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SOME REACTIONS OF DINITROGEN COMPLEXES OF ARYLDICYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

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Summary

The reduction of dinitrogen to NH_3 and N_2H_4 upon thermolysis of $(Cp_2TiR)_2N_2$ ($R = C_6H_5$, *m*-, *p*-$CH_3C_6H_4$, $CH_2C_6H_5$) is reported. The amounts of NH_3 obtained from the reactions of $(Cp_2TiR)_2N_2$ with sodium naphthalene, n-BuLi and i-PrMgCl are discussed.

Introduction

Organometallic dinitrogen complexes of transition metals are the subject of research in many laboratories. (For a review see ref. 1.) We recently reported the preparation and some properties of complexes of the type $(Cp_2TiR)_2N_2$ with Cp = π-cyclopentadienyl, and $R = C_6H_5$, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$ [2]. The IR-spectra of these compounds show no absorptions which can be assigned to ν(NN). This led us to the conclusion that the compounds are probably centrosymmetric, with the dinitrogen coordinated at the metal either end-on or edge-on.

On reaction of the complexes with HCl, Br_2, I_2, CO, H_2 or CH_3COCl, dinitrogen gas was liberated; no other nitrogen-containing products were observed. Reactions aimed at asymmetric coordination of the N_2-ligand [3] with metal halides $AlCl_3$, $SbCl_5$, $TiCl_4$, $TiCl_3$ and with Et_3Al also resulted in the liberation of dinitrogen [4].

We now describe experiments on reactions of the complexed dinitrogen ligand.

Results and discussion

Nitrogen reduction during thermolysis of $(Cp_2TiR)_2N_2$ and Cp_2TiR

Thermal decomposition of $(Cp_2TiR)_2N_2$ results in quantitative formation of RH, partial liberation of nitrogen and production of a complex Ti-containing residue of unknown structure [5]. In a typical experiment with $(Cp_2TiC_6H_5)_2N_2$, the N_2 released was found to be about 90%; NH_3 and N_2H_4 (traces) were detected in the hydrolyzed residue. We report investigations on the residues of a number of thermolyses, performed under various conditions of temperature and N_2-pressure (0-100 atm) in the solid state or in solution. The residues were treated with HCl in ether and after working up tests were made for NH_3, N_2H_4 and amines. In all cases substantial amounts of ammonia and traces of hydrazine were found. Tests for amines were negative. Some of the experiments are summarized in Table 1, together with the results of thermolyses of some nitrogen-free compounds Cp_2TiR in a nitrogen atmosphere. The reproducibility was rather poor and no straight-forward trends in NH_3 yields are evident. Generally the highest yields of NH_3 were found when the thermolyses were performed on the solid dinitrogen complexes, even when the experiments were carried out in vacuum under continuous pumping. This implies that during the thermal decomposition some of the complexed dinitrogen stays on the metal and is reduced when the group R splits off as RH. In solution the dinitrogen complexes dissociate completely under the conditions used into N_2 and Cp_2TiR [2]. The nitrogen reduction probably results from the reaction of N_2 with reactive species formed during the thermal decomposition of Cp_2TiR. This also explains the results obtained with the compounds Cp_2TiR ($R = o\text{-}CH_3C_6H_4$, $2,6\text{-}(CH_3)_2C_6H_3$), which do not form dinitrogen complexes.

Nitrogen reduction by reaction with sodium naphthalene, n-BuLi and i-PrMgCl

High yields of NH_3 were obtained after addition of $(Cp_2TiR)_2N_2$ to a solution of sodium naphthalene ($NaC_{10}H_8$) in THF under N_2 at —78°C, warming the reaction mixture to room temperature during 0.5 h and working up with HCl in ether. Up to 2 moles of NH_3 per mole of $(Cp_2TiR)_2N_2$ were found (Fig. 1; $R = m\text{-}CH_3C_6H_4$). Tests for N_2H_4 showed its presence up to a Na/Ti ratio of 4. Tests for amines were negative. Similar results were obtained when the experiments were performed under argon. Obviously, there is a fast reaction of $NaC_{10}H_8$ with the solid dinitrogen complex and not with a decomposition product of this complex. This is shown by experiments in which $(Cp_2Ti\text{-}m\text{-}CH_3C_6H_4)_2N_2$ was dissolved in THF at 0°C (which results in a quantitative liberation of the complexed dinitrogen [4]) followed by addition of $NaC_{10}H_8$; the yield of NH_3 was sharply decreased. Under the conditions used we obtained about 1 mole of NH_3 per mole of $(Cp_2Ti\text{-}m\text{-}CH_3C_6H_4)_2N_2$. This experiment suggests that in this case a reduction product of Cp_2TiR is formed which is capable of binding N_2 and reducing it. The nature of this intermediate is still unclear.

