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Group 3 metal complexes based on a chiral tetradentate diamine-diamide ligand: Synthesis and use in polymerization of (D,L)-lactide and intramolecular alkene hydroamination catalysis

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Abstract

New amido complexes [Me_2PMEN]Ln(N(SiR_3)$_2$) (Ln = Y, SiR_3 = $SiMe_3$, **2**; Ln = Nd, SiR_3 = $SiMe_3$, **3**; Ln = La, SiR_3 = $SiHMe_2$, **4**) based on the chiral tetradentate diamine-diamide ligand [Me_2PMEN]$^{2-}$, derived by double deprotonation of the parent tetraamine *N*,*N*′-dimethyl-*N*,*N*′-bis[(*S*)-2-methylpyrrolidine]ethylenediamine ([Me_2PMEN]H_2, **1**), have been readily prepared by amine elimination protocols. Complex **2** was shown to be active for the ring-opening polymerization of *racemic*-lactide at room temperature in toluene to yield isotactic-enriched polylactides (P_m up to 70%) with relatively narrow polydispersities (M_w/M_n = 1.32–1.67), but poor initiation efficiency. Complex **2** is also highly active for the room temperature hydroamination/cyclization of some aminopentene and aminohexene derivatives, though those reactions proceed with low enantioselectivities (up to 11% ee).

Keywords: Homogeneous catalysis; Hydroamination; Lanthanides; N ligands; Polymerization

1. Introduction

Organometallic complexes of group 3 and lanthanide elements based on polyamine/amide ligands have received growing attention in the past decades [1]. One of the initial driving forces for this work is the longstanding interest in the design of non-metallocene single-site catalysts for the polymerization of α-olefins [2]. Post-lanthanidocene complexes [3] have also some obvious potential in other topical catalytic reactions, for instance, ring-opening polymerization (ROP) of cyclic polar monomers such as lactides [4,5] and hydroamination of alkenes [6]. In particular, chiral metal complexes that incorporate readily available chiral amine ligands for exploitation in stereoselective catalysis are molecules of growing interest [7]. Thus, some of us have recently studied the structure and reactivity of Zr and Ti complexes that incorporate an original tetradentate diamine-diamide ligand [Me_2PMEN]$^{2-}$, derived by double deprotonation of the parent tetraamine *N*,*N*′-dimethyl-*N*,*N*′-bis[(*S*)-2-methylpyrrolidine]ethylenediamine [8]. In this contribution, we describe new Y, La and Nd complexes based on this chiral ligand, which is readily prepared in enantiomerically pure form starting from cheap, commercially available (*S*)-(2-hydroxymethyl)pyrrolidine. The potential usefulness of these new group 3 metal complexes for lactide polymerization and asymmetric intramolecular hydroamination was also investigated.

2. Results and discussion

2.1. Synthesis and characterization of amido-[Me_2PMEN] group 3 metal complexes

The amine elimination reaction between the diproteo ligand H_2[Me_2PMEN] (**1**) and yttrium and neodymium Ln(N($SiMe_3$)$_2$)$_3$ precursors takes place readily at room temperature in toluene solution to afford the corresponding amido group 3 metal complexes **2** and **3**, respectively (Scheme 1). Complexes **2** and **3** were isolated in high yield after simple workup as

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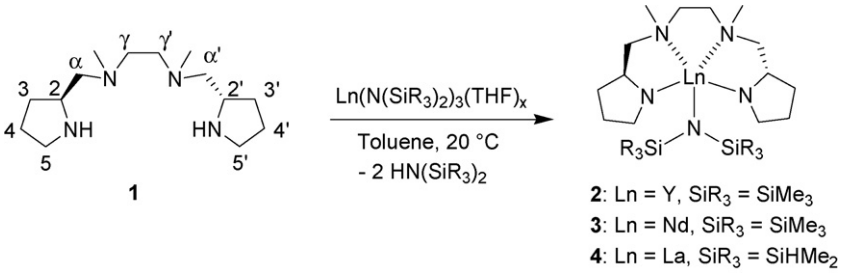


