

Binuclear Titanium Catalysts Based on Methylene-Bridged Tridentate Salicylaldiminato Ligands for Ethylene Homoand Copolymerization

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Abstract A series of methylene-bridged salicylaldiminato tridentate [ONS] ligands bearing different alkylthio sidearms and the corresponding binuclear titanium complexes (Ti_2^{a} , Ti_2^{b} , Ti_2^{c}) were synthesized and characterized by elemental analysis, ESI-MS, FT IR, ¹H and ¹³C NMR. To the best of our knowledge, these were the first non-metallocene tridentate binuclear Ti complexes reported. When activated by modified methylaluminoxane (MMAO), these binuclear Ti complexes displayed extremely high activities in the range of 10^6 g mol⁻¹ h⁻¹ atm⁻¹ for ethylene polymerization and ethylene/ α -olefins copolymerization at atmospheric pressure, producing high molecular weight polymers with narrow polydispersity. Both the catalytic behavior and the spectroscopic characterization indicated that the catalysts assumed symmetric structure and contained single-site active species. Most importantly, the catalytic activities towards ethylene (co)polymerization as well as comonomer incorporation ratios were much higher than that of the corresponding mononuclear complexes. Meanwhile, the properties of polymers and the comonomer incorporation ratios can be effectively tuned by the reaction conditions and the alkylthio side group on ligands. Complex Ti_2^c bearing the long octylthio sidearm showed significantly higher activity for ethylene polymerization than the methylthio functionalized Ti_2^a , presumably due to the increased solubility of the catalyst in the reaction medium. While for copolymerization, complex Ti_2^a demonstrated the highest catalytic activity and comonomer incorporation ratio, due the small steric hindrance of the methylthio side group.

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Graphical Abstract



1 Introduction

Polyolefins are presently the most important and the most produced synthetic polymers and are used in everything from packaging to automotive and electrical components, to lubricants and artificial limbs. Historically, polyolefins were produced using ill-defined but highly active Ziegler-Natta catalyst composed of supported metal halides (typically MgCl₂-supported TiCl₄, which still dominates the market) activated by aluminum alkyls [1]. Beginning in the 1990s, following the great success of Kaminsky's metallocene catalysts [2], significant efforts have been directed toward the development and application of catalysts with various non-metallocene ligands such as diamide, β-diketiminates, iminopyrrolides, amidinates, diimine, alkoxide, aryl oxide, and phenoxyimine [3-24]. These single site molecular catalysts were far better defined and more tunable in terms of structure, activity and selectivity, and the explosion of research advances have led to deeper mechanistic understanding of the catalytic system and production of polyolefin materials with well-defined microstructure and high performance.

Among the non-metallocene candidates, phenoxyimine group 4 transition metal complexes developed by Fujita and co-workers, the so called FI catalyst, exhibited high performances in both catalytic activity and stereoregularity control in olefin polymerization [12–17]. Nevertheless, these FI catalysts required the use of large amount of cocatalyst and showed weak copolymerization capacities for ethylene and other olefins bearing steric hindrance groups due to the crowded coordination environment of bis-ligation. Tang et al. have introduced some sidearms with weak coordination capacity and developed a series of mono-ligated tridentate [ONX] TiCl₃ complexes, where X=O, S, Se, and P [25-30], and found that the catalytic performances were highly dependent on the type and the steric effect of the ancillary sidearm. The complexes bearing the S-Ar/R sidearm were highly active for ethylene polymerization and copolymerization, and showed good capability to incorporate comonomers due partly to the open coordination environment. In addition, the activity is not much diminished even when the amount of MMAO is fairly low (Al/Ti ratio = 100) [27]. Compared with the bis-ligated bidentate complexes, these mono-ligated tridentate complexes were highly stable and could be prepared in one step by simply mixing the tridentate ligands and titanium tetrachloride, without the need to deprotonate the ligands in advance.

