Journal of Organometallic Chemistry, 276 (1984) 171–176
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

FORMATION OF A NITROGEN–CARBON BOND FROM N_2 AND CO. INFLUENCE OF $MgCl_2$ ON THE N_2 REDUCTION PROCESS IN THE SYSTEM $TiCl_4/Mg$

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(Received May 29th, 1984)

Summary

$TiCl_4(THF)_2$ is reduced by Mg in tetrahydrofuran under N_2 to $TiNMg_2Cl_2(THF)$ (I), which reacts further with CO. As a result, $TiCONMg_2Cl_2(THF)$ is obtained, which reacts with CH_3I to produce $(CH_3)_2NCOCH_3$ in 73% yield. This is indicative of the amide character of nitrogen in I. Upon reaction with I_2, the amide nitrogen in I is oxidized to imide. The new compound, TiNMgCl(THF) (II), was found to form Ti(NCO)MgCl(THF) on reaction with CO. $TiCl_4(THF)_2$, recognized as a strong Lewis acid, detaches one Cl^- from $MgCl_2(THF)_2$ formed in the reaction. The $[MgCl(THF)_n]^+$ cation influences the N_2 reduction and determines the amide character of the nitrogen atom in species I.

In many chemical reactions, Groups IA–IIIA elements in non-aqueous solutions having donor properties are used as reducing agents for the transition-metal halogenides MX_n. Such systems, as shown by Vol'pin and Shur [1,2], take up and reduce dinitrogen under mild conditions and give NH_3 under hydrolysis. This is indicative of the splitting of the nitrogen–nitrogen triple bond and the formation of mononitrogen species in these reactions. Such reactions also yield AX, which, in our opinion, can react either with reduced nitrogen or with the substrate MX_n. Particularly active in the N_2 fixation process are low-valent titanium compounds and for this reason we chose them for our studies. When $TiCl_4(THF)_2$ is reduced by magnesium turnings under dinitrogen in tetrahydrofuran (THF), a material formulated as $TiNMg_2Cl_2(THF)$ (I) is formed:

$$2TiCl_4(THF)_2 + 6Mg + N_2 \xrightarrow[293\ K]{THF} \underset{(I)}{2TiNMg_2Cl_2(THF)} + 2MgCl_2(THF)_2 \qquad (1)$$

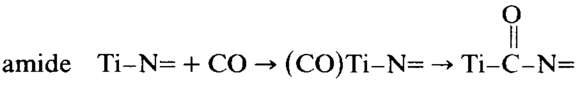
Hydrolysis of I liberates a stoichiometric amount of ammonia [3]. We report herein the results of our attempts to elucidate the properties and reactivity of nitrogen in I and the influence of $MgCl_2(THF)_2$ formed on the course and final result of reaction 1.

0022-328X/84/$03.00

Results and discussion

It should be expected that the nitrogen atom in the $TiNMg_2Cl_2(THF)$ product would appear in one of three possible forms: nitride $Ti{\equiv}N$, amide $T{-}N{=}$, imide $Ti{=}N{-}$, or as a mixture of all three. To define the character of the nitrogen atom in I it was necessary to find a molecule or compound which would react easily with the titanium mononitrogen species, the reaction product of which would be indicative of the character of the nitrogen atom in $TiNMg_2Cl_2(THF)$. Carbon monoxide was found to meet such a requirement. Taking the oxophilic properties of the titanium atom into account [4,5], we expected the reaction product of species I and carbon monoxide to depend upon the character of the nitrogen atom e.g.:

$$\text{nitride}\quad \text{Ti}{\equiv}\text{N} + \text{CO} \rightarrow (\text{CO})\text{Ti}{\equiv}\text{N} \rightarrow \text{TiO}^+ + \text{CN}^- \tag{2}$$



$$\text{amide}\quad \text{Ti}{-}\text{N}{=} + \text{CO} \rightarrow (\text{CO})\text{Ti}{-}\text{N}{=} \rightarrow \text{Ti}{-}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}{-}\text{N}{=} \tag{3}$$

$$\text{imide}\quad \text{Ti}{=}\text{N}{-} + \text{CO} \rightarrow (\text{CO})\text{Ti}{=}\text{N}{-} \rightarrow \text{TiNCO} \tag{4}$$

To illustrate the problem, we have simplified reactions 2–4. The reaction of "titanium nitride" with carbon monoxide should produce cyanate and titanium monoxide compounds because the oxygen atom is more electronegative than the nitrogen atom and would thus form more stable bonds with the titanium atom. Formally, amide has one electron less than nitride, and therefore the reaction should follow equation 3. The properties of the imide nitrogen should be close to those of the nitride nitrogen, and the formation of isocyanate in reaction 4 should be expected.

