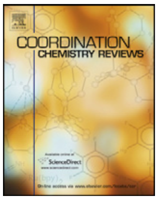
Coordination Chemistry Reviews 254 (2010) 2227–2233

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Well-defined single-site thiobis(phenolate) Group 4 metal catalysts for heterogeneous olefin polymerization

Zofia Janas*

Faculty of Chemistry, University of Wrocław, 14, F. Joliot-Curie, 50-383 Wrocław, Poland

Contents

ARTICLE INFO

Article history:
Received 24 February 2010
Accepted 2 May 2010
Available online 24 May 2010

Keywords:
Heterogeneous polymerization
Thiobis(phenolate) ligands
Titanium
Zirconium
Hafnium

ABSTRACT

The tridentate (OSO-function) thiobis(phenolate) ligand derived from 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] (tbopH$_2$) is an alternative to the cyclopentadienyl ancillary group for Group 4 heterogeneous olefin polymerization. The tbop ligand placed on titanium, zirconium and hafnium forms a wide family of homoleptic compounds as well as heteroleptic alkoxo- and aryloxo-bridged complexes modified with coligands like chlorides, imides, and monoaryloxides. Among these heteroleptic titanium complexes when activated with cocatalysts and supported on MgCl$_2$ are highly effective heterogeneous, well-defined, single-site ethene polymerization catalysts. The active centres of these catalysts consist of Ti(III) species with the alkyl group and the sulfur atom of the tbop ligand coordinated in axial positions. Titanium, zirconium and hafnium systems both heteroleptic and homoleptic show moderate activity in 1-hexene polymerization producing atactic poly(1-hexenes).

1. Introduction

During the past 50 years, since the great Ziegler-Natta discovery, polyolefins have become by far, the highest volume of commercial synthetic polymers. Classical Ziegler-Natta catalysts (Z-N) are heterogeneous and consequently the polymerization process occurs on many different types of active sites. The resulting polymer has a typically broad molecular weight distribution (PDI).

The discovery of homogeneous metallocene catalysts has enabled the production of polyolefins with narrow PDI with control over stereochemistry and molecular branch architecture [1]. Furthermore such catalysts have much higher activities in ethene polymerization than classical Z-N type catalysts.

The replacement of Cp-ligand with hard donor groups led to postmetallocene homogeneous well-defined, single-site catalysts with alternative properties with respect to activity, selectivity, living behaviour, and stability. Systematic ligand design in the past decade explored new families of highly active systems Group 4 metal [2]. Substantial progress in terms of catalysis has appeared using chelating bisphenolate ligands, which have great potential given their ease of modification. First, a large number of possible substituents potentially available for the two phenolate rings may vary the electronic and steric properties of the complexes derived. Secondly, the two phenolate rings may be either directly connected to each other in the *ortho* position (**A**) [2b,3] or linked by a hydrocarbon group (**B**) [2b,4] or bridged by a donor atom such as S [2b,4b,5], S$_2$ [6], SO [7], Te [5c], N [8], P [9] (**C**) to create new types of ligands shown in Fig. 1.

Such modifications resulted in a rich structural variety of bis(phenolate) Group 4 complexes which after activation with aluminium alkyls are active catalysts in homogeneous olefin polymerization processes. The most successful developments in terms of catalysis have appeared using chelating bis(phenolato) ligands, in particular tridentate and tetradentate ligands having an additional neutral donor like sulfur [2b,5,6]. Among them, the titanium complexes $[Ti_2(\mu\text{-}X)_2X_2(tbmp\text{-}\kappa^3O,S,O)_2]$

---

* Tel.: +48 71 3757480; fax: +48 71 3282348.
E-mail address: zj@wchuwr.pl.

0010-8545/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2010.05.008

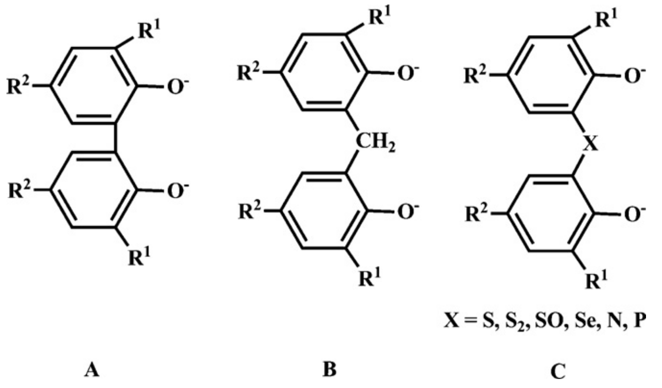


Fig. 1. Representative examples of chelating bis(phenolate) ligands.

derived from the sulfide-linked bisphenol, 2,2'-thiobis(6-*tert*-butyl-4-methylphenol), (tbmpH$_2$) (X = Cl, O^{i}Pr), activated with methylalumoxane (MAO), were first reported by Kakugo et al. to be highly active for the polymerization of ethene, propene, styrene and dienes, as well as the copolymerization of ethene with styrene [10]. These complexes are an order of magnitude more active than systems based on the corresponding methylene-bridged chelating aryloxide complexes, [Ti(mbmp)X$_2$] [mbmp = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)] [2b,4c]. This is in quantitative agreement with a theoretical study reported by Morokuma and co-workers that showed the S-bridged chelating phenolates (**C**) to have lower insertion barriers than their methylene-bridged (**B**) or directly bridged analogues (**A**) (Fig. 1) [11]. The structural data for [Ti$_2$(μ-X)$_2$X$_2$(tbmp-κ^{3}O,S,O)$_2$] complexes reveal long Ti-S distances [2.664(2), X = Cl; 2.724(2), X = O^{i}Pr] [5b,c]. Although the Ti-S interaction in [Ti$_2$(μ-X)$_2$X$_2$(tbmp-κ^{3}O,S,O)$_2$] is weak, it is likely to be of importance in stabilizing the active cationic species [Ti(tbmp-κ^{3}OSO)Me]$^+$, facilitating its formation from the former and MAO and making the coordination of the counterion less tight. It has been predicted that such cationic species act as a “breathing catalyst” with the S atom moving in and out from the metal centre, leading to a lower ethene insertion barrier [11].

