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REACTIONS OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiR}$ COMPOUNDS WITH ORGANIC CYANIDES

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Summary

The syntheses and properties of the titanium(III) complexes $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ ($\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$, C_6F_5 , Cl ; $\text{R}' = \text{CH}_3$, *t*- C_4H_9 , C_6H_5 , *o*- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$) are described. In the complexes the nitrogen atom of the cyanide ligands is coordinated to the metal. The thermal stabilities of the complexes depend markedly on R and R'; on heating they undergo a novel reaction in which two cyanide ligands are coupled by formation of a C—C bond, while the metal is oxidized to titanium(IV).

Introduction

Studies of the thermal decomposition of compounds Cp_2TiR ($\text{R} = \text{aryl}$) led to the concept that for these molecules a vacant metal orbital plays a key role in the decomposition mechanism [1,2]. Stabilization of the Ti—R bond in this type of compounds was achieved e.g., by shielding of the vacant orbital, by complexation with N_2 [2], or by internal coordination (e.g. in $\text{R} = 2\text{-}[(\text{dimethyl}(\text{amino})\text{-phenyl})]$ [3,7].

In order to study the effect of donor molecules on the stability of the Ti—R bond and to explore some reactions of the coordinated ligand we treated Cp_2TiR ($\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$, Cl , C_6F_5) with a range of organic cyanides $\text{R}'\text{CN}$ ($\text{R}' = \text{CH}_3$, *t*- C_4H_9 , C_6H_5 , *o*- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$) and we describe the nature of these reactions, and the properties of the complexes formed.

Results and discussion

Addition of $\text{R}'\text{CN}$ ($\text{R}' = \text{CH}_3$, *t*- C_4H_9 , C_6H_5 , *o*- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$) to cold solutions ($< -10^\circ\text{C}$) of Cp_2TiR ($\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$, C_6F_5 , Cl) gives deep-blue or green solutions. On further cooling and concentration crystalline products of the same colour separate. Chemical analyses, molecular weights

(cryoscopy in benzene), and magnetic properties (one unpaired electron per titanium) of these products are in agreement with their formulation as monomeric complexes $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ (Table 1). $\text{Cp}_2\text{Ti-2,6-(CH}_3)_2\text{C}_6\text{H}_3$ did not react with $\text{R}'\text{CN}$, probably because of the shielding of the vacant coordination site of Ti by the methyl groups [8].

The colours of the solutions of $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ indicate that equilibrium (eq. 1) is established; and shifts to the left on heating. However, upon warming solutions of certain combinations of R and R' (R = C_6H_5 , *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$ and R' = CH_3 , C_6H_5 , *o*- $\text{CH}_3\text{C}_6\text{H}_4$) an irreversible reaction sets in. Yellow

TABLE 1
ANALYTICAL DATA OF THE COMPOUNDS $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$