Reaction with N_2

For examination of all the nitrogen compounds, after completion of reaction 1, only excess magnesium turnings were removed. This post-reaction mixture was denoted as **A**; the same product, but containing the ^{15}N isotope, was denoted as $\mathbf{A}_1$. ^{15}N NMR examination did not explain explicitly in what form the nitrogen atom appears in this product. The ^{15}N NMR spectrum shows only one broad signal (300 ppm), with a maximum at 0 ppm. $NH_4{}^+$ was used as the reference, with the assumption of δ -353 ppm [6]. The width of the observed signal proved only that the nitrogen atom in $\mathbf{A}_1$ is bonded to the paramagnetic titanium atoms.

Reaction with carbon monoxide

In the reaction of **A** with carbon monoxide, $CO/Ti = 1$ was fixed. The IR spectrum of the new product (**B**) does not show either $\nu(CO)$ or $\nu(NCO)$ frequencies. Mass spectrometric measurements of **B** allowed the TiCON(THF) fragment and the $Mg(CN)_2(THF)_2$ compound to be identified. After evaporation of **B** in vacuo to dryness, the residue was treated with methyl iodide (CH_3I) to form *N,N*-dimethylacetamide, $(CH_3)_2NCOCH_3$, in 73% yield (calculated from the amount of fixed dinitrogen). The formation of $(CH_3)_2NCOCH_3$ in the reaction with CH_3I confirmed the mass spectrometric results about the appearance of the $-CON{=}$ group in the reaction product **B**. It was not known, however, which one, the carbon atom or the nitrogen atom, formed the bonding with the titanium atom. To answer this question, we studied the reaction between A_1 containing ^{15}N isotope and ^{13}CO. The product $\mathbf{B}_1$ was examined by ^{13}C NMR. The spectrum shows two signals: a broad one at 125.5 ppm indicating that the ^{13}C atom of the –CON= group is bonded to the paramagnetic titanium atom; and a second one at 155.3 ppm, with $J(^{13}C-^{15}N)$ 5.6 Hz. This value is in good agreement with the value (6.1 Hz) observed for the $^{13}C^{15}N^-$ ion [7]. The observed signal therefore derives from $Mg(CN)_2(THF)_n$. The IR spectrum of **B** shows only one very weak band at 2030 cm^{-1}, originating from $\nu(CN^-)$. Attempts to isolate magnesium cyanate in a pure form failed. For this reason, the number of THF molecules in the formula $Mg(CN)_2(THF)_n$ was denoted by "n". The IR spectra suggest that only a very small amount of nitrogen produced the cyanate in the reaction with CO. Product **A** is, in our opinion, practically the same as species I, and the nitrogen atom in it formally has the amide character.

$$TiNMg_2Cl_2(THF) + CO \rightarrow \underset{(II)}{TiCONMg_2Cl_2(THF)} \qquad (5)$$

That the reaction of CH_3I with compound II produced 73% $(CH_3)_2NCOCH_3$ could be due to the fact that the reaction did not go to completion.

Reaction with I_2

To obtain additional confirmation of the amide character of the nitrogen atom, species I was oxidized with diiodine [8]. In this reaction, TiNMgCl(THF) (III) was formed. Compound III entered into stoichiometric reaction with carbon monoxide to yield the isocyanate Ti(NCO)MgCl(THF) (IV) (ν(NCO) 2197 cm^{-1},s).

$$\underset{(III)}{TiNMgCl(THF)} + CO \xrightarrow[293\ K]{THF} \underset{(IV)}{Ti(NCO)MgCl(THF)} \qquad (6)$$

This means that during the reaction with I_2, the nitrogen atom changes its character from an amide to an imide one, and the course of reaction 6 is similar to that of reaction 4 postulated by us.

