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 ($L = PEtPh_2$, $PBuPh_2$), which were unstable in air. The compounds were characterised by elemental analysis and by the reactions with iodine, hydrochloric acid, and carbon tetrachloride:

$$FeH_2L_3 + I_2 \rightarrow H_2 + FeI_2L_2 + L \quad (1)$$

$$FeH_2L_3 + 2\,HCl \rightarrow 2\,H_2 + FeCl_2L_2 + L \quad (2)$$

$$FeH_2L_3 + 2\,CCl_4 \rightarrow 2\,CHCl_3 + FeCl_2L_2 + L \quad (3)$$

The i.r. spectrum of $FeH_2(PEtPh_2)_3$ (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:

$$FeH_2L_3 + N_2 \rightarrow FeH_2N_2L_3 \quad (4)$$

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:

$$FeH_2N_2(PEtPh_2)_3 + I_2 \rightarrow H_2 + N_2 + FeI_2(PEtPh_2)_2 + PEtPH_2 \quad (5)$$

$$FeH_2N_2(PEtPh_2)_3 + 2\,HCl \rightarrow 2\,H_2 + N_2 + FeCl_2(PEtPh_2)_2 + PEtPh_2 \quad (6)$$

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

$$FeH_2N_2(PEtPh_2)_3 \rightleftharpoons H_2 + FeH(C_6H_4PEtPh)N_2(PEtPh_2)_2 \quad (7)$$

This reaction shows that in the dihydrido-nitrogen-complex 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 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:

$$FeH_2N_2(PEtPh_2)_3 + AlEt_3 \rightarrow FeH_2N_2(PEtPh_2)_2 + Et_3AlPEtPh_2 \quad (8)$$

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

$$FeH_2L_3 + CO \rightarrow FeH_2COL_3 \quad (9)$$

$$FeH_2N_2L_3 + CO \rightarrow FeH_2COL_3 + N_2 \quad (10)$$

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