Activation of Molecular Oxygen, Hydrogen, Carbon Monoxide, and Olefins by a Ruthenium(II) Complex

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Summary Dichlorotris(triphenylarsine)ruthenium(II), dissolved in benzene, readily activates molecular O_2, H_2, CO, and olefins to give new catalytic species of importance in homogeneous catalysis; the oxygen complex is the first known example of a 1 : 1 paramagnetic complex of a d^6 metal ion.

THE complex, dichlorotris(triphenylarsine)ruthenium(II)[1] in benzene solution rapidly absorbs molecular oxygen, at room temperature and atmospheric pressure in a 1 : 1 ratio to give a dark brown complex of composition $RuCl_2(AsPh_3)_3(O_2)$, (I) (m.p. > 300 °C, decomp.). Its i.r. spectrum shows a band at 880 cm^{-1} assigned to O–O stretch of the triangular Ru–O_2 group.[2–4] The oxygen complex (I) is paramagnetic, $\mu_{eff} = 2\cdot90$ B.M., corresponding to two unpaired electrons. E.s.r. studies of (I) are being continued and it seems probable that the unpaired electrons are mostly centred on a molecular orbital which is predominantly $\pi^*(O_2)$. Most of the well characterized molecular oxygen complexes of the d^8 and d^{10} species Ir^I, Ni^0, Pd^0, and Pt^0 [3,4] are diamagnetic except for a Rh^I–O_2 complex in dimethylacetamide of undetermined composition that was reported to be paramagnetic.[5] Complex (I) thus seems to be the first example of a well characterized paramagnetic 1 : 1 oxygen complex of a d^6 system. The n.m.r. spectrum of (I) shows a doublet centred at δ 7·4 p.p.m. which indicates the presence of two mutually *trans* and a *cis* triphenylarsine ligand. Complex (I) reacts with SO_2 to give a sulphato-complex, confirmed by its i.r. spectra.[6] In benzene solution, (I) oxidises triphenylphosphine to triphenylphosphine oxide. This reaction is being studied.

On passing molecular hydrogen into a solution of (I), the O–O band at 880 cm^{-1} disappears, the solution becomes wine red and a band at 1960 cm^{-1} due to hydride stretch appears. This displacement reaction is reversible and the oxygen complex (I) is reformed on passing molecular oxygen through the hydrido-complex.

A solution of (I) rapidly takes up CO to give a dicarbonyl species (i.r. 1950 cm^{-1} and 2100 cm^{-1}) with the displacement of molecular oxygen. The carbonyl complex is quite stable and failed to react with molecular oxygen.

A solution of dichlorotris(triphenylarsine)ruthenium(II) in benzene forms a complex with maleic acid (II). A solution containing (II) activates molecular oxygen (i.r. 885 cm^{-1}). Complex (II) reacts with molecular hydrogen causing the catalytic reduction of maleic to succinic acid. The kinetics and mechanism of this reaction are being studied further.

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