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Journal of Organometallic Chemistry 484 (1994) C10–C12

Journal of Organometallic Chemistry

Preliminary communication

Facile α-H Elimination in cationic zirconium alkyl complexes: formation of μ-CH_2 complexes as a possible deactivation pathway in polymerization catalysis

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Received 26 May 1994

Abstract

The fulvalene complex $\{CpZr(CH_3)_2\}_2(\eta^5:\eta^5\text{-}C_{10}H_8)$ reacts with $[CPh_3][B(C_6F_5)_4]$ at −60°C in the absence of donor ligands with elimination of methane, to give the dinuclear μ-CH_2 complex $[(CpZr)_2(\mu\text{-}CH_3)(\mu\text{-}CH_2)(\eta^5:\eta^5\text{-}C_{10}H_8)]^+$. The relevance of this very facile α-H elimination process as a pathway in the deactivation of homogeneous Ziegler catalysts is discussed.

Keywords: Zirconium; α-H elimination; Ziegler catalysts, Olefin polymerization

Base-free cationic Group 4 metal alkyls of the general formula $[Cp_2M\text{–}R]^+$ (1) (M = Ti, Zr, Hf) are highly active catalysts for the polymerization of olefins [1–3]. We have recently reported the formation of dinuclear methyl complexes of the type $[\{Cp_2M(CH_3)\}_2(\mu\text{-}CH_3)]^+$ (2) (M = Zr, Hf) by the treatment of $Cp_2M(CH_3)_2$ with $[CPh_3][B(C_6F_5)_4]$ at low temperature, to give thermally stable catalysts for the polymerization of ethylene and propene, and have demonstrated that catalytic activity depends on the dissociation of **2** into $Cp_2M(CH_3)_2$ and the active species **1** (Scheme 1) [4].

By contrast, the analogous reaction of the fulvalene complex **3** [5] with $[CPh_3][B(C_6F_5)_4]$ in dichloromethane at −60°C leads to the immediate formation of the red μ-CH_2 complex **4** [Eq. (1)] in quantitative yield, as indicated by ^{1}H-NMR spectroscopy. The compound is isolated as a burgundy–red solid by the addition of cyclopentane to the reaction mixture. The same product is formed at room temperature in either dichloromethane or toluene.

Attempted recrystallizations were unsuccessful and led to less pure material. Monitoring the reaction by NMR at −60°C gave no indication of the expected intermediate $[(CpZrCH_3)_2(\mu\text{-}CH_3)(\eta^5:\eta^5\text{-}C_{10}H_8)]^+$, which evidently undergoes very facile α-H abstraction leading to the evolution of methane to give the bridging methylene complex **4**. The μ-CH_2 ligand is identified in the ^{1}H-NMR spectrum by a set of two doublets at $\delta = 4.35$ and 9.91 for the two inequivalent hydrogens, and by a low field ^{13}C-NMR signal at $\delta = 188.2$. Well-defined products of α-H abstraction from zirconium alkyls are very rare; examples include neutral complexes containing bridging neohexylidene ligands between zirconium and aluminium [6] and a recently reported mononuclear zirconium benzylidene complex [7]. In either case the α-H abstraction requires irradiation or warming to much higher temperature.

Mülhaupt and coworkers [8] noted that the kinetics of propene polymerization with a Cp_2ZrCl_2/methylaluminoxane catalyst can be interpreted by assuming a reversible and an irreversible deactivation process, with both processes being second-order in [Zr]. It is tempting to speculate that the equilibrium $\mathbf{2} \rightleftharpoons \mathbf{1} + Cp_2MMe_2$ provides a model for the reversible deactivation process; i.e. **2** is a temporarily dormant state, while the formation of a μ-CH_2 species of type **4** is irreversible. Although it has not yet been possible to identify μ-al-

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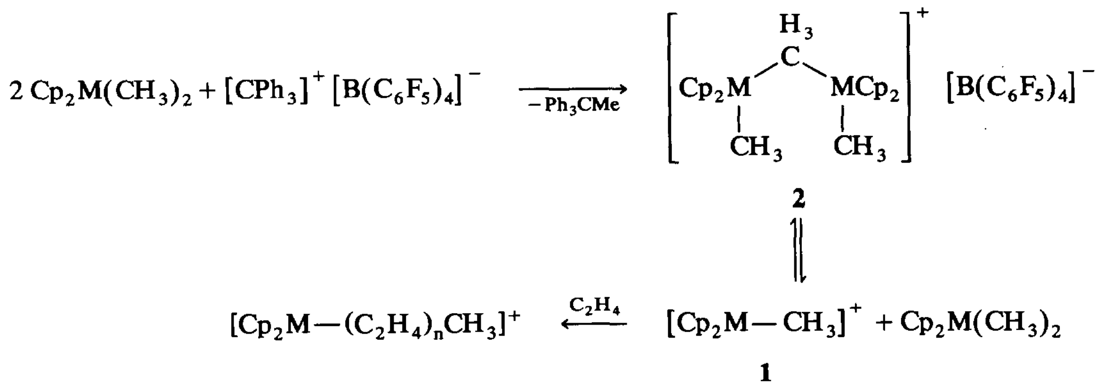
0022-328X/94/$07.00
SSDI 0022-328X(94)05066-K

