Chinese Chemical Letters 33 (2022) 2402–2406

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Well-defined phosphate yttrium dialkyl complexes for catalytic stereo-controllable 1,4-polymerization of isoprene

Pusu Yang[a], Hui-Zhen Du[a], Xiang-Yu Zhang[a], Yong-Liang Xia[a], Jun-Tao Sun[a], Qian Peng[a], Bing-Tao Guan[b,*]

[a] *College of Chemistry, Nankai University, Tianjin 300071, China*
[b] *Department of Chemistry, Fudan University, Shanghai 200438, China*

ARTICLE INFO

Article history:
Received 23 July 2021
Revised 15 November 2021
Accepted 23 November 2021
Available online 27 November 2021

Keywords:
Phosphate
Yttrium alkyls
Isoprene
Stereo-controllable
1,4-Polymerization

ABSTRACT

Oxygen ligation is envisioned to provide a stable and distinctive coordination environment to the strongly oxophilic rare-earth metals. However, the well-defined dialkyl complexes bearing oxyanion ancillary ligand had been rarely addressed for the instability of the complexes and the shortage of easily available ligands. Herein, we report the synthesis of phosphate ligated dialkyl yttrium complexes (PYR_2) featuring a high stability and a tunable ligand. Treated with the borate reagent, the phosphate yttrium complex displays high activity and selectivity in the catalytic *cis*-1,4-polymerization of isoprene (up to 96.5%). Furthermore, using $AlMe_3$ as an additive, the stereoselectivity switches to *trans*-1,4-polymerization (up to 92.0%).

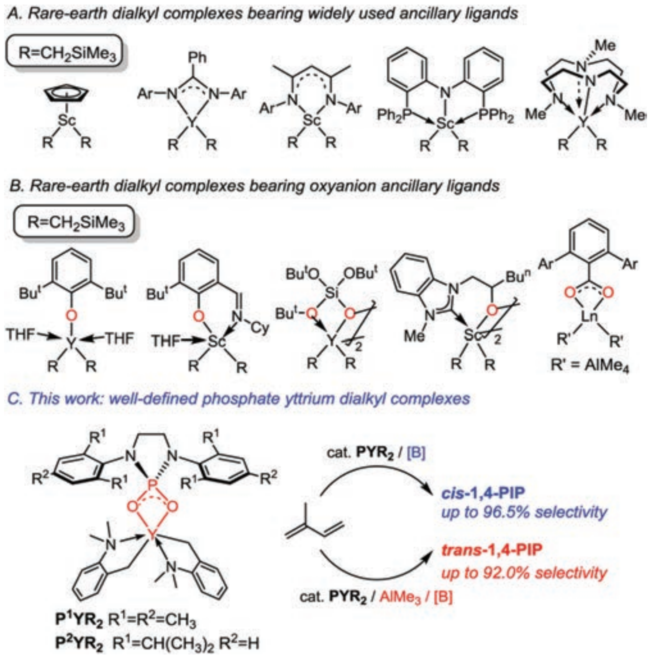
Polyisoprene (PIP) with well-defined microstructure represents an essential class of functional material in elastomers and plastics [1–3]. The huge demand of them thereby promotes an impressive development of rare-earth metal catalysts [4–6], which achieved the selective synthesis of *cis*-1,4-PIP, [7–26] *trans*-1,4-PIP [27–33] and 3,4-PIP [34–39]. It is noteworthy that some catalytic systems were reported to enable a switch of the selectivity by a slight modification of the metal center, ancillary ligand, or cocatalysts [40–54]. For example, Anwander found that the lanthanum fluorenyl half-sandwich catalyst efficiently produced *trans*-1,4-PIP (80%), while the lutetium complex gave access to higher *cis*-1,4-contents (78.2%) [40]. Arnold discovered that half-sandwich scandium borohydrides complexes with different NHC ligands could swtich the stereoselectivity in the isoprene polymerization (94% *trans*-1.4 and 80% *cis*-1.4) [41]. Hou and Zhang reported that the yttrium amidinate complex, by addition of $AlMe_3$, were transformed to heterotrinuclear Y/Al complex, which could dramatically switch the regio- and stereoselectivity of isoprene polymerization (from 3,4-isospecific to 1,4-*cis* selective) [46,47]. In these cases, the precise control on the regio- and stereoselectivity definitely displays the state of the art in catalyst design. A tailor-made catalyst with new structure, good stability, high catalytic activity and selectivity, however, is still highly desired in both academic and industrial fields.

