Formation of aromatic amines from dinitrogen complexes [Cp$_2$TiAr]$_2$N$_2$ (Ar = C$_6$H$_5$, m-CH$_3$C$_6$H$_4$)

E.G. Berkovich [a], V.S. Lenenko [b], L.I. Vyshinskaya [c], G.A. Vasil'eva [c], V.B. Shur [b,*],
M.E. Vol'pin [b,1]

[a] *Department of Organic Chemistry, The Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel*
[b] *A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 117813, Russia*
[c] *Institute of Chemistry, N.I. Lobachevsky Nizhegorodsky State University, Gagarin St. 23, Nizhny Novgorod 603600, Russia*

Abstract

It has been shown that the reaction of the dinitrogen complex [Cp$_2$TiC$_6$H$_5$]$_2$N$_2$ with a mixture of C$_6$H$_5$Li and Li in ether results in the formation of ammonia and aniline after hydrolysis. Under optimum conditions, the yield of aniline is 12 mol% per initial complex and the ammonia yield is 36 mol%. In the absence of lithium neither ammonia nor aniline are formed, while in the absence of phenyllithium only ammonia is produced. The interaction of [Cp$_2$TiC$_6$H$_5$]$_2$N$_2$ with p-, m- and o-tolyllithium reagents in the presence of lithium also gives aromatic amines and ammonia after hydrolysis. Similar results have been obtained for the dinitrogen complex [Cp$_2$Ti(m-CH$_3$C$_6$H$_4$)]$_2$N$_2$. The mechanism of the reaction found is discussed. © 1997 Elsevier Science S.A.

Keywords: Dinitrogen complexes; Titanium; Aryllithiums; Lithium; Aromatic amines

1. Introduction

Currently, a large variety of nitrogen-fixing systems based on transition metal compounds and reducing agents in aprotic media are known (e.g. see reviews in Refs. [1–3]). These systems readily react with molecular nitrogen at room temperature reducing it to nitrido derivatives which give ammonia upon hydrolysis. In a number of cases, varying amounts of hydrazine are detected in the products of the dinitrogen reduction. It has also been reported that in the interaction of dinitrogen with similar systems aromatic amines can be obtained.

The highest activity in the formation of arylamines is displayed by the systems Cp$_2$TiCl$_2$ (Cp$_2$TiPh$_2$) + PhLi in ether and Cp$_2$TiPh$_2$ + Li in THF which are capable of converting molecular nitrogen into aniline in a yield of 10–15 mol% per titanium atom (20 °C, P$_{N_2}$ ~ 100 atm) [1,2,4]. Besides aniline, quite large amounts of ammonia

are also produced on hydrolysis of the reaction products of both systems with dinitrogen.

Important information for understanding the mechanism of nitrogen fixation by similar systems has been obtained from studies on the reactivities of molecular nitrogen complexes. It has been established that the coordinated N$_2$ molecule in a number of such complexes (primarily of titanium) readily forms ammonia and/or hydrazine (after hydrolysis) under the action of sufficiently strong reducing agents in aprotic media [1,3,5]. Attempts were also made to obtain aromatic amines from the dinitrogen complexes under reductive conditions, but these attempts were unsuccessful for a long time.

In 1973, Shilov and coworkers reported the formation of small amounts of aniline (after hydrolysis) in the reaction of phenyllithium with the hydrazido titanium derivative (Cp$_2$Ti)$_2$N$_2$MgCl that was isolated from the products of the reaction of N$_2$ with the system Cp$_2$TiCl$_2$ + i-PrMgCl in ether at −60 °C [6]. In the present work, we describe the first examples of the aromatic amine formation from the dinitrogen complexes. A preliminary account of this work is given in Ref. [7].

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* Corresponding author.
[1] Deceased on September 28, 1996.

2. Results and discussion

The dinitrogen complexes $[Cp_2TiAr]_2N_2$ (Ar = C_6H_5, m-$CH_3C_6H_4$) described by Teuben and coworkers [8–10] were chosen. These complexes are readily reduced with sodium naphthalide in THF to give ammonia and hydrazine (after hydrolysis) in close to quantitative total yield [11–13]. On using n-BuLi as the reducing agent, the yields of ammonia and hydrazine decrease and in the reaction of $[Cp_2TiAr]_2N_2$ with i-PrMgCl only ammonia is formed [11,12]. Neither aromatic nor aliphatic amines were detected in these reactions.

Our attempts to convert a dinitrogen ligand in the complexes $[Cp_2TiAr]_2N_2$ into amines by the reaction of $[Cp_2TiAr]_2N_2$ with aromatic organolithium compounds in ether also failed. However, we could observe such a reaction when $[Cp_2TiAr]_2N_2$ was treated with a mixture of ArLi and metallic lithium.