It was intriguing whether the thiobis(phenolate) Group 4 metal complexes would also generate highly effective catalysts in heterogeneous olefin polymerization, more often used by industry than the homogeneous one.

This report shows our progress in the field of postmetallocene systems based on the Group 4 metal complexes with the tridentate (OSO-function) thiobis(phenolato) ligand, derived from the 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenol] (tbopH$_2$) (Fig. 2).

Except for the S-bridge, the tbop ligand has an extra attractive feature, that is, the long sterically hindered auxiliary 4-(1,1,3,3-tetramethylbutyl) groups. These substituents sufficiently increase solubility of the catalysts in hydrocarbons and create highly active heterogeneous catalytic systems similar to the so-called Kakugo homogeneous ones.

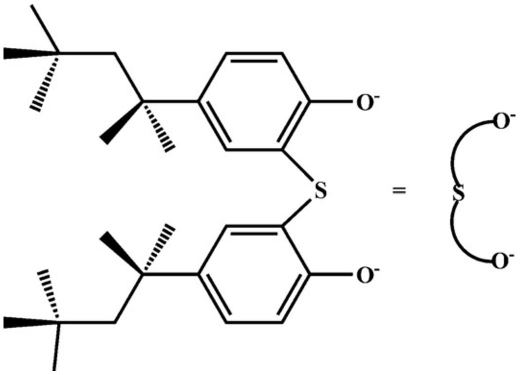


Fig. 2. The 2,2′-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolate] (tbop) ligand.

2. Synthesis and structure of thiobis(phenolate) Group 4 metal complexes

Generally, two routes are used to achieve neutral bis(phenolate) complexes: (a) a σ-bond metathesis reaction between the bis(phenol) and an appropriate homoleptic metal precursor enabling either alkane, alcohol, amine, or HCl elimination; (b) salt elimination reactions between bis(phenolate) Group 1–3 metal salts and MCl$_n$. The convenient route for the preparation of heteroleptic Group 4 metal complexes with the tbop ligand was a direct reaction between MX$_4$ (M = Ti, Zr, Hf; X = Cl, OMe, OEt) and tbopH$_2$ with concomitant elimination of HCl or alcohol.

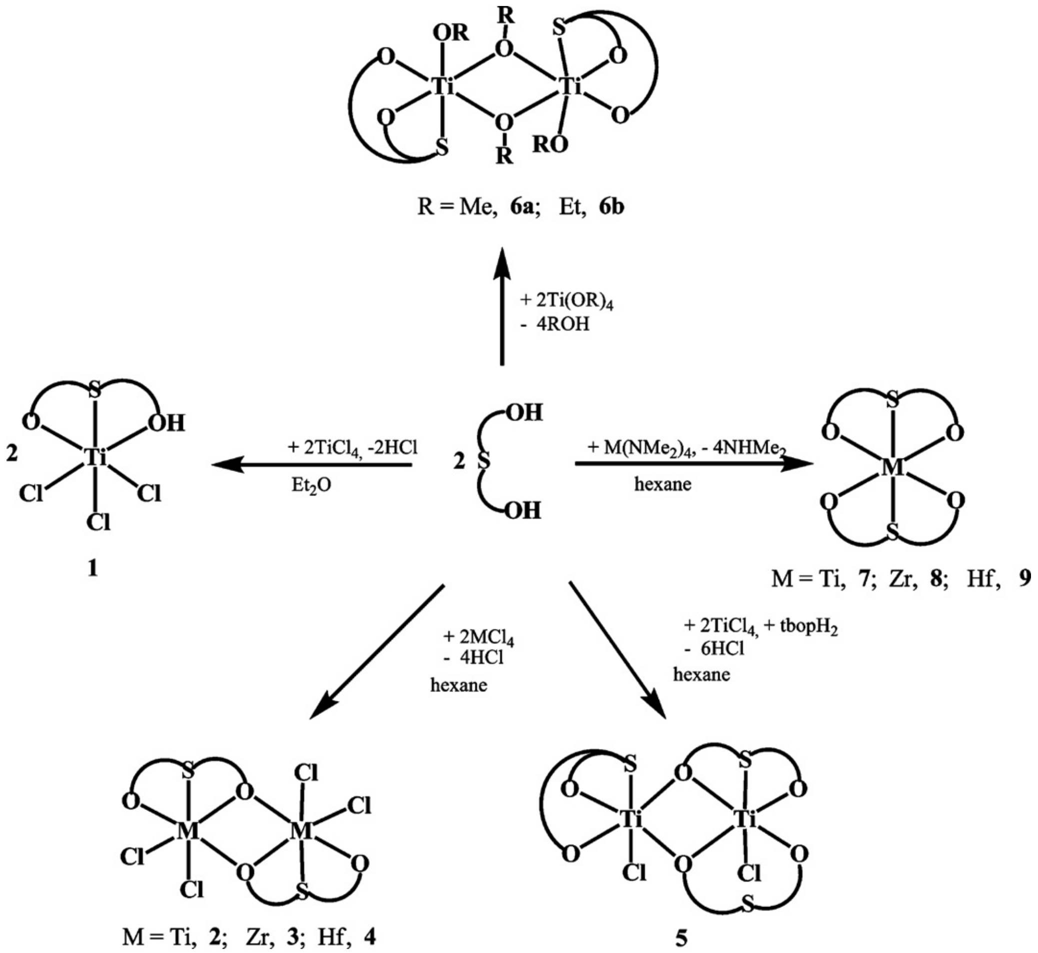
Depending on the stoichiometry and the nature of solvent mononuclear [TiCl$_3$(tbopH-κ^{3}O,S,O)] (**1**) and dinuclear [M$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_4$] (M = Ti, **2**; Zr, **3**; Hf, **4**), [Ti$_2$(μ-tbop-κ^{3}O,S,O)(μ-tbop-κ^{2}O,O)(tbop-κ^{3}O,S,O)Cl$_2$] (**5**) and [Ti$_2$(μ-OR)$_2$(OR)$_2$(tbop-κ^{3}O,S,O)$_2$] (R = Me, **6a**; R = Et, **6b**) complexes have been obtained with high yield (Scheme 1) [12a,b,e]. Homoleptic complexes [M(tbop-κ^{3}O,S,O)$_2$] (M = Ti, **7**; Zr, **8**; Hf, **9**) were prepared via different procedures *e.g.* the σ-bond metathesis reaction between the tbopH$_2$ and [Ti(NMe$_2$)$_4$] in a 2:1 molar ratio gave **7** whereas zirconium and hafnium analogues **8** and **9**, respectively were prepared efficiently by the reaction of 2 equiv of the tbopH$_2$ with MCl$_4$ with elimination of 4 equiv of HCl (Scheme 1) [12b,d,e] The structures of **1**, **5** and **6b** in the solid state were confirmed by X-ray crystallography. These studies showed that in all cases metal centres adopt octahedral geometry and are doubly bridged by oxygen atoms of the tbop or OR groups in dinuclear complexes **5** and **6b**, respectively.

