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β -Diketiminato 3d-metal compounds: Synthesis, characterization and catalytic behavior towards ethylene

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ABSTRACT

The lithium β -diketiminate (1c, [Li{N(2,6-^{*i*}Pr₂C₆H₃)C(Ph)CHC(^{*t*}Bu)NH}]₂ represented as (LiL)₂) reacted with 3d-metal (II) chlorides to afford the corresponding compounds (2–7). All metal compounds were fully characterized by elemental, spectroscopic analyses and the single-crystal X-ray diffraction. The coordination geometries around the metals are shown to be tetrahedral within the trinuclear Co₂Li compound (2), planar in ML₂ (M = Co, 3), pseudo-tetrahedral conformation in the ML₂ with M as Mn (4), Fe (5) or Zn (6), and square planar in the dinickel compound (7). Indicated by the trimetallic Co₂Li compound 2, a six-membered ring is constructed of three metal atoms and three bridged chlorides as a twisted conformation. An inversion center is present in the centroid of the Ni₂Cl₂ four-membered ring within compound 7. The plausible mechanism of forming ML₂ was proposed through the chloro-bridged multinuclear compounds on the basis of isolated intermediates of trinuclear (2) and dinuclearic (7) compounds. Upon treatment with methylaluminoxane (MAO), the nickel compound 7 possessed good activity towards ethylene oligomerization, whereas the other metal compounds showed moderate activities towards ethylene polymerization.

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1. Introduction

The 1,5-diazapentadienyls (known as β -diketiminates) have attracted attention due to their physical properties [1-6], and their exploitations as ancillary ligands in transition metal chemistry [7,8] since 1960s. Lappert et al. have reported a number of symmetric β -diketiminato ligands and metal compounds thereof [9– 15], and a number of review articles have also recently appeared [16,17]. β -Diketiminate metal compounds can in general be reported by a number of structural types, for example, ML_2 (L = ${N(R)C(Ph)}_{2}CH, M = Co [9,10], M = Mn, Fe, Ni or Cu [18], ML(\eta^{3} C_{3}H_{5}$ (L = {N(SiMe_{3})C(Ph)}₂CH, M = Ni, Pd) [18], [KL(THF)₃]₂ $(L = Si(Me)_2 \{NC(Ar)\}_2 CH, Ar = 4^{-t}BuC_6H_4\}$ [19] and their derivatives [20-28]. In the case of the dinuclear compounds, the species are dominated by halo-bridged structures. Various metals have been employed such as palladium $[PdL(\mu-Cl)]_2$ (L = {N(SiMe_3)C(Ph)}_2CH) [18] or {C(Me)N(Ph)}₂CH [29–31], zinc $[ZnL(\mu-F)]_2$ [32], chromium $[CrLCl(\mu-Cl)]_2$ (L = {C(Me)N(2,6-^{*i*}Pr₂C₆H₃)}₂HC) [33,34], nickel $[NiL(\mu-Cl)]_2$ (L = {C(Me)N(Ar)}_2CH) [35–38], or =CH(dmpz)_2 [39], $[NiL(\mu-Cl)]_2 \cdot 2CH_3OH$ [40], $[NiLCl(\mu-Cl)]_2$ [41,42] and cobalt $[CoL(\mu-Cl)]_2$ (L = {C(Me)N(Ar)}_2CH) [38]. We note that some dinickel compounds have shown catalytic behavior in ethylene polymerization and oligomerization [35]. Recently β -diketiminato zirconium compounds have intensively been investigated in ethylene polymerization [43–47], and extensive research has been conducted with the nonsymmetrical N^N β -diketiminato ligands, (2-C₅H₅N)C(H)C(Ph)N(SiMe₃) [48] and N(SiMe₃)₂C(C₅H₅N)CHC(^tBu) [49,50]. However, there are no reports containing mononuclear, dinuclear and trinuclear complexes and understanding the formation mechanism.

The nonsymmetrical β -diketiminato ligand (1c, [Li{N(2,6- ${}^{i}Pr_{2}C_{6}H_{3}C(Ph)CHC({}^{t}Bu)NH\}]_{2}$ (LiL)₂) has been reacted with various metal chlorides. The trinuclear chloro-bridged compound $[(CoL)_2(\mu-Cl)_3Li(THF)_2]$ (2) was isolated, and transformed into the ML_2 compound (M = Co, **3**). Typical ML_2 derivatives were isolated when the metal is Mn (4), Fe (5) or Zn (6), as well as a chlorobridged dinickel compound $[(NiL)_2(\mu-Cl)_2, 7]$. Interest in nickel compounds chelating P[^]P, N[^]O, P[^]N and N[^]N ligands is the catalysis center around their use as for ethylene oligomerization and polymerization [51-54]. The catalytic activity was explored for the dinickel compound $[(NiL)_2(\mu-Cl)_2, 7]$ with high activity observed in ethylene oligomerization, whereas the other metal complexes showed only moderate activities towards ethylene oligomerization. Herein the synthesis and characterization of the title compounds are reported in detail as well as the catalytic behavior in ethylene oligomerization.



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2. Experimental

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Hexane, tetrahvdrofuran, toluene and diethyl ether are dried using sodium potassium alloy and distilled under nitrogen prior to use. Dichloromethane is distilled over CaH₂. The PhMeC=N($2,6^{-i}Pr_2C_6H_3$) (1a) was prepared according to the literature [55,56]. The NMR spectra were recorded on a Bruker DKX-300 spectrometer with TMS as an internal standard. Elemental analyses were performed with a Flash EA 1112 microanalyzer. The polymerization grade ethylene was supplied by Beijing Yansan Petrochemical Co. The Et₂AlCl (1.90 M in toluene) and methylaluminoxane (MAO, 1.46 M in toluene) solution were purchased from Ablemarle Corporation. Deuterated solvents C₆D₆ and CDCl₃ were dried over activated molecular sieves (4 Å) and freshly distilled before use. GC was performed with a VARIAN CP-3800 gas chromatograph equipped with a flame ionization detector and a 30-m (0.2 mm i.d., 0.25 µm film thickness) CP-Sil 5 CB column. Melting points of polyolefins were measured on a Perkin-Elmer DSC-7 differential scanning calorimetry (DSC) analyzer. Under a nitrogen atmosphere, a sample of about 2–6 mg was heated from 20 to 160 °C at a rate of 10 °C/min and kept for 5 min at 160 °C to remove the thermal history, then cooled at a rate of 10 °C/min to 20 °C. The DSC trace and the melting points of the samples were obtained from the second scanning run.