Dialkyl rare-earth complexes bearing a monoanionic ancillary ligand have recently drawn much attention, serving as efficient catalysts for the polymerization and functionalization reactions of alkenes [55–60]. Most of these ligands feature delocalized carbanions or multidentate nitrogen anions structures (Scheme 1A). According to the strong oxophilicity of rare-earth metals, oxyanions are supposed to have great potential for acting as suited ancillary ligands [61–75]. Based on this assumption, Evans synthesized dialkyl rare-earth complexes adopting steric bulky 2,6-di–*tert*-butylphenol as an ancillary ligand [61,62]. Subsequently, functionalized phenols [63–67], silanols [68,69], alkoxy NHCs [70,71] were also introduced into the ancillary ligand family (Scheme 1B). Anwander reported the synthesis of various alkylated carboxylate rare-earth complexes that catalyzed *cis*-1,4-polymerization of isoprene [72]. These oxyanion ligands moved down a new path for the synthesis of dialkyl rare-earth complexes, whereas most of these complexes were not stable enough, presumably because of the easy ligand redistribution and complex aggregation reactions. Nevertheless, further studies about dialkyl rare-earth complexes bearing oxyanion ligands remain sluggish due to a lack of ligand diversity. Although some lanthanide carboxylates [76–79] and phosphates [80–85] were used as catalyst procursors in polymerization process, the well-defined alkyl complexes are yet undeveloped and the role of ligands is still obscure. Thus, we are quite

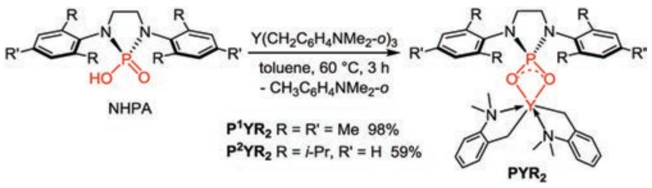
---

* Corresponding author.
E-mail address: bguan@fudan.edu.cn (B.-T. Guan).

https://doi.org/10.1016/j.cclet.2021.11.064
1001-8417/© 2021 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.



Scheme 1. Examples of rare-earth dialkyl complexes.



Scheme 2. Synthesis of phosphate yttrium dialkyl complexes.

curious about that if phosphates could be applied as anion ligands for dialkyl rare-earth complexes; a positive answer to this question could provide further insight about oxyanion ancillary ligands and also an attractive alternative catalyst. Herein, we reported the synthesis of well-defined phosphate yttrium dialkyl complexes and their catalytic application in stereo-controllable 1,4-polymerization of isoprene (Scheme 1C).

The oxophilicity of rare-earth metals would definitely provide a strong interaction between the metal ion and the phosphate anion. This strong bonding, however, together with the small steric hindrance of the oxyanions, would probably result in the bridging interaction and ligand redistribution. To avoid the possible side reactions, we proposed to start with tris(aminobenzyl) yttrium complex, whose alkyl anion has a "built-in" chelating amino group. Thinking of the widely used *N*-heterocyclic carbene ligands, we synthesized two *N*-heterocyclic phosphorodiamidic acids (NHPAs) bearing similar skeleton structures and tunable steric parameters [86,87]. The acid-base reaction between NHPAs and $Y(CH_2C_6H_4NMe_2\text{-}o)_3$ took place smoothly at 60 °C in toluene and afforded the *N*-heterocyclic phosphate yttrium bis(aminobenzyl) complexes **PYR₂** after 3 h (Scheme 2). Both complexes were fully characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy, and their structures in solid state were determined by single-crystal X-ray diffraction (XRD). These characterizations reveal the similar structures of the two phosphate yttrium complexes, as shown in Fig. 1. The phosphate anion is bonded to the yttrium center in κ^2 fashion through two oxygen atoms. The yttrium atom is well located on the OPO rigid frame to form a planar quadrilateral. In a simplified view, the phosphate ligand creates a well-defined steric pocket, along with the κ^2 coordination from the aminobenzyl ligands, conducing to enhance the stability of **PYR₂**. Through comparison with the two phosphate yttrium complexes, it is showed that the Y-O bond lengths in **P²YR₂** (2.306(2) Å) are longer than those in **P¹YR₂** (2.282(2) Å). We speculated that the larger steric hindrance from the isopropyl groups increases the distance between phosphate and yttrium atom.

