Dalton
Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 4236

www.rsc.org/dalton

PAPER

A bulky silyl shift-directed synthesis of a silyl-linked amidinate-amidine and its Zr(IV) complex†

Hong-Bo Tong, Min Li, Sheng-Di Bai, Shi-Fang Yuan, Jian-Bin Chao, Shuping Huang* and Dian-Sheng Liu*

Received 6th September 2010, Accepted 3rd February 2011
DOI: 10.1039/c0dt01177k

A novel silyl-linked amidinate-amidine monoanionic ligand **3** was synthesized by double additions of PhCN starting from silyl-linked bis(amino) monoanion **2**, which underwent an intramolecular Li/H metathesis and double silyl shift. The related Zr(IV) complex **4** was prepared and confirmed by X-ray diffraction revealing a structural rearrangement from its precursor. The mechanisms for the reaction processes have been proposed. Each of compounds **2**, **3** and **4** was characterized by NMR spectroscopy, elemental analysis and X-ray diffraction. Complex **4** exhibited moderate activity for ethylene polymerization in the presence of methylalumoxane (MAO).

Introduction

Amidinate compounds are well known and have been paid considerable attention in searching for novel spectator ligands.[1–3] The ease of tuning the electronic and steric properties by variation of substituents on the conjugated N–C–N backbone make these ligands versatile and comparable with the ubiquitous cyclopentadienyl species. Also based on the similar convenience, a special branch of linked bis(amidinate) ligands has attracted our interest in recent years. This new family of bianionic ligands has been explored because of the advantage of affording both dinuclear and mononuclear complexes, such as types **I** and **II** (Chart 1) which were investigated in our laboratory.[4,6] The related transition metal derivatives were assumed to be useful in asymmetric synthesis.[4,5] Type **II** complexes display close contact between the two amidinate moieties.[6–9] For relevant work on the isomerization processes of organosilyl groups in silylamines, a combined experimental–theoretical study has been made recently by Klingebiel and co-workers.[10]

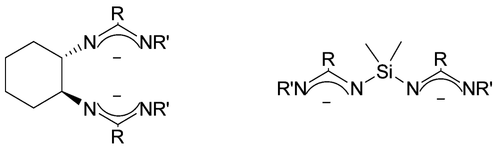


Chart 1

There have been no monoanionic analogues of type **II** reported so far, due to the tendency of intermolecular Li/H metathesis.[6] In our further research of type **II** complexes, the modification of the silyl by linking with a electron donor group led to an unusual monoanionic analogue of type **II**. To the best of our knowledge, this is the first example of a silyl-linked amidinate-amidine monoanion.

Herein, the synthesis of a silyl-linked amidinate-amidine ligand with an electron donor group (here NMe_2) has been described. The mechanisms of the reaction processes are proposed and configuration changes of the ligand caused by the donor group discussed. The corresponding Zr(IV) complex **4** was tested as a catalyst for ethylene polymerization.

Experimental

All manipulations and reactions were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. Solvents were pre-dried over sodium, distilled from sodium–potassium alloy (hexane), sodium–benzophenone (diethyl ether, tetrahydrofuran) and stored over molecular sieves (4 Å). Deuterated solvent (C_6D_6) was dried over sodium–potassium alloy. All solvents were degassed prior to use. Chemicals were purified by distillation before use except for the commercial sample of *n*-butyllithium in hexane (2.72 mol dm^{-3}, Alfa Aesar Corporation). ^1H, ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer. Elemental analyses were performed on a Vario instrument.

Synthesis and characterization

$[SiMe(NMe_2)(PhNH)_2]$ (1). A stirred solution of aniline (9.3 g, 100 mmol) in hexane (150 cm^3) was treated with $LiBu^n$ (37 cm^3, 100 mmol, 2.72 M in hexane) at 0 °C. The reaction mixture was stirred at room temperature for 3 h and then $Cl_2SiMe(NMe_2)$ (7.9 g, 50 mmol) was slowly added at −78 °C. After stirring for a further 10 h at room temperature, the mixture was filtered, and the filtrate was distilled by distillation at 120 °C under 5–6 mmHg to give a very viscous oil $[(Me_2N)SiMe(PhNH)_2]$.

