Reactions of a Dihydride of Ruthenium(II) with Small Molecules

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Summary The complex dihydridotris(triphenylphosphine)-ruthenium(II) reacts in the solid state directly with gases such as nitrogen, carbon monoxide, nitric oxide, sulphur dioxide, and nitrosyl chloride.

WE report the formation and reactions of a dihydride of ruthenium(II), $[RuH_2(PPh_3)_3]$. The complex, unlike the corresponding dichloride and hydridochloride[1,2] behaves as a co-ordinately unsaturated molecule, readily reacting at room temperature in solid state reactions with gaseous small molecules.

Reaction of dichlorotris(triphenylphosphine)ruthenium(II) with triethylamine in benzene under hydrogen gives a colourless precipitate of $[RuH_2(PPh_3)_3]$, which is extremely sensitive to air but is stable under argon. The i.r. spectrum shows a relatively broad band of medium intensity at 1950 cm^{-1} (νRuH).

The solid dihydride reacts almost instantly with carbon monoxide and nitrogen, forming $[RuH_2(CO)(PPh_3)_3]$ and $[RuH_2(N_2)(PPh_3)_3]$, respectively. The i.r. spectra show bands, at 1943 (νCO), 1905 and 1965 cm^{-1} (νRuH) for the carbonyl compound, and 2147 (νN_2), 1924 and 1948 cm^{-1} (νRuH) for the nitrogen complex, in good agreement with previously recorded values.[2,3] By passing carbon monoxide over the nitrogen compound the dihydridocarbonylruthenium(II) complex is obtained.

Reaction of the colourless dihydride with nitric oxide gives deep-red crystals which analyse for $[Ru(NO)_2(PPh_3)_2]$. This compound is stable to air and halogenated solvents and can be recrystallized from benzene solutions. An analogous iron complex[4] is known, but it is rare for ruthenium to co-ordinate more than one nitrosyl group. The nitrosyl stretching frequencies at 1630 and 1675 cm^{-1} are low for ruthenium chemistry. Sulphur dioxide reacts similarly, to give a bright-yellow product, $[Ru(SO_2)_2(PPh_3)_2]$. The i.r. spectrum contains bands due to co-ordinated sulphur dioxide but no hydride bands.

Nitrosyl chloride gas co-ordinates both NO^+ and Cl^- when passed over the dihydride, giving a light-yellow compound, $[RuCl_3NO(PPh_3)_2]$ recently reported as a precursor in the formation of the nitrosyl-ruthenium analogue to Vaska's compound.[5]

Satisfactory elemental analysis have been obtained for all the compounds. They are all diamagnetic.

The complex has been assigned as a dihydride for the following reasons. Passage of argon or hydrogen over $[RuH_2(N_2)(PPh_3)_3]$ generates the starting material. Addition of measured amounts of carbon monoxide and sulphur dioxide lead to pressure drops in the system corresponding to the following reactions:

$$[RuH_2(PPh_3)_3] + CO \rightarrow [RuH_2(CO)(PPh_3)_3]$$

$$[RuH_2(PPh_3)_3] + 2SO_2 \rightarrow [Ru(SO_2)_2(PPh_3)_2] + H_2 + PPh_3$$

The mass spectra of these residual gases show only traces of molecular hydrogen in the CO reaction and appreciable amounts in the SO_2 case.

Recently, a solvent system of phosphineruthenium(II) hydride species which interacts with molecular nitrogen, has been reported.[6]

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