Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 1610

www.rsc.org/dalton

PAPER

Novel heteroligated titanium complexes with fluorinated salicylaldiminato and β-enaminoketonato ligands: synthesis, characterization and catalytic behavior in vinyl addition polymerization of norbornene†

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Received 14th September 2010, Accepted 14th November 2010
DOI: 10.1039/c0dt01225d

A series of heteroligated (salicylaldiminato)(β-enaminoketonato)titanium complexes of the general formula [3-Bu^t-2-OC$_6$H$_3$CH═N(C$_6$F$_5$)][PhN═C(CF$_3$)CHC(R)O]TiCl$_2$ (**3a**: R═Ph, **3b**: R═C$_6$H$_4$Ph(*p*), **3c**: R═C$_6$H$_4$Ph(*o*), **3d**: R = 1-naphthyl, **3e**: R = C$_6$H$_4$F$_2$(2,6), **3f**: R = C$_6$H$_4$Cl$_2$(2,5), **3g**: R═C$_6$F$_4$(2,3,5,6)OMe(4)) were synthesized. The structure of complexes **3d**, **3f–g** were determined by single crystal X-ray diffraction analysis. The X-ray crystallographic analysis indicated these complexes adopted a distorted octahedral geometry around the titanium center. Upon activation with modified methylaluminoxane, complexes **3a–g** exhibited moderate to good catalytic activity for norbornene (NB) vinyl addition polymerization, producing moderate molecular weight polynorbornenes under mild conditions. The introduction of electron-withdrawing groups can greatly enhance the catalytic activity. Significantly, the heteroligated titanium complexes displayed greatly improved activity for vinyl addition polymerization of NB compared to homoligated counterparts, which may stem from the suitable combinations of electronic and steric effects.

Introduction

Polycycloolefins, *via* vinyl addition, have been widely used as high performance materials in the microelectronics industry because of their special properties (*e.g.* good heat resistivity and excellent dielectric properties), which led to increasing interest in the field of polyolefin research.[1] Of these cycloolefins with strained rings, norbornene (NB) is one of the most representative and industrially available examples. Vinyl addition polymerization of NB was first studied with TiCl$_4$/R$_3$Al in the early 1960s, but these systems and subsequent zirconocenes showed very low activities.[2] Thereafter, late transition-metal catalysts became the focus of attention because they displayed high activity for vinyl addition polymerization of NB.[3] A large number of complexes based on nickel,[4–5] palladium[6–7] chromium,[8] cobalt[8b,9] and copper[10] were subsequently reported for efficient NB vinyl addition polymerization. Palladium and nickel complexes were two typical and important types for NB vinyl polymerization. For example, cationic palladium complexes, such as [Pd(CH$_3$CN)$_4$]-[BF$_4$]$_2$, exhibited high catalytic activity and produced high molecular weight polymers that were soluble in organic solvents and possessed high *T*g's > 350 °C. However, palladium is very expensive. Research in our group and other groups indicated well-defined neutral nickel(II) complexes were efficient catalysts for vinyl polymerization of NB in the presence of methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), producing high molecular weight and amorphous poly(NB)s.[11–12] However, early transition metal complexes attracted little attention for NB vinyl addition polymerization despite the fact that they have been tested as active catalyst precursors for ethylene/NB copolymerization and ring-opening metathesis polymerization.[13–15]

Recently, some group IV single-site catalyst systems were reported for the vinyl addition polymerization of NB.[16–17] To the best of our knowledge, there have been only a few successful titanium complexes reported dealing with the vinyl addition homo-polymerization of NB. The half sandwich titanocene pre-catalyst (^{t}BuN-Me$_2$Si-Flu)TiMe$_2$[16d–e] showed good activities in the region of 10^6 g PNB /mol$_{Ti}$ h at 20 and 40 °C activated with MMAO. Complex (2-Me$_4$Cp-4,6-^{t}Bu$_2$-PhO)TiCl$_2$ also displayed catalytic activity up to 10^6 g PNB/mol$_{Ti}$ h in the presence of ^{i}Bu$_3$Al and Ph$_3$CB(C$_6$F$_5$)$_4$.[17a] However, from the structural point of view, all these titanium complexes were constrained geometry catalysts (CGCs)[17a] and low activities of about 10^3 g PNB/mol$_{Ti}$ h were observed in non-CGC systems.[16a–b] Hence, it would be interesting to know whether the constrained geometry of the titanium complexes was necessary for the achievement of high activity for vinyl addition polymerization of NB. Accordingly, we were prompted to synthesize some new non-bridged titanium complexes for NB polymerization based on the ligand-oriented catalyst design.

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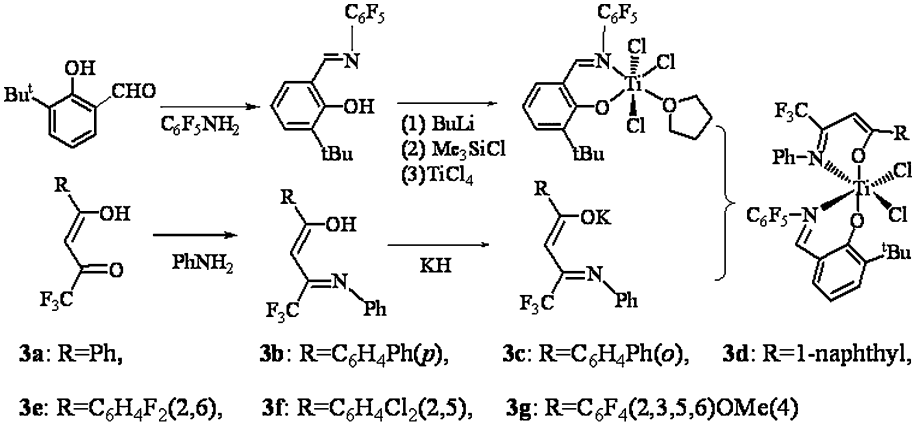
† CCDC reference numbers 791299–791301. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01225d



Scheme 1 General synthetic route of the heteroligated titanium complexes.

