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Preliminary communication

A NEW PRODUCT FROM THE REACTION OF CYCLOOCTATETRAENE WITH $Ru_3(CO)_{12}$: CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)$

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Summary

The synthesis and crystal and molecular structure of $Ru_3(CO)_6(\eta^5\text{-}C_8H_9)(\eta^7\text{-}C_8H_9)$ are described.

In the course of studies [1] on carbonylruthenium complexes of pentalene, we investigated thoroughly the reaction of cyclooctatetraene with $Ru_3(CO)_{12}$, and found that, in addition to the previously-established products [2, 3], two others were formed in low yield. One of these, the pentalene complex $Ru_3(CO)_8(C_8H_6)$, has recently been described [4]; the other is the subject of this note.

The infrared spectrum (ν(CO)(hexane) 2012m, 1987s, 1954s, 1931m, 1830w cm^{-1}) of the new red crystalline complex (I) (m.p. 194°) strongly resembles that of $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ (II), whose molecular structure we have reported [5]. Taken in conjunction with analytical data, and mass and ^1H NMR spectra [τ 4.73m (3H), 4.82t (1H), 5.94t (2H), 6.93t of d (2H), 7.46m (8H), 8.50m (1H), 8.75m (1H)] this suggested a related structure with formulation $Ru_3(CO)_6(C_8H_9)_2$, which has now been confirmed by a single-crystal X-ray diffraction study.

Crystals of I are monoclinic (space group $C2/m$), with a = 24.934(11), b = 12.632(6), c = 14.669(8) Å and β = 114.31(2)°. Data were collected on an automated Nonius CAD-3 diffractometer with Mo-K_α radiation up to a $2\theta_{max}$ of 45°. The solution was solved by heavy atom methods and refined anisotropically to an R factor of 5.9% for 2211 non-zero reflections.

There are two independent (and essentially identical) molecules in the unit cell, each bisected by a crystallographic mirror plane. The molecular framework, shown in Fig. 1, consists of an Ru_3 triangle with dimensions Ru(1)—Ru(2) =

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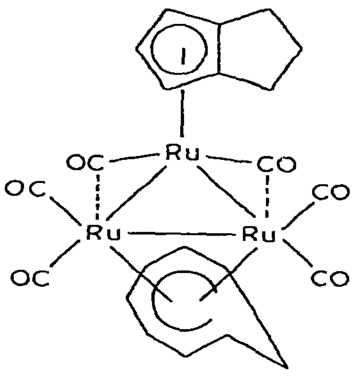
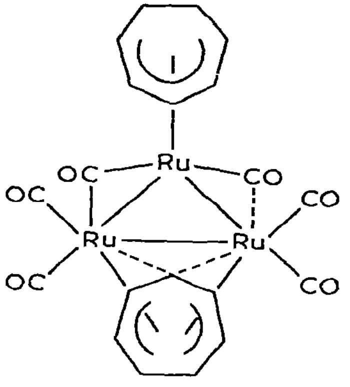


(I)



(II)

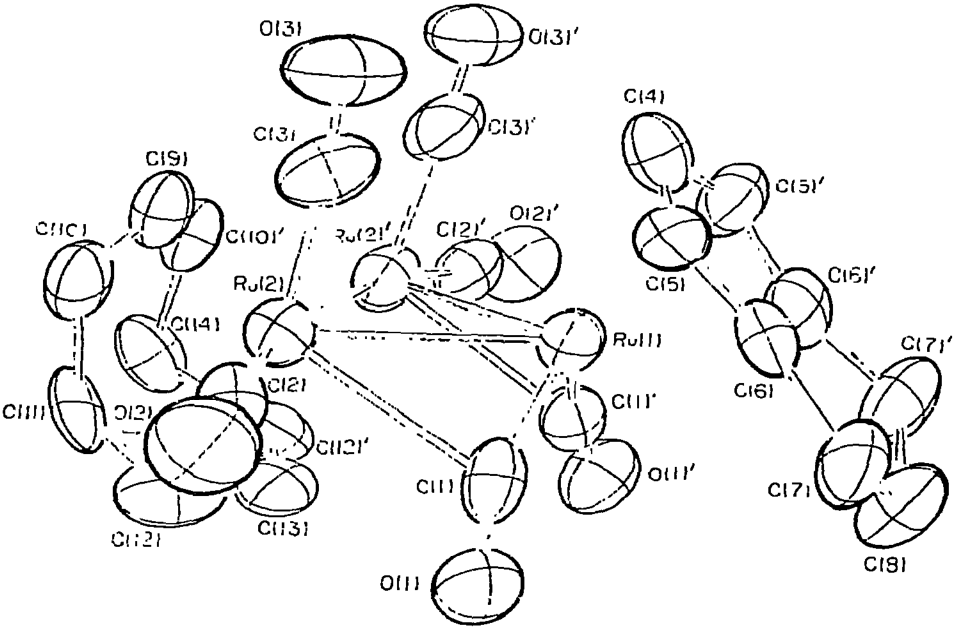


Fig. 1. The molecular geometry of $Ru_3(CO)_6(C_8H_9)_2$. The methylene carbons in the molecule are C(7), C(8), C(7)' and C(14).