Similar structural trends appear for complexes [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_2$(OAr)$_2$] (**10**), [M$_2$(μ-tbop-κ^{3}O,S,O)$_2$(OAr)$_4$] (M = Zr, **11**; Hf, **12**; HOAr = 2,6-diisopropylphenol) and [Ti$_2$(μ-tbop-κ^{3}O,S,O)$_2$(N^{t}Bu)$_2$(H$_2$N^{t}Bu)$_2$] (**13**) achieved by the substitution of chlorides in **2**–**4** with diisopropylphenolato or *tert*-butylimido groups (Scheme 2) [12b,e,f]. On the basis of structures **10**–**13** it has been predicted that complexes **2**–**4** are dimers with metal centres doubly bridged by oxygen atoms of the tbop ligands and terminally coordinated chlorides. This is in contrast to reported by Nakamura and Okuda, [Ti$_2$(μ-Cl)$_2$Cl$_2$(tbmp-κ^{3}O,S,O)$_2$], which has doubly chloride-bridged titanium atoms and facially coordinated tbmp ligands [5c]. It seems most likely that the reason for these structural differences is the presence of the bulky ^{t}Bu substituents at *ortho* positions in the tbmp ligand.

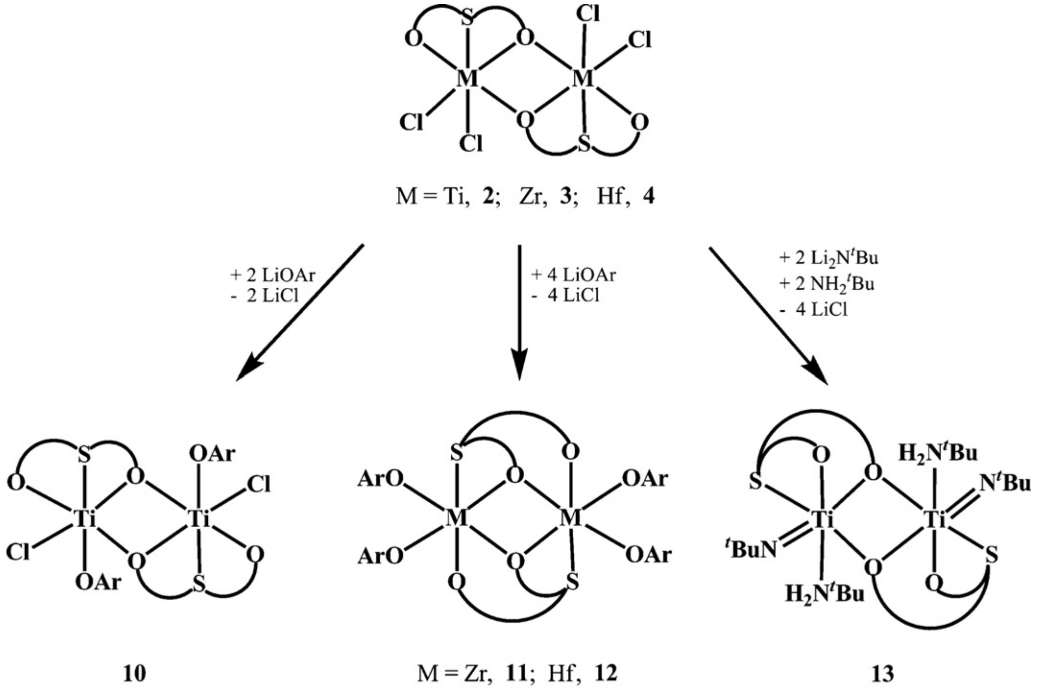
The route based on the use of the tbop-aluminium precursor [Al$_2$(μ-OEt)$_2$(tbop-κ^{3}O,S,O)$_2$] towards MCl$_4$ (M = Ti, Zr, Hf) proved to be an excellent method to extend a family of Group 4 metal complexes of polynuclear homo- and heterometallic compounds (Scheme 3) [12c,e].

