

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), $[\text{RuH}_2(\text{PPh}_3)_3]$. 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 $[\text{RuH}_2(\text{PPh}_3)_3]$, 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 $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ and $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$, 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.

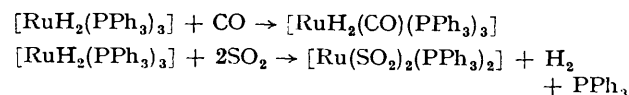
Reaction of the colourless dihydride with nitric oxide gives deep-red crystals which analyse for $[\text{Ru}(\text{NO})_2(\text{PPh}_3)_2]$. This compound is stable to air and halogenated solvents and can be recrystallized from benzene solutions. An analogous iron complex⁴ is known, but it is rare for 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, $[\text{Ru}(\text{SO}_2)_2(\text{PPh}_3)_2]$. 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, $[\text{RuCl}_3\text{NO}(\text{PPh}_3)_2]$ 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 $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ 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:



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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