Reduction of Nitrogen to Hydrazine in a Binuclear Complex of Iron

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Summary A binuclear molecular nitrogen complex has been isolated from the system $(Ph_3P)_2FeCl_3$ + Pr^iMgCl + N_2; in the presence of HCl, partial reduction of the co-ordinated N_2 to N_2H_4 takes place.

IT was shown recently that a molecular nitrogen complex is formed in the system: $(Ph_3P)_2FeCl_3$ + Pr^iMgCl + N_2 in ether solution at low temperautres.[1] Reaction of the complex with gaseous HCl leads to reduction of some of the N_2 to N_2H_4 together with evolution of N_2.

The amount of N_2H_4 formed per complexed nitrogen molecule is approximately 10% and this does not depend on the time of the reaction nor on the ratio of the components. The maximum yield of the complex is obtained with a $(Ph_3P)_2FeCl_3$: Pr^iMgCl ratio of 1:5, at $-50°$, and N_2 pressure $\geqslant$ 200 mmHg.

Reduction of molecular nitrogen in the co-ordination sphere of complexes is unusual; therefore we were careful to show that the reduction of the complex takes place only in the presence of HCl and no hydrazine derivative is formed beforehand.

The following evidence supports this:

(i) The complex decomposes slowly in solution with evolution of N_2 at 0 °C and quickly at 20 °C. No N_2H_4 was obtained on further addition of HCl.

(ii) Carbon monoxide replaces nitrogen in the complex to give $(Ph_3P)_2Fe(CO)_3$ and small amounts of $Ph_3PFe(CO)_4$ (from i.r.),[2] which do not give N_2H_4 in the presence of HCl.

(iii) Hydrazine, formed after partial thermal decomposition of the complex, prepared with $^{14}N_2$, under $^{15}N_2$ at 0 °C, contains increased amounts of $^{15}N_2$. This result also shows that the decomposition of the complex is partially reversible.

(iv) When HBr is used instead of HCl the yield of N_2H_4 is lowered. Virtually no N_2H_4 was obtained after decomposition of the complex by ethanol or water.

The complex was precipitated by the addition of pentane at -50 °C after preliminary removal of excess of RMgCl by 1,4-dioxan.

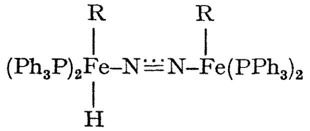
The red complex is stable in an inert atmosphere at temperatures below 0 °C and is oxidised quickly in air.

Decomposition of the complex by ethanol or H_2O results in formation of gaseous N_2, H_2 (with D_2O a mixture of HD, H_2, and D_2), and propane; the ratio $Fe:N_2:H_2:PrH$ is approximately 1:0·5:0·5:1; *i.e.* two Fe atoms apparently form the complex with a molecule of nitrogen. According to the phosphorus analysis the complex contains two molecules of Ph_3P per Fe atom.

The complex, prepared from $(C_6D_5)_3P$, has a band at 1761 cm^{-1}, which may be attributed to ν_{N-N} since it is shifted to 1704 cm^{-1} when $^{14}N_2$ is substituted by $^{15}N_2$. This low frequency corresponds to a low N–N bond order with considerable electron transfer from the two Fe atoms to the nitrogen molecule. The intensity of the band at 1761 cm^{-1} is about 100 times lower than in mononuclear $M-N_2$ complexes, providing additional evidence for the bimetallic structure of the complex.[3]

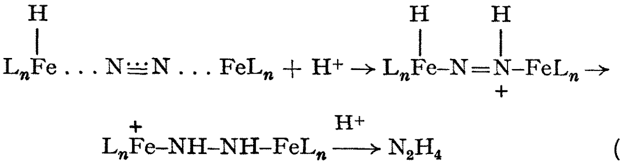
A second, low intensity, ν_{N-N} band at 2016 cm^{-1} (shifts to 1950 cm^{-1} with $^{15}N_2$), may be due to small amounts of a mononuclear complex. Both bands (1760 and 2016 cm^{-1}) disappear when the complex is heated.

The binuclear complex contains co-ordinated ether (i.r.), its analysis is consistent with the structure:



$$\overset{\displaystyle R}{\underset{\displaystyle H}{(Ph_3P)_2Fe}}-N\overset{\cdots}{=}N-\overset{\displaystyle R}{Fe}(PPh_3)_2$$

The reduction of N_2 in the complex by HCl may take place by the mechanism shown in equation (1).



$$L_n\overset{\displaystyle H}{Fe}\ldots N\overset{\cdots}{\equiv}N\ldots FeL_n + H^+ \rightarrow L_n\overset{\displaystyle H}{Fe}-N=\underset{+}{\overset{\displaystyle H}{N}}-FeL_n \rightarrow$$

$$L_n\overset{+}{Fe}-NH-NH-FeL_n \xrightarrow{H^+} N_2H_4 \qquad (1)$$

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[3] Yu. G. Borodko, and A. E. Shilov, *Uspekhi Khim.*, 1969, **38**, 761.

[4] Yu. G. Borodko, V. B. Panov, O. N. Efimov, and A. E. Shilov, *Zhur. fiz. Khim.*, 1971, **45**, 248.