Journal of Organometallic Chemistry, 434 (1992) C1–C5
Elsevier Sequoia S.A., Lausanne
JOM 22856PC

Preliminary communication

Base-free cationic 14-electron alkyls of Ti, Zr and Hf as polymerisation catalysts: a comparison

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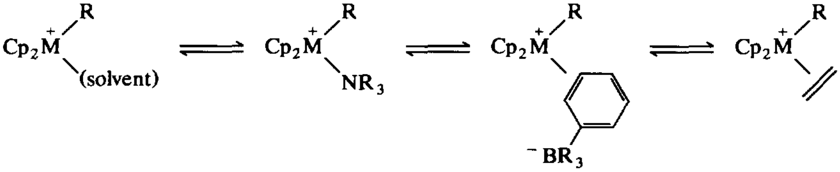
(Received March 25, 1992)

Abstract

The reaction of Cp'_2MMe_2 (M = Ti, Zr, or Hf) with either $[CPh_3]^+$ or $[PhNHEt_2]^+$ salts of non-coordinating anions gives new cationic $[Cp'_2MMe]^+$ catalysts. The ethene polymerisation activity increases in the order $M = Ti \ll Hf < Zr$; the activity of the Zr and Hf complexes is comparable with that of Cp_2MCl_2/methylaluminoxane systems ($Cp' = C_5H_4SiMe_3$).

The role of cationic 14-electron complexes of Group 14 metals of the type $[Cp_2M-R]^+$ as the active species in the homogenous polymerisation of olefins is now well established by a number of model [1], theoretical [2] and catalytic [3,4] studies. We have recently shown that "base-free" alkyl cations of titanium and zirconium can be generated under mild conditions by protolysis of Cp'_2MMe_2 with $[PhNHMe_2]BPh_4$ in weakly coordinating solvents such as dichloromethane and that multiple alkene insertion and polymer chain growth occur on exposure to ethene [4]. These complexes possess moderate polymerisation activity for ethene and propene at atmospheric pressure. In addition to catalyst deactivation by trace impurities, the activity of such systems is limited by the presence of a number of potential ligands, such as the solvent, the amine, and particularly the BPh_4^- anion [3h,5], which compete effectively with the olefinic substrate for a vacant coordination site on the metal centre. The catalytic activity is therefore a function of the equilibrium established, *e.g.* between species **A–D**, and shows pronounced solvent and anion dependence [3i,6]:



(A) **(B)** **(C)** **(D)**

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We have attempted to evaluate the influence of species such as **B** and **C**. Anion coordination (*cf.* **C**) can be virtually eliminated by using fluorinated anions such as $[\mathrm{B\{C_6H_3(CF_3)_2\}_4}]^-$ [6,8] and in particular Turner's $[\mathrm{B(C_6F_5)_4}]^-$ [7,9*]. The influence of the amine (structure **B**) can be demonstrated by using two methods of generating the cationic metal alkyl complexes, one involving reaction with triphenylcarbenium salts (eq. 1), and the other protolysis of metal dialkyls with anilinium salts (eq. 2):

$$\mathrm{Cp'_2MMe_2 + [CPh_3]^+[BR_4]^- \longrightarrow [Cp'_2MMe]^+[BR_4]^- + Ph_3CMe} \qquad (1)$$

(**1**) (**2a**, $\mathrm{R = C_6H_3(CF_3)_2}$; (**3**)
2b, $\mathrm{R = C_6F_5}$)

$$\mathrm{Cp'_2MMe_2 + [PhNHEt_2]^+[BR_4]^- \longrightarrow}$$

(**1**) (**2c**, $\mathrm{R = C_6F_5}$)

$$\mathrm{[Cp'_2MMe(PhNEt_2)]^+[BR_4]^- + CH_4} \qquad (2)$$

(**4**)

The triphenylcarbenium salts **2a** and **2b** were obtained by metathesis of $[\mathrm{CPh_3}]\mathrm{BF_4}$ with $\mathrm{Na[B\{C_6H_3(CF_3)_2\}_4]}$ [8] and $\mathrm{Li[B(C_6F_5)_4]}$ [10], respectively [11*]. The generation of metal alkyl cations **3** according to eq. 1 was verified by ^{1}H NMR spectroscopy by treating $\mathrm{Ind_2TiMe_2}$ with **2a** in $\mathrm{CD_2Cl_2}$ at −45°C. The formation of $[\mathrm{Ind_2TiMe}]^+$ [4] is accompanied by that of $\mathrm{Ph_3CMe}$. At −60°C in the presence of an excess of $\mathrm{Ind_2TiMe_2}$ an unstable dinuclear intermediate is observed, as indicated by two singlets at $\delta = -0.56$ and -1.59 in a ratio 2:1:

$$2\,\mathrm{Ind_2TiMe_2} \xrightarrow{\mathrm{CPh_3^+}} [\mathrm{Ind_2Ti(Me)(\mu\text{-}Me)Ti(Me)Ind_2}]^+ \xrightarrow{\mathrm{CPh_3^+}} [\mathrm{Ind_2TiMe}]^+$$