2.1. Preparations of ligands 1a-1d

2.1.1. [LiCH₂PhC= $N(2,6^{-i}Pr_2C_6H_3)$] (**1b**)

To the solution of **1a** (0.56 g, 2 mmol) in 25 ml THF at $-78 \,^{\circ}$ C, LDA (0.21 g, 2 mmol) was added. The mixture was stirred for 2 h at $-78 \,^{\circ}$ C, then warmed to room temperature for 5 h. The resultant solution was concentrated under vacuum and layered with hexane to give the light yellow solid. Recrystallization from its THF solution gave colorless crystals **1b** (0.56 g, 1.96 mmol) in 98% yield. ¹H NMR (300 MHz C₆D₆): δ 0.81–0.88 (d, 2H, CH₂), 0.93–0.94 (d, 4H, THF), 1.04–1.06, 1.34–1.36 (2d, 12H, CH(CH₃)₂), 2.99–3.11 (d, 4H, THF), 3.58–3.62 (m, 2H, CH(CH₃)₂), 3.72 (s, H, NH), 6.79–6.81 (m, 1H, Ph), 6.85–6.97 (m, 3H, Aryl), 7.09–7.12 (d, 2H, Ph), 7.78–7.81 (d, 2H, Ph). ¹³C NMR (75 MHz C₆D₆): δ 16.60 (CH₂), 16.72 (THF), 19.43, 19.44 (CH(CH₃)₂), 59.30 (THF), 63.06 (CH(CH₃)₂), 112.50 (p-Ar), 114.64 (m-Ar), 117.58 (o-Ph), 118.08 (p-Ph), 135.85 (m-Ph), 141.40 (ipso-CPh), 145.17 (ipso-CAr), 152.34 (ipso-CAr-N), 172.98 (N=C).

2.1.2. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^{t}Bu)NHLi]_2$ (**1***c*)

To the solution of **1b** (0.57 g, 2 mmol) in 25 ml THF at 0 °C, ^tBuCN (0.22 ml, 2 mmol) was added dropwise to form a rose red solution, which gradually disappeared and changed to a brown solution. The mixture was then warmed up to room temperature and kept stirring for 12 h. Then 25 ml hexane was layered on the red solution, and the precipitate was observed and collected as light yellowish solid of **1c** (0.72 g, 0.97 mmol) in 97% yield. *Anal.* Calc. for C₅₀H₆₄N₄Li₂: C, 81.62; H, 8.74; N, 7.59. Found: C, 81.64; H, 8.71; N, 7.62%. ¹H NMR (C₆D₆): δ 0.79–0.79 (d, 6H, CH(CH₃)₂), 1.02–1.04 (d, 6H, CH(CH₃)₂), 1.10 (s, 9H, C(CH₃)₃), 2.74–2.75 (m, 2H, CH(CH₃)₂), 5.04 (s, 1H, CH), 7.06–7.08 (m, 3H, aryl), 7.13–7.57 (m, 5H, Ph). ¹³C NMR (C₆D₆): δ 21.43 (CH, ⁱPr), 23.75 (CH₃, ⁱPr), 27.77 (CH₃, ^fBu), 28.83 (C, ^fBu), 89.73 (CH), 123.51 (aryl), 124.00–126.59 (Ph), 130.64 (ipso-CPh), 135.69 (ipso-CⁱPr), 145.73 (ipso-CAr), 165.62 (N=C), 166.08 (ipso-C^tBu). ⁷Li NMR (C₆D₆): δ 1.52.

2.1.3. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^{t}Bu)NH_2]$ (1d)

To the solution of 1c (0.74 g, 1 mmol) in 25 ml diethyl ether at 0 °C, distilled water (0.08 ml, 4 mmol) was slowly added. The

resultant solution was stirred overnight. The yellow solution was concentrated under vacuum and purified on a silica gel column using petroleum ether/ether (3:1) as the eluent to get the product **1d** (0.64 g, 1.8 mmol) in 90% isolated yield as colorless crystals, mp: 81–83 °C. *Anal.* Calc. for $C_{25}H_{34}N_2$: C, 82.69; H, 9.28; N, 3.85. Found: C, 82.71; H, 9.26; N, 3.86%. ¹H NMR (C_6D_6): δ 0.77–0.79 (d, 6H, CH(CH₃)₂), 0.97–0.99 (d, 6H, CH(CH₃)₂), 1.17 (s, 9H, C(CH₃)₃), 2.87–2.89 (m, 2H, CH(CH₃)₂), 3.69 (NH₂), 4.95 (s, 1H, CH), 6.82 (m, 3H, aryl), 7.04 (m, 5H, Ph). ¹³C NMR (C_6D_6): δ 21.30 (CH, ⁱPr), 23.90 (CH₃, ⁱPr), 27.38, 28.57 (CH₃, ^tBu), 35.30 (C, ^tBu), 89.58 (CH), 121.75 (aryl), 126.77–127.10 (Ph), 137.05 (ipso-CPh), 139.66 (ipso-CⁱPr), 145.54 (ipso-CAr), 165.68 (N=C), 166.24 (ipso-C^tBu).

2.2. Synthesis of late-transition compounds 2-7

2.2.1. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^tBu)NH]_2Co_2(\mu-Cl)_3Li \cdot 2THF(2)$

To the solution of **1c** (0.74 g, 1 mmol) in 25 ml THF at -78 °C, the CoCl₂ (0.26 g, 2 mmol) was added. The resulting mixture was stirred for 10 min, then warmed up to room temperature and stirred for 24 h. Volatile compounds were removed, and the resulting residues were solvated in 50 ml CH₂Cl₂. The filtrate was concentrated and crystallized as black-green crystals **2** (0.46 g, 0.42 mmol) in 42% yield, mp: 167–170 °C (with dec). *Anal.* Calc. for C₅₈H₈₀Cl₃Co₂LiN₄O₂: C, 63.50; H, 7.30; N, 5.11. Found: C, 63.55; H, 7.29; N, 5.13%.

