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## INSERTION OF CO<sub>2</sub> INTO THE METAL–NITROGEN BOND FORMED IN THE REACTION WITH MOLECULAR NITROGEN

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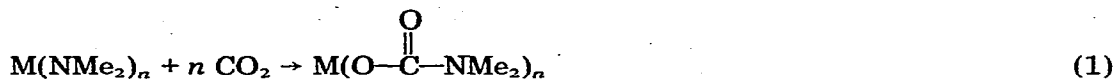
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### Summary

The fixation reaction of carbon dioxide was examined in the following systems; MCl<sub>4</sub>–Mg–THF–N<sub>2</sub> (M = Ti, V) and Cp<sub>2</sub>TiCl<sub>2</sub>–Mg–THF–N<sub>2</sub>. In these systems insertion of CO<sub>2</sub> into the metal–nitrogen bond has been found, which results in the formation of the isocyanate compounds [(THF)<sub>3</sub>Cl<sub>2</sub>Mg<sub>2</sub>OM(NCO)] and Cp<sub>2</sub>TiNCO. In the Cp<sub>2</sub>TiCl<sub>2</sub>–Mg–THF–N<sub>2</sub>–CO<sub>2</sub> system the Cp<sub>2</sub>Ti(CO)<sub>2</sub> carbonyl was also formed.

### Introduction

The insertion of carbon dioxide into the metal–nitrogen [1–7], M–NR<sub>2</sub>, bond has been the subject general investigation for many years. These reactions were found to proceed as shown in eq. 1 and 2. First the carbon dioxide molecule is



M = Ti, Zr, V, Mo;  $n = 4$

M = Nb, Ta;  $n = 5$

M = Bi;  $n = 3$

or



fixed by the nitrogen electron pair and then the M–O– $\overset{\overset{O}{\parallel}}{C}$ –NMe<sub>2</sub> bond is formed [6].

We have undertaken studies on the insertion of carbon dioxide into the metal–nitrogen bond formed in the reaction of the transition metal compound, in a low oxidation state, with molecular nitrogen. As the subject of our studies we have chosen the systems [8,9] MCl<sub>4</sub>–Mg–THF (M = Ti, V) and Cp<sub>2</sub>TiCl<sub>2</sub>–Mg–THF,

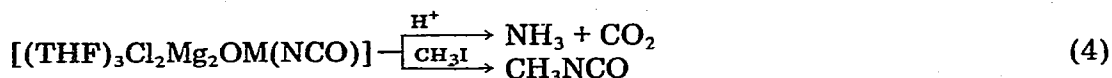
which are capable fixation and reduction of nitrogen. The reaction products under hydrolysis yield stoichiometric amounts of ammonia.

## Results

In the  $MCl_4$ -Mg-THF system, a solution of  $TiCl_4 \cdot 2 THF$  or  $VCl_4$  in tetrahydrofuran (THF) was treated with metallic magnesium (chips) in  $Mg/MCl_4$  1 : 3 under a nitrogen atmosphere. In the reaction time the solution changed colour from yellow to black in the case of the titanium compound and from red to black with the vanadium compound. The nitrogen fixation was observed according to the reaction given in eq. 3.



After the nitrogen fixation reaction was finished, nitrogen was replaced by carbon dioxide. In 45 min one carbon dioxide molecule was fixed per one titanium or vanadium atom. During the carbon dioxide fixation the compound  $[(THF)_3Cl_2Mg_2OM(NCO)]$ , of a constant stoichiometric composition, precipitated from the solution. When treated with acid this compound suffered decomposition with liberation of stoichiometric amounts of ammonia and carbon dioxide. Reaction with methyl iodide yielded  $CH_3NCO$  (eq. 4).



The IR spectrum of  $[(THF)_3Cl_2Mg_2OM(NCO)]$  showed new bands at 2235 and 2197  $cm^{-1}$  (Table 1). Those bands were not observed however, either for  $NMMg_2Cl_2THF$  compounds, or for  $[THFTi(OOCH)_2MgCl_{1.5}]$ , formed [10] in the  $TiCl_4$ -Mg-THF- $CO_2$  system. These bands shifted 10  $cm^{-1}$  towards lower frequencies, 2225 and 2187  $cm^{-1}$  after the reaction with carbon dioxide when the nitrogen isotope  $^{15}N \equiv ^{15}N$  was introduced.