Ru(1)—Ru(2)' = 2.835 Å and Ru(2)—Ru(2)' = 2.853 Å. The two carbonyl groups on Ru(1) are asymmetrically bridged[*], with Ru(1)—C(1) = 1.86 Å, Ru(2)—C(1) = 2.54 Å, and the angle Ru(1)—C(1)—O(1) = 160.9°. There are two distinct C_8H_9 ligands (one bicyclic and the other monocyclic) in the molecule, which can be represented schematically as I.

The evidence for formulation of the bicyclic η^5-C_8H_9 tetrahydropentalenyl

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[*] For other examples of asymmetrically bridged carbonyl groups, see refs. 5 and 6.

ligand is unambiguous. The unsaturated portion of the ligand [atoms C(4), C(5), C(6), C(5)′, C(6)′] is coordinated to Ru(1) with molecular parameters expected of a cyclopentadienyl-type interaction (Ru—C distances in the range 2.23-2.28 Å and C—C distances in the range 1.37-1.44 Å), while the atoms in the saturated portion of the ligand are all non-bonding to Ru(1) and are separated from each other by typical C—C single bond distances of 1.52-1.56 Å.

In contrast to the planar bicyclic C_8H_9 ligand, the monocyclic C_8H_9 ligand is decidedly non-planar and coordinates through seven carbon atoms by wrapping itself around one of the edges of the Ru_3 triangle. The unique methyiene group in this ligand is located at one of the "hinged" positions (i.e. at one of the two positions where a bend in the ligand occurs) and is shown in the figure as C(14)[*]. A non-bonding Ru(2)′····C(14) distance of 2.91 Å clearly characterises C(14) as of the CH_2 group, while a close Ru(2)—C(11) distance of 2.21 Å identifies C(11) as of a CH group. The remaining C(H) carbons of this unique ligand are all within bonding distance of either (or both) of Ru(2) or Ru(2)′. Thus Ru(2)—C(10) = Ru(2)′—C(10)′ = 2.194 Å, and Ru(2)—C(12) = Ru(2)′—C(12)′ = 2.275 Å, while C(9) and C(13) are equidistant (Ru(2)—C(9) = Ru(2)′—C(9) = 2.525; Ru(2)—C(13) = Ru(2)′—C(13) = 2.710 Å) from Ru(2) and Ru(2)′.

It is difficult to represent satisfactorily the bonding of the ligand to Ru(2) and Ru(2)′ in any manner more exact or revealing than that shown in I and, like II, the compound $Ru_3(CO)_6(C_8H_9)_2$ (I) is evidently highly electron-delocalised.

Formation of the tetrahydropentalenyl ligand in reactions of cyclooctatetraene with metal carbonyls has been observed previously [7]. Although complexes of monocyclic C_8H_9 with one metal atom are known [8], we believe, however, that in $Ru_3(CO)_6(C_8H_9)_2$ there exists the first example of this ligand as a bridge between two metals.

If, reasonably [9], one attributes ^{1}H NMR signals at τ 4.73(2H), 4.82(1H) and 7.46(6H) in the spectrum of $Ru_3(CO)_6(C_8H_9)_2$ to the tetrahydropentalenyl ligand, the remaining signals (τ 4.73(1H), 5.94t(2H), 6.93t of d(2H), 7.46(2H), 8.50m(1H) and 8.75(1H)) demand that a mirror plane bisects the monocyclic C_8H_9, which is not apparent in the molecular structure established by X-ray. Whether some low energy fluxional process produces this as a time-averaged effect is as yet undetermined. At —60° some broadening of the signals at τ 5.94 and 6.93 occurs, but low solubility of the complex hinders the attainment of lower temperature spectra.

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[*] Actually the crystallographic mirror plane which bisects the Ru_3 triangle causes the methylene group to be disordered over both "hinged" positions. Thus, C(11) and C(14) appear superimposed in electron density maps as an extremely elongated region of electron density. Fortunately, it was possible in the least-squares refinement to resolve this into two distinct half-atoms. Figure 1 shows an isolated molecule with C(11) and C(14) properly resolved.

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