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REDOX REACTION OF ARENETITANIUM(II) COMPLEXES WITH CYCLOPENTADIENE LEADING TO (η^5-CYCLOPENTADIENYL)TITANIUM(III) COMPLEXES: AN EPR STUDY

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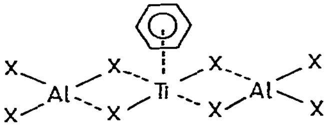
Summary

Bis(dichloroalanedi-μ-chloro)(η^6-arene)titanium(II) complexes are readily oxidised by cyclopentadiene to yield (η^5-cyclopentadienyl)bis(dichloroalanedi-μ-chloro)titanium(III). Upon further addition of cyclopentadiene the $AlCl_4$ ligand is replaced by cyclopentadienyl to give (di-η^5-cyclopentadienyl)(dichloroalanedi-μ-chloro)titanium(III). Similar reactions were observed with bis(dibromoalanedi-μ-bromo)(η^6-benzene)titanium(II). The structures of both the initial and final complexes are confirmed by this redox reaction.

Introduction

Bis(dichloroalanedi-μ-chloro)(η^6-benzene)titanium(II) (Ia) was prepared some time ago [1—4] and appeared to be an effective and specific catalyst for butadiene cyclotrimerisation [5,6]. Recently, the bromo- (Ib) and iodo-substituted derivatives of Ia were synthesised and the titanium(II) → arene nature of the charge transfer band of their electronic spectra was established [7]. In this paper the interaction of Ia and Ib with cyclopentadiene (CpH) is described, and the resulting (η^5-cyclopentadienyl)titanium(III) complexes are identified by means of their EPR spectra.

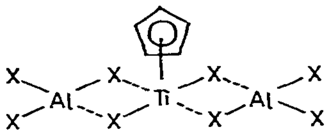


(Ia, X = Cl ; Ib, X = Br)

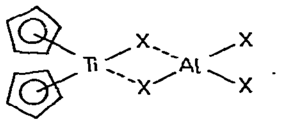
Results and discussion

Stepwise additions of CpH up to the molar ratio 1/1 with respect to titanium(II) complexes turned the red-violet colour of Ia and the blue colour of Ib solutions in benzene to light green. Simultaneously, the solutions, which were initially EPR inactive even at 77 K, developed EPR signals of intensities proportional to the amount of added CpH.

The eleven-line EPR spectrum at $g = 1.973$ shown in Fig. 1A was obtained after treatment with CpH of Ia containing benzene or hexamethylbenzene. It was easily assigned to (η^5-cyclopentadienyl)bis(dichloroalanedi-μ-chloro)titanium(III) (IIa) because the g-value and the hyperfine splitting arising from the interaction of the unpaired electron of titanium(III) with two equivalent aluminium nuclei, a(Al) 0.59 mT, agreed exactly with those reported for IIa prepared by the reduction of $CpTiCl_3$ with aluminium powder in the presence of an excess of $AlCl_3$ [8]. In that case IIa arose from the addition of two molecules of $AlCl_3$ to $CpTiCl_2$ formed by the reduction. Complex IIa was also formed in the action of a protonic acid (HCl or H_2O) on (di-η^5-cyclopentadienyl)(dichloroalanedi-μ-chloro)titanium(III) (IIIa) in the presence of $AlCl_3$ [8]. In this case one cyclopentadienyl ligand was displaced by the action of the acid $HAlCl_4$.



(IIa, X = Cl ; IIb, X = Br)



(IIIa, X = Cl ; IIIb, X = Br)

The identity of compound IIa as prepared from Ia was confirmed by observation of the reversal of the last reaction. The known EPR spectrum of IIIa showing the six-line structure (a(Al) 0.70 mT) at $g = 1.976$ [8,9] was obtained (Fig. 1B) when at least a two-fold excess of CpH was added to the solution of IIa prepared from Ia. The large excess of CpH was necessary to complete the formation of IIIa because a considerable amount of CpH was consumed in a simultaneous polymerisation. Most of the solution turned to a yellow gel and the concentration of IIIa in the remaining yellow solution as indicated by the integrated EPR spectrum was less than the initial concentration of IIa. The missing IIIa was probably trapped in the gel. In this reaction the $AlCl_4$ ligand was displaced by a strongly coordinating cyclopentadienyl anion according to equation 1.

$$\text{IIa} + \text{CpH} \rightleftharpoons \text{IIIa} + [HAlCl_4] \qquad (1)$$

It is likely that the complex acid initiating the polymerisation is removed from the system by the polymerisation, and the above equilibrium is shifted towards complete formation of IIIa.