2.2.2. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^{t}Bu)NH]_2Co(3)$

Method one: To the solution of 1c (0.74 g, 1 mmol) in 25 ml THF at -78 °C, the CoCl₂ (0.13 g, 1 mmol) was added. The resulting mixture was stirred for 10 min, then refluxed for 3 h. Volatile compounds were removed, and the resulting residues were extracted in 50 ml toluene. The filtrate was concentrated and crystallized as red crystals **3** (0.62 g, 0.73 mmol) in 73% yield.

Method two: The compound **2** (0.55 g, 0.5 mmol) was refluxed in toluene for 12 h. The filtrate was concentrated and crystallized as red crystals **3** (0.32 g, 0.41 mmol) in 82% yield. Mp: 252–254 °C (with dec). *Anal.* Calc. for $C_{50}H_{66}N_4$ Co: C, 76.79; H, 8.51; N, 7.16. Found: C, 76.80; H, 8.50; N, 7.15%.

2.2.3. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^{t}Bu)NH]_2Mn$ (4)

Using the same procedure as compound **2**, the compound **4** was isolated as brown crystals (0.60 g, 0.76 mmol) in 76% yield, mp: 182–184 °C (with dec). *Anal.* Calc. for $C_{50}H_{66}N_4Mn$: C, 77.18; H, 8.48; N, 7.21. Found: C, 77.22; H, 8.45; N, 7.20%.

2.2.4. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(tBu)NH]_2Fe$ (5)

Using the same procedure as compound **2**, the compound **5** was obtained as red crystals (0.47 g, 0.6 mmol) in 60% yield, mp: 188–189 °C (with dec). *Anal.* Calc. for $C_{50}H_{66}N_4$ Fe: C, 77.21; H, 8.24; N, 7.21. Found: C, 77.15; H, 8.26; N, 7.19%.

2.2.5. $[N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^tBu)NH]_2Zn$ (6)

Using the same procedure as compound **2**, the compound **6** was obtained as light-yellow crystals (0.67 g, 0.85 mmol) in 85% yield, mp: 226–229 °C (with dec). ¹H NMR (300 MHz CDCl₃) δ 0.838 (s, 18H, C(CH₃)₃), 1.11–1.24 (m, 6H, CH(CH₃)₂), 3.43 (m, 2H, CH(CH₃)₂), 4.80 (s, 1H, CH), 5.83 (s, 1H, NH), 6.88 (m, 6H, aryl), 7.09 (d, 8H, Ph), 7.26 (d, 2H, Ph). ¹³C NMR (75 MHz CDCl₃) δ 24.13, 25.26 (CH₃, ^{*i*}Pr), 27.84 (CH, ^{*i*}Pr), 28.98 (CH₃, ^{*i*}Bu), 39.39 (C, ^{*i*}Bu), 91.88 (CH), 122.51, 123.38 (aryl), 126.96, 127.63, 129.20 (Ph), 141.93 (ipso-C^{*i*}Pr), 142.98 (ipso-CPh), 147.59 (ipso-CAr), 169.24 (ipso-CPh), 181.40 (ipso-C^{*i*}Bu). *Anal.* Calc. for C₅₀H₆₆N₄Zn: C, 77.20; H, 8.24; N, 7.21. Found: C, 77.13; H, 8.27; N, 7.17%.

2.2.6. $[(N(2,6^{-i}Pr_2C_6H_3)C(Ph)CHC(^{t}Bu)NH)Ni(\mu-Cl)]_2$ (7)

Using the same procedure compound **2**, the compound **7** was obtained as black-red crystals (0.28 g, 0.31 mmol) in 31% yield, mp: 240–242 °C (with dec). ¹H NMR (300 MHz CDCl₃) δ 0.92 (s, 9H, C(CH₃)₃), 0.97–0.99 (d, 6H, CH(CH₃)₂), 2.25–2.27 (d, 6H, CH(CH₃)₂), 3.89 (s, 2H, CH(CH₃)₂), 4.71 (s, 1H, CH), 6.78–6.88 (m, 3H, C₆H₃), 6.88–6.98 (m, 5H, C₆H₅). ¹³C NMR (75 MHz CDCl₃) δ 24.32, 27.32 (CH₃, ⁱPr), 29.38 (CH, ⁱPr), 29.94 (CH₃, ^rBu), 37.75 (C, ^rBu), 95.46 (CH), 124.02, 126.03 (aryl), 127.78, 129.00 (Ph), 141.50 (ipso-CPh), 144.10 (ipso-CAr), 144.69 (ipso-CⁱPr), 161.97 (ipso-CPh), 171.21 (ipso-CⁱBu). Anal. Calc. for C₅₀H₆₆N₄Ni₂Cl₂: C, 65.81; H, 7.24; N, 6.14. Found: C, 65.79; H, 7.27; N, 6.11%.

2.3. X-ray crystallographic studies

The data for **1b**, **1d** and **2–7** compounds were collected with Mo K α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer at 298(2)–173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. A total of N reflections were collected by using ω scan mode. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package [57]. Crystal data and details of data collection and refinements for **1b**, **1d** and **2–7** are summarized in Table 1.

Table 1 Crystal data and structure refinement for compounds 1b, 1d and 2–7.

2.4. Procedure for ethylene oligomerization and polymerization

2.4.1. At 1 atm ethylene

A flame-dried, three-necked flask was loaded with the catalyst precursor and purged three times with nitrogen. Ethylene was then charged in the flask along with freshly distilled toluene and the mixture stirred for 10 min under 1 atm of ethylene pressure. The reaction temperature was controlled with a water bath and the required amount of co-catalyst was then injected with a syringe. The reaction mixture was stirred for the required time and then the reaction was quenched by addition of 5% aqueous hydrogen chloride. The contents and distribution of oligomers were determined by GC. The polymerization reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried in vacuum at 60 °C to a constant weight.

