Ru(1)–C(11) = 2·24(1), Ru(1)–C(12) = 2·22(1), Ru(1)–C(13) = 2·31(1), Ru(2)–C(14) = 2·15(1), Ru(2)–C(3) = 2·43(1), Ru(2)–C(4) = 2·54(1), Ru(2)–C(10) = 2·37(1), Ru(2)–C(9) = 2·29(1), C(1)–C(8) = 1·56(2), C(3)–C(4) = 1·41(2), C(15)–C(16) = 1·34(2), C(9)–C(10) = 1·41(2), C(11)–C(12) = 1·44(2), C(12)–C(13) = 1·41(2) Å.

Attempts to remove the dimer (I) from complexation in $[Ru_2(CO)_5(C_{16}H_{16})]$ have been hindered by the small quantities of the complex available. Treatment of (II) with Ag^+ ion likewise failed to give (I).

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