The experiments were conducted using standard procedures. Finely cut-up lithium metal and the appropriate amount of the dinitrogen complex were added under Ar to a solution of ArLi in ether at $-78\,°C$, then the reaction mixture was warmed gradually $(10–20\,°C\,h^{-1})$ to ambient temperature with vigorous stirring and the mixture was stirred at this temperature for several hours. After standing overnight, the reaction mixture was hydrolysed and analysed for the content of nitrogen-containing products.

The results of the experiments have shown that under the above conditions the interaction of $[Cp_2TiPh]_2N_2$ with a mixture of phenyllithium and lithium lead to the formation of aniline along with ammonia (Table 1). Hydrazine was detected as well, but only in negligible amounts (no more than 1 mol% per initial complex).

At the constant PhLi:$[Cp_2TiPh]_2N_2$ ratio of 9:1, the yield of aniline increases with increasing lithium content in the mixture, reaching 12 mol% at the Li:PhLi:$[Cp_2TiPh]_2N_2$ ratio of 35:9:1. The ammonia

yield attains 36 mol% per mole of the complex under the same conditions. In the absence of lithium, neither aniline nor ammonia are obtained.

Also, aniline formation is not observed when only lithium (without phenyllithium) is introduced in the reaction with $[Cp_2TiPh]_2N_2$. Under such conditions only ammonia is produced. At the constant Li:$[Cp_2TiPh]_2N_2$ ratio of 35:1, the ammonia yield is virtually independent of the phenyllithium content in the system, being 35–36 mol% (PhLi:$[Cp_2TiPh]_2N_2$ = (0–9):1). At the same time, the aniline yield increased with an increase in the amount of phenyllithium, reaching the above-mentioned maximum value (12 mol%) at the Li:PhLi:$[Cp_2TiPh]_2N_2$ ratio of 35:9:1.

Thus, the results obtained show that whereas for ammonia formation from the dinitrogen complex it is sufficient to have in the mixture only lithium, for conversion of dinitrogen ligand into aniline the simultaneous presence of both lithium and phenyllithium in the system is required. It should be noted that the yields of ammonia and aniline are independent of whether the reaction of $[Cp_2TiPh]_2N_2$ with PhLi and Li is carried out under argon or in a dinitrogen atmosphere. This indicates that it is precisely the dinitrogen ligand of the complex that is involved in the reaction with PhLi and Li rather than free dinitrogen which could arise in solution due to decomposition of $[Cp_2TiPh]_2N_2$. When the reaction with PhLi and Li is conducted in the absence of the dinitrogen complex but in N_2 atmosphere, neither ammonia nor amines are detected.

The interaction of $[Cp_2TiPh]_2N_2$ with p-, m- and o-tolyllithium reagents also results in the formation of aromatic amines and ammonia after hydrolysis (Table 1). As a result of the reaction, an amine corresponding to the aryl radical of the starting organolithium compound forms predominantly. Thus, in the interaction of $[Cp_2TiPh]_2N_2$ with p-tolyllithium and lithium, p-toluidine is primarily formed, the reaction of $[Cp_2TiPh]_2N_2$ with m-tolyllithium and lithium leads to the formation

Table 1
Yields of aromatic amines and ammonia in the reactions of $[Cp_2TiC_6H_5]_2N_2$ and $[Cp_2Ti(m$-$CH_3C_6H_4)]_2N_2$ with a mixture of ArLi and Li in ether [a]

Complex	ArLi	Yield (mol% per mole of complex)		Amine ratio (%)			
		NH$_3$	Amines	Aniline	Toluidines		
					ortho-	meta-	para-
$[Cp_2TiC_6H_5]_2N_2$	C_6H_5Li	36	12	100	—	—	—
	o-$CH_3C_6H_4Li$	38	9	15	80	5	—
	m-$CH_3C_6H_4Li$	39	4	15	—	85	—
	p-$CH_3C_6H_4Li$	32	3	13	—	—	87
$[Cp_2Ti(m$-$CH_3C_6H_4)]_2N_2$	C_6H_5Li	14	3	88	—	12	—
	o-$CH_3C_6H_4Li$	28	6	—	80	20	—
	m-$CH_3C_6H_4Li$	13	2	—	—	100	—
	p-$CH_3C_6H_4Li$	23	3	—	—	13	87

[a] The molar ratio Li:ArLi:complex is 35:9:1; the initial concentration of the complex (0.6–1.0 g) is ca. 0.11 M.