The reaction between diiodine and species I can be written as:

$$Ti{-}N(MgCl)_2 + \tfrac{1}{2}I_2 \rightarrow [ITi{-}N(MgCl)_2] \xrightarrow[-MgClI]{} Ti{=}N(MgCl) \qquad (7)$$

For simplification, the coordinated THF molecules were omitted from reaction 7. In the first stage of the reaction, the titanium atom undergoes oxidation to form, probably, the unstable intermediate compound [I–Ti–N(MgCl)$_2$]; as a result of reductive elimination Ti=N(MgCl) arises. This reaction most probably follows the pattern of amide deprotonation or imide protonation reactions [9].

$$M^n{=}NH \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} M^{n+1}{-}NH_2 \qquad (8)$$

Reaction 8 can be regarded as the oxidative addition or reductive elimination process, depending on its direction.

Reaction with $MgCl_2$

The amide character of the nitrogen atom in species I suggests that the magnesium atom forms the direct bond with the nitrogen atom. This type of bond has previously been proposed for, e.g., nitrogen species obtained by the reduction of titanium compounds with RMgX [10,11] or with metallic magnesium [12]. It was interesting to find out whether magnesium chloride would react with the $TiCl_4(THF)_2$ compound in THF. The compound $[TiCl_4(\mu\text{-}Cl)_2Mg(THF)_4]$ (V) was obtained by mixing $TiCl_4(THF)_2$ and $MgCl_2(THF)_2$ in a 1/1 molar ratio, in tetrahydrofuran [13].

$$TiCl_4(THF)_2 + MgCl_2(THF)_2 \xrightarrow[293\ K]{THF} \underset{(V)}{[TiCl_4(\mu\text{-}Cl)_2Mg(THF)_4]} \quad (9)$$

However, when the same compounds are mixed in a 1/2 molar ratio, compound VI is produced [14].

$$TiCl_4(THF)_2 + 2MgCl_2(THF)_2 + THF \rightarrow \underset{(VI)}{[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5THF]} \quad (10)$$

The structures of V and VI have been resolved by X-ray analysis. In $[TiCl_4(\mu\text{-}Cl)_2Mg(THF)_4]$, the titanium and magnesium atoms are bonded through two chlorine atoms [13]. Compound VI has an ionic structure [14] and is composed of a $[TiCl_5(THF)]^-$ anion and a $[(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]^+$ cation. The structures of both compounds proved that $TiCl_4(THF)_2$ is a strong Lewis acid and prefers Cl^- anions to the THF molecule; for this reason, it removes two chlorides from $MgCl_2(THF)_2$ and forms compound V in reaction 9. In reaction 10, $TiCl_4(THF)_2$ removes Cl^- from bis(tetrahydrofuran)magnesium chloride to form the $[MgCl(THF)_n]^+$ cation and the $[TiCl_5(THF)]^-$ anion. $[MgCl(THF)_n]^+$ finds a better donor than THF in the chloride from magnesium chloride and in the presence of "excess" $MgCl_2(THF)_2$ (1/2) forms $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$.

$$[MgCl(THF)_n]^+ + MgCl_2(THF)_2 \xrightarrow{THF} [(THF)_3Mg(\mu\text{-}Cl)_3Mg(THF)_3]^+ \quad (11)$$

It was interesting to discover whether bis(tetrahydrofuran)magnesium chloride would behave similarly in the presence of other non-metal acids, e.g. in the presence of the $[NBu_4]^+$ cation.

$$2[NBu_4][BF_4] + 2MgCl_2(THF)_2 \xrightarrow{THF}$$

$$[NBu_4]_2[MgCl_4]\cdot 2THF + [Mg(THF)_n][BF_4]_2 \quad (12)$$

X-Ray analysis revealed that the bis(tetra-n-butylammonium) tetrachloromagnesate(II)-bis(tetrahydrofuran) crystals formed are composed of a $[MgCl_4]^{2-}$ anion, a $[NBu_4]^+$ cation and two THF molecules, non-coordinated with the metal ion, built into a crystal lattice [15]. From equation 12, it follows that also $[Mg(THF)_n][BF_4]_2$,besides $[NBu_4]_2[MgCl_4]\cdot 2THF$, should be formed. However, all attempts to isolate it in a pure form failed. In reaction 12, the magnesium atom exhibits amphoteric behaviour since $MgCl_2(THF)_2$ is a donor and an acceptor, Cl^- all-in-one and, this being so, the $[Mg(THF)_n]^{2+}$ cation and the $[MgCl_4]^{2-}$ anion are formed.

