Kinetics and Stoichiometry of Nitrogen Fixation with $TiCl_3$-Mg and VCl_3-Mg in Tetrahydrofuran

Akio YAMAMOTO, Shigeo GO,* Masaharu OOKAWA, Mitsuaki TAKAHASHI,
Sakuji IKEDA, and Tominaga KEII*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro, Tokyo
**Department of Chemical Engineering, Tokyo Institute of Technology, Meguro, Tokyo*

(Received May 15, 1972)

The kinetics and stoichiometry of nitrogen fixation with $TiCl_3$–Mg and VCl_3–Mg in tetrahydrofuran (THF) systems were studied. The systems react with molecular nitrogen at room temperature and normal pressure giving magnesium dichloride and nitrogen-containing complexes of compositions $[MNMg_2Cl_2(THF)]$, where M= Ti and V, according to the stoichiometry: $MCl_3(THF)_3+\frac{5}{2}Mg+\frac{1}{2}N_2\rightarrow[MNMg_2Cl_2(THF)]+\frac{1}{2}MgCl_2(THF)_2$. Properties of the isolated nitrogen-containing complexes were examined. Reactions under argon and hydrogen gave hydride-containing complexes. The initial rate of nitrogen fixation was first order with respect to the amounts of MCl_3, Mg, and nitrogen pressure. A mechanism involving the complexation of N_2 with dimeric M(II) species followed by rate-determining process to react with magnesium is proposed and discussed.

Since the discovery of Vol'pin and Shur that molecular nitrogen can be fixed under mild conditions by mixed systems of transition metal compounds and reducing agents,[1] there have been reported a number of systems which react with molecular nitrogen.[2] Among these systems, early transition metal compounds in combination with reducing agents contrast in their ability to fix molecular nitrogen with later transition metal compounds which often form stable dinitrogen complexes but the coordinated N_2 ligand can not be readily reduced. A variety of N_2-fixing systems based mostly on titanium compounds have been reported and the mechanism of nitrogen fixation has been studied to some extent. As the apparently simplest N_2-fixing systems we have selected the $TiCl_3$–Mg[3] and VCl_3–Mg systems in tetrahydrofuran (THF) and studied the mechanism of nitrogen fixation by kinetic as well as preparative methods.

Results

Stoichiometry and Kinetics of Nitrogen Fixation. $TiCl_3(THF)_3$ and $VCl_3(THF)_3$ in the presence of magneiusm in tetrahydrofuran react at room temperature and normal pressure with molecular nitrogen. The amounts of molecular nitrogen absorbed by the $TiCl_3$–Mg and VCl_3–Mg systems were equivalent to the amounts of ammonia formed after the hydrolysis of the system. Figure 1 shows typical kinetic runs of N_2 fixation with $TiCl_3$–Mg system; the VCl_3–Mg system behaves similarly but with much slower absorption. In no case the amount of ammonia formed per mole of $TiCl_3$ or VCl_3 exceeded one mole at ambient temperature and pressure. Figure 1 also indicates that the N_2 absorption starts after an induction period. This induction period can be shortened to some extent by using fine powder of magnesium or by pretreatment of magensium with iodine but can not be removed completely. As will be described later this induction period can be ascribed to the period of reduction of Ti(III) to Ti(II) or V(III) to V(II).

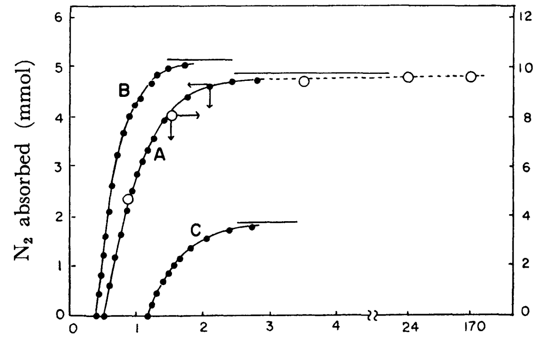


Fig. 1. N_2 absorption and ammonia formation by $TiCl_3$–Mg system at 20°C. ●: Amount of N_2 absorbed in mmol; ○: Amount of ammonia formed after hydrolysis. Curve A: $TiCl_3$, 1.50 g, reduced with 2.0 g of Mg. B: $TiCl_3$, 1.58 g; Mg, 4.0 g. C: $TiCl_3$, 0.57 g; Mg, 3.0 g. Horizontal lines for the curves indicate the calculated values for absorption of 0.5 mol of N_2 per titanium.

The kinetic experiment were carried out mostly with the $TiCl_3$–Mg system which absorbs nitrogen more rapidly than the VCl_3–Mg system. The kinetic curves shown in Fig. 1 have been replotted in Fig. 2 to indicate that the rate of N_2 absorption is first-order with respect to the concentration of a titanium species which is able to combine with molecular nitrogen.

$$r = d[NH_3]/dt = k[Ti] \qquad (1)$$

Figure 3 illustrates the kinetic curves of magnesium consumption by the $TiCl_3$–Mg sytem under nitrogen and under argon. Evidently the rate of magnesium consumption under nitrogen is much faster than that under argon after the first 0.5 g-atom of magnesium per titanium was consumed, although the ultimate

---

[1] M. E. Vol'pin and V. B. Shur, *Nature,* **209**, 1236 (1966).

[2] For recent reviews, see a) R. Murray and D. C. Smith, *Coord. Chem. Rev.*, **3**, 429 (1968); b) K. Kuchynka, *Catal. Rev.*, **3**, 111 (1969); c) G. Henrici Olivé and S. Olivé, *Angew. Chem.*, **81**, 679 (1969); d) T. Ito and A. Yamamoto, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 598 (1970); e) Yu. G. Borod'ko and A. E. Shilov, *Usp. Khim.*, **38**, 761 (1969); f) M. E. Vol'pin and V. B. Shur, *Organometal. Reactions*, **1**, 55 (1970); g) R. F. Gould, Ed., "Bioinorganic Chemistry, Adv. Chem. Series 100, Am. Chem. Soc., (1971); h) E. E. van Tamlen, *Accounts Chem. Res.*, **3**, 361 (1970); i) J. Chatt, *Platinum Metals Rev.*, **13**, 9 (1969); *Proc. Roy. Soc., Ser. B*, **172**, 327 (1969); j) M. Ichikawa, *Kagaku no Ryoiki*, **24**, 863 (1970).

[3] For a preliminary communication, see A. Yamamoto, M. Ookawa, and S. Ikeda, *Chem. Commun.*, **1969**, 841.

