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BINUCLEAR DINITROGEN COMPLEXES OF ARYL- AND BENZYLDICYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

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SUMMARY

The preparation of the deep-blue diamagnetic dinitrogen complexes $(Cp_2TiR)_2N_2$ with $R=C_6H_5$, *o*-, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$ is described. Their chemical and physical properties confirm the formulation in which the R groups are σ-bonded to the Cp_2Ti moiety, and the two nitrogen atoms are equivalent. The heats of formation of the complexes from Cp_2TiR and N_2 in toluene have been determined from spectrophotometric data; for $R=C_6H_5$, *o*-, *m*-, *p*-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$, the values are −18, −9, −17, −20, −17 and −14 kcal·mol^{-1}, respectively. The solid complexes vary markedly in thermal stability, and are extremely air sensitive. The complexed nitrogen can be completely reduced with sodium naphthalene; after hydrolysis of the products, NH_3 and N_2H_4 are obtained. In the thermolysis of the solids, some of the nitrogen is reduced.

INTRODUCTION

Several organometallic compounds of titanium have been found to promote the reduction of N_2 under mild conditions; for a review see ref. 1. The intermediate formation of dinitrogen complexes of titanium has been assumed by several authors, but very little is known about such complexes, and none had been isolated until recently. Van Tamelen *et al.* reported the formation of $(Cp_2TiN_2)_2$ ($Cp=\pi$-C_5H_5) in benzene solution[2]. Evidence for the occurrence of binuclear dinitrogen complexes in reaction mixtures of Cp_2TiCl_2 and RMgCl ($R=C_2H_5$, i-C_3H_7) at low temperatures was described by Shilov *et al.*[3]. More recently the formula $(CpC_5H_5RTi)_2N_2$ was assigned to these complexes[4], by analogy with the complex $(Cp_2TiC_6H_5)_2N_2$, which we had isolated and characterized, and described in a preliminary communication[5]. At about the same time Brintzinger *et al.*[6–8] reported the dinitrogen complexes of decamethyltitanocene, $\{[C_5(CH_3)_5]_2Ti\}_2N_2$, and of titanocene, Cp_2TiN_2.

We describe below our further investigations on the synthesis and properties of the dinitrogen complexes $(Cp_2TiR)_2N_2$.

RESULTS AND DISCUSSION

Reaction of Cp_2TiR with nitrogen in solution

When toluene solutions of Cp_2TiR[9] having $R=C_6H_5$, *o*-, *m*-, *p*-$CH_3C_6H_4$,

C_6F_5, $CH_2C_6H_5$ (but not for R=2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$, C_5H_5) were cooled in a nitrogen atmosphere, an intense blue colour was observed. This colour disappeared when the solution was warmed and reappeared when it was cooled again. The colour also disappeared on evacuation of the system, and reappeared when nitrogen was readmitted. Under argon no blue colour was visible even on cooling, but when nitrogen was bubbled through the solution immediately turned blue. Thus there was clearly a completely reversible formation of a complex of Cp_2TiR with nitrogen.

The visible spectra of the solution show an intense charge-transfer band at about 600 nm, which is responsible for the deep blue colour of the complexes. The position of the peak depends slightly on the group R, λ_{max} being nearly the same for the aryl complexes with R=C_6H_5, *o*-, *m*-, *p*-$CH_3C_6H_4$ (about 615 nm). For R=C_6F_5 and $CH_2C_6H_5$ slightly different values were found (Table 1). From absorbance measurements on solutions of CpTi(*p*-$CH_3C_6H_4$) in toluene, ε was calculated to be 4–5 × 10^4 $l \cdot mol^{-1} \cdot cm^{-1}$, but an exact determination of ε was not possible. Intense absorptions at about 600 nm due to dinitrogen complex formation have been reported by other authors. Brintzinger *et al.* reported a maximum at 597 nm ($\varepsilon > 10^4$) for $(Cp_2Ti)_2N_2$[8]. Shilov *et al.* observed the formation of the bright blue (λ_{max} 610 nm) complexes $(CpC_5H_5RTi)_2N_2$ in the system $Cp_2TiCl_2/RMgX/N_2$ in ether (R=C_2H_5, i-C_3H_7)[3,4].

