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REACTIONS OF BIS(η^5-CYCLOPENTADIENYL)TITANIUM(III) COMPOUNDS WITH ISOCYANIDES

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Summary

Reactions of Cp_2TiR (R = Cl, C_6F_5, C_6H_5, o-$CH_3C_6H_4$) with R'NC (R' = o-$CH_3C_6H_4$, 2,6-$(CH_3)_2C_6H_3$) give two types of products: terminally coordinated adducts, $Cp_2TiR \cdot CNR'$, and insertion products, $Cp_2TiC(R){=}NR'$, i.e. iminoacyl derivatives. Insertion of the isocyanide group into the Ti—R bond was followed by IR spectroscopy for Cp_2Ti-o-$CH_3C_6H_4 \cdot$ 2,6-$(CH_3)_2C_6H_3NC$. The iminoacyl compounds are readily oxidized by X_2 (X = I, SC_6H_5) to give $Cp_2Ti(X)C(R){=}NR'$. The C=N group in the latter compound is η^2-coordinated to titanium.

Introduction

Recently we reported the reactions of Cp_2TiR (R = Cl, aryl) with cyanides, R'CN (R' = alkyl, aryl). Formation of adducts $Cp_2TiR \cdot NCR'$ occurred [1] which, in several cases, depending on R and R', was followed by formation of a diimine compound by coupling of two ligated cyanides [2]. This interesting activation prompted us to investigate the reactions of Cp_2TiR with isocyanides.

Results and discussion

Owing to the high reactivity of isocyanides and formation of untractable by-products, we restricted our investigations to the less reactive, *ortho*-substituted aryl isocyanides: o-$CH_3C_6H_4NC$ and 2,6-$(CH_3)_2C_6H_3NC$. We brought these ligands into reaction with Cp_2TiR, R = Cl, C_6F_5, C_6H_5, o-$CH_3C_6H_4$, 2,6-$(CH_3)_2$-C_6H_3. Depending on R, two kinds of products are formed, which have the same stoichiometry but very different properties, viz., adducts $Cp_2TiR \cdot CNR'$ and insertion products $Cp_2TiC(R){=}NR'$. For R = 2,6-$(CH_3)_2C_6H_3$ no reaction occurred, owing to blocking of the coordination site on the metal by steric hindrance [3]. For R = Cl, C_6F_5 dark adducts are formed. The compounds are air-sensitive and soluble in toluene, but only slightly soluble in pentane or

TABLE 1

ELEMENTAL ANALYSIS

Adduct	Color	Yield (%)	Analyses: found (calcd.) (%)				
			C	H	Cl	N	Ti
$Cp_2TiCl \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$	d. green	60	65.94(66.18)	5.55(5.52)	10.37(10.30)	3.84(4.06)	14.24(13.90)
$Cp_2TiCl \cdot o\text{-}CH_3C_6H_4NC$	d. green	60	65.19(65.35)	5.27(5.14)	10.82(10.74)	4.10(4.23)	15.12(14.49)
$Cp_2TiC_6F_5 \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$	purple	70	62.95(63.02)	4.44(3.99)		3.09(2.94)	10.19(10.06)
Iminoacyl complexes	Color	Yield (%)	C	H	I	N	Ti
I: $Cp_2TiC(C_6H_5)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	d. green	20	77.40(77.72)	6.25(6.21)			12.22(12.40)
II: $Cp_2TiC(o\text{-}CH_3C_6H_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	d. green	[a]	76.82(78.00)	6.79(6.50)		3.22(3.50)	12.05(11.98)
III: $Cp_2Ti(I)C(C_6H_5)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	yellow	60	59.38(58.49)	5.15(4.68)	23.00(24.75)	2.63(2.73)	9.52(9.34)
IV: $Cp_2Ti(SC_6H_5)C(C_6H_5)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	yellow	55	75.31(75.15)	6.09(5.86)		2.77(2.83)	9.75(9.68)
VI: $Cp_2Ti(SC_6H_5)C(o\text{-}CH_3C_6H_3)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$	yellow	30	75.37(75.44)	6.18(6.09)		2.62(2.75)	9.20(9.41)

[a] Compound II did not crystallize well.

ether. The analyses (Table 1) are in agreement with the formula $Cp_2TiR \cdot R'NC$. The IR spectra show, in addition to the characteristic η^5-Cp, R and R′ absorptions, a shift of the $\nu(N{\equiv}C)$ band to higher wave numbers (Table 2) compared with the free isocyanides, as expected for terminal coordination [4]. Magnetic measurements show one unpaired electron per titanium (Table 2). The adducts are stable up to 130°C and react with I_2 according to eq. 1:

$$Cp_2TiR \cdot R'NC + \tfrac{1}{2}I_2 \rightarrow Cp_2Ti(I)R + R'NC \qquad (1)$$