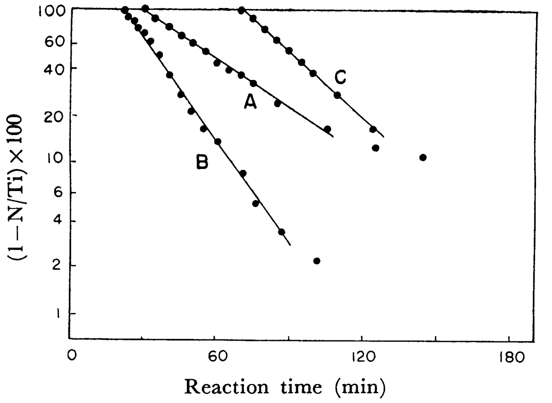


Fig. 2. First order plots of Fig. 1. Legends are the same with Fig. 1. N/Ti in the ordinate represents the number of moles of NH_3 produced per mol of $TiCl_3$ added.

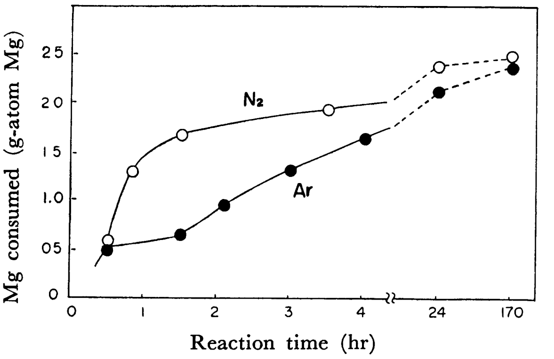


Fig. 3. Consumption of magnesium with time by $TiCl_3$-Mg system. $TiCl_3$, 1.50 g; Mg, 2.0 g, 20°C.
○, under nitrogen; ●, under argon.

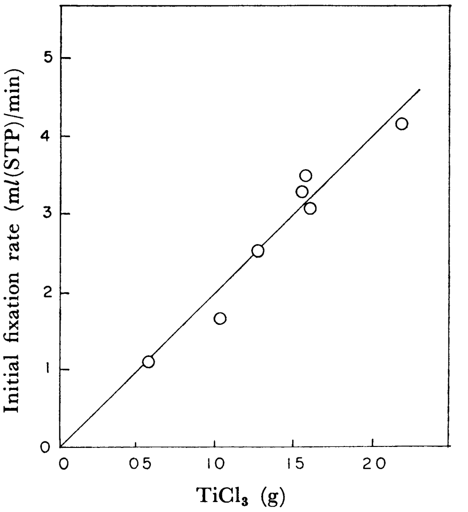


Fig. 4. Relationship between the initial rate of nitrogen fixation and the amount of $TiCl_3$ used.

amount of magnesium consumed is almost the same in either case. (2.5 g-atoms Mg per Ti or V.)

Figures 4, 5, and 6 show the dependences of the initial rate of N_2 fixation on the amount of $TiCl_3$ used, the amount of Mg consumed in the nitrogen fixation (the amount consumed in the induction period is excluded) and on the nitrogen pressure. It can be seen that the initial rate of N_2 fixation is first order with respect to these quantities. From the result of the temperature dependence of the initial rate, the activation energy for this process was estimated as 5 kcal/mol.

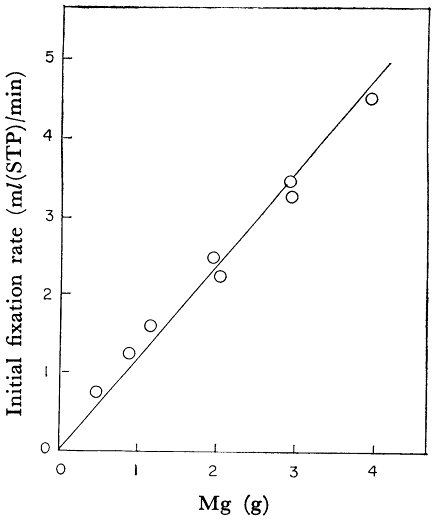


Fig. 5. The dependence of the initial rate of nitrogen fixation on the amount of Mg. The amount of Mg in the abssisae indicates the amount of Mg used for nitrogen fixation, *i.e.*, the amount of Mg consumed in the induction period is substracted from the total amount of Mg used. $TiCl_3$, 1.50 g; P_{N_2}, 62 cmHg; temperature, 20°C.

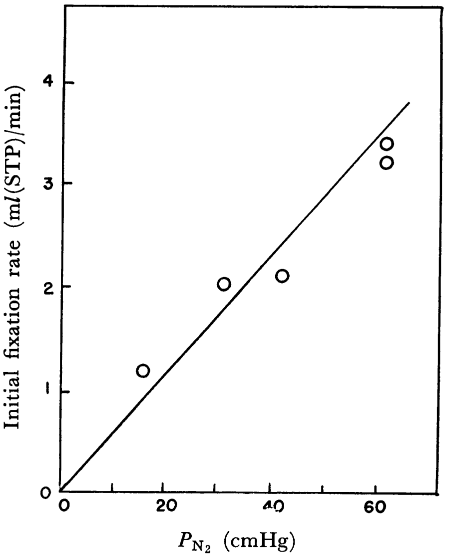


Fig. 6. The dependence of the initial rate of nitrogen fixation on nitrogen pressure at 20°C. $TiCl_3$, 1.50 g; Mg, 3.0 g; total pressure, 76 cmHg with argon as diluent.

In both cases of $TiCl_3$–Mg and VCl_3–Mg the total amounts of magnesium consumed per mole of $TiCl_3$ or VCl_3 did not exceed 2.5 g-atoms but there was some difference observed between the $TiCl_3$–Mg and VCl_3–Mg systems in the relationships between the amount of N_2 fixed and the amount of Mg consumed. As Fig. 7 shows, in both cases with $TiCl_3$ and VCl_3, no N_2 absorption takes place until 1/2 g-atom of magnesium is consumed, and beyond this stage the amount of N_2 fixed increases linearly with the Mg consumption. In the case with $TiCl_3$–Mg system, 1 mol of NH_3 is produced by consumption of 2 g-atoms of Mg, and the system consumes further 0.5 g-atom of Mg without

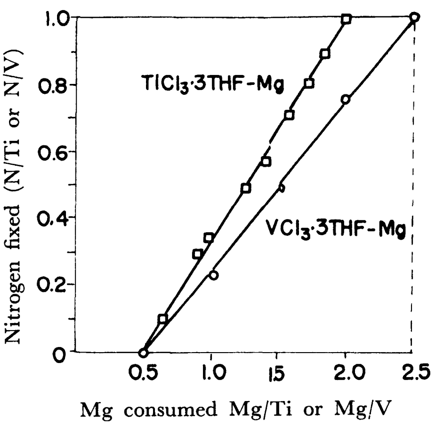


Fig. 7. The relationships between the amount of Mg consumed and the amount of nitrogen fixed by $\mathrm{TiCl_3(THF)_3}$–Mg (□) and $\mathrm{VCl_3(THF)_3}$-Mg system (○).