Since 2000s, there have also been growing interests in binuclear and multinuclear complexes for olefin polymerization [31-54]. As compared to the mononuclear analogues, it was shown that introduction of a proximate metal center could significantly enhance catalytic activity, modify polyolefin molecular weight, branch structure, and increase comonomer enchainment selectivity as a result of the cooperative effects between adjacent catalytic centers. Heterobimetallic catalysts are also capable of producing LLDPE with ethylene as the sole feed [39, 41, 53]. However, compared with the mononuclear complexes, the research on the design and synthesis, and the catalytic performance and mechanism for binuclear complexes is far from enough. Most of these works were focused on metallocene and late transition metal complexes, while non-metallocene early transition metal binuclear complexes have rarely been reported, due probably to the difficulty in synthesis.

Marks' group systematically studied a series of binuclear catalysts, including metallocene and late transition metal complexes, and found that the binuclear catalysts were more efficient in terms of activity and commoner insertion than their mononuclear analogues [31–41]. Recently they also reported a class of early transition bimetallic catalysts (as shown below, **I**) [35]. However, the salicylaldimine ligated mononuclear complexes demonstrated low activity (~10³ g mol⁻¹ h⁻¹ atm⁻¹), whilst the binuclear analogue demonstrated moderate activity (~10⁴ g mol⁻¹ h⁻¹ atm⁻¹). Ma Yuguo et al. lately reported a bidentate salicylaldimine heteroligated binuclear Ti(IV) catalyst (shown below, **II**) with high activity (over 10⁶ g mol⁻¹ h⁻¹ atm⁻¹), yet the synthesis was very tedious [54].





Thus, in order to take the advantage of the open coordination environment of tridentate ligands and the cooperative effect of binuclear complexes, we tethered a series of tridentate [ONS] salicylaldiminato ligands bearing various S-R (R=methyl, propyl, octyl) sidearms with a methylene group and prepared the corresponding Ti complexes. To the best of our knowledge, these are the first non-metallocene tridentate binuclear Ti complexes reported. The structures of the ligands and complexes were characterized by spectroscopic techniques and elemental analysis, and the catalytic performances for ethylene homo- and co-polymerization were investigated. High activities over 10^6 g mol⁻¹ h⁻¹ atm⁻¹ were obtained. Meanwhile, the binuclear catalysts showed 28% increase of activity for ethylene polymerization and significantly increased enchainment of α -olefins such as 1-hexene and 1-octene as compared with the mononuclear analogues, clearly demonstrating the cooperativity between the two metal centers.

2 Experimental Section

2.1 Materials and Characterization

All manipulations involving air- and/or moisture-sensitive compounds were performed under dry nitrogen using standard Schlenk-line and glovebox. Toluene and hexane were purified by distillation over sodium/benzophenone ketyl, while CH_2Cl_2 was refluxed over CaH_2 . Gases and other solvents were purified by standard techniques. Modified methylaluminoxane (MMAO) was purchased from Akzo Chemical as a 7 wt.% solution in heptane. All other chemical reagents were used as received unless noted otherwise. Compounds 2, 3, alkylthio anilines and mononuclear Ti complex Ti_1^c (Scheme 1) were synthesized according to the literature [29].

¹H and ¹³C NMR spectra of ligands and complexes were recorded on a Bruker Avance III 400 MHz spectrometer with tetramethylsilane as an internal standard. Elemental analyses were carried out using Vario EL 111. ¹³C NMR spectra of polymers were obtained on a Varian XL 300 MHz spectrometer at $120 \,^{\circ}\text{C}$ with $o-C_6D_4Cl_2$ as the solvent. IR spectra were collected with a Nicolet Nexus 470 Fourier transform infrared (FTIR) spectrometer. Mass spectra were measured by an Agilent ESI-Q-TOF MS 6520 instrument. DSC measurements were performed on a Netzsch DSC200 F3 instrument at a heating rate of 10°C/min from 20 to 160°C, with the melting points obtained from the endothermic peak of the second heating scan. The M_n and M_w/M_n of the polymers were determined at 150°C with a Viscotek 350A HT-GPC System using a polystyrene calibration. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of 1.0 mL min^{-1} .