In the reaction of Cp_2TiR, R = C_6H_5, o-$CH_3C_6H_4$, with R′NC at −78°C, adduct formation again occurs initially, but the adducts formed are thermally unstable. Only for the combination of Cp_2Ti-o-$CH_3C_6H_4$ and 2,6-$(CH_3)_2C_6H_3NC$ could the adduct be isolated at low temperatures. Its IR spectrum shows $\nu(N{\equiv}C)$ at 2090 cm^{-1}, which represents a shift of 40 cm^{-1} to lower wave number compared with the uncoordinated ligand. This shift is taken as evidence for strong back-bonding, as in the case of the cyanide adducts [1]. This results in activation of the N≡C bond and leads to insertion of the isocyanide group into the Ti—R bond with formation of an iminoacyl compound, Cp_2TiC(o-$CH_3C_6H_4$)=N-2,6-$(CH_3)_2C_6H_3$. This insertion was also followed by IR spectroscopy. At room temperature the spectrum of the adduct of Cp_2Ti-o-$CH_3C_6H_4$ and 2,6-$(CH_3)_2$-C_6N_3NC (Nujol mull) changes slowly; the $\nu(N{\equiv}C)$ band at 2090 cm^{-1} vanishes and at the same time a new band at 1560 cm^{-1} appears, its intensity increasing steadily (Fig. 1). The new band is ascribed to a C=N bond; it is also present in the final product from $Cp_2TiC_6H_5$ and 2,6-$(CH_3)_2C_6H_3NC$. Reaction of Cp_2TiR, R = C_6H_5 and o-$CH_3C_6H_4$ with o-$CH_3C_6H_4NC$ yielded oily, untractable products which could not be purified. The iminoacyl complexes $Cp_2TiC(R)$=N-2,6-$(CH_3)_2C_6H_3$ (I, R = C_6H_5; II, R = o-$CH_3C_6H_4$) are green and very air-sensitive. They are readily soluble in toluene, the lower alkanes, and ether. Product I was obtained crystalline and analytically pure. It possesses one unpaired electron per titanium atom, while molecular-weight determinations by cryoscopy in

TABLE 2

SPECTROSCOPIC AND PHYSICAL DATA

Adducts	$\nu(N{\equiv}C)$ (cm^{-1})	$\Delta\nu(N{\equiv}C)$ (cm^{-1})[a]	$\mu(\mu_\beta)$
$Cp_2TiCl \cdot$ 2,6-$(CH_3)_2C_6H_3NC$	2140	+25	1.56
$Cp_2TiCl \cdot$ o-$CH_3C_6H_4NC$	2135	+20	
$Cp_2TiC_6F_5 \cdot$ 2,6-$(CH_3)_2C_6H_3NC$	2140	+25	1.70
	2115	0	

Iminoacyl complexes	$\nu(N{=}C)$ (cm^{-1})	$\mu(\mu_\beta)$	δ ^{13}C(—C=N—) (ppm)[b]	Mol. weight (calcd.)
I	1573	1.83		385(386)
II	1560			
III	1665	diamagn.	215.0	
IV	1655	diamagn.	230.0	475(495)
V	1665	diamagn.	[c]	
VI	1655	diamagn.	226.6	

[a] ν(CN) (complexes) — ν(CN) (free ligand). [b] In $CDCl_3$ solution relative to TMS. [c] V was not obtained sufficiently pure.

