Isolation of a Binuclear Complex Intermediate in the Reaction of Molecular Nitrogen with Titanium Compounds

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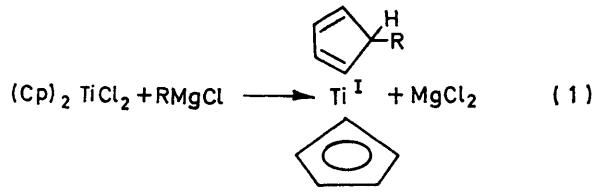
Summary An unstable binuclear titanium complex with molecular nitrogen has been isolated at low temperatures and its composition has been determined; the complex is an intermediate in the reduction of dinitrogen to hydrazine and ammonia.

REVERSIBLE formation of bright blue unstable binuclear complexes (λ_{max} 610 nm) with reduced titanium compounds has been observed[1,2] in the system $(Cp)_2TiCl_2$–RMgX–N_2 (Cp = π-C_5H_5; R = Pr^i or Et) at low temperatures (−100 to −80 °C). The complexes are apparently intermediates in the reduction of N_2.

Recently Brintzinger reported[3] that a similar blue dititanium complex with dinitrogen is formed when N_2 reacts with a particular form of $(Cp)_2Ti$. Also Teuben and Meijer isolated a blue dinitrogen–dititanium complex (λ_{max} 616 nm) in the reaction of N_2 with $(Cp)_2TiPh$ which they considered to be a derivative of Ti^{III}.[4]

In the present work we prepared an analogous complex by the reaction of Pr^iMgCl with $(Cp)_2TiCl$ in solution in ether under N_2 at −80 to −100 °C. The solution of $(Cp)_2TiCl$ was prepared by reduction of Cp_2TiCl_2 with K–Na alloy. The blue precipitate formed was thoroughly washed at −80 °C with dimethyl ether. The residue contains no Mg

and Cl and, after being dried *in vacuo*, is a dark blue powder which is stable at −100 °C but slowly decomposes at −70 °C with evolution of N_2.



(1)

Decomposition by HCl and MeOH gives propane (C_3H_7D in the case of MeOD) and dinitrogen, the ratio Ti : N_2 : PrH being 1 : 0·5 : 1. Subsequent reaction with O_2 in the presence of HCl leads to $(Cp)_2TiCl_2$. No other products (*e.g.* NH_3 or N_2H_4) except gaseous N_2 are formed from the complexed nitrogen during solvolysis. Thus the formula of the complex is $[(Cp)_2RTi)]_2N_2$, in agreement with results[4] which show a dinitrogen molecule as a bridge between two Ti atoms. We believe, however, that the species reacting with N_2 are not necessarily $(Cp)_2Ti^{III}R$ but may be derivatives (**1**) of univalent titanium formed according to equation (1).

With excess of Pr^iMgCl slow transformation of the blue complex into a black one takes place in ether solution at −60 °C. The decomposition of the latter by HCl produces N_2H_4 in almost quantitative yield based on complexed dinitrogen. Considerable amounts of hydrazine were also detected after the purified solid complex had been set aside with a solution of Pr^iMgCl in ether at −60 °C for several hours and subsequently hydrolysed with aqueous HCl. Subsequent reduction to the ammonia derivative which forms NH_3 during hydrolysis occurs at temperatures > 0 °C. These results indicate that the blue complex is an intermediate in the reduction of molecular nitrogen, though the necessity for the presence of an excess of reducing agent shows that the composition of the complex must change before it is able to reduce N_2.

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