of m-toluidine, while o-toluidine along with traces of the meta-isomer are obtained in the case of o-tolyl-lithium. Besides toluidines, small amounts of aniline are also produced in all these reactions (toluidines:aniline ratio is about 87–85:13–15). The yield of amines substantially decreases on going from phenyllithium to tolyllithium reagents, whereas the amount of ammonia formed is virtually independent upon the nature of organolithium compound. Similar results were obtained on studying the reaction of dinitrogen complex $[Cp_2Ti(m-CH_3C_6H_4)]_2N_2$ with aryllithiums and lithium (Table 1). However, the use of $[Cp_2Ti(m-CH_3C_6H_4)]_2N_2$ instead of $[Cp_2TiPh]_2N_2$ leads to a decrease in the yields of both amines and ammonia.

In order to clarify the function of the organolithium compounds and metallic lithium in the reaction, experiments with stepwise addition of the reagents were carried out.

In one set of the experiments (see Table 2), the complex $[Cp_2TiPh]_2N_2$ was added to metallic lithium in ether at $-78\,°C$ and the resulting mixture was gradually warmed $(10\text{–}20\,°C\,h^{-1})$ under stirring to the temperature of $t\,°C$ and then stirred at this temperature for a certain period of time. After that, an ether solution of PhLi was added and the temperature of the reaction mixture was gradually raised to room temperature in standard mode. The hydrolysis of reaction products and analyses were carried out next day.

The results obtained are given in Table 2 where the first line refers to ordinary reaction conditions, i.e. when phenyllithium was mixed with the complex and lithium at $-78\,°C$. It is seen that an increase in temperature and time of preliminary contact of $[Cp_2TiPh]_2N_2$ with Li (before the addition of PhLi) decreases steadily the yield of aniline, while the ammonia yield was little affected. The last line in Table 2 corresponds to a run when PhLi was added to a mixture of the complex and lithium in the very end of the standard procedure, i.e. at room temperature next day. Under such conditions, as in the case of the reaction of $[Cp_2TiPh]_2N_2$ with Li in the absence of PhLi, very little aniline is obtained and

Table 2
Aniline and ammonia yields under conditions of preliminary contact of $[Cp_2TiPh]_2N_2$ with lithium in ether and subsequent addition of phenyllithium [a]

Temperature t (°C)	Reaction time with Li at $t\,°C$ before addition of PhLi (h)	Yield (mol%)	
		NH$_3$	PhNH$_2$
−78	0	36	12
−50	3	41	8
−40	3	36	5
+20	0	42	1
+20	15	38	0.5

[a] The molar ratio Li:PhLi:$[Cp_2TiPh]_2N_2$ is 35:9:1; the initial concentration of the complex in ether is 0.2 M (0.5–0.8 g of $[Cp_2TiPh]_2N_2$); PhLi was introduced in the reaction as a 1.3 M solution in ether.

Table 3
Aniline and ammonia yields under conditions of preliminary contact of $[Cp_2TiPh]_2N_2$ with phenyllithium in ether and subsequent addition of lithium [a]

Temperature t (°C)	Reaction time with PhLi at $t\,°C$ before addition of Li (h)	Yield (mol%)	
		NH$_3$	PhNH$_2$
−78	0	36	12
−50	0.5	27	5
−50	3	18	2
−20	0	2	0.3

[a] The molar ratio Li:PhLi:$[Cp_2TiPh]_2N_2$ is 35:9:1; the initial concentration of the complex is ca. 0.11 M (0.6–1.0 g of $[Cp_2TiPh]_2N_2$).

only ammonia is produced. From this it follows, in particular, that aniline formation in the reaction of $[Cp_2TiPh]_2N_2$ with PhLi and Li proceeds not due to the reaction of phenyllithium with nitrido derivatives, resulting from the reduction of $[Cp_2TiPh]_2N_2$ with metallic lithium and giving ammonia upon hydrolysis, but in a different way.

In another set of experiments (see Table 3), a reverse order for mixing the reagents was used: first, the dinitrogen complex was added to a solution of phenyllithium in ether at $-78\,°C$, then the mixture was gradually warmed under stirring to the temperature of $t\,°C$ and, after stirring at this temperature for a certain period of time, lithium metal was added. The reaction was further carried out by a standard procedure (see above).

It turned out that in such a manner of mixing the reagents an increase in temperature and time of preliminary contact of the complex with PhLi (before the addition of Li) leads to a rapid decrease in the yield of not only an aniline but also ammonia. As seen from Table 3, when lithium is introduced in the system $[Cp_2TiPh]_2N_2 + PhLi$ at $-20\,°C$ (see last line in Table 3), only traces of ammonia and aniline are obtained which corresponds in fact to the results of the reaction of $[Cp_2TiPh]_2N_2$ with PhLi in the absence of Li when neither ammonia nor aniline form at all.

