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# INCORPORATION OF MOLECULAR NITROGEN INTO AMIDES AND IMIDES BY USE OF TITANIUM-NITROGEN COMPLEXES

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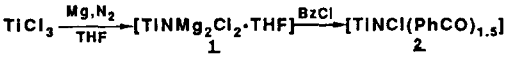
***Abstracts**---Molecular nitrogen was incorporated into amides and imides by the reaction of titanium-nitrogen complex 1 [TiNMg$_2$Cl$_2$·THF] prepared from TiCl$_3$ and Mg under N$_2$ in THF with acyl chlorides 3. The cyclic imides 10, 12, 14 and quinazoline 16 were obtained by the reaction of isocyanate complex[3THF·Mg$_2$Cl$_2$O·TiNCO](6) generated by fixation of CO$_2$ into titanium-nitrogen complex 1 with the corresponding cyclic acid anhydrides 9, 11, 13 and benzoxazone 15.*

Since the discovery of Vol'pin and Shur that molecular nitrogen can be fixed by Cp$_2$TiCl$_2$ and RMgBr under mild conditions,[1] many metal-nitrogen complexes have been synthesized from a variety of transition metals.[2] However, in spite of the impressive development there are few reports about the incorporation of molecular nitrogen into organic compounds *via* these metal-nitrogen complexes. The process reported by Yamamoto is very fascinating because the TiCl$_3$-Mg-THF system can react with an atmosphere of molecular nitrogen at room temperature to afford TiNMg$_2$Cl$_2$·THF(1). This compound then produced the benzoyl-titanium-nitrogen complex[TiNCl(PhCO)$_{1.5}$](2) by treatment with benzoyl chloride(Scheme 1).[3] Now we want to report the result of our research concerning the direct incorporation of molecular nitrogen into the organic compounds, especially heterocyclic compounds, *via* titanium-nitrogen complex 1. When the complex 2 prepared from the complex 1 and benzoyl chloride was treated with water at room temperature, benzamide 4a was obtained in 17% yield based on benzoyl-titanium-nitrogen complex 2. The result indicates that molecular nitrogen was incorporated into benzamide under very mild conditions(Scheme 2).

**Scheme 1**



$$\mathrm{TiCl_3} \xrightarrow[\mathrm{THF}]{\mathrm{Mg,N_2}} \underset{1}{[\mathrm{TiNMg_2Cl_2{\cdot}THF}]} \xrightarrow{\mathrm{BzCl}} \underset{2}{[\mathrm{TiNCl(PhCO)_{1.5}}]}$$

**Scheme2**

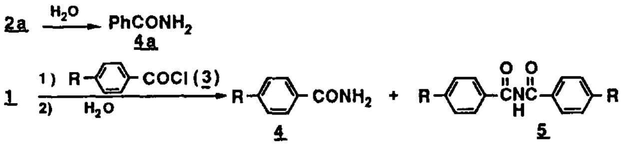
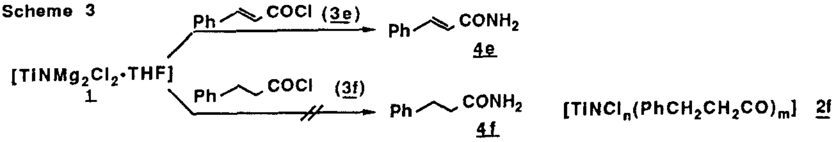


Table 1 ; Reaction of Metal-Nitrogen Complex with Aroyl Chloride

| Run | Aroyl chloride(eq.) | R | | Metal | Temp.[a] | Yield[b](%) of 4 | 5 |
|---|---|---|---|---|---|---|---|
| 1 | 3a | H | (1.8) | $TiCl_3$ | r.t. | 11 | 7 |
| 2 | 3a | H | (1.8) | $TiCl_3$ | reflux | - | 17 |
| 3 | 3a | H | (4.5) | $TiCl_3$ | r.t. | 40 | 12 |
| 4 | 3a | H | (4.5) | $TiCl_3$ | reflux | 36 | 29 |
| 5 | 3a | H | (12) | $TiCl_3$ | r.t. | 41 | 24 |
| 6 | 3b | Me | (4.5) | $TiCl_3$ | r.t. | 34 | 3 |
| 7 | 3c | MeO | (4.5) | $TiCl_3$ | r.t. | 49 | - |
| 8 | 3d | MeOOC | (4.5) | $TiCl_3$ | r.t. | 15 | 4 |
| 9 | 3a | H | (3.0) | $Cp_2TiCl_2$ | r.t. | 22 | 12 |
| 10 | 3a | H | (3.0) | $VCl_3$ | reflux | 4 | 12 |

