

## THE APPLICATION OF $^{13}\text{C}$ AND $^1\text{H}$ NMR SPECTROSCOPY TO THE INVESTIGATION OF THE DINITROGEN FIXATION PROCESS IN THE SYSTEM $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-Mg}$

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### Summary

The  $\text{N}_2$  reduction reaction in the system  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-Mg}$  in tetrahydrofuran was examined. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR results as well as the chemical properties of the products formed revealed that the reaction yielded a mixture of compounds in which the titanium atom was bonded both to the  $\mu\text{-}(\eta^5\text{:}\eta^5\text{-fulvalene})$  ligand and to the cyclopentadienyl ligands. In this system dinitrogen undergoes reduction to  $\text{N}^{3-}$ , which then forms  $\text{M}_3\text{N}$  bridges ( $\text{M} = \text{Ti}, \text{Mg}$ ). The nitride nitrogen may readily be oxidized to imide nitride  $\text{N}^{-1}$ , which may react further, e.g. with carbon monoxide to produce isocyanates, or, with excess oxidizing agent  $\text{N}_2$ . THF in this system undergoes polymerisation. In addition, a  $-\text{OC}_4\text{H}_9$  alkoxy group is formed which makes the substitution of the cyclopentadienyl group bonded to the titanium atoms possible.

### Introduction

The discovery in 1964 by Vol'pin and Shur of the reduction of  $\text{N}_2$  by the  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{RMgX}$  system [1] led several workers to postulate the presence of the  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$  intermediate in these dinitrogen fixation systems; these studies have already been covered in the review literature [2–7].

The possibility that a "real" titanocene,  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ , might indeed bind dinitrogen, stimulated a great deal of efforts to synthesize it. However, up to the present titanocene has never actually been isolated as a discrete chemical compound. Only two "titanocene" complexes obtained in uncontrolled reduction reactions of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  have been reasonably well characterized. These are the fulvalene bridged, green, very air-sensitive bis( $\eta$ -cyclopentadienyltitanium)dihydride [8],  $\mu\text{-}(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)\text{-}\mu(\text{H}_2)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$  and the bridging  $\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$  [9]. Some "titanocenes" are known to bind  $\text{N}_2$  directly, to produce complexes in which dinitrogen is fixed by end-on and side-on bridging between titanium atoms [10–15].

$(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2/\text{RMgX}$  is the most effective reducing system which reduced dinitrogen stoichiometrically to ammonia [16]. Various combinations of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  with Li, Na, K, Cs, Mg, Ce, La and alkali metal-arene radical anions likewise reduce  $\text{N}_2$  to ammonia [3,17,18]. The specific organometallic titanium species responsible for  $\text{N}_2$  reduction has not been identified [2,7].

The mechanism of the reduction of  $\text{N}_2$  in the above system has been the subject of several investigations [19–22]. Van der Weij et al. [21,22] reported, that if  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  was reduced with  $\text{Pr}^{\text{I}}\text{MgCl}$  or sodium naphthalide under dinitrogen, one  $\text{C}_5\text{H}_5$  group was removed from the titanium atom. The loss of this group forms the compounds  $(\text{C}_5\text{H}_5)_2\text{Mg}$  or  $\text{C}_5\text{H}_5\text{Na}$ , as was evidenced by  $^1\text{H}$  NMR and by the reaction with  $\text{FeCl}_2$ , which yielded ferrocene.

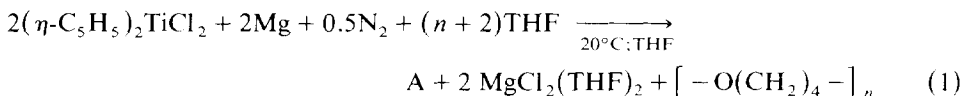
We have undertaken the studies by  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy of the mechanism of reduction of  $\text{N}_2$  in the  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-Mg}$  system. Our purpose was the elucidation of the behaviour of cyclopentadienyl groups in the uncontrolled reduction reaction of bis( $\eta$ -cyclopentadienyl)titanium dichloride under dinitrogen and the characterisation of the chemical properties of nitrogen fixed under these conditions.

## Results and discussion

### *Reactions in the system $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{-Mg}$*

During the reduction of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  (1 g; 4 mmol) with excess metallic magnesium (3 g) in tetrahydrofuran (50  $\text{cm}^3$ ) dinitrogen is fixed (24 h) in a ratio  $\text{N}_2:2\text{Ti} = 0.5$ . As a result product A was formed for which no  $\nu(\text{Ti}\equiv\text{N})$  and  $\nu(\text{N-N})$  frequencies were observed in the IR spectrum. Elemental analysis revealed that in that product the  $\text{Ti}:\text{N}:\text{Mg}:\text{Cl}$  ratio was 1:0.5:2:1.