The complexes of group 4 transition metals bearing two phenoxy-imine chelate ligands (FI catalysts)[18–19] and bis(β-enaminoketonato) chelate ligands[20] are successful single site catalysts for ethylene/NB copolymerization, some of which displayed living catalytic nature and produced copolymers with NB incorporation up to 50 mol%. However, pentafluorinated complex $\{3\text{-Bu}^t\text{-(O)}C_6H_3CHN(C_6F_5)\}_2TiCl_2$ **1** showed almost no activity for NB polymerization due to its bulky hindrance.[21] The bis(β-enaminoketonato)titanium catalysts **2** exhibited very low activity for NB polymerization because of the less positive charge on the metal which would mitigate the coordination of NB to the metal center.[21] We reasoned an alternative approach to synthesizing complexes for high NB polymerization would be producing hybrids with a combination of two different ligands from **1** and **2**, affording catalysts with strong electron-withdrawing groups and an inherently open structure. We previously reported a family of heteroligated (salicylaldiminato)(β-enaminoketonato)titanium complexes which displayed high activities for ethylene/NB copolymerization with high NB incorporation,[22a] suggesting such catalysts might possess potential for NB homo-polymerization. Considering the fact that the variation of the ligand structure may lead to profound changes in the catalytic activity and the property of polymer, we were prompted to design and synthesize complexes **3a**–**g** with different electronic property and steric hindrance for comparison, investigating their NB vinyl addition polymerization behavior. As expected, the introduction of strong electron-withdrawing groups to β-enaminoketonato ligand of the complexes led to good catalytic activity (about 3.8×10^5 $g_{polymer}/mol_{Ti}$ h) for NB vinyl addition polymerization. The results discussed here would provide a new strategy to design catalysts for special olefin polymerization.

Results and discussion

Synthesis and characterization of the titanium complexes

A general synthetic route for the heteroligated titanium complexes used in this study[22] is shown in Scheme 1. β-Enaminoketone ligands were prepared following our reported method[23] while salicylaldiminato ligand was synthesized according to the procedures reported previously.[18b] A tandem sequence of Claisen condensation between methyl ketones and ethyl trifluoroacetate and the condensation of the resulting β-diketone with aniline in acidic toluene was used to synthesize the new β-enaminoketones in moderate to high yields (55–82%). Salicylaldiminato ligand was synthesized in high yield (80%) by the Schiff base condensation of the corresponding fluorine-containing aniline with $3\text{-Bu}^t\text{-(O)}C_6H_3CHO$ using an acid as a catalyst. The systematic synthesis of heteroligated complexes required a stepwise approach through a mono(ligand) intermediate. First, treatment of $TiCl_4$ in toluene with the trimethylsilyl ether derivatives of an iminophenol provided a facile route to complex $\{3\text{-Bu}^t\text{-(O)}C_6H_3CHN\,(C_6F_5)\}TiCl_2(THF)$. Then, deprotonation of the β-enaminoketonates with KH in dichloromethane solution afforded the corresponding potassium salts. Subsequently, **3a**–**g** were prepared through overnight reactions between mono(salicylaldiminato)titanium complex and (β-enaminoketonato) potassium salts at −78 °C, giving dark red solids. Finally, purification by precipitation from dichloromethane/hexane at room temperature formed the desired complexes as dark red needles or solids in good yields (**3a**, 55%; **3b**, 65%; **3c**, 63%; **3d**, 58%; **3e**, 68%; **3f**, 55%; **3g**, 72%).

All the heteroligated titanium complexes were well soluble in toluene, dichoromethane, tetrahydrofuran and other organic solvents. Complexes **3a**–**g** were well identified by ^1H and ^{13}C NMR in $CDCl_3$ solution at 25 °C as well as elemental analyses. The ^1H NMR spectra showed a single set of resonances for titanium-bonded salicylaldiminato and β-enaminoketonato ligands in a 1 : 1 ratio. The peaks at 8.26 and 6.60 ppm can be assigned to the typical methine protons of CH=N on salicylaldiminato and β-enaminoketonato ligands, respectively, while the peaks in the range of 7.7–6.7 ppm can be ascribed to the 10 hydrogen atoms on the phenyl ring as shown by Fig. 1. Besides, no spectral changes were observed in d_l-choroform solutions of **3a**–**g** stored in an inert atmosphere at room temperature over 24 h, indicating the complexes were stable and resistant to ligand redistribution reactions.

It is well-known that there are a number of possible geometric isomers for octahedral complexes with two bidentate monoanionic ligands. In addition, the geometry calculated to be most stable for these systems is that in which the two anionic functions are *trans* and the two chlorides *cis* to one another, respectively.[18d] Both complexes **1** and **2** featured such geometric isomers. To further confirm the structures of these new complexes, crystals of **3d** and **3f**–**g** suitable for X-ray diffraction were grown in CH_2Cl_2/hexane solution. The crystallographic data together

Table 1 Crystal data and structure refinements for complex **3d** and **3f–g**

Complex	**3d**	**3f**	**3g**
Formula	$C_{38}H_{28}Cl_4F_8N_2O_2Ti \cdot 1/2CH_2Cl_2$	$C_{33}H_{22}Cl_4F_8N_2O_2Ti$	$C_{68}H_{44}Cl_4F_{24}N_4O_6Ti_2$
Formula weight	858.91	820.23	1706.68
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a/Å	14.6015(7)	13.5344(5)	21.5519(8)
b/Å	15.5255(7)	12.2293(4)	11.7525(5)
c/Å	17.1760(8)	20.8540(8)	27.6927(11)
α (°)	90	90	90
β (°)	97.235(1)	99.9460(10)	96.1620(10)
γ (°)	90	90	90
V/Å^3	3862.7(3)	3399.8(2)	6973.7(5)
Z	4	4	4
D_c/Mg m^{-3}	1.524	1.602	1.626
Absorption coefficient (mm^{-1})	0.574	0.645	0.502
F(000)	1792.0	1648	3424
Crystal size/mm	0.23 × 0.11 × 0.09	0.34 × 0.23 × 0.11	0.32 × 0.21 × 0.11
θ range (°)	1.77 to 26.24	1.94 to 26.07	0.95 to 26.08
Reflections collected	21431	18614	38066
Independent reflections	7736 (R_{int} = 0.0276)	6720(R_{int} = 0.0338)	13799(R_{int} = 0.0276)
Data/restraints/parameters	7736/0/499	6720/0/454	13799/0/969
GOF on F^2	1.051	1.026	1.032
R_1	0.0513	0.0354	0.0463
wR_2	0.1496	0.0774	0.1159
Largest diff. peak and hole/e Å^{-3}	1.099 and –0.914	0.296 and –0.355	1.703 and –1.531

