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Complexation of Cp_2MCl_2 in a chloroaluminate molten salt: relevance to homogeneous Ziegler–Natta catalysis

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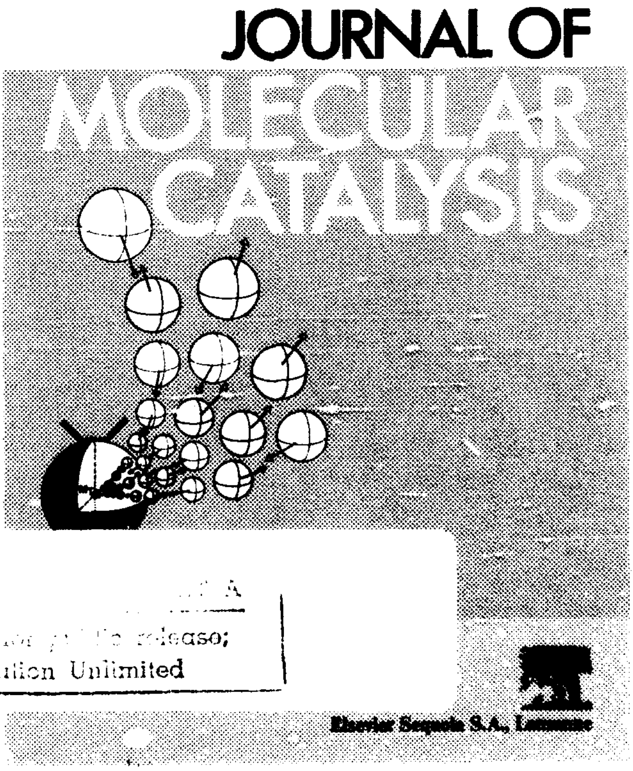

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Complexation of Cp_2MCl_2 in a chloroaluminate molten salt: relevance to homogeneous Ziegler–Natta catalysis

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Abstract

Ethylene polymerization via Ziegler–Natta catalysis occurs in the ambient-temperature molten salt $AlCl_3 \cdot MEIC$ (MEIC = 1-ethyl-3-methylimidazolium chloride) employing Cp_2TiCl_2 as the catalyst and $AlCl_{3-x}R_x$ (R = Me, Et) as a cocatalyst. Catalysis occurs only in melts with $AlCl_3$:MEIC molar ratios > 1. Cp_2ZrCl_2 and Cp_2HfCl_2 with $AlCl_{3-x}R_x$ cocatalysts are not catalytically active in acidic melts. ^1H NMR studies indicate formation of a strong 1:1 complex between Cp_2TiCl_2 and $AlCl_3$, while Zr and Hf form much weaker 1:1 complexes due to strong Zr–Cl and Hf–Cl bonding. This stronger M–Cl bonding for Zr and Hf is proposed to preclude the initiation reaction for ethylene polymerization in the molten salt.

Introduction

The ambient-temperature chloroaluminate molten salt $AlCl_3 \cdot MEIC$ (MEIC = 1-ethyl-3-methylimidazolium) offers a unique medium for studying chloride and $AlCl_3$ complexation [1–3]. It has controllable Lewis acidity and donor/acceptor properties through variation of the $AlCl_3$:MEIC molar ratio [2, 4]. In basic melts ($AlCl_3$MEIC molar ratio < 1), the dominant anions are Cl^- and $AlCl_4^-$, making possible studies of Cl^- complexation. In acidic melts ($AlCl_3$:MEIC molar ratio > 1), the dominant anions are $Al_2Cl_7^-$ and $AlCl_4^-$, making possible studies of $AlCl_3$ complexation. Additionally, the molten salt is stable at subambient and elevated (> 200 °C) temperatures, and it has negligible or low vapor pressure over this wide temperature range. Some Lewis acid-catalyzed organic reactions have been studied in the melts, which were found to be excellent media [5].

We have recently found that ethylene polymerization takes place in the $AlCl_3 \cdot MEIC$ molten salt employing Cp_2TiCl_2 as the catalyst and $AlCl_{3-x}R_x$ (R = Me, Et) as a cocatalyst. Catalysis does not occur in basic melts, where preliminary electrochemical experiments indicate Cp_2TiCl_3 is formed. Acidic melts containing Cp_2ZrCl_2 and Cp_2HfCl_2 as catalysts and $Al_2Me_3Cl_3$ as cocatalyst showed no catalytic activity up to 65 °C. This is consistent with the reported

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observation that Cp_2ZrCl_2 is not a catalyst in the presence of $AlCl_{3-x}R_x$; however, cyclopentadienyl complexes of Zr are catalytic in the presence of aluminoxanes [6, 7]. Similarly, indenyl complexes of Zr and Hf are catalytic in the presence of aluminoxanes [8, 9].