During hydrolysis of A with dilute sulphuric acid (1:1; 20  $\text{cm}^3$ ) 75% of the fixed dinitrogen produced ammonia and 25% was liberated as  $\text{N}_2$ .



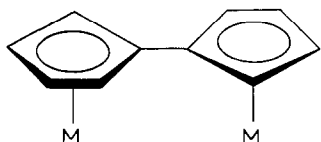
Product A reacted with carbon monoxide in a ratio  $\text{CO}:\text{Ti}$  of about 1.7 to form reaction mixture B, for which bands at 1881 vs and 1965 vs  $\text{cm}^{-1}$ , characteristic of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  were observed in the IR spectrum, but the  $\nu(\text{NCO})$  band was not visible [23]. After evaporation of the reaction mixture B in vacuo the residue reacted with methyl iodide,  $\text{CH}_3\text{I}$ , to form *N,N*-dimethylacetamide,  $(\text{CH}_3)_2\text{NCOCH}_3$ , in 18% yield, calculated from amount of fixed dinitrogen. The amide group in B is formed as the result of reduction of the isocyanate group by a titanium atom at a low oxidation state [23]. This was confirmed by the formation of a mixture of  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NCO})\text{I}$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  during reaction of carbon monoxide with product A and oxidized by iodine with  $\text{I}_2:\text{Ti} = 1$ . The  $\text{Cp}_2\text{Ti}(\text{NCO})\text{I}$  [IR  $\nu(\text{NCO})$  2230s and 2198m  $\text{cm}^{-1}$ ] [24] is formed in 16% yield basing on fixed dinitrogen. The product A can also be oxidized with carbon dioxide and in this case a mixture of  $(\eta\text{-C}_5\text{H}_5)_2\text{TiNCO}$ ,  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$  and  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCO}_3$  is formed [25].

When A is oxidized, in excess, e.g.  $\text{I}_2:\text{Ti} \approx 5$ , then about 60% of the fixed dinitrogen is liberated as  $\text{N}_2$  and after hydrolysis of the oxidized product the residual

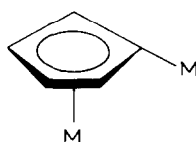
amount of the fixed nitrogen forms ammonia. Hence, it follows that at least 40% of the fixed nitrogen in A existed as the  $N^{3-}$  nitride. On the other hand, the direct hydrolysis of A produced  $NH_3$  in 75% yield. This difference reveals that in A 35% of the fixed nitrogen undergoes oxidation to the imide nitrogen or, with excess oxidizing agent, undergoes further oxidation to  $N_2$ , or reacts with carbon monoxide to form the isocyanide group. To find out whether the reduction reaction of  $N_2$  in the  $(\eta-C_5H_5)_2TiCl_2$ -Mg system was accompanied by elimination of the cyclopentadienyl ring, dry HCl was passed through the post-reaction mixture, which was next evaporated to dryness in vacuo. The residue was extracted with n-pentane, and a 12% yield of  $(\eta-C_5H_5)TiCl_3$  was obtained. When  $FeCl_2$  was added to the post-reaction mixture (A), and when after 24 h the THF was evaporated under vacuo, and next the mixture was extracted with n-pentane and sublimed, ferrocene was obtained in about 8% yield.

### $^{13}C$ and $^1H$ NMR measurements

Precise  $^{13}C$  and  $^1H$  NMR measurements were made to elucidate the course of reaction 1 and to examine the structure and properties of the components of the product A. For cyclopentadienyltitanium compounds the  $^{13}C$  NMR spectroscopic method has proved to be the best. In the  $^{13}C$  NMR spectrum of a fulvalene compound the characteristic pattern of a  $\mu-(\eta^5 : \eta^5\text{-fulvalene})$  ligand is observed [27],



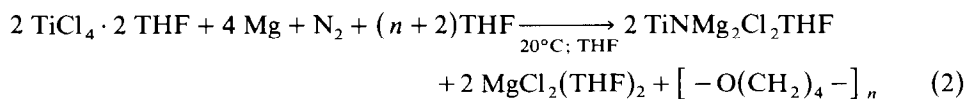
$\mu-(\eta^5 : \eta^5\text{-fulvalene})$



$\mu-(\eta^5 : \eta^1\text{-cyclopentadienyl})$

i.e. C(2) is shifted from C(3) by ca. 2 ppm and C(1) from C(2) by ca. 25 ppm. For the  $\mu(\eta^5 : \eta^1\text{-cyclopentadienyl})$  group C(2) is shifted from C(3) by ca. 20 ppm. The  $(\eta-C_5H_5)_2Ti$  group has one signal because of the rotation of cyclopentadienyl rings.