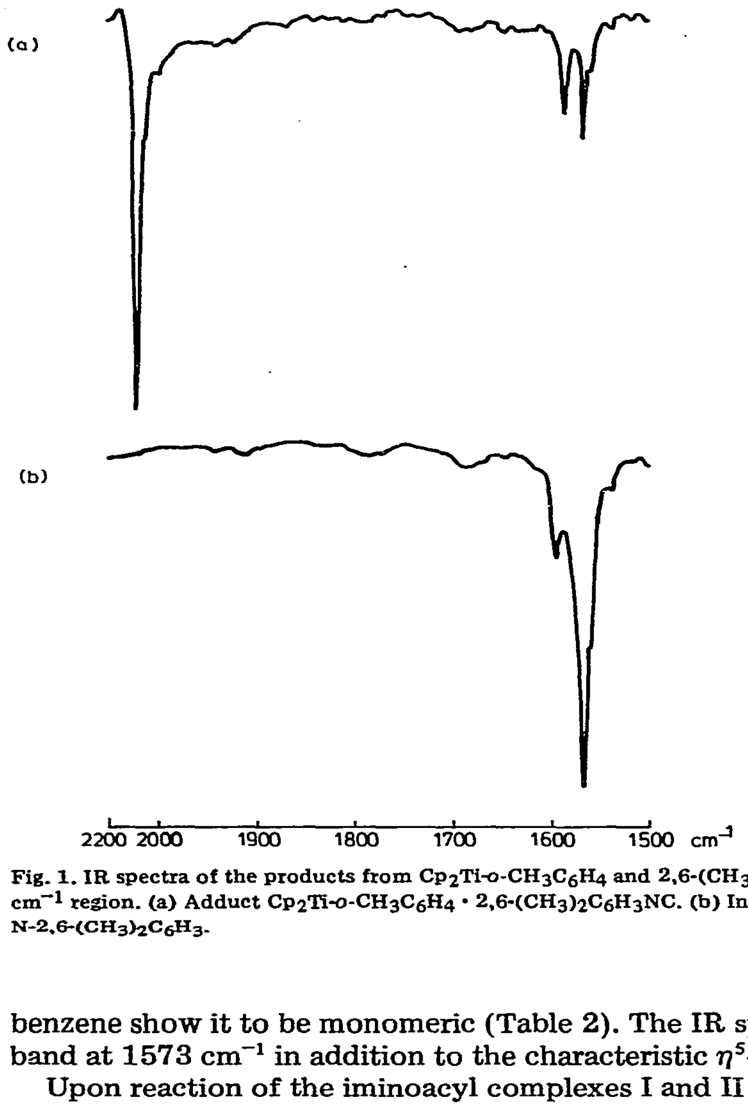

Fig. 1. IR spectra of the products from Cp_2Ti-o-$CH_3C_6H_4$ and 2,6-$(CH_3)_2C_6H_3NC$ in the 2200—1500 cm^{-1} region. (a) Adduct Cp_2Ti-o-$CH_3C_6H_4 \cdot$ 2,6-$(CH_3)_2C_6H_3NC$. (b) Insertion product Cp_2TiC(*o*-$CH_3C_6H_4$)=N-2,6-$(CH_3)_2C_6H_3$.

benzene show it to be monomeric (Table 2). The IR spectrum shows a ν(C=N) band at 1573 cm^{-1} in addition to the characteristic η^5-Cp, R and R′ absorptions.

Upon reaction of the iminoacyl complexes I and II with an excess of HCl in ether the iminoacyl ligand is liberated (eq. 2).

$$Cp_2TiC(R){=}NR' + 3\ HCl \rightarrow Cp_2TiCl_2 + RC(H){=}NR' \cdot HCl + \tfrac{1}{2}H_2 \qquad (2)$$

With I_2 and $C_6H_5SSC_6H_5$, I and II react according to eq. 3:

$$Cp_2TiC(R){=}NR' + \tfrac{1}{2}X_2 \rightarrow Cp_2Ti(X)C(R){=}NR' \qquad (3)$$

(III, R = C_6H_5; X = I) (V, R = *o*-$CH_3C_6H_4$; X = I)
(IV, R = C_6H_5; X = SC_6H_5) (VI, R = *o*-$CH_3C_6H_4$; X = SC_6H_5)

The yellow products III, V, VI are poorly soluble in pentane or ether; IV can be recrystallized from ether and VI from toluene. The analyses (Table 1) are in agreement with their formulation as III—VI. Molecular-weight determination by cryoscopy in benzene (Table 2) show IV to be monomeric. The IR spectra show ν(C=N) at about 1665 cm^{-1} (III, V) or 1655 cm^{-1} (IV, VI). ^{13}C NMR spectra in $CDCl_3$ gave resonances for the iminoacyl carbon at low field; δ = 215.0, 230.0 and 226.6 ppm for III, IV, VI, respectively.