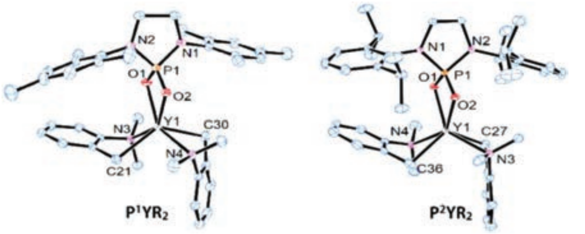
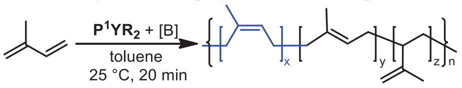


Fig. 1. ORTEP structure of PYR_2 complexes with thermal ellipsoids set at 30% probability. Hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths [Å] and angles [°]: (**P¹YR₂**, left) Y1-O1 2.282(2), Y1-O2 2.277(2), Y1-C21 2.435(3), Y1-C30 2.435(3), Y1-N3 2.533(2), Y1-N4 2.522(2), O1-Y1-O2 63.63(8), P1-O1-Y1 96.19(1), P1-O2-Y1 96.12(1), O1-P1-O2 103.99(1). (**P²YR₂**, right) Y1-O1 2.306(2), Y1-O2 2.300 (2), Y1-C27 2.439(3), Y1-C36 2.436(3), Y1-N3 2.525(2), Y1-N4 2.533(2), O1-Y1-O2 62.86(6), P1-O1-Y1 96.23(8), P1-O2-Y1 96.48(8), O1-P1-O2 104.30(1).

As part of our continuing investigations into isoprene polymerization, we then used the **PYR₂** as catalysts for further exploration. The neutral **P¹YR₂** alone proved to be inactive for the isoprene polymerization (Table 1, entry 1). However, once activited with 1 equiv. of borate reagent $[Ph_3C][B(C_6F_5)_4]$, **P¹YR₂** at room temperature demonstrated high catalytic activity: 1000 equiv. of isoprene were converted quantitatively into PIP within 20 min (entry 2). Remarkably, the polymer product features a high *cis*-1,4 content (93.7%). GPC curve indicated that the PIP obtained is unimodal with a M_n of 2.6×10^5 and a narrow molecular weight distribution (PDI = 1.4). The catalytic polymerization under lower temperature took place smoothly and gave PIP with even higher *cis*-1,4 content (96.5%) as well as higher molecular weight ($M_n = 3.6 \times 10^5$) (entry 3). We next carried out the catalytic polymerization with various [Isoprene]/[**P¹YR₂**] ratios varying from 600 to 5000 (entries 4–9). All the reactions produced PIP with high efficiency (yields > 98%) and excellent selectivity (*cis*-1,4 selectivity: 92.6%–96.5%). Furthermore, the molecular weight of the resultant PIP increases linearly with the amount of the isoprene monomers (see Supporting information for details), while the molecular weight distribution still keeps narrow (1.4–1.6). The phosphate yttrium complex here displayed a very high catalytic activity and thus provided an approach for the synthesis of high-molecular-weight *cis*-1,4-PIP (M_n up to 1.06×10^6). Considering the important roles of alkylaluminum compounds in polymerization, we further carried out the catalytic polymerization reaction in the presence of trialkylaluminum reagents (entries 10 and 11). $Al(iBu)_3$, a well-known chain transfer reagent, led to the decrease of the molecular-weight ($M_n = 1.9 \times 10^5$), as expected. Unlike some known findings [46,48] that addition of $AlMe_3$ could increase the *cis*-1,4 content of PIP, the addition of 5 equiv. of $AlMe_3$ herein greatly increased the *trans*-1,4 content (44.1%).

The catalytic system **P²YR₂**/$[Ph_3C][B(C_6F_5)]_4$ exhibited lower *cis*-1,4 selectivity in the polymerization of isoprene, but higher initiation efficiency (42.1%), compared to the catalytic system **P¹YR₂**/$[Ph_3C][B(C_6F_5)]_4$ (25.9%), producing the PIP product with 83.3% *cis*-1,4, 5.3% *trans*-1,4 and 11.4% 3,4 contents (Table 2, entry 1). This result suggested that the steric effect of the two *ortho*-substituted *N*-aryl rings might be a contributing factor of the *cis*-1,4 selectivity. The bulky *o*-isopropyl in *N*-aryl rings led to the decrease of *cis*-1,4 selectivity [11,16]. The catalytic system containing 5 equiv. of $AlMe_3$ surprisingly switched the stereoselectivity

