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SYNTHESIS AND PROPERTIES OF DICYCLOPENTADIENYLTITANIUM(III) NEO-PENTYL. REACTIVITY OF SOME NITROGEN-FREE TITANIUM(III) COMPOUNDS IN NITROGEN FIXATION

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Summary

Reaction of Cp_2TiCl with $(CH_3)_3CCH_2MgCl$ yields $Cp_2TiCH_2(CH_3)_3$; this compound reacts with N_2 at —90°C to give the complex $[Cp_2TiCH_2C(CH_3)_3]_2N_2$ (ΔH_f —12 kcal mol^{-1}). In presence of sodium naphthalene ($NaC_{10}H_8$) or i-PrMgCl, $Cp_2TiCH_2C(CH_3)_3$ is active in reducing dinitrogen. The results obtained in the systems $Cp_2TiR/NaC_{10}H_8/THF/N_2$ with R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, *m*-$CH_3C_6H_4$ and 2,6-$(CH_3)_2C_6H_3$ are reported, together with some reactions of Cp_2TiCl_2, $Cp_2TiCH_2C(CH_3)_3$ and $Cp_2TiCH_2Si(CH_3)_3$ with i-PrMgCl. The results indicate that in all these systems the same reduction mechanism is operative, viz. the mechanism described recently for the system $(Cp_2Tiaryl)_2N_2/NaC_{10}H_8/THF/N_2$; removal of one of the Cp groups from the titanium atom is the first step in the reduction reaction.

Introduction

The preparation of the compounds Cp_2TiR (R = C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, C_6F_5, $CH_2C_6H_5$) and of the dinitrogen complexes $(Cp_2TiR)_2N_2$ (R = C_6H_5, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$) was described previously [1,2]. Recently, we reported studies of the reduction of dinitrogen in the system $(Cp_2TiR)_2N_2/NaC_{10}H_8/THF/N_2$ [3,4]. The first step in the reduction involves the removal of one Cp group per titanium atom as CpNa, while the group R remains attached to the titanium atom during the reduction. Our results indicated a reduction mechanism different from that proposed by Shilov et al. for the system $Cp_2TiCl/RMgCl/ether/N_2$ (R = Et, i-Pr), although the latter also accept the formation of $(Cp_2TiR)_2N_2$ as an intermediate [5,6]. Rupture of the Ti—R bond is assumed, whereas the Cp_2Ti structure is assumed to stay intact. The disagreement between the proposed mechanisms prompted us to reinvestigate the reaction of Cp_2TiCl with alkylating agents such as RMgX and

RLi and to study the activity of these reaction mixtures in the reduction of dinitrogen.

The reaction of Cp_2TiCl_2 or Cp_2TiCl with RMgCl or RLi (R = Me, Et, i-Pr) has been described in a number of papers. Brintziner [7] and Henrici-Olivé and Olivé [8] concluded from ESR studies on reaction mixtures that hydride species $Cp_2TiH_2^-$ (R = Et, i-Pr) or Cp_2TiR (R = Me) are formed. The existence of Cp_2TiMe during electrochemical reduction of $Cp_2Ti(Me)Cl$ was also assumed by Chivers and Ibrahim [9], but Cp_2TiMe could not be isolated. Better results were obtained by Shilov et al. [5] who reported the isolation of thermally instable $(Cp_2TiR)_2N_2$ (R = Et, i-Pr) at low temperatures. The compound $Cp_2TiCH_2Si(CH_3)_3$ was obtained in good yield from the reaction of Cp_2TiCl with $LiCH_2Si(CH_3)_3$ in ether [10]. However, in toluene a fast disproportionation to $Cp_2Ti[CH_2Si(CH_3)_3]_2$ occurred [11].

Results and discussion

Reaction of Cp_2TiCl with RMgCl (R = Me, Et, i-Pr, n-Bu, t-Bu, n-C_5H_{11}) at 0°C in ether or pentane gave brown to purple mixtures from which Cp_2TiR could not be obtained. Extraction with toluene yielded dark-brown Mg- and Cl-containing products of irreproducible, non stoichiometric composition. In solution a slow decomposition occurred, with evolution of gases and partial loss of the Cp_2Ti structure. Subsequent reaction with HCl/ether gave purple $[(Cp)_2C_{10}H_8Ti_2Cl_2]$, indicating the abstraction of H from the Cp groups and formation of a fulvalene group [12—14]. With RLi similar changes were observed, but again no products could be identified. From the reaction of Cp_2TiCl and RMgCl (R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$) in pentane, green products were obtained, which were characterized as Cp_2TiR. $Cp_2TiCH_2Si(CH_3)_3$ has been described before [10] and our results are in complete agreement with the published data *. Disproportionation reactions, as described by Green and Lucas [11], were not observed.

