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Synthesis and crystal structures of novel β -diketiminato-lithium, iron, cobalt, nickel, zirconium complexes and their catalytical behaviors in polymerization of ethylene

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Abstract

Treatment of azaallyl-lithium $[\text{LiN}(\text{R})\text{C}(\text{Bu}')\text{CHR}]$ with equal portion of 1-piperidinecarbonitrile gave mix-substituted β -diketiminato-lithium **2**. Double ratio of **2** with FeCl_2 , CoCl_2 and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ yielded the β -diketimate iron **3**, cobalt **4**, nickel **5**, or equivalent of ZrCl_4 led to zirconium complex **6**, respectively. The structural features of these complexes were described, and the catalytical behaviors of the complexes **3–6** for the polymerization of ethylene were investigated.

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Keywords: β -Diketimate; Crystal structures; Catalysis; Zirconium; Transition metal

1. Introduction

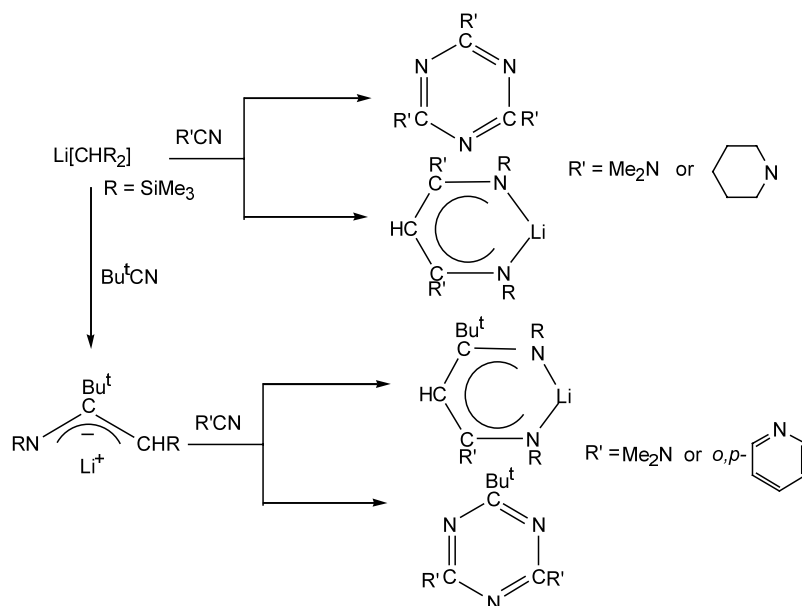
The β -diketiminato ligand is an important chelating system in coordination chemistry. Combining with some later transition metals, the complexes have been used as catalysts for the polymerization of olefin yielding α -olefin and polymer products with high molecular weights or having some special functional polymer materials [1–4]. In 1994, Lappert's group devised a new synthetic method to prepare this type of compound via interaction of LiCHR_2 (or later related lithium trimethylsilylmethyls) and α -hydrogen-free nitrile $\text{R}'\text{CN}$, and the first fully characterized crystalline alkali metal β -diketimate $[\text{Li}\{(\text{N}(\text{R})\text{C}(\text{Ph}))_2\text{CH}\}_2]$ [5,6]. Recently, we reported that addition reactions of the reagent $\text{Li}[\text{CHR}_2]$ ($\text{R} = \text{SiMe}_3$) or derived 1-azaallyl-

lithium $[\text{LiN}(\text{R})\text{C}(\text{Bu}')\text{CHR}]_2$ with cyanoamine could lead to β -diketiminato-lithium and, interestingly, symmetrically and mix-substituted triazines at mild condition (Scheme 1) [7].

In this paper we report our proceeding studies on addition reaction of azaallyl-lithium reagent $[\text{LiN}(\text{R})\text{C}(\text{Bu}')\text{CHR}]_2$ ($\text{R} = \text{SiMe}_3$) with 1-piperidinecarbonitrile, and the synthesis and characterization of the β -diketiminato-lithium, iron, cobalt, nickel and zirconium. Our interesting focus on the catalytic behavior by: (i) introducing an electronegative substituted group of piperidino on the five-member NCCCCN moiety—the coordinative environment of the β -diketiminato ligand; and (ii) changing the transition metal of the β -diketiminato compound. The investigation showed that the catalytic activities was increased as the order diketiminato $\text{Ni} > \text{Zr} > \text{Co} > \text{Fe}$ and, interestingly, the β -diketiminato-zirconium mixed with nickel chloride could significantly increase the catalytic activities in the polymerization of ethylene.

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Scheme 1. Synthetic routes to β -diketiminato-lithium and triazines.