Conclusion

Up-to-date studies on the reactivity of bis(tetrahydrofuran)magnesium chloride have revealed that the magnesium atom in THF solution under acid treatment can produce the following ions: $[Mg(THF)_n]^{2+}$, $[MgCl(THF)_n]^+$, $[Mg_2(\mu\text{-}Cl)_3(THF)_6]^+$ and $[MgCl_4]^{2-}$. This indicates that reaction 1 proceeds, in reality, in an acid medium and it is obvious that the nitrogen atom in the $TiNMg_2Cl_2(THF)$ species has only the amide character (reactions 7 and 8).

Experimental

All reactions were carried out under dinitrogen using dried THF and conventional Schlenk apparatus. Tetrahydrofuran was distilled under N_2 from sodium and benzophenone. $TiCl_4(THF)_2$ and $MgCl_2(THF)_2$ were obtained by literature methods [16,17]. Grignard Mg turnings and THF were obtained from POCh, Gliwice; isotopic dinitrogen, $^{15}N_2$, (98.7%) was from VEB Technische Gase, Leipzig; and carbon monoxide, ^{13}CO, (99.8%) and THF-d_8 were from Isocomerz GmbH, Berlin (G.D.R.). ^{13}C NMR spectra were recorded on a Jeol-JNM-PS-100 instrument in THF-d_8 and ^{15}N NMR spectra on a JEOL-400 instrument in THF-d_8 in a co-axial cell, using NH_4NO_3 as the standard. Microanalyses were performed at the University of Wrocław.

Reaction of $TiCl_4(THF)_2$ with Mg under N_2 in tetrahydrofuran

$TiCl_4(THF)_2$, 2.1 g (6.3 mmol), was dissolved in THF (50 cm^3) under dinitrogen and excess magnesium turnings (3 g) were added under stirring. The reaction was exothermic and the colour of the solution turned from yellow to black. After 2 h, 70 cm^3 of N_2 was fixed and then unreacted magnesium was filtered off. Such a prepared solution was denoted as **A**, while the same mixture obtained under $^{15}N_2$ was denoted as $\mathbf{A}_1$.

Reaction of A with carbon monoxide

The post-reaction mixture **A** was left under carbon monoxide, under stirring. The amount of carbon monoxide fixed in 5 h was CO/Ti = 1. After evaporation of THF in vacuo, the residue was transferred under dinitrogen to a glass ampoule filled with 2 cm^3 of CH_3I; the ampoule was sealed and heated for 24 h at 373 K. The solution in the ampoule was removed from the precipitate and analysed by GLC (3 m column; 6% Carbowax 20M; 0.8% KOH; Chromosorb N, temperature 498 K). *N,N*-Dimethylamide was detected in a 73% yield, calculated with respect to the fixed dinitrogen.

Reaction of A_1 with ^{13}CO

The post-reaction mixture of $\mathbf{A}_1$ was evaporated in vacuo to dryness and then dissolved in THF-d_8 (10 cm^3) and left under ^{13}CO, under stirring. After 5 h, the solution was filtered and analysed by ^{13}C and ^{15}N NMR methods.

Reaction of A with I_2

To the post-reaction mixture of **A** was added I_2 (0.8 g; 3.15 mmol) under dinitrogen, upon stirring. The white precipitate formed was filtered off. Pentane (5 cm^3) was added to the filtrate. A dark-brown precipitate settled, which was filterd off, washed with n-pentane (3 × 10 cm^3), and dried in vacuo. Found: C, 25.01; H, 4.31; N, 6.89; Cl, 18.79; Mg, 12.61; Ti, 24.17%. TiNMgCl(THF) calcd.: C, 24.79; H, 4.12; N, 7.22; Cl, 18.30; Mg, 12.55; Ti, 24.72%.