The pure complex IIa was prepared by subsequent additions of CpH to the benzene solution of Ia until the electron absorption spectrum indicated complete disappearance of the latter. The amount of CpH consumed was about 1.2 times as large as the amount of Ia because some CpH was probably polymerised when local excess of CpH reacted with already formed IIa. The polymer

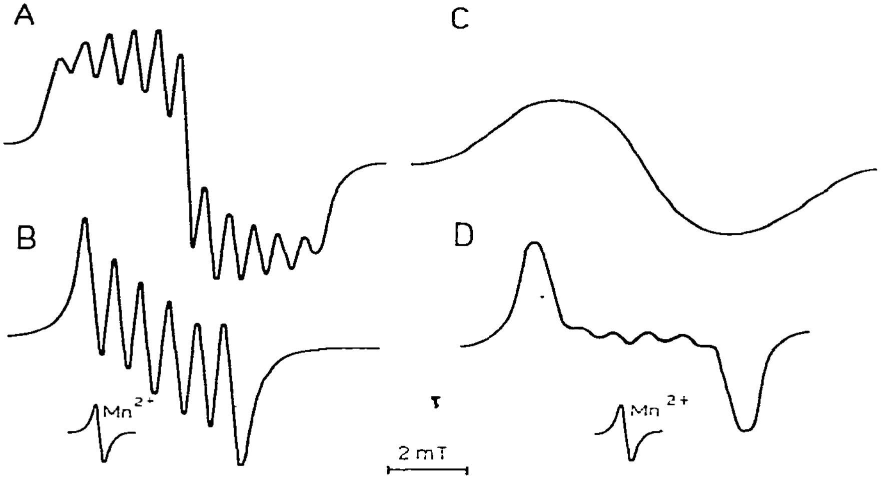


Fig. 1. EPR spectra of the reaction mixtures containing arenetitanium(II) complexes and CpH in molar ratios: A, CpH/Ia 1; B, CpH/Ia ~ 100; C, CpH/Ib 1; D, CpH/Ib ~ 100 ($g(Mn^{2+}) \sim 1.980$).

co-product was removed as a yellow precipitate after the addition of n-hexane to the concentrated solution of IIa. The resulting clear green solution yielded light green crystals by partial evaporation and cooling. The electronic absorption spectrum of the recrystallised IIa in benzene solution exhibited a charge transfer band at 370 nm ($\epsilon \sim 1100$) and a broad band at 660—665 nm ($\epsilon \sim 60$) due to the *d—d* transition.

The addition of an approximately equimolar amount of CpH to the solution of the bromo derivative Ib yielded a species with an EPR spectrum consisting of a broad line (ΔH 4.2 mT) at $g = 1.988$ (Fig. 1C). Addition of a large excess of CpH to this solution resulted in the appearance of a badly resolved six-line EPR spectrum a(Al) 0.83 mT at $g = 1.984$ (Fig. 1D) which can be assigned without doubt to IIIb. The appearance of the latter spectrum provides evidence that the broad line spectrum belongs to IIb, the expected eleven-line structure of which is obscured by considerable line broadening, which is also observed in the spectrum of IIIb.

The transformation of the complexes Ia and Ib into IIa and IIb, respectively, under the action of CpH is evidence for a redox reaction in which one electron from titanium(II) is transferred to CpH and the π-bonded arene molecule is released. Hydrogen formed in the reaction must be partially consumed in the reaction with benzene and/or with CpH, since less than a stoichiometric amount of gaseous H_2 was found above the frozen reaction mixtures. The overall process can be described as follows

$$Ti^{2+} + CpH \rightarrow Ti^{3+} + (CpH)^{-} \rightarrow Cp\text{-}Ti^{2+} + \dot{H}$$

The redox reaction is probably assisted by the acidic nature of CpH and by stabilisation of the product by the cyclopentadienyl ligand, but it clearly demonstrates the electron-donating ability of arenetitanium(II) complexes indicated so far by the titanium(II) → arene character of their charge transfer absorption band [7]. The complete consistency of the present results with the literature data [8] confirms the correctness of the structure proposed for both complexes Ia and IIa.