N_2 absorption. On the other hand, for $\mathrm{VCl_3}$–Mg system the production of 1 mol of NH_3 is performed by consumption of 2.5 g-atoms of magnesium.

Taking into account the amounts of magnesium chloride formed and of nitrogen-containing titanium and vanadium complexes isolated from the reaction systems *(vide infra)*, the stoichiometries of the overall reactions for $\mathrm{TiCl_3}$–Mg and $\mathrm{VCl_3}$–Mg systems can be expressed by:

$$\mathrm{TiCl_3(THF)_3} + \frac{5}{2}\mathrm{Mg} + \frac{1}{2}\mathrm{N_2} \rightarrow \underset{\mathbf{1}}{[\mathrm{TiNMg_2Cl_2(THF)}]} + \frac{1}{2}\mathrm{MgCl_2(THF)_2} \qquad (2)$$

$$\mathrm{VCl_3(THF)_3} + \frac{5}{2}\mathrm{Mg} + \frac{1}{2}\mathrm{N_2} \rightarrow \underset{\mathbf{3}}{[\mathrm{VNMg_2Cl_2(THF)}]} + \frac{1}{2}\mathrm{MgCl_2(THF)_2} \qquad (3)$$

When these N_2 fixing systems are reduced with magnesium prior to contact with N_2 under argon beyond the oxidation state of Ti(II) and V(II), the ability of the systems to fix nitrogen is reduced as illustrated in Fig. 8. When $\mathrm{VCl_3(THF)_3}$ is reduced with magnesium until 0.5 g-atom of Mg is consumed, no loss in the N_2 fixing ability is observed. Further usage of magnesium reduces the ability of the system to fix nitrogen and after consumption of 2.5 g-atoms of Mg the system does not show any more reactivity toward nitrogen. Similarly the titanium system which has been reduced with 2.5 g-atoms of magnesium does not react with nitrogen any more. The presence of other ligands such as triphenylphosphine and 2,2′-dipyridyl hinders the nitrogen fixation. The system containing $\mathrm{TiCl_2(acac)(THF)_2}$[4] and magnesium in THF did not react with nitrogen.

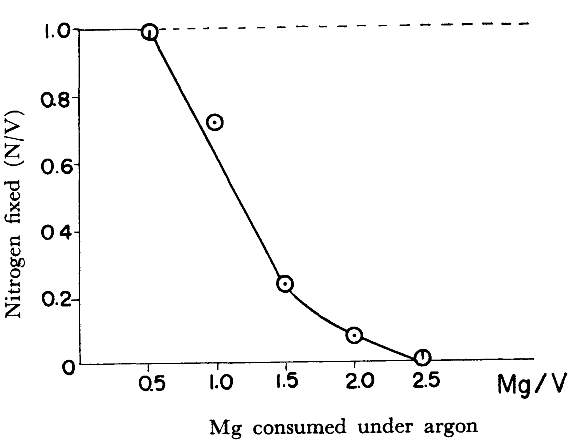


Fig. 8. Residual N_2-fixing capability of $\mathrm{VCl_3(THF)}$-Mg system after controlled reduction of $\mathrm{VCl_3(THF)_3}$ with limited amount of Mg under argon.

$\mathrm{TiCl_3(THF)_3}$–Mg and $\mathrm{VCl_3(THF)_3}$–Mg systems react with molecular hydrogen with the similar color change of the systems to the reduction under nitrogen or argon. The reactivity of the $\mathrm{TiCl_3(THF)_3}$–Mg system was higher than that of the $\mathrm{VCl_3(THF)_3}$–Mg system: The $\mathrm{TiCl_3(THF)_3}$–Mg system absorbed 2.7 mol of H_2 per titanium in 18 hr whereas the latter system absorbed the same amount of hydrogen per vanadium in 3 weeks. The addition of hydrogen gas to the nitrogen gas competitively inhibits the nitrogen fixation: in an experiment with a 1 : 1 mixture of N_2 and H_2 2.6 mol of the gas was absorbed but only 0.25 mol of N_2 was fixed per titanium without formation of NH_3 in the gas phase.

The $\mathrm{TiCl_3(THF)_3}$–Mg system reacted with propylene, absorbing 1.6 mol of propylene per titanium in 40 hr at room temperature and atmospheric pressure. Formation of propylene dimers including 2-methylpentane, 1-hexene and 2-hexene in a ratio of 4 : 2 : 1 was confirmed by gas chromatography. Under similar conditions the system absorbed 4 mol of ethylene in 15 hr yielding mainly ethane along with 1-butene, *n*-butane, and other hydrocarbons.

Separations of Low Valent Titanium and Vanadium Complexes. *(i) Titanium Complexes:* From the reaction system containing $\mathrm{TiCl_3(THF)_3}$, magnesium and molecular nitrogen, a titanium complex containing nitrogen was isolated. After the system absorbed 0.5 mol of N_2 per titanium consuming 2.5 g-atoms of magnesium with the color change from blue through green to black, unreacted magnesium was removed and black benzene soluble diamagnetic powder of a composition $[\mathrm{TiNMg_2Cl_2(THF)}]$ (**1**) was separated from benzene-insoluble crystals of $\mathrm{MgCl_2(THF)_2}$. Complex **1** and other titanium or vanadium complexes to be described later were not obtained as crystals and we can not claim that they are unequivocally pure. However, they were homogeneous as far as one can judge from column chromatography of the THF solutions using sucrose, $MgCO_3$ or Na_2CO_3 and from the analytical data which always gave the same compositions. The titanium complex **1** contained a small amount of titanium hydride as detected by evolution of hydrogen on reaction of **1** with iodine. Complexes **1** gave one mole of ammonia per titanium on reactions with water and ethanol. The reaction of **1** with dry hydrogen chloride proceeded as follows:

$$[\mathrm{TiNMg_2Cl_2(THF)}] + 6\mathrm{HCl} \xrightarrow[\mathrm{THF}]{} \mathrm{NH_4Cl} + \mathrm{TiCl_3(THF)_3} + 2\mathrm{MgCl_2(THF)_2} + \mathrm{H_2}$$

---

[4] A. Yamamoto, M. Murai, N. Oshima, and S. Ikeda, unpublished.