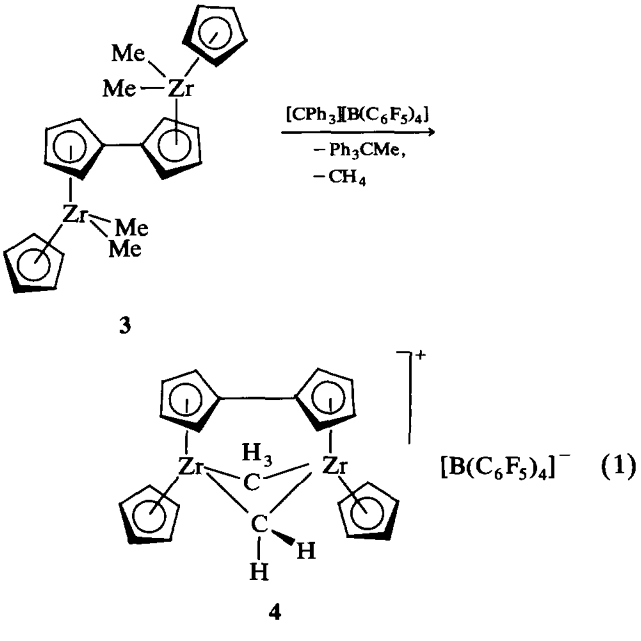


Scheme 1.

kylidene complexes in such polymerisation systems, the very facile formation of **4** suggests that α-H abstraction processes must be considered as plausible side-reactions in homogeneous polymerization catalysts which may possibly contribute to catalysts decay. However, complex **4** is not catalytically inactive and does polymerise ethylene, although its productivity is more than an order of magnitude lower than that of $[Cp_2ZrMe]^+$ under comparable conditions [9]. It appears therefore that if bridging alkylidene complexes are involved in catalyst deactivation, they may contribute to the overall reduction in activity but may not necessarily represent the end-products of the deactivation process [10].

Experimental section

All reactions were carried out under strictly anaerobic conditions following procedures detailed elsewhere [3]. Synthesis of **4** was carried out at both −60°C and room temperature, with identical results. The solubility of **3** in CD_2Cl_2 at low temperature is limited, and a suspension was used. 500 mg (1.0 mmol) **3** was suspended in 20 ml dichloromethane. A solution of 0.91 g (1.0 mmol) $[CPh_3][B(C_6F_5)_4]$ in 10 ml CH_2Cl_2 was added, and the mixture was stirred for 30 min while the solution turned clear red. On addition of 20 ml cyclopentane a burgundy–red, very air-sensitive solid was obtained (1.0 g, 0.87 mmol, 87%). ^{1}H-NMR (CD_2Cl_2, −50°C): −1.67 (s, 3 H, μ-CH_3), 4.35 (d, 1 H, $J_{HH} = 8.25$ Hz, μ-CH_2), 6.38 (s, 10 H, Cp), 6.11 (m, 4 H), 6.23 (m, 2 H), 6.92 (m, 2 H) ($\eta^5:\eta^5$-$C_{10}H_8$), 9.91 (d, 1 H, $J_{HH} = 8.25$ Hz, μ-CH_2). ^{13}C-NMR (CD_2Cl_2, −60°C): 62.59 (μ-CH_3), 109.36, 109.54, 110.76, 112.72, 113.47 ($\eta^5:\eta^5$-$C_{10}H_8$), 188.19 (μ-CH_2). The resonances of the anion correspond to free $[B(C_6F_5)_4]^-$ and are omitted.



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Acknowledgement

This work was supported by the Science and Engineering Research Council and by BP Chemicals Ltd., Sunbury. T.C. is grateful to Consejeria Educación (CAM) for a fellowship.

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[9] Catalyst generated in-situ from 26.8 μmol **3** and 25.4 μmol $[CPh_3][B(C_6F_5)_4]$ in 20 ml toluene at 21°C under 1 bar ethylene, giving an average productivity of 9.2×10^4 g PE $\{(\text{mol } \mathbf{4})\text{h}\}^{-1}$. The reactions were terminated by methanol injection after 5 min.

[10] For Cp_2ZrCl_2/Al_2Et_6 ethylene polymerization catalysts side reactions involving β-H elimination leading to ethylene-bridged binuclear compounds, such as $[Cp_2Zr(ClAlEt_3)]_2(\mu\text{-}CH_2CH_2)$, have been observed. For a summary of the reaction pathways see H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, *18* (1980) 99.