The results obtained can be explained by the reaction sequence in Scheme 1. The symbol $[Ti \cdot N_2 \cdot Ti]$ in the scheme designates a reactive dinitrogen complex generated from $[Cp_2TiAr]_2N_2$ and being really responsible for the formation of the amines and ammonia in the reaction with aryllithium and lithium. According to Van der Weij [12] and Van der Weij and Teuben [13], the interaction of $[Cp_2TiAr]_2N_2$ with sodium naphthalide in
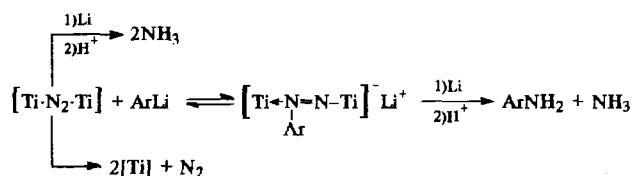
Scheme 1.

THF leads to elimination of one of the Cp rings from each Cp_2Ti moiety, whereas σ-aryl groups remain bonded to titanium. On the basis of these and some other data, the authors have proposed a mechanism of the reduction of dinitrogen ligand including transformation of the initial $[Cp_2TiAr]_2N_2$ into reactive intermediate $[CpTiAr]_2N_2$ which reacts further with sodium naphthalide to give ammonia and hydrazine after hydrolysis. An analogous mechanism (via the intermediate formation of $[CpTiAr]_2N_2$) has also been postulated for the reduction of dinitrogen ligand in $[Cp_2TiAr]_2N_2$ under the action of i-PrMgCl and n-BuLi in ether [12,14]. Similar reactive intermediates containing σ-bonded aryl groups (along with dinitrogen ligand) could be generated from $[Cp_2TiAr]_2N_2$ in our case as well.

According to the proposed mechanism in Scheme 1, three main processes occur in the interaction of [Ti $\cdot$ N$_2$ $\cdot$ Ti] with ArLi and Li.

(1) The reduction of coordinated N_2 molecule in [Ti $\cdot$ N$_2$ $\cdot$ Ti] by lithium to give nitrido derivatives yielding ammonia upon hydrolysis.

(2) The nucleophilic attack on the dinitrogen ligand in [Ti $\cdot$ N$_2$ $\cdot$ Ti] by aryllithium to form aryldiazenido derivative, subsequent reaction of which with lithium affords the corresponding arylamine and ammonia.

(3) The irreversible decomposition of the complex with the formation of dinitrogen.

The important feature of the proposed mechanism is that the step of an addition of aryl anion to dinitrogen ligand in [Ti $\cdot$ N$_2$ $\cdot$ Ti] is assumed to be reversible. In such a case, if lithium is absent in the system, aryl-diazenido derivative will gradually decompose because of irreversible decay of [Ti $\cdot$ N$_2$ $\cdot$ Ti] with liberation of N_2, and hence, neither amines nor ammonia will form. For the same reason, the yields of amines and ammonia should decrease when lithium is introduced in the system after the initial dinitrogen complex was first allowed to stand with organolithium compound at a temperature above $-78\,°C$ (see Table 3). If the reaction is carried out under standard conditions, metallic lithium present in the mixture traps the intermediate aryl-diazenido derivative reducing it to equimolar amounts of the corresponding amine and ammonia. As NH_3 is also formed due to the reaction of [Ti $\cdot$ N$_2$ $\cdot$ Ti] with lithium, the amount of ammonia always exceeds the yield of the amines.

When only lithium is first introduced in the reaction with $[Cp_2TiAr]_2N_2$, and the organolithium compound is added later, at higher temperatures (Table 2), the yield of the amines should also decrease due to consumption of the dinitrogen complex for the reaction with lithium and for the decomposition with evolution of N_2. At the same time, the use of such a procedure should not affect significantly the yield of ammonia, since ammonia arises from both the reaction of the dinitrogen complex with lithium and the reaction of lithium with the intermediate

aryldiazenido derivative. In the limiting case, when only lithium is introduced in the system, only ammonia is formed.

The possibility of the nucleophilic attack on the dinitrogen ligand by aryl anion has been demonstrated previously by Sellmann and Weiss on the example of the reaction of phenyllithium with mononuclear dinitrogen complex of manganese $CpMn(CO)_2(N_2)$ [15]:

$$Cp(CO)_2Mn(N_2) + PhLi \xrightarrow[THF]{-30\,°C} [Cp(CO)_2Mn-\underset{Ph}{N}=N]^- Li^+$$
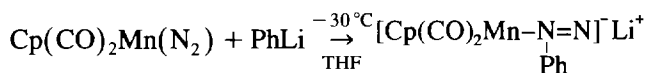
The formation of amines is not reported in this work.

