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Synthesis and ROMP activity of aminophenol-substituted tungsten(VI) and molybdenum(VI) complexes

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Abstract

Tungsten(VI) and molybdenum(VI) complexes $[MO(L^1)Cl_2]$ and $[M(X)(L^2)Cl_3]$ (X = O, NPh) with tridentate aminobis(phenolate) ligand L^1 = methylamino-N,N-bis(2-methylene-4,6-dimethylphenolate) and bidentate aminophenolate ligand L^2 = 2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenolate) were prepared and characterised. These complexes are principally stable in open atmosphere under ambient conditions. When activated with Et_2AlCl, they exhibited high activity in ring-opening metathesis polymerisation (ROMP) of 2-norbornene (NBE) and its derivatives. Especially complexes $[M(NPh)(L^2)Cl_3]$, which are easily available from corresponding metal oxides MO_3 by a simple three-step synthesis, were found very efficient ROMP catalysts for NBE (M = Mo, W) and 2-norbornen-5-yl acetate (M = Mo).
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1. Introduction

Olefin metathesis reaction has become a standard procedure to manipulate carbon–carbon bonds in the syntheses of polymers, fine-chemicals and pharmaceuticals [1]. Modern, well-defined catalysts for olefin metathesis comprise a high-valent metal ion (Mo, W or Re) surrounded by alkoxido and imido spectator ligands and a reactive carbene ligand [2]. However, these catalysts are highly sensitive to atmospheric oxygen and moisture and are rather expensive. Similarly, the costs of well-defined Ru alkylidene complexes [3] represent an important disadvantage for their practical application. On the other hand, a number of relatively cheap Mo(VI) and W(VI) complexes with labile ligands can be activated by main-group organometallics

to obtain active catalysts [4–6]. It is assumed that the main role of these activators consists in the substitution of two labile ligands on a transition metal with alkyl groups. The resultant organometallic intermediate would then undergo an α-elimination reaction to give the corresponding alkylidene complex. Recently, W and Mo complexes with chelating aryloxo ligands have attracted attention as very active catalyst precursors for controlled ROMP [7–9]. Especially, W(VI) phenolate complexes with additional oxo and imido ligands were reported as precursors for highly efficient as well as highly stereoselective ROMP catalysts [9]. Preparation of these complexes was simple in comparison with that of well-defined carbene complexes. For practical reasons, these aryloxo complexes were studied mainly in the polymerization of 2-norbornene (NBE) and dicyclopentadiene (DCPD); therefore there is no information about their efficiency in the metathesis of polar substituted monomers.

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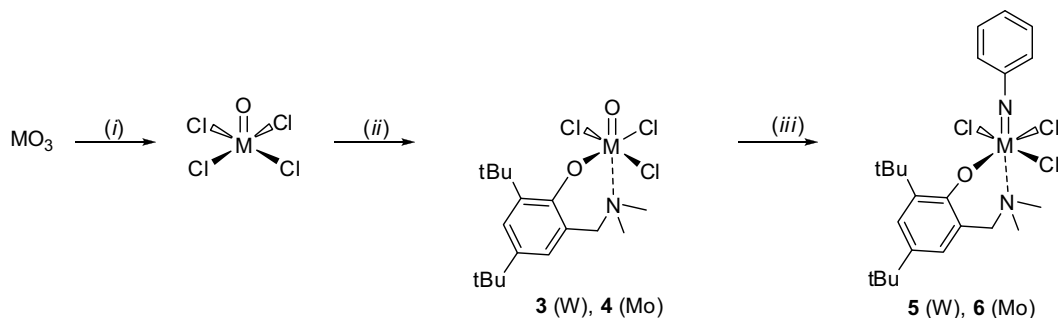
Scheme 1. Preparation of aminophenol complexes. Conditions: (i) SOCl$_2$, reflux. (ii) HL^2, PhMe, reflux, 2 h (**3**) or 3 h (**4**). (iii) PhNCO, PhMe, reflux, 2 h.
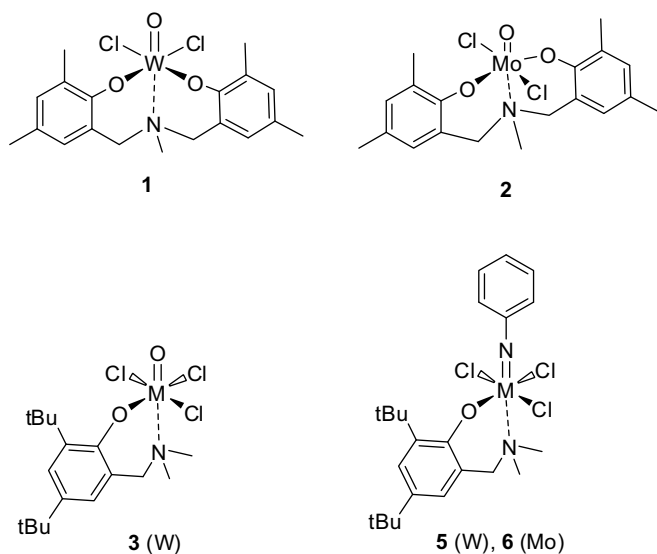