Institute of Applied Chemistry, Shanxi University, Tiayuan, 030006, China

† CCDC reference numbers 761269–761271. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01177k

Table 1 Crystal and refinement data for **2–4**

	2	**3**	**4**
Chemical formula	$C_{38}H_{60}Li_2N_6O_2Si_2$	$C_{58}H_{60}Li_2N_{10}Si_2$	$C_{37}H_{46}Cl_3N_5O_2SiZr$
M_r	702.98	967.22	818.45
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	11.089(3)	10.660(4)	14.7016(17)
b/Å	12.471(3)	11.667(6)	20.676(2)
c/Å	17.197(4)	12.924(7)	26.029(3)
α/°	81.586(4)	115.39(4)	90.00
β/°	75.624(4)	97.71(3)	90.506(2)
γ/°	67.478(4)	105.45(4)	90.00
V/Å^3	2124.5(9)	1341.5(11)	7911.6(16)
Z	2	1	8
T/K	213(2)	213(2)	213(2)
No. reflections measured	8820	6270	32332
No. independent reflections	7344	4518	13925
R_{int}	0.0370	0.0271	0.0529
Final R_1 values ($I > 2\sigma(I)$)	0.0700	0.0705	0.0732
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1176	0.1652	0.1432
Final R_1 values (all data)	0.1288	0.0823	0.1048
Final $wR(F^2)$ values (all data)	0.1375	0.1728	0.1557
CCDC number	761269	761270	761271

{[SiMe(NMe$_2$)(PhNH)PhNLi(OEt$_2$)]$_2$} (2). To a stirred solution of **1** (1.56 g, 10 mmol) in hexane (30 cm^3) was slowly added LiBu^n (3.7 cm^3, 10 mmol, 2.72 M in hexane) at −78 °C and the reaction mixture was warmed to room temperature and stirred for 10 h, then solvent was carefully removed *in vacuo* after which the residue was recrystallized in Et$_2$O to give colorless crystals of **2**. Yield: 3.12 g (89%), 136–138 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ (ppm) 0.46 (s, 3H, Si$\mathrm{C}H_3$), 1.09–1.13 (t, J_{HH} = 1.8 Hz, 6H, OCH$_2$CH_3), 2.19 (s, 1H, NHPh), 2.46 (s, 6H, N(CH_3)$_2$), 3.21 (q, J_{HH} = 1.8 Hz, 4H, OCH_2CH$_3$), 6.83–7.17 (m, 10H, 2Ph); ^{13}C NMR (75.1 MHz, 298 K, C$_6$D$_6$): δ (ppm) 146.3, 129.2, 127.7, 127.38, 127.1 (Ph), 65.2 (OCH$_2$CH$_3$), 36.0 (N(CH$_3$)$_2$), 14.9 (OCH$_2$$CH_3$), −5.1 (Si$CH_3$). Found: C, 64.0; H, 8.1; N 12.0. Calc. for (C$_{19}$H$_{30}$LiN$_3$OSi)$_2$: C, 64.1; H, 8.2; N, 11.95%.

{[SiMe(NMe$_2$){NC(Ph)NH(Ph)}{(NC(Ph)N(Ph)Li)}]$_2$} (3). To a stirred solution of **2** (1.05 g, 3 mmol) in Et$_2$O (20 cm^3) was added PhCN *via* syringe (0.3/0.6 cm^3, 3/6 mmol) at 0 °C and the mixture was slowly warmed to room temperature and stirred for a further 5 h. Then the mixed solution was carefully concentrated *in vacuo* to afford colourless crystals of **3**. Filtering the solution of unreacted starting material purified the product **3**. Yield: 0.60/1.28 g (41.5/88.5%); mp 173–175 °C. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ (ppm) 0.36 (s, 6H, Si$\mathrm{C}H_3$), 2.55 (s, 12H, N(CH_3)$_2$), 2.76 (s, 2H, NHPh), 6.83–7.47 (m, 20H, C$_6$$H_5$); ^{13}C NMR (75.1 MHz, 298 K, C$_6$D$_6$): δ 165.1 (NCN of amidinate), 164.2 (NCN of amidine), 120.2, 124.6, 124.7, 124.8, 125.0, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 128.3, 128.3, 128.5, 128.6, 128.8, 129.2, 137.0, 142.9, 150.6, 152.2, 152.8 (Ph), 38.4 (N(CH$_3$)$_2$), 37.41 (N(CH$_3$)$_2$), 1.2 (SiCH$_3$). Found: C, 72.1; H, 6.1; N, 15.0. Calc. for C$_{58}$H$_{60}$Li$_2$N$_{10}$Si$_2$: C, 72.0; H, 6.25; N, 14.5%.