TABLE 1

ABSORPTION MAXIMA IN THE VISIBLE RANGE AND HEATS OF FORMATION OF COMPLEXES $(Cp_2TiR)_2N_2$ IN TOLUENE

R	λ_{max} (*nm*)	ΔH^0 (*kcal·mol*$^{-1}$)
C_6H_5	615	−18
o-$CH_3C_6H_4$	614	−9
m-$CH_3C_6H_4$	613	−17
p-$CH_3C_6H_4$	616	−20
C_6F_5	588	−17
$CH_2C_6H_5$	628	−14

The formation of the complex as a function of the concentration of Cp_2TiR, and of the nitrogen pressure, P_{N_2}, was studied spectrometrically for R=C_6F_5 (λ_{max} 588 nm). Plots of the absorbance, *A*, of the dinitrogen complex *vs*., the square of the concentration of $Cp_2TiC_6F_5$ and the nitrogen pressure, P_{N_2}, are given in Fig. 1. Assuming that the solutions of the dinitrogen complex follow the Lambert–Beer Law, it is seen from Fig. 1 that the concentration of the complex is quadratic with respect to the concentration of $Cp_2TiC_6F_5$ and linear with respect to the nitrogen pressure, which is directly proportional to the nitrogen concentration in solution. This indicates the following equilibrium in the solutions:

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

Analogous experiments on the other complexes confirmed the results given above, but because of thermal decomposition of the compounds Cp_2TiR (R=C_6H_5, *m*-,

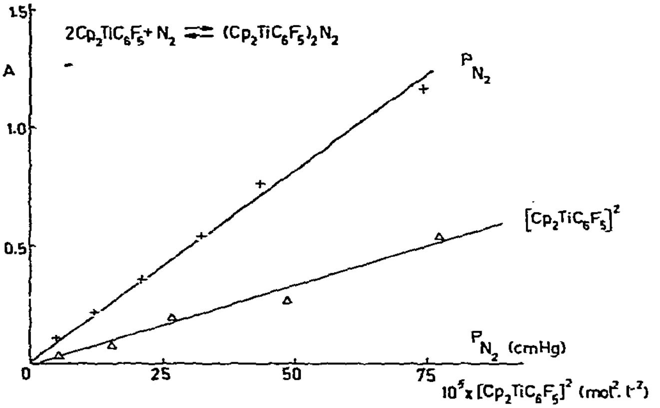


Fig. 1. Absorbance, A, of $(Cp_2TiC_6F_5)_2N_2$ (in toluene solution, 0.2 cm cell) plotted *vs.* P_{N_2} ($[Cp_2TiC_6F_5]$ 1.2×10^{-2} M, −31°), and *vs.* $[Cp_2TiC_6F_5]^2$ (P_{N_2} 750 mmHg, −26°).

p-$CH_3C_6H_4$, $CH_2C_6H_5$) in solution the results were less accurate.

The heat of formation of the complexes, ΔH^0, in toluene solution was calculated from the change of the absorbance at λ_{max} with temperature. At temperatures at which the concentration of the complexes is much smaller than that of Cp_2TiR and N_2 in the solutions, the expression:

$$\frac{-\Delta H^0}{R} = \frac{\mathrm{d} \ln K}{\mathrm{d}T^{-1}}$$

can be approximated by:

$$\frac{-\Delta H^0}{R} = \frac{\mathrm{d} \ln x}{\mathrm{d}T^{-1}} = \frac{\mathrm{d} \ln A}{\mathrm{d}T^{-1}},$$

where x indicates the concentration of $(Cp_2TiR)_2N_2$ and A the absorbance of the dinitrogen complex in solution at λ_{max}. In Fig. 2 log A is plotted *vs.* T^{-1} for $Cp_2Ti(p$-$CH_3C_6H_4)$ in toluene. Similar plots were obtained for the other complexes. ΔH^0 values calculated from these plots are given in Table 1. The value of ΔH (−5 kcal·mol^{-1}) reported by Shilov and Likhtenshtein[10] for the complex $[Cp(C_5H_5$–i-$C_3H_7)Ti]_2N_2$ may be compared with the data for the complexes described in this paper.