Scheme 1. Synthesis of amido group 3 metal complexes (the atom numbering used for the $[Me_2PMEN]^{2-}$ ligand is shown for pro-ligand **1**).

crystalline solids. The bis(dimethylsilyl)amido lanthanum complex **4** was prepared in an analogous way starting from the bis(THF) adduct $La(N(SiHMe_2)_2)_3(THF)_2$; monitoring of the reaction by ^1H NMR evidenced the release of two equiv of free amine $HN(SiHMe_2)_2$. The three complexes are all readily soluble at room temperature in toluene and benzene, and less soluble in pentane.

The identity of complexes **2–4** was established on the basis of elemental analysis and NMR spectroscopy. Attempts to grow suitable crystals for X-ray diffraction studies have failed so far. Despite the C_2 symmetry of the $[Me_2PMEN]^{2-}$ ligand, the ^1H NMR spectrum of diamagnetic yttrium complex **2** in benzene-d_6 at 300 K features a complete set of well resolved resonances indicative of a non-symmetric (C_1) species on the NMR time scale (Fig. 1); in particular, two singlets are observed for the N–CH_3 groups, as well as two multiplets and four multiplets for the H-2 and H-5 hydrogens, respectively. Consistently, the ^{13}C NMR spectrum contains one resonance for each individual carbon atom. A complete assignment of ^1H and ^{13}C resonances for **2** was possible on the basis of COSY, HMBC and HMQC experiments. The ^1H NMR spectrum of **3** in toluene-d_8 at 300 K showed, despite its paramagnetic Nd center, relatively sharp and

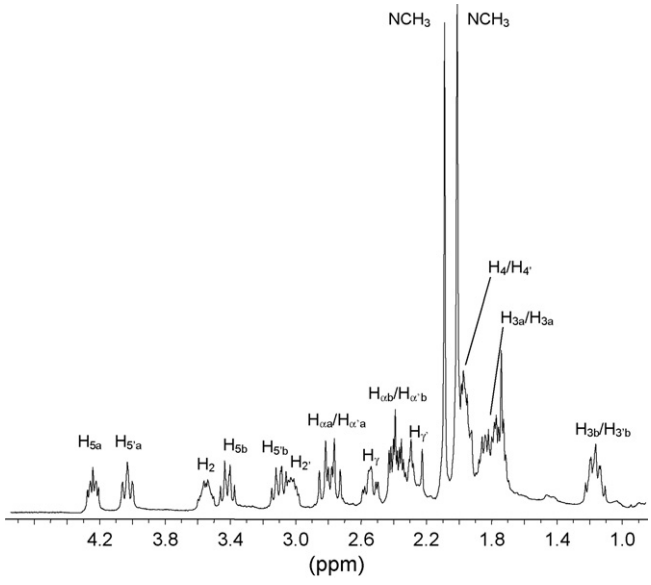
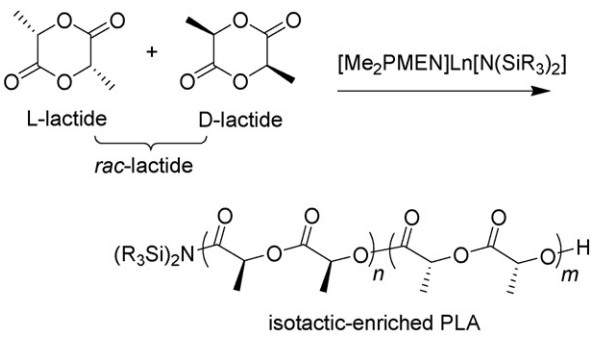


Fig. 1. Detail of the ^1H NMR spectrum of complex **2** (300 MHz, benzene-d_6, 300 K) (for atom numbering, see Scheme 1; descriptors a and b refer to the two hydrogen atoms of methylene groups).