2. Results and discussion

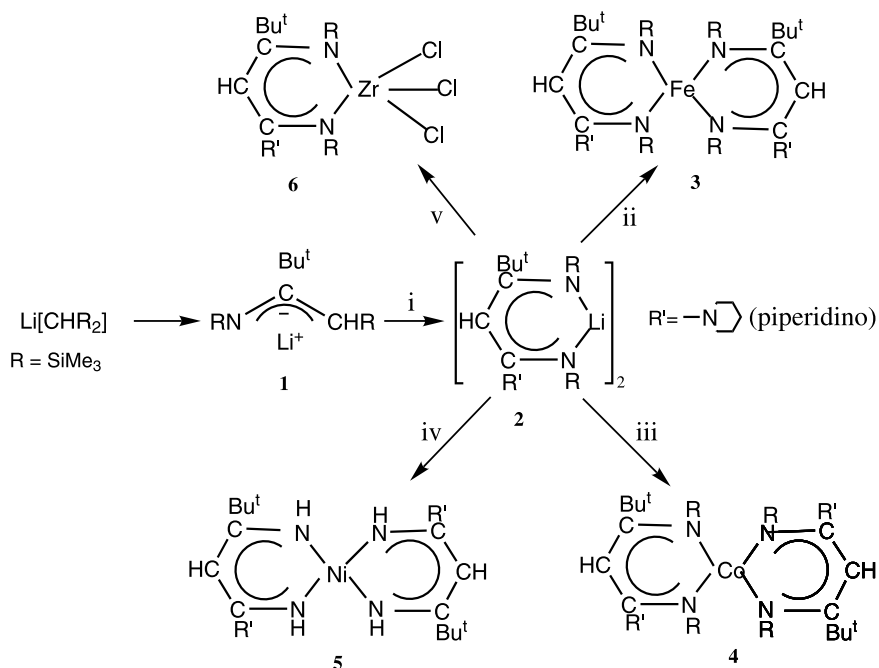
2.1. Synthesis of complexes 2–6

The synthetic routes to complexes 2–6 are illustrated in Scheme 2.

The azaallyl-lithium compound $[\text{LiN}(\text{R})\text{C}(\text{Bu}^t)\text{CHR}]_2$ ($\text{R} = \text{SiMe}_3$) (**1**) was prepared in an early work [8]. The reaction of **1** with an equimolar portion of $\text{R}'\text{CN}$ ($\text{R}' =$

piperidino) in polar solvent such as Et_2O gave $[\text{Li}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHC}(\text{R}')\text{N}(\text{R})\}]_2$ (**2**).

Treatment double ratio of **2** with FeCl_2 or CoCl_2 in Et_2O at -78°C led to red crystalline complexes $[\text{Fe}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHC}(\text{R}')\text{N}(\text{R})\}]_2$ (**3**) or $[\text{Co}\{\text{N}(\text{R})\text{C}(\text{Bu}^t)\text{CHC}(\text{R}')\text{N}(\text{R})\}]_2$ (**4**), respectively. Their suitable single crystals were obtained by recrystallization in dichloromethane.

Scheme 2. Synthetic routes to complexes 3–6. Reagents and conditions: (i) $\text{R}'\text{CN}$ ($\text{R}' = \text{piperidino}$), Et_2O ; (ii) FeCl_2 , Et_2O , -78°C ; (iii) CoCl_2 , Et_2O , -78°C ; (iv) NiCl_2 , $\text{Et}_2\text{O}-\text{H}_2\text{O}$; (v) ZrCl_4 , Et_2O , -78°C .

Treatment double ratio of **2** with NiCl₂ could not isolate the corresponding Ni complex in our case. It was noted that the bulky effect of the trimethylsilyl groups on the β-diketiminato ligand normally gave a tetrahedral complex. Due to the d⁸ configuration Ni preferred a planar geometry and might not easily to give a tetrahedral complex in this case. However, using NiCl₂·6H₂O instead of NiCl₂ gave crystalline [Ni{NHC–(Bu')CHC(R')NH}]₂ (**5**) in high yield (80%) and as a result the trimethylsilyl groups inevitably were hydrolyzed.

Treatment of an equimolar portion of **2** with ZrCl₄ in Et₂O at –78 °C led to Zr[N(R)C(Bu')CHC(R')N(R)]Cl₃ (**6**). A suitable single crystal was obtained by recrystallization in dichloromethane.

2.2. Characterization of 2–6

The β-diketiminato-complexes **2–6** were characterized by ¹H-NMR, X-ray diffraction and for **3–6** elemental analysis. Their analytical data were satisfactory. The ¹H-NMR spectrum of paramagnetic **4** showed a substantial peak-broadening effect with three broad peaks at δ 1.6, 3.0, and 8.1.

2.3. The molecular structure of complexes 2–6

The molecular structures of complexes **2–6** are shown in Figs. 1–5 and the selected bond lengths and angles are shown in Tables 1–5, respectively. Crystallographic data for complexes **2–6** are listed in Table 6.

2.3.1. The molecular structure of complex 2

Molecular structure of compound **2** (Fig. 1) is a dimer built around a nearly planar LiNLiN ring (mean deviation 0.08 Å); the angles at the nitrogen atoms being narrower [75.8(3) and 76.3(3)°] than those at the Li atoms [102.8(3), 104.9(3)°]. One lithium atom is coordinated with three N and three C atoms (η⁵), and the other with four N and four C atoms, including an N atom from piperidino group. The intramolecular Li–N_{sp³} bond distances [2.007(8) and 2.045(8) Å] are close to the intermolecular Li–N_{sp³} [2.028(7) and 2.046(7) Å].

Angles N–C–C in the two LiNCCCC ring are almost same [126.4(4) and 126.3(3)°], but N–Li–N are 104.6(3) and 98.2(3)°, and C–C–C are 131.5(4) and 129.9(3)°, respectively. The NCCCCN fragment is planar (mean deviation 0.07 Å). The two lithium atoms are about 0.98 and 1.17 Å out of the two plane NCCCCN rings, respectively. Thus the fragment can be rendered as a six-electron-donor with some degree of π-electron delocalization, although the pairs of N–C [1.298(4) and 1.374(4) Å] and C–C bonds [1.367(4) and 1.464(5) Å] are far from being identical.

