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Fixation of Nitrogen by a $TiCl_3$–Mg System. Isolation and Properties of Titanium Complexes Containing Reduced Nitrogen

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Summary From a system of $TiCl_3$, tetrahydrofuran, magnesium, and nitrogen, titanium complexes containing reduced nitrogen have been isolated.

We report the isolation and properties of titanium complexes containing reduced nitrogen.

A nitrogen-containing complex was prepared by reducing $TiCl_3,3THF$ (THF = tetrahydrofuran) with magnesium in THF in an atmosphere of nitrogen at room temperature and normal presure.[1] The solution absorbs half a mole of N_2, consuming 2·5 g.-atoms of magnesium per titanium, with evolution of heat and with a colour change from light blue to black. From a comparative study with stepwise additions of sodium amalgam to $TiCl_3,3THF$ it was concluded that the reaction of nitrogen with the titanium complex takes place when the bivalent titanium complex is reduced.[2] From the THF solution, benzene-insoluble $MgCl_2,2THF$ was recovered. A benzene-soluble diamagnetic complex of composition $[TiNMg_2Cl_2,THF]$ (I) was isolated as black air-sensitive powder which gives one mole of NH_3 per titanium on hydrolysis. In contrast to the N_2-co-ordinated Group VIII transition-metal complexes, (I) releases no N_2 on pyrolysis at 200°. The overall reaction can be expressed by:

$$TiCl_3,3THF + \tfrac{5}{2}Mg + \tfrac{1}{2}N_2 \rightarrow$$
$$[TiNMg_2Cl_2,THF] + \tfrac{1}{2}MgCl_2,2THF$$

(I)

The magnesium in (I) can be partly or completely removed by addition of various reagents. The addition of pyridine to (I) in THF led to the formation of a black complex of composition $[TiNMgCl_{0\cdot5},py]$ (II) and $MgCl_2,2py$. The reaction of (I) with bipyridyl in THF gave zerovalent $Mg(bipy)_3$ obtained as dark reddish violet needles and black powder with a composition $[TiNMg_{1\cdot5}Cl_2,1\cdot5bipy,THF]$ (III). The magnesium in (III) could be further removed by the reaction with pyridine as $MgCl_2,2py$ leaving a titanium complex [TiNMgCl py] (IV). Complete removal of the magnesium from (I) was achieved by reaction with benzoyl chloride. Magnesium was removed as $MgCl_2,2THF$ and a dark green powder of composition $[TiNCl(COPh)_{1\cdot5}]$ (V) was obtained. These titanium–nitrogen complexes were not obtained as crystals but are considered homogeneous as far as one can judge from column chromatography of the THF solutions using sucrose, $MgCO_3$, or Na_2CO_3.

The $TiCl_3$–THF–Mg system reacts with molecular hydrogen as well as with nitrogen, absorbing over 3 moles of H_2 per titanium at room temperature and atmospheric pressure. The nitrogen complex (I) in THF solution in the presence of magnesium also reacts with hydrogen under the same conditions. The reaction is slow but continues as long as an excess of magnesium is present; in the absence of magnesium no reaction takes place. Unreacted magnesium and magnesium hydride separated from the THF solution,[3] as proved by the evolution of hydrogen on reaction with iodine. The THF-soluble fraction contained $MgCl_2,2THF$ and a titanium complex which was isolated as a black benzene-soluble powder of composition $[TiNMg_4Cl_{1\cdot5}H_2,2THF]$ (VI). The presence of two hydridic hydrogens in the complex is supported by the evolution of 1·0 mole of hydrogen per titanium on reaction of the complex with iodine. The reaction with dry hydrogen chloride also liberates hydrogen.

Each of these complexes (I)—(VI) liberates one mole of ammonia per titanium on hydrolysis. The i.r. spectra of these complexes above 400 cm.$^{-1}$ showed no distinct band assignable to the N_2 stretch or metal–nitride stretch. Two structures are possible which are compatible with the i.r. spectra and the chemical behaviour of the complexes: (1) an N_2-bridged binuclear structure with low N–N bond order; and (2) a nitride structure with low Ti–N bond order. It seems certain that the bound nitrogen is in a considerably reduced state, as it readily reacts with protic reagents such as water, alcohol, and hydrogen chloride, liberating ammonia.

One remarkable feature of the present system is its capacity for activating both molecular nitrogen and hydrogen under mild conditions. The incorporation of hydrogen into the titanium complex as a hydride and the succeeding transfer to magnesium without reaction with the reduced nitrogen is noteworthy in view of the susceptibility of the nitrogen–titanium complexes to attack by protic reagents.

A similar system composed of VCl_3 and magnesium in THF is also active in nitrogen fixation.

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[1] This system was reported by S. Go, K. Soga, Y. Hattori, and T. Keii at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1968.

[2] M. E. Vol'pin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Comm.*, 1968, 1074.

[3] Recently the formation of sodium hydride by a titanium compound–sodium naphthalenide–H_2 system was reported; E. E. van Tamelen and R. B. Fechter, *J. Amer. Chem. Soc.*, 1968, **90**, 6854.