well resolved resonances, which are spread from ca. δ 50 to −30 ppm. Though exact assignment was impossible, the number of resonances suggests that complex **3** is dissymmetric in toluene solution on the NMR timescale, as observed for **2**. On the other hand, the ^1H NMR spectrum of lanthanum complex **4** at 300 K in benzene-d_6 contains very broad signals in the range δ 4–0 ppm, indicative of a fluxional behavior which was not investigated in details. It is noteworthy that no resonances unambiguously attributable to a THF molecule were observed, which is consistent with the results of elemental analysis of **4** that indicate a THF-free complex (see Section 4).

2.2. Ring-opening polymerization of rac-lactide

The prepared $[Me_2PMEN]Ln(N(SiR_3)_2)$ complexes are active in the ROP of *racemic*-lactide under mild conditions (Scheme 2). Representative results are summarized in Table 1. Yttrium complex **2** allows complete conversion of 200 equiv. of lactide within 15 min at room temperature in toluene at [*rac*-LA] = 1.0 mol L^{-1} (entry 5). Polymerizations with this yttrium initiator/catalyst proceed much more slowly in THF (entries 1/4), presumably because of competitive coordination between the monomer and this donor solvent, as often observed in this type of ROP reactions promoted by oxophilic meta-based systems [9]. This difference in activity between toluene and THF solvent is not observed with complex **4** (entries 8/10); however, this lanthanum complex is significantly less active than its yttrium parent **2** in toluene medium (e.g., entries 2/9 and 4/10). Polymerizations of *rac*-lactide with $[Me_2PMEN]Ln(N(SiR_3)_2)$ complexes show overall a moderate degree of control: (i) The



Scheme 2. ROP of *rac*-lactide promoted by $[Me_2PMEN]Ln(N(SiR_3)_2)$ complexes **2** and **4**.

Table 1
Polymerization of *rac*-lactide promoted by [Me_2PMEN]Ln($N(SiR_3)_2$) complexes **2** and **4**[a]

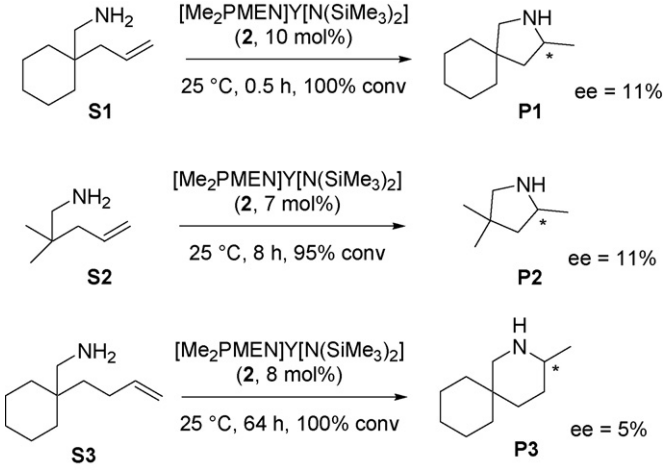
Entry	Complex	Solvent	T (K)	[LA]/[Ln]	Time[b] (min)	Yield[c]	$M_{n,exp}$[d] (g/mol)	M_w/M_n[d]	P_m[e] (%)
1	**2**	THF	298	100	10	27	49,600	1.72	47
2	**2**	Toluene	273	100	15	72	59,000	1.61	68
3	**2**	Toluene	273	200	10	35	89,600	1.32	71
4	**2**	Toluene	298	100	5	72	42,700	1.54	64
5	**2**	Toluene	298	200	10	93	58,700	1.67	66
6	**2**	Toluene	323	100	10	64	41,000	1.39	63
7	**2**	Toluene	323	200	10	71	42,700	1.39	63
8	**4**	THF	298	100	10	28	37,300	1.35	56
9	**4**	Toluene	273	100	15	5	31,700	1.53	50
10	**4**	Toluene	298	100	10	32	27,600	1.49	53
11[f]	**2**	Toluene	298	100	10	95	49,300	1.43	>99