2.3.2. The molecular structure of complex 3

For complex **3** the dihedral angle between N(1)–Fe(1)–N(2) and N(1A)–Fe(1)–N(2A) is 65.1°; both angles of N(1)–Fe(1)–N(2) and N(1A)–Fe(1)–N(2A) are 89.48(10)°; N(1)–Fe(1)–N(1A) and N(2)–Fe(1)–N(2A) are 92.93(14) and 122.65(15)°, respectively. So it is a marked distorted tetrahedral geometry. Comparing with Co^{II}, Fe^{II} has a lower tendency to form tetrahedral complex. Here the reason is mainly due to bulky effect of trimethylsilyl groups on N atoms. It is noted that dihedral angle between C(1)–C(3)–N(1) and

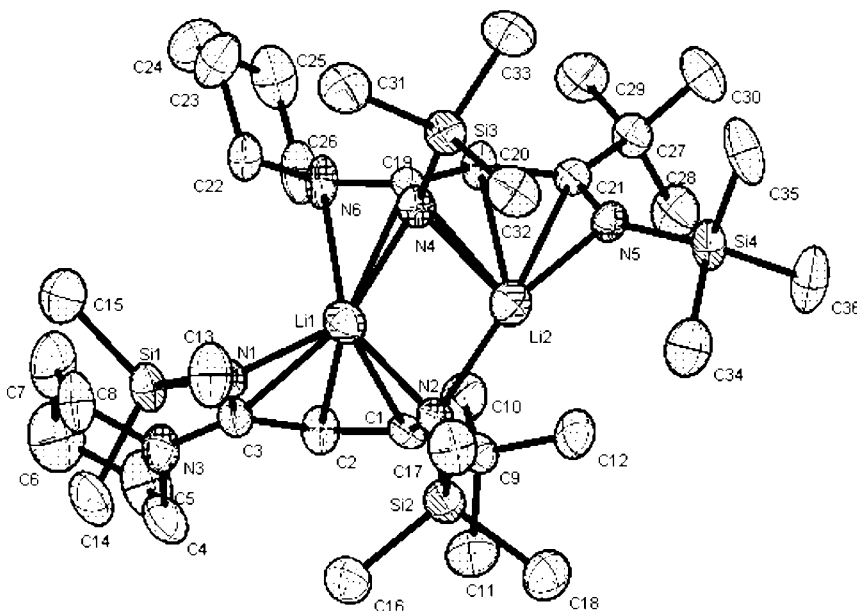


Fig. 1. Molecular structure of complex **2**.

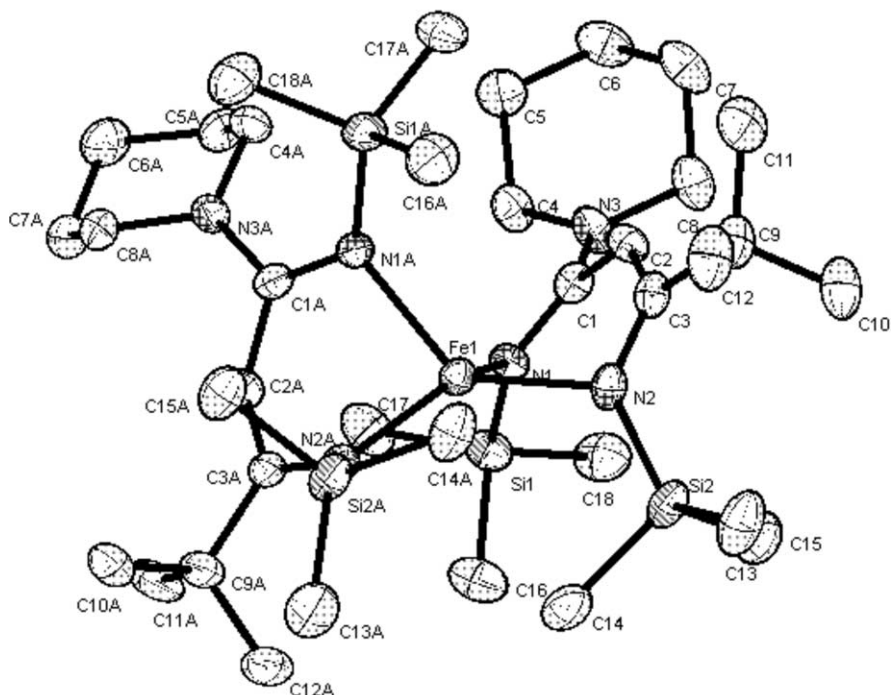


Fig. 2. Molecular structure of complex 3.

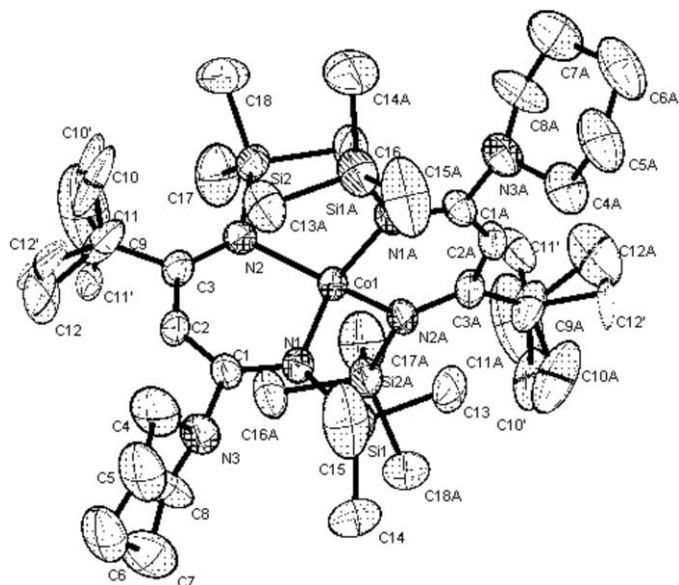


Fig. 3. Molecular structure of complex 4.

C(1)–C(3)–N(2) was 8.3° , and thus N(1)–C(1)–C(3)–N(2) [NC–CN] can be regarded in a plane (mean deviation 0.04 \AA). However, dihedral angles between C(1)–C(2)–C(3) or N(1)–Fe(1)–N(2) and NC–CN are 16.3 and 56.4° , respectively. That means the C(2) and Fe(1) atoms actually are out the planes (average vertical distance from Fe(1) and C(2) to the plane NC–CN are ca. 1.23 and 0.17 \AA , respectively). For this reason we would like to regard the ligand being a η^5 -bonding mode.