The results of  $^{13}C$  and  $^1H$  NMR measurements of the product A are shown in Fig. 1a. This spectrum was recorded after the THF had been evaporated under vacuo and the residue dissolved in benzene- $d_6$ . To explain the origin of signals 1–4 and 1'–4' in the  $^{13}C$  NMR spectrum and of signals 1–3 in the  $^1H$  NMR spectrum identical measurements were made for the product of reaction 2 which did not contain cyclopentadienyl rings [28].



The spectrum shown in Fig. 1b exhibits similar signals with identical  $\delta$  values, which are presented in the Experimental. These values indicate that the  $N_2$  fixation reactions 1 and 2 are accompanied by polymerization of the THF, which is reflected in the  $^{13}C$  NMR spectra (Figs. 1a and 1b), as the signals 1–4 derive from the  $[-O(CH_2)_4-]_n$  structure. The signals 1'–4' could be attributed to the carbons of

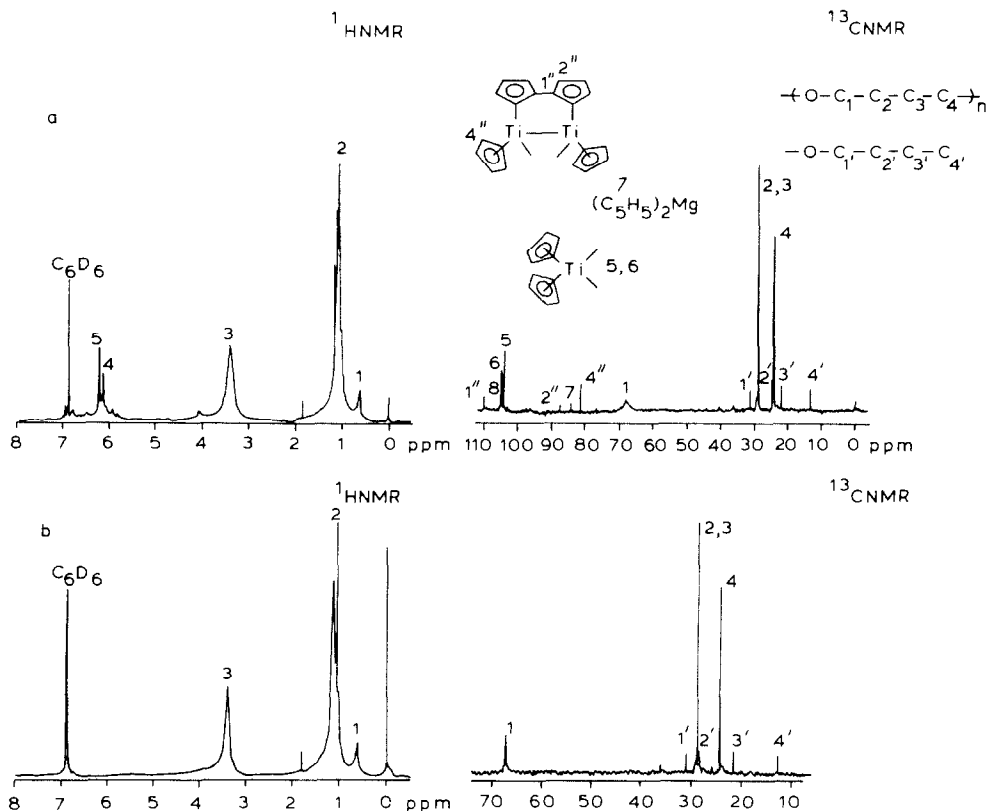


Fig. 1. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra: a) reaction product A, b) product of reaction 2.