2.4.2. At 10 atm ethylene

A 250-ml stainless steel reactor equipped with a mechanical stirrer and a temperature controller was heated under vacuum at least 2 h at above 80 °C, then cooled to the required reaction temperature under ethylene atmosphere and charged with toluene, the desired amount of cocatalyst, and a toluene solution of catalytic precursor; the total volume was 100 ml. The reactor was sealed and pressurized to the desired ethylene pressure, and the ethylene pressure was maintained with feeding of ethylene. After the reaction was carried out for the required period, the pressure was released. A small amount of the reaction solution was collected, the reaction in this small sample was terminated by the addition

Compound	1b	1d	2	3	4	5	6	7
Formula Formula weight	C ₃₂ H ₄₈ LiNO ₃ 501.65	C ₂₅ H ₃₄ N ₂ 362.54	C ₅₈ H ₈₂ Cl ₃ Co ₂ LiN ₄ O ₂ 1098.43	C ₅₀ H ₆₆ CoN ₄ 782.00	C ₅₀ H ₆₆ N ₄ Mn 778.01	C ₅₀ H ₆₆ N ₄ Fe 778.92	C ₅₀ H ₆₆ N ₄ Zn 788.44	C ₂₅ H ₃₃ ClN ₂ Ni 455.69
Т(К)	173(2)	223(2)	293(2)	173(2)	223(2)	223(2)	293(2)	293(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	triclinic
Space group	ΡĪ	ΡĪ	C2/c	C2/c	C2/c	Pccn	Pccn	ΡĪ
a (Å)	9.5595(19)	11.025(4)	29.686(7)	13.182(3)	17.198(6)	14.064(5)	13.964(14)	9.647(3)
b (Å)	11.331(2)	11.156(3)	10.206(2)	21.701(4)	12.821(7)	16.974(6)	16.985(15)	10.275(5)
c (Å)	14.764(3)	11.566(4)	20.220(5)	15.162(3)	20.655(11)	18.841(6)	18.834(15)	13.052(6)
α (°)	86.47(3)	66.354(6)	90	90	90	90	90	88.28(4)
β (°)	81.59(3)	64.955(4)	104.547(4)	96.22(3)	93.07(8)	90	90	68.91(3)
γ (°)	73.86(3)	62.488(4)	90	90	90	90	90	88.78(4)
V (Å ³)	1519.2(5)	1105.11(6)	5930(2)	4311.9(15)	4547(4)	4498(4)	4467(7)	1206.5(9)
μ (mm ⁻¹)	0.068	0.063	0.736	0.436	0.327	0.372	0.587	0.927
Ζ	2	2	4	4	4	4	4	2
$\rho_{\rm calc} ({\rm g/cm^3})$	1.097	1.090	1.230	1.205	1.136	1.150	1.172	1.254
θ (°)	1.39-27.49	2.18-25.01	1.42-25.01	1.82-27.48	1.98-25.00	1.88-25.01	2.16-25.01	1.67-25.01
Index ranges	$-12 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 13$	$-34 \leqslant h \leqslant 35$	$-17 \leqslant h \leqslant 17$	$-20 \leqslant h \leqslant 20$	$-16 \leq h \leq 16$	$-16 \leqslant h \leqslant 16$	$-11 \leqslant h \leqslant 11$
	$-14 \leqslant k \leqslant 14$	$-13 \leqslant k \leqslant 12$	$-12 \leqslant k \leqslant 10$	$-21 \leqslant k \leqslant 28$	$-10 \leqslant k \leqslant 15$	$-17 \leqslant k \leqslant 20$	$-20 \leqslant k \leqslant 14$	$-12 \leqslant k \leqslant 11$
	$-17 \leqslant l \leqslant 19$	$-11 \leqslant l \leqslant 13$	$-23 \leqslant l \leqslant 23$	$-19 \leqslant l \leqslant 19$	$-22 \leqslant l \leqslant 24$	$-13 \leqslant l \leqslant 22$	$-22 \leqslant l \leqslant 21$	$-10 \leqslant l \leqslant 15$
Number of reflections collected	18 468	4289	11 217	17 453	8864	16 531	17 082	4940
Number of independent reflections (R _{int})	6937 (0.0251)	3675 (0.0345)	5096 (0.0767)	4822 (0.0457)	3916 (0.0564)	3878 (0.0657)	3909 (0.0593)	4129 (0.0287)
Number of	363	251	370	277	256	256	256	269
Goodness-of-fit (GOF) on F^2	1.112	1.300	1.282	1.190	1.202	0.919	1.007	1.145
$F(0 \ 0 \ 0)$	548	396	2328	1684	1676	1680	1696	484
Completeness to θ (%)	99.3	94.2	97.5	97.4	97.5	97.7	99.1	96.9
Final R indices	$R_1 = 0.0652$,	$R_1 = 0.1477$,	$R_1 = 0.1266$,	$R_1 = 0.0713$,	$R_1 = 0.0781$	$R_1 = 0.0661$	$R_1 = 0.0576$,	$R_1 = 0.0784$
$[I > 2\sigma(I)]$	$wR_2 = 0.1795$	$wR_2 = 0.3757$	$wR_2 = 0.3301$	$wR_2 = 0.1946$	$wR_2 = 0.1980$	$wR_2 = 0.1960$	$wR_2 = 0.1677$	$wR_2 = 0.2232$
R indices (all data)	$R_1 = 0.0689$,	$R_1 = 0.1650$,	$R_1 = 0.1788$,	$R_1 = 0.0756$,	$R_1 = 0.1018$,	$R_1 = 0.1003$,	$R_1 = 0.0825$,	$R_1 = 0.0870$,
. ,	$wR_2 = 0.1830$	$wR_2 = 0.4033$	$wR_2 = 0.3610$	$wR_2 = 0.1979$	$wR_2 = 0.2259$	$wR_2 = 0.2440$	$wR_2 = 0.1903$	$wR_2 = 0.2411$
Largest difference in	0.430 and	0.669 and	0.793 and -1.043	0.818 and	0.619 and	0.729 and	0.771 and	0.562 and
peak and hole (e $Å^3$)	-0.342	-0.672		-0.618	-0.594	-0.489	-0.412	-1.445

of 5% aqueous hydrogen chloride, and the organic layer was analyzed by gas chromatography (GC) for determining the composition and mass distribution of oligomers obtained. The polymerization reaction was quenched by addition of acidic ethanol. The precipitated polymer was washed with ethanol several times and dried in vacuum.

