A New Dimer of Cyclo-octatetraene and its Tricarbonylruthenium Complex: Crystal and Molecular Structure of $[Ru(CO)_3(C_{16}H_{16})]$

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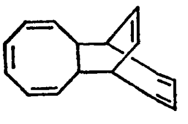
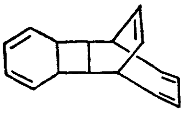
Summary A new dimer of cyclo-octatetraene and its tricarbonylruthenium complex $[Ru(CO)_3(C_{16}H_{16})]$ are formed on reaction of cyclo-octatetraene with $[H_4Ru_4(CO)_{12}]$; the molecular structure of $[Ru(CO)_3(C_{16}H_{16})]$ has been determined by *X*-ray diffraction.

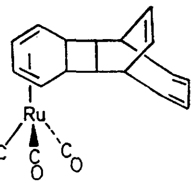
ALTHOUGH cyclo-octatetraene has four known dimers, it shows no tendency towards Diels–Alder self-addition, and a dimer of structure (I), or its tautomer (II), has not been reported. We have now identified such a dimer, which adopts the tautomeric form (II), and also its tricarbonylruthenium complex (III), both formed from reaction of cyclo-octatetraene with the hydrido-carbonylruthenium cluster $[H_4Ru_4(CO)_{12}]$.[1,2] Typically, $[H_4Ru_4(CO)_{12}]$ (1 g) is treated (20 h) with freshly distilled cyclo-octatetraene (6 cm³) in heptane (150 cm³) at reflux; additional products are known carbonylruthenium complexes of cyclo-octatetraene or cyclo-octatriene and a complex of (I), $[Ru_2(CO)_5(C_{16}H_{16})]$, which is described in detail in the succeeding communication.[3] Chromatography does not efficiently separate (II) from (III), and the dimer is best obtained by subjecting the mixture to Ce^{IV} oxidation. In this way the $Ru(CO)_3$ group is removed and approximately 300 mg of the dimer is isolated per g of $[H_4Ru_4(CO)_{12}]$ employed. Reaction of $[Ru_3(CO)_{12}]$ with cyclo-octatetraene does, we have found, yield some (III) but no free dimer.



(I)



(II)



(III)

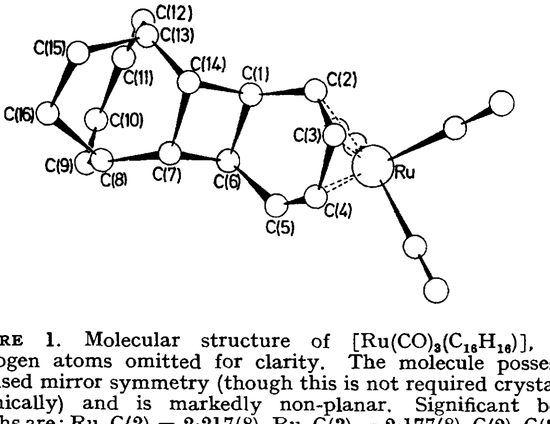


FIGURE 1. Molecular structure of $[Ru(CO)_3(C_{16}H_{16})]$, the hydrogen atoms omitted for clarity. The molecule possesses idealised mirror symmetry (though this is not required crystallographically) and is markedly non-planar. Significant bond lengths are: Ru–C(2) = 2·217(8), Ru–C(3) = 2·177(8), C(2)–C(3) = 1·413(11), C(3)–C(4) = 1·410(14), C(1)–C(14) = 1·555(9), C(1)–C(6) = 1·536(10), C(14)–C(7) = 1·534(11), C(15)–C(16) = 1·29(2), C(11)–C(10) = 1·43(2), C(11)–C(12) = 1·30(1), C(13)–C(15) = 1·51(1) Å. The molecule 'folds' along the lines C(2)—C(5), C(1)—C(6), C(14)—C(7), and C(13)—C(8), the angle between the plane defined by [C(13), C(12), C(8), and C(9)] and that defined by [C(8), C(13), C(15), and C(16)] being *ca.* 120°.