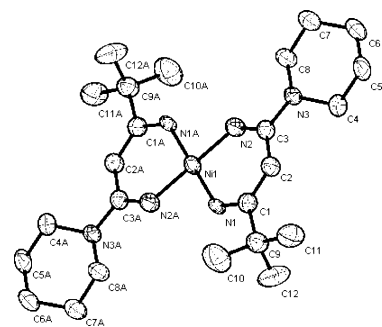


Fig. 4. Molecular structure of complex 5.

Due to a C_2 -axis is present across Fe(1) and the center point of N(1)–N(1A), the two β -diketiminato ligands in one complex molecular are equivalent.

2.3.3. The molecular structure of complex 4

In the complex 4, a C_2 symmetric axis is present across Co(1) and the center point of N(1)–N(1A); the two β -diketiminato ligands in one complex molecular are equivalent. The centric cobalt atom Co(1) has a tetrahedral arrangement and is bonded by four nitrogen atoms from two ligands with bond length ranging from $1.987(5)$ to $2.023(5) \text{ \AA}$. The four atoms N(1), C(1), C(3) and N(2) are almost in the same planar (mean deviation 0.0016 \AA). The dihedral angle between N(1)–C(1)–C(3)–N(2) and N(1)–Co(1)–N(2) is 0.1° and between N(1)–C(1)–C(3)–N(2) and C(1)–C(2)–C(3) is 0.3° , respectively. So each of the six-membered metallacycles is coplanar. Dihedral angle between N(1)–Co(1)–N(2)

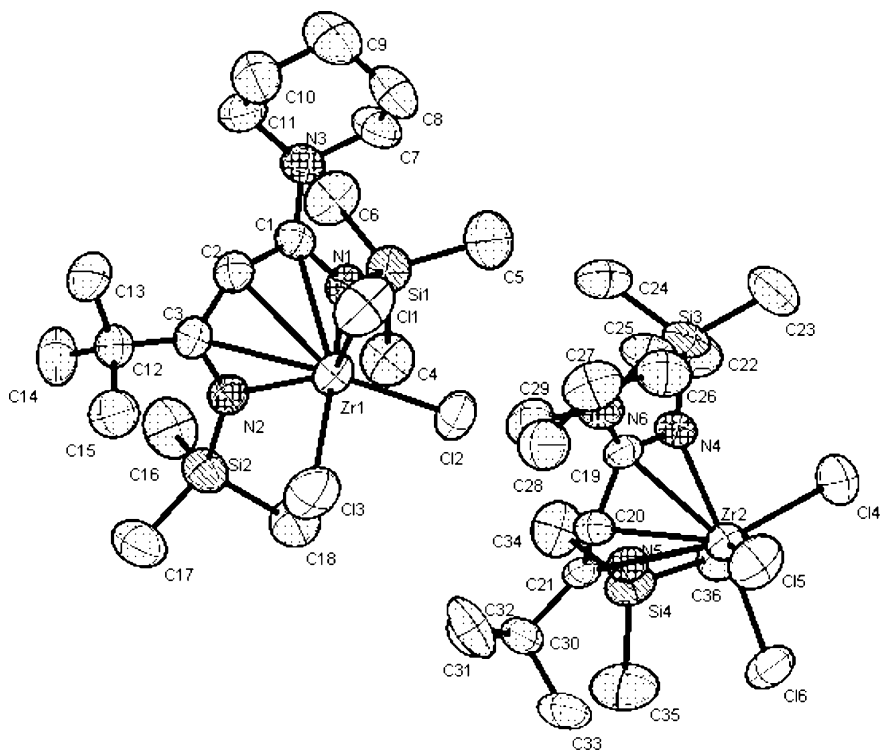


Fig. 5. Molecular structure of complex 6.

Table 1
Some selected bond lengths (Å) and angles (°) for complex 2

<i>Bond lengths</i>	
Li(1)–N(1)	1.962(7)
Li(1)–N(2)	2.007(8)
Li(1)–N(4)	2.028(7)
Li(1)–N(6)	2.716(7)
Li(2)–N(2)	2.046(7)
Li(2)–C(19)	2.523(7)
Li(2)–C(20)	2.780(7)
Li(2)–C(21)	2.664(7)
N(1)–C(3)	1.298(4)
N(2)–C(1)	1.374(4)
C(1)–C(2)	1.367(4)
C(2)–C(3)	1.464(5)
<i>Bond angles</i>	
N(2)–Li(1)–N(4)	104.9(3)
N(2)–Li(2)–N(4)	102.8(3)
Li(1)–N(2)–Li(2)	76.3(3)
Li(1)–N(4)–Li(2)	75.8(3)
N(1)–Li(1)–N(2)	104.6(3)
N(2)–C(1)–C(2)	126.4(4)
C(1)–C(2)–C(3)	131.5(4)
N(4)–Li(2)–N(5)	98.2(3)
N(4)–C(19)–C(20)	126.3(3)
C(19)–C(20)–C(21)	129.9(3)

Table 2
Some selected bond lengths (Å) and angles (°) for complex 3

<i>Bond lengths</i>	
Fe(1)–N(1)	2.113(3)
Fe(1)–N(2)	2.056(3)
C(1)–N(1)	1.315(4)
C(3)–N(2)	1.353(4)
C(1)–C(2)	1.441(4)
C(2)–C(3)	1.383(4)
Fe(1)–C(1)	2.809(3)
Fe(1)–C(2)	2.929(3)
Fe(1)–C(3)	2.741(3)
<i>Bond angles</i>	
N(1)–Fe(1)–N(2)	89.48(10)
N(2)–Fe(1)–N(2A)	122.65(15)
N(1)–Fe(1)–N(1A)	92.93(14)
N(1)–C(1)–C(2)	123.4(3)
C(1)–C(2)–C(3)	128.2(3)
Fe(1)–N(1)–C(1)	107.74(19)

2.3.4. The molecular structure of complex 5

Ni complex has a planar geometry different from **3** and **4** because of a loss of the two trimethylsilyl groups. Two of the six-membered metallacycles are coplanar. The piperidino rings adopt chair conformation. The whole structure of complex **5** is centro-symmetric.

