

DIMERIZATION OF ORGANIC CYANIDES LIGATED TO DI- η^5 -CYCLOPENTADIENYLARYLTITANIUM(III)

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(Received December 12th, 1977)

Summary

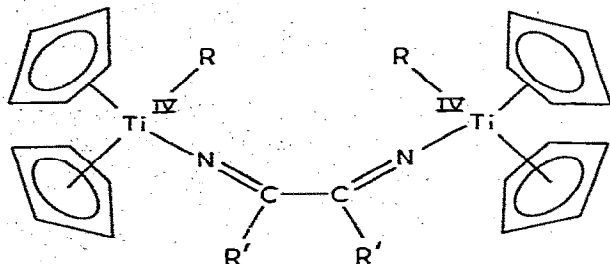
Reactions of Cp_2TiR ($\text{R} = \text{C}_6\text{H}_5$, *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $\text{CH}_2\text{C}_6\text{H}_5$, C_6F_5 , Cl) with $\text{R}'\text{CN}$ ($\text{R}' = \text{C}_6\text{H}_5$, *o*- $\text{CH}_3\text{C}_6\text{H}_4$, CH_3) have been studied. The products, $(\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN})_2$, identified by chemical and physical methods, form a new class of compounds, in which two Cp_2TiR groups are connected by a bridging diimine ligand formed by oxidative coupling of two cyanide ligands via the cyanide carbon atoms. The metal is formally oxidized to titanium(IV).

Introduction

In a previous paper [1] we described the adducts $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$, in which the cyanide is terminally coordinated to the metal. These adducts react at higher temperatures to give, depending upon R' , products having the same stoichiometry but very different properties. These products are also obtained when the starting materials Cp_2TiR and $\text{R}'\text{CN}$ are mixed in solution. We have studied this reaction for various combinations of Cp_2TiR and $\text{R}'\text{CN}$, and the results are presented below.

Results and discussion

Reaction of Cp_2TiR with $\text{R}'\text{CN}$ in solution or in some cases of the solid adducts $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ gives titanium–diimine compounds of structure I. This



(I)

TABLE 1

COMBINATIONS OF Cp_2TiR AND $R'CN$ AND SOME OF THEIR SPECTROSCOPIC PROPERTIES

Cp_2TiR R =	$R'CN$ R' =	$\nu(C=N)$ (cm^{-1})	Colour	PMR ($\delta(TMS) = 0$ ppm) ^a		
				$\delta(Cp)$	$\delta(R)$	$\delta(R')$
C_6H_5	C_6H_5	1655	yellow	5.80	6.66	7.50
C_6H_5	<i>o</i> - $CH_3C_6H_4$	2190 ^b	dark-blue			
C_6H_5	<i>p</i> - ClC_6H_4	1648	yellow	5.75	6.70	7.40
C_6H_5	CH_3	1705	yellow	5.93	6.70	2.02
<i>o</i> - $CH_3C_6H_4$	C_6H_5	1658	yellow			
<i>o</i> - $CH_3C_6H_4$	<i>o</i> - $CH_3C_6H_4$	1651	orange			
<i>o</i> - $CH_3C_6H_4$	<i>p</i> - ClC_6H_4	1648	yellow			
<i>o</i> - $CH_3C_6H_4$	CH_3	1700	yellow			
<i>m</i> - $CH_3C_6H_4$	C_6H_5	1658	yellow	5.96	6.70	1.81
<i>m</i> - $CH_3C_6H_4$	<i>o</i> - $CH_3C_6H_4$	1640	orange			7.73
		1648				
<i>m</i> - $CH_3C_6H_4$	CH_3	1700	yellow			
<i>p</i> - $CH_3C_6H_4$	C_6H_5	1657	yellow			
<i>p</i> - $CH_3C_6H_4$	<i>o</i> - $CH_3C_6H_4$	1638	orange	5.43	6.32	2.02
<i>p</i> - $CH_3C_6H_4$	CH_3	1695	yellow			7.28
$CH_2C_6H_5$	C_6H_5	1655	yellow			2.52
$CH_2C_6H_5$	<i>o</i> - $CH_3C_6H_4$	1660	orange			
C_6F_5	<i>p</i> - ClC_6H_4	1650	orange			
Cl	C_6H_5	1665	orange			

^a In $CDCl_3$ solution. ^b Formation of the adduct was established, no dimerisation occurred.

reaction was studied for the combinations of R and R' given in Table 1. The yellow to orange dimers are stable in air, diamagnetic and poorly soluble in the common organic solvents (toluene, ether, pentane) in contrast with the primary adducts [1]. The conversion of $Cp_2TiCl \cdot C_6H_5CN$ into the dimer was followed by IR spectroscopy (Fig. 1). The absorption at 2235 cm^{-1} ($\nu(C\equiv N)$) gradually vanishes when a Nujol mull is heated at 120°C , and a new band at 1665 cm^{-1} appears and increases steadily in intensity. This new band and also the other features of the appearing spectrum are found in the IR spectra of the final products studied (Table 1). The relation between the peaks indicated the formation of a C=N bond.

