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

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Summary

The first step in the reduction of the dinitrogen ligand in $(Cp_2TiR)_2N_2$ (R = C_6H_5, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$) by sodium napthalene ($NaC_{10}H_8$) involves the removal of one Cp group per titanium atom. The resulting diimide precursor reacts with a second mole of $NaC_{10}H_8$ 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 $(Cp_2TiR)_2N_2$ (R = C_6H_5, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$) under the action of a number of reducing agents [1], of which sodium naphthalene ($NaC_{10}H_8$) appeared to be the most effective. NH_3 and some N_2H_4 were obtained after acidification of the reaction mixture; with 2 or more moles of $NaC_{10}H_8$ 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 Cp_2Ti structure was almost completely destroyed.

In the present paper we report some experiments on the mechanism of the reduction in the system $(Cp_2TiR)_2N_2/NaC_{10}H_8/THF/N_2$.

Results and discussion

An indication of the mechanism of the reduction of dinitrogen in the system $(Cp_2Tiaryl)_2N_2/NaC_{10}H_8/THF/N_2$ was obtained by investigation of the titanium-containing compounds after quenching the reaction mixture with HCl in ether. Since two moles of $NaC_{10}H_8$ 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 $CpTiCl_3$. Only small amounts of Cp_2TiCl_2 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 $NaC_{10}H_8$ in excess, a sharp decrease of the organotitanium products was observed. For instance, if the reduction reaction was performed with 4 eq. of $NaC_{10}H_8$ during 24 h at 25° C, neither $CpTiCl_3$ nor Cp_2TiCl_2 was obtained after quenching. With a ratio $Na/Ti < 2$ the yield of $CpTiCl_3$ and reduced nitrogen decreased, whereas the amount of Cp_2TiCl_2 increased; the latter probably originates from unreacted starting material which, on reaction with HCl, reacts according to eq. 1 [2].

$$(Cp_2TiR)_2N_2 + 4\ HCl \rightarrow 2Cp_2TiCl_2 + 2\ RH + N_2 + H_2 \qquad (1)$$

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 $(Cp_2TiR)_2N_2$ and $NaC_{10}H_8$ 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 η^5-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-d^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 η^5-bonded Cp group, a σ-bonded aryl group and nitrogen.

$$\tfrac{1}{2}(Cp_2TiR)_2N_2 + 2\ NaC_{10}H_8 \rightarrow CpNa + 2\ C_{10}H_8 + [CpTiRN]Na \qquad (2)$$

The formation of CpNa was also demonstrated by addition of $FeCl_2$ prior to HCl. Cp_2Fe 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 $CpTiCl_3$ and reduced nitrogen were obtained as in experiments without $FeCl_2$ indicating that $FeCl_2$ does not interfere in the reduction process. (In the absence of $NaC_{10}H_8$, $FeCl_2$ reacted with $(Cp_2TiR)_2N_2$ with liberation of N_2; the Cp_2Ti structure remained intact and no Cp_2Fe was formed.) The amounts of CpNa, calculated from the amounts of Cp_2Fe (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 $NaC_{10}H_8$ is used, a sharp

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* 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 η^5-bonded Cp group (δ 5.7 ppm) were observed with intensities corresponding to an equimolar mixture of these components.

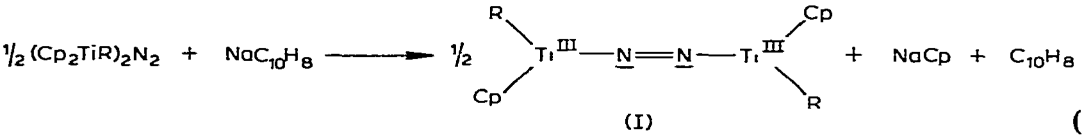
TABLE 1

RELATIVE AMOUNTS OF CpNa FORMED IN THE REACTION OF $(Cp_2TiC_6H_5)_2N_2$ WITH $NaC_{10}H_8$

Na/Ti	Reaction time (h)	T (°C)	CpNa/Ti
1.88	2.0	−20	0.98
1.96	1.5	+20	1.00
1.84	0.75	+20	0.96
4.03	1.0	+20	1.21
1.0	1.0	+20	0.5—0.7

decrease of the amount of CpNa formed is observed. Obviously, another reaction in which $NaC_{10}H_8$ is consumed also takes place.

Information about the mechanism of the reduction reaction was also obtained from a study of the yields of NH_3 and N_2H_4 after quenching the mixtures of $(Cp_2TiR)_2N_2$ and $NaC_{10}H_8$ (Na/Ti ~ 2) with HCl in water [*]. If the reduction is carried out at −78° C, N_2H_4 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, NH_3 is also found after acidification (a maximum of 0.09 NH_3/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).