2.3.5. The molecular structure of complex 6

In complex **6**, there are two independent Zr complex molecules found in the unit cell in which the bond distances and angles have no significant differences.

and N(1A)–Co(1)–N(2A) is 90.8°, and then the two planes are mutual perpendicular giving a nearly rigorously tetrahedral configuration. The two piperidino rings adopt chair conformation.

Table 3
Some selected bond lengths (Å) and angles (°) for complex 4

<i>Bond lengths</i>	
Co(1)–N(2)	2.023(5)
Co(1)–N(1)	1.987(5)
N(1)–C(1)	1.338(7)
N(2)–C(3)	1.358(7)
C(1)–C(2)	1.387(7)
C(2)–C(3)	1.375(8)
C(3)–C(9)	1.527(10)
C(1)–N(3)	1.465(8)
<i>Bond angles</i>	
N(1)–Co(1)–N(2)	102.97(19)
Co(1)–N(1)–C(1)	114.9(4)
N(1)–C(1)–C(2)	127.5(6)
C(1)–C(2)–C(3)	134.3(6)
C(2)–C(1)–N(3)	116.9(5)
C(2)–C(3)–C(9)	123.9(6)
N(1)–C(1)–N(3)	115.5(5)
N(2)–C(3)–C(9)	123.9(6)
N(1)–Co(1)–N(1A)	110.4(3)
N(1A)–Co(1)–N(2A)	102.97(19)
N(1)–Co(1)–N(2A)	112.1(2)
N(2)–Co(1)–N(1A)	112.1(2)

Table 4
Some selected bond lengths (Å) and angles (°) for complex 5

<i>Bond lengths</i>	
Ni(1)–N1	1.845(3)
Ni(1)–N2	1.855(3)
N(1)–C(1)	1.321(4)
N(2)–C(3)	1.317(4)
C(1)–C(2)	1.375(5)
C(2)–C(3)	1.416(5)
N(3)–C(3)	1.394(4)
C(1)–C(9)	1.533(5)
<i>Bond angles</i>	
N(1)–Ni(1)–N(1A)	180.00(16)
N(1)–Ni(1)–N(2)	91.25(12)
N(1)–C(1)–C(2)	123.1(3)
N(2)–C(3)–C(2)	120.5(3)
C(1)–C(2)–C(3)	124.0(3)
C(2)–C(1)–C(9)	121.1(3)
C(1)–C(9)–C(11)	113.5(3)
N(3)–C(4)–C(5)	112.7(3)

Zirconium atom is coordinated to a β -diketiminato-anion group in a η^5 -bonding mode, thus forming around the metal a distorted trigonal bipyramidal environment. The Zr(1)–C(2) [2.537(4) Å] is shorter than Zr(1)–C(1) and Zr(1)–C(3) [2.635(4) and 2.603(4) Å]. The dihedral angle between C(1)–C(3)–N(1) and C(1)–C(3)–N(2) is 4.2°, thus the four atoms N(1)–C(1)–C(3)–N(2) is actually in a plane, and between N1–Zr1–N2 and N1–C1–C3–N2 is 78.8°, which is similar to that between N–Zr–N and N–C–C–N of the other molecule. So the six-membered metallacycle Zr–N–C–C–C–N adopt boat conformation, and the distances from Zr(1) or C(2) to planar N(1)–C(1)–C(3)–N(2) are ca. 1.58 and 0.29 Å, respectively.

Table 5
Some selected bond lengths (Å) and angles (°) for complex 6

<i>Bond lengths</i>	
C(1)–N(1)	1.336(4)
C(1)–C(2)	1.456(5)
C(2)–C(3)	1.398(5)
C(3)–N(2)	1.347(4)
Zr(1)–N(1)	2.185(3)
Zr(1)–N(2)	2.145(3)
Zr(1)–C(1)	2.635(4)
Zr(1)–C(2)	2.537(4)
Zr(1)–C(3)	2.603(4)
Zr(1)–Cl(1)	2.4111(13)
Zr(1)–Cl(2)	2.4087(11)
Zr(1)–Cl(3)	2.4497(13)
<i>Bond angles</i>	
Cl(1)–Zr(1)–Cl(2)	101.44(5)
Cl(2)–Zr(1)–Cl(3)	91.02(4)
Cl(1)–Zr(1)–Cl(3)	94.04(5)
N(1)–Zr(1)–N(2)	83.79(11)
Cl(1)–Zr(1)–N(1)	100.99(9)
Cl(1)–Zr(1)–N(2)	131.84(9)
Cl(2)–Zr(1)–N(1)	86.18(8)
Cl(2)–Zr(1)–N(2)	126.72(9)
Cl(3)–Zr(1)–N(1)	164.96(9)
Cl(3)–Zr(1)–N(2)	86.09(9)

2.3.6. A comparison of structure data for complexes 3–6

Sketched structures of the complexes 3–6 are shown in Fig. 6 and some important geometric data (bond lengths in Å, angles in °) are listed in Table 7.