the alkoxide group,  $\text{OC}_4\text{H}_9$ . This conclusion has found its confirmation in the  $^1\text{H}$  NMR spectrum. The block of signals 2 could be attributed to the methylene groups of the chain and signal 3 to the methylene group bound to oxygen. Signal 1 originates from the  $-(\text{CH}_2)_3\text{CH}_3$  methyl group. Additional confirmation of our conclusions was obtained experimentally. The reaction products whose spectra are shown in Fig. 1 ( $\text{HCl}$ , 1:1;  $10\text{ cm}^3$ ) produced butanol under hydrolysis. The position of signals 2'' and 1'' (Fig. 1a) in the  $^{13}\text{C}$  NMR (87.18 and 110.03 ppm) shows a pattern characteristic of a  $\mu(\eta^5: \eta^5\text{-fulvalene})$  ligand, i.e.  $\text{C}(1'')\text{-C}(2'')$  is shifted by ca. 22 ppm as in bis( $\eta^5: \eta^5\text{-fulvalene}$ )dicobalt(III), hexafluorophosphate [27]. The signal 4'' for 81.16 ppm originates from the  $\text{C}_5\text{H}_5$  group of that compound. Signals 5 and 6 in the  $^{13}\text{C}$  NMR spectrum (104.05 and 104.48 ppm) are indicative of the presence of nonequivalent  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$  groups, as was also evidenced by the  $^1\text{H}$  NMR spectra (signals 4 and 5, Fig. 1a). This spectrum shows also the protons in the range 4–6 ppm, most probably due to the shift of titanium atoms towards the  $\text{C}(1'')$ ,  $\text{C}(2'')$  and  $\text{C}(5'')$  carbons of the fulvalene ring, causing an electron density increase and shielding of the 2 and 5 protons, as for the  $\alpha$ -ferrocenylcarbonium ion [29].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the products shown in Fig. 1 indicate the

presence of a small amount of bis(cyclopentadienyl)magnesium,  $(C_5H_5)_2Mg$  [30,31].

Analysis of the  $^{13}C$  and  $^1H$  NMR spectra suggests that the product A could be a mixture of at least two compounds. To find out which compounds they might be,

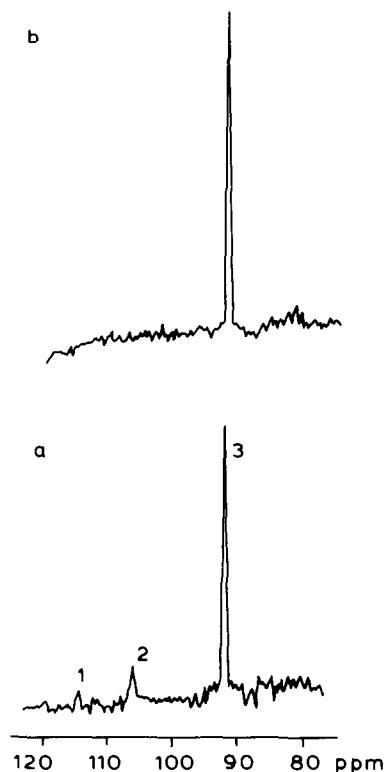
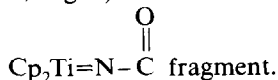


Fig. 2. The  $^{13}C$  NMR spectrum: a) of the reaction product of A with carbon monoxide, b) of the product obtained from the reaction between stoichiometrically oxidized A with  $I_2$  and carbon monoxide.

studies with carbon monoxide were carried out. When A was treated with carbon monoxide, the  $^{13}C$  NMR spectrum of the newly formed product (B) revealed the presence of the carbonyl compound  $(\eta-C_5H_5)_2Ti(CO)_2$  as the main product (signal 3; Fig. 2) and showed a signal (1) with  $\delta$  118.94 ppm, deriving most probably from a

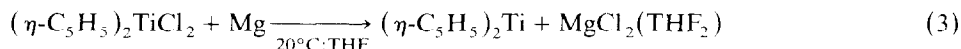


In this spectrum is also present a signal (2), at  $\delta$  105.48 ppm, close to that of signal 8 in the spectrum of the product A. Signal 2 could originate from the cyclopentadienyl rings of  $\mu(\eta^5: \eta^5-C_{10}H_8)-\mu(H)_2(\eta-C_5H_5)_2Ti_2$ , a compound which reacts neither with  $N_2$  nor with CO [32,33].

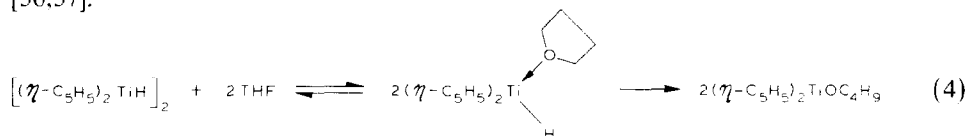
It is interesting that after oxidation of product A with a stoichiometric amount of  $I_2$ , followed by the reaction with CO, the  $^{13}C$  NMR spectrum of post-reaction mixture is similar to that of the product (B) (Fig. 2), which is the evidence that under these conditions the fixed nitrogen undergoes oxidation first: a confirmation of our prior conclusion drawn from the studies of the chemical properties of the nitrogen fixed in A.