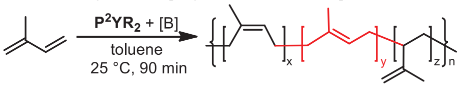
Table 1
P^1YR_2 catalyzed *cis*-1,4-polymerization of isoprene. [a]



Entry	IP (equiv.) [b]	Yield (%)	Selectivity (x / y / z) [c]	M_n (10^5) [d]	PDI [d]	T_g (°C) [e]	eff. (%)[k]
1[f]	1000	–	–	–	–	–	–
2	1000	99	93.7 / 2.3 / 3.6	2.6	1.4	−62	25.9
3[g]	1000	99	96.5 / 0.7 / 2.8	3.6	1.4	−63	18.7
4	600	98	93.8 / 2.8 / 3.4	1.8	1.4	−62	22.3
5	800	98	93.5 / 3.1 / 3.4	2.3	1.5	−62	23.2
6	1200	98	93.7 / 2.8 / 3.5	3	1.4	−62	26.7
7	1500	99	92.6 / 3.6 / 3.8	3.5	1.5	−62	28.6
8	2000	99	95.1 / 1.7 / 3.2	4.8	1.5	−62	28.1
9	5000	95	94.4 / 1.7 / 3.8	10.6	1.6	−64	30.5
10[h,i]	1000	97	93.9 / 2.0 / 3.9	1.9	3	−64	34.8
11[h,j]	1000	95	50.6 / 44.1 /5.3	2.6	2.1	−63	24.9

[a] Reaction conditions: **P^1YR_2** (10 μmol), $[Ph_3C][B(C_6F_5)_4]$ (10 μmol), toluene (5 mL), room temperature, 20 min, unless otherwise noted.
[b] Equiv. = [isoprene]/[**P^1YR_2**].
[c] Selectivity ratio of *cis*-1,4/*trans*-1,4/3,4 determined by ^1H and ^{13}C NMR spectroscopy.
[d] Determined by GPC with respect to a polystyrene standard.
[e] Determined by DSC.
[f] Without $[Ph_3C][B(C_6F_5)_4]$.
[g] 0 °C.
[h] 60 min.
[i] 5 equiv. of $Al(iBu)_3$ as additive.
[j] 5 equiv. of $AlMe_3$ as additive.
[k] Initiation efficiency = M_n (calculated)/M_n (measured).

Table 2
P^2YR_2 catalyzed 1,4-polymerization of isoprene. [a]



Entry	$AlMe_3$ (equiv.) [b]	Yield (%)	Selectivity (x / y / z) [c]	M_n (10^5) [d]	PDI [d]	T_g (°C) [e]	eff. (%)[k]
1[f]	–	99	83.3 / 5.3 / 11.4	1.6	1.6	−58	42.1
2	1	80	85.4 / 4.2 / 10.4	2.6	1.7	−59	21.0
3	2	84	81.5 / 4.3 / 13.2	2.7	2.5	−58	21.2
4	3	93	19.5 / 75.7 / 4.8	1.9	2	−66	33.3
5	4	89	11.3 / 85.1 / 2.3	1.9	1.7	−69	32.0
6	5	99	8.2 / 89.4 / 2.4	3.6	1.4	−68	18.7
7	10	83	6.1 / 92.0 / 1.9	1.3	1.5	−68	43.4
8[g]	5	82	48.7 / 36.8 /15.4	2.6	1.4	−57	21.5
9[h]	5	98	85.8 / 1.8 / 12.4	1.1	2.3	−54	60.7
10[i]	5	–	–	–	–	–	
11[j]	5	–	–	–	–	–	

[a] Reaction conditions: **P^2YR_2** (10 μmol), $[Ph_3C][B(C_6F_5)_4]$ (10 μmol), toluene (5 mL), isoprene (10 mmol), room temperature, 90 min.
[b] Equiv. = $[AlMe_3]/[P^2YR_2]$.
[c] Selectivity ratio of *cis*-1,4/*trans*-1,4/3,4 determined by ^1H and ^{13}C NMR spectroscopy.
[d] Determined by GPC with respect to a polystyrene standard.
[e] Determined by DSC.
[f] 20 min.
[g] 5.0 equiv. of $AlEt_3$ as additive.
[h] 5.0 equiv. of $Al(iBu)_3$ as additive.
[i] Without **P^2YR_2**.
[j] Without $[Ph_3C][B(C_6F_5)]_4$.
[k] Initiation efficiency = M_n (calculated)/M_n (measured).