There are significant structural differences among these complexes. Complexes 3 and 4 have a tetrahedral or distorted tetrahedral metal environment, but in an important respect of coordination way the metallacycle ring skeleton in 4 (Co) is planar whereas in 3 the Fe atom is out of the NC–CN plane. Nickel complex 5 adopts a square planar geometry and zirconium complex 6 is in a distorted trigonal bipyramidal environment. In complexes 4 and 5, the MNCCCN (M = Co or Ni) ring is planar and the β -diketiminato ligand behaves in identical chelating fashion via terminal N atoms. In complexes 3 and 6, the six-membered metallacyclic ring is in boat form and the β -diketiminato ligand could be regarded as being η^5 -bonding mode though the bond distances of Fe–C (2.741–2.929 Å) in complex 3 are relatively long.

2.4. Application of complexes 3–6 in the polymerization of ethylene

Complexes 3–6 were used as catalysts in the polymerization of ethylene. Results are listed in Table 8. Compared with Cp_2ZrCl_2 they were shown low activity in pressure of 0.038 MPa of ethylene. Compound 5 had higher catalytic efficiency than other three complexes. Their catalytical activity conforms to the order: Ni 5 > Zr 6 > Co 4 > Fe 3. The catalytic behaviors of the transition metal complexes especially for olefin are

Table 6
Summary of crystallographic data for 2–6

Complex	2	3	4	5	6
Empirical formula	C ₃₆ H ₇₆ Li ₂ N ₆ Si ₄	C ₃₆ H ₇₆ FeN ₆ Si ₄	C ₃₆ H ₇₆ CoN ₆ Si ₄	C ₂₄ H ₄₄ N ₆ Ni	C ₁₈ H ₃₈ Cl ₃ N ₃ Si ₂ Zr
<i>M</i>	719.27	761.24	764.32	475.36	550.26
Temperature (K)	193(2)	153(2)	193(2)	193(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> <i>b</i> <i>cn</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	9.6464(19)	10.8759(11)	16.9343(12)	6.662(2)	11.6805(10)
<i>b</i> (Å)	28.865(6)	19.905(2)	15.8231(11)	9.714(3)	16.7608(15)
<i>c</i> (Å)	16.194(3)	20.692(2)	17.5757(13)	10.144(3)	28.557(3)
α (°)	90	90	90	79.894(4)	90
β (°)	91.160(4)	100.640(2)	90	86.603(4)	96.280(2)
γ (°)	90	90	90	88.102(4)	90
<i>U</i> (Å ³)	4508.3(15)	4402.5(15)	4709.5(6)	645.0(3)	5557.2(8)
<i>Z</i>	4	4	4	2	8
μ (mm ⁻¹)	0.162	0.482	0.495	1.548	0.779
Reflections collected	18 528	7617	15 843	2657	22 743
Independent reflections	7935	3843	4115	2206	9808
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0703	0.0571	0.0791	0.0607	0.0416
<i>wR</i> ₂ (all data)	0.0914	0.1447	0.1795	0.1224	0.0919

influenced by electronic configuration and coordinative unsaturated degree of central metal as well as coordinate type. With the increase of the ion radius from Fe to Ni atom, their coordinative unsaturated degree are increased too and thus the nickel complex has a relatively high catalytic activity, which may be an important factor for catalytic activity of the β -diketiminato transition metal compound catalyst.

It is also our interest to know the influence on catalytic behavior by introducing an electronegative substituted group into the ligand. We deduced that

reducing donor effect of the coordinative N atoms might be beneficial to the catalytic activity of the β -diketiminato Group IV metal compound. Therefore, the polymerization test was designed to make a comparison between complex **6** (which contains an electronegative substituted group of piperidino) and Zr[N(R)C(Bu^t)CHC(R')N(R)]Cl₃ (R' = Ph) (being made in an early work [9]). It was shown that the catalytic activity of the former (complex **6**) was relatively higher than the latter (the former 2.09 gPE (mol M h)⁻¹, while the latter 1.80 gPE (mol M h)⁻¹; toluene =

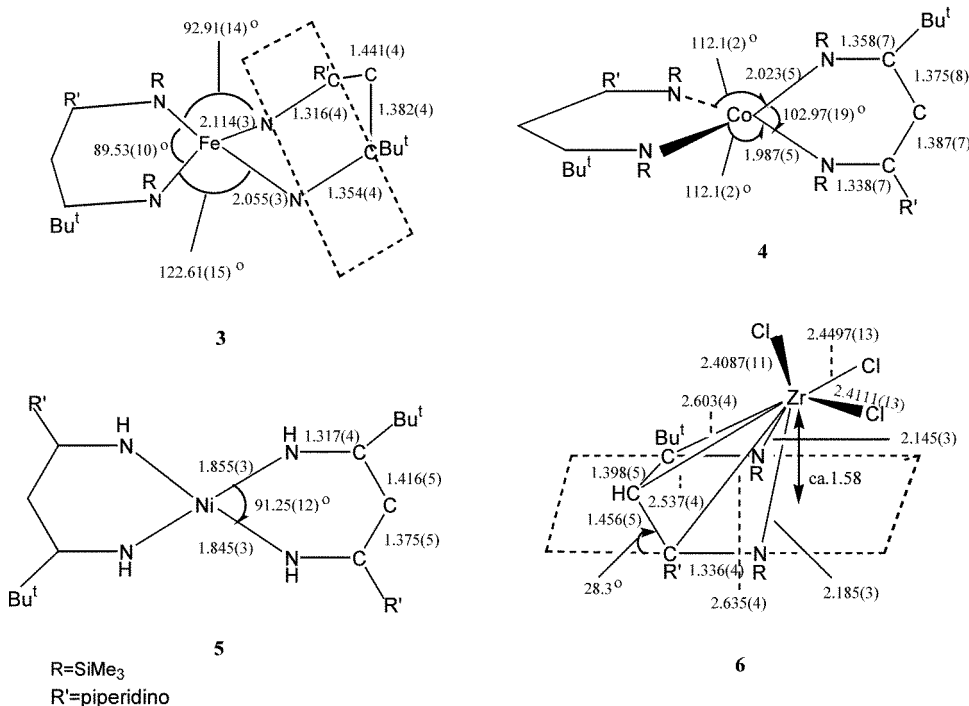


Fig. 6. Selected geometric parameters for crystalline 3–6.