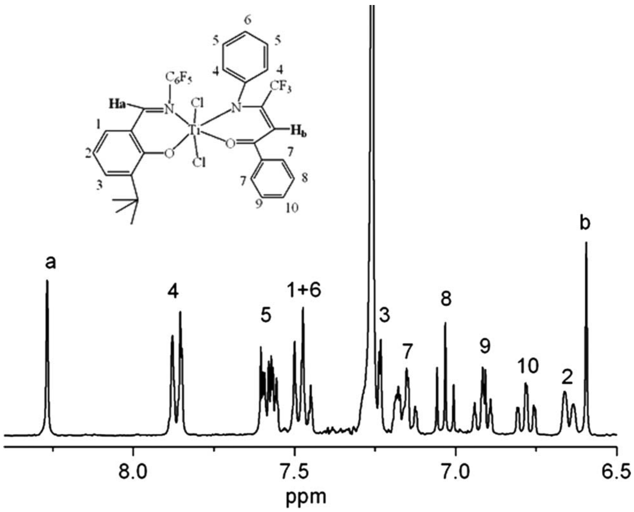


Fig. 1 ^{1}H NMR spectrum of compound **3a**.

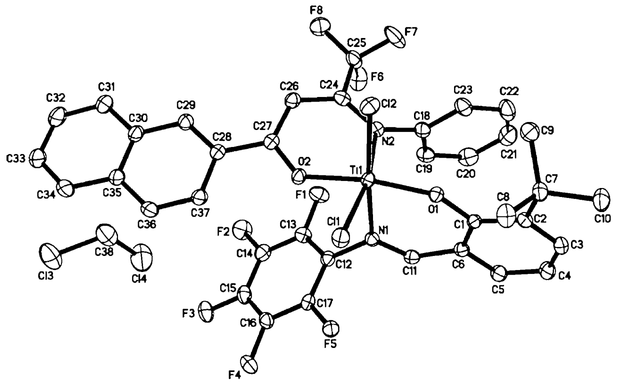


Fig. 2 Thermal ellipsoid plot of complex **3d** (30% probability displacement ellipsoids).

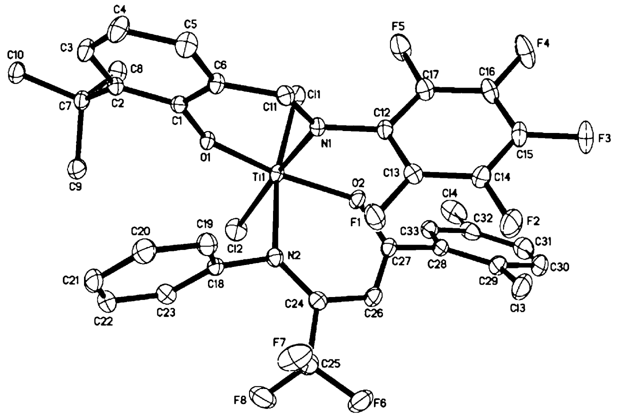


Fig. 3 Thermal ellipsoid plot of complex **3f** (30% probability displacement ellipsoids).

with the collection and refinement parameters were summarized in Table 1. The molecular structures and the ORTEP diagrams for **3d** and **3f–g** were shown in Fig. 2–4, while selected bond lengths and angles were given in Table 2. X-Ray crystallographic analysis displayed they featured a distorted octahedral geometry in which the titanium was bound to two *cis*-coordinated [N,N] chelating ligands (*trans*-O,O) and the two chlorine atoms (*cis*-Cl,Cl) in the solid state, just as those reported previously.[22] In the unit cell of **3d**, there is a CH_2Cl_2 solvent molecule per Ti(IV) complex, while in the unit cell of complex **3g** there are two crystallographically independent molecules with only minor differences from each other (*e.g.*, bond angles O(1)-Ti(1)-O(2), N(1)-Ti(1)-N(2), O(4)-Ti(2)-O(5) and N(3)-Ti(2)-N(4) are 167.01, 165.62, 83.70 and 82.75°, respectively). Although the Ti–O, Ti–N, Ti–Cl bond distances for complexes **3d** and **3f–g** are similar to

Table 2 Selected bond lengths [Å] and angles[°]

Complex	3d	3f	3g	1
Bond distances				
Ti–Cl(1/3)	2.2955(9)	2.2797(7)	2.2834(8) 2.2846(9)	2.2876(7)
Ti–Cl(2/4)	2.2702(9)	2.2612(7)	2.2639(8) 2.2544(9)	2.2578(8)
Ti–O(1/4)	1.814(2)	1.8164(14)	1.8209(18) 1.8282(19)	1.841(1)
Ti–O(2/5)	1.931(2)	1.9218(14)	1.9500(19) 1.9459(19)	1.845(1)
Ti–N(1/3)	2.206(2)	2.2439(17)	2.226(2) 2.245(2)	2.234(2)
Ti–N(2/4)	2.164(2)	2.2219(18)	2.213(2) 2.209(2)	2.217(2)
Bond angles				
Cl(1/3)-Ti-Cl(2/4)	95.92(4)	97.11(3)	99.78(3) 99.51(4)	96.42(3)
O(1/4)-Ti-O(2/5)	163.67(9)	163.53(6)	167.01(8) 165.62(9)	163.61(6)
N(1/3)-Ti-N(2/4)	86.45(9)	83.16(6)	83.70(8) 82.75(8)	86.94(7)

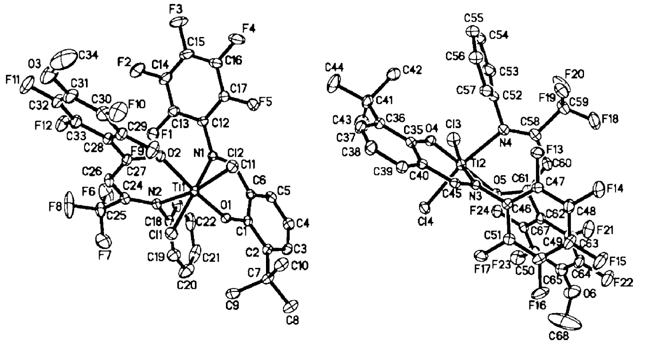


Fig. 4 Thermal ellipsoid plot of complex **3g** (30% probability displacement ellipsoids).