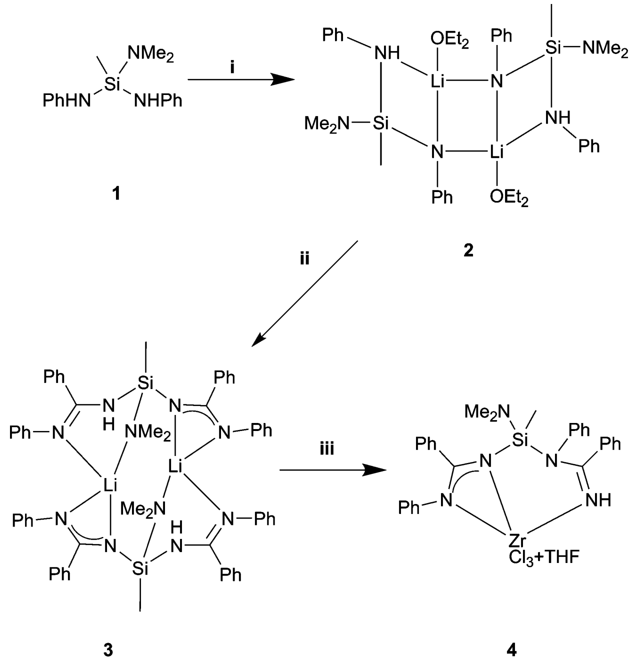
SiMe(NMe$_2$){NC(Ph)NH(Ph)}{(NC(Ph)N(Ph)ZrCl$_3$(THF))·THF} (4). To a solution of **3** (1.45 g, 3.0 mmol) in Et$_2$O (20 cm^3) at −78 °C was added ZrCl$_4$ (0.70 g, 3.0 mmol) and the reaction mixture was warmed to room temperature and stirred for a further 10 h, then the solvent was removed *in vacuo* and extracted with CH$_2$Cl$_2$. The volatiles were evaporated *in vacuo* and the residue was recrystallized in THF to give yellow crystals of **4**. Yield: 1.93 g (66.5%), ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): δ 0.19 (s, 3H, Si$\mathrm{C}H_3$), 1.17 (m, J_{HH} = 7.2, 4H, THF), 2.25 (s, NHPh), 2.74 (s, 6H, N(CH_3)$_2$), 3.43 (m, J_{HH} = 7.2, 4H, THF), 6.58–7.47 (m, 10H, Ph); ^{13}C NMR (75.1 MHz, 298 K, C$_6$D$_6$): δ (ppm) 149.6 (NCN of amidinate), 149.99 (NCN of amidine), 116.50, 122.43, 122.8, 123.1, 124.6, 125.0, 126.1, 126.3, 126.5, 126.7, 127.3, 127.5, 127.6, 127.8, 127.9, 128.1, 129.0, 134.6, 134.9, 149.27 (Ph), 90.8 (N(CH$_3$)$_2$), 67.6 (OCH$_2$CH$_2$ of THF), 25.5 (OCH$_2$$CH_2$ of THF), 3.6 (SiCH$_3$). Found: C, 54.5; H, 5.3; N, 8.5. Calc. for C$_{37}$H$_{46}$Cl$_3$N$_5$O$_2$SiZr: C, 54.3; H, 5.7; N, 8.6%.