Depending on the titanium precursor, TiCl$_4$ or [Ti(OEt)$_4$] two chemically and structurally different compounds, trinuclear homometallic [Ti$_3$(μ-OEt)$_2$(μ-tbop-κ^{3}O,S,O)$_2$Cl$_6$] (**14**) and tetranuclear heterometallic [Ti$_2$Al$_2$(μ-OEt)$_6$(μ-tbop-κ^{3}O,S,O)$_2$(OEt)$_4$] (**15**) species are produced, respectively [12c,e]. Three octahedral titanium atoms in **14** are double bridged by oxygen atoms of the tbop and the ethoxo ligands to form a Ti$_3$O$_4$ core. The discrete molecular unit of **15** contains a core of two peripheral octahedral titanium atoms and two internal trigonal bipyramidal aluminium atoms linked by oxygen atoms from the six OEt groups.

However, the use of the same preparative methodology with zirconium and hafnium tetrachlorides led to trinuclear heterometallic

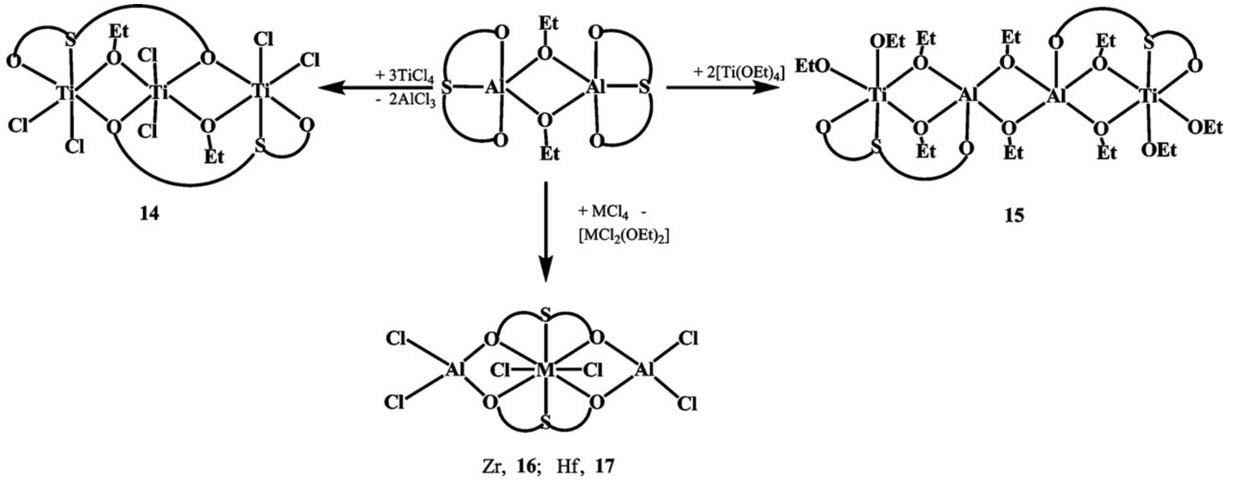


Scheme 1.



HOAr = 2,6-diisopropylphenol

Scheme 2.



Scheme 3.

