

Preliminary communication

The reaction of dodecacarbonyltriruthenium with bicyclo[3.2.1]-2,6-octadiene

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The ability of dodecacarbonyltriruthenium to abstract hydrogen from a range of organic molecules has been previously documented^{1,2}. In this communication we present an example of hydride ion abstraction from a cyclic diolefin by this carbonyl to yield a complex in which a novel bonding pattern is observed between the olefin and the metal cluster.

Dodecacarbonyltriruthenium reacts with bicyclo[3.2.1]-2,6-octadiene in benzene under reflux to produce a yellow complex which has been characterised by analytical and spectroscopic techniques as the dihydride $H_2 Ru_3(CO)_9(C_8H_8)$. In this molecule the organic moiety is complexed to the metal cluster by two metal-carbon σ -bonds and one metal-olefin bond (see Fig. 1)^{★★★}. The remaining double bond is not coordinated to the cluster. The major evidence for this structure stems from the 100 MHz ¹H NMR spectrum which exhibits the following features at 30°: a broad doublet at τ 3.96 (1H, H₂), a broad doublet at τ 4.70 (1H, H₃), a complex multiplet at τ 7.13 (2H, H₁ and H₅); two four line multiplets centred at τ 7.70 (1H, H_{4 α}), a doublet at τ 8.08 (1H, H_{4 β}), a doublet at τ 8.11 (1H, H_{8 α}) a doublet of triplets at τ 8.69 (1H, H_{8 β}) and finally a broad resonance at τ 28.3 (2H, bridging hydrides) (J_{12} , 5.5; J_{23} , 10.0; J_{34} , 3; $J_{4\alpha 4\beta}$, 18.7; $J_{4\alpha 5}$, 4.5; $J_{18\alpha}$ and $J_{58\alpha}$, 4.0; $J_{8\alpha 8\beta}$, 10.5 cps). These assignments are based on double irradiation experiments and on a comparison of the 60 and 100 MHz spectra. Further confirmation is provided by the spectrum of the D₃ derivative. The presence of the two hydrido ligands is clearly indicated by the appearance of the broad resonance at τ 28.3; this separates into two well resolved doublets (τ 25.83 and 30.82) at -48° indicating the inequivalence of the hydrogens in the

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^{★★★}This bonding arrangement is different to that recently established in $HRu_3(CO)_9(C_{12}H_{15})$; a product generated from the reaction of cyclo-1,5,9-decatrienes with $Ru_3(CO)_{12}$ which involves a dehydrogenation step and the formation of a π -allyl-metal bond and two metal-carbon σ -bonds²

complex with rapid intramolecular exchange under ambient conditions ($E_a = 8.01 \pm 0.36$ kcal/mole, $\Delta S^\ddagger = -18.4 \pm 1.4$ e.u. (25°)). In agreement with the supposition that the second double bond is not coordinated to the cluster the chemical shifts observed for the

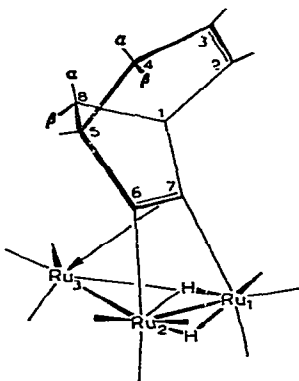


Fig. 1. Molecular structure of $H_2Ru_3(CO)_9(C_8H_8)$.

protons H_2 and H_3 are similar to those recorded for the free diene. In the structure show each ruthenium obeys the E.A.N. rule★ and it is mainly for this reason that we choose to associate the two H-ligands with Ru_1 and Ru_2 .

The formation of this complex may be viewed as an oxidative-addition of the olefinic C-H grouping to the $Ru_3(CO)_{12}$ cluster; two of the ruthenium being formally oxidised to Ru^{II} . Such a reaction is obviously of some importance in studies of the isomerisation of dienes by this carbonyl and is actively under further study.

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REFERENCES

- 1 see e.g. B.F.G. Johnson, J. Lewis and I.G. Williams, *J. Chem. Soc., A*, (1970) 1100 and references therein.
- 2 M.I. Bruce, M.A. Cairns, A. Cox, M. Green, M.D.H. Smith and P. Woodward, *Chem. Commun.*, (1970) 735.

★E.A.N. rule = effective atomic number rule.