Cp_2TiR R	R'CN R'	Yield (%)	Analysis (found (calcd.) (!))			
			Ti	C	H	N
C_6H_5	t- C_4H_9	80	14.25 (14.26)	74.34 (74.55)	7.15 (7.15)	4.10 (4.14)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	55	12.42 (12.43)	76.85 (78.00)	6.40 (6.20)	^a
$\text{CH}_2\text{C}_6\text{H}_5$	t- C_4H_9	35	13.74 (13.61)	74.29 (75.00)	7.39 (7.39)	3.65 (3.98)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	35	11.81 (11.98)	76.52 (78.00)	6.61 (6.50)	^a
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	t- C_4H_9	65	13.72 (13.61)	74.97 (75.00)	7.52 (7.39)	3.71 (3.98)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	50	11.81 (11.98)	77.08 (78.00)	6.72 (6.50)	3.81 (3.50)
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	t- C_4H_9	85	13.52 (13.61)	74.60 (75.00)	7.45 (7.39)	4.09 (3.98)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	55	12.03 (11.98)	77.06 (78.00)	6.73 (6.50)	^a
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	t- C_4H_9	65	13.71 (13.61)	74.86 (75.00)	7.48 (7.39)	3.88 (3.98)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	60	11.85 (11.98)	77.73 (78.00)	6.72 (6.50)	3.17 (3.50)
C_6F_5	CH_3	65	12.30 (12.41)	56.22 (55.95)	3.67 (3.36)	3.50 (3.62)
	t- C_4H_9	75	11.16 (11.19)	58.96 (58.88)	4.65 (4.44)	3.22 (3.27)
	C_6H_5	65	10.89 (10.69)	61.52 (61.60)	3.53 (3.35)	3.23 (3.13)
	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	65	10.22 (10.36)	62.53 (62.34)	3.95 (3.68)	2.96 (3.03)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	65	10.08 (10.06)	62.92 (63.03)	4.18 (3.99)	2.95 (2.94)
						^a
Cl	CH_3	70	18.72 (18.69)	56.61 (56.20)	5.27 (5.07)	^a
	t- C_4H_9	50	15.96 (16.16)	60.57 (60.70)	6.46 (6.41)	4.51 (4.72)
	C_6H_5	65	15.11 (15.13)	64.69 (64.45)	4.86 (4.74)	4.27 (4.42)
	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	75	14.55 (14.49)	65.43 (65.36)	5.30 (5.14)	4.25 (4.24)
	2,6-(CH_3) $_2\text{C}_6\text{H}_3$	80	13.81 (13.90)	65.99 (66.20)	5.56 (5.52)	3.98 (4.06)

^a Not determined.

or orange products of composition $[\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}]_2$ are then formed in which the metal is oxidized from titanium(III) to titanium(IV), while the two $\text{R}'\text{CN}$ ligands are coupled via the cyanide carbon atoms. The solid complexes $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ (same combinations R and R' as given above) undergo a similar reaction on warming. This reaction is under investigation.

The complexes $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ are very air-sensitive and readily soluble in toluene or THF, but only slightly soluble in aliphatic solvents. As expected for complexes of this structure, reaction with HCl in ether proceeds according eq. 2.

The IR spectra show the absorptions characteristic of the groups $\eta^5\text{-C}_5\text{H}_5$, R' and R. The $\nu(\text{CN})$ absorptions (Table 2) are found in the 2200—2300 cm^{-1} range; they lie at higher frequencies than those in the corresponding free cyanides, indicating that in the complexes the cyanide function is σ -bonded to the metal [4]. Exceptions are the 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CN}$ complexes with $\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4\cdot\text{CH}_2\text{C}_6\text{H}_5$, in which $\nu(\text{CN})$ is lower than in the free cyanide, indicating enhanced π -back bonding in the complexes [5].

The UV-Vis spectra of the aryl cyanide complexes show a characteristic intense band at 550—650 nm ($\epsilon > 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$). This absorption, which is also present in a solution containing both Cp_2TiR ($\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$) and $\text{R}'\text{CN}$ ($\text{R}' = \text{C}_6\text{H}_5$, *o*- $\text{CH}_3\text{C}_6\text{H}_4$) demonstrates the presence of the cyanide complexes at low temperature. This band probably is associated with a

TABLE 2
 $\nu(\text{CN})$ AND DECOMPOSITION TEMPERATURES OF THE COMPLEXES $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$

Cp_2TiR R	$\text{R}'\text{CN}$ R'	$\nu(\text{CN})$ (cm^{-1})	$\Delta\nu(\text{CN})^b$	Decomposition temperature ($^\circ\text{C}$)	
				$\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$	Cp_2TiR [1]
C_6H_5	<i>t</i> - C_4H_9	^a		120	29
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2204	—11	164	
$\text{CH}_2\text{C}_6\text{H}_5$	<i>t</i> - C_4H_9	^a		53	43
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2200	—15	152	
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	<i>t</i> - C_4H_9	2235	—2	70	95
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_4$	2203	—12	115	
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	<i>t</i> - C_4H_9	^a		110	<20
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2207	—8	160	
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	<i>t</i> - C_4H_9	^a		104	<20
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2205	—10	128	
C_6F_5	CH_3	2273	+19		106
	<i>t</i> - C_4H_9	2261	+24	142	
	C_6H_5	2240	+18		
	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	2231	+1		
Cl	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2205	0	164	
	CH_3	2274	+20		
	<i>t</i> - C_4H_9	2266	+29	102	
	C_6H_5	2235	+13		
	<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	2235	5		
	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$	2235	+20	191	