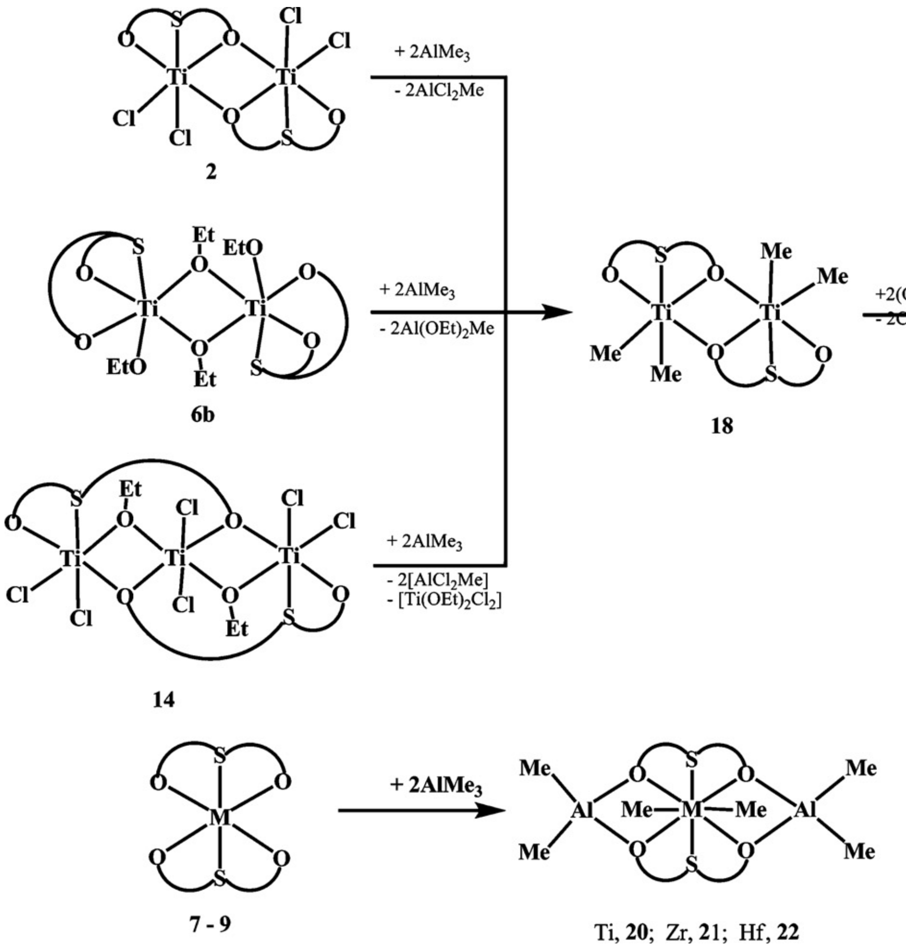
complexes [M(tbop-κ^3O,S,O)$_2$Cl$_2$(μ-AlCl$_2$)$_2$] (M = Zr, **16**, X; Hf, **17**) for which the single-crystal X-ray diffraction analysis showed zirconium and hafnium centres to have eight-coordinate dodecahedral geometry (Scheme 3) [12f]. The formation of compounds **16** and **17** occurs via the double exchange of chlorides and the tbop groups and as a result ionic [M(tbop-κ^3O,S,O)$_2$Cl$_2$]$^{2-}$ and [AlCl$_2$]$^+$ species are formed. In the latter, coordinatively unsaturated aluminium atoms bind to the oxygen atoms of the tbop ligands to achieve tetrahedral geometry and in consequence molecular complexes are created. Complexes **16** and **17** are the first examples of eight-coordinate, thiobis(phenolate) dichloride zirconium and hafnium compounds. The migration of the tbop ligand from the aluminium precursor to the more acidic titanium centres is a very important property of these systems in view of the nature of the catalytic active sites. This indicates that the tbop ligand will remain at the coordination sphere of Group 4 metals upon their activation with coocatalyst to generate catalytic active centres.

Thus, the tbop ligand has an excellent potential to create a wide family of neutral Group 4 mononuclear or polynuclear metal complexes. In most of them metal centres adopt octahedral geometry in which the Ti-S bond lengths vary in the range 2.888(2)–2.587(2) Å [12a–c], substantially longer than a Ti–S single bond (typically 2.3–2.4 Å). The Ti–S distances reported for so-called Kakugo's precatalysts [Ti$_2$(μ-X)$_2$X$_2$(tbmp-κ^3O,S,O)$_2$] [X = Cl, 2.719(1) Å; O^{i}Pr, 2.664(2) Å] are shorter than the longest one found in the tbop-based titanium complexes [5b,c]. The Zr–S [2.848(1) Å] and Hf–S [2.820(2) Å] bond lengths in octahedral complexes show a significant decrease on going from Zr to Hf [12f]. This structural feature presumably reflects a decrease in oxophilicity in descending through the Group 4 metals, although the influence of the crystal packing is not excluded. However, the second factor seems to be most likely because both Zr–S and Hf–S distances in the eight-coordinate complexes **16** and **17** are similar according to Zr and Hf covalent radius [12d,f]. In the context of a "breathing catalyst" it could be expected that complexes having a significant longer M–S distance would be effective catalysts for olefin polymerization processes.

3. Ethene and 1-hexene polymerization by thiobis(phenolate) Group 4 metal catalysts

The original intention was to apply complexes **1**–**17** as catalyst precursors for olefin polymerization. Catalysts for ethene polymerization, based on these compounds were prepared in *n*-hexane by milling a slurry of MgCl$_2$ with the precatalyst (10:1) and aluminium cocatalyst [12a–c,e]. The polymerization of ethene was performed in a two-step process. The aim of the first step (very low Al:M molar ratio, normal pressure of monomer, very low rate of polymerization) was to prepare granules of polymer containing a dispersed catalyst. These granules acted as a "microreactor" in the second step of polymerization with a high rate (Granular Reactor Technology). This method gave polyethene (PE) yields twice as high as those obtained with a single stage activation process. The ethene polymerization tests showed that only systems based on titanium heteroleptic complexes **1**, **2**, **5**, **6**, **10**, **13**–**15** formed very active catalysts according to the Gibson's scale [2a]. The catalyst based on complex **10** exhibited the highest catalytic activity (707 kg PE/g Ti/h) [12b]. This is close to the homogeneous [Ti$_2$(μ-X)$_2$X$_2$(tbmp)$_2$]/MAO (820 kg PE/g Ti/h for X = Cl and 677 kg PE/g Ti/h for X = O^{i}Pr; 293 K, 3 MPa, 0.001 mmol catalyst, 5.17 mmol MAO, toluene) systems [10a,b]. However, generally, the activities of the remaining systems are comparable and range from 465 to 314 kg PE/g Ti/h [12a–c,e]. This suggested that independently of the structure of the titanium precursor and its modification with colligands like Cl, OR, NR, ethene polymerization process occurred on similar active sites. The molecular weights of the polymers produced with these systems under the same conditions range from 924,000 to 1,269,000 g/mmol. The polydispersities, PDI, are close to 3 and are more narrow than those reported for homogeneous catalysts based on [Ti$_2$(μ-X)$_2$X$_2$(tbmp)$_2$] (PDI = 11.9) [2b]. It would appear that for the polymerization of ethene, activation of these systems affords well-defined, single-site active species. This indicates that the cocatalyst does not abstract the tbop ligand from the titanium centres.