from *cis*-1,4 to *trans*-1,4-polymerization, thus affording the polymers with contents of 89.4% *trans*-1,4 units (entry 6). The *trans*-1,4-polymerization took place much more slowly (90 min). The significantly increased molecular weight ($M_n = 3.6 \times 10^5$) revealed an obvious decreased efficiency of the catalyst (18.7%), which hinted a dramatic structure change of the catalytic species. We speculated that the heteronuclear Y/Al complex formed *in-situ* might be the possible cataytic species in the *trans*-1,4-polymerization [9,28,46]. To find out more details, we carefully examined the polymerization with different $[AlMe_3]/[$**P^2YR_2**$]$ ratios. 1 or 2 equiv. of $AlMe_3$ did not obviously change the regioselectivity (entries 2 and 3). Using 3 equiv. of $AlMe_3$ as additive resulted in a noticeable increase of the *trans*-1,4 selectivity from 5.3% to 75.0% (entry 4). When 4 equiv. of $AlMe_3$ or more was added, the PIP was obtained with higher *trans*-1,4 content (85.1%–92%) (entries 5 and 7). It is suggested that 4 equiv. of $AlMe_3$ was necessary for the formation of the heterotrinuclear Y/Al complex [46]. It is noteworthy that 10 equiv. of $AlMe_3$ as additive gave the PIP with lower molecular weight ($M_n = 1.3 \times 10^5$) but similar narrow molecular weight distribution (PDI = 1.5), suggesting that the excess amount of $AlMe_3$ may act as a chain transfer reagent to interrupt the growing polymer chain and tune the molecular weight. For comparison, the PIP obtained with the system **P^2YR_2**/$[Ph_3C][B(C_6F_5)]_4/AlEt_3$ or $Al(iBu)_3$ failed to achieve high *trans*-1,4 contents (entries 8 and 9). This observation showed that the *trans*-1,4 selectivity might be influenced by the steric effect of the aluminum alkyls ($AlMe_3 > AlEt_3$

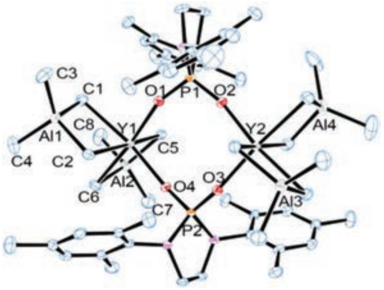


Fig. 2. ORTEP structure of $\mathbf{[P^1Y(AlMe_4)_2]_2}$ with thermal ellipsoids set at 30% probability. Hydrogen atoms and solvents have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Y1-O1 2.188(2), Y1-O4 2.194(2), Y1-C1 2.621(4), Y1-C2 2.527(4), Al1-C1 2.062 (4), Al1-C2 2.074(4), O1-Y1-O4 95.883(8), O1-P1-O2 108.205(1), P1-O1-Y1 161.082(1), C1-Y1-C2 82.598(1), C1-Al1-C2 110.499(2), C3-Al1-C4 118.280(2).

$>$ Al(iBu)$_3$) [21]. Control experiments were conducted that the isoprene polymerization could not be initiated without either borate reagent or $\mathbf{P^2YR_2}$, indicating that the cationic Y/Al species may account for the *trans*-1,4-polymerization of isoprene (entries 10 and 11). To gain further insight into the possible heterotrinuclear Y/Al species, we carried out the reaction between phosphate yttrium dialkyl complexes and 4 equiv. of AlMe$_3$. A crystal of a phosphate bis(tetramethylaluminate) yttrium complex $\mathbf{[P^1Y(AlMe_4)_2]_2}$ suit for X-ray diffraction analysis was surprisingly obtained (Fig. 2). Compared to the crystal structure of $\mathbf{P^1YR_2}$, this dimer complex $\mathbf{[P^1Y(AlMe_4)_2]_2}$ features a quite different coordination environment around the yttrium metal center. The huge change of the catalyst structure might result in the different coordination and insertion mode of isoprene, leading to *trans*-1,4-polymerization of isoprene (Table 1, entry 11). The synthesis and isolation of heteronuclear Y/Al complex $\mathbf{[P^2Y(AlMe_4)_2]_2}$ and catinoic species of $\mathbf{[P^1Y(AlMe_4)_2]_2}$ were tried but failed, possibly because of their thermal instability.