3. Results and discussion

3.1. Synthesis and characterization

The stoichiometric reaction of 2,6-diisopropyl-*N*-(1-phenylethylidene)benzenamine (CH₃(Ph)C=N(2,6-^{*i*}Pr₂C₆H₃), **1a**) [55] with lithium diisopropylamide (LDA) in THF quantitatively formed the lithium compound CH₂(Ph)C(2,6-^{*i*}Pr₂C₆H₃)NLi-3THF (**1b**). Further reaction of **1b** with an equivalent of ^{*t*}BuCN in THF gave the nonsymmetrical β -diketiminato lithium complex (**1c**) *via* a C–C coupling reaction. Quenching the ether solution of **1c** with water, *N*-(3-amino-4,4-dimethyl-1-phenylpent-2-enylidene)-2,6-diisopropylbenzenamine (HL, **1d**) was obtained, which proved the formula LiL and was consistent with the elemental and NMR analysis. Referring to the β -diketiminato lithium analogs [9–12,48–50], the β -diketiminato lithium (**1c**) is reasonably assumed as dimer (LiL)₂ (Scheme 1).

The β -diketiminato lithium (1c) was reacted with various transition metal (II) chlorides to form the corresponding metal compounds (2–7) (Scheme 1). The trinuclear compound $[CoL]_2(\mu$ -Cl)_3Li(THF)₂ (2) was recrystallized from its THF solution at room temperature; and was shown a twisted conformation with three bridging chlorides, two cobalt atoms and one lithium. The compound 2 was refluxed in toluene and produced a trinuclear CoL₂ compound (3), which was also isolated by refluxing the mixture of 1c with CoCl₂ in THF. The typical pseudo-tetrahedral ML₂ compounds for Mn (4), Fe (5) and Zn (6) were easily isolated from the correspondent reactions of 1c with the respective metal (II) chloride. In the reaction of nickel dichloride, however, a chloro-bridged dinickel compound [NiL(μ -Cl)]₂ (7) with a planar square geometry was isolated.

All β -diketiminato metal compounds were slightly sensitive in solution, but stable in the solid state. The microanalysis data of all compounds **1b**, **1d** and **2–7** were in agreement with the proposed structures, and the compounds **1a–1d**, **6** and **7** were characterized by NMR spectroscopy; moreover, the molecular structures of compounds **1b**, **1d** and **2–7** were confirmed by single-crystal

X-ray diffraction analysis. Except for nickel, the commonly reported ML_2 compounds (**D**) [58] were observed for all metals. The trimetallic compound (**2**, **B** type) proved to be an intermediate in forming CoL₂ (**3**, **D** type). Elimination of LiCl and THF within compound **B** happened, the chloro-bridged dinickel compound [NiL(μ -Cl)]₂ (**7**) was formed (represented as **C**). Therefore, the initial step in the reaction of the metal (II) chlorides with **1c** would form the chloro-metal bonding in intermediate **A**, which further rearrange to form the trimetallic compound **B**. It would be better to isolate all types of the compounds with the same metal, but their analogs provided enough information for a plausible reaction mechanism as shown in Scheme 2.

3.2. Crystal structures

The molecular structure of **1b** is illustrated in Fig. 1, and its selected bond lengths and angles are tabulated in Table 2. The



Scheme 2. Plausible mechanism for forming multinuclear metal compounds.



Scheme 1. Synthesis of compounds 1-7.





Fig. 2. ORTEP drawing of **1d** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Fig. 1. ORTEP drawing of **1b** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) for $\mathbf{1b}$ and $\mathbf{1d}$

1b			
Bond lengths N(1)–C(1) N(1)–C(9) N(1)–Li(1) Li(1)–O(2)	1.3572(18) 1.4209(17) 1.994(3) 2.064(3)	C(1)-C(2) C(1)-C(3) Li(1)-O(1) Li(1)-O(3)	1.359(2) 1.495(2) 1.967(3) 2.028(3)
Bond angles C(1)-N(1)-C(9) C(9)-N(1)-Li(1) N(1)-C(1)-C(3) 1d	113.89(11) 110.98(11) 115.32(12)	C(1)-N(1)-Li(1) N(1)-C(1)-C(2) C(2)-C(1)-C(3)	134.85(12) 127.29(14) 117.36(14)
Bond lengths N(1)–C(13) C(13)–C(14) N(2)–C(21)	1.284(6) 1.439(7) 1.330(6)	N(1)-C(1) C(14)-C(21) C(21)-C(22)	1.429(6) 1.355(7) 1.545(7)
Bond angles C(13)-N(1)-C(1) C(21)-C(14)-C(13) N(2)-C(21)-C(22)	122.0(4) 126.1(4) 115.8(4)	N(1)-C(13)-C(14) N(2)-C(21)-C(14) C(14)-C(21)-C(22)	121.2(4) 121.3(4) 122.8(4)

lithium atom is coordinated with an κ^1 -enamido ligand and three THF molecules, consistent with the use of a bulky enamido ligand along with coordinated THF molecules [13]. The bond distance of Li–N is 1.994(3) Å and the length of C(1)–C(2) is 1.359(2) Å. The dihedral angle of the aryl ring and phenyl ring to the plane C(2)–C(1)–C(3)–N–Li are 87.18° and 47.20°, respectively.

In the NCCCN moiety of compound **1d** (Fig. 2 and Table 1), the bond distances N(1)–C(13), C(13)–C(14), C(14)–C(21) and N(2)–C(21) are 1.284(6), 1.439(7), 1.355(7) and 1.330(6) Å, respectively, and their bond features alternately appear as double and single ones. The bond angles of N(1)–C(13)–C(14), C(13)–C(14)–C(21) and C(14)–C(21)–N(2) are 121.2(4)°, 126.1(4)° and 121.3(4)°, respectively, indicate that the NCCCN moiety is a near coplanar system. Due to the steric strain of the bulky 2,6-diisopropylphenyl, the dihedral angles of the aryl or phenyl to the NCCCN plane are 81.62° and 62.95°, respectively.