Table 7
Selected structural data for complexes 3–6

Complex	3	4	5	6
M–N(1)	2.113(3)	1.987(5)	1.845(3)	2.185(3)
M–N(2)	2.056(3)	2.023(5)	1.855(3)	2.145(3)
C(1)–N(1)	1.316(4)	1.338(7)	1.321(4)	1.336(4)
C(1)–C(2)	1.441(4)	1.387(7)	1.375(5)	1.456(5)
N–M–N	89.53(10)	102.97(19)	91.25(12)	83.79(11)
Geometry	Distorted tetrahedral	Tetrahedral	Square planar	Distorted trigonal bipyramidal
MNCCCN	Boat	Coplanar	Coplanar	Boat
Bonding mode	η^5	Didentical	Didentical	η^5

Table 8
Data for ethylene polymerization catalyzed by complexes 3–6/MAO system

Complex	Cat. (mg)	Yield of PE (mg)	Activity gPE (mol M h) ⁻¹
3	2.6	1.20	3.51×10^2
4	1.8	7.50	3.18×10^3
5	2.5	166	3.15×10^4
6	1.7	28.9	9.36×10^3
Cp ₂ ZrCl ₂	3.3	694	1.22×10^5

Polymerization conditions: toluene = 50 ml, MAO = 2 ml (0.14 mol l⁻¹), *P* = 0.038 MPa, *T* = RT, *t* = 1 h, M = Fe, Co, Ni, Zr.

50 ml, MAO = 2 ml, *P* = 0.020 MPa, *T* = RT, *t* = 4 h). It seems that the substituted group of piperidino has no significant influence on the catalytic activity. The investigation on this aspect is still under way.

2.5. Catalytic efficiency of compound 6 by adding transition metal chlorides

There is considerable current interest in the use of various Group 4 metal(IV) chloride as polymerization catalysts [10], particularly those of zirconium [9]. In order to investigate the influence of other transition metal as additive on the catalytical behavior of complex 6, metal chlorides such as NiCl₂·6H₂O, PdCl₂, FeCl₂·4H₂O, CoCl₂ and RuCl₂·*n*H₂O were used. Their corresponding activities and amounts are shown in Table 9. Interestingly, NiCl₂·6H₂O evidently increased (about 10 times) the catalytical activity of complex 6; but others such as CoCl₂ and PdCl₂ had no positive influence and even made the catalyst decreased or lost activity. The reason that NiCl₂·6H₂O increased the catalytical activity of complex 6 is of the possibility to partly form nickel complex with diimino ligands and produce the active center on nickel.

3. Experimental

3.1. Materials and procedures

All reactions were performed under Ar using standard Schlenk techniques [11,12]. Solvents were dried and

distilled over K–Na alloy under Ar prior to use. The compound LiCHR₂ were prepared by known procedures [9,13]; others were purchased and purified by standard procedures. The NMR spectra were recorded on Bruker DKX300 instrument, and solvent resonances were used as the internal references for ¹H spectrum. Elemental analyses were carried out using a Vario EL-analyzer (Germany).

3.2. $[\text{Li}\{\overline{\text{N}(\text{R})\text{C}(\text{Bu}^i)\text{CHC}(\text{R}')\text{N}(\text{R})}\}]_2$ (*R* = SiMe₃, *R'* = piperidino) (2)

Trimethylacetonitrile (0.81 cm³, 7.13 mmol) was added dropwise to a stirred solution of LiCH(SiMe₃)₂ (1.18 g, 7.13 mmol) in Et₂O (ca. 20 cm³) at 0 °C for 30 min. The mixture was warmed slowly to room temperature (r.t.) and stirred for 2 h. To the solution 1-piperidinecarbonitrile (0.79 g, 7.13 mmol) was added dropwise at –78 °C. The mixture was slowly warmed to r.t. and stirred for a further 12 h. The solvent was removed in vacuo. The residue was dried at 75 °C/10⁻² Torr for 1 h, then dissolved in C₆H₁₄ (ca. 3–5 cm³) and filtered. By concentrating filtrate white crystalline complex 2 (1.48 g, 58.9%) was obtained. ¹H-NMR (300 MHz, C₆D₆): δ 0.3–0.5 (s, 18H, SiMe₃), 1.12 (s, 9H, Buⁱ), 1.51 (s, 6H, CH₂), 3.18–3.21 (d, 4H, CH₂), 5.29 (s, 1H, CH).

3.3. $[\text{Fe}\{\overline{\text{N}(\text{R})\text{C}(\text{Bu}^i)\text{CHC}(\text{R}')\text{N}(\text{R})}\}]_2$ (3)

Iron dichloride (0.1205 g, 0.95 mmol) was added slowly to a solution of compound 2 (0.682 g, 1.90 mmol) in ether (20 cm³) at –78 °C. The mixture was warmed slowly to r.t. and stirred for overnight. The solvent was removed in vacuo; the residue was extracted with CH₂Cl₂ and filtered. The filtrate was concentrated to give red crystals of compound 3 (0.296 g, 41.0%). Anal. Found: C, 55.50; H, 9.98; N, 11.01. C₃₆H₇₆FeN₆Si₄ requires: C, 56.80; H, 10.06; N, 11.04%. ¹H-NMR (300 MHz, CDCl₃): δ 0.3–0.5 (s, 18H, SiMe₃), 1.3 (s, 9H, Buⁱ), 1.7 (s, 6H, CH₂), 3.4 (d, 4H, CH₂), 5.5 (s, 1H, CH).