those for complex **1**,[18d] the bond angles between the ligands (O–Ti–O, N–Ti–N and Cl–Ti–Cl) are rather different. Complex **3d** has the narrower Cl–Ti–Cl angles while complexes **3f–g** have wider Cl–Ti–Cl and narrower N–Ti–N angles relative to those for their analogue complex **1**, which may be caused by the different electron withdrawing group R. It was noted that complex **3g** possessed the widest Cl–Ti–Cl and O–Ti–O angles and the narrowest N–Ti–N angles among these catalysts, which probably originated from the four fluorine atoms in the phenoxy benzene ring of the β-enaminoketonato ligand. For most of these complexes, stronger electron-withdrawing groups in the phenoxy benzene ring of the β-enaminoketonato would result in wider Cl–Ti–Cl and O–Ti–O bond angles and a narrower N–Ti–N angle as indicated by the corresponding data of complex **3g** in Table 2. Besides, wider Cl–Ti–Cl and O–Ti–O bond angles demonstrated an inherently more open nature of the catalyst, which would provide a larger aperture of the coordination sphere favoring easy access of norbornene to propagate.

Norbornene polymerization results

The results of the NB polymerization using complexes **3a–g** in the presence of various cocatalysts at different reaction temperatures were summarized in Table 3. Upon activation with modified methyl aluminoxanes (MMAO), complexes **3a–g** showed moderate to high activity for NB polymerization to produce high molecular weight polymers (entries 1–7) while catalyst **1** displayed almost no activity due to its highest steric hindrance among them (entries 8). It is well known that the activity greatly depends on the structure of complexes. Complexes **3e–g** with strong electron-withdrawing groups in the phenoxy benzene ring showed much higher activities than **3a** for NB polymerization at 40 °C (entries 5–7), whereas **3b–d** with electron-donating substituents on the phenolate group displayed lower catalytic activity (entries 1–4), suggesting electronic effect plays a significant role in NB polymerization. On the other hand, the catalytic activity order of **3a** > **3d** > **3b** > **3c** indicated the bulkiness of the ligand would hinder the access of NB to coordinate to the active center and thus decreased the activity. Accordingly, the poly(NB)s with higher molecular weight (MW) were achieved by the complexes displaying higher activities.

In order to determine suitable NB polymerization conditions, we focused on **3g** due to its higher activity to further investigate the effect of the reaction time, temperature and monomer concentration. There was obvious reduction in catalytic activity of **3g** for NB polymerization with the increase of reaction time (entries 9–11). The MW of the resultant polymer enhanced, while the molecular weight distributions (MWDs) broadened. These results might derive from the deactivation of the titanium center caused by the polymer precipitation during the polymerization process due to the low solubility of the poly(NB)s in toluene. As can be seen by Fig. 5, the catalytic activity and the MW of the resultant polymer increased with enhancement in polymerization temperature from 0–40 °C (entries 11–13) and began to decrease with further increasing the polymerization temperature (entries 14–15). In addition, the increase of NB concentration also resulted in the enhancement of the catalytic activity and MW of the resultant polymer as expected.

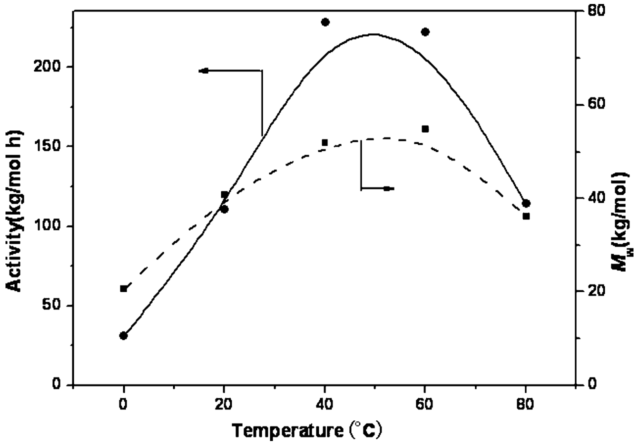


Fig. 5 Plots of reaction temperature *versus* catalytic activity and the molecular weight of poly(NB)s obtained by **3g**/MMAO system.

The polymerizations activated with different cocatalysts were also investigated under the same monomer concentration at 40 °C. The obtained results were listed in Table 3. The activity of the dried MAO system was similar to that of MMAO system (entries 7 and 17). On the other hand, though no activity was observed in the absence of $^iBu_3Al$ (entry 19), the borate/$^iBu_3Al$

Table 3 Norbornene polymerization results catalyzed by complexes **3a–g**

Entry	Cat.	Cocatalyst.	Al/Ti	Time (min)	Temp .(°C)	Polymer (mg)	Activity[b]	M_w[c](kg mol^{-1})	M_w/M_n[c]
1[a]	**3a**	MMAO	500	5	40	36	43.2	34.0	1.60
2	**3b**	MMAO	500	5	40	22	26.4	24.7	1.96
3	**3c**	MMAO	500	5	40	16	19.2	20.3	1.89
4	**3d**	MMAO	500	5	40	26	31.2	28.8	1.62
5	**3e**	MMAO	500	5	40	112	134.4	44.7	1.88
6	**3f**	MMAO	500	5	40	152	182.4	48.3	1.90
7	**3g**	MMAO	500	5	40	190	228.0	51.9	1.97
8	**1**	MMAO	500	5	40	trace	—	—	—
9	**3g**	MMAO	500	15	40	415	166.0	58.8	1.99
10	**3g**	MMAO	500	30	40	520	152.0	60.4	2.18
11	**3g**	MMAO	500	60	40	888	88.8	64.2	2.29
12	**3g**	MMAO	500	5	0	26	31.2	20.6	1.81
13	**3g**	MMAO	500	5	20	92	110.4	40.8	1.90
14	**3g**	MMAO	500	5	60	185	222.0	54.8	2.04
15	**3g**	MMAO	500	5	80	95	114.0	36.2	2.38
16[d]	**3g**	MMAO	500	5	40	210	252.0	56.9	1.98
17[e]	**3g**	dry MAO	500	5	40	172	206.4	52.1	1.80
18[f]	**3g**	$Ph_3CB(C_6F_5)_4/(^iBu)_3Al$	40	5	40	202	242.4	53.7	1.72
19	**3g**	$Ph_3CB(C_6F_5)_4$	0	5	40	trace	—	—	—
20[g]	**3g**	$B(C_6F_5)_3/Me_3Al$	10	5	40	trace	—	—	—
21[g]	**3g**	$B(C_6F_5)_3/Et_3Al$	10	5	40	trace	—	—	—
22	**3g**	$AlMe_3$	500	5	40	n.o.	—	—	—
23	**3g**	AlEt3	500	5	40	n.o.	—	—	—
24[h]	**3g**	MMAO/Me3Al	500/10	5	40	52	62.4	10.3	2.66
25[i]	**3g**	MMAO/Et3Al	500/10	5	40	22	26.4	8.2	2.88

