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THE HAMMETT RELATIONSHIP IN $CpTiCl_2OPhX$ ($X = CH_3O$, CH_3, Cl, NO_2) + $BuLi(Et_2AlCl)$ CATALYTIC SYSTEMS

W. SKUPIŃSKI and A. WASILEWSKI

Department of Chemistry, Technical University (Politechnika) 00-662 Warszawa, Koszykowa 75 (Poland)

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Summary

The $CpTiCl_2OPhX$ ($X = CH_3O$, CH_3, Cl, NO_2) + BuLi system is active in olefin hydrogenation, while the $CpTiCl_2OPhX + Et_2AlCl$ system is active in olefin polymerization. In both cases a linear relationship between the Hammett substituent constants and the catalytic activity of the investigated systems is found. The ρ constant for these two reactions is negative. The same relationship is found between the $g_{\parallel}$ constants of the EPR signals of the titanium(III) complexes obtained.

Introduction

In our previous paper [1] we presented the physicochemical properties of the titanium complexes $CpTiCl_2OPhX$ ($X = Me$, Cl, NO_2), which were prepared by the following reaction:

$$XPhOH + CpTiCl_3 \rightarrow XPhOTiCpCl_2 + HCl\uparrow \qquad (1)$$

We found a relationship between the wave number of some IR bands, the τ values of the aromatic proton bands in the NMR spectra, and the values of the σ Hammett substituent constant for the phenyl rings of the titanium(IV) complexes obtained. This paper deals with the catalytic and physicochemical properties of systems prepared by reduction of the titanium(IV) complexes with an excess of BuLi or Et_2AlCl.

Experimental

The $CpTiCl_2OPhX$ compounds were prepared as described in our previous paper [1]. In addition, *para*- and *meta*-methoxy derivatives were prepared. Both isomers are oils- *para* being red and *meta* red-orange in colour. In their IR spectra they display bands due to the Ti–O–R grouping as follows: *meta* isomer: 1416, 1106, 608, 485 cm^{-1}; *para* isomer: 1414, 1100, 548, 475 cm^{-1}. In the ^1H NMR spectra the cyclopentadienyl and phenyl protons are located as follows: *meta* isomer: Cp(H), δ

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7.03 (s); Ph(H), 1.10 (m); *para* isomer: Cp(H), δ 6.90 (s), Ph(H), 6.73 (m) (where s stands for singlet and m multiplet).

All these values correlate directly with the σ Hammett constants of the phenoxy ring substituents (for values of other $CpTiCl_2OPhX$ compounds see our previous paper [1]).

The reduction reactions of the titanium(IV) complexes obtained with an excess of BuLi or Et_2AlCl were carried out at room temperature: (1) 0.35 mmol of $CpTiCl_2OPhX$ in benzene (1 *M*) was treated with 1 mmol of BuLi in hexane (3 *M*); (2) 0.3 mmol of $CpTiCl_2OPhX$ in benzene (1 *M*) was treated with 1.2 mmol of Et_2AlCl in heptane (1 *M*).
After 10 min the solutions were taken for reaction or for the EPR measurements.

Cyclopentene ($C_5^=$) was used for the hydrogenation, which was carried out as a static reaction in the presence of the BuLi-reduced systems at room temperature under normal pressure. The $C_5^=/Ti$ ratio was 10/1 and the $H_2/C_5^=$ ratio 4/1. The progress of the reaction was monitored by GLC.

Ethylene ($C_2^=$) was used for polymerization, which was carried out in an autoclave in the presence of the Et_2AlCl-reduced systems at room temperature under a fixed pressure of 7×10^5 Pa.

NMR measurements were carried out using a Tesla BS487C80 MHz spectrometer, IR spectra were recorded on a UR 10 Carl Zeiss instrument (Jena) and EPR spectra were recorded using a Wrocław 200 spectrometer at room temperature.

Results and discussion

EPR measurements

The homogeneous yellow or red benzene solutions of the $CpTiCl_2OPhX$ compounds changed colour after addition of the reducing agents. In the case of BuLi, dark brown or black solutions were obtained. EPR measurements gave wide singlets characteristic of the anisotropic, axial symmetry of titanium(III) complexes. The values of the $g_\perp$ and $g_\parallel$ constants are given in Table 1.