Evidence for the diamagnetism of the complexes in solution was obtained from ESR spectra of solutions (10^{-3}–10^{-4} M) of Cp_2TiR in toluene. Under nitrogen these solutions gradually turned blue on cooling to −95°, and the intensity of the Cp_2TiR signal at $g = 1.95$[9] decreased and finally vanished completely without the appearance of another signal. When the experiment was repeated in an argon atmosphere, neither the blue colour nor the disappearance of the ESR signal were observed. The low solubilities of the complexes at the temperatures at which they are formed have so far prevented the recording of their NMR spectra.

The solid complexes $(Cp_2TiR)_2N_2$

The solid dinitrogen complexes $(Cp_2TiR)_2N_2$ ($R = C_6H_5$, o-, m-, p-$CH_3C_6H_4$, C_6F_5, $CH_2C_6H_5$) were obtained by slow cooling of ca. 0.1 M toluene solutions of

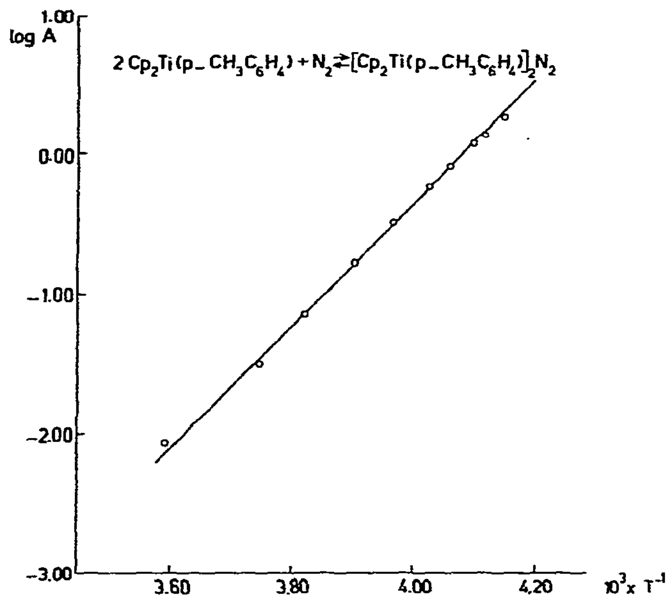


Fig. 2. Plot of log *A* *vs.* T^{-1} for $[Cp_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$ in toluene. $[Cp_2Ti(p\text{-}CH_3C_6H_4)]3 \times 10^{-3}$ *M*, P_{N_2} 750 mmHg, 0.2 cm cell.

Cp_2TiR under nitrogen (1 atm.). The complexes separated as glittering purple to blue-black crystals. After removal of the mother liquor and washing with n-pentane, the crystals were dried in vacuum at −20°. In general, the products thus obtained contained some trapped toluene (about 5% by weight). For the complexes with $R = C_6H_5$, *m*-, *p*-$CH_3C_6H_4$, $CH_2C_6H_5$ the toluene could be largely removed by continuous extraction with n-pentane at −20°, but because of the low thermal stability complete removal of toluene without considerable decomposition was not achieved for $R = o\text{-}CH_3C_6H_4$, C_6F_5. The amount of nitrogen consumed in reaction (1) and the results of elementary analyses of the solid complexes (Table 3) were in agreement with the formula $(Cp_2TiR)_2N_2$. Attempts to prepare analogous complexes with $R = C_5H_5$, 2,6-$(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$ were not successful; even concentrated solutions of Cp_2TiR at −78° gave no indication of complex formation.

The thermal stabilities of the dinitrogen complexes varied markedly (Table 3). The stability sequence (with exception of $R = C_6F_5$) appeared to be opposite to that for the nitrogen-free compounds Cp_2TiR[9]. The nature of the group R, in particular the presence or absence of substituents on the *ortho* positions of the aryl group, seems to govern the thermal stabilities of the two types of compounds. The instability of dinitrogen complexes with di-*ortho* substituted aryl groups [$R = 2,6\text{-}(CH_3)_2C_6H_3$, 2,4,6-$(CH_3)_3C_6H_2$] and the low stability of the complex with $R = o\text{-}CH_3C_6H_4$ are probably caused by steric hindrance due to the *ortho* substituents. The thermal decomposition of the dinitrogen complexes gave almost quantitative formation of N_2 and RH; a black residue remained, in which the Cp_2Ti structure was no longer present, as in the case of the nitrogen-free compounds Cp_2TiR[9]. In the case of $(Cp_2TiC_6H_5)_2$-N_2, about 10% of the complexed nitrogen was reduced during the thermolysis and found as ammonia after acidification with hydrogen chloride. Details on the thermolysis of $(Cp_2TiR)_2N_2$ and Cp_2TiR will be given in a future paper.