As mentioned above, small amounts of aniline along with toluidines are detected in the products of the reaction of $[Cp_2TiPh]_2N_2$ with the tolyllithium reagents and lithium. This result can be explained by the reversible aryl groups exchange between the dinitrogen complex and the organolithium compound. The exchange processes of such a type have been observed by Van der Weij [12] in the reaction of $[Cp_2TiAr]_2N_2$ with i-PrMgCl in ether. As concerns the formation of small amounts of m-toluidine in the interaction of $[Cp_2TiPh]_2N_2$ with o-tolyllithium in ether, this fact seems to be due to the isomerization of the σ-bonded to titanium o-tolyl group (resulting from the above exchange reaction) to the m-tolyl group via intermediate benzyne complexes according to the mechanism proposed in Ref. [16].

3. Experimental details

The reactions were conducted in an argon atmosphere with careful exclusion of air and moisture. Diethyl ether was purified in the usual manner and freshly distilled over sodium and lithium aluminium hydride under Ar before use. The starting dinitrogen complexes, $[Cp_2TiC_6H_5]_2N_2$ and $[Cp_2Ti(m-CH_3C_6H_4)]_2N_2$, were prepared by procedures described in Refs. [9,12]. The aromatic organolithium compounds (phenyllithium, p-, m- and o-tolyllithiums) were obtained by the conventional method: by the reaction of the corresponding aryl bromide with lithium in dry ether under Ar. The analyses of the aromatic amines were performed by GLC on a column (2.8 m × 4 mm) with 5% Tween-20 on Chromosorb G treated with a methanol solution of KOH (chromatograph Chrom-2 with flame ionization detector, column temperature 132 °C, carrier gas N_2 (50 ml min^{-1}), internal standard: naphthalene).

3.1. Reaction of $[Cp_2TiPh]_2N_2$ with a mixture of PhLi and Li in ether

12.6 ml of 1 M solution of PhLi in ether and 0.34 g (49 mmol) of lithium were placed into two-neck flask under Ar. The reaction mixture was cooled to $-78\,°C$

and $[Cp_2TiPh]_2N_2$ (0.81 g, 1.4 mmol) was rapidly added under Ar. The reaction mixture was then warmed gradually to room temperature with vigorous stirring in the following mode: -70 to $-50\,°C$ in 1 h ($20\,°C\,h^{-1}$), -50 to $-30\,°C$ in 2 h ($10\,°C\,h^{-1}$), -30 to $+20\,°C$ in 2.5 h ($20\,°C\,h^{-1}$). In the range from -50 to $-30\,°C$, the colour of the solution changed from dark blue to brown. The reaction mixture was stirred at room temperature for an additional 2–3 h and allowed to stand overnight under Ar. Next day, the mixture was cooled to $-78\,°C$, then 10 ml of 10 M solution of HCl in EtOH and 20 ml of 7% aqueous HCl were added with vigorous stirring under Ar after which the temperature was gradually raised to 20 °C.

The further work-up was conducted in air. An ether layer was separated and the acid aqueous layer was extracted several times with ether. The ether extracts and ether layer were combined and washed with 7% aqueous HCl. The combined acid aqueous layers were diluted with water to 100 ml and divided into two equal portions. One portion was analysed by the Kjeldahl method for the total amount of aniline and ammonia. Another portion was analysed for the content of aniline. The amount of ammonia was calculated from the difference in these two analyses.

To determine aniline, the acid aqueous solution (50 ml) was cooled to 0 °C, alkalized with 40% KOH to a strong alkaline reaction and extracted several times with ether. The combined ether extracts were dried with anhydrous Na_2SO_4, evaporated to a small volume (1–2 ml) and analysed by GLC for aniline.

The other portion (50 ml) of the acid aqueous solution was diluted with water, 5–10 ml of concentrated H_2SO_4 was added, and the mixture was evaporated to half its original volume. The residue was alkalized with 40% KOH to a strong alkaline reaction, and ammonia and aniline were distilled off together with water into a flask containing excess 0.1 N HCl. The titration of the excess acid gave the total amount of ammonia and aniline.

The results of the analyses: aniline yield is 12 mol%, ammonia yield is 36 mol%.

Other experiments, including those with stepwise addition of the reagents, were carried out by a similar procedure (for the order and conditions for mixing the reagents see Tables 2 and 3).

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