

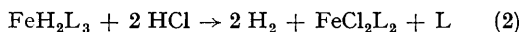
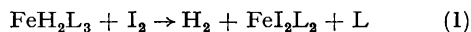
Nitrogen Fixation: Hydrido- and Hydrido-nitrogen-complexes of Iron(II)

By A. SACCO* and M. ARESTA

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

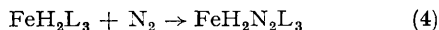
As an extension of studies on the fixation of molecular nitrogen under mild conditions by hydrido-complexes of transition metals,¹ we report the preparations and reactions of hydrido- and hydridonitrogen-complexes of iron(II).

Treatment of iron(II) chloride dihydrate and tertiary phosphine with sodium borohydride in ethanol, under hydrogen or argon, gave the yellow crystalline compounds, FeH_2L_3 (L = PEtPh_2 , PBuPh_2), which were unstable in air. The compounds were characterised by elemental analysis and by the reactions with iodine, hydrochloric acid, and carbon tetrachloride:



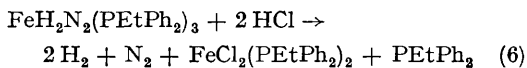
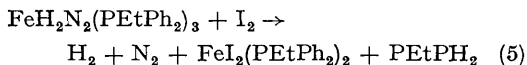
The i.r. spectrum of $\text{FeH}_2(\text{PEtPh}_2)_3$ (Nujol), shows bands of medium intensity at 1922 and 1860 cm^{-1} (Fe-H stretch) whereas the corresponding deuterio-complex has bands at 1382 and 1335 cm^{-1} .

These compounds readily react with nitrogen at room temperature and atmospheric pressure, both in solution and in the solid state, according to the equation:



The i.r. spectra of dihydrido-nitrogen-complexes show absorption at 2055—2060 (*vs.* co-ordinated N—N stretch), 1950—1960 w, and 1855—1863 cm^{-1} (Fe-H stretch).

The $\text{FeH}_2\text{N}_2(\text{PEtPh}_2)_3$ is a yellow crystalline diamagnetic compound, which decomposes *in vacuo* at 80° with evolution of hydrogen and nitrogen. It reacts quantitatively with iodine and with hydrochloric acid:



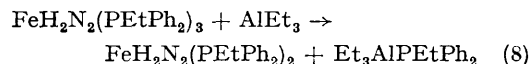
In sunlight, in the solid state, it undergoes a reversible reaction:



This reaction shows that in the dihydrido-nitrogen-complex the Fe-N₂ bond is stronger than the Fe-H bond; after the initial loss of hydrogen, a rapid migration of the hydrogen atom from the

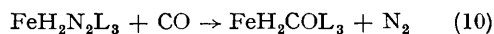
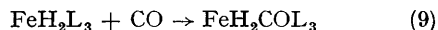
ligand to the metal occurs. This type of hydrogen migration is well known.²

The dihydrido-nitrogen-complex reacts with AlEt_3 in benzene solution:



In the penta co-ordinated dihydridonitrogen-complex the absorption band due to the co-ordinated N-N stretch is shifted to 1989 cm.^{-1} .

Both the dihydrido- and the dihydridonitrogen-complexes react with carbon monoxide at room temperature and atmospheric pressure:



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¹ A. Sacco and M. Rossi, *Chem. Comm.*, 1967, 316; *Inorg. Chim. Acta*, 1968, 2, 127.

² J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 1965, 843; M. A. Bennet and D. L. Milner, *Chem. Comm.*, 1967, 581; G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, 1968, 90, 2278.