Chart 1. W(VI) and Mo(VI) complexes prepared and used as catalyst precursors in this study.

We have earlier introduced a family of aminobis(phenolato) complexes of Mo(VI) and W(VI) and acquired some tentative results on their activity in ROMP of NBE [10]. In preliminary tests, the obtained activities has been disappointingly low, possibly due to the rigid ligand framework, which prevents the necessary reorientation of the coordination sphere. Thus, we decided to prepare new W(VI) and Mo(VI) complexes with bidentate aminophenolate ligand and compare their suitability as catalyst precursors in ROMP of NBE DCPD and 2-norbornen-5-yl acetate (NBEAc). Catalyst precursors studied in this work are shown in Scheme 1 (Chart 1).

2. Results and discussions

2.1. Preparation of catalyst precursors

Earlier, we reported a high-yield synthesis of *cis*-[WOCl$_2$(L^1)] (**1**) (L^1 = methylamino-*N,N*-bis(2-methylene-4,6-dimethylphenolate) dianion) in addition to some preliminary results on ROMP of norbornene [10a]. *trans*-[MoOCl$_2$(L^1)] (**2**) was also previously prepared by the

chlorination reaction of [{MoO$_2$(L^1)}$_2$] [10e], however in the present study it was synthesised straightforwardly in a high-yield by heating [MoO$_2$Cl$_2$(dmf)$_2$] (dmf = dimethylformamide) with a stoichiometric amount of methylamino-*N,N*-bis(2-methylene-4,6-dimethylphenol), H$_2$L^1 in a toluene suspension. This monooxido complex is formally
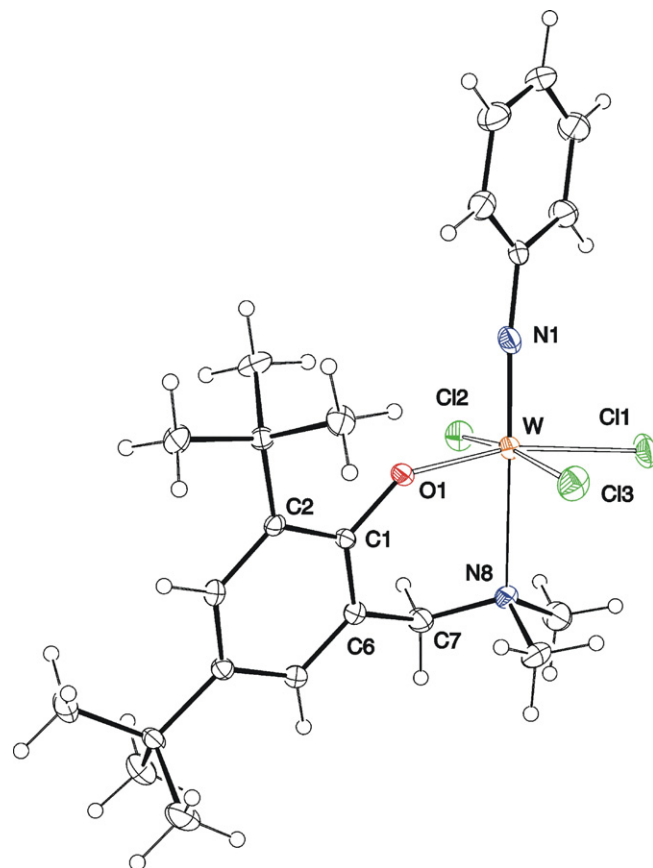