The nitrogen bound in complex **1** can not be removed readily except by treatment with protic reagents. On heating the complex at 200°C no dinitrogen was released. The gas evolved by the thermal decomposition of the complex contained THF as the main decomposition product together with 1-butene, 2-butene, ethylene, propylene, ethane, butane and hydrogen which may be generated by decomposition of THF bound in complex **1**. The pyrolysis residue contained still 1 atom of nitrogen per titanium and some THF.

In order to find how nitrogen is bound in the complex, the following reactions of **1** were carried out. A part of magnesium contained in **1** was removed on reaction of **1** with pyridine yielding $MgCl_2(Py)_2$ and a black complex with a composition of $[TiNMgCl_{0.5}(THF)]$. The complex obtained by the reaction of **1** with pyridine released one mole of ammonia per titanium on hydrolysis.

A part of magnesium in **1** was removed also as a zerovalent complex with addition of 2,2′-dipyridyl. On reaction of **1** with 2,2′-dipyridyl in THF, reddish purple crystals which are soluble in THF were obtained and identified as $Mg(dipy)_3$ by elemental analysis. After the removal of $Mg(dipy)_3$, a THF-insoluble residue with a composition of $[TiNMg_{1.5}Cl_2(dipy)_{1.5}(THF)]$ remained. Further removal of magnesium from this residue by reaction with pyridine gave $MgCl_2(Py)_2$ and a black powder with a composition of $[TiNMgCl(Py)_2]$. THF in **1** was not replaced by a soft base such as triphenylphosphine.

Complete removal of magnesium component from **1** was achieved by using benzoyl chloride in THF. The reaction yielded $MgCl_2(THF)_2$, some polymer of THF and a dark green substance with an approximate composition of $[TiNCl(C_6H_5CO)_{1.5}]$. The polymer of THF is considered to be formed by cationic polymerization. The mode of combination of benzoyl chloride component with titanium was not clear. In none of the complexes which were obtained by various treatments of **1** the decrease of the nitrogen to titanium ratio was observed.

Complex **1** dissolved in THF showed no reactivity toward nitrogen but still reacted with hydrogen in the presence of magnesium. The system slowly absorbed hydrogen and the reaction continued as long as excess magnesium was present. From the system excess magnesium and a gray powder which are insoluble in THF were separated. The gray powder released hydrogen on reaction with iodine and probably contains magnesium hydride beside unreacted magnesium. As described in the preparation of **1**, $MgCl_2(THF)_2$ was separated from the system and a black powder of a composition of $[TiH_2NMg_3Cl_{1.5}(THF)_2]$ (**2**) was isolated. The reaction of iodine with **2** released one mole of H_2 per titanium. The nitrogen in **2** is still bonded with titanium after the reaction of **1** with hydrogen as revealed by the formation of 1 mol of ammonia and of ammonium chloride respectively on reactions of **2** with water and hydrogen chloride.

(ii) Vanadium Complexes. *a. Under Nitrogen:* In a similar manner to the $TiCl_3$–Mg system, $VCl_3(THF)_3$ was reduced in THF with magnesium under nitrogen. The color of the THF solution changed from red through green to black. $MgCl_2(THF)_2$ and a vanadium complex of a composition $[VNMg_2Cl_2(THF)]$ (**3**), were separated from the system. Complex **3**, diamagnetic ($\chi = 0.0113 \times 10^{-6}\ g^{-1}$) and very sensitive to air, gave 1 mol of ammonia per vanadium on hydrolysis. On iodolysis **3** released 0.026 mol of H_2 per vanadium thus showing the presence of a small amount of hydride ingredient as in titanium complex **1**. Thermal decomposition of **3** over 200°C for 10 hr released no nitrogen but hydrogen together with THF, 1-butene, *n*-butane, *trans*- and *cis*-2-butenes, propylene, ethylene, ethane, and methane were detected in the gas evolved. These products may be formed by decomposition of THF in **3**. The pyrolysis residue still contained nitrogen as proved by the formation of 1 mol of ammonia per vanadium on hydrolysis of the residue.

b. Under Argon: From the $VCl_3(THF)_3$–Mg system reacted under argon a diamagnetic vanadium complex of composition $[VHMg_2Cl_{1.5}(THF)]$ (**4**) and $MgCl_2(THF)_2$ were separated. The presence of hydride was deduced from the amount of H_2 produced on iodolysis of **4**. The IR spectrum of **4** was very similar to that of **3** and no band ascribable to ν(V–H) was detected.

c. Under Hydrogen: When $VCl_3(THF)_3$ was reduced with magnesium in THF under hydrogen at ambient temperature and pressure, the system absorbed hydrogen slowly but steadily over a long period; 3.5mol of H_2 was absorbed per mol of the vanadium complex in 35 days. The diamagnetic vanadium complex separated from the system has the composition of $[VH_2MgCl(THF)_2]$ (**5**). The amount of hydridic hydrogen in the complex was deduced from the amount of hydrogen produced on iodolysis.

Chemical Properties of $[VNMg_2Cl_2(THF)]$ ***3***. In order to examine the properties of **3**, the following reactions of **3** were carried out. Complex **3** dissolved in THF reacted in the presence of magnesium with hydrogen at room temperature and atmospheric pressure. The reaction proceeded slowly but steadily as long excess magnesium was present. More than 10 mol of H_2 per the vanadium complex was absorbed in a month. From the system black powder with a composition of $[VN(H)_2Mg_5Cl_2(THF)_2]$ (**6**) and magnesium hydride were separated.

Complex **3** as well as other vanadium complexes prepared under argon and hydrogen reacts with ethylene forming ethane. In the presence of hydrogen complex **3** catalyzes the hydrogenation of ethylene. The formation of amine was not detected.

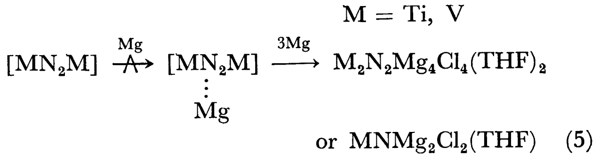
Complex **3** reacted with various organic halides. The reaction of benzyl chloride with **3** took place with evolution of heat, and $MgCl_2(THF)_2$, dibenzyl, and a vanadium complex with a composition of $[VNMgCl_{1.5}(THF)]$ were formed. By the reaction of **3** with chlorotriphenylmethane, a part of magnesium in **3** was removed as $MgCl_2(THF)_2$ and a black complex of a composition $[VNMgCl_2(THF)]$ was obtained. A similar reaction with methyl iodide released 0.5 mol of methane per vanadium with partial removal of magnesium chloride from **3**. A part of magnesium in **3** was also removed as magnesium chloride on reaction with benzoyl chloride accompanied by the formation of a polymer of THF.

