ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 590 (1999) 115–117

Journal of Organometallic Chemistry

Note

Titanium and zirconium complexes bearing (*S*,*S*′)-ferrocenyldithiolate ligands

Vernon C. Gibson *, Nicholas J. Long [1], Jeff Martin, Gregory A. Solan, Joanne C. Stichbury

Department of Chemistry, Imperial College, South Kensington, London SW7 2AY, UK

Received 15 June 1999; received in revised form 14 July 1999

Abstract

The ferrocenyldithiolate complexes of formula $\{(C_5H_4S)_2Fe\}M(NMe_2)_2$ (M = Ti or Zr) can be prepared in good yield by treatment of $M(NMe_2)_4$ with $\{(C_5H_4SH)_2Fe\}$ at elevated temperature; in the presence of trimethylaluminium (TMA)–methylaluminoxane (MAO) both complexes polymerize ethylene under mild conditions. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferocene dithiolate; Titanium; Zirconium; Ethene polymerization

1. Introduction

Recent advances in α-olefin polymerization have identified a number of non-cyclopentadienyl ligands as suitable supports for Group 4 transition metal centres [1]. In particular, dianionic chelate ligands (L_2^{2-}) have been at the forefront of many of these advances with a number of diamide [2–6] and dialkoxide [7,8] systems displaying moderate to high productivities. While ligand steric effects can strongly influence the productivity of these systems and the microstructure of the polymer, changes to the electronic environment of the active site also play a most significant role.

We decided to target ligands that contain, either within the ligand backbone or as pendant groups, redox-active centres, which would offer an opportunity to change quite dramatically the electronic environment of the active site. Herein, we report on the facile synthesis of titanium and zirconium complexes bearing chelating dianionic (*S*,*S*′)-ferrocenyldithiolate ligands in which the ferrocenyl moiety is contained within the backbone of the ligand, and some preliminary results on their ability to polymerize ethylene. Chelating dithiolate ligands of this type have not previously been used to support polymerisation active centres of the Group 4 metals, and indeed, to our knowledge there have been no previous reports of ferrocenyldithiolate ligands attached to early transition metals.

Some mid-to-late transition metal and main group derivatives have, however, been reported. Dilworth and Ibrahim have described the bis(chelate) complex $[ReO\{(C_5H_4S)_2Fe\}_2][PPh_4]$, prepared by treatment of $\{(C_5H_4SH)_2Fe\}$ with $Re(O)Cl_3(PPh_3)_2$ [9], while Seyferth and co-workers have reported the palladium species $\{(C_5H_4S)_2Fe\}Pd(PPh_3)$ [10], which was subsequently characterised by X-ray diffraction [11]. Akabori et al. [12] have described analogous Pt(II) and Pd(II) complexes. The ligand has also been used to form 'spiro' ferrocenophanes, where the two ferrocenyl units are linked by a central bridging element, i.e. Si, Ge, Sn [13].

2. Experimental

The ferrocenyl dithiol ligand $\{(C_5H_4SH)_2Fe\}$ was prepared from a lithium aluminium hydride reduction of 1,2,3-trithia-[3]ferrocenophane [14] and added to a

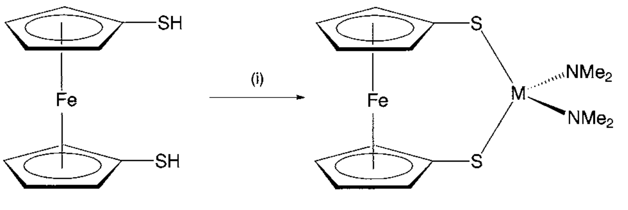
---

* Corresponding author. Fax: + 44-171-594-5810.

E-mail address: v.gibson@ic.ac.uk (V.C. Gibson)

[1] Also corresponding author.

PII: S0022-328X(99)00426-X



M = Ti **1**, Zr **2**

Scheme 1. (i) $M(NMe_2)_4$, C_7H_8, 40–50°C, N_2.

toluene solution of either $Ti(NMe_2)_4$ or $Zr(NMe_2)_4$ at elevated temperatures for 48 and 18 h, respectively, leading to elimination of two equivalents of Me_2NH and the formation of the air-sensitive, red diamagnetic ferrocenyldithiolate complexes $\{(C_5H_4S)_2Fe\}M(NMe_2)_2$ (M = Ti **1**, Zr **2**) in good yield (**1** 59%, **2** 68%) (Scheme 1)[2].