Synthesis of $[TiCl_4(\mu\text{-}Cl)_2Mg(THF)_4]$

3.6 g (10.7 mmol) of $TiCl_4(THF)_2$ and 2.5 g (10.7 mmol) of $MgCl_2(THF)_2$ were dissolved in 50 and 30 cm^3, respectively, of hot THF (343 K) under N_2 and stirring. Next, at room temperature, the solutions were mixed and left for crystallization. After 24 h, yellow crystals were filtered off and washed with tetrahydrofuran (3 × 5 cm^3). Yield: 59%. Found: C, 24.19; H, 4.11; Cl, 26.68; Mg, 2.96; Ti, 6.03%. $C_{16}H_{32}Cl_6MgTi$ calcd.: C, 24.42; H, 4.03; Cl, 26.78; Mg, 3.06; Ti, 6.03%.

Synthesis of $[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)]$

2.1 g (6.3 mmol) of $TiCl_4(THF)_2$ and 2.1 g (12.6 mmol) of $MgCl_2(THF)_2$ were dissolved in 25 and 31 cm^3, respectively, of hot THF (343 K) under N_2 and stirring. Next, at room temperature, the solutions were mixed and left for crystallization. After 24 h, yellow crystals were filtered off and washed with THF (3 × 5 cm^3). Yield: 48%. Found: C, 38.03; H, 6.39; Cl, 31.91; Mg, 5.52; Ti, 5.51%. $C_{28}H_{56}Cl_8Mg_2Ti$ calcd.: C, 37.97; H, 6.33; Cl, 32.65; Mg, 5.49; Ti, 5.41%.

Acknowledgement

The authors are grateful to Prof. D. Sellmann, Erlangen-Nürnberg University, for allowing us to carry out studies with the $^{15}N_2$ isotope in his laboratory.

References

1 M.E. Vol'pin and V.B. Shur in New Trends in the Chemistry of Nitrogen Fixation, Academic Press, New York, 1980, p.67.
2 M.E. Vol'pin and V.B. Shur, J. Organomet. Chem., 200(1980)319.
3 A. Yamamoto, S. Go, M. Ookawa, M. Tahahashi, S. Iked and T. Keii, Bull. Chem. Soc. Jn., 45(1980)3110.
4 T.-L. Ho, Synthesis, (1979)1.
5 P. Sobota, B. Jeżowska-Trzebiatowska, Coord. Chem. Rev., 26(1978)71.
6 J. Chatt, M.E. Fakley, R.L. Richards, J. Mason and I.A. Stenhouse, J. Chem. Res. (S), (1979)322.
7 M. Sano, Y. Yashikawa and H. Yamatera, Inorg. Chem., 21(1982)2520.
8 P. Sobota and Z. Janas, J. Organomet. Chem., 243(1983)35.
9 R.A. Henderson, G. Davies, J.R. Dilworth and R.N.F. Thoeneley, J. Chem. Soc., Dalton Trans., (1981)40.
10 Yu.G. Borodko, I.N.Ivleva, L.M. Kachipina, S.I.Salienko, A.K. Shilova and A.E. Shilov, Chem. Commun., (1972)1178.
11 Yu.G. Borodko, I.N. Ivleva, L.M. Kachipina, E.F. Kvashina, A.K. Shilova and A.E. Shilov, Chem. Commun., (1973)169.
12 P. Sobota, B. Jeżowska-Trezbiatowska and Z. Janas, J. Organomet. Chem, 118(1976)253.
13 J.C.J. Bart, I.W. Bassi, M. Calcatera, E. Albizzati, U. Giannini and S. Parodi, Z. Anorg. All. Chem., 482(1981)121.
14 P. Sobota, J. Utko and T. Lis, J. Chem. Soc., Dalton Trans., in press.
15 P. Sobota, T. Płuziński and T. Lis, in press.
16 L.E. Mazner, Inorg. Synth., 21(1982)135.
17 E.C. Ashby and R.C. Arnott, J. Organomet. Chem., 14(1968)1.