$Cp_2TiCH_2C(CH_3)_3$ is a green very air-sensitive compound of moderate thermal stability (decomp. temp. 25°C). The IR spectrum shows absorption bands at 3070w, 1450w, 1350w, 1120w, 1010s and 795vs cm^{-1}, characteristic of η^5-bonded cyclopentadienyl groups. Other absorption bands are found at 2920m, 2850sh, 2840w, 1255w, 1220m, 1200w, 1060w, 895m and 500w cm^{-1}. The UV-V spectrum showed absorptions at 646 nm ($\epsilon = 50$) and 448 nm ($\epsilon = 350$), resembling the values obtained for Cp_2Tiaryl [1] and $Cp_2TiCH_2Si(CH_3)_3$ (632 ($\epsilon = 40$); 455 ($\epsilon = 450$)). The ESR spectrum of the compound in toluene shows a singlet centered at g 1.960. Magnetic susceptibility measurements on the solid confirm the paramagnetic behaviour (μ = 1.65 BM). Molecular-weight determinations in benzene show the compound to be monomeric ($M = 240 \pm 10$). The chemical properties are in agreement with the formulation $Cp_2TiCH_2C(CH_3)_3$ (eq. 1,2):

$$Cp_2TiCH_2C(CH_3)_3 + HCl \rightarrow Cp_2TiCl + C(CH_3)_4 \quad (1)$$

$$Cp_2TiCH_2C(CH_3)_3 + 3/2\ Br_2 \rightarrow Cp_2TiBr_2 + BrCH_2C(CH_3)_3 \quad (2)$$

In pentane and toluene the compound reacts with N_2 to form dark blue solu-

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* Chivers and Ibrahim mentioned the formation of $Cp_2TiCH_2C(CH_3)_3$ during the reaction of Cp_2TiCl with $LiCH_2C(CH_3)_3$ [15], but did not give details.

tions (λ_{max} 639 nm, $\epsilon > 10^4$), from which at −90°C black crystals separate. By analogy with our results for $Cp_2Tiaryl$ [2] and with observations by Shilov et al. [5], we formulate the product as $[Cp_2TiCH_2C(CH_3)_3]_2N_2$. Measurements of the optical density at 639 nm at several temperatures enabled us to establish the heat of formation of the dinitrogen complex as −12 kcal mol^{-1}. This value is close to those reported for the compounds $(Cp_2TiR)_2N_2$ with R = aryl [2], but rather different from the value of −5 kcal mol^{-1} reported by Shilov et al. for the complex with R = i-Pr [16,17]. We could not isolate the pure dinitrogen complex because it decomposed rapidly above −60°C with formation of $Cp_2TiCH_2C(CH_3)_3$, according to eq. 3.

$$[Cp_2TiCH_2C(CH_3)_3]_2N_2 \rightarrow 2\ Cp_2TiCH_2C(CH_3)_3 + N_2 \qquad (3)$$

Surprisingly $Cp_2TiCH_2Si(CH_3)_3$ in pentane does not form observable amounts of a dinitrogen complex, even at temperatures as low as −125°C.

Reduction of the dinitrogen ligand of $[Cp_2TiCH_2C(CH_3)_3]_2N_2$ was achieved by addition of $NaC_{10}H_8$ or of i-PrMgCl. The reduction of dinitrogen with $NaC_{10}H_8$ under similar conditions proceeds in the way reported for the system based on $(Cp_2Tiaryl)_2N_2$ [4]. Maximum N_2-reduction (N(red)/Ti ratio about 1) was observed for Na/Ti $\geqslant$ 2.

Because of the thermal instability of the complex $[Cp_2TiCH_2C(CH_3)_3]_2N_2$ even at low temperatures, we investigated the reactions of the nitrogen-free compounds Cp_2TiR (R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$, m-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$) with $NaC_{10}H_8$ in THF under N_2 and Ar. These complexes were selected because of their differing behaviour towards dinitrogen. For R = $CH_2C(CH_3)_3$ an instable dinitrogen complex is formed and for R = m-$CH_3C_6H_4$ a stable complex; for R = $CH_2Si(CH_3)_3$ and 2,6-$(CH_3)_3C_6H_3$ no dinitrogen complexes are known, in the latter case probably for steric reasons [18]. The reactions were performed under N_2 (1 atm) with a Na/Ti ratio of about 2; the results observed after quenching are given in Table 1. At −78°C almost all the reduced nitrogen was recovered as N_2H_4. At +25°C a mixture of NH_3 and N_2H_4 was obtained. During the reduction the Cp_2Ti-structure is lost and CpTi-species are obtained ($CpTiCl_3$ is the main Ti-containing product after quenching with HCl/ether), which indicates the formation of CpNa as in the case of $(Cp_2Tiaryl)_2N_2$ [4]. This was confirmed by the