(3)

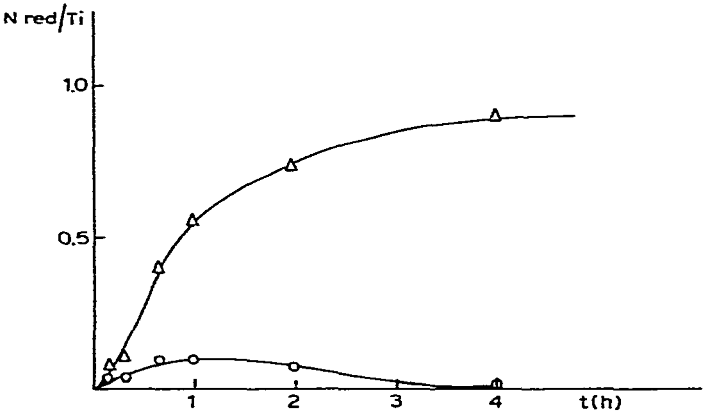


Fig. 1. Yields of NH_3(○) and N_2H_4(△) obtained from the system (Cp₂Ti m-$CH_3C_6H_4)_2N_2/4NaC_{10}H_8$/THF/$N_2$ after various reaction times at −78°C.

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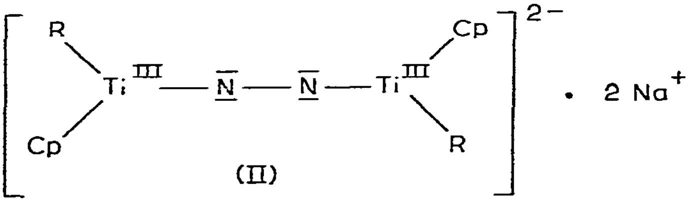
[*] The use of HCl in water, H_2SO_4 or CF_3COOH results in the formation of more N_2H_4 and less NH_3, compared to the yields obtained with HCl in ether. The total amount of reduced nitrogen is not affected.

Reaction with HCl at this stage produces N_2H_2 (eq. 4) which decomposes [5] according to eq. 5.

$$\mathrm{I} + 6\,\mathrm{HCl} \rightarrow 2\,\mathrm{CpTiCl_3} + 2\,\mathrm{RH} + \mathrm{N_2H_2} + \mathrm{H_2} \tag{4}$$

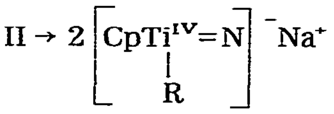
$$3\,\mathrm{N_2H_2} \rightarrow 2\,\mathrm{NH_3} + 2\,\mathrm{N_2} \tag{5}$$

In a second step the diimide precursor reacts with the second mole of $NaC_{10}H_8$ to form the hydrazine precursor II which will produce $CpTiCl_3$ and N_2H_4 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).



(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 NH_3/Ti and about 0.15 N_2H_4/Ti are formed. This indicates a facile splitting of the N—N bond in II without additional reductant $NaC_{10}H_8$. An ammonia precursor (III) is formed, probably according to eq. 6.



$$\mathrm{II} \rightarrow 2\left[\begin{array}{c}\mathrm{CpTi^{IV}{=}N}\\ |\\ \mathrm{R}\end{array}\right]^{-}\mathrm{Na^+} \tag{6}$$

(III)

This reaction appeared to be irreversible. The time during which the reaction mixture is stirred at room temperature does not affect the yields of NH_3 and N_2H_4. Variation of the solvent (1,2-dimethoxyethane, diethyleneglycoldimethylether, THF/1,4-dioxan 1 : 1) resulted in essentially the same ratio of NH_3 and N_2H_4. 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/H_2O 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 N_2 in the related alkyl compounds $(Cp_2TiR)_2N_2$ [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 $(Cp_2Ti)_2N_2$ 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 $(Cp_2TiR)_2N_2$ 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. $(Cp_2TiR)_2N_2$ 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 Chrisp [9]. NH_3 was determined in the Analytical Department of this University under the supervision of Mr. A.F. Hamminga.

Determination of CpNa

$(Cp_2TiR)_2N_2$ was added to freshly prepared solutions of $NaC_{10}H_8$ 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 $FeCl_2$ 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 $CpTiCl_3$ and Cp_2TiCl_2

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. $CpTiCl_3$ was obtained by extraction of the solid residue with n-pentane. Subsequently, Cp_2TiCl_2 was washed out with 1,2-dichloroethane.

Determination of N_2H_4 and NH_3

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 $NaC_{10}H_8$ 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 NH_3 and N_2H_4.

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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