Fig. 1. Crystal structure of **5**. Thermal ellipsoids have been drawn by 30% probability. Selected bond distances (Å) and angles (°): W–N1: 1.730(3); W–O1: 1.870(2); W–Cl2: 2.3514(9); W–Cl1: 2.3551(9); W–Cl3: 2.3725(10); W–N8: 2.452(3). N1–W–O1: 99.02(11); N1–W–Cl2: 94.32(10); O1–W–Cl2: 92.88(7); N1–W–Cl1: 94.87(9), O1–W–Cl1: 165.82(7); Cl2–W–Cl1: 88.85(4); N1–W–Cl3: 94.41(10); O1–W–Cl3: 89.42(7); Cl2–W–Cl3: 170.51(4); Cl1–W–Cl3: 86.71(4); N1–W–N8: 177.41(12); O1–W–N8: 80.78(9); Cl2–W–N8: 83.12(7); Cl1–W–N8: 85.47(7).
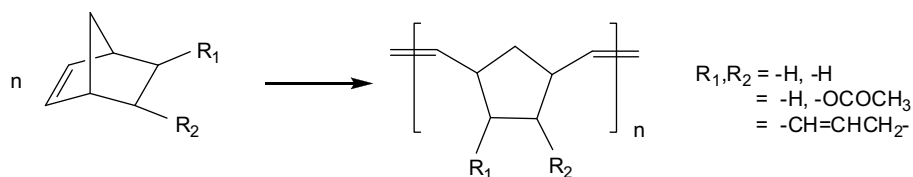
Scheme 2. ROMP of norbornene and its derivatives.

generated by a condensation reaction of a Mo=O group with two phenol moieties of the ligand molecule. According to the literature examples on the related reactions [11], we may suggest that in the first step the ligand H_2L^1 is coordinated to the MoO_2Cl_2 unit as a neutral nitrogen donor. This is subsequently followed by an addition of OH group across one of the Mo=O bonds to form an intermediate $MoO(OH)Cl_2(HL^1)$, which immediately reacts further to eliminate water and yield the ultimate product.

A stoichiometric reaction of a phenolic precursor HL^2 with $WOCl_4$ in a refluxing toluene solution leads to the selective substitution of one of the chlorides with a phenoxide group. Evaporation of the solvent and HCl co-product afforded complex 3 as a dark red crystalline solid. Solid compound is stable for several hours in open atmosphere, but it decomposes slowly in solution to form a pale gray deposit. Nevertheless, complex 3 was stable enough for catalyst tests and for further synthesis. In situ prepared MoOCl_4 seems to react similarly as $WOCl_4$, but our attempts to isolate and characterise the formed molybdenum compound 4 failed due to the low stability of the dark blue product. However, the dark blue crude mixture, which contains supposedly an adequate amount of 4, was used in the preparation of an imido derivative (see below).

Transition metal oxido compounds are known to react with alkyl and aryl isocyanates to produce corresponding metal imido complexes [12]. When complex 3 was heated in toluene solution with one equivalent of phenyl isocyanate, the reaction proceeded efficiently to produce imido derivative 5. This dark red tungsten compound is surprisingly stable under ambient atmosphere, and it was easily purified by crystallization from hot acetonitrile. Intense blue molybdenum compound 6 was prepared directly by the three-step reaction from MoO_3 without isolation or purification of the intermediates. The complex 6 is less stable in solution at elevated temperature than its tungsten counterpart, for example, it decomposed in hot acetonitrile solution during attempted crystallization. However, 6 is stable when dissolved in organic solvents at room temperature, so it could be purified by column chromatography and used in catalyst tests. Consequently, the total yield of 6 was noticeably lower than that for 5.

The solid-state structure of 5 was verified by X-ray diffraction (Fig. 1). As expected, the central W(VI) ion is surrounded by one terminal phenyl imido group, one bidentate aminophenolate and three chlorides. The NMe_2 group of the chelating ligand is bonded trans to the imido ligand, whereas the phenoxide oxygen and chlorides are arranged equatorially. The W–N1 distance of 1.730(3) Å is typical for phenyl imido double bond [13–15], while other intramolecular contacts to the W(VI) ion are comparable with those found for oxotungsten(VI) complexes with aminobis(phenol)s [10a]. Consequently, the overall

Table 1
Results of ROMP experiments with W and Mo aminophenolato complexes applied as catalyst precursors