[a] General conditions [LA] = 0.5–1.0 mol/L, T = 20 °C.
[b] Reaction time was not necessarily optimized.
[c] Yield of isolated polylactide, consistent within ±5% with monomer conversion as determined by ^{1}H NMR.
[d] Experimental (uncorrected) M_n and M_w/M_n values determined by GPC in THF vs. polystyrene standards.
[e] P_m is the probability of meso linkages between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum.
[f] L-Lactide was used instead of *rac*-lactide.

molecular weight distributions, though always unimodal and relatively narrow, are well above unity, in the range 1.32–1.72; these are usual polydispersity values for amido [–$N(SiMe_3)_2$, –$N(SiHMe_2)_2$]-metal initiators [5b], which are known to be less nucleophilic than other initiating groups such as alkoxides [9b,10]. (ii) In direct line with this latter observation, the experimental number-average molecular weights of the polylactides are always significantly higher than the calculated values, calling for low initiation efficiencies. (iii) The microstructure of the polymers, as determined by homo-decoupled ^{1}H NMR experiments [9,11], shows a noticeable enrichment in isotactic enchainments with a probability of meso linkages between monomer units (P_m) up to ca. 70% (entries 2 and 3). Similar to our observations with [amino-ether-bis(phenolate)]-lanthanide systems [9], decreasing the temperature resulted in a slight enhancement in stereoselectivity using **2** as the initiator (entries 2–7). Changing the solvent (toluene, THF) also affected the stereoselectivity in a quite sensitive manner (entries 1/4). On the other hand, the influence of these two factors was much less sensitive with the lanthanum complex **4** (entries 8/10). Polymerization of L-lactide by **2** (entry 11) resulted in pure isotactic PLA; the decoupled ^{1}H NMR spectrum of the polymer showed one sharp resonance for the methine region. This observation supports the lack of base-promoted epimerization of L-lactide or PLA and argues against an anionic polymerization mechanism being operative [12].

2.3. Asymmetric intramolecular hydroamination

Intramolecular asymmetric hydroamination reactions are nowadays explored by numerous groups as an efficient atom economical way towards the formation of valuable nitrogen-containing heterocycles. Various chiral non-cyclopentadienyl lanthanide complexes proved indeed active to perform such transformations, as was reported in the last 3 years [13]. In this context, complexes **2** and **3** were tested for the hydroamination/cyclization of some aminoalkenes. As can be seen from Scheme 3, complex **2** allowed the rapid cyclization of *C*-(1-allyl-cyclohexyl)-methylamine (**S1**) in less than half an hour at room temperature, albeit with the formation of the expected corresponding spiropyrrolidine (**P1**) with a low ee (11%). Complex **2** is active enough to catalyze this transformation at 0 °C (3.5 h for 100% conversion) but the selectivity was only marginally improved (13% ee). 2,2-Dimethyl-pent-4-enylamine (**S2**), renowned as the test substrate to classify the efficiency of hydroamination catalysts [13], was cyclized into **P2** with a nearly quantitative conversion at room temperature within 8 h. Unfortunately, pyrrolidine **P2** was obtained in only 11% ee. Furthermore, catalyst **2** was tested in the more challenging synthesis of spiropiperidine **P3**. This product was interestingly obtained by cyclization of the corresponding aminohexene **S3** at room temperature after 64 h reaction time. 3-Methyl-2-aza-spiro[5,5]undecane **P3** was obtained with only 5% ee. However, to the best of our knowledge, this reaction represents the first room temperature synthesis of a piperidine derivative obtained



Scheme 3. Asymmetric intramolecular hydroamination of primary aminoalkenes promoted by [Me_2PMEN]Y($N(SiR_3)_2$) (**2**).

by aminoalkene hydroamination promoted by non-metallocene lanthanide complexes.