X-Ray crystallography

X-Ray diffraction data of **2**, **3** and **4** were collected with graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer, equipped with an Oxford Cryosystems CRYOSTREAM device. The collected frames were processed with the proprietary software SAINT and an absorption correction was applied (SADABS) to the collected reflections.[11] The structures of the molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL.[12,13] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and allowed to ride on the respective parent atoms. Pertinent crystallographic data and other experimental details are summarized in Table 1. Compound **2** exhibits a severely disordered Et$_2$O of the carbon atoms (C37a, C37b, C38a, C38b) which was resolved by using SIMU, DELU and EADP restraints. Compound **4** shows a slightly disordered THF of the carbon atoms (C67–C70, C71–C74) which was treated by using DFIX restraints.

Results and discussion

The silyl-linked diamine [(Me$_2$N)SiMe(PhNH)$_2$] **1** (Scheme 1) was chosen as precursor and was prepared by a common procedure reported in literature.[6] The synthesis of **1–4** is shown in Scheme 1.



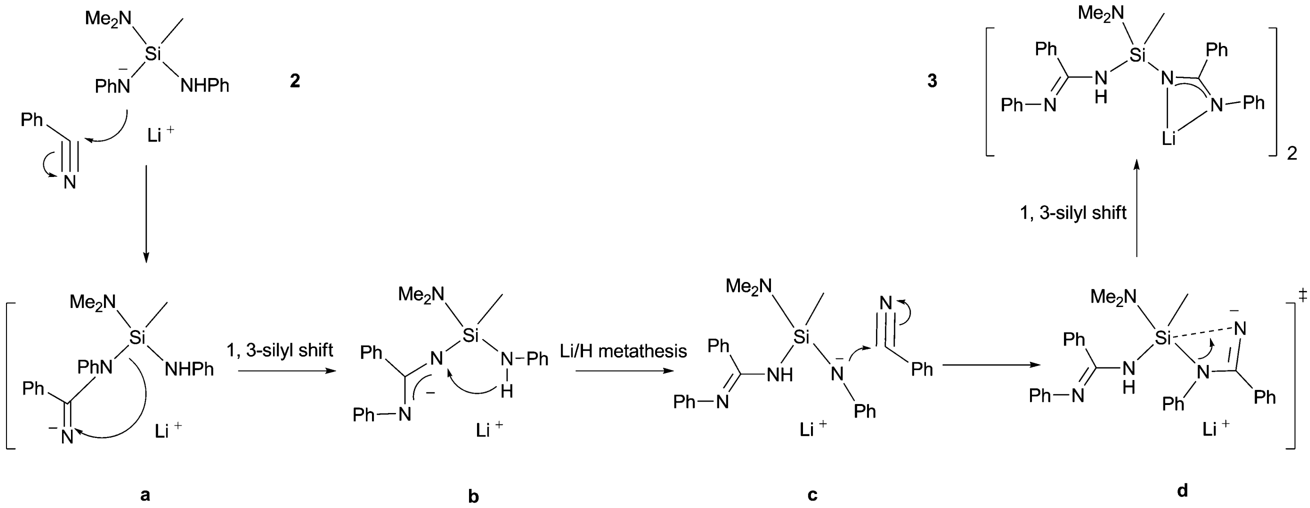
Scheme 1 Synthesis of compounds **2–4**. *Reagents and conditions*: (i) 1 equiv. LiBu^n, hexane and Et$_2$O, −78 °C; (ii) 1 or 2 equiv. PhCN, Et$_2$O, 0 °C; (iii) ZrCl$_4$, −78 °C, extraction with CH$_2$Cl$_2$, recrystallization from THF.

Treatment of diamine **1** with 1 equiv. of LiBu^n gave compound **2**. Compound **2** was crystallized in Et$_2$O and characterized by single-crystal X-ray diffraction. Compound **2** reacted with PhCN to provide **3** (silyl-linked amidinate-amidine ligand), which was characterized by single-crystal X-ray diffraction. Interestingly, the expected silyl-linked bis(amidinate) ligand (type **II**, Chart 1) was not isolated from the addition reaction of **2** to PhCN. In addition, the monoanion **3** was always isolated whether using a 1 : 1 molar ratio (41.5% yield) or 1 : 2 molar ratio (88.5% yield) of **2** to PhCN. Our original design was to introduce a electron donor group (NMe$_2$) on the silyl-bridge, however, the NMe$_2$ group changed the basicity of the terminal PhNH group, which promoted an intramolecular Li/H metathesis before a further addition to PhCN, and led to the silyl-linked amidinate-amidine monoanion **3** (Scheme 1). In contrast, for the dimethylsilyl-linked monoanion analogue, such a result had not been observed in our previous work.[6] This strongly suggests an intimate relation between NMe$_2$ group modification and the intramolecular Li/H metathesis.