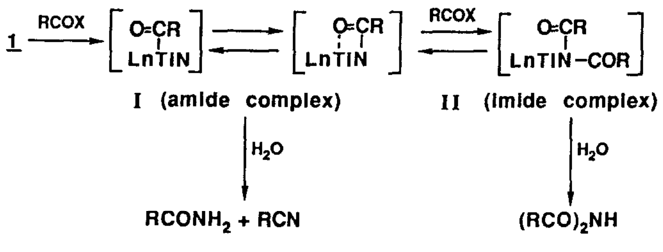
a; all reactions run in THF under nitrogen overnight.
b; based on transition metal

Scheme 3



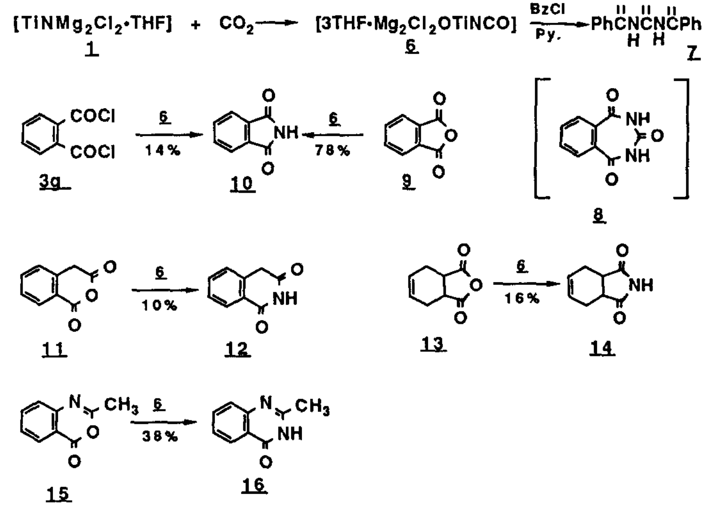
Thus, various aroyl chlorides were allowed to react with titanium-nitrogen complex $TiNMg_2Cl_2{\cdot}THF$(1) prepared from $TiCl_3$ and Mg in THF under $N_2$ *in situ*. The results are summarized in Table 1. Similarly, the titanium-nitrogen complex prepared from $TiCl_4$ or $Cp_2TiCl_2$ gave the same products in each case. Furthermore vanadium-nitrogen complex prepared from $VCl_3$, Mg and molecular nitrogen afforded also benzamide(4a) in a similar manner. It was very interesting that a fair amount of benzimide (5a) was obtained in addition to benzamide 4a. In some cases, a small amount of benzonitrile was detected from the spectral data.[4] The higher temperature improved the yield of the product 4 and 5 and the increased amount of aroyl chloride also improved the yield. The reaction of titanium-nitrogen complex 1 with unsaturated acid chloride 3e gave amide 4e, but saturated acid chloride 3f did not afford amide 4f because decarbonylation from acyl-nitrogen complex 2f followed by β-hydride elimination occurred. A solution of titanium-nitrogen complex 1 and benzoyl chloride was refluxed in benzene overnight to give a black precipitate, which was insoluble in THF and benzene. The infrared spectrum(νmax 1610 $cm^{-1}$) of this complex was clearly different from that of benzoyl-titanium-nitrogen complex 2. Hydrolysis of this complex afforded imide 5a(52% yield) and amide 4a(15% yield). On the basis of these results, the reaction should proceed as shown in Scheme 4. Since the amide 4 was obtained from aroyl-titanium-nitrogen complex I(amide complex), the imide 5 must be derived from imide complex II.[5]