Scheme 1 Structure of mononuclear Ti complex Ti₁^c

2.2 Ethylene Polymerization and Copolymerization

A flame-dried Schlenk flask purged with N_2 was filled with ethylene gas. 30 mL of freshly distilled toluene was added and raised to the reaction temperature for 10 min. MMAO was then injected using a syringe and the mixture was stirred for 5 min. The polymerization was initiated by adding a solution of the titanium complex in toluene with a syringe. After a desired time, the polymerization was quenched with acidified ethanol (100 mL, 8 vol.% HCl in ethanol). The precipitated polymer was filtered off, washed with ethanol, then dried under vacuum overnight at 60 °C till a constant weight. For copolymerization, α -olefins (1-hexene, 1-octene) and MMAO were injected in sequence via a syringe.

2.3 Synthesis of the Ligands and Binuclear Titanium Complexes

The synthesis of the methylene-bridged salicylaldiminato tridentate [ONS] ligands La–Lc and the corresponding binuclear Ti complexes Ti_2^a – Ti_2^c is shown in Scheme 2.

2.3.1 Synthesis of the Methylene-Bridged Salicylaldiminato Tridentate [ONS] Ligands (La, Lb and Lc)

To a 100 mL 3-neck flask were added 0.92 g (2.5 mmol) of **3**, 0.695 g (5 mmol) of methylthio aniline, 30 mL of ethanol, and 0.31 mL of formic acid, and heated to reflux for 12 h. The mixture was then vacuum dried, and recrystallized with ethanol to afford **La** as a yellow solid (1.2 g, 80%)



Scheme 2 Synthesis of the methylene-bridged salicylaldiminato tridentate [ONS] ligands and the corresponding Ti complexes

yield). ¹H NMR (400 MHz, ppm, CDCl₃): δ 13.46 (s, 2H, OH), 8.56 (s, 2H, N=CH), 7.0–7.27 (m, 12H, ArH), 3.91 (s, 2H, CH₂), 2.47 (s, 6H, CH₃), 1.47 (s, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CDCl₃): δ 162.8 (CH=N), 159.0, 145.8, 137.9, 134.7, 131.5, 130.6, 130.4, 127.2, 125.3, 124.9, 119.0, 117.4 (Ar–*C*), 40.4, 35.0, 29.4, 14.8. ESI-MS [*m*/*z* (%)]: 611 (100) [M⁺]. Anal. Calcd for C₃₇H₄₂N₂O₂S₂: C, 72.75; H, 6.93; N, 4.59%. Found: C, 72.88; H, 6.46; N, 4.25%. IR (KBr, cm⁻¹): 2957, 2917, 1614, 1566, 1437, 1266, 1203, 1160, 805, 755.

Ligand Lb was synthesized with a similar procedure as for La. Yield: 85%. ¹H NMR (400 MHz, CDCl₃): δ 13.5 (s, 2H, OH); 8.5 (s, 2H, CHO); 6.9–7.4 (m, 12H, ArH); 4.0 (s, 2H, CH₂); 2.9 (tr, 4H, CH₂); 1.8 (m, 4H, CH₂); 1.4 (s, 18H, C(CH₃)₃); 1.05 (m, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.0 (*C*H=N), 159.1, 147.0, 137.9, 133.1, 131.5, 130.6, 130.4, 127.5, 127.0, 126.0, 119.1, 118.0 (Ar–*C*), 40.4, 35.0, 34.3, 29.5, 22.4, 13.7. ESI-MS [*m*/*z* (%)]: 663 (100), 666 (33) [M⁺]. Anal. Calcd for C₄₁H₅₀N₂O₂S₂: C, 73.83; H, 7.56; N, 4.20%. Found: C, 73.29; H, 7.31; N, 4.38%. IR (KBr, cm⁻¹): 2959, 2872, 1614, 1567, 1438, 1269, 1202, 1159, 802, 755.