Discussion

Comparison of the reductions of $TiCl_3(THF)_3$ and $VCl_3(THF)_3$ with magnesium under nitrogen, argon, and hydrogen clearly indicates the striking similarity of the two systems belonging to the IVth and Vth groups in the periodic table. The stoichiometries of the N_2-fixation reactions given by Eqs. (2) and (3) are satisfactorily substantiated from the analyses of the products as well as from kinetic studies. Clearly the induction periods observed in the nitrogen fixation with these systems are due to the one electron reductions of $TiCl_3(THF)_3$ and $VCl_3(THF)_3$ with 0.5 g-atom of Mg accompanied by the formation of 0.5 mol of $MgCl_2$. Similar induction period has been reported in the nitrogen fixation by $VCl_3(THF)_3$–lithium naphthalide system.[5] Examination of the visible spectrum of the $VCl_3(THF)_3$–Mg system after the one electron reduction revealed the formation of a divalent vanadium species as shown by the presence of absorption maxima at 410 and 650 nm which can be compared with the spectrum of known $VCl_2(THF)_2$ at 407 and 643 nm.[6] Similarly the absorption band at 380 nm observed in the induction period of the N_2-fixing $TiCl_3$–Mg system may be due to the divalent titanium species. Accompanying the change of the electronic spectrum the ESR spectrum of the $VCl_3(THF)_3$–Mg system changed with increasing amount of magnesium added to the system. Vanadium having the nuclear spin of 7/2 gives 8 hyperfine splittings but the shape of the ESR spectrum changed depending on the amount of Mg consumed. The ultimate reduction products of VCl_3–Mg system which consumed 2.5 g-atoms of magnesium per vanadium were diamagnetic and showed no ESR absorption. The ESR spectra of the intermediate reduction products prepared under nitrogen and argon were identical. The ultimate oxidation states of titanium and vanadium complexes after absorption of 2.5 g-atoms of Mg (**1** and **3**) are difficult to assign, since the magnesium contained in the complexes can be removed by reactions with organic nitrogen bases as Mg(II) in one case and as Mg(0) in the other, although the diamagnetism of **1** and **3** suggests Ti(0) and V(I) as the formal oxidation states. Some ESR studies on VCl_3–alkali naphthalide system have been reported.[5,7]

From the kinetics of nitrogen fixation by $TiCl_3$–Mg system, the initial rate of nitrogen absorption after the induction period was shown to be first order with respect to the amounts of $TiCl_3$, of Mg and the pressure of nitrogen, whereas the stoichiometry of the nitrogen fixation (Eq. 2) shows that half a molecule of nitrogen combines with mole of titanium and vanadium. As a reasonable explanation compatible with these results we assume a dimeric titanium or vanadium species which combines with molecular nitrogen and the N_2 complex thus formed is further reduced reacting with magnesium in the succeeding rate determining step:

$$[M]_2 + N_2 \rightleftarrows [MN_2M] \qquad M = Ti, V \tag{4}$$



$$[MN_2M] \overset{Mg}{\nrightarrow} \underset{\substack{\vdots \\ Mg}}{[MN_2M]} \xrightarrow{3Mg} M_2N_2Mg_4Cl_4(THF)_2 \text{ or } MNMg_2Cl_2(THF) \tag{5}$$

As the N_2-binding species, divalent and univalent transition metal may be considered but the latter appears to be less probable. The experiment shown in Fig. 8 indicates that VCl_3–Mg which reacted with 1.0 g-atom of Mg per vanadium under argon has the N_2-fixing ability of about 70%. This system would be expected to show the full N_2-fixing ability if V(I) formed by stepwise reduction of V(III) should be responsible as the N_2-binding species.

Therefore we propose the divalent vanadium and titanium compounds as the N_2 binding species. Negligible absorption of nitrogen in the divalent state of vanadium and titanium at room temperature and normal pressure may be understood if the equilibrium (4) is on the side of dissociation. Recent isolations of titanium[8–10] and molybdenum[11] complexes with N_2, as the bridging ligand between two metal atoms, lend support to the assumption. We are presently investigating the possibility of identifying the species with a composition $[Ti(II)\cdot N_2\cdot Ti(II)]$ or $[V(II)\cdot N_2\cdot V(II)]$. We do not have at present any information about the state of aggregation of the divalent titanium and vanadium species to combine with nitrogen but $TiCl_3(THF)_3$ is reported to be dimeric.[12]

Alternative pathway to the above mechanism is that a monomeric species combines with N_2 followed by a rapid combination with another monomeric species forming a bridged N_2 complex. Van Tamelen presented evidence to indicate the formation of TiN_2 type complex.[2h,13]

The linear relationship between the amount of magnesium consumed and the amount of N_2 fixed (Fig. 7) suggests that stepwise change of the oxidation states of titanium and vanadium is not involved during the consumption of Mg between 0.5 and 2.0 g-atoms in the titanium system and between 0.5 and 2.5 g-atom in the vanadium system. Probably the reaction of

---

[5] T. P. M. Beelen and W. Van Erk, *Rec. Trav. Chim. Pays-Bas*, **90**, 1197 (1971).

[6] H. J. Seifert and T. Auel. *J. Inorg. Nucl. Chem.*, **30**, 2081 (1968).

[7] G. Henrici-Olivé and S. Olivé, *J. Organometal. Chem.*, **9**, 325 (1967).

[8] J. H. Teuben and H. J. de Liefde Meijer, *Rec. Trav. Chim. Pays-Bas*, **90**, 360 (1971).

[9] A. E. Shilov, A. K. Shilova, and E. F. Krashina, *Kinet. Katal.*, **10**, 1402 (1969).

[10] J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **93**, 2045 (1971); R. H. Marvich and H. H. Brintzinger, **93**, *ibid.*, 2046 (1971).

[11] M. L. H. Green and W. E. Silverthorn, *Chem. Commun.*, **1971**, 557.

[12] R. J. H. Clark, J. Lewis, D. Machin, and R. S. Nyholm, *J. Chem. Soc.*, **1963**, 379.

[13] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *J. Amer. Chem. Soc.*, **91**, 1551 (1969).

magnesium with the previously assumed N_2-bridged species (Eq. 5) is irreversible and once the nitrogen is partially reduced in the titanium or vanadium complex, further reaction with magnesium would take place preferentially with the nitrogen bound, partially reduced species, leaving the other species the full capacity to combine with molecular nitrogen. This assumption is supported by Fig. 3 which shows much faster rate of Mg consumption under nitrogen than under argon and by Fig. 8 which demonstrates that the system reacted with 1.5 g-atoms of Mg under argon still shows considerable capacity to combine with nitrogen.