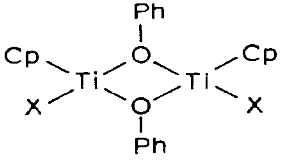
The $g_\perp$ constants are larger than the $g_\parallel$ constants for all the titanium(III) complexes obtained, and are very close to the g_e value (for a free electron) of 2.0023. These facts suggest tetrahedral symmetry for the titanium(III) complexes obtained and unpaired electron localization on the $d_{x^2-y^2}$ orbital [2]. The values of the $g_\parallel$ constant are very sensitive to ligand–metal ion interactions within the complex [3]. The values of the $g_\parallel$ constant of the investigated titanium(III) complexes show very great changes depending on the kind of substituent in the phenoxy ring (which must

TABLE 1

VALUES OF THE $g_\parallel$ AND $g_\perp$ CONSTANTS OF THE EPR SPECTRA OF THE $CpTiCl_2OPhX$ ($X = OCH_3, CH_3, Cl, NO_2$)+BuLi SYSTEM

X	*p*-CH_3	*m*-CH_3	H	*p*-Cl	*m*-NO_2	*p*-NO_2
σ	−0.17	−0.07	0	0.23	0.71	1.24
$g_\perp$	1.991	1.984	1.981	1.992	2.033	2.007
$g_\parallel$	1.975	1.,976	1.978	1.984	2.002	2.003

be in the coordinative sphere of the titanium(III) ions in our systems). The strongest electron-accepting nitro groups shifted the values of the $g_{\parallel}$ constant towards g_e values. The $g_{\parallel}$ constant of these compounds equals 2.002. This means that the unpaired electron is almost completely delocalized from the titanium ion to the ligands [3]. The strongest electron-donating substituents in the phenoxy ring are responsible for the values of $g_{\parallel}$ typical for tetrahedral titanium(III) complexes (~ 1.97) [4]. The correlation between the $g_{\parallel}$ constant values of all the investigated titanium(III) complexes and the Hammett factors of the phenoxy ring substituents gives direct agreement (see Fig. 1). This proves the strong influence of the phenoxy ring donor-acceptor properties on the unpaired electron density around the metal ions in the titanium(III) complexes under investigation, where acceptor groups, such as nitro groups, withdraw electrons from the metal ion and donor groups, such as alkyl groups, increase the electron density around titanium(III). This means that this influence must occur thanks to interaction between the unpaired electron localized on the titation $d_{x^2-y^2}$ orbital and the phenoxy ring. This interaction can occur only when the $d_{x^2-y^2}$ orbital is involved in a direct bond with the phenoxy ring. Thus it is reasonable to accept that this orbital is in the phenoxy oxygen–titanium bond. On the basis of the known dimeric forms of alkoxy titanium(III) complexes [5] and the considerations described above, the titanium(III) complexes obtained should have a dimeric structure with oxygen as the bridging atoms:



where X = alkyl, halogen or hydrogen.

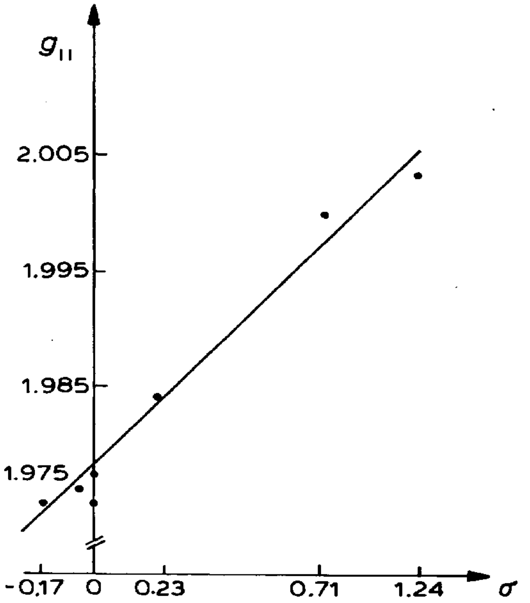


Fig. 1. Relationship between the values of σ and $g_{\parallel}$.

Hydrogenation and polymerization of olefins

Cyclopentene hydrogenation in the presence of the BuLi-reduced systems is rather slow. For a $C_5^=/Ti$ ratio of 10/1, statistically only one olefin molecule is hydrogenated on one titanium(III) complex after 1 h on the most active system (*p*-methoxy), which is more than 7 times more active than the least active (*p*-nitro) one (see Table 2).

Ethylene polymerization in the presence of the Et_2AlCl-reduced systems is a more efficient reaction. In 1 h, according to statistics, about 150 ethylene molecules polymerize on one titanium complex on the least active system (*p*-NO_2) and about 300 ethylene molecules are polymerized on the most active (*p*-OCH_3) catalyst (see Table 3).