^a Could not be observed. ^b $\nu(\text{CN})$ (complex) — $\nu(\text{CN})$ (free ligand).

transfer of charge from the metal to the aryl cyanide π -system. Similar but far more intense absorptions were observed for the corresponding dinitrogen complexes, $(\text{Cp}_2\text{TiR})_2\text{N}_2$ [1]. The alkyl cyanide complexes, on the other hand, show a low intensity band ($\epsilon \sim 50 \text{ l mole}^{-1} \text{ cm}^{-1}$) at 700–800 nm.

The effect of coordination of the cyanide molecule on the thermal stability of the Ti—aryl band is overshadowed by the enhanced reactivity of the cyanide itself. This is demonstrated by the observed irreversible dimerization reaction mentioned above. In the compounds $[\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}]_2$ the Ti—aryl bond stays intact up to 200°C for the phenyl cyanide derivatives. Only in complexes in which the reactions of the cyanide are hindered by bulky groups ($\text{R}' = t\text{-C}_4\text{H}_9$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$) is there no dimerization, and so a study of the stability of the Ti—R bond in $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ was possible. Studies in solution were not possible because of equilibrium 1 lies too well over to the left at higher temperature. From the decomposition temperatures of the solid compounds (Table 2) it follows that the Ti—R bond is stabilized and that the order of stability is the same as observed for the N_2 complexes: $o\text{-CH}_3\text{C}_6\text{H}_4 < \text{C}_6\text{F}_5 < \text{CH}_2\text{C}_6\text{H}_5 < \text{C}_6\text{H}_5$, $\sim m\text{-CH}_3\text{C}_6\text{H}_4 \sim p\text{-CH}_3\text{C}_6\text{H}_4$.

In a limited number of cyanide complexes the thermal decomposition is simple: quantitative formation of RH and $\text{R}'\text{CN}$ was found for $\text{R} = o\text{-CH}_3\text{C}_6\text{H}_4$ and $\text{R}' = t\text{-C}_4\text{H}_9$. This reaction is similar to the thermal decomposition of the N_2 complexes $(\text{Cp}_2\text{TiR})_2\text{N}_2$ viz. liberation of the complexed ligand followed by RH formation. For the other $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ complexes the thermal decomposition is more complicated, and the yields of $\text{R}'\text{CN}$ and RH are much smaller. This indicates that the decomposition of these complexes follows more than one path of comparable activation energy. However, for all the complexes it is clearly demonstrated that the Ti—R bond is stabilized by the coordination of the cyanide.

Experimental

All experiments were carried out under argon. Commercially available cyanides were used without further purification, 2,6-dimethylphenyl cyanide was prepared according to Vogel [6]. Cp_2Ti —aryl compounds were prepared as described before [1]. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

IR spectra (Nujol mull) were obtained using a Hitachi EPI-G spectrophotometer. Decomposition temperatures were determined with a low-temperature DTA apparatus (heating rate 2 à 3°C/min).

Synthesis

Preparation of $\text{Cp}_2\text{Ti-p-CH}_3\text{C}_6\text{H}_4 \cdot 2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CN}$. To a solution of 960 mg $\text{Cp}_2\text{Ti-p-CH}_3\text{C}_6\text{H}_4$ in pentane 450 mg 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3\text{CN}$ was slowly added at 0°C, to give a precipitate of dark blue lustrous crystals. After washing and drying in vacuo, 895 mg of analytically pure $\text{Cp}_2\text{Ti-p-CH}_3\text{C}_6\text{H}_4 \cdot 2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CN}$ (60%) was isolated, and sealed in ampoules.

The other complexes were prepared in essentially the same way but in the case of Cp_2TiCl toluene was used as solvent. The results are summarized in Table 1.

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