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ON THE MECHANISM OF THE REDUCTION OF MOLECULAR NITROGEN WITH ARYLDICYCLOPENTADIENYLTIITANIUM(III) COMPLEXES

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Summary

The first step in the reduction of the dinitrogen ligand in (Cp₂TiR)₂N₂ (R = C₆H₅, m-, p-CH₃C₆H₄, C₆F₅, CH₂C₆H₃) by sodium naphthalene (NaC₁₀H₈) involves the removal of one Cp group per titanium atom. The resulting diimide precursor reacts with a second mole of NaC₁₀H₈ with formation of a hydrazine precursor. This compound is thermally unstable and decomposes to an ammonia precursor. A minor part of the hydrazine precursor abstracts a proton from the solvent.

Introduction

Recently, we reported the reduction of the dinitrogen ligand in (Cp₂TiR)₂N₂ (R = C₆H₅, m-, p-CH₃C₆H₄, C₆F₅, CH₂C₆H₃) under the action of a number of reducing agents [1], of which sodium naphthalene (NaC₁₀H₈) appeared to be the most effective. NH₃ and some N₂H₄ were obtained after acidification of the reaction mixture; with 2 or more moles of NaC₁₀H₈ per Ti over 90% of the complexed dinitrogen was reduced. Furthermore, it was observed, that the group R remained attached to the titanium atom during the reduction, whereas the Cp₂Ti structure was almost completely destroyed.

In the present paper we report some experiments on the mechanism of the reduction in the system (Cp₂TiR)₂N₂/NaC₁₀H₈/THF/N₂.

Results and discussion

An indication of the mechanism of the reduction of dinitrogen in the system (Cp₂Tiaryl)₂N₂/NaC₁₀H₈/THF/N₂ was obtained by investigation of the titanium-containing compounds after quenching the reaction mixture with HCl in ether. Since two moles of NaC₁₀H₈ per titanium give almost complete reduction of the dinitrogen ligand [1], the experiments were carried out with a Na/Ti ratio of
about 2. After quenching of the reaction mixture with HCl in ether at —78°C, up to 70% of the titanium was recovered as a pentane-soluble, moisture-sensitive fraction, which consisted mainly of CpTiCl₂. Only small amounts of Cp₂TiCl₂ were obtained (20% or less) together with traces of unidentified inorganic titanium compounds. Variation of the temperature of the reduction reaction * (between —78 and 25°C) and reaction time (from 0.5 to 24 h) had only a minor effect on the composition of the titanium-containing products. However, with NaC₁₀H₈ in excess, a sharp decrease of the organotitanium products was observed. For instance, if the reduction reaction was performed with 4 eq. of NaC₁₀H₈ during 24 h at 25°C, neither Cp₂TiCl₃ nor Cp₂TiCl₂ was obtained after quenching. With a ratio Na/Ti < 2 the yield of Cp₂TiCl₃ and reduced nitrogen decreased, whereas the amount of Cp₂TiCl₂ increased; the latter probably originates from unreacted starting material which, on reaction with HCl, reacts according to eq. 1 [2].

\[(\text{Cp}_2\text{TiR})_2\text{N}_2 + 4 \text{HCl} \rightarrow 2\text{Cp}_2\text{TiCl}_2 + 2 \text{RH} + \text{N}_2 + \text{H}_2 \]  

(1)  

The formation of monocyclopentadienyltitanium compounds suggests the removal of one of the two Cp groups from the titanium atoms as CpNa in an early stage of the reduction process. Evidence for the formation of CpNa after mixing (Cp₂TiR)₂N₂ and NaC₁₀H₈ in THF was obtained from IR and NMR spectroscopy. THF was removed (25°C, vacuum) from the reaction mixture and naphthalene was washed out quantitatively with pentane. The IR spectrum of the resulting solid showed the absorptions of the \( \eta^8 \)-CpTi group, the ligand R and peaks characteristic of CpNa; magnetic measurements showed the solid to be diamagnetic. The NMR spectrum of the mixture dispersed in THF-\( \delta^8 \) showed only the absorption of CpNa (δ 5.63 ppm) [3]. At extremely high amplification also broad absorptions were observed around 2.2 ppm and between 5 and 9 ppm, indicating that the titanium-containing part of the reduced complex is only sparingly soluble in THF **. The overall reduction reaction at 25°C can be visualized as given in eq. 2, where the titanium complex contains a \( \eta^8 \)-bonded Cp group, a \( \sigma \)-bonded aryl group and nitrogen.