A similar reaction was carried out in the system:  $Cp_2TiCl_2$ -Mg-THF (eq. 5 and 6). A solution of  $Cp_2TiCl_2$  (2.5 g,  $10^{-2}$  mol) in tetrahydrofuran was treated with an excess of metallic magnesium (1 g) under a nitrogen atmosphere. After

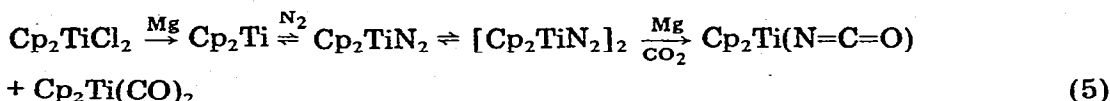


TABLE 1

IR STRETCHING FREQUENCIES ( $cm^{-1}$ , s, strong; w, weak)

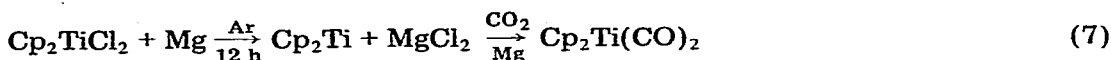
Compounds	$\nu(^{14}N=C=O)$	$\nu(^{15}N=C=O)$	$\Delta\nu$
[(THF) <sub>3</sub> Cl <sub>2</sub> Mg <sub>2</sub> OTi(NCO)]	2235w	2225w	10
	2197s	2187s	10
[(THF) <sub>3</sub> Cl <sub>2</sub> Mg <sub>2</sub> OV(NCO)]	2235w	2225w	10
	2197s	2187s	10
Cp <sub>2</sub> TiNCO	2242w	2230w	12
	2202s	2190s	12



about 60 ml of nitrogen had been fixed at room temperature, nitrogen was replaced by carbon dioxide.

In 45 min one carbon dioxide molecule was fixed per titanium atom. Such a reaction most probably yielded dicyclopentadienyttitanium isocyanate,  $\text{Cp}_2\text{Ti-NCO}$ . Its IR spectra presented two bands at 2242 and 2202  $\text{cm}^{-1}$  which were shifted 12  $\text{cm}^{-1}$  towards lower frequencies; to 2230 and 2190  $\text{cm}^{-1}$ , when the  $^{15}\text{N}=\text{N}$  nitrogen isotope was introduced into the reaction. From the filtrate, after evaporation of THF under vacuum to dryness, a red-brown compound was obtained. Its IR spectra showed two intense bands at 1957 and 1870  $\text{cm}^{-1}$ . Iodine treatment of a solution of the compound in THF resulted in the liberation of carbon monoxide.

If the in  $\text{Cp}_2\text{TiCl}_2\text{-Mg-THF}$  system the reaction was carried out for 12 h under an argon atmosphere and then with the argon replaced by carbon dioxide, the black colour of the solution turned red-brown. After evaporation of the solution under vacuum to dryness the red-brown carbonyl  $\text{Cp}_2\text{Ti}(\text{CO})_2$  remained

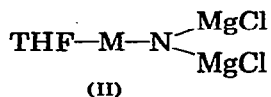
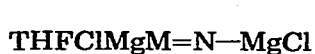


which showed, in the IR spectra, two intense bands at 1957 and 1870  $\text{cm}^{-1}$ .

## Discussion

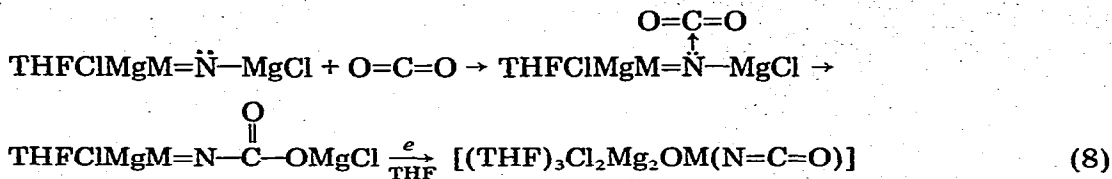
The appearance of the new bands in the infrared spectra, as the result of the reaction of carbon dioxide with the nitrogen titanium and vanadium compounds, allowed us to consider those bands as originating from the bond formed between nitrogen and carbon dioxide. These bands cannot be derived from the  $\nu(\text{N}\equiv\text{N})$  stretching vibration, since the isotope effect of  $^{15}\text{N}_2$  nitrogen for this type of compound amounts to  $\Delta \nu$  40  $\text{cm}^{-1}$  [11], and their hydrolysis yields ammonia and carbon dioxide. The formation of ammonia and carbon dioxide in hydrolysis is evident, since the isocyanate acid is unstable and in acid solution decomposes to ammonia and carbon dioxide.