Ligand Lc was synthesized with a similar procedure as for La. Yield: 75%. ¹HNMR (400 MHz, ppm, CDCl₃): δ 13.53 (s, 2H, OH), 8.54 (s, 2H, N=CH), 7.32–7.00 (m, 12H, ArH), 3.92 (s, 2H, CH₂), 2.91 (s, 4H, SCH₂), 1.69 (m, 4H, CH₂), 1.47 (m, 10H, CH₂), 1.27 (s, 18H, C(CH₃)₃), 0.87 (t, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.2 (CH=N), 159.5, 138.4, 135.0, 132.9, 132.7, 131.7, 131.4, 130.0, 127.6, 126.5, 120.5, 118.9 (Ar–C), 40.6, 35.0, 33.1, 31.8, 29.5, 29.4, 29.3, 29.2, 29.0, 22.6, 14.1. ESI-MS [*m*/*z* (%)]: 804 (100), 806 (16) [M⁺]. Anal. Calcd for C₅₁H₇₀N₂O₂S₂: C, 75.88; H, 8.74; N, 3.47%. Found: C, 75.32; H, 8.96; N, 3.75%. IR (KBr, cm⁻¹): 2950, 2925, 2857, 1613, 1565, 1467, 1437, 1364, 1268, 1202, 1158, 803, 756.

2.3.2 Synthesis of the Binuclear Ti Complexes

Synthesis of the binuclear Ti complexes Ti_2^{a} : 0.61 g (1 mmol) of ligand La was added to a 100 mL Schlenk flask, dissolved in 15 mL of CH₂Cl₂. A solution of TiCl₄ (0.28 mL, 2.6 mmol) in CH₂Cl₂ (15 mL) was added to another 100 mL Schlenk flask. The ligand solution was then slowly added to the TiCl₄ solution at -78 °C. After 4 h, the mixture was slowly warmed to RT, then heated to 35 °C for 24 h under stirring. The solvent was vacuum dried to afford Ti_2^{a} as a red brown solid (0.6 g, 65%). ¹H NMR (400 MHz, CD₂Cl₂): 8.76 (s, 2H, N=CH), 7.69–7.19 (m, 12H, ArH), 4.17 (s, 2H, CH₂), 3.05 (s, 6H, CH₃), 1.28 (s, 18H, C(CH₃)₃). ¹³C NMR (101 MHz, CD₂Cl₂): δ 162.4 (CH=N), 159.5, 154.5, 148.2, 145.3, 138.4, 136.1, 134.0, 129.7, 129.0, 128.2, 125.1, 122.7 (Ar–C), 53.4, 31.6,

22.7, 14.1. ESI-MS [m/z (%)]: 915 (100), 917 (15) [M⁺]. Anal. Calcd for C₃₇H₄₀Cl₆N₂O₂S₂Ti₂: C, 48.45; H, 4.40; N, 3.05%. Found: C, 48.87; H, 4.12; N, 3.43%. IR (KBr, cm⁻¹): 2959, 1632, 1548, 1387, 1266, 856, 759, 608.

Ti₂^b was prepared using the same procedure as for **Ti**₂^a. Yield: 98.2%. ¹H NMR (400MHz,CDCl₃): 8.7 (s, 2H, CHO); 7.1–7.7 (m, 12H, ArH); 4.1 (s, 2H, CH₂); 2.48 (tr, 4H, CH₂); 2.05 (m, 4H, CH₂); 1.55 (s, 18H, C(CH₃)₃); 1.13 (m, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 162.9 (CH=N), 159.4, 152.6, 145.0, 142.6, 136.3, 136.2, 134.0, 131.4, 131.3, 130.3, 128.0, 119.3 (Ar–C), 53.4, 48.0, 35.4, 29.8, 21.8, 13.4. ESI-MS [*m*/*z* (%)]: 971 (100), 973 (86) [M⁺]. Anal. Calcd for C₄₁H₄₈Cl₆N₂O₂S₂Ti₂: C, 50.59; H, 4.97; N, 2.88%. Found: C, 50.06; H, 4.25; N, 3.12%. IR (KBr, cm⁻¹): 2963, 2869, 1626, 1548, 1386, 1271, 1109, 857, 758, 612.