The complexed nitrogen was readily released as N_2 when the complexes $(Cp_2TiR)_2N_2$ were brought into solution at room temperature or when they were treated with, *e.g.*, H_2, CO, HCl or Br_2. No nitrogen compounds (ammonia, hydrazine, or amines) were found among the reaction products. Under vacuum at room temperature the solid complexes decomposed with the formation of Cp_2TiR and N_2.

The chemical properties of the complexes $(Cp_2TiR)_2N_2$ are quite similar to those of the nitrogen-free compounds Cp_2TiR[9]. They were very sensitive towards oxygen and water. Slow oxidation led to yellow polymeric products of an irreproducible and non-stoichiometric composition. Violent reactions occurred with chlorine-containing solvents; Cp_2TiCl_2 was found among the products. With HCl at −78° a fast reaction was observed:

$$(Cp_2TiR)_2N_2 + 2\,HCl \rightarrow 2\,Cp_2TiCl + 2\,RH + N_2$$

With bromine the complexes reacted according to:

$$(Cp_2TiR)_2N_2 + 3\,Br_2 \rightarrow 2\,Cp_2TiBr_2 + 2\,RBr + N_2$$

These reactions have been studied quantitatively. The results, given in Table 2, provide strong evidence for the presence of the Cp_2Ti moiety and Ti–R σ-bonds in the dinitrogen complexes[11]. Magnetic-susceptibility measurements between 4.2 and 100 K showed the complexes to the diamagnetic in the solid state.

The IR spectra of the solid complexes in Nujol are given in Fig. 3. Because of the extensive thermal decomposition at room temperature, no spectra could be obtained for R=o-$CH_3C_6H_4$, C_6F_5. Absorptions characteristic for π-bonded cyclopentadienyl groups are found at about 3100 w, 1440 m, 1360 w, 1120 vw, 1020–1010 m and 810 vs cm^{-1}[12]. All spectra show the bands characteristic of phenyl or substituted phenyl groups[13]. The IR spectra of the complexes $(Cp_2TiR)_2N_2$ are very similar to those of the corresponding compounds Cp_2TiR, Cp_2VR and Cp_2TiR_2[9,14], suggesting a close similarity in structure and bonding. There are no absorptions in the 2200–1900 cm^{-1} range assignable to $\nu(N{\equiv}N)$. Therefore, we assume that the complexes $(Cp_2TiR)_2N_2$ are centrosymmetric. The absence of the $\nu(N{\equiv}N)$ absorption in the titanocene complex $(Cp_2Ti)_2N_2$ was likewise interpreted as being due to a centrosymmetric Ti–N_2–Ti structure[8].

TABLE 2

REACTION OF $(Cp_2TiR)_2N_2$ WITH HCl AND Br_2

R	*HCl, yield (%) of*		*Br_2, yield(%) of*	
	RH	*Cp_2TiCl_2*	*RBr*	*Cp_2TiBr_2*
C_6H_5	97	93	92	101
m-$CH_3C_6H_4$	96	88	92	100
p-$CH_3C_6H_4$	97	82	94	103
C_6F_5	87	63	[a]	[a]
$C_6H_5CH_2$	87	76	97	100

[a] Not determined.