Despite showing no activity in ethene polymerization, zirconium and hafnium complexes **3**, **4**, **11**, **12**, **16** and **17** upon activation with Al^{i}Bu$_3$ and supported on MgCl$_2$ in *n*-hexane acted as catalysts in 1-hexene polymerization process to produce 31–43 kg mol^{-1} of atactic poly(1-hexenes) [12f]. The activity of the catalysts was practically independent of temperature (293 or 323 K) and of the geometry of zirconium and hafnium sites in those precursors. Lower activity or its lack was achieved for systems activated with MAO in either homogeneous or heterogeneous systems. The polymers had very high molecular weight of a range 518,000–937,000 g/mmol and narrow molecular weight distribution. These results are in contrast to [Zr(tbmp-κ^3O,S,O)Cl$_2$]/MAO homogeneous system which does not polymerize 1-hexene [2b]. It has been suggested that the tbmp ligand steric hinders the 2,1-insertion of 1-hexene. However, the corresponding double sulfur donor system [Zr(dtbmp-κ^4OSSO)(bn)$_2$]/B(C$_6$F$_5$)$_3$ having the same substituents at the phenolate groups like the tbmp, effectively polymerizes 1-hexene (80 kg mol^{-1}) and reveals an



Scheme 4.

atactic structure of poly(1-hexene) with relatively low molecular weight (7400 g/mmol) [6j]. In this context the activity of the $[Ti_2(tbmp\text{-}\kappa^3O,S,O)_2(\mu\text{-}Cl_2)_2Cl_2]$/MAO [2b], and our $[Ti(tbop\text{-}\kappa^3O,S,O)_2Me_2(\mu\text{-}AlMe_2)_2]$/$Al^iBu_3$/$MgCl_2$ system [12f], in aspecific polymerization of 1-hexene affording atactic poly(1-hexene) is not comprehensible. Thus, so far accessible data have not been indicative of factors determining the activity, molecular weight and stereoregularity of 1-hexene polymerization by the sulfur donor based systems and further studies in this area are essential to explain this problem.

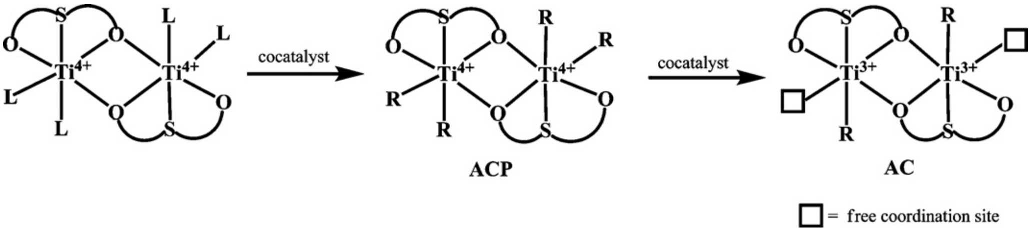
4. Nature of thiobis(phenolate) titanium active sites

To confirm the foregoing suggestions on single-site active centres created by the tbop-Ti systems and to approach their nature, the reactivity of the complexes described towards $AlMe_3$ was investigated. Reactions of heteroleptic complexes **2**, **6b** and **14** with stoichiometric amount of $AlMe_3$ gave the same organometallic compound $[Ti_2(\mu\text{-}tbop\text{-}\kappa^3O,S,O)_2Me_4]$ (**18**) (Scheme 4) [12a,e]. Octahedral titanium atoms in the dimer **18** are doubly bridged via oxygen atoms of the tbop ligands while methyl groups are situated in terminal positions. However in the presence of ethoxo groups deriving from byproducts $[Al(OEt)_2Me]$ or $[Ti(OEt)_2Cl_2]$ the substitution of one Me group at each titanium atom by OEt occurs and as a result compound $[Ti_2(\mu\text{-}OEt)_2(tbop\text{-}\kappa^3O,S,O)_2Me_2]$ (**19**) is formed [12a,e]. The X-ray crystallography of **19** showed it to be a dimer in which in contrast to **18**, the tbop ligands are facially capped to octahedral titanium atoms whereas ethoxo groups are engaged in bridging the metal centers.

The interaction of homoleptic compounds **7**–**9** with $AlMe_3$ leads to the formation of heterotrinuclear organometallic compounds $[M(tbop\text{-}\kappa^3O,S,O)_2Me_2(\mu\text{-}AlMe_2)_2]$ (M = Ti, **20**; Zr, **21**; Hf, **22**) (Scheme 4), methyl analogues of **16** and **17** [12d].

These investigations demonstrate that aluminium alkyls do not abstract the tbop ligand from Group 4 metal centres and cause only the migration of the coligands (Cl, OEt). This confirms that the tbop ligand is strongly bonded to the Group 4 metals and plays a crucial role in the formation of the active species.

The presence of alkyl groups attached to Ti, Zr and Hf centres in **18**–**22** and additional $AlMe_2$ moieties in molecules **20**–**22** lead to the belief that these compounds would act as olefin polymerization catalysts. Polymerization tests on complexes **18**–**22** showed a lack of activity towards ethene. However the use of an excess of cocatalyst showed systems based on **18** and **19** to be highly active catalysts. Monitoring the reaction of compound **18** with an excess of $AlMe_3$ at room temperature in toluene (conditions close to practical polymerization) by the ESR spectrum at 290 K showed a superposition of several signals (where two signals dominated) with shifted *g*-factors (compared to organic radicals) at $g = 1.982$ and $g = 1.949$ [13]. Such low values of *g*-factor are typically exhibited by paramagnetic Ti(III) complexes [14]. This provided evidence that Ti(III) species are vital to generate the active centres for ethene polymerization process in the systems discussed. Examination of the structural features in complexes **5**, **6b**, **13**, **15** and **19** showed that the Ti–S distance strongly depends on the donor atom axially situated to the sulfur atom of the tbop ligand. The Ti–S bond length decreases in the following order **19** > **15** > **6b** > **5** > **13** according to the order of decreasing *trans* influence of the ligands



Scheme 5.