When $TiCl_3(THF)_3$ was reduced with sodium amalgam under nitrogen, the system became heterogeneous when 2.7 equivalents of Na was consumed with the N_2 fixation of 0.35 mol per titanium. In a similar experiment with $VCl_3(THF)_3$ using 5 equivalents of sodium amalgam per vanadium the fixation of nitrogen after 1 day was almost negligible. These results show the suitability of magnesium in the N_2 fixation and suggest its particular role in the reduction of the combined nitrogen.

The mode of combination of magnesium with titanium or vanadium presents a difficult problem to explain. The magnesium content in the benzene-soluble vanadium complexes **3**—**6** varies depending on the preparative conditions and magnesium in [$TiNMg_2Cl_2(THF)$] **1** can be removed either in zerovalent or in divalent state as described earlier. Magnesium is supposed in these complexes to be present in the vicinity of titanium or vanadium and of chlorine, and can be driven in different ways depending on the reagent to attack magnesium. It is clear that the nitrogen in these complexes is not present in the form of magnesium nitride since the removal of magnesium takes place leaving the nitrogen in the complexes intact.

Evidently the nitrogen in the complexes is bound with titanium or vanadium but we can not conclude from the available data whether it is in the form of nitride or exists as the bridging ligand. The absence of the N_2 stretch band in the IR spectrum above 1600 cm^{-1} excludes the possibility of the presence of N_2 ligand as in later transition metal–N_2 complexes.[2] No distinct band assignable to metal-nitride stretch was observed above 400 cm^{-1} and the possibility of N_2-bridged binuclear structure with low N-N bond order can not be excluded, although the failure of detection of hydrazine after hydrolysis of the nitrogen-containing complexes favors the nitride structure.

Tetrahydrofuran in complexes **1**—**6** appears to be bonded with titanium or vanadium. Symmetric and antisymmetric stretching bands of C–O–C bond of THF were observed at 860 and 1015 cm^{-1} for titanium complex **1** and at 875 and 1026 cm^{-1} for vanadium complex **3** in comparison with those of free THF at 910 and 1075 cm^{-1} and of $MgCl_2(THF)_2$ at 890 and 1040 cm^{-1}. The tetrahydrofuran is bonded with titanium very strongly in complex **1** and thermal decomposition of **1** at 200°C could not remove all THF in the complex and the decomposition was accompanied by partial decomposition of the THF ligand whereas THF in $MgCl_2(THF)_2$ was easily removed.

The presence of a small amount of hydridic hydrogen in complexes **1** and **3** and of one hydridic hydrogen in complex **4** prepared under argon should be explained by hydrogen abstraction from THF by titanium or vanadium. This result may be understood as the indication of the reactivity of the low valent vanadium and titanium complexes toward hydrogen in the absence of nitrogen.

The high reactivities of the low valent titanium and vanadium complexes are reflected in their reactions with various reagents. The reactions with organic halides may probably proceed through oxidative addition reactions which yield unstable transition metal-alkyl complexes. The formations of dibenzyl in the reaction of benzyl chloride and of methane in the reaction of methyl iodide with **3** support the above assumption.

The catalytic activities of the low valent complexes in the dimerization and hydrogenation of olefins may be understood by assuming titanium and vanadium hydrides as the active species which can be formed by the reaction with molecular hydrogen and also by hydrogen abstraction from THF.

The $TiCl_3$–Mg and VCl_3–Mg systems described here react with molecular nitrogen and hydrogen respectively but no ammonia was formed in the presence of both reactants except after hydrolysis. Previously we considered necessary conditions for ammonia synthesis from N_2 and H_2 by a transition metal complex to proceed including the activation of N_2 and H_2 and transfer of hydrogen from the activated hydrogen to nitrogen.[14] The present systems are capable to activate both N_2 and H_2 but apparently the conditions for hydrogen transfer to occur are not fulfilled. Interestingly complexes **1** and **3** containing nitrogen catalyze the hydrogenation of magnesium to magnesium hydride. Complex **1** or **3** containing reduced nitrogen reacts with hydrogen forming a titanium hydride or vanadium hydride complex but the hydride formed is passed to magnesium, not to nitrogen, giving magnesium hydride despite the high reactivity of the bound nitrogen toward protonic reagents. Apparently the bound nitrogen in the complex has anionic nature and so does the hydride formed by the reactions of titanium or vanadium complex with molecular hydrogen, thus the hydrogen transfer of the hydride to the bound nitrogen may be hindered. Finding a proper method to make this hydrogen transfer possible seems a key problem for the catalytic formation of NH_3 from N_2 and H_2 to proceed under mild conditions.

Experimental

Materials. Titanium trichloride was used by dissolving in THF or after conversion to $TiCl_3(THF)_3$ by refluxing in THF for several hours and then purifying by recrystallization from THF.

Found: C, 39.2; H, 6.6; Cl, 28.0; Ti, 13.2% μ_{eff} 1.91 B. M. Calcd for $C_{12}H_{24}O_3Cl_3Ti$: C, 38.9; H, 6.5; Cl, 28.7; Ti, 12.9%.

---

[14] A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *ibid.*, **93**, 371 (1971).

Vanadium trichloride was always used as $VCl_3(THF)_3$. VCl_3 which was prepared by the reaction of V_2O_5 with S_2Cl_2[15] was converted to the THF adduct which was purified by recrystallization from THF.

Found: C, 37.7; H, 6.2; Cl, 28.0; V, 13.9% μ_{eff}, 2.95. B. M. Calcd for $C_{12}H_{24}O_3Cl_3V$: C, 38.6; H, 6.5; Cl, 28.5; V, 13.9%.

Nitrogen, hydrogen, and argon gases were dried and deoxygenated by passing through columns of $CaCl_2$, P_2O_5, and activated copper. Solvents were dried by usual methods and deoxygenated by distillation under nitrogen or argon. Granular or powder magnesium was used; in some experiments granular magnesium was pretreated with iodine and washed with THF. Sodium amalgam was prepared by the reaction of sodium with mercury in Nujol; the sodium content was 0.2%.

Analytical Methods. Analysis of Ti, V, Mg, and Cl was carried out after hydrolysis of a sample (0.1—0.6 g) with 20% sulfuric acid. Titanium was precipitated by Cupferron (nitrosophenylhydroxylamine) and determined as TiO_2 by gravimetric method. Vanadium was determined in a similar method as V_2O_5. Magnesium was analyzed after removal of titanium or vanadium component from the sample by titration with ethylenediaminetetracetic acid. Chlorine content was determined by Mohr method with silver nitrate. The amount of nitrogen fixed by the complex was determined by Kjeldahl method and referred to as N* in analytical data to distinguish when necessary from the amount of total nitrogen content N obtained by microanalysis. The microanalysis was performed by Mr. T. Saito of our laboratory.