The observed frequencies are the same as those for the titanium [12] isocyanate compound  $[(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NCO})]$ , 2235 and 2196  $\text{cm}^{-1}$ . The changes in the  $\nu(^{14}\text{N}=\text{C}=\text{O})$  frequency vibration calculated for  $\nu(^{15}\text{N}=\text{C}=\text{O})$  from the formula:  $\nu(^{15}\text{N}=\text{C}=\text{O}) = \nu(^{14}\text{N}=\text{C}=\text{O}) \cdot \sqrt{u_1/u_2}$  ( $u_1$  reduced mass  $^{14}\text{N}=\text{C}=\text{O}$ ;  $u_2$  reduced mass of  $^{15}\text{N}=\text{C}=\text{O}$ ) is equal to 14  $\text{cm}^{-1}$  which is in good agreement with the observed effect. The formulas proposed by Yamamoto et al. [8] for the nitrogen compounds  $\text{THFCl}_2\text{Mg}_2\text{MN}$  ( $\text{M} = \text{Ti}, \text{V}$ ), synthesized in the  $\text{MCl}_3\text{-Mg-THF-N}_2$  systems give no explanation of the carbon dioxide insertion reaction. From the isocyanine formation in the reaction with carbon dioxide and from the fact that the reaction was rapid (45 min) structures I or II could be proposed for these compounds. Structure I is more probable as it contains two magnesium



atoms in two different oxidation states;  $Mg^0$  and  $Mg^{2+}$  as previously reported [8].

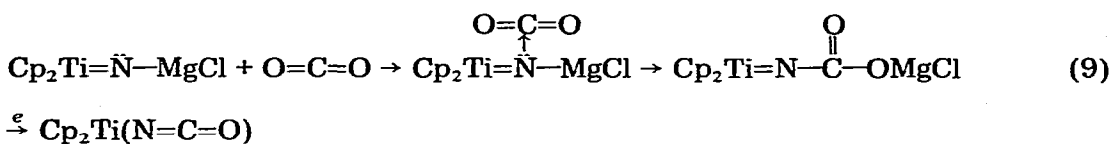
The mechanism of the reaction could be written as in eq. 8.



At first the carbon dioxide molecule, the electron acceptor, was fixed by the free electron pair on the nitrogen atom, which was transferred into the antibonding  $2\pi_u$  orbital of the carbon dioxide molecule. For this reason the carbon dioxide molecule changed its configuration from linear to angular and formed

the  $M=\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OMgCl}$  bond. This bond undergoes reduction, under the influence of either the magnesium, titanium, or vanadium atom present in the compound, yielding isocyanate. The final reaction product  $[(\text{THF})_3\text{Cl}_2\text{Mg}_2\text{OM}(\text{N}=\text{C}=\text{O})]$  is most probably a mixture in spite of its constant stoichiometric composition.

The reaction occurring in the  $\text{Cp}_2\text{TiCl}_2-\text{Mg}-\text{THF}$  system could be presented in a similar way (eq. 9). The reduction of  $\text{Cp}_2\text{TiCl}_2$  with metallic magnesium



under a nitrogen atmosphere probably yields  $\text{Cp}_2\text{Ti}=\text{N}-\text{MgCl}$ , which in reaction

with carbon dioxide gives rise to the intermediate  $\text{Cp}_2\text{Ti}=\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OMgCl}$  compound, which is further reduced. Formation of the  $\text{Cp}_2\text{Ti}(\text{CO})_2$  carbonyl indicates the presence of free  $\text{Cp}_2\text{Ti}$  in solution. This compound can both fix and reduce carbon dioxide in the presence of Mg, as in the reaction carried out first under argon and then under carbon dioxide (eq. 10).