[a] Polymerization conditions: Ti = 10 μmol, [NB] = 1.0 mol L^{-1}, solvent = toluene, total volume = 30 mL, cocatalyst = MMAO unless specially noted. [b] kg PE/mol$_{Ti}$ h bar. [c] Determined by GPC data in 1,2,4-trichlorobenzene *versus* polystyrene standard. [d] [NB] = 4.0 mol L^{-1}. [e] Cocatalyst = 232 mg dry MAO. [f] Cocatalyst = $Ph_3CB(C_6F_5)_4$ + $(^iBu)_3Al$, B/Ti = 2, $(^iBu)_3Al$ = 400 μmol. [g] B/Ti = 9, Me_3Al = 100 μmol. [h] MMAO/Me_3Al/Ti = 500/10/1. [i] MMAO/Et_3Al/Ti = 500/10/1.

system showed the same activity as that of MMAO system (entry 18) because of the better separation of the ion pair. In the case of **3g**/$B(C_6F_5)_3/R_3Al$ (R = Me, Et), no or low activity were observed (entries 20–23). The addition of R_3Al (R = Me, Et) to the **3g**/MMAO catalyst system decreased both the catalytic activity and the MW of the resultant poly(NB)s (entries 24–25), which indicated the chain transfer reactions caused by R_3Al.

As is well-known, in the vinyl addition polymerization of NB, chain termination *via* β-hydrogen elimination is prohibited because the β-hydrogen of the propagation chain end is at the *endo* position of the NB unit.[16e,24] Besides, the chain transfer to monomer should also be impossible because of the sterically hindered propagation chain end and NB monomer.[16e,24] Thus, we proposed the major chain transfer reaction might transfer to aluminium. To further confirm our speculation, we increased the MMAO and dry MMAO dosage and investigated their polymerization behavior. As can be seen by Fig. 6, the catalytic activity of both systems increased. Though the MW of the resultant poly(NB)s increased with enhancement of dry MMAO dosage, the MW of the polymer obtained by **3g**/MMAO system reduced, indicating chain transfer to aluminium occurred in **3g**/MMAO system, which is consistent with our speculation.

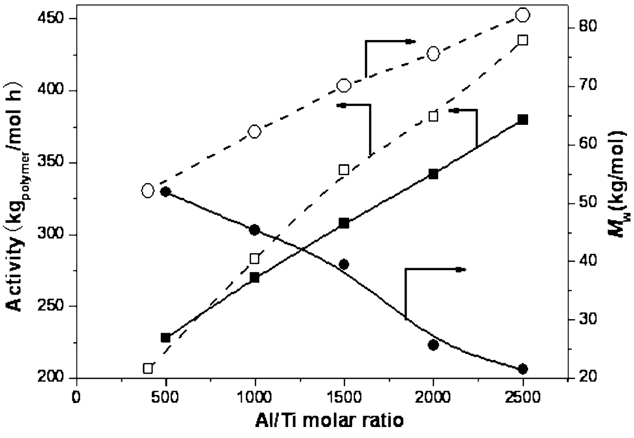


Fig. 6 Plots of Al/Ti molar ratio *versus* the catalytic activity and molecular weight of the resultant polymer obtained by **3g** (10 μmol catalyst, polymerization time 5 min, reaction temperature 40 °C). The solid line(—) and dashed line(- - -) display the MMAO and dry MMAO systems, respectively.

The ^{13}C NMR spectra of all the poly(NB)s obtained were similar and indicative of the vinyl addition of NB irrespective of the activator employed.[16d–e] Fig. 7(a) showed the ^{13}C NMR spectrum of polymer obtained by **3g**/MMAO system. Though the signals of the saturated carbons were split into several peaks due to the different stereoisomers of the NB unit, reference to polynorbornenes,[25] and norbornene hydrotrimers[26] allowed assignments of the ^{13}C signals reported in Fig. 7. The presence of signals from 28 to 55 ppm and absence of peaks at 20–24 ppm indicated the poly(NB)s were *exo* enchained.[27] The signals at 29–33.5 ppm and 35–38.5 ppm can be assigned to C5/C6 and C7, while the peaks at 38.5–44 ppm and 47.5–55 ppm can be ascribed to C1/C4 and C2/C3, respectively. The distribution of the stereotriad sequences of the poly(NB)s is determined from the C1 and C4 regions (C1/C4 at 38.8 ppm in the *mm* triad, at 40.3 ppm in the *mr* triad and at 41.3 ppm in the *rr* triad).[16a] The high intensity peak at 40.4 ppm of C1/C4 suggested that the inserted NB units of poly(NB)s obtained by **3g**/MMAO

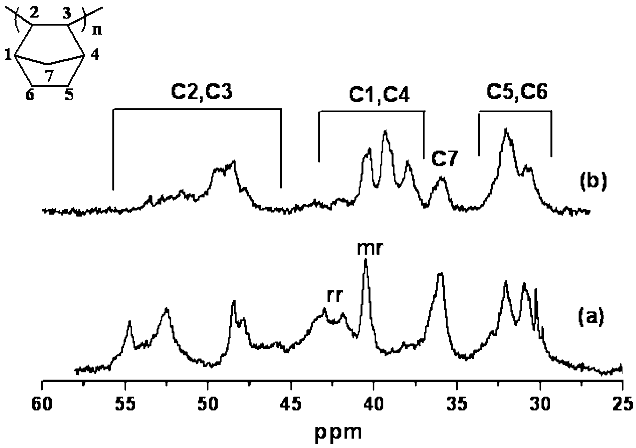


Fig. 7 (a) ^{13}C NMR spectrum of poly(NB)s obtained with **3g**/MMAO(entry 7 of Table 3).(b) ^{13}C NMR spectrum of poly(NB)s obtained with neutral nickel complexes bearing salicylaldiminato ligands reported previously.

can be predominantly heterotactic with very small amount of isotactic units, while our previously reported poly(NB)s achieved by neutral nickel complexes bearing salicylaldiminato ligands displayed typical atactic units as shown by Fig. 7(b).[11a] In addition, only one peak of C7 assigned indicated an overlapping of *rr* and *mr* triad sequences, because a mixture of *rr* and *mr* would probably resolve and overlap. These results were similar to those of poly(NB)s produced with Ni(dpm)$_2$,[25] but different from those obtained by (^{t}BuN-Me$_2$Si-Flu)TiMe$_2$[16d–e] and [(η^3-crotyl)Ni(1,4-COD)]PF$_6$ with three and two peaks assigned to C7, respectively.