The parent neodymium complex **3** was also used as catalyst in the transformation of **S1** but was found to be less active than complex **2**. 3-Methyl-2-aza-spiro[4,5]decane **P1** was indeed obtained with 72% conversion and 12% ee, after 20 h reaction time.

3. Conclusion

In conclusion, we have readily prepared new amido–lanthanide complexes derived from a chiral tetradentate N_4-ligand. Those complexes, in particular the yttrium derivative **2**, feature significant catalytic activity in the isospecific ring-opening polymerization of racemic lactide, as well as for the asymmetric room temperature hydroamination/cyclization of aminoalkenes. Though, the overall performances of these catalytic processes are plagued by the poor degree of control of the polymerization and the low enantioselectivity of the formed amines, respectively.

4. Experimental section

4.1. General considerations

Synthesis of lanthanide complexes and catalytic experiments were carried out under a purified argon atmosphere using standard Schlenk techniques or in a high performance (<1 ppm O_2, <2 ppm H_2O) glove box. Solvents (toluene, benzene, pentane, THF) and deuterated solvents ([D_6]benzene, [D_8]toluene, [D_8]THF/99.5% D, Eurisotop) were freshly distilled from Na/K alloy under nitrogen and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. The H_2(Me_2PMEN) ligand [8] and lanthanide precursor La[$N(SiHMe_2)_2$]$_3$(THF)$_2$ [14], were prepared following reported procedures. Racemic lactide and *S*-lactide (Aldrich) were recrystallized twice from dry toluene and then sublimed under vacuum at 50 °C. *C*-(1-allyl-cyclohexyl)-methylamine **S1** [13e], 2,2-dimethyl-pent-4-enylamine **S2** [13d], and *C*-(1-but-3-enyl-cyclohexyl)-methylamine **S3** [13e] were prepared according to reported procedures.

4.2. Instruments and measurements

NMR spectra were recorded on Bruker AC-300 and AC-500 spectrometers in Teflon valve NMR tubes at ambient temperature (300 K). ^{1}H and ^{13}C chemical shifts are reported in ppm versus $SiMe_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was made from multinuclear 1D (^{1}H, ^{13}C{^{1}H}) and 2D (COSY, HMQC, HMBC,) NMR experiments. Coupling constants are given in Hertz. Size exclusion chromatography (SEC) of PLAs was performed in THF at 20 °C using a Waters SIS HPLC pump, a Waters 410 refractometer, a DAD-UV detector and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration. Microstructure of PLAs was measured by homodecoupling ^{1}H NMR spectroscopy at 20 °C in $CDCl_3$ on a Bruker AC-500. Enantiomeric excesses of the products obtained by intramolecular hydroamination were determined by GC or HPLC analyses after derivatization, and compared to racemic products prepared with Y[$N(TMS)_2$]$_3$. The methods detailed for each compound have been previously reported [13e].

4.3. [Me_2PMEN]Y{$N(SiMe_3)_2$} (2)