The amount of coordinated THF in complexes was determined by displacing the coordinated THF with 2,2′-dipyridyl and by analyzing the liberated THF by gas chromatography. This method is not quite quantitative but can be used as a measure to estimate the number of the coordinated THF approximately. In the case of $TiCl_2(acac)(THF)_2$[4] we have confirmed that 85% of THF for the theoretical value was released.

Because the complexes obtained are very air-sensitive, considerable difficulties were encountered in analysis. Furthermore, since the amount of THF contained in complexes varied, the absolute percentage of the analytical data can not be regarded as the criteria for purity. Therefore the empirical composition based on the ratio of atoms and THF in the complexes will be given below in most places.

IR spectra were recorded in KBr discs with Hitachi EPI-G3 and Shimadzu IR 27C spectrophotometers. Electronic spectrum was measured with a Shimadzu SV-50 spectrophotometer and ESR spectra was recorded on a Jeolco JES 3B-X.

Kinetic Studies. Kinetics studies were carried out using a 1-liter glass flask with a magnetic stirrer in a thermostatted bath regulated within 0.1°C. $TiCl_3$ was added to 100 m*l* of THF containing Mg and the time was measured from the point of addition. Previous dissolution of $TiCl_3$ somewhat shortened the induction period but no change in the essential feature of the N_2 absorption rate was observed. The absorption rate was followed by a gas flow meter, keeping the pressure constant by an oil seal and removing the moisture of the flowing gas by passing through a P_2O_5 column. The reaction with argon diluent was carried out as follows; after all the reagents were introduced into the reactor under argon, the pressure of argon was adjusted to a given pressure and N_2 was introduced. The reaction was terminated by removing the gas and solvent *in vacuo*. The amount of nitrogen fixed was determined as ammonia after hydrolysis with sulfuric acid and the amount of magnesium consumed was measured by weighing the unreacted magnesium which was separated from the solution, washed with THF and dried *in vacuo*.

Isolation and Reactions of Complexes. Since the complexes were isolated in a similar way some typical examples will be given.

1. *[$TiNMg_2Cl_2(THF)$]* **1**: $TiCl_3(THF)_3$ (18 g, 50 mmol) was dissolved in 150 m*l* of THF under nitrogen and the solution was added to 12 g of magnesium. The color of the solution changed slowly from blue through green to black with evolution of heat and absorption of N_2 which was measured by a gas burette. The absorption of N_2 stopped after several hours but the contact of the solution with nitrogen was continued for 24 hr to complete the reaction. The total amount of nitrogen absorbed was 0.5 mol per titanium. Unreacted magnesium was separated by filtration and the black THF solution was evaporated to dryness at room temperature. The residue was extracted with benzene *in vacuo* until no benzene-soluble dark substance remained. The white residue (5.7 g) was recrystallized from THF-hexane mixture as white needles. The benzene soluble fraction was dissolved again in THF and precipitated by addition of a controlled amount of hexane. The dark precipitate thus obtained was dried *in vacuo* to yield black very air-sensitive powder (11.2 g).

The white needles readily lose THF on drying and the amount of THF varied depending on the extent of drying. The ratio of magnesium to chlorine of the powder obtained on drying the crystals was 1 : 1.94, thus indicating the compound as $MgCl_2$ probably coordinated with 2 mol of THF in the crystalline state.

The benzene soluble fraction obtained as black powder analyzed as follows: Ti, 18.3; Mg, 17.6; Cl, 23.8; N, 4.7; THF, 24.5; C, 21.6; H, 4.5%. The empirical composition based on the ratio of atoms and THF: $TiMg_{1.9}Cl_{1.8}N_{0.94}(THF)_{0.89}$.

Reactions of **1** *a. Iodolysis* of this complex (0.32 g) released 1.89 m*l* at STP of H_2 which was measured by a Toepler pump and identified by mass spectrometry. The amount of H_2 evolved corresponded to 6.34% per titanium.

b. With HCl: **1** dissolved in THF (0.439 g, 1.67 mmol as calculated from the Ti content) reacted with dry hydrogen chloride consuming 10.07 mmol (6.02 mmol/Ti) and evolved 1.26 mmol (0.76 mol/Ti) of H_2.

c. With Pyridine: The reaction of **1** (2.3 g) in 100 m*l* of THF with pyridine (13.2 g) caused the precipitation of a black substance. Extraction of the system with THF and recrystallization from THF gave colorless crystals.

Found: C, 47.4; H, 4.0; N, 10.8; Cl, 28.3; Mg, 9.65%. Calcd for $MgCl_2(C_5H_5N)_2$: C, 47.4; H, 4.0; N, 11.1; Cl, 28.1; Mg. 9.60%.

Analysis of the black precipitate purified by repeated reprecipitation from pyridine-THF-hexane mixture: Ti, 22.7; Mg, 13.6; Cl, 8.62; N*, 6.31. Empirical composition: $TiMg_{1.2}Cl_{0.5}N^*_{0.95}$

d. With 2,2′-Dipyridyl: Addition of THF solution of dipyridyl (20 g) to the black THF solution containing 5.2 g of **1** caused the color change to reddish violet and a precipitate was formed. Extraction of a THF soluble fraction from the system gave dark reddish violet crystals which are very sensitive to air.

Found: Mg, 4.6; C, 69.5; H, 5.7; N, 15.9%; Atomic ratio: Mg, 1.0; C, 30; H, 26; N, 6.0.

The THF insoluble fraction could not be purified because of the lack of appropriate solvent.

---

[15] H. Funk and C. Muller, *Z. Anorg. Allg. Chem.*, **244**, 94 (1940).

Found: Ti, 9.9; Mg, 7.2; Cl, 13.9; N*, 2.9; C, 46.7; H, 4.8; N, 10.4%. Empirical formula: $TiMg_{1.4}Cl_{1.9}M^*_{1.0}C_{19}H_{23}(N\text{–}N^*)_{2.6}$.

Reaction of the THF-insoluble fraction with pyridine gave homogeneous black solutiom. Addition of THF formed the black precipitate which was separated from the solution and analyzed after reprecipitation from pyridine–THF mixture.

Found: Ti, 17.6; Mg, 0.87; Cl, 10.1; N*, 4.4; C, 36.4; H, 3.7; (N–N*), 9.2%. Empirical formula: $TiMg_{0.87}Cl_{0.78}N^*_{0.86}C_{8.3}H_{10}(N\text{–}N^*)_{1.8}$. From the solution white crystals of $MgCl_2(C_2H_5N)_2$ were isolated.

e. With Benzoyl Chloride: $[TiNMg_2Cl_2(THF)]$ **1** (2.1 g, 8.2 mmol) was dissolved in 50 m*l* of THF and a THF solution containing 3.5 g of benzoyl chloride was added at room temperature. The black solution turned dark green with addition of benzoyl chloride. On cooling the mixture with addition of *n*-hexane colorless plates of $MgCl_2(THF)_2$ separated out. After removal of the white crystals, all the titanium complex was precipitated with addition of *n*-hexane and the precipitate was washed to remove excess benzoyl chloride. The precipitate was extracted with benzene, purified and analyzed as usual.