TABLE 2

CYCLOPENTENE HYDROGENATION IN THE PRESENCE OF THE $CpTiCl_2OPhX$ + BuLi SYSTEM (ρ −0.65)

X	*p*-OCH_3	*p*-CH_3	*m*-CH_3	H	*m*-OCH_3	*p*-Cl	*m*-NO_2	*p*-NO_2
$k\dfrac{\text{mol}C_5^=}{\text{mol Ti}^{III}\,h^{-1}}$	0.69	0.62	0.48	0.46	0.40	0.35	0.23	0.1

TABLE 3

ETHYLENE POLYMERIZATION IN THE PRESENCE OF THE $CpTiCl_2OPhX$ + $AlEt_2Cl$ SYSTEM (ρ −0.20)

X	*p*-OCH_3	*p*-CH_3	*m*-CH_3	H	*m*-OCH_3	*p*-Cl	*m*-NO_2	*p*-NO_2
$k\dfrac{\text{mol}C_2^=}{\text{mol Ti}^{III}\,h^{-1}}$	300	290	270	265	245	238	200	150

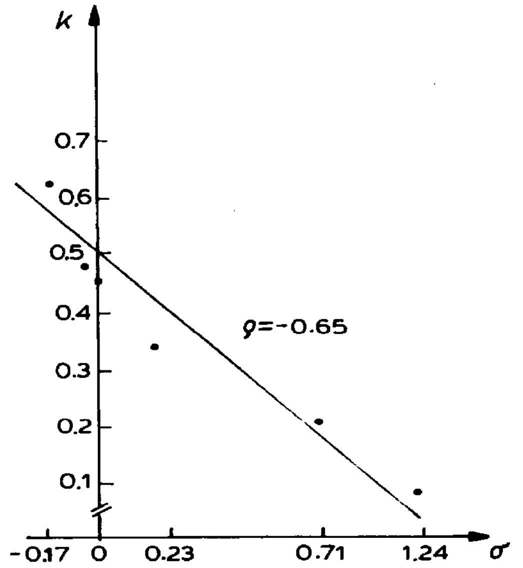


Fig. 2. Relationship between the values of σ and k for cyclopentene hydrogenation (k = mol $C_5^=$/mol Ti^{III} h^{-1}).

The activity of both systems correlates with the Hammett constants of the phenoxy ring substituents for the hydrogenation and polymerization reactions, respectively (see Figs. 2 and 3).

For both reactions, the more electron-donating the phenoxy ring in the titanium(III) complexes, the more unpaired electron density around titanium(III) ions, thus the catalysts are more active and the reactions are more efficient. The greater differences between the activities of the particular catalytic systems in the hydrogenation reactions that those observed in the polymerization of ethylene allows us to suppose that cyclopentene hydrogenation is more sensitive to electron density around titanium(III) ions in the investigated systems than ethylene polymerization.

If we use the formalism of the Hammett equation to discuss the results obtained and the particular catalyst we treat as a reagent in the catalytic path in both reactions, we can discuss the ρ constant defined as

$$\rho = \log(k/k_0)\sigma$$

where k is the reaction rate for compounds having the substituent Hammett constant and k_0 is the reaction rate for H as the substituent [6].

For the systems we investigated, ρ is -0.65 for the hydrogenation reaction and -0.20 for the polymerization reaction. The low values of both ρ constants suggest that both reactions go through several transition stages in which the catalyst participates. Some of these transition stages are accelerated by decreasing electron density around titanium(III) ions in the catalyst species (these reactions have a positive ρ constant). The rest of the transition stages must be accelerated by increasing electron density around titanium(III) ions (these reactions have a negative ρ constant. The sum of the ρ constants of all these transition stages for both reactions is negative. This means that the reactions in both catalytic paths with negative values play the most important role. Thus increasing electron density

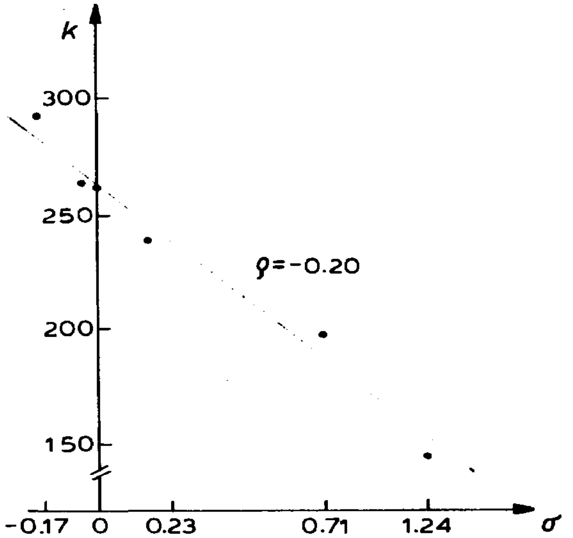


Fig. 3. Relationship between the values of σ and k for ethylene polymerization (k = mol $C_2^=$/mol Ti^{III} h^{-1}).

around titanium(III) ions in the investigated systems is responsible for their higher catalytic activity. This increase of electron density is more important for the hydrogenation reaction – the ρ constant is more negative.

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