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Synthesis and catalytic activity in ethylene polymerization of cyclopentadienylterbium dibromides with pyrazole or triphenylphosphine ligand

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Abstract

Organoterbium compounds $TbBr_2CpHPz$ and $TbBr_2CpPPh_3$ were obtained by reaction of pyrazole or triphenylphosphine ligands with cyclopentadienylterbium dibromide. These compounds were characterized by elemental analysis, complexometric titration with EDTA, thermal analysis, vibrational spectra in the infrared region and ¹H NMR. In a preliminary catalytic study, these compounds were active in ethylene polymerization when MAO was used as cocatalyst, producing low crystalline polyethylene. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The synthesis and characterization of organolanthanide compounds containing cyclopentadienyl (Cp) ligand and its derivatives have been largely investigated in the literature [1]. The most important features in obtaining a stable organolanthanide compound are the optimization of eletrostatic interactions by using stable organic anions and the saturation of the coordination sphere of the metal with bulky ligands to sterically inhibit decomposition reactions [1]. The use of Cp derivatives and neutral ligands therefore has led to compounds with better characteristics, and opened the possibility of applications in different fields as catalysis.

Ethylene polymerization reactions catalyzed by organolanthanide compounds are one of their most studied applications [2]. Catalytic systems based on hydride and alkyl derivatives have been investigated. Some examples in ethylene polymerization are $[LaH(C_5Me_5)_2]_2$ with catalytic activity of 146 400 gPE mmol⁻¹ h⁻¹ bar⁻¹ [3], and and $Lu(\eta^5-C_5Me_5)_2CH_3^{\cdot}$ ether (66 gPE mmol⁻¹ $h^{-1} bar^{-1})$ [4].

In an attempt to contribute to the application of organolanthanides as catalysts for olefin polymerization, we have been investigating catalytic systems based on MAO (methylaluminoxane), an industrially important cocatalyst that affords highly active and long lived catalytic systems [5]. In this work we report the synthesis of the organoterbium compounds containing N- or P-donor ligands, TbCpBr₂L, L = pyrazole (HPz) or triphenylphosphine (PPh₃) and the preliminary catalytic studies in ethylene polymerization using these compounds activated by MAO.

2. Experimental details

All manipulations were performed under prepurified argon. Solvents were dried by standard techniques and thoroughly deoxygenated before use. Anhydrous terbium tribromide was obtained as described by Brown et al. [6]. The compound $\text{TbBr}_2\text{Cp}(\text{THF})_3$ was prepared by the reaction of anhydrous terbium tribromide with cyclopentadienylsodium in THF according to method

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described by Maggin et al. [7] for cyclopentadienyllanthanide dichlorides. NaCp (Aldrich) and MAO, 10 wt% in toluene suspension (Akzo), were used as received.

Microanalysis (%C, %H, %N) were performed in a Perkin-Elmer CHN 2400 equipment. Percentage of Ln was determined by complexometric titration with EDTA [8]. Percentage of Br was determined by argentimetric titration [9]. Thermogravimetric (TG) and derived thermogravimetric (DTG) curves were recorded on a Shimadzu Thermogravimetric Analyzer-TGA-50, heating 2-5 mg samples in a platinum crucible from 25 to 850 °C at 20 °C/min in air (50.0 ml/min) using 2–5 mg samples in a platinum crucible. Infrared spectra were recorded on FTIR-BOMEM MB-102, from 4000 to 200 cm⁻¹, using Nujol or Fluorolube mulls between cesium iodide windows. ¹H NMR spectra were recorded on a Bruker-DPX 300 MHz spectrometer, using acetone-d₆ or chloroform-d as solvents and TMS as internal reference. Differential Scanning Calorimetry (DSC) measurements were performed on a DSC 2910 TA Instruments. The samples were heated from 25 to 200 °C at a heating rate of 10 °C/min. The melting temperature values (T_m) and the heat of fusion $(\Delta H_{\rm f})$ were taken from the second heating curve. The degree of crystallinity was calculated from $\Delta H_{\rm f}$, using the equation $w_{\rm CH} = \Delta H_{\rm f} \times 100/288$ [10].