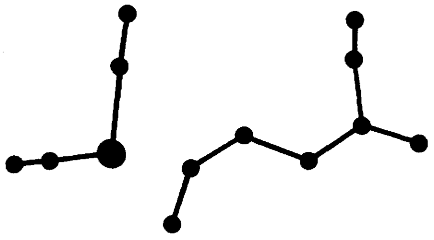


FIGURE 2. Cross section through the mirror plane of the $[Ru(CO)_3(C_{16}H_{16})]$ molecule to show the dihedral angular relationships.

N.m.r. spectra of the colourless, crystalline, slightly air- and light-sensitive dimer (m.p. 78—79°) are compatible with the structure (II). Thus, the ^1H n.m.r. spectrum shows 10 olefinic [τ 4·15 (6H, m) and 4·35 (4H, m)] and 6 aliphatic [τ 6·70 (2H, m) and 7·25 (4H, m)] protons, while the ^{13}C n.m.r. spectrum reveals three sp^3 and five sp^2 carbon environments [at 33·2, 34·1, 52·1, 121·0, 124·2, 126·3, 128·1 and 135·8 p.p.m. (downfield of Me_4Si)].

We have so far been unable to obtain crystals of the dimer suitable for an *X*-ray diffraction study. However, the ^1H [τ 4·28 (8H, m), 6·53 (2H, m) 7·22 (4H, m), and 8·34 (2H, m)] and ^{13}C (33·9, 41·2, 43·5, 62·9, 87·7, 124·5, 125·9, and 135·2 p.p.m.) n.m.r. spectra of the very pale yellow crystalline $[Ru(CO)_3(C_{16}H_{16})]$ [III; m.p. 115—118°; ν_{CO} (hexane) 2061s, 1995s, and 1986s cm⁻¹] clearly suggested its identity as a complex of the new dimer, and that the dimer, whatever its structure, had not suffered any gross structural change on complexation. In particular, the ^{13}C n.m.r. spectrum of the complex differs from that of the dimer (II) only in the shift to high field of two pairs of formerly olefinic carbon atoms now brought into complexation with ruthenium. A single crystal *X*-ray diffraction study on (III) has unequivocally established the molecular structure (Figures) and, by implication, that of the new dimer.

Crystals of (III) are monoclinic, space group *P*2/*n*, with 4 molecules in a unit cell of dimensions $a = 12{\cdot}801(4)$, $b = 6{\cdot}640(1)$, $c = 19{\cdot}678(5)$ Å, $\beta = 103{\cdot}06°$. The structure was solved by conventional heavy-atom methods from data collected on a Syntex $P2_1$ 4-circle diffractometer to $2\theta = 50°$ (Mo-K_α *X*-radiation). For the 1991 independent reflections R = 0·036.

It is the tub conformation adopted by cyclo-octatetraene which precludes its Diels-Alder self-addition. It is attractive, therefore, to believe that (II) and (III) are formed *via* the tricarbonylruthenium complex of cyclo-octatetraene, $[Ru(CO)_3(C_8H_8)]$, an *X*-ray diffraction study[4] of which has shown that the (instantaneously) unco-ordinated 1,3-diene fragment of the ring is held very nearly planar, thus allowing its involvement in thermal $[4+2]\pi$ cycloadditions. In support of this premise we have observed that treatment of $[Ru(CO)_3(C_8H_8)]$ with cyclo-octatetraene does yield (III). Whether Diels–Alder addition of cyclo-octatetraene to $[Ru(CO)_3(C_8H_8)]$ occurs directly onto the co-ordinated olefin or *via* preliminary co-ordination[5] to ruthenium is of importance; in either event (III) would not be formed directly and subsequent steps are required.

We note, finally, that reaction of $[Fe(CO)_3(C_8H_8)]$ with cyclo-octatetraene yields complexes of dimers of the olefin,[6] but not of (II). The iron analogue of (III) is, however, readily obtained from $Fe_2(CO)_9$ and (II).

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