## Conclusions

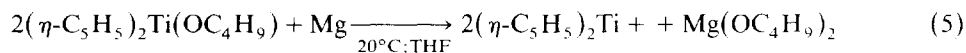
Our results together with the literature data revealed that the  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$  formed in the first stage was unstable.



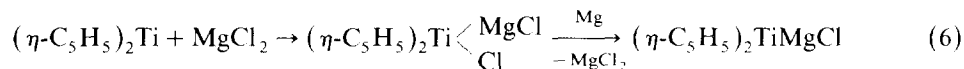
The formation of the bis( $\eta$ -cyclopentadienyl)titanium intermediate is responsible for the very complicated reaction pathway under these conditions. Titanocene most likely undergoes rearrangement by  $\alpha$ -hydrogen abstraction to yield  $\mu(\eta^5 : \eta^5\text{-C}_{10}\text{H}_8)\text{-}\mu(\text{H})_2(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}_2$  and also probably the  $[(\eta\text{-C}_5\text{H}_5)_2\text{TiH}]_2$  hydride compound [36,37].



$[(\eta\text{-C}_5\text{H}_5)_2\text{TiH}]_2$  is unstable at room temperature and by reaction with THF the alkoxy compound [14] is formed. The alkoxy compound undergoes reduction since reaction 1 proceeds in the presence of excess magnesium.



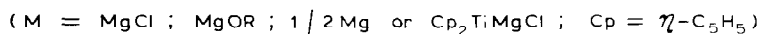
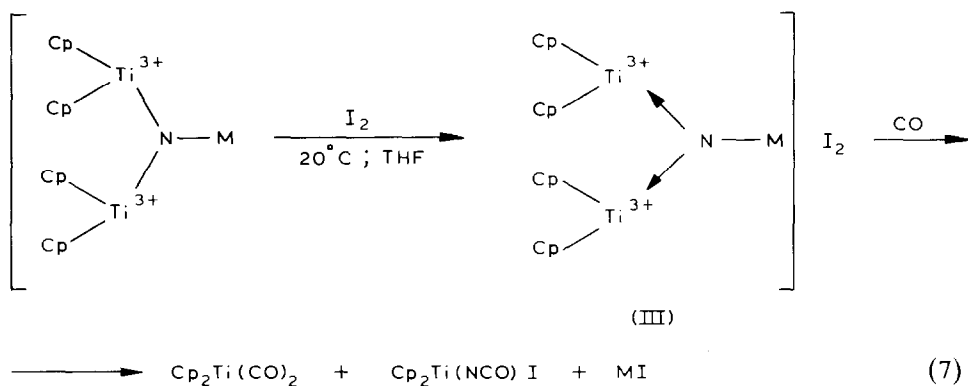
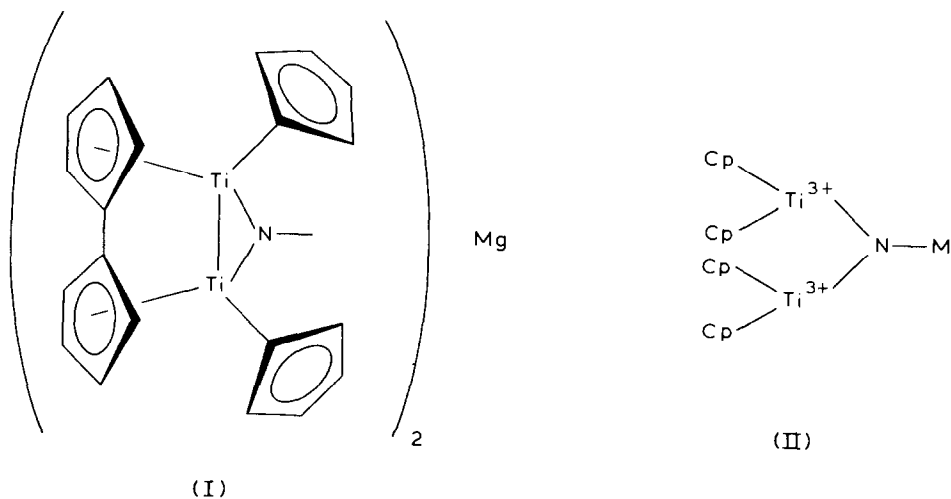
That the alkoxy group is combined with magnesium is evidenced by the similar  $\delta$  values in the  $^1\text{H}$  NMR spectrum (Figs. 1a and 1b). Titanocene could also react with the magnesium chloride, formed in reaction 3.