The proposed mechanism for the formation of **3** is described as following (Scheme 2): (1) addition of PhCN to **2** led to the silyl-linked amino-amidine intermediate **a**, (2) a subsequent 1,3-silyl group shift (N to N′) to form a silyl linked amino-amidinate intermediate **b**, (3) an intramolecular Li/H metathesis leading to **c**, (4) a further addition reaction of PhCN to give the final product **3** with a η^3-conjugated skeleton by a 1,3-silyl shift (N to N′). The result strongly suggests that compound **3** is a thermodynamically favourable product and **d** may exist as an intermediate in this process.

As illustrated in Scheme 1, treatment of **3** with ZrCl$_4$ gave the corresponding Zr(IV) complex **4**. Interestingly, X-ray analysis showed that **4** has a different molecular skeleton from its precursor **3**. The proposed mechanism for the formation of **4** is illustrated in Scheme 3. First, the reaction might lead to the amidinated Zr intermediate coordinated with one of N atoms which is less hindered; second, it undergoes a cleavage of a Si–N′ bond and formation of a Si–N bond corresponding to a bulky silyl group shift (N to N′) leading to the N–C–N–Si–N–C–N skeletal rearrangement. The driving force is probably steric as it leads to coordination of the less bulky amino group.

In order to gain further insight into the reaction process, a variable-temperature ^{7}Li NMR study of compound **3** has been performed in d^8-toluene. As illustrated in Fig. 1, from −20 to 20 °C, there was only one ^{7}Li signal at ~1.62 ppm for compound **3**. From 20 to 70 °C, no other ^{7}Li signals were found; the only change was in the width of signal. Thus, we believe that compound **3** can not transfer to intermediate **d** without ZrCl$_4$. Hence we propose a mechanism for the conversion from compound **2** to **3** *via* a double 1,3-silyl shift and a Li/H metathesis step. When **3** reacted with ZrCl$_4$, the ligand moved back *via* a 1,3-silyl shift to form **4** (Scheme 3). The rearrangement interaction of



Scheme 2 Synthesis mechanism of silyl-linked amidinate-amidine lithium compound **3**, **a–d** are proposed as intermediates in this process.

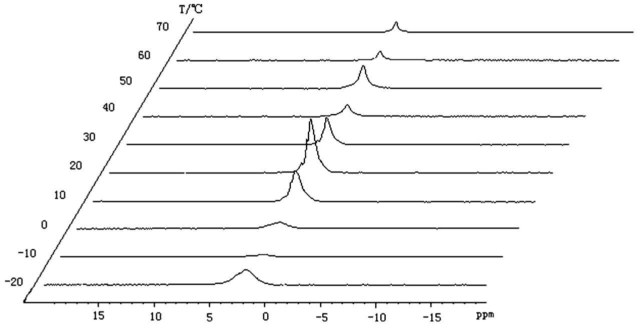
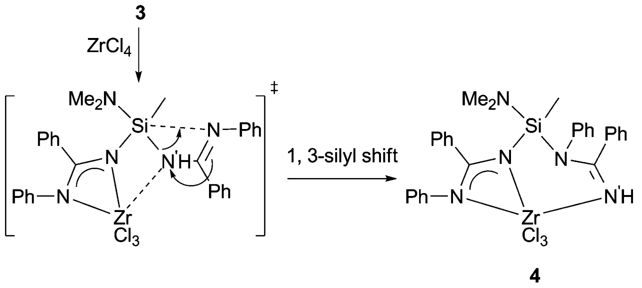


Fig. 1 Variable-temperature ^{7}Li NMR studies of compound **3** in d^8-toluene.