The reduction of the dinitrogen complexes by n-BuLi was studied in THF, toluene and diethyl ether. The results obtained in toluene are shown in Fig. 1 ($R = m\text{-}CH_3C_6H_4$). Essentially the same results were found in THF and diethyl ether. The NH_3 production with this reducing agent is about half of that observed with $NaC_{10}H_8$. This can be ascribed to the lower reactivity of n-BuLi then of $NaC_{10}H_8$. The reaction takes place only at temperatures at which the equilibrium (eqn. 1) is partly shifted to the right; reaction of Cp_2TiR with n-BuLi causes a decrease in the NH_3 production. Hydrazine was present up to a Li/Ti ratio of 4.

TABLE 1

AMMONIA DETERMINATIONS ON HYDROLYZED RESIDUES OF THERMOLYZED $(Cp_2TiR)_2N_2$

R	Conditions of thermolysis	NH_3/Ti
C_6H_5	80°C, 2 h, solid, vac.	0.12
	20°C, 72 h, toluene, N_2, 1 atm	0.05
	80°C, 24 h, toluene, N_2, 1 atm	0.08
	80°C, 24 h, toluene, N_2, 20 atm	0.10
	80°C, 24 h, toluene, N_2, 40 atm	0.13
m-$CH_3C_6H_4$	80°C, 1 h, solid, vac.	0.08
	80°C, 1 h, solid, N_2, 1 atm	0.18
	80°C, 2 h, benzene, N_2, 1 atm	0.08
p-$CH_3C_6H_4$	80°C, 1 h, solid, vac.	0.11
	80°C, 1 h, solid, N_2, 1 atm	0.07
	80°C, 1 h, benzene, N_2, 1 atm	0.16
$CH_2C_6H_5$	55°C, 1 h, solid, N_2, 1 atm	0.21
	20°C, 20 h, benzene, N_2, 1 atm	0.16
o-$CH_3C_6H_4$ [a]	120°C, 1 h, solid, N_2, 1 atm	0.01
	80°C, 24 h, benzene, N_2, 1 atm	0.18
2,6-$(CH_3)_2C_6H_3$ [a]	240°C, 1 h, solid, N_2, 1 atm	0.01

[a] Investigated as Cp_2TiR.

$$(Cp_2TiR)_2N_2 \rightleftharpoons 2Cp_2TiR + N_2 \qquad (1)$$

When i-PrMgCl was used as the reducing agent low yields of NH_3 (NH_3/Ti ~0.15) were obtained (Fig. 1; R = m-$CH_3C_6H_4$). No detectable amounts of N_2H_4

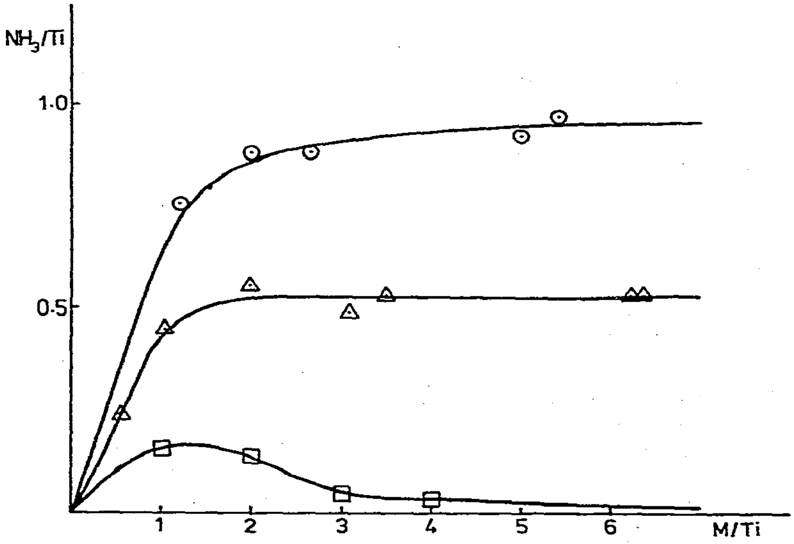

Fig. 1. Yield of NH_3 after reaction of $(Cp_2Ti$-m-$CH_3C_6H_4)_2N_2$ with sodium napthalene (⊙), n-BuLi (△) and i-PrMgCl (□).