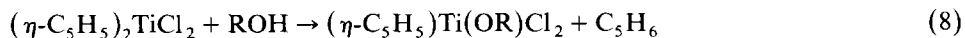
As the result of oxidative addition of  $\text{MgCl}_2$ ,  $\text{Cp}_2\text{Ti}(\text{Cl})\text{MgCl}$  is formed which next undergoes reduction. This reaction explains the formation of the  $-\text{Ti}-\text{MgCl}$  bond, as suggested by elemental analysis of the product A.

The reactions discussed here have a direct influence on the  $\text{N}_2$  fixation process. Dinitrogen forms a bridge between the titanium compounds in which the titanium is in oxidation state two  $\text{Ti}^{2+}$ . The coordinated dinitrogen ( $\mu_2\text{-N}_2$ ) coordinates by its free electron pairs of the titanium compounds present in solution which alone are not capable of  $\text{N}_2$  fixation, e.g.  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}-\text{MgCl}$ . The products of such a reaction are compounds in which dinitrogen is coordinated in the  $\mu_3\text{-N}_2$  and  $\mu_4\text{-N}_2$  states, and which undergoes further reduction by magnesium. The final products are compounds of the type I and II.

The number of compounds in the mixture A may be greater, because of the possibility of other combinations. However, the bridge bonding of nitrogen between the titanium and M atoms remains always the basic element. For simplification, we have considered here only the case where the cyclopentadiene rings only are involved. The type I and II bonding forms explain the properties of the fixed nitrogen. In the oxidation process the nitride nitrogen,  $\text{N}^{3-}$ , undergoes oxidation to the imide nitrogen,  $\text{N}^{-1}$ , capable of formation of stable bonds with the titanium atoms [37]. The compound III reacts with CO in the disproportionation reaction [23,26,37,38] and consequently the compounds described in eq. 7 are formed. The compound  $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}-\text{N}=\text{N}-\text{Ti}(\eta\text{-C}_5\text{H}_5)_2$  cannot be formed in reaction 1, be-



cause it is unstable under these conditions [19,20]. The presence of (η-C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> after hydrolysis and of ferrocene after the reaction with FeCl<sub>2</sub> can be explained equally well in terms of the reaction with (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg and the electrophilic influence of the alkoxy group OC<sub>4</sub>H<sub>9</sub>. The exchange of a cyclopentadienyl group for an alkoxy group, under the influence of alcohol has been reported [39,40].



It seems very likely that in our case the mechanism of the exchange of cyclopentadienyl groups follows a similar pattern. The (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mg compound can react with the MgCl<sub>2</sub> formed in reaction 1, to produce C<sub>5</sub>H<sub>5</sub>MgCl [31]. The latter compound is responsible for the presence of mainly bis(η-cyclopentadienyl)-type titanium compounds in the investigated system.

## Experimental

All manipulations were carried out under pure, dry argon and dinitrogen, using Schlenk tube and vacuum line techniques. THF was purified before use by distillation under argon from sodium and benzophenone. The  $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  was obtained commercially from Fluka AG; Grignard Mg turnings and THF were obtained from POCH-Gliwice and  $\text{C}_6\text{H}_6$  from IBJ Swierk/Otwock.

*Reaction of bis( $\eta$ -cyclopentadienyltitanium) dichloride with magnesium under dinitrogen*  
 $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$  (1.8 g, 7.5 mmol) was dissolved in tetrahydrofuran (50 cm<sup>3</sup>) under dinitrogen and excess of magnesium turnings (3 g) was added upon stirring. The reaction was exothermic and the colour of the solution turned from red through green to red-brown. After 24 h 39 cm<sup>3</sup> N<sub>2</sub> was fixed. The post-reaction mixture [M] was evaporated under vacuo. Next, unreacted magnesium was filtered off. The residue was extracted with benzene to leave MgCl<sub>2</sub>. Benzene solution (product A) was examined by <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy. After evaporation to dryness the elemental analysis was performed.