The PMR spectra of the dimers in $CDCl_3$ are all very similar, and show a singlet at about $\delta 6.0$ ppm, and two broad resonances at about 6.6 and 7.6 ppm. The integration ratio is in accordance with the assignment to Cp, R and R' protons, respectively. The Cp and R protons are found at positions characteristic for tetravalent titanium compounds e.g. $Cp_2Ti(R)X$ [2]. The UV-vis spectra of the dimers are also closely similar to spectra of $Cp_2Ti(R)X$ [6] (Table 1). Because of the poor solubility of the dimers, determination of the molecular weight (by cryoscopy in benzene) was possible only for the final product of the reaction of $Cp_2TiC_6H_5$ with *p*- ClC_6H_4CN . The observed value of 805 (calcd. 785) shows that the formulation as a dimer is correct.

Reaction of HCl in ether with the product from Cp_2Ti -*o*- $CH_3C_6H_4$ and C_6H_5CN yields Cp_2TiCl_2 (80%), $C_6H_5CH_3$ (70%) and, after hydrolysis of the reaction mixture, benzil, $C_6H_5C(=O)C(=O)C_6H_5$ (60%), formed by hydrolysis of the diimine (eq. 1).

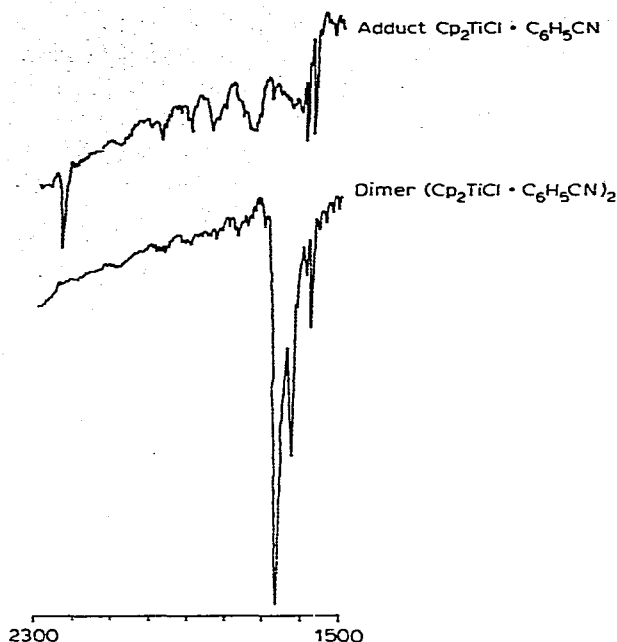
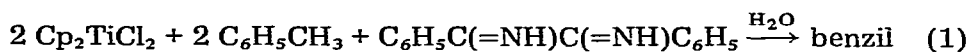
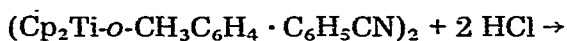
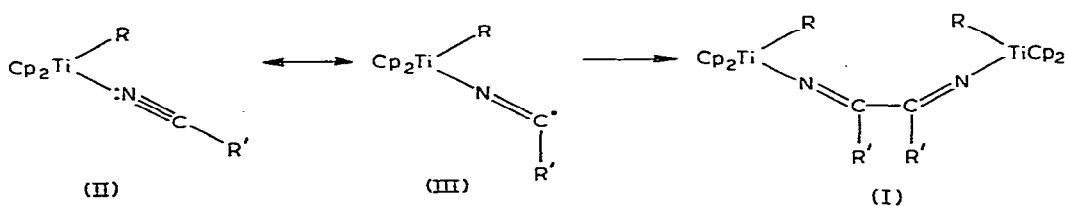


Fig. 1. IR spectra of the products from Cp_2TiCl and $\text{C}_6\text{H}_5\text{CN}$ in the $2300\text{--}1500\text{ cm}^{-1}$ region.



Reaction of the product of $o\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$ and $\text{Cp}_2\text{Ti}-o\text{-CH}_3\text{C}_6\text{H}_4$ with ethereal HCl gives Cp_2TiCl_2 (45%), $\text{C}_6\text{H}_5\text{CH}_3$ (95%) and, after work up, the yellow-white crystalline diimine, $o\text{-CH}_3\text{C}_6\text{H}_4\text{C}(=\text{NH})\text{C}(=\text{NH})\text{C}_6\text{H}_4\text{-}o\text{-CH}_3$ (65%), which is stable towards hydrolysis. Details are described in the Experimental part. The formation of the dimer can be rationalized as outlined in Scheme 1.

SCHEME 1



The first step in the reaction of Cp_2TiR with $\text{R}'\text{CN}$ is coordination of the cyanide to the metal. Solutions of aryl cyanide and Cp_2TiR , mixed at low temperatures, indeed show the intense absorption at $600\text{--}650\text{ nm}$ ($\epsilon > 10^3\text{ l mol}^{-1}\text{ cm}^{-1}$) characteristic for the adducts $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ ($\text{R}' = \text{aryl}$) [1]. Dimerization then proceeds via III, which is a canonical form of the adduct II. The contribution of III to the actual bonding situation in the adducts is related to the extent

of backbonding between the metal and the cyanide function. Evidence for strong backbonding is found in the lowering of $\nu(\text{C}\equiv\text{N})$ of the adducts compared with the free ligand [3]. EPR spectra of the adducts confirm this observation. The singlet signal ($g \approx 1.95$) observed for Cp_2TiR [5] changes into a 3-line spectrum for the $\text{Cp}_2\text{TiR} \cdot \text{R}'\text{CN}$ adducts ($g \approx 1.99$, a 2.45 Hz for $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4\text{-}2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{CN}$) due to interaction with ^{14}N . This demonstrates the delocalization of the unpaired electron from titanium to the cyanide function.