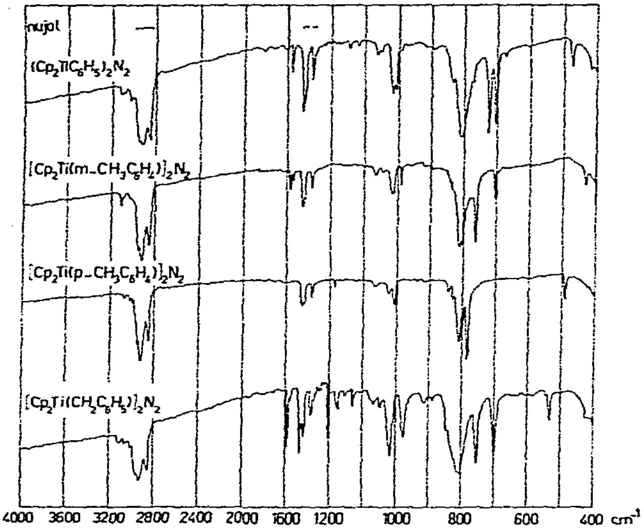
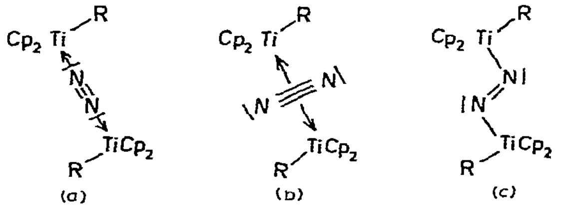


Fig. 3. IR spectra of $(Cp_2TiC_6H_5)_2N_2$, $[Cp_2Ti(m\text{-}CH_3C_6H_4)]_2N_2$, $[Cp_2Ti(p\text{-}CH_3C_6H_4)]_2N_2$, $(Cp_2TiCH_2C_6H_5)_2N_2$ in Nujol. The Nujol absorptions are indicated at the top of the figure.

The exact structure of the complexes, especially the bonding of the dinitrogen group, cannot be deduced unequivocally from the results obtained. The presence of the Cp_2Ti moiety, R groups σ-bonded to the metal and the complexed N_2 group, is well established by the stoichiometry of the compounds, their IR spectra, the reactions with Br_2 and HCl and the observed equilibrium (1) in solution. Several centrosymmetric arrangements of these groups are possible:



In structure (c) the metal may be regarded as Ti^{IV}; in structures (a) and (b) the diamagnetism of the complexes could be explained by interaction of the odd electrons of the two Ti^{III} atoms via the antibonding π-orbitals of the dinitrogen ligand.

Shilov *et al.*[4] suggest that the group R is bonded to a C_5H_5 ring, and that the dinitrogen complexes are in fact cyclopentadiene-cyclopentadienyl derivatives of titanium(I). In our opinion this view conflicts with the IR spectra and the chemical properties of the complexes described here.

The dinitrogen group in $(Cp_2TiR)_2N_2$ can readily be reduced. Partial reduction (NH_3/Ti 0.14) was observed after the thermolysis of $(Cp_2TiC_6H_5)_2N_2$. Complete reduction could be achieved by adding the complexes at $-78°$ to solutions of sodium naphthalene in THF. After stirring for 2 h at $-20°$ an excess of HCl in ether was added. Ammonia and hydrazine were found in the reaction mixture; the ratio

$N(N_2H_4)/N(NH_3)$ being about unity; the Cp_2Ti structure was destroyed. In some experiments traces of other nitrogen compounds (amines) were also present. The relative amounts of ammonia and hydrazine appeared to depend on the reaction temperature rather than on the Na/Ti ratio. A detailed account of this nitrogen reduction reaction will be published separately.

EXPERIMENTAL

The experiments were performed in an atmosphere of purified nitrogen or argon using Schlenk-type glassware. Ether and THF were distilled from KOH and dried over sodium. Toluene (Merck *p.a.*) and n-pentane (Merck *p.a.*) were stored over sodium. Prior to use the solvents were freed from oxygen by repeated degassing and saturating with nitrogen. Cp_2TiCl was prepared as described in the literature[15], and purified by sublimation (180°/0.1 mmHg) or recrystallization from toluene. Good results were also obtained when Cp_2TiCl was prepared by reducing Cp_2TiCl_2 with one equivalent of i-C_3H_7MgCl:

$$Cp_2TiCl_2 + \text{i-}C_3H_7MgCl \xrightarrow{\text{ether}} Cp_2TiCl + MgCl_2 + C_3H_7^{\bullet}$$

Cp_2TiCl thus prepared was used without isolation or purification.