Ti₂^c was prepared using the same procedure as for **Ti**₂^a. Yield: 70%. ¹H NMR (400 MHz, ppm, CDCl₃): δ 8.72 (s, 2H, N=CH), 7.65–7.25 (m, 12H, ArH), 4.09 (s, 2H, CH₂), 3.50 (s, 4H, SCH₂), 2.00 (m, 4H, CH₂), 1.55 (m, 10H, CH₂); 1.27 (s, 18H, C(CH₃)₃), 0.87 (t, 6H, CH₃). ¹³C NMR (101 MHz, CDCl₃): δ 163.0 (*C*H=N), 161.7, 150.5, 137.5, 136.3, 136.1, 134.3, 134.2, 131.5, 130.3, 128.8, 128.0, 119.4 (Ar–*C*), 46.3, 35.3, 31.8, 29.9, 29.8, 29.1, 29.0, 28.8, 28.1, 22.6, 14.1. ESI-MS [*m*/*z* (%)]: 1113 (100) [M⁺]. Anal. Calcd for C₅₁H₆₈Cl₆N₂O₂S₂Ti₂: C, 55.00; H, 6.15; N, 2.52%; Found: C, 55.22; H, 6.34; N, 2.29%. IR (KBr, cm⁻¹): 2923, 2850, 1602, 1545, 1391, 1263, 864, 752, 623.

3 Results and Discussion

3.1 Synthesis of Binuclear Ti Complexes

Methylene-bridged bis(salicylaldehyde) 3 was synthesized through two steps with o-^tbutyl phenol as starting material according to the reference [55], which then reacted with alkylthio aniline to obtain the methylene-bridged bis-salicylaldiminato tridentate [ONS] ligands La-Lc. The ligands reacted directly with excess TiCl₄ to form the binuclear Ti complexes $Ti_2^{a}-Ti_2^{c}$, with no need to deprotonate with a base. This procedure is much simpler than that for the synthesis of bidentate binuclear Ti(IV) complexes [34], and the products were also more stable. The structures of the free ligands and the corresponding binuclear Ti complexes were confirmed by ¹H NMR, ¹³C NMR, ESI-MS, FT IR and elemental analysis. The ¹H NMR of La and the responding complex Ti_2^a was shown in Fig. 1. Notable changes for Ti_2^a were the disappearance of OH resonance at $\delta 13.46$ ppm, and the shift of the thiomethyl from 2.47 to 3.05 ppm. The ¹H NMR spectra also proved that the molecule adopted a symmetric geometry.



Fig. 1 ¹H NMR spectra of ligand La and complex Ti₂^a

3.2 Ethylene Polymerization

The binuclear Ti complexes $Ti_2^a - Ti_2^c$ were examined for ethylene polymerization under MMAO activation, with the results summarized in Table 1. Overall, these binuclear complexes showed very high activity (over 10^6 g mol⁻¹ h⁻¹ atm⁻¹) under suitable conditions. The melting points (T_m) of the products were about 133 °C, which were typical of high-density polyethylene. This was in full accordance with the ¹³C NMR spectra (not shown), which showed no branches on the polymer backbone.

The influences of different reaction conditions such as the reaction temperature and Al:Ti molar ratio upon the catalytic behaviors of Ti₂^c/MMAO were also studied. The

optimum activity was achieved with Al:Ti=1500 at 55 °C under ethylene pressure of 1.0 atm (Table 1, entry 8).