The redox reaction with CpH can be used for the identification of the structure of various modified arenetitanium(II) complexes [10] which possess catalytic activity for the cyclotrimerisation of butadiene. In this way the presence of the bivalent titanium can be demonstrated without complete destruction of its complex (cf. decomposition with water yielding H_2 [1—3], and important information about the structure of the original titanium(II) complex can be obtained from the EPR spectrum of the titanium(III) containing product. The electron transfer from arenetitanium(II) complexes to other olefinic compounds is under study.

Experimental

EPR spectra were measured on an ERS-220 spectrometer in the X-band at room temperature. Electronic absorption spectra were taken on an Optica Milano CF-4N spectrometer in the region 320—1000 nm.

Chemicals

Complexes Ia, Ib and Ia containing hexamethylbenzene were prepared and purified as described elsewhere [7]. Benzene was refluxed for 6 h over $LiAlH_4$ and fractionated. After degassing on a vacuum line it was distilled into an ampoule containing μ-(η^5:η^5-fulvalene)di-μ-hydrido(di-η^5-cyclopentadienyltitanium) (FDHT). The next day it was distilled into a storage vessel containing solid Ia. n-Hexane was purified in the same manner. Cyclopentadiene (CpH) was prepared by thermolysis of dicyclopentadiene (Fluka). Freshly prepared CpH was degassed and distilled on to solid FDHT in vacuo. This procedure was repeated with fresh FDHT, and the CpH containing FDHT was stored at 77 K.

Procedure

All the titanium compounds used were very sensitive to oxygen and moisture, and so all operations were performed under high vacuum (10^{-5} mmHg) using metal valves, Teflon stopcocks, and glass breakseals. The reaction of 10^{-2} *M* benzene solutions of Ia and Ib with CpH was carried out in an all-glass apparatus equipped with an EPR sample tube and a quartz cuvette (ϕ 1 mm or 1 cm). The gaseous CpH was admitted to a magnetically stirred titanium(II) solution at room temperature. The amount of added CpH was measured by the decrease of CpH pressure in a calibrated reservoir.

Preparation of IIa. CpH in approximately equimolar amount was added to the solution of Ia, the reaction apparatus was sealed off and the electronic absorption and EPR spectra were recorded including integrations. This procedure was repeated after sealing the apparatus to the vacuum line by the breakseals until the formation of IIa was indicated to be complete by both spectroscopic methods. Pure IIa was obtained as light green crystals by adding n-hexane to the concentrated benzene solution and by cooling the clear solution. Compound IIa was readily soluble in benzene and only slightly soluble in n-hexane.

References

1 G. Natta, G. Mazzanti and G. Pregaglia, *Gazz. Chim. Ital.*, 89 (1959) 2065.
2 H. Martin and F. Vohnwinkel, Chem. Ber., 94 (1961) 2416.
3 H. de Vries, Rec. Trav. Chim. Pays-Bas, 81 (1962) 359.
4 R. Gieżyński, S. Dzierzogowski and S. Pasynkiewicz, J. Organometal. Chem., 87 (1975) 295.
5 F. Vohnwinkel, Trans. N.Y. Acad. Sci., 26 (1964) 446.
6 Dzierzgowski, R. Gieżyński, S. Pasynkiewicz and M. Niżyńska, J. Mol. Catal., 2 (1977) 253.
7 H. Antropiusová, K. Mach and J. Zelinka, Transition Met. Chem., 3 (1978) 127.
8 G. Henrici-Olivé and S. Olivé, Makromol. Chem., 121 (1969) 70.
9 G. Henrici-Olivé and S. Olivé, J. *Organometal. Chem.*, 21 (1970) 377.
10 K. Mach, H. Antropiusová and J. Poláček, Transition Met.Chem., in press.