Catalyst precursor	Monomer	Monom./W (Mo) mole ratio	Reaction time (h)	Temperature (°C)	Polymer yield (%)	Polymer 10^{-3} M_w (M_n)	cis content (%)
1[a]	NBE	100	5	60	0.8	– insol.	– insol.
1	NBE	100	3	60	89	– insol.	– insol.
1	DCPD	200	3	60	93	– insol.	– insol.
1	NBEAc	60	9	60	31	530 (83)	65
2	NBE	100	2	rt	77	– insol.	– insol.
2	NBEAc	60	9	60	33	710 (200)	48
3[b]	NBE	100	2	rt	100	– insol.	– insol.
3[b]	NBEAc	60	9	60	49	370 (39)	69
5	NBE	120	2	rt	100	– insol.	– insol.
5	NBEAc	60	9	60	14	450 (96)	82
6[a]	NBE	100	5	60	0	– insol.	– insol.
6	NBE	120	1	rt	95	– insol.	– insol.
6	NBEAc	60	7	60	72	740 (95)	86
6[c]	NBEAc	330	4	60	100	710 (100)	86

Benzene, $Et_2AlCl/W(Mo)$ mole ratio = 5, initial catalyst precursor concentration $[c]_o$ = 3 mmol/l.
[a] Without Et_2AlCl.
[b] Catalyst precursor soluble only partially.
[c] $[c]_o$ = 1.5 mmol/l.

structure of **5** is closely similar to that found for [W(NPh)(OC$_6$H$_2$(CH$_2$NMe$_2$)$_2$-2,6-Me-4)Cl$_3$] [13].

2.2. Catalyst tests

The complexes synthesized were used as catalyst precursors in the ROMP of NBE, DCPD, and NBEAc (Scheme 2).

The results on the catalyst tests are presented in Table 1. It was found that the use of aluminium co-catalyst Et$_2$AlCl was necessary to obtain any activity. Polymerisation of DCPD and NBE yielded rubber-like materials in nearly quantitative yields, but these polymers were not characterised due to the poor solubility. It is known that in ROMP of functionalized cycloolefins, W and Mo based catalysts exhibit generally lower activity because of the interaction of monomer polar groups with catalyst components [16]. Therefore, the application of elevated temperature, prolonged reaction times and higher catalyst to monomer mole ratios is recommended in these cases. Under such conditions high molecular weight poly(NBEAc)s were prepared with all catalytic systems tested. Polymers were white solids well soluble in common organic solvents. The cis double bond content (determined as the signal ratio at $\delta = 41.7$ ppm and 47.2 ppm in ^{13}C NMR spectra [17]) varied from 0.48 to 0.82 according to the catalyst precursor used. The highest *cis*-selectivity was achieved with complexes having phenylimido ligands **5** and **6**. Mo complex **6** exhibited the highest activity delivering high molecular weight poly(NBEAc) in a quantitative yield at relatively low catalyst/monomer molar ratio (1/330). This activity was significantly higher than that of classical systems based on W and Mo chlorides [17–19].

3. Conclusion

New W(VI) and Mo(VI) complexes with tridentate aminobis(phenolate) and bidentate aminophenolate ligands were prepared. Most of them are long-time stable in open atmosphere under ambient conditions. In combination with Et$_2$AlCl, these complexes can be applied in ROMP of norbornene and its derivatives. Especially complexes [M(NPh)(L^2)Cl$_3$] (L^2 = 2,4-di-*tert*-butyl-6-((dimethylamino)methyl)phenolate), stable on air, exhibited high activity in ROMP of NBE and for M = Mo also high activity and cis selectivity in ROMP of NBEAc.

4. Experimental

4.1. General comments

WOCl$_4$ [20] and ligand precursors H$_2$L^1 [21] and HL^2 [22] were prepared and purified according to the literature. Other chemicals were of reagent grade and were used as purchased. ^{1}H NMR (400 MHz) and ^{13}C spectra (100 MHz) were recorded in CDCl$_3$ solutions and were referenced to SiMe$_4$ and/or to the sol-

vent signal ($\delta_C = 77.00$ ppm). Reactions were carried out under a N$_2$ atmosphere by using standard bench-top techniques.