A typical catalytic run consisted of bubbling ethylene at 1 atm through 6.8 g of an acidic 1.1:1.0 $AlCl_3$:MEIC melt containing 0.022 g Cp_2TiCl_2 (17 mM) and 0.118 g $Al_2Me_3Cl_3$ (330 mM in methyl) for 10 min at 25 °C. Quenching of the catalytic mixture with 150 ml methanol resulted in precipitation of the polyethylene (PE), while the catalyst and melt components remained in solution. The PE was isolated by centrifugation, giving a yield of 0.020 g or a catalytic activity of 0.023 (g PE) min^{-1} (mmol $Ti)^{-1}$ atm^{-1}. Catalytic activities were in the range of 0.02 to 0.15 (g PE) min^{-1} (mmol $Ti)^{-1}$ atm^{-1} using either 1.1:1.0 or 1.5:1.0 $AlCl_3$:MEIC melts as solvents. These catalytic activities are low relative to other homogeneous systems [10]; however, they are in the same range as that reported for the cationic complex $Cp_2ZrMe(THF)^+$ [11]. The low catalytic activity may be attributed to several factors, including inherently lower activity of the Ti complex in the melts, low solubility of ethylene in the melts, or the presence of alkylimidazole impurities which, as nitrogen bases, block the Ti active sites.

A study of the $AlCl_3$ complexation of Cp_2MCl_2 (M = Ti, Zr, and Hf) in acidic melts was performed to gain an understanding of the catalytic activity of Cp_2TiCl_2 and the lack of activity for Cp_2ZrCl_2 and Cp_2HfCl_2. Solutions of the three complexes were prepared in a neutral melt ($AlCl_3$:MEIC molar ratio = 1), where $AlCl_4^-$ is the only anion present. The proton chemical shifts of the Cp rings were monitored as a function of added $AlCl_3$, Fig. 1. As the melts become acidic, all the complexes show a downfield shift of the Cp

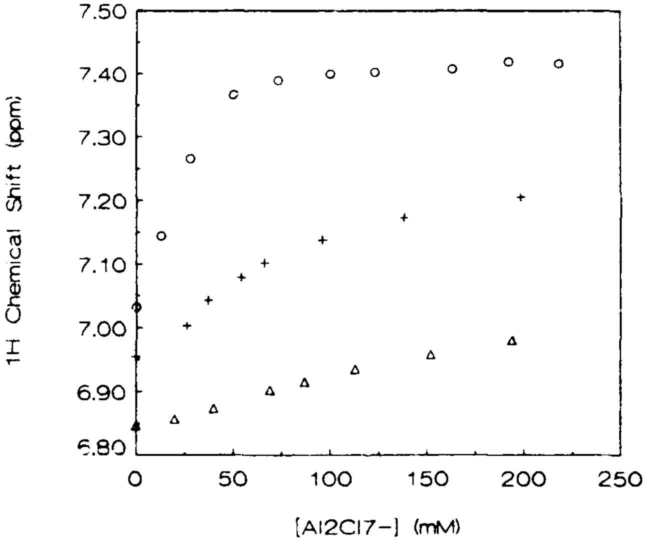

Fig. 1. Chemical shift of ^{1}H NMR resonance for the Cp protons in (○) Cp_2TiCl_2 (58 mM), (+) Cp_2ZrCl_2 (16 mM) and (△) Cp_2HfCl_2 (72 mM).

protons, indicative of removal of electron density from the complex. Similar behavior has been reported for a ^{13}C NMR study of $Cp_2TiClEt/AlEtCl_2$ in d_8-toluene [12]*. Additionally, the potential of the one-electron reduction of Cp_2TiCl_2 shifts approximately 1.2 V positive in going from a basic to an acidic melt, emphasizing the removal of electron density from the Ti complex in acidic melts [13]. The two complexation reactions which may occur are shown in eqns. (1) and (2):

$$Cp_2MCl_2 + Al_2Cl_7^- \rightleftharpoons Cp_2MCl(AlCl_4) + AlCl_4^- \tag{1}$$

$$Cp_2MCl(AlCl_4) + Al_2Cl_7^- \rightleftharpoons \begin{cases} Cp_2M(AlCl_4)_2 \\ \quad\text{or} \\ Cp_2MCl(Al_2Cl_7) \end{cases} + AlCl_4^- \tag{2}$$

Structures for $Cp_2MCl(AlCl_4)$ (M = Ti [14] and Zr [15]) have been reported. In both complexes, $AlCl_4^-$ is coordinated in a monodentate fashion, forming a M−Cl−Al bridging structure.