Grignard reagents (about 0.7–1.0 *M*) were prepared in ether and stored under nitrogen. C_6H_5Br and $C_6H_5CH_2Cl$ were distilled before use; the other organic bromides were used as they were purchased. The Grignard reagents were syringed into the reaction vessels. At the same time 1,4-dioxane in an amount equimolar to the Grignard reagent was added in order to precipitate the magnesium halides formed and to decrease the reducing action of the reagent[16].

Elementary analyses for C, H and N (Dumas) were carried out by the Microanalytical Department of this University under supervision of Mr. W. M. Hazenberg; Ti was analyzed in our laboratory under supervision of Drs. B. P. Knol. Gas chromatographic analyses were performed with a F&M model 720 gas chromatograph. IR spectra were recorded on Nujol suspensions with a Hitachi EPI-G spectrophotometer. Absorption spectra in the visible range were recorded with a Perkin–Elmer EPS-3T spectrophotometer. Magnetic susceptibilities were determined with a vibrating-sample magnetometer (PAR magnetometer type 150 D). Decomposition temperatures were determined with a melting-point microscope on samples sealed in glass capillaries under nitrogen.

All complexes were prepared in essentially the same way, and so only the synthesis of $[Cp_2Ti(m\text{-}CH_3C_6H_4)]_2N_2$ is described in detail. The synthesis of $(Cp_2TiC_6H_5)_2N_2$ was described previously[5]. Yields, decomposition temperatures and analytical data are given in Table 3.

Bis(m-tolyldicyclopentadienyltitanium)dinitrogen

A mixture of 7.6 mmol of Cp_2TiCl, an equimolar amount of 1,4-dioxane, and 50 ml of ether was stirred vigorously at −20°, and 10.5 ml of a 0.69 *M* solution of $m\text{-}CH_3C_6H_4MgBr$ in ether was added dropwise during 2 h. The solvent then was removed in vacuum at −20°. The residue was stirred with 35 ml of toluene in vacuum at 0°. The resulting green solution of $Cp_2Ti(m\text{-}CH_3C_6H_4)$ was filtered and nitrogen

TABLE 3

YIELDS, DECOMPOSITION TEMPERATURES, AND ANALYTICAL DATA FOR THE COMPLEXES $(Cp_2TiR)_2N_2$

R	*Yield* (%)	*Decomp.* (°C)	*Analysis, found (calcd.) (%)*			
			C	*H*	*Ti*	*N*[a]
C_6H_5	56	67	71.55	5.81	17.76	
			71.11	5.72	17.62	4.83
			(71.38)	(5.62)	(17.79)	(5.20)
$o\text{-}CH_3C_6H_4$	50	< −20				[b]
$m\text{-}CH_3C_6H_4$	47	67	72.12	6.51	16.75	4.50
			72.07	6.31	16.76	4.50
			(72.09)	(6.05)	(16.91)	(4.95)
$p\text{-}CH_3C_6H_4$	54	63	73.29	6.28	15.91	4.68[c]
			73.68	6.39	16.03	4.68
			(72.09)	(6.05)	(16.91)	(4.95)
C_6F_5	61	10				[b]
$CH_2C_6H_5$	17	44	73.33	6.70	16.15	4.14[c]
			73.10	6.79	16.18	4.15
			(72.09)	(6.05)	(16.91)	(4.95)

[a] Partial reduction of the complexed N_2 during the combustion is probably responsible for the low nitrogen values. [b] Because of the low thermal stability of the complexes no analytical data were obtained. [c] These results are compatible with the presence of about 4–5% toluene, which was confirmed by IR spectroscopy and GLC.

gas was admitted. The solution immediately turned intensely blue. On slow cooling to −78° the dinitrogen complex separated as a black crystalline layer. After decantation of the mother liquor and washing with *n*-pentane, the $[Cp_2Ti(m\text{-}CH_3C_6H_4)]_2N_2$ was dried in vacuum at −20°, sealed in ampoules under nitrogen, and stored at −80°. Yield 1.7 mmol (47%).