In conclusion, *N*-heterocyclic phosphate ancillary ligand was designed and proved to be suitable for the synthesis and isolation of yttrium dialkyl complexes, which could be conveniently prepared *via* the acid-base reactions between tris(aminobenzyl) yttrium complex and *N*-heterocyclic phosphoric acid. Activated by $[Ph_3C][B(C_6F_5)]_4$, the yttrium complexes $\mathbf{PYR_2}$ exhibit high catalytic activities for *cis*-1,4-selective (up to 96.5%) polymerization of isoprene. The stereoselectivity was dramatically switched from *cis*-1,4 to *trans*-1,4-polymerization (up to 92.0%) when using AlMe$_3$ as an additive. Considering various easily available phosphoric acids including the chiral ones, we could expect a nice synthetic value and diversified catalytic applications of phosphate ligated metal complexes in near future. Along this line, the synthesis of *N*-heterocyclic phosphate complexes with other metals and also with chiral phosphoric acids are currently ongoing in our laboratory.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We gratefully acknowledge the support from the Fudan University. We thank Prof. Li Pan (Tianjin Univ.), Prof. Jian-Hua Cheng (CIAC, China) for their helpful suggestions. This project was supported by National Natural Science Foundation of China (Nos. 21890722 and 21950410519), National Natural Science Foundation of Tianjin (No. 19JCYBJC20100).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2021.11.064.