TABLE 1

CONDITIONS AND RESULTS OF THE REACTIONS IN THE SYSTEM $Cp_2TiR/2NaC_{10}H_8/THF/N_2$

R	Reaction temp. (°C) [a]	Reaction time (h)	N(red)/Ti [b]	CpNa/Ti [b]
$CH_2C(CH_3)_3$	−78	3	0.69	
	+25	1	0.94	1.00
$CH_2Si(CH_3)_3$	−78	3	0.82	
	+25	1	0.89	1.00
m-$CH_3C_6H_4$	−78	3	0.88	
	+25	1	0.79	1.00
2,6-$(CH_3)_2C_6H_3$	−78	3	0.01	
	+25	1	0.18	0.26
	+25	24	0.36	0.65

[a] In all cases the reagents were mixed at −78°C. [b] Determinations of N(red) and CpNa involved separate runs.

formation of Cp_2Fe after addition of $FeCl_2$ to the reduced mixture before hydrolysis. For R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$ and *m*-$CH_3C_6H_4$ the amount of Cp_2Fe obtained corresponds to the formation of 1 mole of CpNa per mole of Cp_2TiR (Table 1). For R = 2,6-$(CH_3)_2C_6H_3$ the reduction of nitrogen is very slow and inefficient.

Under argon the reaction of the compounds Cp_2TiR with $NaC_{10}H_8$ in THF is very slow, and even after 24 h at 25°C the formation of CpNa is incomplete (R = *m*-$CH_3C_6H_4$: CpNa/Ti = 0.9) and some starting material remains. The rate of the reaction of Cp_2Ti-2,6-$(CH_3)_2C_6H_3$ with $NaC_{10}H_8$ was not affected by this change of atmosphere. Subsequent exposure of the reduced mixtures to N_2 did not lead to N_2-complexation and/or reduction.

From these results we conclude that the reduction process of N_2 proceeds via the Cp abstraction of the dinitrogen complexes $(Cp_2TiR)_2N_2$ with R = $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$ and *m*-$CH_3C_6H_4$, although the concentration of these complexes may be very low. The N_2-free complexes react only slowly with $NaC_{10}H_8$, possibly with formation of the coordinatively highly unsaturated, very reactive CpTiR, which in the absence of N_2 reacts further to give complexes which are inactive in the reduction of N_2. It appears from these experiments that $Cp_2TiCH_2Si(CH_3)_3$ also forms a complex with dinitrogen which is probably very unstable.

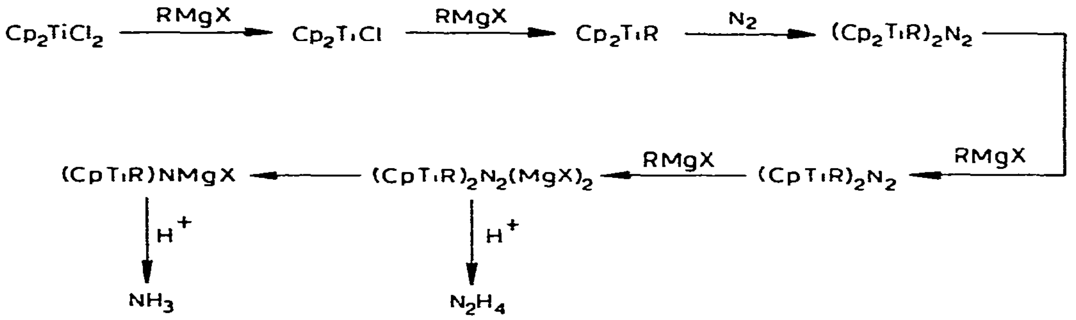
The reactivity of Cp_2TiR with R = $CH_2C(CH_3)_3$ and $CH_2Si(CH_3)_3$ towards i-PrMgCl is larger than that of the Cp_2Tiaryl compounds. Up to 0.65 N(red)/Ti was found, cf. [3]. Cp_2Fe was formed on addition of $FeCl_2$, indicating the removal of one Cp group per titanium during the reduction reaction. Again the similarity with the system $(Cp_2\text{Tiaryl})_2N_2/NaC_{10}H_8/THF/N_2$ is striking.

