Reaction of Benzylideneacetone with (Cyclo-octa-1,5-diene)tricarbonylruthenium

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Summary The preparation and *X*-ray structural analysis of μ-hydrido-μ-(3,4-h^2: 4-O-h^2-benzylideneacetonato)hexacarbonyldiruthenium(Ru–Ru) are reported.

Studies on tricarbonyliron complexes of α,β-unsaturated ketones[1,2] have shown that the ligand is attached to the metal atom in a manner analogous to that found for π-(1,3-

diene) complexes.[3] Although the same mode of bonding has been observed in complexes of other heterodienes,[4,5] the possibility arises that the lone pair of electrons of the heteroatom is involved in the formation of a ligand–metal σ-bond.[5,6]

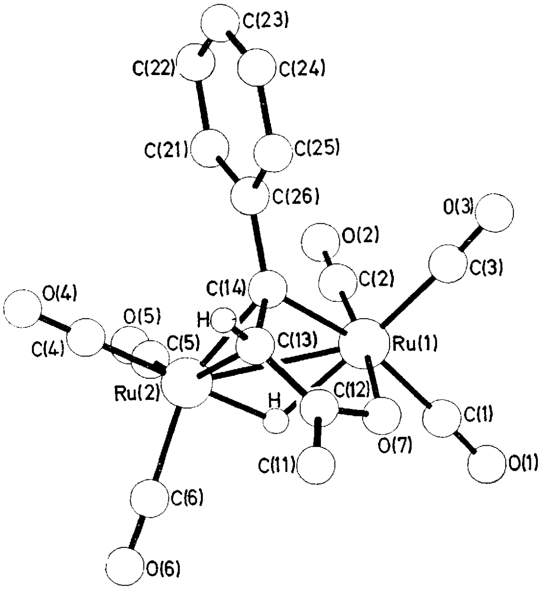

FIGURE. The molecule of $H(C_{10}H_9O)Ru_2(CO)_6$.

We now report the preparation and structural characterisation of a complex of composition $C_{10}H_{10}ORu_2(CO)_6$ (I), the only organometallic product of the reaction of benzylideneacetone with (cyclo-octa-1,5-diene)tricarbonylruthenium (II), and formulated as μ-hydrido-μ-(3,4-h^2:4-*O*-h^2-benzylideneacetonato)-hexacarbonyldiruthenium(Ru–Ru) (Figure) on the basis of its i.r., mass, and ^1H n.m.r. spectra and of single-crystal *X*-ray analysis.

(Cyclo-octa-1,5-diene)tricarbonylruthenium[7] (440 mg) was treated (1 h; 70°C) under nitrogen with benzylideneacetone (440 mg) in benzene. Purification by chromatography followed by sublimation yielded $H(C_{10}H_9O)Ru_2(CO)_6$ (51%) as reasonably air stable orange crystals, τ2·46—2·91 (m, 5H, Ph), 6·49 [s, 1H, H(13)], 7·89 (s, 3H, Me), 22·6 (s, 1H, bridging hydride). In the solid state, as in hydrocarbon solutions, complex (I) undergoes thermal decomposition (*ca.* 90°C) to produce $Ru_3(CO)_{12}$ and a material insoluble in most organic solvents. The crystals used in the *X*-ray study were obtained by slow evaporation of a n-heptane solution of the complex.

The crystals of $H(C_{10}H_9O)Ru_2(CO)_6$ are monoclinic: a = 9·676(6), b = 16·129(10), c = 14·472(10) Å, β = 125·83(2)°; space group $P2_1/c$; D_c = 1·87 g/cm³, Z = 4. The stereochemistry shown in the Figure corresponds to a structural analysis based on 1409 unique non-zero intensities (Mo-K_α, two circle diffractometry). The data were corrected for absorption (μ = 16·45 cm^{-1}) and the structure solved by Patterson and Fourier procedures and refined by full-matrix least-squares with anisotropic temperature factors for the ruthenium atoms only. At the present state of refinement the conventional R factor is 0·039.

The Ru(1)–Ru(2) = 2·862(3) Å bond length is identical to that found in $(C_8H_8)Ru_2(CO)_6$ [2·865(2) Å].[8] Including the bridging hydrogen but excluding the metal–metal bond, the co-ordination is approximately octahedral at Ru(1) and trigonal bipyramidal distorted towards octahedral at Ru(2). Each ruthenium atom carries three carbonyls with Ru–C-(av) = 1·88 Å and C–O(av) = 1·15 Å. The O(7), C(11), C(12), C(13), and C(14) atoms of the organic ligand lie in one plane (within ±0·03 Å) and show the following bond lengths: O(7)–C(12) = 1·259(13), C(11)–C(12) = 1·513(18), C(12)–C(13) = 1·423(13), and C(13)–C(14) = 1·462(14) Å. This ligand is attached to Ru(2) through C(13) and C(14) in a π-olefinic manner [Ru(2)–C(13) = 2·226(12), Ru(2)–C(14) = 2·077(11) Å] and to Ru(1) by a carbon–metal σ-bond [Ru(1)–C(14) = 2·093(11) Å] and an oxygen–metal dative σ-bond [Ru(1)–O(7) = 2·103(7) Å; Ru(1)–O(7)–C(12) = 111·0(6)°]. No other bonding from the ligand to the metal atoms is observed [Ru(1)–C(12) = 2·81, Ru(2)–C(12) = 2·96, Ru(1)–C(13) = 2·86 Å]. Thus, one lone pair of electrons of the oxygen atom is involved in the bonding of the hetero-diene to the dimetal unit and the C(14)–H bond has undergone oxidative addition to form an additional carbon–metal σ-bond [Ru(1)–C(14)]. A similar σ-attachment to the metal atom in a mononuclear manganese complex has been described in the literature.[9] With one hydrogen atom removed from its molecule, benzylideneacetone donates five electrons to the metal cluster, which is the number of electrons required by the $HRu_2(CO)_6$ unit for the complex to obey the effective atomic number rule.

H(4) (metal hydride) and H(13) were located in difference Fourier syntheses and all the hydrogen atoms were included in the refinement. H(4) bridges Ru(1) and Ru(2), and the distances Ru(1)–H(4) = 1·85(12) Å and Ru(2)–H(4) = 1·64(11) Å and angle Ru(1)–H(4)–Ru(2) = 110(6)° are, within the experimental error, similar to those observed in the ruthenium ethylidyne complex $H_3Ru_3(CO)_9CCH_3$.[10]

The complex $H(C_{10}H_9O)Ru_2(CO)_6$ constitutes one of the few examples of ruthenium compounds involving two metal atoms and illustrates the now well established ability of ruthenium carbonyl compounds to abstract hydride ions from olefins.

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