The observation that bulky groups R' , e.g. $t\text{-C}_4\text{H}_9$ and $2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3$, impede the dimerization of the cyanide ligand is explained in terms of steric hindrance at the reactive cyanide carbon atom. The coupling shows similarity to that reported for NbCl_4 and CH_3CN [4] but no other examples are known to the authors. In view of the activating properties of Cp_2TiR for the dimerization of organic cyanides, analogous reactions with other unsaturated substrates such as isocyanides, acetylenes, and olefins are under investigation.

Experimental

All experiments were carried out in an inert atmosphere (N_2 or Ar). Commercially available cyanides were distilled before use, compounds Cp_2TiR were prepared as described previously [5]. Elemental analyses were performed at Microanalytical Department of this University under supervision of Mr. A.F. Hamminga.

Synthesis

Preparation of $[(\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4)_2(\text{C}_6\text{H}_5\text{CN})_2]$. To a solution of 1 mmol of $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4$ in 25 ml of hexane 1 equivalent of $\text{C}_6\text{H}_5\text{CN}$ in hexane was slowly added at room temperature. A yellow crystalline product formed. After addition of the cyanide the mother liquor was decanted, the residue washed with hexane, and dried in vacuo. The compound was sealed in ampoules under N_2 ; yield 55%.

Other compounds were prepared in essentially the same way. The purity of the compounds is much affected by the ease of formation of the dimer and purity of the starting materials. Often some solvent and free cyanide is incorporated into the products. In the case of the reaction of $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4$ with the various cyanides (Table 2), the reaction conditions were optimized, and in

TABLE 2
ANALYSES OF $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4$ WITH $\text{R}'\text{CN}$

R'	Analysis (found (calcd.) (%))				
	Ti	C	H	N	Yield (%)
C_6H_5	12.51 (12.85)	76.68 (77.21)	6.21 (5.89)	3.61 (3.75)	60
$o\text{-CH}_3\text{C}_6\text{H}_4$	12.02 (12.41)	77.68 (77.72)	6.86 (6.22)	3.31 (3.63)	70
CH_3	15.48 (15.46)	73.35 (73.54)	6.58 (6.45)	4.52 (4.51)	80

the case of thermally instable $\text{Cp}_2\text{Ti-aryl}$ compounds, the reactions were carried out at 0°C .

Reaction with HCl

$\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4\text{-}o\text{-CH}_3\text{C}_6\text{H}_4\text{CN}$ dimer (3 mmol) were treated with an excess of HCl in ether at -78°C . The mixture was slowly warmed to room temperature and the ether and volatile reaction products were evaporated off and condensed at -196°C . GLC analysis of the condensate showed $\text{C}_6\text{H}_5\text{CH}_3$ in 95% yield. The residue was washed with 0.5 ml $(\text{C}_2\text{H}_5)_2\text{NH}$ in 15 ml of hexane and with 15 ml of hexane (2 X). The washings were combined and cooled. A yellow-white product crystallized, which was identified as $o\text{-CH}_3\text{C}_6\text{H}_4\text{C(=NH)C(=NH)-}o\text{-CH}_3\text{C}_6\text{H}_4$. IR: $3280, 3180\text{ cm}^{-1}$ (N—H stretch), 1593 cm^{-1} (C=N stretch); NMR (CCl_4 , internal standard TMS): δ 2.13 (multiplet, 3), 6.86 (multiplet, 4), 9.8—10.9 (multiplet, 1) ppm; mass spectrum: $M^+ m/e$ 236; yield 65%. This diimine is stable in air and reacts with HCl to the corresponding HCl salt. IR: $3000\text{--}2500\text{ cm}^{-1}$ (N—H⁺ stretch), 1660 cm^{-1} (C=N stretch). The red residue left was characterized as Cp_2TiCl_2 , yield 45% (IR, UV).

Reaction of " $\text{Cp}_2\text{Ti-}o\text{-CH}_3\text{C}_6\text{H}_4\text{-C}_6\text{H}_5\text{CN}$ " dimer with HCl in ether was carried out as described above. After evaporation of the volatile products the residue was treated with 10 ml of ether and 1 ml of H_2O , and subsequently washed with 10 ml of hexane (2 X). Drying and evaporation of the combined hexane and ether extracts gave benzil; yield 65%. The yield of Cp_2TiCl_2 (70%) was determined in a separate run.

Acknowledgements

The authors thank Dr. H.J. de Liefde Meijer and Prof. Dr. F. Jellinek for stimulating discussions. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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