The molecular structure of the trinuclear cobalt compound $(CoL)_2(\mu$ -Cl)_3Li-2THF (**2**) is shown in Fig. 3, while the selected bond



Fig. 3. ORTEP drawing of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: -x, y, -z + 1/2.

lengths and angles are tabulated in Table 3. The cluster $M_2Li(\mu-Cl)_3$ core is a six-membered chelate ring with a twisted conformation. Each Co atom is coordinated to two chloride ions and a μ,η -NCCCN ring of the β -diketiminato ligand, whereas the cationic four coordinate lithium is bound by two chlorides and two THF molecules. The Co–Cl [C1(2)] bond distances are 2.340(3) Å, which are slightly longer than data observed in the compounds [CoL(μ -Cl)]₂ [38] and CoLCl₂Li(THF)₂(L=(N(Dipp)C(Me))₂CH) (2.293–2.295 Å) [59],

Table 3	
Selected bond lengths (Å) and angles (°) for 2 .	

Bond lengths			
Co-N(2)	1.929(8)	C(13)-C(20)	1.377(13)
Co-N(1)	1.954(7)	C(20)-C(21)	1.395(14)
N(1)-C(13)	1.342(12)	N(2)-C(21)	1.304(13)
N(1)-C(1)	1.457(11)	C(13)-C(14)	1.521(13)
C(21)-C(22)	1.552(13)	Cl(1)–Li	2.361(15)
Co-Cl(1)	2.287(3)	Co-Cl(2)	2.340(3)
Bond angles			
Bond angles N(2)-Co-N(1)	96.0(3)	C(1)-N(1)-Co	122.1(6)
Bond angles N(2)-Co-N(1) C(13)-N(1)-Co	96.0(3) 118.8(6)	C(1)-N(1)-Co C(21)-N(2)-Co	122.1(6) 125.5(7)
Bond angles N(2)-Co-N(1) C(13)-N(1)-Co N(1)-Co-Cl(1)	96.0(3) 118.8(6) 114.8(2)	C(1)-N(1)-Co C(21)-N(2)-Co C(1)-N(1)-Co	122.1(6) 125.5(7) 122.0(5)
Bond angles N(2)-Co-N(1) C(13)-N(1)-Co N(1)-Co-Cl(1) N(1)-Co-Cl(2)	96.0(3) 118.8(6) 114.8(2) 118.8(2)	C(1)-N(1)-Co C(21)-N(2)-Co C(1)-N(1)-Co N(2)-Co-Cl(2)	122.1(6) 125.5(7) 122.0(5) 101.9(3)
Bond angles N(2)-Co-N(1) C(13)-N(1)-Co N(1)-Co-Cl(1) N(1)-Co-Cl(2) Cl(1)-Co-Cl(2)	96.0(3) 118.8(6) 114.8(2) 118.8(2) 105.29(10)	C(1)-N(1)-Co C(21)-N(2)-Co C(1)-N(1)-Co N(2)-Co-Cl(2) N(2)-Co-Cl(1)	122.1(6) 125.5(7) 122.0(5) 101.9(3) 120.3(3)
Bond angles N(2)-Co-N(1) C(13)-N(1)-Co N(1)-Co-Cl(1) N(1)-Co-Cl(2) Cl(1)-Co-Cl(2) Co-Cl(1)-Li	96.0(3) 118.8(6) 114.8(2) 118.8(2) 105.29(10) 99.4(4)	C(1)-N(1)-Co C(21)-N(2)-Co C(1)-N(1)-Co N(2)-Co-Cl(2) N(2)-Co-Cl(1) Co-Cl(2)-Co'	122.1(6) 125.5(7) 122.0(5) 101.9(3) 120.3(3) 102.42(16)

and Co(OMes₂)₂Li(THF)₂(μ -Cl)₂ Li(THF)₂ (2.297(1)Å) [60]; whilst the bond lengths of Co-Cl [Cl(1) and μ -Cl(1)'] 2.287(3) Å are in agreement with the observations (2.293-2.297 Å) related the Co-Cl-Li fragments [58]. The Cl(2) atom lies in the plane of the Co-Co-Li, however, the Cl(1) and Cl(1)' atoms are out of Co-Cl(2)-Co-Li plane with one above and another below. The distances of Cl(1) and Cl(1)^r to the Co-Cl(2)-Co-Li plane are equal at 4.56 Å, and the dihedral angle between Co–Cl(1)'–Li and Co–Cl(2)– Co-Cl(1)-Li is 75.71°. The Li-Cl and Li-O distances [2.361(15) and 1.938(17) Å] are also similar to previously reported compounds [59–64]. Regarding the β -diketiminato moiety, the bond distances Co-N [1.956(7) and 1.920(7) Å] and the bond angle N-Co-N (96.0°) are typical for β -diketiminato compounds [9–18,59–73]. The dihedral angles between C(13)-C(20)-C(21) or N(1)-Co-N(2) and N(1)-C(13)-C(21)-N(2) are 16.33° and 36.88°, whilst the dihedral angle between C(13)-C(20)-C(21) and N(1)-Co-N(2) is 20.56°. The MNCCCN backbone features a full-boat conformation which is wider than that of compounds 3-7. The dihedral angles of the aryl and phenyl to the six-membered metallic ring are 75.81° and 55.88°, respectively.

The molecular structures of cobalt **3**, manganese **4**, iron **5** and zinc **6** complexes possessed a similar distorted tetrahedral geometry (Figs. 4–7), and their selected bond lengths and angles are illustrated in Tables 4 and 5, respectively.

The metal cores of compounds 3-6 are coordinated by four nitrogen atoms of two β -diketiminato ligands, and the sixmembered metalocyclic rings adapt shallow boat-shaped conformations. The two six-membered rings are either orthogonality (4, 5, 6) (cf. the dihedral angle at the metal M, which increases in the sequence Mn (48°) < Fe (63.02°) < Zn (64.46°) , as shown in Table 5) or co-planarity (3, Co (5.35°)). The difference is attributed to steric effects. The bond distances of Mn-N in compound 4 are in the range [2.071(3)–2.114(3) Å], which are a little longer than the M–N bond in its analogs, for example Co-N [1.880(3)-1.962(2) Å] in 3, Fe-N [1.978(3)-2.044(3) Å] in 5, Zn-N [1.955(3)-2.038(3) Å] in 6. These are caused by the differences of their ionic radii and electrophilic behaviors. The bond angle $[N(1)-Co-N(2)^{\prime} 88.84(11)^{\circ}]$ in **3** and $[N(1)-Mn-N(2) 87.85(13)^{\circ}]$ in **4** are smaller than [N(1)-Fe-N(2)]91.24(13)°] in **5** and [N(1)–Zn–N(2) 93.12(11)°] in **6**. The dihedral angles of the aryl and phenyl to the six-membered metal rings decrease in the sequence **3** (84.80° and 77.83°) > **4** (83.52° and 60.21°) > 5 (82.24° and 50.17°) > 6 (82.43° and 49.23°).