The ^1H-NMR spectra of **1** and **2** are consistent with their formulation with two sets of pseudo triplets for the two pairs of inequivalent cyclopentadienyl protons and a singlet for the equivalent methyl resonances of the two monodentate dimethylamide ligands (n.b. a pseudo triplet is seen due to incomplete resolution of the expected doublet of doublets splitting pattern from the coupling of magnetically inequivalent, albeit very similar, protons — a common feature in monosubstituted cyclopentadienyl rings). The fast atom bombardment (FAB) mass spectra of **1** and **2** display fragmentation peaks corresponding to the loss of dimethylamide or methyl groups from their molecular ion peaks. While complex **1** is moderately soluble in C_6D_6, complex **2** is insoluble but can be solubilised (for NMR purposes) in $CDCl_3$. To date, it has not proved possible to obtain X-ray-quality crystals of these complexes.

Both complexes were tested as ethylene polymerization procatalysts[3]. Pretreatment of **1** and **2** with trimethylaluminium (TMA), to convert the complexes to their dimethyl derivatives [15], followed by exposure to ethylene (1 atm) in the presence of methylaluminoxane (MAO) (200 equivalents) at 25°C gave active catalysts. Solid polyethylene [0.025 g (using **1**) and 0.750 g (using **2**)] was obtained in both cases with productivities of 3 g $mmol^{-1}$ h^{-1} bar^{-1} for **1** and 15 g $mmol^{-1}$ h^{-1} bar^{-1} for **2**[4]. GPC data[5] for the polyethylene product obtained using **2** shows a broad molecular weight distribution (pdi = 37) with an M_{pk} at 34 000. In both cases the polymers retained a pale yellow coloration in spite of extensive washing with acidified methanol.

3. Conclusions

In conclusion, ferrocenyldithiolate ligands have been successfully introduced onto titanium and zirconium and preliminary studies show that both complexes are active for ethylene polymerization. Experiments are in progress to chemically and electrochemically change the electronic properties of the ferrocenyl-containing ligand and to probe these effects on ethylene polymerization. These studies will form the basis of future publications.

Acknowledgements

BP-Amoco Ltd and the EPSRC (studentship to J.M.) are thanked for their financial support and Dr G. Audley is thanked for GPC measurements.

References

[1] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428.

---

[2] Synthesis of **1**: a solution of $\{(C_5H_4SH)_2Fe\}$ (0.80 g, 3.2 mmol) in toluene (100 ml) was added by cannula to a solution of $Ti(NMe_2)_4$ (0.72 g, 3.2 mmol) in toluene (100 ml). The mixture was heated to 40°C for 48 h under a slow stream of nitrogen to displace any $HNMe_2$ evolved. A purple–red coloured precipitate formed during this time. The solution was allowed to cool to room temperature and the supernatant liquid removed by cannula filtration. The precipitate was collected and washed with cold pentane (3 × 100 ml) and dried under reduced pressure for 12 h to afford $\{(C_5H_4S)_2Fe\}Ti(NMe_2)_2$ (**1**) (0.72 g, 59%). ^1H-NMR (C_6D_6): δ 4.05 (app. tr, 4H, Cp-*H*], 3.99 (app. tr, 4H, Cp-*H*), 3.34 (s, 12H, N*Me*$_2$). FAB MS: 370 [M^+–Me], 340 [M^+–NMe_2]. Synthesis of **2**: complex **2** was prepared using a similar procedure to that outlined above, employing equimolar (3.0 mmol) quantities of $\{(C_5H_4SH)_2Fe\}$ and $Zr(NMe_2)_4$. The mixture was heated to 50°C for 18 h to give a blood-red coloured precipitate. On cooling, the precipitate was collected and washed with cold pentane (3 × 100 ml) and dried under reduced pressure for 12 h to afford $\{(C_5H_4S)_2Fe\}Zr(NMe_2)_2$ (**2**) (0.87 g, 68%). ^1H-NMR ($CDCl_3$): δ 4.30 (app. tr, 4H, Cp-*H*], 4.19 (app. tr, 4H, Cp-*H*), 2.43 (s, 12H, N*Me*$_2$). FAB MS 369 [M^+–NMe_2–Me], 339 [M^+–$2NMe_2$].