The thermal property of poly(NB)s with M_w about 52 kg mol^{-1} obtained by **3g**/MMAO and neutral nickel(II) salicylaldiminato complex previously reported,[11a] for comparison, were studied by thermogravimetric analysis (TGA). Both samples were stable up to 400 °C under a nitrogen atmosphere. Only about 3.3% weight loss was recorded at 449 °C for the sample catalysed by **3g** (Fig. 8a), but about 10% weight loss was detected at 442 °C for poly(NB)s by neutral nickel(II) salicylaldiminato complex (Fig. 8b), which is consistent with their ^{13}C NMR analyses. In addition, the poly(NB)s catalysed by **3g** were much more stable than those by (^{t}BuN-Me$_2$Si-Flu)TiMe$_2$.[16d–e] DSC experiment was also performed but no melting transition heating to 400 °C was observed under a nitrogen atmosphere. In addition, it is very difficult to determine the glass transition temperature (T_g) of the poly(NB)s because T_g should be very close to their decomposition temperature.

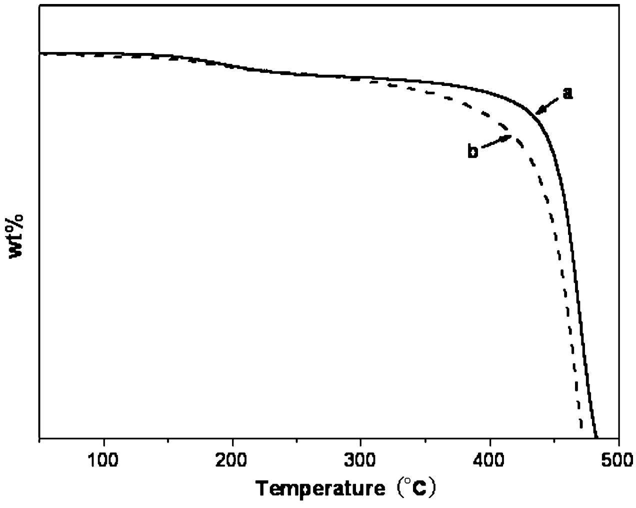


Fig. 8 TGA thermograms of poly(NB)s with M_w about 52 kg mol^{-1} obtained from the complex **3g (a)** and neutral nickel(II) salicylaldminato complex **(b)**.

Conclusions

We have synthesized and characterized a series of new heteroligated titanium complexes which were used as efficient catalysts for NB polymerization. The catalytic activities were greatly enhanced with increase of the electron-withdrawing groups and decrease of the steric bulkiness of groups attached to the β-enaminoketonato ligand. In addition, the cocatalyst type also played an important role in the catalytic activity. The poly(NB)s obtained were predominantly heterotactic and stable up to 450 °C, which showed moderate solubility in halogenated aromatic hydrocarbons for the determination of MW. The ^{13}C NMR analyses of the polymer suggested that the catalytic polymerization occurred *via* vinyl addition mechanism.

Significantly, the heteroligated titanium complexes effectively combined the more open nature required for NB incorporation and displayed greatly improved activity for vinyl addition polymerization of NB compared to homoligated counterparts. Though it was not clear why such a ligand combination was needed for good activity of NB polymerization in detail, we supposed the ligand differences might result in faster rates for NB insertion and slower rates for chain transfer to aluminium. The nature of the metal, the steric and electronic properties of the ligand play important roles in determining the olefin insertion at octahedral catalysts, while the suitable combinations of these effects may result in an improved olefin polymerization behavior. Thus, we believe this may help to design catalysts for special olefin polymerization. Moreover, from the structural point of view, these catalysts were the first titanium complexes which displayed good catalytic activity for NB polymerization with unsymmetrical and non-constrained geometry.

Experimental section

General procedure and materials

All manipulation of air- and/or moisture-sensitive compounds were carried out under a dry argon atmosphere by using standard Schlenk techniques or under a dry argon atmosphere in an MBraun glovebox unless otherwise noted. All solvents were purified from MBraun solvent purification system (SPS). The NMR data of the ligands and complexes used were obtained on a Bruker 300 MHz spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C) at ambient temperature, with CDCl$_3$ as the solvent (dried by MS 4 Å). The NMR data of the copolymers were obtained on a Varian Unity-400 MHz spectrometer at 135 °C, with *o*-C$_6$D$_4$Cl$_2$ as a solvent. Elemental analyses were recorded on an elemental Vario EL spectrometer. The weight-average molecular weight (M_w) and the polydispersity index (PDI) of polymer samples were determined at 135 °C by a PL-GPC 220 type high-temperature chromatograph equipped with three Plgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL min^{-1}. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd).

$TiCl_4$ and Me_3SiCl were purchased from Aldrich. KH (40% mineral oil suspension) was purchased from Aldrich and washed with light petroleum. Modified methylaluminoxane (MMAO, 7% aluminium in heptane solution), R_3Al, $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$ were purchased from Akzo Nobel Chemical Inc. Norbornene was purchased from Aldrich and purified by sublimation under reduced pressure before use. The stock solution of NB was prepared in toluene (6.07 M). The other reagents and solvents were commercially available.