\[\frac{1}{2}(\text{Cp}_2\text{TiR})_2\text{N}_2 + 2 \text{NaC}_{10}\text{H}_8 \rightarrow \text{CpNa} + 2 \text{C}_{10}\text{H}_8 + [\text{CpTiRN}]\text{Na} \]  

(2)  

The formation of CpNa was also demonstrated by addition of FeCl₂ prior to HCl. Cp₂Fe was formed; it was extracted from the reaction mixture with pentane and quantitatively determined by UVV spectroscopy. After treatment of the residue with HCl in ether, essentially the same yields of Cp₂TiCl₃ and reduced nitrogen were obtained as in experiments without FeCl₂ indicating that FeCl₂ does not interfere in the reduction process. (In the absence of NaC₁₀H₈, FeCl₂ reacted with (Cp₂TiR)₂N₂ with liberation of N₂; the Cp₂Ti structure remained intact and no Cp₂Fe was formed.) The amounts of CpNa, calculated from the amounts of Cp₂Fe (c.f. [4]), and given in Table 1, show that for a Na/Ti ratio of about 2 one Cp group is removed per titanium atom. At higher Na/Ti ratios a second Cp group is split off, but only at a much slower rate. If one eq. of NaC₁₀H₈ is used, a sharp

* In all cases the reactions were started at —78°C and subsequently warmed to the temperatures given.

** Traces of moisture completely changed the NMR spectrum. Then absorptions assignable to CpH, to RH and to a \( \eta^8 \)-bonded Cp group (δ 5.7 ppm) were observed with intensities corresponding to an equimolar mixture of these components.
Table 1

<table>
<thead>
<tr>
<th>Na/Ti</th>
<th>Reaction time (h)</th>
<th>T (°C)</th>
<th>CpNa/Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.88</td>
<td>2.0</td>
<td>−20</td>
<td>0.98</td>
</tr>
<tr>
<td>1.96</td>
<td>1.5</td>
<td>+20</td>
<td>1.00</td>
</tr>
<tr>
<td>1.84</td>
<td>0.75</td>
<td>+20</td>
<td>0.96</td>
</tr>
<tr>
<td>4.03</td>
<td>1.0</td>
<td>+20</td>
<td>1.21</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>+20</td>
<td>0.5−0.7</td>
</tr>
</tbody>
</table>

decrease of the amount of CpNa formed is observed. Obviously, another reaction in which NaC₁₀H₈ is consumed also takes place.

Information about the mechanism of the reduction reaction was also obtained from a study of the yields of NH₃ and N₂H₄ after quenching the mixtures of (C₅H₅)₂TiN₂ and NaC₁₀H₈ (Na/Ti ~ 2) with HCl in water * . If the reduction is carried out at −78° C, N₂H₄ is the main product (Fig. 1). In about 4 h, essentially all the complexed nitrogen is reduced to a hydrazine precursor. With shorter reaction times, however, NH₃ is also found after acidification (a maximum of 0.09 NH₃/Ti was obtained after 1 h of reduction). This is explained by assuming that the first step in the reduction is the formation of a diimide precursor, I (eq. 3).

\[
\begin{align*}
\frac{1}{2} (C₅H₅)₂Ti(NR₂) & \rightarrow \frac{1}{2} Ti \overset{III}{\equiv} N \overset{III}{\equiv} N \overset{R}{\equiv} CP \overset{R}{\equiv} CP + NaCP + C₁₀H₈ \newline
\end{align*}
\]

(3)

Fig. 1. Yields of NH₃(•) and N₂H₄(△) obtained from the system (C₅H₅)₂Ti m-CH₃C₆H₄₂₅N₂/4NaC₁₀H₈/-THF/N₂ after various reaction times at −78°C.

* The use of HCl in water, H₂SO₄ or CF₃COOH results in the formation of more N₂H₄ and less NH₃, compared to the yields obtained with HCl in ether. The total amount of reduced nitrogen is not affected.
Reaction with HCl at this stage produces N₂H₂ (eq. 4) which decomposes [5] according to eq. 5.

\[ \text{I} + 6 \text{HCl} \rightarrow 2 \text{Cp}_2\text{TiCl}_3 + 2 \text{RH} + \text{N}_2\text{H}_2 + \text{H}_2 \]  \hspace{1cm} (4)

\[ 3 \text{N}_2\text{H}_2 \rightarrow 2 \text{NH}_3 + 2 \text{N}_2 \]  \hspace{1cm} (5)

In a second step the diimide precursor reacts with the second mole of NaC₁₀H₈ to form the hydrazine precursor II which will produce CpTiCl₃ and N₂H₄ upon addition of HCl. After a reaction time of 4 h at −78° C and acidification with HCl in water at −78° C hydrazine is indeed obtained in high yields (Fig.1).