The ethylene polymerisation activity [12*] of a series of complexes $[\mathrm{(C_5H_4SiMe_3)_2MMe}]^+$ in dichloromethane and toluene under comparable conditions decreases in the order $\mathrm{M = Ti \ll Hf < Zr}$ (Table 1). In agreement with earlier results, titanium catalysts are moderately active in dichloromethane at or below 0°C [4,6]. The influence of the counterion, even of $[\mathrm{B(C_6F_5)_4}]^-$, is small in dichloromethane where solvent coordination is thought to be important (run 2), and there is no substantial improvement if toluene is used as the reaction medium. The molecular weight of polymers from titanium catalysts is relatively low. By contrast, the activity of zirconium alkyl cations is substantially higher (runs 4–6), and although the Cp ligands were not specially chosen to maximise catalytic activity, a productivity corresponding to up to about 2.8 tons PE per mol Zr complex per hour was observed. This activity significantly exceeds that reported recently for catalysts based on metallacarborane anions [3k], and is comparable with that of conventional $\mathrm{Cp_2ZrCl_2}$/methylaluminoxane catalysts under 1.7 atm of ethene [13].

The activities of systems generated according to eqs. 1 and 2 in the presence and absence of amine were very similar, and suggest that at the low catalyst concentrations employed ($1.1 - 1.5 \times 10^{-4}$ *M*) complexes of type **4** are essentially

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* Reference number with asterisk indicates a note in the list of references.

Table 1

Comparison of ethene polymerisation activity of $[Cp'_2MMe]^+$ catalysts (M = Ti, Zr and Hf; $Cp' = C_5H_4SiMe_3$) [a]

Run no.	Cp'_2MMe_2 M (μmol)	Cocatalyst (μmol)	Solvent	Temperature (°C)	Time (s)	Productivity kg PE/(mol 3·h)	Turnover no. N_t (s^{-1})	M_w [b] ($\times 10^{-3}$)	M_n [b] ($\times 10^{-3}$)	M_w/M_n
1	Ti (144)	**2a** (140)	CH_2Cl_2	0	240	35	0.35	13.3	6.01	2.2
2	Ti (180)	**2c** (180)	CH_2Cl_2	0	240	54	0.54			
3	Ti (21)	**2b** (7.3)	toluene	21	120	82	0.82			
4	Zr (15)	**2b** (3.6)	toluene	21	120	1542	15.3			
5	Zr (10)	**2b** (1.8)	toluene	21	120	2333	23.2	203	92.5	2.2
6	Zr (15)	**2c** (1.4)	toluene	21	120	2870	28.5	382	144.6	2.6
7	Hf (31)	**2b** (6.6)	toluene	21	120	796	7.9			
8	Hf (18.6)	**2b** (3.3)	toluene	41	120	1200	11.9	34.9	15.2	2.3

[a] For polymerisation conditions see ref. 12*. [b] By GPC, PLgel column, 1,2-dichlorobenzene, 140°C.

dissociated and diethylaniline coordination (*cf*. structure **B**) is not a limiting factor for the catalytic activity.

The activity of hafnium cations is somewhat less than that of zirconium catalysts. There is a marked activity increase with temperature, with a corresponding decrease in polymer molecular weight. This temperature dependence mirrors that of Cp_2MCl_2/MAO catalysts [13]. In all cases the polymers produced have a narrow molecular weight distribution typical for chemically homogeneous catalytic sites.

Related cationic zirconium alkyls with stereorigid chelating Cp ligands are active for the iso- and syndio-specific polymerisation of propene [14]. While this work was in progress, the use of **2b** to generate highly active isospecific polymerisation catalysts was reported [15].

Acknowledgements. This work was supported by the Science and Engineering Research Council. We are grateful to Dr. S. Holding (RAPRA Technology Ltd.) for GPC measurements.

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11 Selected spectroscopic data: **2a**, yellow crystals; ^1H NMR (400 MHz, CD_2Cl_2): $[CPh_3]^+$: 8.22 (t, *p*-H), 7.84 (t, *m*-H), 7.64 (d, *o*-H); $[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]^-$: 7.55 (s, br, *p*-H), 7.23 (t, br, *o*-H); ^{19}F NMR (CD_2Cl_2, rel. $CFCl_3$): -56.0. **2b**, yellow crystals; ^1H NMR: $[CPh_3]^+$: 8.27, 7.88, 7.67; $[B(C_6F_5)_4]^-$: ^{19}F NMR ($CDCl_3$, rel. $CFCl_3$): -125.7 (s, br), -156.1 (t, *J* 20.6 Hz), -160.0 (t, br, *J* *ca.* 18 Hz).

12 Polymerisation conditions: Aliquots of toluene solutions of **1** and **2** were injected under argon into a glass reactor charged with 12 mL of toluene and thermostated to the given temperature. The mixture was allowed to react with vigorous stirring for 120 s before the argon was replaced by ethylene (1 bar). The reaction was terminated by injecting methanol (2 mL). The polymer was washed with methanol and aqueous HCl and dried at 70°C. For reactions in dichloromethane, **1** (M = Ti) and **2** were injected at −78°C, ethene was admitted and the mixture warmed to 0°C.

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