As the temperature was raised from 25 to 65 °C, the catalytic activity remained at high level, and a maximum activity of 2.43×10^6 g mol⁻¹ h⁻¹ atm⁻¹ was achieved at 55 °C (Table 1, entry 4). The activity slightly decreased as the polymerization temperature further increased to 65 °C (Table 1, entry 5). The temperature also had great influence on the molecular weight of the products. With the temperature increase, the $M_{\rm w}$ of the polymer decreased from 8.74×10^4 g mol⁻¹ at 25 °C to 1.16×10^4 g mol⁻¹ at 65 °C (Fig. 2), indicating that the high polymerization temperature might promote chain transfer reaction.

The influence of Al/Ti molar ratio was investigated by maintaining the temperature at 55 °C, and the maximum activity was achieved with an Al/Ti ratio of 1500 (Table 1, entry 8). The catalyst maintained high activity of over 10⁶ g mol⁻¹ h⁻¹ atm⁻¹ even at a low Al/Ti ratio of 500. The molecular weight of the polyethylene was sensitive to the Al/Ti ratio and decreased from 5.09×10^4 to 1.48×10^4 g mol⁻¹ with the increase of the Al/Ti ratio from 500 to 2500, suggesting that chain transfer to aluminum compounds occurred in the process.

The influences of the alkylthio sidearm on catalytic performance were also investigated. Under the same condition, the activity of the three binuclear complexes increased in the order of $Ti_2^{c} > Ti_2^{b} > Ti_2^{a}$ (Table 1, entry 8, 10, 11), it appeared that the longer the alkyl group, the higher the homopolymerization activity. This is somehow different from the corresponding mononuclear complexes observed by Tang et al. [29], where the activities were similar. For ethylene homopolymerization, the steric hindrance of the substituents in the mononuclear Ti complexes appeared to

Table 1 The results of ethylene polymerization catalyzed by binuclear Ti complexes binuclear Ti complexes binuclear Ti complexes	Entry	Cat. (µmol)	Al/Ti	Temp (°C)	PE (g)	Act ^a	Tm ^b (°C)	Mw ^c (10 ⁴ g/mol)	PDI ^c
	1	Ti ₂ ^c (2)	2000:1	25	0.3922	1.17	141.6	8.74	3.56
	2	${Ti_2}^{c}(2)$	2000:1	35	0.3941	1.18	_	_	_
	3	${Ti_2}^{c}(2)$	2000:1	45	0.5057	1.52	136.9	3.24	2.52
	4	${Ti_2}^{c}(2)$	2000:1	55	0.8105	2.43	_	_	-
	5	${Ti_2}^{c}(2)$	2000:1	65	0.5425	1.63	133.7	1.16	2.35
	6	${Ti_{2}}^{c}(2)$	500:1	55	0.4213	1.26	136.4	5.09	2.75
	7	${Ti_2}^{c}(2)$	1000:1	55	0.5645	1.69	-	-	-
	8	${Ti_2}^{c}(2)$	1500:1	55	0.8537	2.56	135.4	1.57	2.48
	9	${Ti_2}^{c}(2)$	2500:1	55	0.5705	1.71	134.9	1.48	2.27
	10	$Ti_{2}^{a}(3)$	1500:1	55	0.7479	1.50	130.8	0.79	2.71
	11	$Ti_{2}^{b}(2)$	1500:1	55	0.7425	2.24	133.4	1.45	2.78
	12	${Ti_1^{c}}(4)$	1500:1	55	0.6682	2.00	130.8	0.95	2.79

