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EPR spectra of products of the reaction of di-η^5-cyclopentadienyl(diethylalanedi-μ-chloro)titanium(III) with C_1 compounds

S.K. Tyrlik *, A. Korda,

Laboratory of Homogenous Catalysis, Institute of Organic Chemistry, Polish Academy of Sciences, 00-961 Warszawa, Kasprzaka 44 (Poland)

L. Poppe,

Institute of Physical Chemistry, Polish Academy of Sciences, 00-961 Warszawa, Kasprzaka 44 (Poland)

A. Rockenbauer and M. Györ

Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest II, Pustaszeri ut.59 (Hungary)

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Abstract

The outcome of the reaction of di-η^5-cyclopentadienyl(diethylalanedi-μ-chloro)titanium(III) (IA) with MeOH depends strongly on the molar ratio: with IA/CH_3OH < 0.75 the methanol cleaves the Al–Et bond; with higher ratios solvated Cp_2TiCl is formed. The compounds HCHO, CO_2, $HCONH_2$, HCO_2CH_3 and $(CH_3O)_2CO$ react with IA at the Al–Et bond to give new paramagnetic dimers independent of the molar ratio. The chlorinated species CH_xCl_{4-x} ($x = 0$–2) either oxidize titanium(III) to titanium(IV) or give unidentified paramagnetic species.

Introduction

Low valent titanium is known to show a strong affinity for oxygen [1]. Although the majority of known titanium systems involve titantium(II) or a lower oxidation state, there are recent reports that the titanium(III) complexes can also be active in oxygen abstraction from organic compounds; e.g. in reaction 1:

$$2[CpTi(Cl)_2(THF)_{1.5}] + CH_2O \rightarrow [CpTi(Cl)_2]_2O + CH_2{=}CH_2 \qquad (1)$$

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* Adress correspondence to this author; current adress: Institute of Industrial Chemistry, Warsaw, Rydygiera 8 (Poland).

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However, there has been no report of a process in which titanium activates oxygen-containing organic compounds in the following way:

$$R_xC\ldots O + [Ti] \rightarrow R_xC^\star + O^\star \tag{2a}$$

$$\text{organic material} + R_xC^\star + O^x \rightarrow \text{products of O incorporation} + \text{products of } R_xC \text{ incorporation} \tag{2b}$$

In this connection oxygenated C_1 compounds are of obvious interest. We are seeking possible applications of oxygenated C_1 compounds in reactions with condensed aromatic or hydroaromatic systems in order to produce aliphatic or functionalized aromatic chemicals:

$$\left\{\begin{array}{c}\text{Condensed aromatics}\\ \text{or hydroaromatics}\end{array}\right\} + \text{oxygenated } C_1\text{'s} \xrightarrow{[Ti]} \text{aliphatics or functionalized aromatics} \tag{3}$$

Reaction of [Ti] with oxygenated C_1' could therefore provide an entry to this chemistry. Following this approach we have studied reactions of di-η^5-cyclopentadienyl(diethylalanedi-μ-chloro)titanium(III), $Cp_2TiCl_2AlEt_2$ (IA) with C_1 species. Since IA contains Al–Et bonds it can be expected [6] to undergo reactions of the types:

$$>Al{-}R + R'OH \rightarrow\ >AlOR' + RH$$

$$>Al{-}R + R'_2C{=}O \rightarrow\ >AlOCR'_2R$$

Compound IA is a paramagnetic species belonging to the class of heterobinuclear cyclopentadienyl complexes $Cp'_2TiX_2AlY_2$ (I) for which the ESR spectra have been studied [3]. Reactions of IA with oxygenated C_1's could produce paramagnetic species as follows: (1) compounds of the types $[Cp_2Ti(Cl)] \leftarrow$[oxygen in Cl_1] or $Cp_2Ti(OCH_3)$, as products of decomposition of the heterobinuclear dimer. (2) Compounds in which Al–Et bonds have been cleaved with preservation of the dimer structure.

In addition, diamagnetic titanium(IV) compounds, such as $[Cp_2Ti(Cl)_2]O$ or $Cp_2Ti(Cl)OC(R_2)C(R_2)O(Cl)TiCp_2$, can be formed from ketones, $R_2C{=}O$. It was also of interest to find out whether chlorinated C_1 compounds oxidize the titanium(III) in IA.

This paper describes the paramagnetic reaction products of the above reactions.

Results and discussion

Reaction of $Cp_2TiCl_2AlEt_2$ (IA) with CH_3OH

Compound IA was prepared by treating Cp_2TiCl_2 with $AlEt_3$ in a 1/1 molar ratio in tetralin. The molar ratios CH_3OH/IA are based on the amount of Cp_2TiCl_2 initially taken and since the reaction of Cp_2TiCl_2 with $AlEt_3$ is probably not quantitative, the actual CH_3OH/[Ti] ratios may be somewhat higher.