References

[1] E. Ceauşescu, Stereospecific Polymerization of Isoprene, 1st ed., Pergamon, Oxford, 1983.
[2] J. Song, B. Huang, D. Yu, J. Appl. Polym. Sci. 82 (2001) 81–89.
[3] J.E. Puskas, E. Gautriaud, A. Deffieux, J.P. Kennedy, Prog. Polym. Sci. 31 (2006) 533–548.
[4] L. Porri, A. Giarrusso, 5-Conjugated diene polymerization, in: G. Allen, J.C. Bevington (Eds.), Comprehensive Polymer Science and Supplements, Pergamon, Amsterdam, 1989, pp. 53–108.
[5] Z. Hou, Y. Wakatsuki, Coord. Chem. Rev. 231 (2002) 1–22.
[6] Z. Zhang, D. Cui, B. Wang, B. Liu, Y. Yang, Polymerization of 1,3-conjugated dienes with rare-earth metal precursors, in: P.W. Roesky (Ed.), Molecular Catalysis of Rare-Earth Elements, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 49–108.
[7] S. Arndt, K. Beckerle, P.M. Zeimentz, T.P. Spaniol, J. Okuda, Angew. Chem. Int. Ed. 44 (2005) 7473–7477.
[8] L. Zhang, T. Suzuki, Y. Luo, M. Nishiura, Z. Hou, Angew. Chem. Int. Ed. 46 (2007) 1909–1913.
[9] M. Zimmermann, N.Å. Frøystein, A. Fischbach, et al., Chem. Eur. J. 13 (2007) 8784–8800.
[10] Y. Yang, B. Liu, K. Lv, et al., Organometallics 26 (2007) 4575–4584.
[11] W. Gao, D. Cui, J. Am. Chem. Soc. 130 (2008) 4984–4991.
[12] K. Lv, D. Cui, Organometallics 29 (2010) 2987–2993.
[13] D. Li, S. Li, D. Cui, X. Zhang, Organometallics 29 (2010) 2186–2193.
[14] Y. Luo, S. Fan, J. Yang, J. Fang, P. Xu, Dalton Trans. 40 (2011) 3053–3059.
[15] Y. Pan, T. Xu, G. Yang, K. Jin, X. Lu, Inorg. Chem. 52 (2013) 2802–2808.
[16] J. Zhang, Z. Hao, W. Gao, et al., Chem. Asian J. 8 (2013) 2079–2087.
[17] S. Sun, H. Ouyang, Y. Luo, et al., Dalton Trans. 42 (2013) 16355–16364.
[18] L. Li, C. Wu, D. Liu, S. Li, D. Cui, Organometallics 32 (2013) 3203–3209.
[19] S. Liu, G. Du, J. He, et al., Macromolecules 47 (2014) 3567–3573.
[20] L. Guo, X. Zhu, S. Zhou, et al., Dalton Trans. 43 (2014) 6842–6847.
[21] L. Guo, X. Zhu, G. Zhang, et al., Inorg. Chem. 54 (2015) 5725–5731.
[22] M. Deng, S. Chi, Y. Luo, New J. Chem. 39 (2015) 7575–7581.
[23] L. Shi, Q. Su, J. Chen, X. Li, Y. Luo, Dalton Trans. 45 (2016) 1391–1397.
[24] P. Zhang, H. Liao, H. Wang, et al., Organometallics 36 (2017) 2446–2451.
[25] M. Bonath, C.O. Hollfelder, D. Schädle, et al., Eur. J. Inorg. Chem. 2017 (2017) 4683–4692.
[26] C. Yu, P. Zhang, F. Gao, S. Zhang, X. Li, Polym. Chem. 9 (2018) 603–610.
[27] F. Bonnet, M. Visseaux, D. Barbier-Baudry, E. Vigier, M.M. Kubicki, Chem. Eur. J. 10 (2004) 2428–2434.
[28] M. Zimmermann, K.W. Törnroos, R. Anwander, Angew. Chem. Int. Ed. 47 (2008) 775–778.
[29] L. Annunziata, M. Duc, J. Carpentier, Macromolecules 44 (2011) 7158–7166.
[30] W. Rong, D. Liu, H. Zuo, et al., Organometallics 32 (2013) 1166–1175.
[31] H. Liu, J. He, Z. Liu, et al., Macromolecules 46 (2013) 3257–3265.
[32] L.N. Jende, C. Maichle-Mössmer, R. Anwander, Chem. Eur. J. 19 (2013) 16321–16333.
[33] S. Fadlallah, M. Terrier, C. Jones, et al., Organometallics 35 (2016) 456–461.
[34] L. Zhang, Y. Luo, Z. Hou, J. Am. Chem. Soc. 127 (2005) 14562–14563.
[35] G. Du, Y. Wei, L. Ai, et al., Organometallics 30 (2011) 160–170.
[36] A.A. Kissel, D.M. Lyubov, T.V. Mahrova, et al., Dalton Trans. 42 (2013) 9211–9225.
[37] B. Liu, L. Li, G. Sun, et al., Macromolecules 47 (2014) 4971–4978.
[38] C. Yao, D. Liu, P. Li, et al., Organometallics 33 (2014) 684–691.
[39] F. Kong, M. Li, X. Zhou, L. Zhang, RSC Adv. 7 (2017) 29752–29761.
[40] D. Diether, K. Tyulyunov, C. Maichle-Mössmer, R. Anwander, Organometallics 36 (2017) 4649–4659.
[41] F. Bonnet, C.E. Jones, S. Semlali, et al., Dalton Trans. 42 (2013) 790–801.
[42] Y. Yang, K. Lv, L. Wang, Y. Wang, D. Cui, Chem. Commun. 46 (2010) 6150–6152.
[43] R. Tanaka, K. Yuuya, H. Sato, et al., Polym. Chem. 7 (2016) 1239–1243.
[44] N.Y. Rad'Kova, A.O. Tolpygin, V.Y. Rad'Kov, et al., Dalton Trans. 45 (2016) 18572–18584.
[45] R. Tanaka, Y. Shinto, Y. Nakayama, T. Shiono, Catalysts 7 (2017) 284.
[46] L. Zhang, M. Nishiura, M. Yuki, Y. Luo, Z. Hou, Angew. Chem. Int. Ed. 47 (2008) 2642–2645.
[47] X. Yu, Q. You, X. Zhou, L. Zhang, ACS Catal. 8 (2018) 4465–4472.
[48] C. Döring, W.P. Kretschmer, R. Kempe, Eur. J. Inorg. Chem. 2010 (2010) 2853–2860.
[49] L. Wang, D. Liu, D. Cui, Organometallics 31 (2012) 6014–6021.
[50] F. Chen, S. Fan, Y. Wang, J. Chen, Y. Luo, Organometallics 31 (2012) 3730–3735.
[51] L. Luconi, D.M. Lyubov, A. Rossin, et al., Organometallics 33 (2014) 7125–7134.
[52] B. Liu, G. Sun, S. Li, D. Liu, D. Cui, Organometallics 34 (2015) 4063–4068.
[53] J. Chen, Y. Gao, S. Xiong, et al., ACS Catal. 7 (2017) 5214–5219.
[54] G. Zhang, S. Wang, X. Zhu, et al., Organometallics 36 (2017) 3812–3822.
[55] A.A. Trifonov, D.M. Lyubov, Coord. Chem. Rev. 340 (2017) 10–61.
[56] M. Nishiura, F. Guo, Z. Hou, Acc. Chem. Res. 48 (2015) 2209–2220.
[57] S. Arndt, J. Okuda, Adv. Synth. Catal. 347 (2005) 339–354.
[58] P.M. Zeimentz, S. Arndt, B.R. Elvidge, J. Okuda, Chem. Rev. 106 (2006) 2404–2433.