We were puzzled by the differences between our mechanism and that suggested by Shilov et al. for the system Cp_2TiCl_2/i-PrMgCl/ether/N_2 [6]. The assumed decomposition of the intermediate $(Cp_2Tii\text{-}Pr)_2N_2$ at −60°C with formation of $(Cp_2Ti)_2N_2$ seems unlikely and formation of compounds containing $(Cp)_2C_{10}H_8Ti_2$ units is expected instead, cf. [19]. These discrepancies prompted us to repeat some of the experiments reported by Shilov et al. [6]. After warming a mixture of Cp_2TiCl_2 and 4 eq. of i-PrMgCl in ether during 3 h from −60°C to room temperature and quenching with HCl/ether at −78°C, we obtained 46% Cp_2TiCl_2, 40% CpTi compounds (mainly $CpTiCl_3$) and 49% N(red) (37% NH_3 and 6% N_2H_4), relative to the starting material Cp_2TiCl_2. Addition of $FeCl_2$ to the reaction mixture prior to hydrolysis yielded 22% of Cp_2Fe, indicating the presence of at least 44% of CpMgCl in the reaction mixture. The removal of Cp groups from the Cp_2Ti species was also confirmed by adding 1,4-dioxan to the reaction mixture, evaporating the solution and heating it in vacuum to sublime out a white cristalline solid which was identified as the dioxan complex of Cp_2Mg.

Variation of the reaction conditions gave different amounts of the products. After 1 h stirring at −50°C about 70% Cp_2TiCl_2 was recovered whereas only 28% N(red) was formed (14% NH_3, 7% N_2H_4). Evidently, the amount of N(red) formed corresponds to the amount of Cp_2TiCl_2 that has reacted. From our results we conclude that Cp_2TiCl_2 is involved in the reduction reaction as indicated in Scheme 1.

Apparently the reduction of dinitrogen in the presence of Cp_2TiR with R = alkyl and the reducing agents $NaC_{10}H_8$ or i-PrMgCl follows the pathway described previously for $[Cp_2\text{Tiaryl}]_2N_2$ [4].

SCHEME 1



Experimental

All experiments were performed under purified nitrogen or argon, using Schlenk-type glassware. Solvents were purified by standard methods and freed from oxygen by repeated degassing and saturation with nitrogen. $Cp_2TiCH_2Si(CH_3)_3$ was prepared as described by Chivers and Ibrahim [10]. Cp_2Ti-2,6-$(CH_3)_2C_6H_3$ and Cp_2Ti-*m*-$CH_3C_6H_4$ were prepared as described previously [1]. Ferrocene was determined quantitatively by UV-V spectrometry with a Perkin—Elmer EPS-3T spectrophotometer. The amount of hydrazine was measured as described by Watt and Chrisp [20].

Ti, C and H analyses and NH_3 determination were carried out in the analytical department of this university under supervision of Mr. A.F. Hamminga.

Preparation of $Cp_2TiCH_2C(CH_3)_3$

20 ml of 0.52 *M* $(CH_3)_3CCH_2MgBr$ in ether was added during 1 h to 2.19 g of Cp_2TiCl (10.3 mmol) in 100 ml of n-pentane at −10°C with vigorous stirring. After stirring for 2 h, the solution was filtered and cooled to −78°C. $Cp_2TiCH_2C(CH_3)_3$ separated as small green crystals. The mother liquor was removed and the crystalline material was recrystallized from pentane and dried at 0°C in vacuum. Yield: 1.0 g $Cp_2TiCH_2C(CH_3)_3$ (4.0 mmol). (Found: C, 71.18; H, 8.51; Ti, 18.89; mol.wt. 240 ± 10. $C_{15}H_{21}Ti$ calcd.: C, 72.29; H, 8.49; Ti, 19.22%; mol.wt. 249.)

Reactions with $NaC_{10}H_8$

Cp_2TiR was added to freshly prepared solutions of $NaC_{10}H_8$ in THF, at −78°C. The mixture was stirred for the time and at the temperature given in Table 1. CpNa and N(red) were determined in separate experiments. The amounts of CpNa formed were determined from the yields of Cp_2Fe obtained after stirring the reaction mixtures for 1 h at room temperature in the presence of a fourfold excess of $FeCl_2$; ferrocene was extracted from the evaporated reaction mixtures with n-pentane and purified by sublimation. N(red) was determined after quenching the reaction mixture with HCl/H_2O and evaporation in vacuum. The residue was extracted with 0.1 *M* HCl/H_2O and the extracts were analyzed for NH_3 and N_2H_4.

Reactions with i-PrMgCl

To a solution of Cp_2TiR in THF, 2 eq. of i-PrMgCl in ether were added at —78° C. The mixture was allowed to warm to room temperature during about 3 h. Subsequently a fivefold excess of HCl/ether was added at —78° C. After evaporation in vacuum, the residue was extracted with 0.1 *M* HCl/H_2O. The collected HCl/H_2O fractions were analyzed for NH_3 and N_2H_4.

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