Reaction with hydrogen chloride

Hydrogen chloride (3 mmol) in 3 ml of ether was added to 0.5 mmol of $(Cp_2TiR)_2N_2$ in 7 ml of n-pentane at −78°. A reaction rapidly took place and RH, N_2 and a green precipitate of Cp_2TiCl were formed.

$$(Cp_2TiR)_2N_2 + 2\,HCl \rightarrow 2\,Cp_2TiCl + 2\,RH + N_2$$

On warming to room temperature the Cp_2TiCl was oxidized by the excess of hydrogen chloride according to the equation:

$$Cp_2TiCl + HCl \rightarrow Cp_2TiCl_2 + \tfrac{1}{2}\,H_2$$

The RH reaction products were quantitatively determined by gas chromatography and identified by their retention times. After washing with n-pentane, the amount of Cp_2TiCl_2 formed was determined spectrometrically in 1,2-dichloroethane solution (λ_{max} 525 nm, ε $2.00 \times 10^2\ l \cdot mol^{-1} \cdot cm^{-1}$; λ_{max} 392 nm, ε $2.39 \times 10^3\ l \cdot mol^{-1} \cdot cm^{-1}$). The results are presented in Table 2.

Reaction with bromine

Bromine (1.6 mmol) was added to a mixture of 0.5 mmol of $(Cp_2TiR)_2N_2$ and

10 ml of n-pentane at −78°. The mixture was slowly warmed to room temperature and stirred for about 2 h. RBr and a precipitate of Cp_2TiBr_2 were formed according to:

$$(Cp_2TiR)_2N_2 + 3\,Br_2 \rightarrow 2\,Cp_2TiBr_2 + 2\,RBr + N_2$$

The RBr was quantitatively determined by gas chromatography and identified by its retention time. The amount of Cp_2TiBr_2 was spectrometrically determined in 1,2-dichloroethane solution (λ_{max} 428 nm, ε 3.26×10^3 $l \cdot mol^{-1} \cdot cm^{-1}$). The results are given in Table 2.

Thermal decomposition of $(Cp_2TiC_6H_5)_2N_2$

$[(Cp_2TiC_6H_5)_2N_2]$ (0.78 mmol) was heated at 150°. A rapid evolution of N_2 took place during about 5 min [0.7 mmol, $N(N_2)/Ti = 0.9$]. (On subsequent heating of the residue to 300° no more N_2 was formed.) Benzene was also formed during the thermolysis. It was pumped off and quantitatively determined by gas chromatography (1.32 mmol, C_6H_6/Ti 0.85). After treatment of the black residue with HCl in ether, no Cp_2TiCl_2 or C_6H_6 were found. The resulting reaction mixture was dried in vacuum and decomposed with H_2SO_4. A Kjeldahl determination on the resulting solution yielded 0.21 mmoles of NH_3 [$N(NH_3)/Ti$ 0.14].

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REFERENCES

1 G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, 8 (1969) 650.
2 E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler and W. Cretney, *J. Amer. Chem. Soc.*, 92 (1970) 5251.
3 A. E. Shilov, A. K. Shilova and E. F. Kvashina, *Kinet. Katal.*, 10 (1969) 1402.
4 A. E. Shilov, A. K. Shilova, E. F. Kvashina and T. A. Vorontsova, *J. Chem. Soc. D*, (1971) 1590.
5 J. H. Teuben and H. J. de Liefde Meijer, *Recl. Trav. Chim. Pays-Bas*, 90 (1971) 360.
6 J. E. Bercaw and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 93 (1971) 2046.
7 R. A. Marvich and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 93 (1971) 2048.
8 J. E. Bercaw, R. H. Marvich, L. G. Bell and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 95 (1972) 1219.
9 J. H. Teuben and H. J. de Liefde Meyer, *J. Organometal. Chem.*, 46 (1972) 313.
10 A. E. Shilov and G. I. Likhtenshtein, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 518.
11 H. J. de Liefde Meijer and F. Jellinek, *Inorg. Chim. Acta*, 4 (1970) 651.
12 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, 91 (1969) 7281.
13 N. B. Colthup, L. H. Daly and S. J. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York, 1964.
14 C. P. Boekel and J. H. Teuben, unpublished results.
15 G. Natta, G. Dallasta, G. Mazzanti, U. Giannini and S. Cesca, *Angew. Chem.*, 71 (1959) 205.
16 A. Jacot-Guillarmod, R. Tabacchi and J. Porret, *Helv. Chim. Acta*, 53 (1970) 1491.