4.2. Reaction of H$_2$L^1 with [MoO$_2$Cl$_2$(dmf)$_2$]

1.00 mmol (345 mg) of [MoO$_2$Cl$_2$(dmf)$_2$] and 1.00 mmol (300 mg) of a ligand precursor H$_2$L^1 were mixed with 30 ml of PhMe. The stirred reaction mixture was heated at reflux temperature for 45 min to obtain a dark blue solution, which was cooled to the room temperature, filtered through a short pad of silica and subsequently evaporated to obtain **2** as a dark blue solid. NMR and elemental analyses match those reported earlier by us [10e]. Yield: 435 mg (90%). ^{1}H NMR (CDCl$_3$): δ 7.10 (s, 2H, ArH), 6.92 (s, 2H, ArH), 4.87 (d, $J = 13.0$ Hz, 2H, Ar–CH$_2$), 3.10 (d, $J = 13.0$ Hz, 2H, Ar–CH$_2$), 2.55 (s, Ar–CH$_3$, 6H), 2.48 (s, 6H, Ar–CH$_3$) 1.85 (s, 3H, N–CH$_3$) ppm. ^{13}C NMR (CDCl$_3$): δ 160.82, 138.90, 130.73, 129.22, 129.10, 128.29, 62.82, 46.79, 21.07, 16.32 ppm. Anal. Calc.: C$_{19}$H$_{23}$Cl$_2$-MoNO$_3$ requires: C, 47.52; H, 4.83; N, 2.92. Found: C, 47.84; H, 5.03; N, 2.68%.

4.3. Reaction of HL^2 with WOCl$_4$

WOCl$_4$ (340 mg, 1.0 mmol) was suspended in 20 ml of CH$_2$Cl$_2$ and subsequently treated with one equivalent of HL^2 (263 mg) to form an intense red mixture. The reaction mixture was allowed to reflux while the reaction was monitored by TLC (PhMe as an eluent). After two hours, the TLC analysis showed a single purple spot ($R_f = 0.85$), which discolours in a minute in air. The volatiles were then evaporated in a vacuum and the solid residue was washed with hexane to obtain **3** as a dark purple crystalline solid. A dissolved product decomposes slowly during purification and analysis processes, but it was stable as a solid and pure enough for further syntheses. ^{1}H NMR (CDCl$_3$): δ 7.42 (1H, s, *ArH*), 7.01 (1H, s, *ArH*), 4.29 (2H, br, N–*CH$_2$*), 2.99 (6H, s, N(*CH$_3$*)$_2$), 1.45 (9H, s, C(*CH$_3$*)$_3$), 1.30 (9H, s, C(*CH$_3$*)$_3$). NMR spectrum comprises also small signals for the free ligand. Anal. Calc.: C$_{17}$H$_{28}$Cl$_3$NO$_2$W requires: C, 35.91; H, 4.96; N, 2.46. Found: C, 35.70; H, 4.83; N, 2.66%.

4.4. Preparation of [W(NPh)(L^2)Cl$_3$]

1.3 mmol of complex [WO(L^2)Cl$_3$] was prepared as described above and dissolved in 15 ml of toluene. 1.4 mmol (0.15 ml) of phenyl isocyanate was added and the purple solution was heated to the reflux temperature for 11/2 h while the reaction was monitored by TLC. Volatiles were then removed in vacuum and the red solid residue was crystallized from 5 ml of hot MeCN to obtain 590 mg (92%) of **5** as an air- and moisture-stable solid. ^{1}H NMR (CDCl$_3$): δ 7.65 (2H, t, $J = 7.9$ Hz, *NArH$_{meta}$*) 7.47 (1H, s, *OArH*), 7.38 (2H, d, $J = 7.5$ Hz, *NArH$_{ortho}$*), 7.09 (1H, t, $J = 7.5$ Hz, *NArH$_{para}$*), 7.07 (1H, s, *OArH*),

4.21 (2H, br, N–CH_2), 3.02 (6H, N(CH_3)$_2$), 1.48 (9H, s, C(CH_3)$_3$), 1.35 (9H, s, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$): δ 156.76, 151.21, 150.37, 140.69, 131.86, 130.16, 127.75, 127.60, 125.29, 124.43, 64.30, 51.43, 35.40, 34.81, 31.55, 30.83. Anal. Calc.: $C_{23}H_{33}Cl_3N_2OW$ requires: C, 42.93; H, 5.17; N, 4.35. Found: C, 42.90; H, 5.13; N, 4.55%.