The proton chemical shifts of the Zr and Hf complexes were fit successfully to a single equilibrium, eqn. (1), using a least squares method [16]. A constant $AlCl_4^-$ activity of one and activities of the other species equal to their concentrations were assumed. The Ti curve indicates an extremely high equilibrium constant for eqn. (1) and can only be assigned a lower limit from the data. The calculated equilibrium constants, K_1, are summarized in Table 1. At high $Al_2Cl_7^-$ concentrations, the ^1H resonances show a more gradual downfield shift in the three complexes. Apparently eqn. (2) becomes important particularly for Ti at high $Al_2Cl_7^-$ concentrations.

It is significant that Ti has the highest K_1 value and is the only complex which demonstrates catalytic activity. Equation (1) may be viewed as a reaction in which formation of the Al−Cl bond occurs at the expense of M−Cl bonding. The M−Cl bond strengths increase in the order Ti−Cl (102.6 kcal mol^{-1}) < Zr−Cl (117.0 kcal mol^{-1}) < Hf−Cl (118.3 kcal mol^{-1}) [17]; therefore, the lower K_1 values for Zr and Hf are indicative of stronger M−Cl bonding in these complexes *vs.* the Ti complex.

TABLE 1

Complexation equilibrium constants for Cp_2MCl_2 in acidic $AlCl_3$·MEIC melts

M	K_1
Ti	$> 10^5$
Zr	21 ± 4
Hf	4.1 ± 0.8

---

*In the melts at ambient temperatures, the Cp_2TiCl_2 complex is slowly reduced to a paramagnetic Ti(III) complex in the presence of alkylaluminums, precluding Cp_2TiCl_2/alkylaluminum NMR complexation studies. For the Zr and Hf complexes, no reduction occurs; however, only alkylaluminum species, no alkylated Zr or Hf complexes, were detected by NMR.

In acidic melts, the precursor to the active Ti catalyst is most likely an alkylated 1:1 $AlCl_3$:Cp_2TiCl_2 complex, which can be written as $Cp_2TiR(AlCl_4)$. Recently, the crystal structure of the complex $Cp_2TiCSi(CH_3)_3{=}C(CH_3)(C_6H_5)^+AlCl_4^-$, formed from reaction of $(C_6H_5)CCSi(CH_3)_3$ with Cp_2TiCl_2 and $MeAlCl_2$ [18], and the demonstration that the cationic complex $Cp_2Zr(CH_3)(THF)^+B(C_6H_5)_4^-$ is a catalyst for ethylene polymerization without the alkylaluminum cocatalyst [11] provide support for the hypothesis that the active homogeneous catalyst is a cationic Cp_2MR^+ species. Based on this, generation of the active polymerization catalyst in the melt may involve loss of $AlCl_4^-$ to form the coordinatively-unsaturated species Cp_2TiR^+ as in eqn. (3):

$$Cp_2TiR(AlCl_4) \rightleftharpoons Cp_2TiR^+ + AlCl_4^- \tag{3}$$

or initiation of polymerization may involve displacement of $AlCl_4^-$ by ethylene to form the complex $Cp_2TiR(CH_2CH_2)^+$ as in eqn. (4):

$$Cp_2TiR(AlCl_4) + CH_2CH_2 \rightleftharpoons Cp_2TiR(CH_2CH_2)^+ + AlCl_4^- \tag{4}$$

In both schemes, the active catalyst is a cationic complex and is generated by breaking of the M—Cl bond, which is considerably stronger for Zr and Hf than for Ti. Therefore, the evidence indicates that the lack of catalytic activity for the Zr and Hf complexes is due to their stronger M—Cl bonding which precludes formation of the active catalyst species.

Because of the large concentration of $AlCl_4^-$ in the melts (>4 M), it seems unlikely that a coordinatively-unsaturated species would exist in the melt, with eqn. (3) being shifted almost entirely to the left. This is especially true since no Cp_2TiR^+ is spectroscopically observed in chloroform solvent when the $AlCl_2R$:Cp_2TiCl_2 molar ratio is only 1:1 [18], indicating the equilibrium constant for eqn. (3) is small. Therefore, although dissociation, eqn. (3), followed by complexation of Cp_2TiR^+ with ethylene cannot be ruled out, we favor eqn. (4) as the step producing the active catalytic species in these melts.

These ambient-temperature molten salts offer a unique medium for the study of $AlCl_3$ complexation to transition metal chlorides. Their high ionic nature and Lewis acidity provide an unusual environment for catalytic processes which we are investigating further.

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