Scheme 3 Proposed mechanism of skeletal rearrangement of **4**.

the silyl-linked-bis(amidinate) ligand with MCl$_4$ (M = Zr, Ti) is not an unprecedented case. In previous studies, the interactions of silyl-linked-bis(amidinato)lithium with ZrCl$_4$ or TiCl$_4$ have been reported to give similar rearrangement of the molecular framework.[8,9]

Compound **2** is a dimer of silyl-linked bis(amino)lithium in which each Li atom is coordinated by three aniline N atoms and one O atom from Et$_2$O (Fig. 2). The central Li atoms and their coordinated N atoms compose three four-membered rings which adopt a nonplanar saddle-shaped conformation. The two Li–O bonds are 1.966(6) and 1.924(7) Å. The three Li–N bonds are in the range of 2.08–2.26 Å. Each of Li1 or Li2 forms a distorted tetrahedral core with the ligands. One of the solvated Et$_2$O molecules is disordered over two positions (Fig. 2). Selected bond lengths and angles for compound **2** are collected in Table 2.

Compound **3** was crystallized as colorless crystals in the solid state. The molecular structure of **3** (Fig. 3) shows a centrosymmetric dimeric arrangement consisting of two lithium silyl-linked amidinate-amidine moieties. Each Li atom is co-ordinated by an amidinate moiety, a terminal N atom of an amidine moiety and an NMe$_2$ moiety with N–Li distances of 2.091(6), 2.111(5), 2.059(6) and 2.130(6) Å, respectively. The coordination geometry around the central Li atoms is distorted tetrahedral with a sum of angles of 649.6° around Li atoms. Selected bond lengths and angles for compound **3** are collected in Table 3.

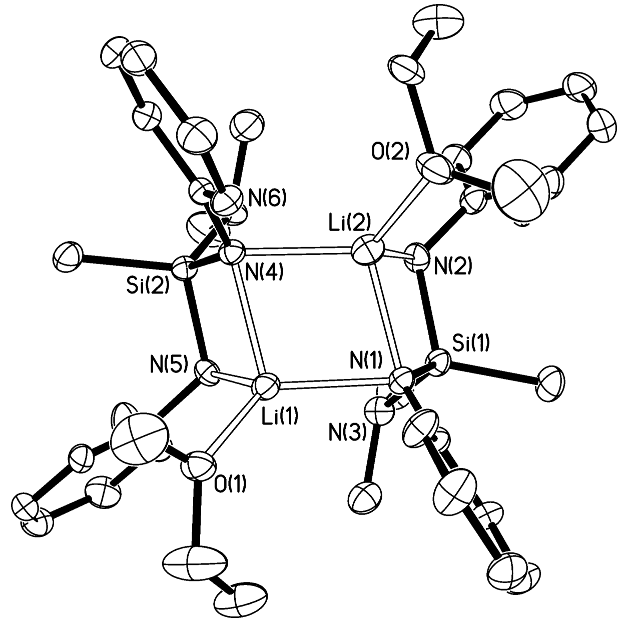


Fig. 2 ORTEP view of **2** with thermal ellipsoids at 30% probability level.

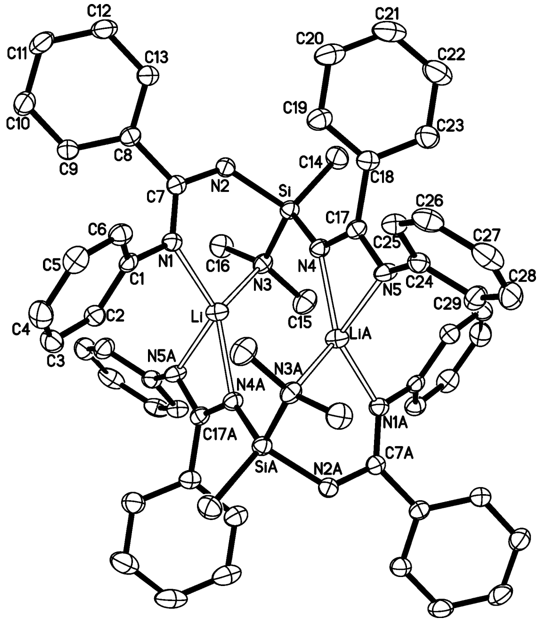


Fig. 3 ORTEP view of **3** with thermal ellipsoids at 30% probability level (symmetry code: $-x$, $-y$, $-z$ for atoms A).

