Isolation of a New Intermediate Complex in the Nitrogen-fixing System $(\pi\text{-}C_5H_5)_2TiCl + MeMgI + N_2$

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Summary A binuclear complex $cp_2TiN_2Ticp_2$ has been isolated at low temperature in the system cp_2TiCl + MeMgI + N_2 ($cp = \pi\text{-}C_5H_5$); it is apparently a di-imide derivative, and initially forms N_2H_2 when decomposed with HCl.

INTENSELY coloured blue complexes, $(cp_2TiR)_2N_2$, have been observed,[1] and in some cases[2,3] isolated, on reduction of cp_2TiCl_2 and cp_2TiCl by RMgX in the presence of dinitrogen. Apparently, the complexes represent the first stage of dinitrogen activation in these N_2-fixing systems.

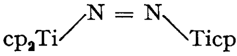
We report the isolation, in a pure state, of a new binuclear complex $(cp_2Ti)_2N_2$, which corresponds to a further stage in the reduction of dinitrogen.

A solution of cp_2TiCl in ether was added to a solution of methylmagnesium iodide (also in Et_2O) at $-70°$ under an atmosphere of argon. The Mg:Ti ratio was 2:1. The argon atmosphere was replaced by an atmosphere of dinitrogen and the dark precipitate which formed was isolated.

The complex is stable at room temperature but loses dinitrogen when heated above 40°.

Elemental analysis, taken in conjunction with the other data given below, indicates that the complex has the formula $(cp_2Ti)_2N_2$.†

Treatment of the complex with methanolic HCl at $-60°$ resulted in the formation of dinitrogen and hydrazine (1:1 molar ratio) and cp_2TiCl. Oxidation of the cp_2TiCl by air in the presence of HCl gave a quantitative yield of cp_2TiCl_2. The molar ratio $(N_2 + N_2H_4):cp_2TiCl_2$ was 1:2. Treatment of the complex $(cp_2Ti)_2N_2$ with a solution of HCl in ether at $-60°$ gave mostly N_2 and ammonia, together with cp_2TiCl_2 (after further oxidation). The yield of ammonia (based on cp_2TiCl_2) was *ca.* 30%, and only traces (*ca.* 2%) of hydrazine were observed in this case. These results suggest that the reaction of the complex with HCl first produces di-imide, which disproportionates either to $N_2 + N_2H_4$ or to $N_2 + NH_3$, depending upon the conditions.

The i.r. spectrum shows an absorbance at 1280 cm^{-1} which may be attributed to ν_{NN} since it is shifted to 1240 cm^{-1} when $^{14}N_2$ is substituted by $^{15}N_2$. It should be noted that ν_{NN} is considerably lower than the lowest frequency for dinitrogen complexes obtained so far [1630 cm^{-1} for *trans*-$Cl(PMe_2Ph)_4ReN_2NbCl)$[5]]. The integrated intensity of the absorption band at 1280 cm^{-1} is of the order 10^3 l mol^{-1} cm^{-2}. The complex could have either a distorted centrosymmetric or a non-centrosymmetric structure *e.g.*,  $cp_2Ti{-}N{=}N{-}Ticp_2$ in which case ν_{NN} would be active in the i.r. spectrum. A band at 3100 cm^{-1} indicates a $\pi\text{-}C_5H_5$ structure.

Magnetic susceptibility measurements give $\mu_{eff} = 1{\cdot}45$ BM at 300 K and 1·1 BM at 77 K per atom Ti. This may be due to exchange interaction as occurs in Ti^{III} complexes.[6]

N_2 in the complex may be reduced further. Thus nitride formation takes place when a solution of LiPh in ether is added to the complex; NH_3 is the only nitrogen containing product obtained on further reaction with HCl.

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† A similar formula has been suggested[4] for the complex observed in the reaction of N_2 with cp_2Ti. However, this complex is more like $(cp_2TiR)_2N_2$ rather than the complex obtained in this work.

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