were found. At higher Mg/Ti ratios the NH_3 production decreased. Probably the enhanced amount of $(i\text{-}Pr)_2Mg$ is responsible for this. This compound reacts (like Et_3Al) with $(Cp_2TiR)_2N_2$ with liberation of the coordinated dinitrogen (cf. introduction). This is confirmed by the fact that when $(i\text{-}Pr)_2Mg$ was added to $(Cp_2Ti\text{-}m\text{-}CH_3C_6H_4)_2N_2$ in ether no nitrogen reduction was observed.

The Grignard reagent is not a sufficiently strong reducing agent to initiate nitrogen reduction under the conditions used. A similar observation was made by Shilov et al. [6], who studied the system $(Cp_2TiR)_2N_2/RMgCl/N_2$ (R = i-Pr). This system is effective in producing N_2H_4 and NH_3. The essential step in the reduction of the complexed dinitrogen is not the action of Grignard reagent in excess, but the formation of $(Cp_2Ti)_2N_2$ from the original dinitrogen complex. $(Cp_2Ti)_2N_2$ essentially is a diimide derivative, which is easily reduced further. Our studies [2,5] on the thermal stabilities of the dinitrogen complexes discussed here, make it clear that significant loss of R groups is unlikely. The reductions we studied take a different route. For the greater part the group R stays on the titanium atom, as is shown by experiments in which DCl/D_2O was used for hydrolysis of the reduced mixture. RD and RH (about 3/1) were found. It is to be noted that the Cp_2Ti-structure is almost completely destroyed if excess $NaC_{10}H_8$ or n-BuLi is used. Considerable amounts of $CpTiCl_3$ were obtained when 1 to 2 equivalents of the reducing agent were used.

The experiments do not permit conclusions on the mechanism of the reduction of the N_2 complexes but do suggest an active role for compounds of the type CpTiR. The traces of N_2H_4 apparently originate from diimine or hydrazine precursors, indicating a stepwise reduction of the dinitrogen molecule. Because of the high efficiency, the reductions with $NaC_{10}H_8$ and n-BuLi seem better suited for studying the reduction pathway than the thermal decomposition or the reactions with i-PrMgCl. A detailed study is in progress.

Experimental

The experiments were performed under purified nitrogen or argon, using Schlenk-type glassware [2]. $(Cp_2TiR)_2N_2$ and Cp_2TiR were prepared as described previously [2]. $(i\text{-}Pr)_2Mg$ was prepared as described by Strohmeier et al. [7]. Hydrazine was determined with *p*-dimethylaminobenzaldehyde [8,9]. Tests for amines were performed as described by Feigl [10]. NH_3 was determined in the Analytical Department of this university under supervision of Mr. A.F. Hamminga.

Nitrogen reduction during thermolyses of $(Cp_2TiR)_2N_2$ and Cp_2TiR

The thermal decompositions were performed as described previously [5]. After removing the volatile components in vacuum, the residues were treated (at −78°C) with HCl in ether in excess, warmed to room temperature, and extracted with 0.1 *M* HCl. The extracts were analyzed for NH_3, N_2H_4 and amines.

Nitrogen reduction by reaction of $(Cp_2TiR)_2N_2$ with sodium naphthalene, n-BuLi and i-PrMgCl

$(Cp_2TiR)_2N_2$ was added to solutions of $NaC_{10}H_8$ in THF, n-BuLi in diethyl ether or toluene, or i-PrMgCl in diethyl ether at −78°C. The reaction mixture was warmed to room temperature during 0.5 h with stirring. After one hour the mixture was cooled to —78°C and an excess of HCl in ether was added. After slowly warming to room temperature the volatile components were removed in vacuum. Non-volatile organic material and soluble Ti-compounds (e.g. $CpTiCl_3$) were removed by washing with pentane. Cp_2TiCl_2 was isolated by extracting the residue with 1,2-$C_2H_4Cl_2$ and identified by IR and UV-V spectroscopy. The remaining materials were dissolved in 0.1 *M* HCl, and analyzed for NH_3, N_2H_4 and amines.

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