R > OR > Cl > NH_2R. Thus, the longest Ti–S distance of 2.985(1) Å was detected in the complex **19** indicating that titanium active species possessing the alkyl group in *trans* position to the sulfur atom may successfully act as a “breathing catalyst”. These results suggest that activation of the thiobis(phenolate) titanium complexes with aluminium alkyls leads in the first step to the formation of the intermediate ACP (active centre precursor) containing two alkyl groups at each titanium centre and in the next step an excess of the cocatalyst causes reduction Ti(IV) to Ti(III) generating active species (AC) (Scheme 5).

5. Conclusions

The tridentate thiobis(phenolate) ligand (tbop) incorporated with Group 4 metals generates a large family complexes. Depending on a kind of coligand it can be coordinated to the metal center in a facial or bridging manner to form either heteroleptic or homoleptic, mononuclear and polynuclear, molecular compounds. The tbop ligand is strongly bonded to Group 4 metals and upon activation with the cocatalyst does not migrate to the aluminium centre generating solely in the case of heteroleptic titanium systems, single-site catalysts for heterogeneous ethene polymerization. Independent of the coligands and the tbop-coordination bonding mode, the same organometallic titanium compound, considered as the active centre precursor, is formed upon treatment of the tbop-titanium species with $AlMe_3$. The catalytic active sites are believed to consist of a Ti(III) species with the alkyl group coordinated in axial position to the sulfur atom of the tbop ligand.

The lack of catalytic activity of systems based on the homoleptic Group 4 metal complexes in ethene polymerization can arise from the fact that in the presence of aluminium alkyls they form coordinatively saturated species, and there is no vacancy for the incoming olefin. However it remains to be explored why the zirconium and hafnium tbop-based systems do not catalyze ethene polymerization while all the systems described here, are active towards 1-hexene producing polyhexenes with a narrow molecular weight distribution.

Acknowledgements

The author thanks her motivated co-workers who contributed to the results and also the State Committee for Scientific Research (Poland) for financial support of this work (grant no. N204089 31/2127).