Toluene 30 mL, 1 atm ethylene pressure, reaction time 5 min

^aActivity, 10^6 g mol⁻¹ h⁻¹ atm⁻¹

^bMelting temperature determined by DSC

^cDetermined by GPC using polystyrene standard



Fig. 2 GPC traces of PE samples from entries 2, 3, and 6 in Table 1

have little effect on activity, due to the wide open coordination environment of the tridentate complexes and the small size of ethylene monomer. Therefore, the difference in activity here may be due to their different solubilities. The complex $\mathbf{Ti_2}^a$ bearing a methylthiol group had the lowest solubility and consequently lowest catalytic activity. Tang also found that the increase of solubility could increase the catalytic activity of phenoxy-imine [ONS] trident Ti complexes. The molecular weight of the polyethylene catalyzed by the binuclear complexes increased in the same order (Fig. 3), with the products catalyzed by $\mathbf{Ti_2}^c$ of the highest M_w , which was attributed to the larger steric hindrance of octylthio group that inhibited the chain transfer reaction.

Compared with the mononuclear analogue (Ti_1^c) , the catalytic activity of the binuclear Ti complex Ti_2^c increased modestly by 28%, and the molecular weight produced by Ti_2^c was higher than that by Ti_1^c . However, the molecular weight distribution of the polyethylenes catalyzed by binuclear Ti complexes were within 2–3, similar to that of the mononuclear analogue (Table 1, entry 8 vs. 12).

3.3 Ethylene Copolymerization with α-Olefins

These binuclear Ti complexes were also excellent catalysts for copolymerization of ethylene and α -olefins under MMAO activation. The copolymerization of ethylene with 1-hexene or 1-octene was investigated under similar condition with various feeds of α -olefins and the results were summarized in Table 2.

Comparable high activity (over 2×10^6 g mol⁻¹ h⁻¹ atm⁻¹) with the copolymerzation was observed for all the reaction system. As the feed of 1-hexene was increased from 5 to 15 mmol, the copolymerization activity increases from 2.07 to 2.42×10^6 g mol⁻¹ h⁻¹ atm⁻¹ (Table 2, entry 1–3).



Fig. 3 GPC traces of PE samples from entries 8, 10-12 in Table 1

The products were apparently branched polyethylene, as revealed by the much diminished melting points and the high temperature ¹³C NMR spectra. The 1-hexene incorporation ratio in the copolymer was calculated from the ¹³C NMR spectra [33] and found tunable from 1.4 to 7.3% by varying the initial feed of α -olefin commoners from 5 to 15 mmol (Fig. 4). The melting points of the copolymers also varied from 106.7 to 89.5 °C (Fig. 5).

For ethylene copolymerization, the steric hinderance of the binuclear Ti complexes played important role in catalysts performance. Under the same condition, the binuclear complex Ti₂^a with methylthio sidearm demonstrated the highest catalytic activity and comonomer incorporation ratio, as a result of the small steric hindrance of the side group. Furthermore, higher activity was observed as compared with the mononuclear complex (Table 2, entries 2 vs. 6), and the incorporation of 1-hexene was 6.9, 5.7, and 9.3% respectively for Ti2^c, Ti2^b, and Ti2^a, all of which were significantly higher than the 4.5% ratio obtained by Ti₁^c (Table 2, entries 2, 5, 4, 6, and Fig. 6). It is speculated that the higher catalytic activity and comonomer incorporation ratio are caused by the larger steric hindrance of these binuclear Ti complexes which would reduce the interaction between the catalyst and the cocatalyst molecules and therefore improve the catalytic activity and comonomer incorporation ratio.