Table 9
Results of complex **6** as catalyst for the polymerization of ethylene

Enter	Additive (0.0100 g)	Activity gPE (mol Zr h) ⁻¹	Mw	D	Tm (°C)	Xc (%)
1	–	3.65 × 10 ³	7453	55.06	132.8	60.33
2	NiCl ₂ ·6H ₂ O	1.04 × 10 ⁴	63 961	8.34	131.7	56.61
3	PdCl ₂	0	–	–	–	–
4	FeCl ₂ ·4H ₂ O	6.47 × 10 ³	6103	28.26	133.4	67.92
5	CoCl ₂	1.06 × 10 ³	229 842	58.22	130.9	61.66
6	RuCl ₂ · <i>n</i> H ₂ O	5.00 × 10 ³	470 425	8.25	133.7	70.38

Mcat = 0.0400 g (71.43 μmol), toluene = 50 ml, MAO = 20 ml (1.4 mol l⁻¹), P = 1 atm, T = 40 °C, t = 1 h.

3.4. [Co{N(R)C(Bu')CHC(R')N(R)}]₂ (**4**)

Cobalt dichloride (0.27 g, 2.06 mmol) was added slowly to a solution of compound **2** (1.48 g, 4.12 mmol) in Et₂O (25 cm³) at -78 °C. The resultant green solution was allowed to warm to r.t. and was stirred for overnight. The solvent was removed in vacuo, the residue was extracted with CH₂Cl₂ and filtered. The filtrate was concentrated and crystallized at -30 °C to give red crystal of **3** (0.52 g, 33%). Anal. Found: C, 56.15; H, 9.350; N, 10.99. C₃₆H₇₆CoN₆Si₄ requires: C, 56.57; H, 10.02; N, 11.00%. ¹H-NMR of d⁷ paramagnetic crystalline complex **4** widened all the peaks.

3.5. [Ni{NHC(Bu')CHC(R')NH}]₂ (**5**)

NiCl₂·6H₂O (0.646 g, 2.72 mmol) was added to a solution of compound **2** (0.929 g, 2.59 mmol) in Et₂O (20 cm³) at 0 °C, and degassed water (ca. 20 cm³) was added. The mixed solution was stirred for overnight. The oil layer was dried by MgSO₄ for about 10 h and then concentrated to give block red crystal of **5** (0.49 g, 80%). Anal. Found: C, 60.11; H, 9.05; N, 16.21. C₂₄H₄₄N₆Ni requires: C, 60.64; H, 9.33; N, 17.68%. ¹H-NMR (300 MHz, CDCl₃): δ 1.11 (s, 9H, Bu'), 1.55 (s, 6H, CH₂), 3.08–3.14 (d, 4H, CH₂), 4.38 (s, 1H, CH).

3.6. Zr[N(R)C(Bu')CHC(R')N(R)]Cl₃ (**6**)

Zirconium tetrachloride (0.615 g, 2.64 mmol) was added slowly to a solution of compound **2** (0.948 g, 2.64 mmol) in Et₂O (15–20 cm³) at -78 °C. The resultant pale-yellow solution was allowed to warm to r.t. and was stirred for overnight. The solvent was removed in vacuo. The orange residue was dissolved in CH₂Cl₂ and filtered. The filtrate was concentrated and crystallized at -30 °C to give block yellow crystal of **6** (0.804 g, 56%). Anal. Found: C, 39.45; H, 6.904; N, 7.336. C₁₈H₃₈Cl₃N₃Si₂Zr requires: C, 39.29; H, 6.960; N, 7.636%. ¹H-NMR (300 MHz, CDCl₃): δ 0.3–0.5 (s, 18H, SiMe₃), 1.37 (s, 9H, Bu'), 1.73 (s, 6H, CH₂), 3.49–3.55 (d, 4H, CH₂), 5.56 (s, 1H, CH).

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194394 for complex **2**, No. 192417 for complex **3**, No. 192416 for complex **4**, No. 192418 for complex **5**, and No. 192415 for complex **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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References

- [1] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
- [2] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. 7 (1998) 849.
- [3] D. Pappalardo, M. Mazzeo, S. Antinucci, C. Pellecchia, Macromolecules 33 (2000) 9483.
- [4] M.D. Leatherman, M. Brookhart, Macromolecules 34 (2001) 2748.
- [5] P.B. Hitchcock, M.F. Lappert, D.S. Liu, J. Chem. Soc. Chem. Commun. (1994) 1699.
- [6] L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031.
- [7] Xia Chen, Du Chenxia, Guo Jianping, Wei Xuehong, Liu Diansheng, J. Organomet. Chem. 655 (2002) 89.
- [8] P.B. Hitchcock, M.F. Lappert, D.S. Liu, J. Chem. Soc. Chem. Commun. (1994) 2637.
- [9] M.F. Lappert, D.S. Liu, J. Organomet. Chem. 500 (1995) 203.
- [10] A.D. Horton, Trip 2 (1994) 158.
- [11] D.F. Shriver, M.A. Drezdon, The Manipulation of Air Sensitive Compounds, 2nd ed., Wiley, New York, 1986.
- [12] S. Herzog, J. Dehnert, K. Lühder, Technique of Inorganic Chemistry, vol. VII, Interscience, New York, 1969.
- [13] P.B. Hitchcock, M.F. Lappert, D.S. Liu, et al., J. Chem. Soc. Dalton Trans. (1999) 1263.