References

[1] (a) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143;
(b) W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413;
(c) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253;
(d) H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205;
(e) M. Bochmann, J. Chem. Soc., Dalton Trans. (1996) 255;
(f) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. 34 (1995) 1143.
[2] (a) G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. Engl. 38 (1999) 428;
(b) A. van der Linden, C.J. Schaverien, N. Meijboom, C. Ganter, A.G. Orpen, J. Am. Chem. Soc. 117 (1995) 3008;
(c) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169;
(d) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283;
(e) Y. Suzuki, H. Terao, T. Fujita, Bull. Chem. Soc. Jpn. 76 (2003) 1493;
(f) H. Kawaguchi, T. Matsuo, J. Organomet. Chem. 689 (2004) 4228;
(g) J. Saito, Y. Suzuki, H. Makio, H. Tanaka, M. Onda, T. Fujita, Macromolecules 39 (2006) 4023.
[3] (a) J.B. Alexander, D.S. La, D.R. Cefalo, A.H. Hoveyda, R.R. Schrock, J. Am. Chem. Soc. 120 (1998) 4041;
(b) S.S. Zhu, D.R. Cefalo, D.S. La, J.Y. Jamieson, W.M. Davis, A.H. Hoveyda, R.R. Schrock, J. Am. Chem. Soc. 121 (1999) 8251.
[4] (a) C. Floriani, F. Corazza, W. Lesueur, A. Chiesi-Villa, C. Guastini, Angew. Chem., Int. Ed. Engl. 28 (1989) 66;
(b) F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 30 (1991) 145;
(c) J. Okuda, S. Fokken, H.C. Kang, W. Massa, Chem. Ber. 128 (1995) 221;
(d) S. Fokken, T.P. Saniol, J. Okuda, F.G. Sernetz, R. Mülhaupt, Oranometallics 16 (1997) 4240;
(e) D. Takeuchi, T. Nakamura, T. Aida, Macromolecules 33 (2000) 725;
(f) Y. Takashima, Y. Nakayama, T. Hirao, H. Yasuda, A. Harada, J. Organomet. Chem. 689 (2004) 612.
[5] (a) S. Fokken, T.P. Spaniol, H.C. Kang, W. Massa, J. Okuda, Organometallics 15 (1996) 5069;
(b) L. Porri, A. Ripa, C. Colombo, E. Miano, S. Capelli, S.V. Meille, J. Organomet. Chem. 514 (1996) 213;
(c) Y. Nakayama, K. Watanabe, N. Ueyama, A. Nakamura, A. Harada, J. Okuda, Organometallics 19 (2000) 2498;
(d) F. Amor, S. Fokken, T. Kleinheim, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 621 (2001) 3;
(e) Y. Takashima, Y. Nakayama, H. Yasuda, A. Nakamura, A. Harada, J. Organomet. Chem. 654 (2002) 74;
(f) L.S. Natrajan, C. Wilson, J. Okuda, P.L. Arnold, Eur. J. Inorg. Chem. (2004) 3724.
[6] (a) J. Okuda, S. Fokken, T. Kleinheim, T.P. Spaniol, Eur. J. Inorg. Chem. (2000) 1321;
(b) C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moeller, T.P. Spaniol, J. Am. Chem. Soc. 125 (2003) 4964;
(c) A. Proto, C. Capacchione, V. Venditto, J. Okuda, Macromolecules 36 (2003) 9249;
(d) C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, R. Manivannan, T.P. Spaniol, J. Okuda, J. Mol. Catal. A, Chem. 213 (2004) 137;
(e) K. Beckerle, C. Capacchione, H. Ebeling, R. Manivannan, R. Mulhaupt, A. Proto, T.P. Spaniol, J. Okuda, J. Organomet. Chem. 689 (2004) 4636;
(f) C. Capacchione, F.C. De Carlo, Zannoni, J. Okuda, A. Proto, Macromolecules 37 (2004) 8918;
(g) C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T.P. Spaniol, J. Okuda, Organometallics 24 (2005) 2971;
(h) K. Beckerle, R. Manivannan, H.P. Spaniol, J. Okuda, Organometallics 25 (2006) 3019;
(i) G.-J.M. Meppelder, H.-T. Fan, T.P. Spaniol, J. Okuda, Inorg. Chem. 48 (2009) 7378;
(j) A. Cohen, A. Yeori, I. Goldberg, M. Kol, Inorg. Chem. 46 (2007) 8114.
[7] (a) J. Okuda, S. Fokken, H.-C. Kang, W. Massa, Polyhedron 17 (1998) 943;
(b) C.R. Cornman, K.M. Geiser-Bush, J.W. Kampf, Inorg. Chem. 38 (1999) 4303.
[8] (a) E.Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, Chem. Commun. (2000) 379;
(b) E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 112 (2000) 10706;
(c) S. Groysman, I. Goldberg, Z. Goldschmidt, M. Kol, Inorg. Chem. 44 (2005) 5073;
(d) A. Cohen, J. Kopilov, I. Goldberg, M. Kol, Organometallics 28 (2009) 1391.
[9] (a) S. Priya, M.S. Balakrishna, J.T. Mague, Chem. Lett. 33 (2004) 2166;
(b) L.-C. Liang, Yu.-N. Chang, H.M. Lee, Inorg. Chem. 46 (2007) 2666.
[10] (a) M. Kakugo, T. Miyatake, K. Mizunuma, Chem. Express. 2 (1987) 445;
(b) T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem., Rapid Commun. 10 (1989) 349;
(c) T. Miyatake, K. Mizunuma, M. Kakugo, Macromol. Symp. 66 (1993) 203;
(d) C.J. Schaverien, A.J. van der Linden, A.G. Orpen, Polym. Prepr. (Am. Chem. Polym. Div.) 35 (1994) 672;
(e) Patent, Mitsui Toatsu Chem. Inc. JP 05230133-A, 1992;
(f) F.G. Serenetz, R. Mülhaupt, S. Fokken, J. Okuda, Macromolecules 30 (1997) 1562.
[11] (a) R.D.J. Froese, D.G. Musaev, T. Matsubara, K. Morokuma, J. Am. Chem. Soc. 119 (1997) 7190;

(b) R.D.J. Froese, D.G. Musaev, T. Matsubara, K. Morokuma, Organometallics 18 (1999) 373.

[12] (a) Z. Janas, L.B. Jerzykiewicz, K. Przybylak, P. Sobota, K. Szczegot, Eur. J. Inorg. Chem. (2004) 1639;
(b) Z. Janas, L.B. Jerzykiewicz, K. Przybylak, P. Sobota, K. Szczegot, D. Wiśniewska, Eur. J. Inorg. Chem. (2005) 1063;
(c) Z. Janas, L.B. Jerzykiewicz, P. Sobota, K. Szczegot, D. Wiśniewska, Organometallic 24 (2005) 3987;
(d) D. Wiśniewska, Z. Janas, P. Sobota, L.B. Jerzykiewicz, Organometallics 25 (2006) 6166;
(e) Z. Janas, Wiad. Chem. 60 (2006) 748;
(f) Z. Janas, D. Godbole, T. Nerkowski, K. Szczegot, Dalton Trans. (2009) 8846.

[13] D. Godbole, PhD Dissertation, Faculty of Chemistry, University of Wrocław, Poland, 2008.

[14] (a) K.P. Bryliakov, N.V. Semikolenova, V.A. Zakharov, E.P. Talsi, J. Organomet. Chem. 683 (2003) 23;
(b) V. Ye, W.–J. Wang, S. Zhu, J. Appl. Polym. Sci. 89 (2003) 2474;
(c) L. Bonoldi, L. Abis, L. Fiocca, R. Fusco, L. Longo, F. Simone, S. Spera, J. Mol. Catal. A: Chem. 219 (2004) 47;
(d) T. Gueta-Neyroud, B. Tumanskii, M. Kapon, M.S. Eisen, Macromolecules 40 (2007) 5261;
(e) W.W. Lukens, M.R. Smith III, R. Andersen, J. Am. Chem. Soc. 118 (1996) 1719;
(f) L. Bonoldi, L. Fiocca, R. Fusco, L. Longo, F. Simone, S. Srea, J. Mol. Catal. A: Chem. 219 (2004) 47;
(g) J.W. Pattiasina, H.J. Heeres, F. van Bolhuis, A. Meetsma, J.H. Teuben, A.L. Spek, Organometallics 6 (1987) 1004;
(h) V. Volkis, A. Lisovskii, B. Tumanskii, M. Shuster, M.S. Eisen, Organometallics 25 (2006) 2656.