[59] F.T. Edelmann, Chem. Soc. Rev. 41 (2012) 7657–7672.
[60] M. Nishiura, Z. Hou, Nat. Chem. 2 (2010) 257–268.
[61] W.J. Evans, R.N.R. Broomhall-Dillard, J.W. Ziller, Organometallics 15 (1996) 1351–1355.
[62] M.V. Butovskii, O.L. Tok, V. Bezugly, F.R. Wagner, R. Kempe, Angew. Chem. Int. Ed. 50 (2011) 7695–7698.
[63] A. Lara-Sanchez, A. Rodriguez, D.L. Hughes, M. Schormann, M. Bochmann, J. Organomet. Chem. 663 (2002) 63–69.
[64] D.J.H. Emslie, W.E. Piers, M. Parvez, R. McDonald, Organometallics 21 (2002) 4226–4240.
[65] S.C. Marinescu, T. Agapie, M.W. Day, J.E. Bercaw, Organometallics 26 (2007) 1178–1190.
[66] G. Paolucci, M. Bortoluzzi, M. Napoli, P. Longo, J. Mol. Catal. A: Chem. 287 (2008) 121–127.
[67] G. Paolucci, M. Bortoluzzi, S. Milione, A. Grassi, Inorg. Chim. Acta. 362 (2009) 4353–4357.
[68] N. Dettenrieder, H.M. Dietrich, C. Maichle-Mössmer, R. Anwander, Chem. Eur. J. 22 (2016) 13189–13200.
[69] B.R. Elvidge, S. Arndt, T.P. Spaniol, J. Okuda, Dalton Trans. (2006) 890–901.
[70] S. Long, B. Wang, H. Xie, et al., New J. Chem. 39 (2015) 7682–7687.
[71] P.L. Arnold, Z.R. Turner, R. Bellabarba, R.P. Tooze, J. Am. Chem. Soc. 133 (2011) 11744–11756.
[72] A. Fischbach, F. Perdih, E. Herdtweck, R. Anwander, Organometallics 25 (2006) 1626–1642.
[73] C.S. Tredget, S.C. Lawrence, B.D. Ward, et al., Organometallics 24 (2005) 3136–3148.
[74] W. Miao, S. Li, D. Cui, B. Huang, J. Organomet. Chem. 692 (2007) 3823–3834.
[75] S. Ge, S. Bambirra, A. Meetsma, B. Hessen, Chem. Commun. (2006) 3320–3322.
[76] W.J. Evans, D.G. Giarikos, J.W. Ziller, Organometallics 20 (2001) 5751–5758.
[77] A. Fischbach, F. Perdih, P. Sirsch, W. Scherer, R. Anwander, Organometallics 21 (2002) 4569–4571.
[78] W.J. Evans, D.G. Giarikos, Macromolecules 37 (2004) 5130–5132.
[79] D.M. Roitershtein, A.A. Vinogradov, A.A. Vinogradov, et al., Organometallics 32 (2013) 1272–1286.
[80] P. Laubry, F. Barbotin, US20050130835 A1[P], 2006.
[81] R. Anwander, O. Nuyken, Neodymium Based Ziegler Catalysts: Fundamental Chemistry, Springer, Berlin, 2006.
[82] I.E. Nifant'Ev, A.N. Tavtorkin, A.V. Shlyahtin, et al., Dalton Trans. 42 (2013) 1223–1230.
[83] I.E. Nifant'ev, A.N. Tavtorkin, S.Y.A. Korchagina, et al., Appl. Catal. A 478 (2014) 219–227.
[84] S.K. Gupta, G.A. Bhat, R. Murugavel, Inorg. Chem. 56 (2017) 9071–9083.
[85] I. Carson, M.R. Healy, E.D. Doidge, et al., Coord. Chem. Rev. 335 (2017) 150–171.
[86] H. Huang, J.Y. Kang, Org. Lett. 19 (2017) 5988–5991.
[87] C. Kutzbach, L. Jaenicke, J. Liebigs, Ann. Chem. 692 (1966) 26–41.