In our opinion the insertion reaction, which discovered by us, of carbon dioxide into the bond formed in the reaction of the metal compound with molecular nitrogen will allow to carry on the catalytic processes of the fixation and reduction of nitrogen. Until now the synthesis of nitrogen and nitrate derivatives by reaction of molecular nitrogen with a transition metal compound, required drastic methods which destroyed the system. Application carbon dioxide to the separation of reduced nitrogen from a metal creates new catalytic possibilities for organic synthesis.

## Experimental

### Materials

$\text{TiCl}_4 \cdot 2 \text{THF}$  was obtained by slow addition of  $\text{TiCl}_4$  to tetrahydrofuran un-

der argon with constant stirring. The product was recrystallized from tetrahydrofuran and dried under vacuum.  $VCl_4$  was obtained by direct synthesis from ferrovanadium and chlorine [13].  $VCl_4$  was redistilled under an argon atmosphere. The  $Cp_2TiCl_2$  used was trade from Fluka A.G. The metallic magnesium chips were the same as those used in the Grignard reaction. Tetrahydrofuran was distilled from  $LiAlH_4$  immediately before each reaction. Carbon dioxide was taken from the steel bottle directly and nitrogen and argon gases were dried and deoxygenated by passing through a molecular sieve column and activated copper. The nitrogen isotope containing 95.3%  $^{15}N$  was obtained from VEB Technische Gase—Leipzig.

### Analytical methods

Analyses of Ti, V, Mg and Cl were carried out after hydrolysis of the sample (0.1–0.5 g) with 20%  $H_2SO_4$ . Titanium was determined calorimetrically from  $H_2O_2$  and vanadium gravimetrically as  $V_2O_5$ . Magnesium was analyzed after removal of the titanium or vanadium component from the sample by titration with ethylenediaminetetracetic acid. The chlorine content was determined by the Mohr method with silver nitrate. The amount of nitrogen fixed by the complex was determined by the Kjeldahl method. Reaction with  $CH_3I$  was carried out in a glass-sealed tube at a temperature of 100°C for 10 h.

IR measurements were made in Nujol mulls and KBr discs on a Perkin—Elmer 621 spectrometer. Chromatographic measurements were performed on an N-503 of Polih's production.

### Syntheses

$[(THF)_3Cl_2Mg_2OTi(NCO)] \cdot TiCl_4 \cdot 2 THF$  (3.3 g;  $10^{-2}$  mol) was dissolved in 50 ml THF under nitrogen and the solution was added (0.7 g;  $3 \times 10^{-2}$  mol) to magnesium. The colour of the solution changed from yellow via green and blue to black with evolution of heat and absorption of  $N_2$  which was measured by a gas burette. The total amount of nitrogen absorbed was 0.5 mol per mol of titanium. Next, nitrogen was replaced by carbon dioxide. The total amount of carbon dioxide absorbed was 1 mol per mol of titanium. During the  $CO_2$  fixation a black precipitate formed which, after separation from the solution, was dried under a carbon dioxide atmosphere. (Found: C, 34.27; H, 5.23; Cl, 19.96; Ti, 10.55; Mg, 11.01; N, 3.06  $C_{13}H_{24}Cl_2Mg_2NO_5Ti$ . calcd.: C, 35.37; H, 5.44; Cl, 16.09; Mg, 11.01; Ti, 10.85; N, 3.17%.)

$[(THF)_3Cl_2Mg_2OV(NCO)]$ . This complex was prepared in a similar way as the titanium complex  $[(THF)_3Cl_2Mg_2OTi(NCO)]$ , from 1.37 ml ( $10^{-2}$  mol) of  $VCl_4$  in 50 ml THF and 0.73 g ( $3 \times 10^{-2}$  mol) of magnesium. The total amount of nitrogen and carbon dioxide was 0.5 mol  $N_2$  and 1 mol  $CO_2$  and the colour of the solution turned from red through green to black (Found: C, 34.73; H, 5.18; Cl, 15.87; N, 2.97; V, 11.82; Mg, 10.33  $C_{13}H_{24}Cl_2Mg_2O_5NTi$ . calcd.: C, 35.09; H, 5.39; Cl, 15.97; N, 3.15; V, 11.45; Mg, 10.93%).

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