\[
\begin{array}{c}
\text{R} \\
\text{Cp} \\
\text{Ti} \\
\text{N} \\
\text{N} \\
\text{R} \\
\text{Cp} \\
\text{Ti}
\end{array}
\]  \hspace{1cm} (II)

The hydrazine precursor II is stable only at low temperatures. If the reaction mixture is warmed to room temperature before acidification, up to 0.6 NH₃/Ti and about 0.15 N₂H₂/Ti are formed. This indicates a facile splitting of the N—N bond in II without additional reductant NaC₁₀H₈. An ammonia precursor (III) is formed, probably according to eq. 6.

\[ \text{II} \rightarrow 2 \left[ \text{CpTi}^{IV} \text{—N} \right]^{-} \text{Na}^{+} \]  \hspace{1cm} (6)

This reaction appeared to be irreversible. The time during which the reaction mixture is stirred at room temperature does not affect the yields of NH₃ and N₂H₄. Variation of the solvent (1,2-dimethoxyethane, diethylene glycoldimethylether, THF/1,4-dioxan 1 : 1) resulted in essentially the same ratio of NH₃ and N₂H₄. Obviously, a side reaction occurs in which II abstracts a proton from the solvent. This is strongly supported by the fact that addition of compounds which are more acidic than the solvents used, increase the yield of hydrazine. For instance, the addition of phenylacetylene to the reaction mixture (consisting mainly of II) at −78° C and subsequent warming to room temperature, resulted, after HCl/H₂O addition, in the formation of about 80% hydrazine and only 10% ammonia (N red/Ti ~ 0.9).

The results reported here suggest a mechanism different from that proposed for the reduction of N₂ in the related alkyl compounds (Cp₂TiR)₂N₂ [6], where (in contrast with the aryl compounds) Grignard reagents can be employed successfully to reduce the dinitrogen ligand [1,6]. Rupture of the Ti—alkyl bond, and consequently the formation of (Cp₂Ti)₂N₂ has been proposed as the first step in the reduction. The difference between the two reduction processes is probably due to the great difference in stability of the compounds (Cp₂TiR)₂N₂ with R = alkyl [7] and R = aryl [2]. In both mechanisms the occurrence of bimetallic intermediates is proposed (cf [8]).
The properties of the various intermediates, occurring during the reduction are under investigation.

Experimental

All experiments were performed under purified nitrogen, using Schlenk-type glassware. Solvents were purified by conventional methods and freed from oxygen by repeated degassing and saturation with nitrogen. (Cp₂TiR₂)₃N₂ was prepared as described previously [2]. Ferrocene was determined quantitatively by UV-spectrometry with a Perkin—Elmer EPS-3T spectrophotometer. NMR spectra were recorded on a Jeol 60 HL. The amount of hydrazine was determined according to Watt and Chrip [9]. NH₃ was determined in the Analytical Department of this University under the supervision of Mr. A.F. Hamminga.

**Determination of CpNa**

(Cp₂TiR₂)₃N₂ was added to freshly prepared solutions of NaC₁₀H₈ in THF, at —78°C. After 1 h the reduced complex was allowed to warm to the temperatures and stirred for the times shown in Table 1. Then, about 4 eq. of FeCl₂ were added. The reaction mixture was stirred for one hour and subsequently evaporated to dryness in vacuum. The mixture was extracted with n-pentane. The ferrocene in the collected pentane layers was purified by sublimation.

**Determination of CpTiCl₃ and Cp₂TiCl₂**

The reduced complex was prepared at —78°C as described above. The reaction mixture was either held at —78°C or warmed to —20°C or + 25°C and stirred during 0.5 to 24 h. After cooling the mixture to —78°C, excess of HCl in ether was added. After slowly warming to room temperature the volatile compounds were removed in vacuum. CpTiCl₃ was obtained by extraction of the solid residue with n-pentane. Subsequently, Cp₂TiCl₂ was washed out with 1,2-dichloroethane.

**Determination of N₂H₄ and NH₃**

The reduced complex was prepared at —78°C as described. The results given in Fig. 1 were obtained by stirring the mixture during the given time and quenching with benzyl chloride (to destroy the NaC₁₀H₈ left; this is important at short reaction times) and subsequently with HCl in water at —78°C. After slowly warming to room temperature the volatile compounds were removed in vacuum. The solid residues were extracted with 0.1 M HCl and analyzed for NH₃ and N₂H₄.

The procedure followed if the reaction mixture was allowed to warm to room temperature prior to acidification, was the same except that no benzyl chloride was added.

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