2.1. Synthesis and characterization of compounds

2.1.1. TbBr₂Cp

THF was removed from the compound TbBr_2Cp (THF)₃ (4 mmol) by evaporation under high vacuum at 40 °C for 24 h, yielding an amorphous orange solid (3.6 mmol). Yield: 90%. Calc. Anal. for: TbBr₂Cp: C, 15.64; H, 1.31; Tb, 41.40; Br⁻, 41.63. Found: C, 15.70; H, 1.27; Tb, 41.78; Br⁻, 41.81.

2.1.2. TbBr₂CpHPz and TbBr₂CpPPh₃

A solution of pyrazole (6 mmol) or triphenylphosphine (1 mmol) in 30 ml of toluene was added to a suspension of cyclopentadienylterbium dibromide (1 mmol) in 50 ml of toluene. The resulting mixture was stirred for 24 h at room temperature followed by evaporation under vacuum for 16 h at 30 °C to give the organolanthanide compounds TbBr₂CpHPz (0.75 mmol) and TbBr₂CpPPh₃ (0.8 mmol) as amorphous orange solids. Yields: 75% for TbBr₂CpHPz and 80% for TbBr₂ CpPPh₃. Calc. Anal. for: TbBr₂CpHPz: C, 21.26; H, 2.01; N, 6.20; Tb, 35.16; Br⁻, 35.36. Found: C, 20.92; H, 2.14; N, 6.39; Tb, 35.34; Br⁻, 35.62; For: TbBr₂CpPPh₃: C, 42.75; H, 3.12; Tb, 24.59; Br⁻, 24.73. Found: C, 42.37; H, 3.18; Tb, 24.21; Br⁻, 24.47.

2.2. Catalytic polymerization of ethylene

The polymerization experiments were carried out in a Büchi autoclave at 70 °C, using 50 ml of toluene as

solvent, 3.5–4.5 mg of organolanthanide compound, MAO (10% in toluene) in the molar ratio Al/Ln of 2000 and ethylene (3 bar). Polymerization was interrupted after 2 h by ethanol addition. The polymers formed were washed with ethanol and dried at 50 $^{\circ}$ C for 6 h.

3. Results and discussion

Reaction of TbBr₂Cp with pyrazole or triphenylphosphine in toluene at room temperature yielded amorphous solids, formulated TbBr₂CpHPz and TbBr₂CpPPh₃ according to elemental analysis. Removal of THF from the starting compound was undertaken to facilitate subsequent coordination of the softer N- or P-donor ligands to Tb(III).

The monocyclopentadienyl derivatives are insoluble in THF and present low solubility in acetone, toluene and chloroform. Attempts to grow single crystals from acetone or toluene solutions failed.

Thermal analysis showed that the compounds lose weight gradually with increasing temperature from 25 °C, forming TbOBr at ca. 650 °C under air atmospheres (Table 1). The molar weight of compounds were calculated from TG weight losses, and are in agreement with the expected values based on analytical data presented in experimental section.

Infrared spectra of the compounds (Table 2) exhibit characteristic frequencies of cyclopentadienyl and pyrazole or triphenylphosphine ligands. Assignment of cyclopentadienyl vibrational modes indicated a σ -centered coordination to the lanthanide(III) ions under C5V local symmetry with ionic character [11]. The characteristic frequencies of pyrazole were assigned according to Orza et al. [12] and King [13] indicating the coordination of the neutral ligand. Triphenylphosphine ligand frequencies were assigned according to Whiffen [14], Jensen and Nielsen [15], and Deacon et al. [16]. Some vibrational modes of triphenylphosphine are shifted by coordination of this ligand to metallic ions [14]. In the spectrum of TbBr₂CpPPh₃, only one of these X-sensitive modes, mode t, was shifted to higher wave number (445 cm^{-1}) when compared to free triphenylphosphine (432 cm^{-1}), indicating a probable coordination of PPh₃ to Tb(III).

