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Utilisation of Dinitrogen in the Synthesis of Isocyanate and Amides

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The investigations concerning complexes with end-on or end-on bridging coordinated dinitrogen molecule carried out so far, enabled a partial explanation of the reduction and protonation mechanism of dinitrogen [1, 2]. However little is known hitherto on the properties of nitrogen contained in compounds which are formed in the reaction of N_2 with simple halogen compounds of titanium, vanadium, chromium and others in a reducing medium [3, 4].

It is known that reacting titanium trichloride, metallic magnesium in tetrahydrofuran (THF) under dinitrogen, $TiNMg_2Cl_2THF$(I) is formed. Hydrolysis of this compound liberates the stoichiometric amount of ammonia [5]:

$$2TiCl_3(THF)_3 + 5Mg + N_2 \xrightarrow[-2THF]{} 2TiNMg_2Cl_2THF + MgCl_2(THF)_2 \qquad (1)$$

(I)

Compound (I) reacts easily with Lewis acids like CO_2 or CS_2 and the corresponding isocyanate or thioisocyanate derivatives of titanium with a 50% yield are formed [6].

$$TiNMg_2Cl_2THF + CX_2 \xrightarrow[THF]{} [Ti(NCX)(X)Mg_2Cl_2(THF)_3] \qquad (2)$$

where X = O or S.

In this letter we report the results of the investigation of the properties of the nitrogen atom in compound (I).

Results and Discussion

To explain the mechanism of reaction (2) a similar reaction but with carbon monoxide was performed.

$$TiNMg_2Cl_2THF + CO \rightarrow [A] \xrightarrow{CH_3I} (CH_3)_2NCOCH_3 \qquad (3)$$

As a result of stoichiometric reaction the intermediate [A] is formed. Its IR spectrum does not reveal either ν_{CO} or ν_{NCO} frequencies. However, if intermediate [A] is reacted with methyl iodide, the organic compound N,N-dimethylacetamide is formed with a 73% yield. The obtained N,N-dimethylacetamide demonstrates that intermediate [A] formed in reaction (3) incorporates an isocyanate group which is reductively transformed, in the complex, to $=N-\overset{O}{\overset{\|}{C}}-$ group followed by the reaction of this group with methyl iodide giving $(CH_3)_2NCOCH_3$. These results were additionally confirmed by the following reactions:

$$TiNMg_2Cl_2THF + \tfrac{1}{2}I_2 \rightarrow TiNMgClTHF + MgClI(THF)_2 \qquad (4)$$

(II)

$$TiNMgClTHF + CO \rightarrow [Ti(NCO)MgClTHF] \qquad (5)$$

(III)

Compound (I) undergoes oxidation with the stoichiometric amount of iodide or ferric chloride to give TiNMgClTHF(II). This compound reacts readily with carbon monoxide to form the isocyanate complex [Ti(NCO)MgClTHF](III) with a 50% yield. This fact confirms the above conclusion, since the oxidized compound (II) is unable to reduce the isocyanate group to the amide group.

Compound (II) reacts also with carbon dioxide and again compound (III) is formed in 47% yield, according to the following reaction:

$$TiNMgClTHF + CO_2 \xrightarrow{-O} [Ti(NCO)MgClTHF] \qquad (6)$$

In the IR spectrum of compound (III) the ν_{NCO} frequencies are observed at 2235 cm^{-1} (sh) and 2197 cm^{-1} (s). Titanium compounds in low oxidation states exhibit strong reduction and oxiphillic properties [4], so that in the medium of reaction (6) CO_2 is reduced to CO. The latter reacts with compound (II) according to eqn. (5). It is very likely that in reaction (6), in addition to compound (III), the oxidized form of compound (II) is formed, which could never be isolated in a pure form so far.

During oxidation of compound (I) with excess $FeCl_3$ or I_2 the fixed nitrogen liberates partly in form of N_2 (14%) and after hydrolysis with diluted HCl (1:1) 48% NH_3 is formed.

These results suggest that the nitrogen atom in compound (I) has no nitrile character. It seems likely that in compound (I) the nitrogen atom is partially reduced in part only and similarly as for dinitrogen complexes its total reduction requires a protonated medium.

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