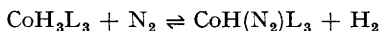


Hydride and Nitrogen Complexes of Cobalt

By A. SACCO and M. ROSSI

(Istituto di Chimica Generale e Inorganica, Università di Bari, Bari, Italy)

RECENTLY a cobalt(0) complex co-ordinated with molecular nitrogen has been described.¹ In the course of our studies on the hydrido-complexes of transition metals, we have found that the trihydrido-complexes of cobalt(III), CoH_3L_3 ($\text{L} = \text{PPh}_3, \text{PEtPh}_2$), obtained by reaction of CoX_2L_2 ($\text{X} = \text{Cl, Br, I}$) with borohydride in the presence of free ligand in ethanol and in an atmosphere of hydrogen or argon, readily react with nitrogen at room temperature and atmospheric pressure according to the following equilibrium:



The equilibrium is quantitatively displaced to the right in a nitrogen atmosphere and to the left in a hydrogen atmosphere.

The trihydrido-complexes are yellow crystalline compounds, unstable to the air, soluble in non-polar solvents.* Their i.r. spectra show two absorption bands of medium intensity at 1745 and 1933 cm^{-1} , in agreement with an octahedral structure with two hydrogen atoms in *trans*-positions.

* Analysis: Calc. for $\text{C}_{54}\text{H}_{46}\text{P}_3\text{Co}$: C, 76.4; H, 5.7; P, 11.0; Co, 7.0. Found: C, 76.0; H, 6.0; P, 11.0; Co, 6.9%.

† Analysis: Calc. for $\text{C}_{54}\text{H}_{46}\text{N}_2\text{P}_3\text{Co}$: C, 74.2; H, 5.3; N, 3.2; P, 10.6; Co, 6.7. Found: C, 73.9; H, 5.5; N, 3.1; P, 10.4; Co, 6.8%.

¹ A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Comm.*, 1967, 79.

² A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.

The nitrogen complexes are orange crystalline compounds, moderately stable to the air, soluble in nonpolar solvents.† Their i.r. spectra show a very strong absorption band at 2080—2084 cm^{-1} , assignable to the co-ordinated N—N stretch, but do not show any band assignable to the Co—H stretch.

However, the presence of the hydrogen atom bound to cobalt is proved by the following:

(1) Thermal decomposition at 100—150° liberates 1.5 mole of gas per mole of complex. (2) The composition of the evolved gas is 66.6% nitrogen and 33.3% hydrogen. (3) By treatment of the nitrogen complex with bisdiphenylphosphinoethane (dp) in anhydrous benzene the known² $\text{CoH}(\text{dp})_2$ is obtained, and one mole of nitrogen is evolved per mole of complex. (4) The nitrogen complex is diamagnetic, in agreement with the magnetic behaviour of a five-co-ordinated cobalt(I) complex.

(Received, February 17th, 1967; Com. 152.)