Found: Ti, 17.6; Cl, 10.9; N*, 4.89; C, 48.5; H, 4.0%. Empirical formula: $TiCl_{0.84}N_{0.95}C_{11}H_4$.

f. With Hydrogen and Magnesium: Complex **1** (2.35 g, 9.2 mmol) dissolved in THF (50 m*l*) was put in contact with 2.3 g of magnesium under hydrogen at room temperature. The system absorbed 3.33 mol of H_2/Ti in 90 hr and still showed ability to react with hydrogen. From the system black powder was separated as the benzene-soluble fraction.

Found: Ti, 13.0; N*, 3.4; Mg, 26.6; Cl, 14.6; C, 25.0 H, 5.0; N, 3.8%. Iodolysis of the powder 0.1164 g (0.318 mmol based on Ti content) in benzene gave 0.318 mmol of H_2 (98.5% based on Ti content). Empirical formula: $TiN_{1.0}(H)_2Mg_{4.0}Cl_{1.5}C_{7.7}H_{16}$(**2**).

2. Preparation of Vanadium Complexes. 2.1 Under Nitrogen: Complex **3** was prepared in a similar way to titanium complex **1** from 28.7 g (75.9 mmol) of $VCl_3(THF)_3$ in 200 m*l* of THF and 18.7 g (0.77 mol) of Mg under nitrogen. The absorption of nitrogen took 15—20 hr at room temperature and the color of the solution turned from red through green to black.

Found: V, 17.5; Mg, 15.9; Cl, 25.5; N, 4.9; C, 21.5; H, 3.8%. Empirical formula: $VMg_{2.1}Cl_{2.1}N_{1.0}C_{5.2}H_{11.0}$. Iodolysis of the complex, 0.311 g, released 0.615 m*l* of H_2 which corresponded to 2.75 mol% of vanadium.

2.2 Under Argon: $VCl_3(THF)_3$ (17.3 g, 46.3 mmol) in 150 m*l* of THF was reduced under argon with 11.4 g (0.47 mol) of magnesium at room temperature. After the reaction for 3 days with the color change of the solution as observed in the reaction under nitrogen, the argon was replaced with nitrogen but no absorption was observed. $MgCl_2(THF)_2$ and benzene-soluble black powder were separated.

Found: V, 20.4; Mg, 18.5; Cl, 21.3; C, 25.6; H, 4.4%. Empirical formula: $VH_{0.6}Mg_{1.9}Cl_{1.5}C_{5.3}H_{10.0}$. Iodolysis of the complex 0.258 g (1.03 mmol) gave 0.303 mol of hydrogen per vanadium.

2.3 Under Hydrogen: $VCl_3(THF)_3$ (22.6 g, 60.4 mmol) dissolved in 200 m*l* of THF was stirred with 29.2 g of Mg under hydrogen at room temperature for 1 month and the system absorbed 3.5 mol of hydrogen per vanaduim. Magnesium chloride and benzene soluble black powder were separated.

Found: V, 19.6; Mg, 17.8; Cl, 11.6; C, 32.8; H, 6.2%. Empirical formula: $V(H)_{1.8}Mg_{1.9}Cl_{0.81}C_{7.1}H_{14.2}$. Hydride content was determined by iodolysis which relaesed 0.90 mol of H_2 per vanadium.

*Reaction of **3**. a. With Hydrogen and Magnesium*: Complex **3** (2.8 g, 9.7 mmol) was dissolved in 80 m*l* of THF and stirred with 4.7 g (0.19 mol) of magnesium at room temperature under hydrogen. The solution absorbed 10 mol of H_2 per vanadium in 40 days. Black powder was recovered from the solution.

Found: V, 11.6; Mg, 28.6; Cl, 16.8; N, 3.0; C, 21.6; H, 4.2%. Empirical formula: $V(H)_{1.9}Mg_{5.2}Cl_{2.1}N_{0.94}C_{7.9}H_{18.5}$. Hydride content was determined by iodolysis which released 0.95 mol of H_2 per vanadium.

b. With Benzyl Chloride: Benzyl chloride 4.8 g (38 mmol) in THF (80 m*l*) was added to **3**(3.7 g, 12.7 mmol) and the reaction took place with evolution of heat. The solution was evaporated to dryness, washed with *n*-hexane and ether, and extracted with benzene. In the ether washing the presence of dibenzyl, mp 51—53.5°C, was detected and identified by comparison of the IR spectrum with authentic sample. As the benzene insoluble residue magnesium dichloride remained and from the benzene extract a nitrogen containing vanadium complex was recovered.

Found: V, 23.2; Mg, 8.8; Cl, 19.3; N, 5.9; C, 27.8; H, 4.6%. Empirical formula: $VMg_{0.79}Cl_{1.2}N_{0.92}C_{5.1}H_{10.1}$. The IR spectrum of this complex was similar to that of **3**.

c. With Chlorotriphenylmethane: Reaction of **3** (4.2 g, 14.4 mmol) with chlorotriphenylmethane (9.4 g, 33.6 mmol) in 60 m*l* of THF took place with evolution of heat and a black benzene soluble powder with a similar IR spectrum to **3** was obtained.

Found: V, 18.4; Mg, 10.3; Cl, 24.6; N, 4.7; C, 22.3; H, 4.1%. Empirical formula: $VMg_{1.1}Cl_{1.9}N_{0.93}C_{5.1}H_{11.4}$. White benzene insoluble crystals were identified as magnesium chloride.

d. With Methyl Iodide: A THF solution containing 8.6 g (60.5 mmol) of methyl iodide was added to 4.5 g (15.5 mmol) of **3**. Reaction took place with evolution of gas. As the benzene soluble powder a vanadium complex was obtained.

Found: V, 18.1; Mg, 15.7; Cl, 23.6; N, 4.8; C, 21.6; H, 3.9%. Empirical Formulas: $VMg_{1.8}Cl_{1.9}N_{0.96}C_{5.2}H_{10.9}$. The IR spectrum of the complex was similar to **3**. By an independent experiment the gas evolved was identified as methane (0.5 mol/V) and traces of ethane and ethylene by mass spectroscopy and gas chromatography.

The authors are grateful for the grant support of this work from the Ministry of Eduction.