Crystal and Molecular Structure of $Rh_2(CO)(NBD)_2(C_8H_8O)$; A Reaction Product of $Rh_6(CO)_{16}$ and Norbornadiene

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Summary The final product from the reaction of norbornadiene and $Rh_6(CO)_{16}$ is a dinuclear species containing the novel C_8H_8O ligand, formally an acylvinyl cyclopentene derivative, which is bound by both σ- and π-bonds to both rhodium atoms.

TREATMENT of $Rh_6(CO)_{16}$ with norbornadiene (NBD) in refluxing methylcyclohexane results initially in the successive replacement of two carbonyl groups by norbornadiene with the formation of $Rh_6(CO)_{14}NBD$, $Rh_6(CO)_{12}(NBD)_2$ and $Rh_6(CO)_{10}(NBD)_3$. On furthei refluxing the deep red solution containing $Rh_6(CO)_{10}(NBD)_3$ suddenly turns orange-yellow and fine yellow needles, only slightly soluble in organic solvents, crystallise. Elemental analyses and mass spectroscopic data for this product are consistent with the empirical formula $Rh_2(CO)_2(NBD)_3$ but the i.r. spectrum (KBr disc) precludes a simple structural species because, in addition to an absorption at 1830 cm^{-1}, indicating the presence of a bridging carbonyl group, a doublet absorption is observed in the organic carbonyl region of the spectrum at 1670 and 1650 cm^{-1}.

It seemed likely that this compound, and the method of its formation, might have some relevance to the mechanism of the well-known metal carbonyl-catalysed coupling reactions of norbornadiene,[1,2] and its molecular structure has been determined by a single-crystal *X*-ray diffraction study.

Crystal data: $C_{23}H_{24}O_2Rh_2$, $M = 538\cdot2$; monoclinic, $a = 14\cdot42$, $b = 6\cdot49$, $c = 21\cdot55$ Å, $\beta = 115\cdot64°$; $U = 1818$ Å^3; D_m (flotation) $= 1\cdot93$, $D_c = 1\cdot966$, $Z = 4$; $F(000) = 1072$; space group $P2_1/c$ (C^5_{2h}, no. 14). The structure analysis was based on 1408 independent reflections [$I_{obs} > 3\cdot5\sigma(I_{obs})$; Nb-filtered Mo-$K_\alpha$, $\lambda = 0\cdot7107$ Å] measured on a Picker four-circle automatic diffractometer, fitted with a scintillation counter using pulse-height discrimination, and R is 0·044.

In the structure (Figure), the two rhodium atoms, each bonded to a bidentate NBD ligand, are bridged on one side by a carbonyl group and on the other by the novel ligand C_8H_8O, formally an acyl vinyl cyclopentene derivative, which is bound by both σ- and π-bonds to both rhodium atoms. The positions of the hydrogen atoms are deduced from the bond lengths which are close to expected values for the single and double bonds indicated.

In addition to the presence of the C_8H_8O ligand there are two other significant features of the structure. Firstly, this molecule represents another example of the increasing number of complexes containing an unsymmetrical carbonyl bridging group.[3] In this case we are concerned with a 'moderately unsymmetrical' bridge, using Cotton's terminology, (Rh–C = 1·99, 2·15 Å) but an examination of intermolecular interactions reveals no obvious explanation for the lack of symmetry on steric grounds. Presumably the lack of symmetry must arise from electronic factors operating to counterbalance those from the C_8H_8O ligand system. Secondly, in contrast to most of the NBD complexes studied crystallographically,[2,4] the NBD ligands themselves are not bonded symmetrically to the rhodium atoms. In each case the bond lengths from the rhodium atom to the centres of the double bonds are significantly different (2·25, 2·02 Å and 2·31, 2·00 Å respectively).

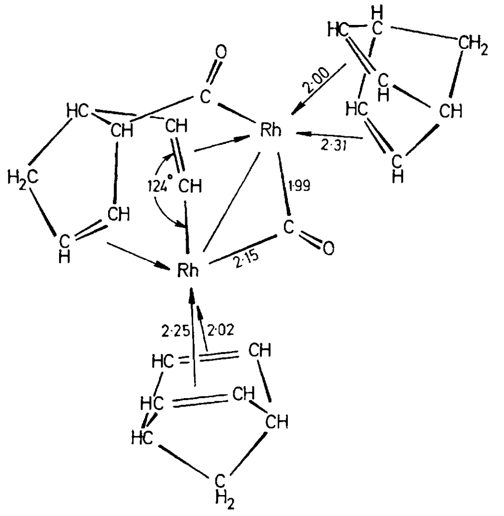

FIGURE. The molecule of $Rh_2(CO)(NBD)_2C_8H_8O$ (bond lengths in Å).

A crystal structure determination of $Rh_6(CO)_{10}(NBD)_3$, the apparent precursor to the dinuclear species, has shown that this molecule is derived from the parent $Rh_6(CO)_{16}$[5] by removing the two terminal carbonyl groups from three of the rhodium atoms, each of which is then bonded to an NBD molecule acting as a bidentate ligand. The relative configurations of the NBD ligands show evidence of steric strain in that they are slightly bent away from each other and the two Rh–Rh distances involved are significantly longer (av. 2·88 Å) than the remaining Rh–Rh distances (av. 2·75 Å), thus making it unlikely that a fourth NBD could be accommodated by further replacement of carbonyl groups. This may account for the NBD ring opening and fragmentation of the cluster into dinuclear units.

The formation of the ligand system C_8H_8O from norbornadiene is certainly unprecedented and may represent an intermediate stage in the ring-opening reaction of NBD which occurs during the retro-Diels Alder reaction to cyclopentadiene and acetylene. In this case the intermediate is fortuitously stabilised by insertion of a carbonyl group and co-ordination to the rhodium carbonyl environment. Furthermore the formation and structure of this complex is relevent to the formation of metallocyclic ring systems, currently of interest as intermediates in the dimerisation and dismutation of olefins.[6]

The compound is probably identical with that reported recently by Kitamura and Joh[7] from the reaction of $Rh_4(CO)_{12}$ and NBD and for which a simple structure was proposed.

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