[3] Polymerization of ethylene. Using **1**: complex **1** (0.004 g, 0.01 mmol) was dissolved in toluene (40 ml). The complex was then pre-alkylated by treating with $AlMe_3$ (0.1 ml, 0.05 mmol, 0.5 M solution in toluene, five equivalents) and stirred vigorously for 20 min. The solution was then treated with MAO (1.2 ml, 2 mmol, 10% solution in toluene) and stirred for a further 20 min. The Schlenk tube was then evacuated and back filled with ethylene (1 bar). The mixture was stirred vigorously for 1 h, during which time solid polyethylene was observed to form. The polymerization test was terminated by removal of the ethylene supply and addition of diluted HCl (100 ml). The polymer was filtered and washed with more acid and methanol (3 × 200 ml) and dried under reduced pressure at 40°C for 24 h. Mass of polymer isolated 0.025 g (3 g $mmol^{-1}$ h^{-1} bar^{-1}). Using **2**: The polymerization was performed as described above using the same relative ratios of reagents but with 0.05 mmol of **2**. Mass of polymer isolated 0.750 g (15 g^{-1} $mmol^{-1}$ h^{-1} bar^{-1}).

[4] GC-MS analysis of the extracted organic phases showed no evidence for lower molecular weight oligomeric fractions.

[5] GPC data for polyethylene obtained using **2**: M_n 7400, M_w 276 000, M_w/M_n 37, M_{pk} 34 000.

[2] V.C. Gibson, B.S. Kimberley, A.J.P. White, D.J. Williams, P. Howard, Chem. Commun. (Cambridge) (1998) 313.

[3] (a) J.D. Scollard, D.H. McConville, J. Am. Chem. Soc. 118 (1996) 10008. (b) J.D. Scollard, D.H. McConville, N.C. Payne, J.J. Vittal, Macromolecules 29 (1996) 5241.

[4] F.G.N. Cloke, T.J. Geldbach, P.B. Hitchcock, J.B. Love, J. Organomet. Chem. 506 (1996) 343.

[5] N.A.H. Male, M. Thornton-Pett, M. Bochmann, J. Chem. Soc. Dalton Trans. (1997) 2487.

[6] F. Jäger, H.W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, Chem. Ber./Recl. 130 (1997) 399.

[7] A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008.

[8] (a) F.G. Sernetz, R. Mülhaupt, S. Fokken, J. Okuda, Macromolecules 30 (1997) 1562. (b) S. Fokken, T.P. Spaniol, J. Okuda, F.G. Sernetz, R. Mulhaupt, Organometallics 16 (1997) 4240.

[9] J.R. Dilworth, S.K. Ibrahim, Trans. Met. Chem. 16 (1991) 239.

[10] D. Seyferth, B.W. Hames, T.G. Rucker, M. Cowie, R.S. Dickson, Organometallics 2 (1983) 472.

[11] M. Cowie, R.S. Dickson, J. Organomet. Chem. 326 (1987) 269.

[12] S. Akabori, K. Kawazoe, T. Kumagai, M. Sato, S. Sato, C. Tamura, Organometallics 6 (1987) 526.

[13] (a) A.G. Osborne, R.H. Whiteley, J. Organomet. Chem. 101 (1975) C27. (b) A. Davison, J.C. Smart, J. Organomet. Chem. 174 (1979) 321. (c) A.J. Blake, R.F. Bryan, R.E. Hollands, S. Lockhart, A.G. Osborne, J. Organomet. Chem. 287 (1985) 39.

[14] J.J. Bishop, A. Davison, M.L. Katcher, W.L. Litchenberg, R.E. Merrill, J.C. Smart, J. Organomet. Chem. 27 (1971) 241.

[15] I. Kim, R.F. Jordan, Macromolecules 29 (1996) 489.