In the NMR spectra of these compounds, broad signals were observed for Cp protons at 10.4 ppm (TbBr₂Cp), 7.0 ppm (TbBr₂CpHPz) and 16.4 ppm (TbBr₂CpPPh₃). Broadening of Cp signals may be related to the paramagnetic nature of Tb(III) [17]. Pyrazole protons of TbBr₂CpHPz yielded sharp signals at 7.0 ppm (doublet, 2H) and 6.3 ppm (triplet, 1H), and a broad signal at 12.0 ppm (N–H). Triphenylphosphine protons in TbBr₂CpPPh₃ originated a multiplet of sharp signals centered at 7.3 ppm.

The organolanthanide compounds TbBr₂Cp, TbBr₂CpHPz and TbBr₂CpPPh₃ presented catalytic

Table 1 Results of thermal analysis of organoterbium compounds

Compound	Weigth loss (%)	<i>m</i> Initial (mg)	m Residue (mg)	Residue	MM exp. (g/mol)	MM calcd. (g/mol)
TbBr ₂ Cp TbBr ₂ CpHPz	31.98 43.38	3.584 4.041	2.314 2.288	TbOBr TbOBr	395 450	384 452
TbBr ₂ CpPPh ₃	60.44	3.351	1.326	TbOBr	644	646

Table 2 Infrared frequencies (cm⁻¹) of organoterbium compounds

$TbBr_2Cp^a$	TbBr ₂ CpHPz ^a	TbBr ₂ CpPPh ₃ ^a	Assignment
_	3161 w	_	v(NH)HPz
3098 vw	3096 vw	3097 vw	v(CH)Cp
2958 w	2959 w	2955 w	v(CH)Cp
_	1647 w	_	$a_1 \gamma(C-H) HPz$
_	1551 w	1571 w	$a_1v(ring)HPz$ or $k v(CC)(a_1)PPh_3$
1408 w	1405 w	1459 w	$n v(CC)(a_1)PPh_3 + v(CC)Cp$
_	_	1303 m	$\omega + i(b2)PPh_3$
_	_	1260 sh	$e \beta$ (C–H)(b2) PPh ₃
_	_	1168 sh	$a \beta$ (C–H)(a1) PPh ₃
_	_	1153 w	$b \beta$ (C–H)(b2) PPh ₃
1096 sh	1082 w	1085 w	q X-sens (a1) PPh ₃ + $v(CC)Cp$
1010 w	1035 w	1026 w	a ₁ δ (CH)HPz or <i>b</i> β (C–H)(a1)PPh ₃ + δ (CH)Cp
_	969 w	968 w	$a_1 v(ring)HPz$ or $h (C-H)(a_2)PPh_3$
_	912 w	_	$a_1\delta(ring)HPz$
888 w	888 w	891 w	$\pi(CH)Cp$
_	821 w	_	$a_2\gamma(C-H)HPz$
769 w	767 sh	767 sh	π (C–H)Cp
_	753 m	739 s	$a_2\gamma$ (C–H)HPz or $f\gamma$ (C–H)(b1)PPh ₃
_	654 w	693 s	$a_2\tau(ring)HPz$ or $\nu Ph(C-C)(b2)PPh_3$
_	620 s	_	$a_2 \tau(ring) HPz$
_	_	503-497 w	y X-sens.(a1)PPh ₃
-	-	445 w	t X-sens.(a1)PPh ₃

^as, strong; m, medium; w, weak; sh, shoulder.

activity of ca. 4.0 gPE mmolTb⁻¹ bar¹ h⁻¹ at 70 °C with Al/Ln ratio of 2000. These activities are in the range of catalytic activities of other compounds contanining PzA as the systems LnBr₂CpPzA/MAO (4.3 and 4.6 gPE mmolLn⁻¹ h⁻¹ bar⁻¹, Ln = Nd and Sm, 70 °C) [18] and LnA₂Cp(PzA)₂/MAO, Ln = Nd, Sm, Eu e Tb, $A = Cl, -CH_3SO_3^-$ (4.0 and 6.4 gPE mmolLn⁻¹ h⁻¹ bar⁻¹, 70 °C) [19,20]. The presence of the neutral soft ligands HPz or PPh₃ caused no steric nor electronic effects on the metal center that could modify catalytic activities.