Marks and Ma also found that the *agostic* interaction between the comonomer and metal center could stabilize the coordinated bimetallic olefin complex and enchain olefin comonomers more easily than mononuclear complex [54]. The molecular weights of the copolymers were found in the range $1.33-1.93 \times 10^4$ g mol⁻¹, and a narrower polydispersity (2.08–2.39) as compared with the homopolymerization was obtained (Fig. 7). **Table 2** Copolymerization of
ethylene and α -olefins catalyzed
by binuclear Ti complexes

Entry	Cat. (µmol)	α -Olefins (mmol)	Poly (g)	Act ^a	Tm (°C)	$M_w^{\ b}$	PDI ^b	Incorp ^b (mol%)
1	Ti ₂ ^c (2)	C6 (5)	0.6887	2.07	106.7	_	_	1.4
2	${Ti_2}^{c}(2)$	C6 (10)	0.7065	2.12	95.4	1.93	2.08	6.9
3	${Ti_2}^{c}(2)$	C6 (15)	0.8079	2.42	89.5	_	_	7.3
4	$Ti_{2}^{a}(2)$	C6 (10)	0.8401	2.52	85.5	1.33	2.14	9.3
5	$Ti_{2}^{b}(2)$	C6 (10)	0.8055	2.42	99.1	1.36	2.39	5.7
6	$\mathbf{Ti_1^c}(4)$	C6 (10)	0.6859	2.05	102.8	1.40	2.29	4.5
7	$Ti_{2}^{a}(2)$	C8 (10)	0.9794	2.94	92.1	1.61	2.20	9.8
8	$Ti_{2}^{b}(2)$	C8 (10)	0.9073	2.72	98.2	1.29	2.42	8.0
9	${Ti_2}^{c}(2)$	C8 (10)	0.7912	2.37	94.8	1.42	2.16	7.9
10	$Ti_{1}^{c}(4)$	C8 (10)	0.7570	2.27	100.7	1.44	2.36	5.9

Toluene 30 ml, 1 atm ethylene pressure, reaction time 5 min, temp 55 °C, Al:Ti 1500 equiv. MMAO ^aActivity, 10^6 g mol⁻¹ h⁻¹ atm⁻¹

^bDetermined by GPC using polystyrene standard







Fig. 5 DSC curves of PE samples from entries 1–3 in Table 2



Fig. 6 NMR spectra of PE samples from entries 2, 4–6 in Table 2

Similarly, for copolymerization with 1-octene, higher activities $(2.37-2.94 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1} \text{ atm}^{-1})$ and comonomer incorporation ratios (7.9–9.8%) are obtained (Table 2, entries 7-10) as compared with the mononuclear complex $(2.27 \times 10^6 \text{ g mol}^{-1} \text{ h}^{-1} \text{ atm}^{-1} \text{ of activity, } 5.9\% \text{ of incorpo-}$ ration ratio). Both these results were higher than that for 1-hexene copolymerization, although 1-octene was a bulkier comonomer. It is likely that 1-octene produced longer branches and rendered the product easier to dissolve, thus facilitated the polymerization reaction. Similar phenomenon has also been observed for the mononuclear complexes [29, 56]. These tridentate binuclear Ti complexes showed better catalytic properties for ethylene-α-olefin copolymerization than the bis-ligated binuclear catalyst FI^2-Ti_2 reported by Ma, which generated similar activities and 1-hexene or 1-octene incorporation ratios as compared to the mononuclear **FI**–**Ti**₁.



Fig. 7 GPC traces of PE samples from entries 2, 4–6 in Table 2

4 Conclusions

Binuclear Ti complexes (Ti2^a-Ti2^c) based on methylenebridged salicylaldiminato tridentate [ONS] ligands bearing different alkylthio sidearms were prepared and examined for ethylene (co)polymerization under MMAO activation. High activity of over 10⁶ g mol⁻¹ h⁻¹ atm⁻¹ was obtained for both homo- and co-polymerization. Compared with the corresponding mononuclear complex, the binuclear catalysts showed increased activity and comonomer insertion ratio. The alkylthio sidearm also significantly influenced the polymerization behavior. Complex Ti₂^c with the long octylthio side group showed higher activity for ethylene polymerization than the methylthio functionalized Ti_2^a , as a result of the increased solubility of the catalyst in toluene. While for copolymerization, complex Ti2^a demonstrated the highest catalytic activity and comonomer incorporation ratio, due the small steric hindrance of the methylthio side group.

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