Scheme 4



The titanium-isocyanate complex[3THF·Mg$_2$Cl$_2$O·TiNCO][6](6) generated by fixation of CO$_2$ to titanium-nitrogen complex 1 was considered to be the same oxidation level as the amide complex 1.[5,7] A solution of complex 6 and benzoyl chloride was stirred at room temperature in pyridine to afford compound 7(27% yield) along with benzamide(12% yield). In this reaction, the central urea group of compound 7 was derived from complex 6. It seems pyridine acted not only as the activating agent of acyl halide but also as a ligand. However, NEt$_3$ and bipyridine did not affect this reaction. Though phthaloyl dichloride 3g was treated with complex 6 in a similar manner for the formation of seven membered ring 8, only phthalimide 10 was obtained in 14% yield. When phthalic anhydride 9 was used instead of phthaloyl dichloride 3g, the same product 10 was obtained though the yield was low(Table 2, Run 1). The yield was improved when pyridine solution of complex 6 and phthalic anhydride 9 was refluxed overnight(Run 2 and 3). Other solvents such as DMF and NMP(*N*-methyl-2-pyrrolidone) containing no pyridine afforded the same results as mentioned above, but solvents such as mesitylene, dichloroethane and dioxane containing pyridine gave the worse results. The use of a large amount of titanium-isocyanate complex 6 raised the yield of the desired product 10(Run 8). Homophthalimide(12) and tetrahydrophthalimide(14) were obtained from corresponding acid anhydride 11 and 13(10% and 16% yields, respectively) in a similar manner. It was interesting that molecular nitrogen could be incorporated into quinazoline 16 via titanium-isocyanate complex 6(Scheme 6).

**Scheme 5**



**Scheme 6**

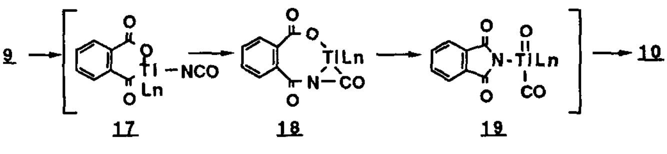


Table 2 ; Reaction of Complex **6** with Phthalic anhydride **9**.

| Run | 6 (eq.) | Temp. | Time (h) | Solvent | Yield(%) of **10**[a] |
|---|---|---|---|---|---|
| 1 | 1 | r.t. | 40 | pyridine | 3 |
| 2 | 1 | reflux | 24 | pyridine | 45 |
| 3 | 1 | reflux | 48 | pyridine | 53 |
| 4 | 1 | reflux | 24 | mesitylene-pyridine | 28 |
| 5 | 1 | reflux | 24 | dichloroethane-pyridine | 19 |
| 6 | 1 | reflux | 24 | dioxane-pyridine | 16 |
| 7 | 1 | 120°C | 24 | DMF | 39 |
| 8 | 3 | 100°C | 24 | NMP | 78[b] |

a; based on complex 6 (2 eq. of phthalic anhydride was used.)
b; based on phthalic anhydride

According to our assumption, this reaction should proceed through the Scheme 2. The oxidative addition of anhydride **9** to the titanium-isocyanate complex **6** should afford complex **17**. Migration of acyl group to nitrogen on titanium might occur to give complex **18**. Then titanium oxide complex should be formed from **18**, which was hydrolyzed to give the cyclic imide **10**.[8]

The results of this research suggest that molecular nitrogen can be used as the resource of nitrogen heterocycles *via* nitrogen-titanium complex **1**. Further studies are in progress.

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## References and Notes

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2. Recent review: a)J. R. Dilworth and R. L. Richards, "*Comprehensive Organometalic Chemistry*", **Vol.8**, p 1073, Pergamon Press (1982). b)T. A. George, In "*Homogeneous Catalysis with Metal Phosphine Complexes*"; L. H. Pinolet, Ed., Plenum Press; p 405 (1983). c)M. Hidai, In "*Molybdenum Enzyme*"; T. G. Spiro, Ed., John Wiley and Sons; p 285 (1985).
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4. van Tamellen has reported that benzonitrile was obtained from benzoyl chloride by use of $Cp_2TiCl_2$-Mg-molecular nitrogen system as a main product. E. E. van Tamellen, and H. Rudler, *J. Am. Chem. Soc.*, **92**, 5253 (1970).
5. When a solution of benzoyl-titanium-nitrogen complex **2** was stirred with toluoyl chloride in benzene at room temperature overnight followed by hydrolysis, toluamide was obtained in 62 % yield. Moreover, a solution of imide complex II(R=Ph) and toluoyl chloride was refluxed in benzene for 48 h followed by hydrolysis to give toluimide in 50 % yield as the sole product. These results suggest that toluoyl group must have exchanged with benzoyl group on titanium of complex **2** or imide complex II.
6. P. Sobota, B. J-Trzebiatowska and Z. Janas, *J. Organometallic Chem.* **118**, 253 (1976).
7. A benzene solution of titanium-isocyanate complex **6** was refluxed with benzoyl chloride overnight followed by treatment with water to give benzamide **4a**(13 % yield) and benzimide **5a**(18 % yield).
8. It seems that carbonyl group on nitrogen of complex **6** served to stabilize the coordinated nitrogen and then it migrated on titanium as ligand.

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