Synthesis of titanium catalysts

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(Ph)O]TiCl$_2$ (3a). To a solution of compound 3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$) (0.69 g, 2 mmol) in dried tetrahydrofuran (20 mL) at −78 °C was added a 2.5 M n-butyllithium hexane solution (0.8 mL, 2 mmol) dropwise over 5 min. The mixture was allowed to warm to room temperature and stirred for 4 h, affording a yellow solution. Then, at 0 °C $(CH_3)_3SiCl$ (4 mmol, 0.5 mL) was added dropwise over 3 min and stirred for 18 h, the formed colorless solution was concentrated and added dried toluene 15 mL, then filtered. The colorless filtrate was added dropwise to a toluene solution of $TiCl_4$ (2 mmol) at 0 °C, and allowed to warm to room temperature, then evaporated under reduced pressure after stirred for 12 h to afford a solid residue, which was needed to recrystallized with dichloromethane and hexane to form dark red solid [3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)]TiCl$_3$(THF). Thereupon, a solution of [3-Bu-2-OC$_6$H$_3$CH=N (C$_6$F$_5$)]TiCl$_3$(THF) (0.78 g, 1.4 mmol) in dichlorometane (10 mL) at −78 °C was treated with [PhN=C(CF$_3$)CHC(Ph)]OK (0.46 g, 1.4 mmol). The reaction mixtures was allowed to warm slowly to room temperature and stirred for 20 h, affording a dark red solution. The solution was filtered to remove KCl and the isolated product was concentrated. Purification by precipitation from dichloromethane/hexane at room temperature gives the desired complex a dark red power in 55% yield. ^{1}H NMR (300 MHZ, CDCl$_3$, 20 °C): δ 8.24 (s, 1H, CH=N), 7.83–7.86 (q, 2H, Ar), 7.54–7.59 (m, 2H, Ar), 7.43–7.48 (t, 2H, Ar), 7.23 (t,1H, Ar), 7.10–7.16 (t, 2H, Ar), 6.99–7.04 (t, 1H, Ar), 6.87–6.92 (t, 1H, Ar), 6.74–6.78 (t, 2H, Ar), 6.62–6.64 (t, 1H, Ar), 6.57 (s, 1H, CH), 1.24 (s, 9H, *t*-Bu). ^{13}C NMR (20 °C): δ 177.3, 172.9, 147.6, 139.4, 136.8, 134.4, 133.7, 129.4, 128.7, 127.9, 126.9, 126.6, 125.8, 123.5, 122.7, 96.3, 35.6, 30.4. Anal. Calc. for $C_{33}H_{24}Cl_2F_8N_2O_2Ti$: C 52.75, H 3.22, N 3.73. Found: C 52.71, H 3.27, N 3.68.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(1-C$_{10}$H$_7$)-O]TiCl$_2$ (3b). Catalyst **3b** was prepared *via* a procedure similar to that for **3a** as a dark red power in 65% yield. ^{1}H NMR (300 MHZ, CDCl$_3$, 20 °C): δ 8.28 (s, 1H, CH=N), 7.92–7.95 (d, 2H, Ar), 7.68–7.71 (m, 4H, Ar), 7.65–7.67 (d, 1H, Ar), 7.56–7.58 (t, 2H, Ar), 7.48–7.50 (t, 1H, Ar), 7.15–7.20 (t, 1H, Ar), 6.92–7.01 (t, 1H, Ar), 6.89–6.91 (t, 1H, Ar), 6.70–6.75 (t, 1H, Ar), 6.60–6.65 (d, 1H, Ar), 6.59 (s, 1H, CH), 1.30 (s, 9H, *t*-Bu). ^{13}C NMR (75.5 MHZ, CDCl$_3$, 20 °C): δ 177.0, 172.5, 160.9, 139.0, 136.5, 135.5, 133.9, 132.8, 130.7, 129.7, 129.4, 129.0, 128.9, 128.8, 128.3, 128.2, 127.8, 127.0, 126.5, 126.3, 125.4, 123.0, 122.8, 96.5, 53.4, 35.2, 30.0. Anal. Calc. for $C_{37}H_{26}Cl_2F_8N_2O_2Ti$: C 55.45, H 3.27, N 3.50. Found: C 55.41, H 3.30, N 3.45.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(*p*-PhPh)O]-TiCl$_2$ (3c). Catalyst **3c** was prepared *via* a procedure similar to that for **3a** as dark red needles in 63% yield. ^{1}H NMR (300 MHZ, CDCl$_3$, 20 °C): δ 8.41 (s, 1H, CH=N), 8.25 (s, 1H, Ar) 7.89–7.97 (d, 1H, Ar), 7.82–7.86 (d, 2H, Ar), 7.75–7.79 (d, 1H, Ar), 7.56–7.61 (q, 5H, Ar), 7.13–7.18 (m, 3H, Ar), 6.98–7.03 (t, 1H, Ar), 6.88–6.91(t, 1H, Ar), 6.75–6.81 (t, 1H, Ar), 6.69 (s,1H, CH), 6.59–6.62 (d, 1H, Ar), 1.30 (s, 9H, *t*-Bu). ^{13}C NMR (75.5 MHZ, CDCl$_3$, 20 °C): δ 176.6, 172.6, 160.8, 157.5, 147.3, 139.7, 138.9, 136.5, 134.0, 132.1, 129.0, 128.4, 128.3, 128.1, 127.6, 127.2, 127.1, 126.5, 126.3, 125.4, 123.1, 122.3, 121.1, 117.3, 96.0, 35.2, 30.0. Anal. Calc. for $C_{39}H_{28}Cl_2F_8N_2O_2Ti$: C 56.61, H 3.41, N 3.39. Found: C 56.59, H 3.39, N 3.35.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(*o*-PhPh)O]-TiCl$_2$ (3d). Catalyst **3d** was prepared *via* a procedure similar to that for **3a** as dark red needles in 58% yield. ^{1}H NMR (300 MHZ, CDCl$_3$, 20 °C): δ 8.13 (s, 1H, CH=N), 7.77–7.79 (d, 1H, Ar),7.47–7.55 (q, 2H, Ar), 7.25–7.48 (m, 6H, Ar), 7.14–7.18 (t, 2H, Ar), 7.08–7.11(q, 1H, Ar), 6.91–6.99 (m, 2H, Ar), 6.70–6.80 (m, 2H, Ar), 6.56–6.58 (d, 1H, Ar), 5.79 (s, 1H, CH), 1.39 (s, 9H, *t*-Bu).^{13}C NMR (75.5 MHZ, CDCl$_3$, 20 °C): δ 176.6, 172.6, 160.8, 158.5, 148.3, 139.9, 138.4, 136.2, 134.3, 132.0, 129.2, 128.3, 128.2, 128.1, 127.6, 127.2, 127.1, 126.5, 126.3, 125.4, 123.1, 122.3, 121.1, 117.3, 96.0, 35.2, 30.0. Anal. Calc. for $C_{39}H_{28}Cl_2F_8N_2O_2Ti$: C 56.61, H 3.41, N 3.39. Found: C 56.55, H 3.37, N 3.36.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(2,6-F$_2$Ph)-O]TiCl$_2$ (3e). Catalyst **3e** was prepared *via* a procedure similar to that for **3a** as dark red needles in 68% yield. ^{1}H NMR (CDCl$_3$, 20 °C): δ 8.18 (s, 1H, CH=N), 7.53–7.58 (t, 1H, Ar), 7.30–7.44 (m, 1H, Ar), 7.13–7.16 (d, 2H, Ar), 7.00–7.07 (t, 1H, Ar), 6.95–6.99 (m, 3H, Ar), 6.76–6.89 (m, 2H, Ar), 6.64–6.67 (d, 1H, Ar), 6.36 (s,1H, CH), 1.35 (s, 9H, *t*-Bu).^{13}C NMR (75.5 MHZ, CDCl$_3$, 20 °C): δ 161.3, 155.0, 147.1, 139.0, 137.2, 135.9, 134.6, 133.9, 132.7, 131.3, 128.9, 127.6, 127.0, 126.5, 123.8, 122.3, 102.2, 77.9, 77.4, 76.9, 35.6, 30.4. Anal. Calc. for $C_{33}H_{22}F_2Cl_2F_8N_2O_2Ti$: C 50.34, H 2.82, N 3.56. Found: C 50.36, H 2.84, N 3.52.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(2,5-Cl$_2$Ph)-O]TiCl$_2$ (3f). Catalyst **3f** was prepared *via* a procedure similar to that for **3a** as dark red needles in 55% yield. ^{1}H NMR (CDCl$_3$, 20 °C): δ 8.19 (s, 1H, CH=N), 7.63 (s,1H, Ar), 7.54–7.57 (d, 1H, Ar), 7.35–7.36 (q, 2H, Ar), 7.15–7.17 (d, 2H, Ar), 6.96–7.07 (m, 2H, Ar), 6.77–6.88 (m, 2H, Ar), 6.73 (s, 1H, Ar), 6.63–6.65 (d, 1H, Ar), 1.36 (s, 9H, *t*-Bu). ^{13}C NMR (75.5 MHZ, CDCl$_3$, 20 °C): δ 161.0, 154.9, 146.9, 139.1, 137.0, 135.8, 134.5, 133.8, 132.5, 131.2, 128.9, 127.5, 126.9, 126.4, 123.6, 122.1, 102.1, 77.8, 77.4, 76.9, 35.6, 30.4. Anal. Calc. for $C_{33}H_{22}Cl_4F_8N_2O_2Ti$: C 48.32, H 2.70, N 3.42. Found: C 48.34, H 2.65, N 3.40.