A solution of H_2[Me_2PMEN] (0.420 g, 1.70 mmol) in toluene (5 mL) was added dropwise to a solution of Y($N(SiMe_3)_2$)$_3$ (0.969 g, 1.70 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 48 h, and volatiles were removed in vacuo to leave **2** as an off-white powder, which was washed with a minimal amount of cold pentane and dried in vacuum (0.850 g, 99%). ^{1}H NMR (C_6D_6, 300 K): δ 4.23 (m, 1H, H-5a), 4.02 (t, 1H, H-5′a), 3.55 (m, 1H, H-2), 3.41 (q, 1H, H-5b), 3.10 (m, 1H, H-5′b), 3.05 (m, 1H, H-2′), 2.78 (m, 2H, H-αa and H-α′a), 2.53 (m, 2H, H-γ), 2.39 (m, 2H, H-αb and H-α′b), 2.29 (m, 2H, H-γ′), 2.08 (s, 3H, NCH_3), 2.00 (s, 3H, NCH_3), 1.96 (m, 4H, H-4 and H-4′), 1.83 (m, 1H, H-3a), 1.76 (m, 1H, H-3′a), 1.16 (m, 2H, H-3b and H-3′b), 0.48 (s, 18H, $SiMe_3$). ^{13}C{^{1}H} NMR (C_6D_6, 300 K): δ 67.94 (C-α), 66.31 (C-α′), 63.05 (C-2 and C-2′), 58.54 (C-γ), 55.18 (C-γ′), 52.68 (C-5), 52.35 (C-5′), 48.43 (NCH_3), 40.98 (NCH_3), 31.86 (C-3), 31.74 (C-3′), 28.08 (C-4), 27.04 (C-4′), 4.80 ($SiMe_3$). Anal. Calcd. for $C_{20}H_{46}N_5Si_2Y$ (501.69 g mol^{-1}): C, 47.88; H, 9.24; N, 13.96. Found: C, 47.68; H, 8.93; N, 13.97.

4.4. [Me_2PMEN]Nd{$N(SiMe_3)_2$} (3)

Complex **3** was prepared as described above for **2** starting from H_2[Me_2PMEN] (0.200 g, 0.80 mmol) and Nd($N(Si(CH_3)_3)_2$)$_3$ (0.508 g, 0.80 mmol) in toluene (10 mL). Complex **3** was isolated as olive green crystals after recrystallization from pentane at −35 °C (0.323 g, 70%). ^{1}H NMR (toluene-d_8, 300 K) (all singlet like resonances): δ 52.67, 49.79, 43.89, 35.5, 35.05, 33.25, 14.14, 10.96, 10.29, 8.99, 7.38, 3.63, 3.05, 2.64, 2.18, −2.81, −3.59, −4.01, −4.62, −4.81, −5.96, −6.62, −9.10 (strong intensity), −19.07, −27.25, −28.34. Anal. Calcd. for $C_{20}H_{46}N_5Si_2Nd$ (577.02 g mol^{-1}): C, 43.12; H, 8.32; N, 12.57. Found: C, 42.64; H, 7.86; N, 12.00.

4.5. [Me_2PMEN]La{$N(SiHMe_2)_2$} (4)

A solution of H_2[Me_2PMEN] (0.100 g, 0.40 mmol) in toluene (5 mL) was added dropwise to a solution of La($N(SiHMe_2)_2$)$_3$(THF)$_2$ (0.217 g, 0.40 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature for 4 days; NMR spectroscopy revealed complete conversion of the reagents with release of 2 equiv. of $HN(SiHMe_2)_2$ (^{1}H NMR: δ = 4.71, 0.11 ppm; ^{13}C NMR: δ = 0.23). The volatiles were removed in vacuo to leave a light yellow-brown viscous oil, which was triturated with pentane (ca. 15 mL) to form a brown precipitate. The brownish powder obtained after evapo-

ration was washed with a minimal amount of cold pentane and dried in vacuum (0.152 g, 70%). The ^{1}H NMR spectra (toluene-d_8 or benzene-d_6, 298 K) featured very broad, uninformative resonances. Anal. Calcd. for $C_{18}H_{42}N_5Si_2La$ (523.64 g mol^{-1}): C, 41.29; H, 8.08; N, 13.37. Found: C, 40.79; H, 8.29; N, 13.33.

4.6. General procedure for rac-lactide polymerization

In the glovebox, a Schlenk flask was charged with a solution of the complex (typically 0.02 mmol, ca. 10 mg) in toluene (0.2 mL) or THF (0.2 mL). To this solution was added rapidly a solution of *rac*-lactide in the appropriate ratio in toluene or THF (3.0 mL). The mixture was immediately stirred with a magnetic stir bar at room temperature. Aliquots were periodically removed with a pipette for monitoring by ^{1}H NMR. After the desired time (typically 10 min), the reaction was quenched with acidic methanol (0.5 mL of a 15 wt% HCl solution in MeOH), and the polymer was precipitated with excess methanol (100 mL). The polymer was then filtered, dried under vacuum to constant weight. Polymerization experiments conducted at 273 and 323 K were conducted similarly by setting the Schlenk flasks at the appropriate temperature.