Coordination of the C=N group

Coordination of a C=N group can occur in two ways for in addition to the bonding of the carbon atom (η^1-) at the metal the nitrogen atom may coordinate at the metal via its lone pair electrons (η^2-). Recently, Adams and Chodosh [5] have studied both coordination modes in Mo complexes; they show that η^2-coordination results in an increase of ν(C=N) and a shift of the ^{13}C resonance of the iminoacyl carbon to a lower field than in the case of η^1-coordination. In our complexes III—VI the C=N stretching frequencies are about 1665 cm^{-1} and 1655 cm^{-1}. These are significantly higher than in η^1-iminoacyl ligands, which generally lie in the range 1580—1620 cm^{-1} [6]. The ^{13}C resonance of the iminoacyl carbon is shifted by —52, —67 and —64 ppm for III, IV and VI, respectively, relative to the free ligand (in $HC(C_6H_5)=N\text{-}2,6\text{-}(CH_3)_2C_6H_3$ the iminoacyl carbon resonates at 162 ppm). For the Mo complexes with η^2-coordination a shift of approximately —40 ppm was observed [5]. Complexes with η^1-coordination did not show this effect. Therefore, it seems a plausible conclusion that the iminoacyl ligands in compounds III—VI have an η^2-coordination.

For I and II the IR spectra (ν(C=N) at 1573 and 1560 cm^{-1}) indicate η^1-coordination. This is unexpected in view of the η^2-coordination in III—VI, where steric hindrance is likely to be stronger than in I or II. In contrast, the high stability and the chemical inertness of I and II (no reaction with N_2 or CO) would be more compatible with η^2-coordination of the iminoacyl ligands. Owing to the paramagnetism of the complexes I and II, no ^{13}C NMR spectra could be obtained to provide more information. An X-ray structure determination is being undertaken to clarify the coordination mode in I.

Experimental

General remarks

All experiments were performed in an inert atmosphere (N_2 or Ar). Compounds Cp_2TiR were prepared as described previously [7]; $2,6\text{-}(CH_3)_2C_6H_3NC$ and $o\text{-}CH_3C_6H_5NC$ according to ref. 8. Elemental analyses were performed at the Microanalytical Department of this University under supervision of Mr. A.F. Hamminga. ^{13}C NMR spectra of IV and VI were recorded on a Varian XL-100 spectrometer by Drs. D. Kok and Dr. O. Possel of the Physical Organic Department of this University. The ^{13}C NMR spectrum of III was recorded by Dr. Ir. C.J. Groenenboom of AKZO Corporated Research, Arnhem on a Bruker WH270 apparatus. Shifts are given relative to TMS (internal standard). IR spectra were recorded on a JASCO-IRA-2 spectrophotometer as Nujol mulls.

Synthesis

Preparation of $Cp_2TiCl \cdot 2,6\text{-}(CH_3)_2C_6H_3NC$. To a solution of 0.27 g of Cp_2TiCl in 30 ml of toluene, 0.17 g of $2,6\text{-}(CH_3)_2C_6H_3NC$ were added at room temperature. Immediately a green precipitate was formed which was recrystallized from hot toluene. After decanting the mother liquor the green needles were washed with n-pentane, dried in vacuo and sealed in ampoules. Yield: 0.25 g (60%). The other adducts were prepared in essentially the same way (Table 1).

Preparation of $Cp_2TiC(C_6H_5)$=N-2,6-$(CH_3)_2C_6H_3$ (I). 1.65 g of $[Cp_2Ti(C_6H_5)]_2N_2$ was stirred in diethyl ether (35 ml) at 0°C in vacuo to remove N_2. To the resulting green solution of $Cp_2TiC_6H_5$ 0.65 g of 2,6-$(CH_3)_2C_6H_3NC$ were added at −78°C. Immediately a purple-blue precipitate was formed which turned to green at slow warming to room temperature. The green precipitate was washed with diethyl ether at −78°C and subsequently recrystallized from diethyl ether. The crystalline product was dried in vacuo and sealed in ampoules. Yield: 0.45 g (20%).

Preparation of $Cp_2Ti(S\text{-}C_6H_5)C(C_6H_5)$=N-2,6-$(CH_3)_2C_6H_3$ (IV). To a solution of 0.70 g of $Cp_2TiC(C_6H_5)$=N-2,6-$(CH_3)_2C_6H_3$ in 150 ml of diethyl ether 0.19 g of $C_6H_5SSC_6H_5$ were added at −78°C and the mixture was slowly warmed to room temperature. A yellow precipitate formed, which was thoroughly washed with n-pentane at −40°C and then recrystallized from diethyl ether. The yellow needles were dried in vacuo and sealed in ampoules. Yield: 0.55 g (60%).

The other products, including those from reaction with I_2, e.g. III, V and VI, were prepared in the same way, except that products III and V were not recrystallized while VI was recrystallized from toluene.

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