### *Elemental analysis*

Titanium was determined colorimetrically, magnesium complexometrically, by means of the EDTA, and Cl<sup>-</sup> by the Mohr method. Nitrogen was determined by usual routine method by distillation of NH<sub>3</sub> with steam and by titration of the excess acid with a base. The liberated N<sub>2</sub> was measured with a burette. Its composition was controlled by GLC (5 m column, molecular sieves X13, temp. 293 K). Found: N, 3.01; Cl, 16.81; Mg, 19.89; Ti, 20.55 corresponding to a Ti : N : Mg : Cl ratio of 1 : 0.5 : 1.95 : 1.1.  $(\eta\text{-C}_5\text{H}_5)\text{TiCl}_3$  was determined after passing gaseous HCl through the solution M.

Ferrocene was detected after introduction of FeCl<sub>2</sub> into the post-reaction mixture M. Determinations were made as reported in literature [21.22].

### *Reaction with carbon monoxide*

The post-reaction mixture M was left under carbon monoxide with stirring. The amount of carbon monoxide fixed in 5 h was CO/Ti  $\approx$  1.7. The IR spectrum in THF shows the frequencies 1881vs and 1965vs cm<sup>-1</sup>.

After evaporation of THF in vacuo the residue was transferred under argon to a glass ampoule filled with 2 cm<sup>3</sup> CH<sub>3</sub>I; the ampoule was sealed and heated for 24 h at 373 K. The solution in the ampoule was removed from the precipitate and analyzed by GLC (3 m column; 6% carbowax 20M; 0.8% KOH; chromosorb N; temp. 498 K) *N,N*-dimethylacetamide was detected in 18% yield, calculated with respect to the nitrogen fixed.

When the post-reaction mixture M was oxidized under M with a stoichiometric amount of I<sub>2</sub> (3.75 mmol; 0.95 g), the N<sub>2</sub> atmosphere was replaced by CO, and the mixture was stirred, the amount of the carbon monoxide fixed in 5 h was CO/Ti  $\approx$  1.

The IR spectrum in THF shows the frequencies 1881vs, 1965vs, 2230m and 2198m cm<sup>-1</sup>;

### *<sup>1</sup>H and <sup>13</sup>C NMR measurements*

The <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker NIC 360 (Figs. 1a and 1b) and Jeol-JNM-PS-100 (Fig. 2) spectrometers.



All measurements were made in benzene- $d_6$  and chemical shifts are in ppm relative to external TMS. Fig. 1a;  $^1\text{H}$  NMR,  $\delta$ ; (1) 0.75; (2) 1.12; (3) 3.42; (4) 6.15; (5) 6.26;  $^{13}\text{C}$  NMR, ( $4'$ ) 13.15; ( $3'$ ) 21.82; ( $2'$ ) 24.83; ( $1'$ ) 31.37; (4) 24.03; (3) 30.25 (2) 29.06 (1) 58.02; ( $4''$ ) 81.16; ( $2''$ ) 84.02; ( $3''$ ) 87.18; ( $1''$ ) 110.04; (5) 104.05; (6) 104.48; (7) 105.48.

Fig. 1b:  $^1\text{H}$  NMR, (1) 0.74; (2) 1.14; (3) 3.42;  $^{13}\text{C}$  NMR, ( $4'$ ) 13.17; ( $3'$ ) 21.85; ( $2'$ ) 28.82; ( $1'$ ) 31.41; (4) 24.52; (3) 30.12; (2) 28.93; (1) 69.28.

Fig. 2a:  $^{13}\text{C}$  NMR, (1) 92.08.

Fig. 2b:  $^{13}\text{C}$  NMR, (1) 92.08.