4.7. General procedure for NMR-scale hydroamination-cyclization of aminoalkenes

In an argon-filled glove box, the appropriate aminoalkene (0.15 mmol) was dissolved in C_6D_6 (0.1 mL) and dried on 4 Å molecular sieves for 2 h. Complexes **2** or **3** (see Scheme 3 for the corresponding catalytic ratio) was introduced into an NMR tube equipped with a Teflon screw cap and dissolved in C_6D_6 (0.5 mL) and the aminoalkene solution was then introduced. The hydroamination reaction was monitored by ^{1}H NMR by observation of the decreasing of the olefinic protons signals. After the reaction time mentioned in Scheme 3, the reaction was quenched with CH_2Cl_2. The enantiomeric excesses were determined either by NMR after reaction with Mosher chloride (for pyrrolidines **P1** and **P2**) or by HPLC after naphthoylation (for piperidine **P3**) [13e].

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References

[1] (a) D.D. Graf, W.M. Davis, R.R. Schrock, Organometallics 17 (1998) 5814–5820;
(b) A. Spannenberg, P. Arndt, R. Kempe, Angew. Chem. Int. Ed. 37 (1998) 832–835;
(c) A. Spannenberg, M. Oberthür, H. Noss, A. Tillack, P. Arndt, R. Kempe, Angew. Chem. Int. Ed. 37 (1998) 2079–2082;
(d) P.W. Roesky, Inorg. Chem. 37 (1998) 4507–4511;
(e) H. Noss, M. Oberthür, C. Fischer, W.P. Kretschmer, R. Kempe, Eur. J. Inorg. Chem. (1999) 2283–2288;
(f) T.I. Gountchev, T.D. Tilley, Organometallics 18 (1999) 2896–2905;
(g) P.W. Roesky, M.R. Bürgstein, Inorg. Chem. 38 (1999) 5629–5632;
(h) P.W. Roesky, Organometallics 21 (2002) 4756–4761;
(i) S. Bambirra, S.J. Boot, D. van Leusen, A. Meetsma, B. Hessen, Organometallics 23 (2004) 1891–1898;
(j) D.V. Vitanova, F. Hampel, K.C. Hultzsch, J. Organomet. Chem. 690 (2005) 5182–5197;
(k) D.V. Vitanova, F. Hampel, K.C. Hultzsch, Dalton Trans. 9 (2005) 1565–1566.
[2] (a) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J.H. Teuben, Chem. Commun. (2001) 537;
(b) C.G. Tazelaar, S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J.H. Teuben, Organometallics 23 (2004) 936–939;
(c) B. Hessen, S. Bambirra, World Patent WO 02/32909 (to ExxonMobil);
(d) J. Gromada, J.-F. Carpentier, A. Mortreux, Coord. Chem. Rev. 248 (2004) 397–410.
[3] (a) W.E. Piers, D.J.H. Emslie, Coord. Chem. Rev. 233–234 (2002) 131–155;
(b) F.T. Edelmann, D.M.M. Freckmann, H. Schumann, Chem. Rev. 102 (2002) 1851–1896.
[4] (a) S. Mecking, Angew. Chem. Int. Ed. 43 (2004) 1078–1085;
(b) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147–6176;
(c) J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, Coord. Chem. Rev. 250 (2006) 602–626;
(d) A. Amgoune, C.M. Thomas, J.-F. Carpentier, Pure Appl. Chem., in press.