Infrared spectra of the produced polyethylene show: (a) bands at 1461, 1360 and 1337 cm⁻¹ assigned to deformation of the methylene groups; (b) bands at 730 and 719 cm⁻¹ assigned to rocking of the methylene groups. Polyethylene absorption band at 730 cm⁻¹ arises from the crystalline regions only and the 721 cm⁻¹ band arises from both crystalline and amorphous regions [21] indicating that the polymer obtained has both regions. The polyethylene presented melting points of 125 °C and degree of crystallinity of 39% ($\Delta H_{\rm f} = 112$ J/g). This low crystallinity indication is also supported by infrared data.

4. Conclusions

The organometallic compounds $TbBr_2CpHPz$ and $TbBr_2CpPPh_3$ have been prepared in good yields by the reaction of mono(cyclopentadienyl)terbium dibromide with pyrazole or triphenylphosphine ligand in toluene in appropriate molar ratio. These organolanthanide compounds are active in ethylene polymerization reaction when MAO is used as cocatalyst, producing low crystallinity polyethylene.

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References

- [1] C.J. Schaverien, Adv. Organomet. Chem. 36 (1994) 283.
- [2] H. Yasuda, Prog. Polym. Sci. 25 (2000) 573.

- [3] G. Jeske, H. Lauke, H. Mauermann, P.N. Sweptson, H. Schumann, T.J. Marks, J. Am. Chem. Soc. 107 (1985) 8091.
- [4] P.L. Watson, J. Am. Chem. Soc. 104 (1982) 337.
- [5] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 428.
- [6] D. Brown, S. Fletcher, D.G. Hollah, J. Chem. Soc. A (1968) 1889.
- [7] R.E. Maggin, S. Manastyrskyj, M. Dubeck, J. Am. Chem. Soc. 85 (1963) 672.
- [8] S.J. Lyle, Md.M. Rahman, Talanta 10 (1963) 1177.
- [9] A.I. Vogel, A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, third ed., Longman, New York, 1961.
- [10] A.P. Gray, Thermochim. Acta 1 (1970) 563.
- [11] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., Wiley, New York, 1997.

- [12] J. Orza, O. Mó, M. Yánez, J. Elguero, Spectrochim. Acta A 53 (1997) 1383.
- [13] S.T. King, J. Phys. Chem. 74 (1970) 2133.
- [14] D.H. Whiffen, J. Chem. Soc. (1956) 1350.
- [15] K.A. Jensen, P.H. Nielsen, Acta Chem. Scand. 17 (1963) 1875.
- [16] G.B. Deacon, R.A. Jones, P.E. Rogasch, Aust. J. Chem. 16 (1963) 360.
- [17] N. Kaltsoyannis, P. Scott, The *f* Elements, Oxford University Press, Oxford, 1999.
- [18] V. Lavini, A. de Souza Maia, I.S. Paulino, U. Schuchardt, W. Oliveira, Inorg. Chem. Commun. 4 (2001) 582.
- [19] R.D. Miotti, A. de Souza Maia, I.S. Paulino, U. Schuchardt, W. Oliveira, Química Nova 25 (2002) 762.
- [20] R.D. Miotti, A. de Souza Maia, I.S. Paulino, U. Schuchardt, W. Oliveira, J. Alloys Compd. 344 (2002) 92.
- [21] S.L. Aggarwal, O.J. Sweeting, Chem. Rev. 57 (1957) 665.