Hydrazine-producing Intermediate in the Nitrogen Fixing System: $cp_2TiCl_2 + Pr^iMgCl + N_2$

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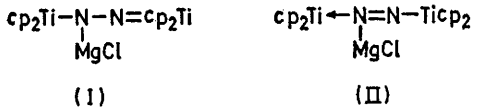
Summary An intermediate paramagnetic complex $(cp_2Ti)_2N_2MgCl$ has been isolated at -60 °C in the system: $cp_2TiCl_2 + Pr^iMgCl + N_2$ in ether ($cp = \pi$-C_5H_5); the complex forms N_2H_4 when decomposed by HCl.

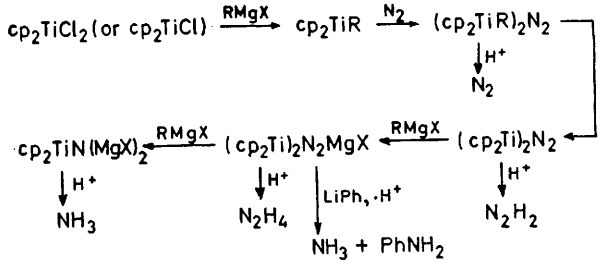
AN unstable complex $(cp_2TiR)_2N_2$ which readily loses N_2 has been observed[1,2] in the system: cp_2TiCl_2 (or cp_2TiCl) + Pr^iMgCl + N_2. Another comparatively stable complex $(cp_2Ti)_2N_2$ has been isolated in the system cp_2TiCl +



(I) (II)

$MeMgI + N_2$.[3] This forms N_2H_2 as an intermediate when decomposed by HCl. The complexes $(cp_2TiR)_2N_2$ and $(cp_2Ti)_2N_2$ can be regarded as two successive intermediates n the reduction of dinitrogen to a nitride.

A solution of Pr^iMgCl in ether was added to solid cp_2TiCl_2 at -60 °C under argon (Mg : Ti = 4). When the solution was filtered and the argon replaced by N_2 a dark precipitate was formed. The product is stable *in vacuo* at room temperature but is rapidly oxidised by air.



SCHEME
cp = cyclopentadienyl

The analysis of the complex corresponds to a formula $(cp_2Ti)_2N_2MgCl$, the complex is paramagnetic, the temperature dependence of magnetic susceptibility obeys the Curie law, the magnetic moment corresponds to one unpaired electron per two titanium atoms ($\mu_{eff} = 1{\cdot}1$ BM per one atom Ti. The e.s.r. spectrum of the solid is a single line with $g = 1{\cdot}975$ and $\nu_{NN} = 1255$ cm^{-1} (shifted to 1215 cm^{-1} when $^{14}N_2$ is substituted by $^{15}N_2$). These results are in agreement with structures (I) or (II). Treatment of the complex with methanolic HCl at -60 °C results in the formation of hydrazine (*ca.* 80%) probably from reaction (1). The remainder of the complexed nitrogen produces free N_2 possibly *via* N_2H_2.

$$(cp_2Ti)_2N_2MgCl \xrightarrow{HCl} (cp_2TiCl)NHNHTicp_2 \xrightarrow{HCl} N_2H_4 \quad (1)$$

Reaction of $(cp_2Ti)_2N_2MgCl$ with excess of Pr^{i}MgCl leads to a nitride which forms NH_3 when decomposed by HCl. The reactions shown in the Scheme account for these results. Reaction of $(cp_2Ti)_2N_2MgCl$ with LiPh instead of Pr^{i}MgCl and subsequent treatment by HCl produces some aniline (*ca.* 1%) together with ammonia. This result shows a possible mechanism for aniline formation in the system $cp_2TiCl_2 + LiPh + N_2$.[4]

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