[5] See for instance;
(a) K.B. Aubrecht, K. Chang, M.A. Hillmyer, W.B. Tolman, J. Polym. Sci., A: Polym. Chem. 39 (2001) 284–293;
(b) A. Alaaeddine, A. Amgoune, C.M. Thomas, S. Dagorne, S. Bellemin-Laponnaz, J.-F. Carpentier, Eur. J. Inorg. Chem. (2006) 3652–3658;
(c) P.B. Hitchcock, Q. Huang, M.F. Lappert, X.-H. Wei, M. Zhou, Dalton Trans. 24 (2006) 2991–2997;
(d) L.F. Sanchez-Barba, D.L. Hughes, S.M. Humphrey, M. Bochmann, Organometallics 25 (2006) 1012–1020.
[6] (a) G. Molander, J.A.C. Romero, Chem. Rev. 102 (2002) 2161–2185;
(b) A.S. Hong, T.J. Marks, Acc. Chem. Res. 37 (2004) 673–686.
[7] (a) M.R. Bürgstein, P.W. Roesky, Organometallics 22 (2003) 1372–1375;
(b) P.W. Roesky, J. Organomet. Chem. 621 (2001) 277–283.
[8] J.-F. Carpentier, A. Martin, D.C. Swenson, R.F. Jordan, Organometallics 22 (2003) 4999–5010.
[9] (a) C.-X. Cai, A. Amgoune, C.W. Lehmann, J.-F. Carpentier, Chem. Commun. (2004) 330–331;
(b) A. Amgoune, C.M. Thomas, T. Roisnel, J.-F. Carpentier, Chem. Eur. J. 12 (2006) 169–179.
[10] (a) M. Cheng, A.B. Attygalle, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 121 (1999) 11583–11584;
(b) H. Ma, J. Okuda, Macromolecules 38 (2005) 2665–2673.
[11] (a) K.A.M. Thakur, R.T. Kean, E.S. Hall, J.J. Kolstad, T.A. Lindgren, M.A. Doscotch, J.I. Siepmann, E.J. Munson, Macromolecules 30 (1994) 2422–2428;
(b) J.E. Kasperczyk, Macromolecules 28 (1995) 3937–3939.
[12] (a) B.M. Chamberlain, Y. Sun, J.R. Hagadorn, E.W. Hemmesch, V.G. Young Jr., M. Pink, M.A. Hillmyer, W.B. Tolman, Macromolecules 32 (1999) 2400–2402;
(b) M.H. Chisholm, N.W. Eilerts, Chem. Commun. (1996) 853–854.
[13] (a) K.C. Hultzsch, Adv. Synth. Catal. 347 (2005) 367–391;
(b) S. Hong, S. Tian, M.V. Metz, T.J. Marks, J. Am. Chem. Soc. 125 (2003) 14768–14783;
(c) P.N. O'Shaughnessy, K.M. Gillespie, P.D. Knight, I. Munslow, P. Scott, Dalton Trans. (2004) 2251–2256;
(d) J.Y. Kim, T. Livinghouse, Org. Lett. 7 (2005) 1737–1739;
(e) D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, J. Org. Chem. 71 (2006) 2514–2517;
(f) D.V. Gribkov, K.C. Hultzsch, F. Hampel, J. Am. Chem. Soc. 128 (2006) 3748–3759;

(g) N. Meyer, A. Zulys, P.W. Roesky, Organometallics 25 (2006) 4179–4182;
(h) M. Rastätter, A. Zulys, P.W. Roesky, Chem. Commun. (2006) 874–876;
(i) M.C. Wood, D.C. Leitch, C.S. Yeung, J.A. Kozak, L.L. Schafer, Angew. Chem. Int. Ed. 45 (2006) 1–5;
(j) D.A. Watson, M. Chiu, R.G. Bergman, Organometallics 25 (2006) 4731–4733.

[14] (a) K.C. Hultzsch, P. Voth, K. Beckerle, T.P. Spaniol, J. Okuda, Organometallics 19 (2000) 228–243;
(b) R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck, M. Spiegler, J. Chem. Soc., Dalton Trans. (1998) 847–858.