Fig. 4. ORTEP drawing of **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: -x, y, -z + 1/2.



Fig. 5. ORTEP drawing of **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent are omitted for clarity. Symmetry operation: -x, -y, -z + 1/2.



Fig. 6. ORTEP drawing of **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent are omitted for clarity. Symmetry operation: -x + 1/2, -y + 1/2, -z.



Fig. 7. ORTEP drawing of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent are omitted for clarity. Symmetry operation: -x + 1/2, -y + 1/2, z.

Table 4

Endocyclic bond	distances	(a-f) (Å) and	angles	$(\alpha - \theta)$	(°) in	the	M{N(Ar)C(Pl	1)CHC
(^t Bu)NH} moieties	s of 3–6 .							

Compound	3	4	5	6
Ph_ e	f ^t Bu			
B				
c	d			
Ň	$\theta \int_{1}^{\varepsilon \dot{N}}$			
Ar a N	N, p			
a (Å)	1.962(2)	2.114(3)	2.046(3)	2.038(3)
b (Å)	1.880(3)	2.071(3)	1.972(3)	1.955(3)
c (Å)	1.351(4)	1.353(5)	1.343(4)	1.331(4)
d (Å)	1.322(4)	1.305(5)	1.319(4)	1.309(4)
e (Å)	1.384(4)	1.395(6)	1.402(5)	1.407(5)
f (Å)	1.398(4)	1.420(6)	1.393(5)	1.389(5)
α(°)	126.6(2)	125.0(3)	123.7(2)	121.5(2)
β(°)	125.1(3)	124.7(3)	124.1(3)	125.3(3)
γ(°)	124.5(3)	129.0(3)	128.6(3)	128.4(3)
δ (°)	120.2(3)	121.5(3)	121.7(3)	122.4(2)
(°) 3	134.6(2)	129.7(3)	128.5(2)	127.0(2)
θ (°)	88.84(11)	87.85(13)	90.91(10)	93.12(11)

Table 5
Selected bond distances $(a-f)$ (Å), angles $(\alpha-\theta)$ (°) and dihedral angles (°) around metal
atoms of 4–6 .

Compound	3	4	5	6
Ar a b	Ph C C IBu	Ph δ β Ar α M	ε θ N	
a (Å)	1.447(4)	1.441(5)	1.447(4)	1.432(4)
b (Å)	1.508(4)	1.503(5)	1.495(5)	1.491(5)
<i>c</i> (Å)	1.542(4)	1.543(5)	1.531(4)	1.540(4)
d (Å)	0.108	-0.292	0.414	0.432
e (Å)	0	-0.210	0.168	0.179
f(Å)	0	0.143	-0.013	-0.029
α (°)	120.08(18)	113.7(2)	115.3(2)	116.0(2)
β (°)	113.3(2)	120.1(3)	119.4(3)	120.5(3)
γ (°)	121.4(3)	120.3(3)	121.0(3)	120.8(3)
δ (°)	113.5(3)	115.0(3)	114.9(3)	113.9(3)
(°) 3	119.4(3)	118.2(3)	120.1(3)	118.8(3)
θ (°)	120.5(3)	120.3(3)	118.2(3)	118.3(3)
Dihedral angle at M (°)	5.35°	48	63.02	64.46

The molecular structure of the nickel compound $(NiL)_2(\mu-Cl)_2$ (7) is illustrated in Fig. 8, and the selected bond lengths and angles are shown in Table 6. The Ni centers adopts a typical square planar coordination geometry, with two N and two bridging Cl atoms occupying the four coordination sites and displaying typical bond lengths and angles. The Ni-N distances [1.818(4) and 1.878(4)Å] are unexpectedly different. The nonbonded Ni…Ni distance [2.8821(17)Å] is shorter than those (Ni···Ni separation 3.2966(8)-3.458(1)Å) reported in the chloro-bridged dinickel compound bearing bulky β -diketiminato ligands [35–37], and longer than the interacting Ni-Ni bond (2.38-2.81 Å) [67-74], suggesting a weak Ni-Ni interaction in compound 7. The bridging Ni-Cl distances [1.869(4) and 1.882(4)Å] are also shorter than previously reported Ni-Cl [2.2997(9)-2.4840(6)Å] [35-37,39, 41,42], perhaps due to the sterically imposing β -diketiminate and the high-spin Ni(II). The bond angle N(1)-Ni-N(2) $(93.81(18)^\circ)$ is typical for β -diketiminato compounds [9-18,35-37]. The dihedral angles between C(9)-C(8)-C(1) or N(1)-Ni-N(2) and N(1)–C(9)–C(1)–N(2) are 2.18° and 7.02° , whilst the dihedral angle between N(1)–Ni–N(2) and Cl(1)–Ni–Cl(1)^{γ} is 2.84°; C(8) and Ni lie on same side. The MNCCCN moiety is a boat conformation as seen in compounds **3–6**. The Cl(1) and Cl(1)'atoms are out the N(1)-Ni-N(2) planes (mean deviation 0.076



Fig. 8. ORTEP drawing of **7** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and solvent are omitted for clarity. Symmetry operation: -x, -y, -z.

Table 6
Selected bond lengths (Å) and angles (°) for 7.