[3-Bu^t-2-OC$_6$H$_3$CH=N(C$_6$F$_5$)][PhN=C(CF$_3$)CHC(2,3,4,6-F$_4$,4-OMePh)O]TiCl$_2$ (3g). Catalyst **3g** was prepared *via* a procedure similar to that for **3a** as dark red needles in 72% yield. ^{1}H NMR (CDCl$_3$, 20 °C): δ 8.11 (s, 1H, CH=N), 7.48–7.51 (d, 1H, Ar), 7.16–7.19 (d, 1H, Ar), 7.07–7.10 (d, 1H, Ar), 6.90–7.01 (m, 2H, Ar), 6.75–6.82 (m, 2H, Ar), 6.58–6.60 (d, 1H, Ar), 6.27 (s, 1H, CH), 4.10 (s, 3H, OMe), 1.32 (s, 9H, *t*-Bu).^{13}C NMR (75.5 MHZ,

$CDCl_3$, 20 °C): δ 173.6, 168.7, 161.1, 157.6, 147.2, 146.7, 143.4, 140.0, 139.0, 137.0, 134.5, 128.9, 127.6, 126.9, 126.4, 125.9, 123.6, 122.1, 121.1, 103.4, 77.4, 62.4, 35.7, 31.9, 30.5. Anal. Calc. for $C_{34}H_{22}Cl_2F_{12}N_2O_2Ti$: C 48.77, H 2.65, N 3.35. Found: C 48.78, H 2.67, N 3.32.

Crystallography studies

Single crystals of complexes **3d** and **3f–g** suitable for X-ray structure determination were grown from a dichlorometane/hexane solution at room temperature in a glovebox, thus maintaining a dry, O_2 free environment. X-ray densities of these complexes were collected with the ω scan mode (185 K) on a Bruker Smart APEX diffractometer with CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption corrections were applied to the data using SADABS program. The crystal structures were solved using the SHELXTL program and refined using full matrix least squares. All the non-hydrogen atoms were refined anisotropically. The crystallographic data together with the collection and refinement parameters are summarized in Table 1.

Procedure for norbornene polymerization

Polymerizations were performed in a 100 mL glass reactor equipped with a seal septum and a magnetic stirrer. At first, the reactor was charged with a stock solution of norbornene in toluene and a prescribed amount of MMAO solution (2.5 M) was added. Additional toluene was added to make up the total volume to 25 mL and the reactor was kept in an ice or oil bath for 30 min to reach reaction temperature. Five mL of the aliquot of catalyst solution in toluene was added to start the polymerization. Temperature was kept constant during polymerization. Polymerization was terminated with acidic methanol. The polymer obtained was adequately washed with methanol and dried under vacuum at 60 °C for 10 h. If the polymerization was activated with dry MAO, the reactor was first charged with a prescribed amount of dry MAO and the NB solution. If the activators are R_3Al and/or perfluorinated boranes, the polymerization procedure is performed as follows: a prescribed amount of NB in toluene and R_3Al in toluene was first added into the reactor and the solution was heated to 40 °C in an oil bath. The polymerization was started by addition of perfluorinated boranes in toluene into the above solution soon after the addition of a precatalyst in toluene. The following procedure is the same as those of polymerizations activated with MMAO.

Acknowledgements

The authors are grateful for subsidy provided by the National Natural Science Foundation of China (Nos. 20734002 and 20923003).

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