With increase in the CH_3OH/[Ti] ratio there is a significant change in the EPR spectrum of the reaction mixture, as can be seen from Fig. 1 and Table 1. Starting from the single line of the initial $Cp_2TiCl_2AlEt_2$ there is a gradual change through a six-line multiplet to a new sharp singlet when there is an excess of CH_3OH. For a ratio of CH_3OH/[Ti] of 0.5/1 (Fig. 3B) the original singlet in the spectrum has

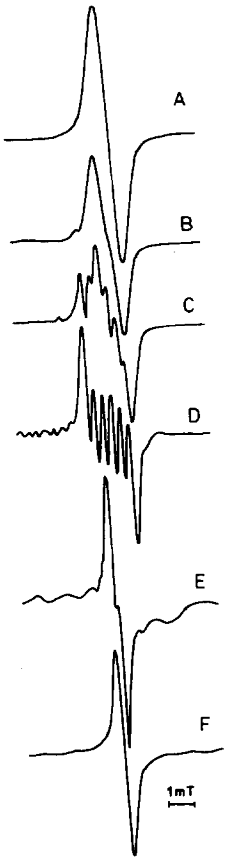

Fig. 1. EPR spectra of reaction products of IA with methanol for various molar ratio of IA to MeOH. A: IA without methanol; B: IA CH_3OH 1/0.5; C: 1/0.75; D: 1/1; E: 1/2; F: 1/5.

become broader, possibly as a result of solvation. With a $CH_3OH/[Ti]$ ratio of 0.75/1 there is a superposition of the spectrum of IA and that of the initial reaction product, which we suggest is a methoxy derivative $Cp_2TiCl_2Al(OCH_3)Et$ (IIA). With a 1/1 ratio, a spectrum (Fig. 1D) that can be ascribed to pure IIA is observed. Comparison of spectrum D ($g = 1.978$, a_{Al} 0.34 mT, a_{Ti} 1.05 mT) with the spectra

Table 1

Spectral parameters of the products from the reaction of $Cp_2TiCl_2AlEt_2$ (IA) with CH_3OH

Molar ratio IA/CH_3OH	g	$H_{1/2}$ (mT)	a_{Al} (mT)	a_{Ti} (mT)
no methanol	1.976	0.8–0.9	–	1.25
1/0.5	1.976	11–12	–	1.23
1/0.75		superposition of two spectra		
1/1	1.978	–	0.34	1.05
1/2	1.979	0.3	–	1.12
1/5	1.979	0.4	–	1.13

of $Cp_2TiCl_2Al(Cl)Et$, $Cp_2TiCl_2AlCl_2$, and their mixtures [4] confirms this assignment. The coupling to aluminium in $Cp_2TiCl_2AlCl_2$ has a value of 0.7 mT and that in $Cp_2TiCl_2Al(Cl)Et$ one of 0.35 mT. The substituent CH_3O is somewhat less electronegative than Cl. The influence of electronegativity of substituents bonded to Al on the spectral parameters of the paramagnetic heterobinuclear dimer has been discussed by Henrici-Olivé [4] and the value of a_{Al} 0.34 mT observed for paramagnetic species in Fig. 1D suggests that the product is $Cp_2TiCl_2Al(OCH_3)Et$ rather than $Cp_2TiCl_2Al(OCH_3)_2$. Further increase in the proportion of CH_3OH does not produce another multiplet but instead gives a species showing a narrow line (Fig. 1E and 1F) with spectral parameters ($g = 1.979$, $H_{1/2}$ 0.4 mT) close to those reported for a THF solution of Cp_2TiCl [5], and the latter is probably the product of the action of an excess of CH_3OH on IA; i.e higher proportions of CH_3OH lead to decomposition of the bimetallic complex.

Reactions with CH_3OH are quite fast, the new spectra appearing within a few minutes. The reaction products are stable in solution for ~ 50 h and so the redox process involved in quenching of titanium(III) must be much slower than the initiated reaction with CH_3OH. The results show that CH_3OH has greater tendency to cleave Al–Et bonds than the $TiCl_2Al$ bridge. Analogous results have been obtained with ethanol.

Reactions of $Cp_2TiCl_2AlEt_2$ with HCHO, CO_2, $HCONH_2$, $HCOOCH_3$ and $(CH_3O)_2CO$

We included reactions of methyl formate and methyl carbonate in this study of reactions of C_1 species because they can be readily prepared from C_1 compunds and do not contain C–C bonds; methyl formate and carbonate are often included in studies of the chemistry and technology of C_1 species [2].