4.5. Preparation of [Mo(NPh)(L^2)Cl$_3$]

1.0 mmol (145 mg) of MoO$_3$ was heated with 3 ml of SOCl$_2$ in the reflux temperature for 5 h until all solid was dissolved. All volatiles were then removed in vacuum and the dark green residue was suspended in 20 ml of CH$_2$Cl$_2$ and subsequently treated with one equivalent of HL^2 (263 mg) to form an intense blue mixture. The reaction mixture was allowed to reflux for 3 h. The solvent was then evaporated in vacuum and the blue solid residue was washed with hexane and then dissolved in 15 ml of toluene. 1.2 mmol (0.13 ml) of phenyl isocyanate was added and the blue solution was heated to the reflux temperature for 2 h while the reaction was monitored by TLC. The blue solution was cooled to the room temperature and filtered through the short pad of silica to obtain 197 mg (35%, based on MoO$_3$) of **6** as an air- and moisture-stable blue solid. ^{1}H NMR (CDCl$_3$): δ 7.83 (2H, t, $J = 7.0$ Hz, NArH_{meta}) 7.57 (2H, d, $J = 7.9$ Hz, NArH_{ortho}), 7.39 (1H, s, OArH), 7.38, (1H, t, $J = 7.0$ Hz, NArH_{para}), 7.12 (1H, s, OArH), 4.15 (2H, br, N–CH_2), 2.90 (6H, N(CH_3)$_2$), 1.46 (18H, s, C(CH_3)$_3$), 1.35 (18H, s, C(CH_3)$_3$). ^{13}C NMR (CDCl$_3$): δ 164.35, 154.74, 154.30, 141.26, 133.01, 130.83, 129.38, 128.78, 126.48, 124.41, 64.46, 51.26, 35.96, 35.45, 31.28, 31.11. Anal. Calc.: $C_{23}H_{33}Cl_3N_2MoO$ requires: C, 49.70; H, 5.98; N, 5.04. Found: C, 49.64; H, 5.84; N, 4.88%.

5. X-ray structure determination of 4

Single-crystal data collections, reduction and subsequent calculations were carried out in University of Jyväskylä essentially similarly as described in our earlier papers [10]. *Crystal data*: $C_{23}H_{33}Cl_3N_2OW$ (**6**); $M_r = 643.71$; red prisms, size (mm) $0.20 \times 0.18 \times 0.10$, monoclinic; space group $P2_1/n$; $Z = 4$; $a = 11.5190(2)$ Å; $b = 16.3500(4)$ Å; $c = 13.6978(3)$ Å; $\beta = 99.110(1)°$; $V = 2547.24(9)$ Å^3; $D_c = 1.679$ Mg m^{-3}; 6286 unique reflections (R(int) = 0.0518), 5136 observed ($I > 2\sigma(I)$), data/restraints/parameters = 6286/0/279, $R_1 = 0.0298$, $wR_1 = 0.0423$ (on $I > 2\sigma(I)$), $R_2 = 0.0626$, $wR_2 = 0.0589$ on all data.

6. Catalytic tests

Polymerization experiments were carried out in a batch stirred glass reactors under vacuum. Benzene (p.a., Lach-Ner, Czech Republic, purified by distillation and dried with calcium hydride) was used as a solvent. NBE (Aldrich, 99%), DCPD (Chemical Plants in Livinov, Czech Republic, stripped by nitrogen), NBEAc (Janssen Chimica, 98% purity, 80% of endo isomer, distilled in a vacuum) were used as

monomers. In a typical experiment 0.01 mmol of a catalyst precursor was placed in the reactor, then 3 ml of solvent and appropriate amounts of monomer were added. The reaction was started by charging Et$_2$AlCl (0.5 ml of 0.1 M solution in benzene from breakable vials). A polymer was isolated by pouring a reaction mixture into methanol, dried in a vacuum at 50 °C and weighed. SEC analyses of polymers were carried out on a Watrex Chromatograph fitted with a differential refractometer Shodex RI 101. A series of two PL-gel columns (Mixed-B and Mixed-C, Polymer Laboratories Bristol, UK) and THF (flow rate 0.7 ml/min) were used. Weight average molecular weight, M_w, and number average molecular weight, M_n, relative to polystyrene standards are reported.

Appendix A. Supplementary material

CCDC 666578 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.007.

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