Bond lengths			
Ni(1)-N(1)	1.818(4)	C(8)-C(9)	1.397(7)
N(1)-C(9)	1.305(6)	N(2)-C(1)	1.328(6)
Ni(1)-N(2)	1.878(4)	C(1)-C(8)	1.392(8)
N(2)-C(14)	1.436(6)	C(1)-C(2)	1.496(7)
Ni(1)-Cl	1.882(4)	Ni(1)-Cl'	1.869(4)
Ni(1)-Ni(1')	2.8821(17)	Cl-Cl'	2.400(9)
Bond angles			
N(1) - Ni(1) - N(2)	93.81(18)	C(1)-N(2)-Ni(1)	124.6(4)
N(2)-C(1)-C(8)	124.3(5)	C(9)-N(1)-Ni(1)	131.0(4)
C(1)-C(8)-C(9)	124.9(5)	N(1)-C(9)-C(8)	120.4(5)
Cl-Ni(1)-Cl'	79.6(2)	Ni(1)-Cl-Ni(1')	100.4(2)

and 0.039 Å) and lie on opposite sides, which may partly be caused by the steric repulsion between the aryl and phenyl groups out-of-the-plane of the NCCCN plane (the dihedral angles 81.52° and 56.43°).

To summarize, the important geometrical parameters associated with compounds **2–7** indicate the bond lengths M–N(Ar) and M–N decrease in the sequence **4** > **5** > **6** > **3** > **2** > **7** with the characteristic M–N(Ar) > M–N. The mean C–N lengths are similar as C(sp2)=N(sp2) bond. The bond angle of N–M–N in **3** [88.84(11)°] and **4** [87.85(13)°] are relatively smaller than those of its analog compounds 90.91(10)° (**5**), 93.12(11)° (**6**), 93.81(18)° (**7**), and 96.0(3)° (**2**), respectively. The compound **2** has a twisted conformation formed by three bridging-chlorides and three metal centers, whereas the compound **3** gives a planar structure. In compounds **4–6**, with a distorted tetrahedral coordination, the dihedral angles between two NMN planes are 48° in **4**, 63.02° in **5** and 64.46° in **6**. Compound **7** adopts a dinuclear square planar geometry.

3.3. Ethylene reactivity

The compounds **2**, **5** and **7** are investigated for their catalytic behavior towards ethylene in the presence of cocatalysts. In general, nickel compounds are the most considered among these compounds, and compound **7** is used in selecting suitable cocatalysts. Using methylaluminoxane (MAO) as cocatalyst showed better activity than that of diethylaluminum chloride (Et₂AlCl) (entries 1–2 in Table 7). The dimerization mostly occurred when using Et₂AlCl. In the presence of MAO, the ratio of Al/Ni and pressure

Table 7

Ethylene oligomerization and polymerization of 2 and 7 system.^a

Entry	Cat.	Cocat.	Al/M	P (atm)	Oligomer	Oligomers (%) ^b				$T_{\rm m}^{\rm e}$ (°C)
					Act. ^c	C₄/∑C	C ₆ /∑C	1-C4		
1	7	Et ₂ AlCl	200	1	14.6	96.91	3.09	61.52	-	
2	7	MAO	1500	1	107	81.3	18.70	50.5	trace	
3	7	MAO	1000	1	79.8	80.3	19.7	41.0	-	
4	7	MAO	2000	1	98.1	80.6	19.4	46.1	-	
5	7	MAO	1500	10	775	73.9	26.1	89.0	1.20	89.6
6	2	MAO	1000	1	2.21	77.4	22.6	69.2	-	
7	2	MAO	1500	1	7.38	70.2	29.8	71.2	-	
8	2	MAO	2000	1	4.54	72.6	27.4	58.2	-	
9	2	MAO	1500	10	31.1	72.8	27.2	86.3	-	

^a Conditions: 5 µmol; 30 min; 30 °C. The total volume: 30 ml toluene for 1 atm or 100 mL toluene for 10 atm.

^e Determined by DSC.

of ethylene were verified (entries 3–5 in Table 7), and the optimum condition with molar ratio of Al/Ni at 1500 was observed to produce butenes and hexenes along with a trace amount of polyethylene (entry 4 in Table 7), but without higher order olefins. When the ethylene pressure was increased from 1 to 10 atm, the catalytic activity increased to 7.75×10^5 g mol(Ni)⁻¹ h⁻¹ (entry 5 in Table 7). Moreover, the fractions of hexenes were significantly improved along with a better selectivity for α -olefins (89.0% for 1-butene of butenes). Such phenomena are explained by the ethylene insertion and chain propagation being enhanced by the increase of ethylene pressure [74]. An activity value for the ethylene polymerization as high as 1.20×10^4 g mol(Ni)⁻¹ h⁻¹ was obtained (entry 5 in Table 7).

The cobalt compound **2** was also investigated in the presence of MAO (entries 6–9 in Table 7), and showed relative lower activities in oligomerization than observed for the nickel compound **7**. Again, the catalytic activity and selectivity of the α -olefins were improved with elevated ethylene pressure (entry 9 in Table 7). Based on the optimum condition observed in the catalytic system of nickel, further investigation were conducted for the iron analogs employing the ratios of Al/M in 1500 at 10 atm of ethylene. The iron compound **5** produces polyethylene with good activity [2.44×10^5 g mol⁻¹(Fe) h⁻¹], whilst the molecular weight (M_w) value of the PE is 130 kg/mol with molecular weight distribution 4.2. The melting point (T_m) value of PE is 134 °C.

Although these compounds had potential as catalysts for either ethylene oligomerization or polymerization, the results obtained here suggested that they are not promising for further consideration.

4. Conclusions

The nonsymmetric β -diketiminato lithium complex (1c) and its corresponding metal compounds 2–7 were synthesized and characterized by elemental and spectroscopic methods, as well as by X-ray crystallographic studies. The isolation of trimetallic, dimetallic and monometallic compounds contributed to a plausible reaction mechanism. Their catalytic behaviors were evaluated with cocatalyst MAO or Et₂AlCl, and the MAO showed better performance, the nickel compound showed good activity in ethylene oligomerization. The variation of nonsymmetric β -diketiminato ligands and their metal compounds is still being explored for their interesting properties in structural and catalytic chemistry.

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Appendix A. Supplementary material

CCDC 759159–759166 contain 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.ica.2011.01.063.

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^b Determined by GC.

^c 10^3 g mol⁻¹(M) h⁻¹.

^d 10^4 g mol⁻¹(M) h⁻¹

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