η^5-Cyclopentadienyl (diethylalanedi-μ-chloro)titanium(III) reacts with all compounds specified above to form paramagnetic species with a six-line multiplet EPR spectrum of type D in Fig. 1. The spectral parameters for a $C_1/[Ti]$ molar ratio of 10/1 are listed in Table 2. The aluminium coupling constants for all products are in the range 0.29–0.34 mT, which suggests that the products are as follows:

$$Cp_2TiCl_2AlEt_2 + \left\{ \begin{array}{l} HCOH \rightarrow Cp_2TiCl_2Al(OCH_2Et)Et \\ CO_2 \rightarrow Cp_2TiCl_2Al[OC(O)Et]Et \\ HC(O)NH_2 \rightarrow Cp_2TiCl_2Al[OC(NH_2)H\ Et]Et \\ HC(O)OCH_3 \rightarrow Cp_2TiCl_2Al[OC(OCH_3)HEt]Et \\ (CH_3O)_2CO \rightarrow Cp_2TiCl_2Al[OC(OCH_3)_2Et]Et \end{array} \right.$$

All the substituents bonded to Al should have similar effects on aluminium and titanium, and thus the spectral parameters of all the products are very similar.

For $C_1/[Ti]$ molar ratios of less than 10, the spectra were of the type A–C in Fig. 1, but the process was slower than in the case of CH_3OH. However with further increase in the proportion of the carbonyl compound the behaviour was not the same as that for CH_3OH, in that the heterobinuclear $Cp_2TiCl_2Al[O(R')(R^2)Et]Et$ dimer was not broken down to Cp_2TiCl. Only for $(CH_3O)_2CO$ did a sharp singlet, which could be tentatively ascribed to Cp_2TiCl solvated with methyl carbonate, appear along with a hyperfine multiplet. The ability of methanol to decompose the

Table 2

Spectral parameters of the products and from IA and carbonyl (C_1 species. Molar ratio IA/C_1 = 1/10

C_1	g	a_{Al} (mT)	a_{Ti} (mT)
HCHO	1.979	0.34	1.01
CO_2	1.978	0.33	–
$HCONH_2$	1.978	0.29	1.1
$HCOOCH_3$	1.977	0.34	1.05
$(CH_3O)_2CO$	1.978	0.34	not visible
very weak multiplet singlet	1.983 $H_{1/2}$ = 0.2	–	–

Table 3

Spectral parameters of the products from IA and CH_2Cl_2 or $CHCl_3$ compounds.

Reagent		g	a_{Al} (mT)	a_{Ti} (mT)
$CHCl_3$	very weak multiplet	1.975	0.34	–
	singlet	1.992		
		$H_{1/2}$ = 0.6		0.6
CH_2Cl	multiplet	1.975	0.34	1.1
	singlet	1.988	–	–

heterobinuclear dimer was further illustrated when methanol was added to the products from IA and C_1 carbonyl species, a sharp singlet being observed.

Reactions of $Cp_2TiCl_2AlEt_2$ with CCl_4, $CHCl_3$ and CH_2Cl_2

Carbon tetrachloride seems to oxidize titanium(III), since the product solution gives no EPR signal. The spectra parameters for the products from $CHCl_3$ and CH_2Cl_2 are listed in Table 3. The origin of the sharp singlet is not clear at present, but the products may be Cp_2TiCCl_3 or $Cp_2TiCHCl_2$ *.

Experimental

$Cp_2TiCl_2AlEt_2$ (IA) was prepared, under argon in a two-necked flask equipped with a rubber septum, stopcock, and magnetic stirrer, from 1 ml (0.25 g) of Cp_2TiCl_2 and 1 ml of $AlEt_3$ in 10 ml of tetralin. (The Cp_2TiCl_2 did not dissolve completely in the tetralin, but did so upon addition of $AlEt_3$ and the solution turned green.) The mixture was stirred for 1 h at room temperature, and a solution obtained in this way was usually used for three reactions with a C_1 compound; e.g. three different amounts of CH_3OH (e.g. 0.33 ml; 0.66 ml; 1.65 ml) were dissolved in 3.3 ml tetralin each (in Schlenk tubes) and one-third of the solution of IA was added to each Schlenk tube from a hypodermic syringe; upon this addition the green

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* A referee has suggested that the spectrum of the product from CH_2Cl_2 is $[Cp_2Ti(\mu\text{-}Cl)]_2$, but the latter has different spectral characteristics [5].

solution of IA turned red or brown depending on the C_1 compound used. These solutions were stirred for ~ 5 min and a few drops were transferred to EPR tubes, all operations being performed under argon. The EPR spectra were recorded at room temperature with a JES-Me3X X-band apparatus (JEOL, Tokyo). Usually at least 3 spectra were recorded, at 0.5 h, 2 h and 24 h, after mixing of the reagents. At least two reproducible runs were carried out for each reaction.

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