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

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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 = PEtPh₂, PBuPh₂), which were unstable in air. The compounds were characterised by elemental analysis and by the reactions with iodine, hydrochloric acid, and carbon tetrachloride:

$$\operatorname{FeH}_{2}L_{3} + I_{2} \to H_{2} + \operatorname{FeI}_{2}L_{2} + L \qquad (1)$$

$$\operatorname{FeH}_{2}L_{3} + 2 \operatorname{HCl} \rightarrow 2 \operatorname{H}_{2} + \operatorname{FeCl}_{2}L_{2} + L$$
 (2)

 $\operatorname{FeH}_{2}L_{3} + 2\operatorname{CCl}_{4} \rightarrow 2\operatorname{CHCl}_{3} + \operatorname{FeCl}_{2}L_{2} + L$ (3)

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:

$$\operatorname{FeH}_{2}L_{3} + \operatorname{N}_{2} \to \operatorname{FeH}_{2}\operatorname{N}_{2}L_{3}$$
 (4)

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 m cm.⁻¹ (Fe-H stretch).

The $FeH_2N_2(PEtPh_2)_3$ 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:

$$\begin{aligned} \operatorname{FeH}_{2}N_{2}(\operatorname{PEtPh}_{2})_{3} + I_{2} \rightarrow \\ H_{2} + N_{2} + \operatorname{FeI}_{2}(\operatorname{PEtPh}_{2})_{2} + \operatorname{PEtPH}_{2} \quad (5) \\ \operatorname{FeH}_{2}N_{2}(\operatorname{PEtPh}_{2})_{3} + 2 \operatorname{HCl} \rightarrow \end{aligned}$$

$$2 H_2 + N_2 + FeCl_2(PEtPh_2)_2 + PEtPh_2$$
 (6)

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

$$\begin{array}{l} {\rm FeH_2N_2(PEtPh_2)_3 \rightleftharpoons} \\ {\rm H_2 + FeH(C_6H_4PEtPh)N_2(PEtPh_2)_2} \end{array} (7) \end{array}$$

This reaction shows that in the dihydrido-nitrogencomplex the Fe-N_2 bond is stronger than the Fe-H bond; after the initial loss of hydrogen, a rapid migration of the hydrogen atom from the

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

The dihydrido-nitrogen-complex reacts with AlEt₃ in benzene solution:

$$\begin{aligned} \text{FeH}_2\text{N}_2(\text{PEtPh}_2)_3 + \text{AlEt}_3 &\rightarrow \\ \text{FeH}_2\text{N}_2(\text{PEtPh}_2)_2 &+ \text{Et}_3\text{AlPEtPh}_2 \end{aligned} \tag{8}$$

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 dihydridonitrogencomplexes react with carbon monoxide at room temperature and atmospheric pressure:

$$\text{FeH}_{2}L_{3} + \text{CO} \rightarrow \text{FeH}_{2}\text{COL}_{3}$$
 (9)

$$\operatorname{FeH}_2\operatorname{N}_2\operatorname{L}_3 + \operatorname{CO} \to \operatorname{FeH}_2\operatorname{COL}_3 + \operatorname{N}_2$$
 (10)

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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.