### Acknowledgement

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### References

- 1 M.E. Volpin and V.B. Shur, *Nature* (London), 209 (1966) 1236.
- 2 M.E. Volpin and V.B. Shur, *J. Organometal. Chem.*, 200 (1980) 319.
- 3 M.E. Volpin and V.B. Shur in *New Trends in the Chemistry of Nitrogen Fixation*, Academic Press, New York 1980, p. 67.
- 4 J.H. Teuben, p. 233.
- 5 A.E. Shilov, *Russ. Chem. Rev.*, 43 (1974) 378.
- 6 E.E. Van Tamelen, *Accounts Chem. Res.*, 3 (1970) 361.
- 7 G.P. Pez and J.N. Armor, *Adv. Organometal. Chem.*, 19 (1981) 1, and references cited therein
- 8 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 94 (1972) 1219.
- 9 G.P. Pez, *J. Amer. Chem. Soc.*, 98 (1976) 8072.
- 10 J.E. Bercaw, *J. Amer. Chem. Soc.*, 96 (1974) 5087; R.D. Sanner, D.M. Duggan, T.C. McKenzie, R.E. Marsh and J.E. Bercaw, *ibid.*, 98 (1976) 8358.
- 11 J.D. Zeinstra, J.H. Teuben and F.J. Jellinek, *J. Organometal. Chem.*, 170 (1979) 39; R.W. van der Weij and J.H. Teuben, *ibid.*, 120 (1976) 223.
- 12 A.E. Shilov, A.K. Shilova and E.F. Krashina, *Kinet. Katal.*, 10 (1969) 1402.
- 13 E.E. van Tamelen, W. Cretney, N. Klaentschi and J.S. Miller, *J. Chem. Soc. Chem. Commun.*, (1972) 481.
- 14 J.E. Bercaw, R.H. Marvich, L.G. Bell and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 94 (1972) 1219.
- 15 G.P. Pez, P. Apgar and R.K. Crissey, *J. Amer. Chem. Soc.*, 104 (1982) 448.
- 16 M.E. Volpin, V.B. Shur and M.A. Ilatovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 9 (1964) 1728.
- 17 E. Bayer and V. Schuring, *Chem. Ber.*, 102 (1964) 3378.
- 18 G. Henrici-Olive and S. Olive, *Angew. Chem. Int. Ed.*, 8 (1969) 650.
- 19 Yu.G. Borodko, I.N. Ivleva, L.M. Kachapina, S.I. Salienco, A.K. Shilova and A.E. Shilov, *J. Chem. Soc. Chem. Commun.*, (1972) 1178.
- 20 Yu.G. Borodko, I.N. Ivleva, L.M. Kachapina, E.F. Kvashina, A.K. Shilova and A.E. Shilov, *J. Chem. Soc. Chem. Commun.* (1973) 169.
- 21 F.W. van der Weij and J.H. Teuben, *J. Organometal. Chem.*, 120 (1976) 223.
- 22 F.W. van der Weij, H. Scholtens and J.H. Teuben, *J. Organometal. Chem.*, 127 (1977) 299.
- 23 P. Sobota and Z. Janas, *Inorg. Chim. Acta. Lett.*, 53 (1981) L11.
- 24 J.L. Burmeister, E.A. Deardorff, A. Jensen and V.H. Christiansen, *Inorg. Chem.*, (1970) 58; J.L. Burmeister, E.A. Deardorff and C.E. Van Dyke, *Inorg. Chem.*, (1969) 170.
- 25 P. Sobota, B. Jezowska-Trzebiatowska and Z. Janas, *J. Organometal. Chem.*, 118 (1976) 253.
- 26 E.J.M. de Boer, L.C.T. Cate, A.G.J. Staring and J.H. Teuben, *J. Organometal. Chem.*, 181 (1979) 61.
- 27 A. Davison and S.S. Wreford, *J. Amer. Chem. Soc.*, 96 (1979) 3017.
- 28 A. Yamamoto, S. Go, M. Ookawa, M. Tahahashi, S. Ikeda and T. Keii, *Bull. Chem. Soc. Jap.* 45 (1972) 3100.
- 29 F.L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, 91 (1969) 1258.

- 30 P.C. Lauterbur and R.B. King, *J. Amer. Chem. Soc.*, 87 (1965) 3266; T. Saito, *Chem. Commun.*, (1971) 1422.
- 31 W.T. Ford and J.B. Grutzner, *J. Org. Chem.*, 37 (1972) 2561.
- 32 F. Calderazzo, J.J. Salzmann and P. Mosimann, *Inorg. Chim. Acta.*, 1 (1967) 65.
- 33 H.H. Brintzinger and J.E. Bercaw, *J. Amer. Chem. Soc.*, 92 (1970) 6182.
- 34 M.E. Volpin, V.A. Dubovitskii, O.V. Nogina and D.N. Kursonov, *Dokl. Akad. Nauk SSSR, Ser. Khim.*, 151 (1963) 1100.
- 35 J.W. Lauher and R. Hoffmann, *J. Amer. Chem. Soc.*, 98 (1976) 1729.
- 36 R.H. Marvich and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 91 (1969) 7301
- 37 P. Sobota, T. Płuziński and S. Rummel, *Tetrahedron* 37 (1981) 939.
- 38 M. Kubota, T.G. Chappell and S.P. Powers, *Inorg. Chem.*, 12 (1979) 3615.
- 39 A.N. Nesmeyanov, O.W. Nogina, A.M. Bierlin, A.S. Girshovich and G.W. Shatalov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1961) 2146.
- 40 A.N. Nesmeyanov, O.W. Nogina, N.A. Lazarieva and V.A. Dubovitskii *Izv. Akad. Nauk SSSR Ser. Khim.*, (1967) 808.