Rhodium(III) Hydrido–Carbonyl Complexes

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Summary The hydrido–carbonyl complexes RhH(CO)(L–L)X_2 (L–L = 2,2-bipyridyl or 1,10-phenanthroline; X = Cl or Br) have been prepared.

THE synthesis of rhodium carbonyl halides is easily effected by bubbling carbon monoxide through a refluxing ethanolic solution of rhodium trichloride.[1] The yellow solution obtained has been shown to contain the anionic complex $[Rh(CO)_2Cl_2]^-$, and solutions containing the bromo-analogue $[Rh(CO)_2Br_2]^-$ are obtained by a halogen exchange reaction using lithium bromide.[2] Recently the preparation of the cationic rhodium(I) complexes $[Rh(CO)_2(L\text{–}L)]^+$ (L–L = 2,2-bipyridyl or 1,10-phenanthroline) by interaction of the chelating agent with a solution of "rhodium perchlorate" through which carbon monoxide had been passed, has been recorded.[3] We now report the isolation of the neutral rhodium(III) complexes, RhH(CO)(L–L)X_2 (L–L = 2,2-bipyridyl or 1,10-phenanthroline : X = Cl or Br) by treatment of the halogenocarbonyl solutions with the appropriate nitrogenous bidentate.

When 2,2-bipyridyl is shaken at room temperature with the chlorocarbonyl solution a light red complex separates after two hours. Three bands in the 2150—1800 cm^{-1} region are present in the i.r. spectrum of this derivative (Table). It is a diamagnetic complex, although analytical data indicate an Rh : Cl ratio of 1 : 2. Performing the reaction in the presence of D_2O gives a compound whose i.r. spectrum showed a marked decrease in the intensity of the upper band (2115 cm^{-1}): the other two bands being unchanged. This may be taken as an indication that the band at 2115 cm^{-1} represents a metal–hydride stretching frequency, and since the complex is a non-electrolyte in nitromethane it is probably best formulated as the rhodium(III) hydride [RhH(CO)(dipy)Cl_2]. A phenanthroline derivative, [RhH(CO)(phen)Cl_2] has also been prepared, and the analogous bromo-species [RhH(CO)(dipy)Br_2] and [RhH(CO)(phen)Br_2] are obtained from the bromocarbonyl solution.

I.r. frequencies (*cm*$^{-1}$) *for the rhodium complexes.**

Compound	CO	M–H
RhH(CO)(dipy)Cl_2	2080, 2060†	2115w
RhH(CO)(phen)Cl_2	2075, 2052	2117w
RhH(CO)(dipy)Br_2	2080, 2060	2115w
RhH(CO)(phen)Br_2	2072, 2045	2110w

* KBr discs; † all bands are strong unless otherwise stated.

All the complexes are diamagnetic and non-electrolytes in nitromethane, and all exhibit a band above 2110 cm^{-1} (Table) which decreases in intensity following the addition of D_2O to the reaction mixture. Although the insolubility of the complexes does not permit an investigation of the n.m.r. spectra or the determination of molecular weights, the compounds are most likely six-co-ordinate monomers. The split nature of the carbonyl bands is probably due to solid-state effects. Satisfactory analytical figures were obtained for all four complexes.

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[1] J. Chatt and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1437.
[2] J. V. Kingston, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 65.
[3] G. K. N. Reddy and C. H. Susheelamma, *Chem. Comm.*, 1970, 54.