Compound **4** was crystallized in THF as yellow crystals in the solid state. X-Ray analysis shows that it is converted as a linked iminoamidinate mononuclear species. Selected bond lengths and angles for compound **4** are collected in Table 4. The ligand around the Zr has a different N–C–N–Si–N–C–N backbone from its precursor **3**. The two N–C–N moieties (amidinate and amidine) exhibit different coordination modes to the metal center; one is ionic chelating and the other is neutral monodentate. Around the central Zr atoms, the three Zr–N bonds are in the range of 2.22–2.28 Å. Atoms Cl(1), Zr(1) and Cl(3) are closely linear and this line is perpendicular to Zr(1)–Cl(2). In the presence of a THF molecule, the Zr adopts a pentagonal bipyramid configuration (Fig. 4).

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Li(1)–N(1)	2.100(6)	Li(2)–N(1)	2.080(7)
Li(1)–N(4)	2.115(6)	Li(2)–N(2)	2.266(6)
Li(1)–N(5)	2.200(6)	Li(2)–N(4)	2.076(7)
Li(1)–O(1)	1.966(6)	Li(2)–O(2)	1.924(7)
N(1)–Li(1)–N(4)	101.5(3)	N(4)–Li(2)–N(1)	103.6(3)
N(1)–Li(1)–N(5)	109.0(3)	N(4)–Li(2)–N(2)	112.1(3)
N(4)–Li(1)–N(5)	78.4(2)	N(1)–Li(2)–N(2)	77.4(2)

Table 3 Selected bond lengths (Å) and angles (°) for compound **3**

Li–N(1)	2.091(6)	Li–N(4A)	2.111(5)
Li–N(3)	2.130(6)	Li–N(5A)	2.059(6)
N(1)–Li–N(4A)	128.9(3)	N(5A)–Li–N(3)	102.7(2)
N(5A)–Li–N(1)	123.5(3)	N(1)–Li–N(3)	100.3(2)
N(5A)–Li–N(4A)	65.98(2)	N(4A)–Li–N(3)	128.2(3)

Table 4 Selected bond lengths (Å) and angles (°) for compound **4**

Zr(1)–N(1)	2.278(4)	Zr(1)–Cl(1)	2.450(2)
Zr(1)–N(4)	2.222(4)	Zr(1)–Cl(2)	2.546(2)
Zr(1)–N(5)	2.238(4)	Zr(1)–Cl(3)	2.456(2)
		Zr(1)–O(1)	2.288(4)
N(5)–Zr(1)–N(1)	135.5(2)	Cl(1)–Zr(1)–Cl(3)	178.8(1)
N(4)–Zr(1)–N(5)	59.1(2)	Cl(1)–Zr(1)–Cl(2)	87.9(1)
N(4)–Zr(1)–N(1)	76.5(2)	Cl(3)–Zr(1)–Cl(2)	93.1(1)

Ethylene polymerization

Recently, the catalytic behavior of transition metal compounds bearing silylamido motifs[14] acting as versatile ligands in various reactive patterns[15–17] has been widely explored.[18–27] Some metal complexes based on diamine ligands have shown to be valuable as olefin polymerization catalysts.[28–33] Here we report the silyl-linked amidinate-amidine chelate Zr(IV) complex **4** and describe its catalytic activity for such application.

The general procedures for ethylene polymerization were adopted as reported in literature.[34] Compound **4** was dissolved in toluene and transferred into an autoclave *via* a syringe. The solution of co-catalyst ($AlEt_3$, $AlEt_2Cl$, MAO or MMAO) in toluene was added *via* a syringe for activation. While stirring, ethylene gas was filled into the reactor at 1 (or 10) atm of ethylene pressure. After stirring for a fixed period of time, the reaction mixture was quenched with 5% HCl/EtOH. The polymer was filtered, washed with ethanol and dried *in vacuo*.

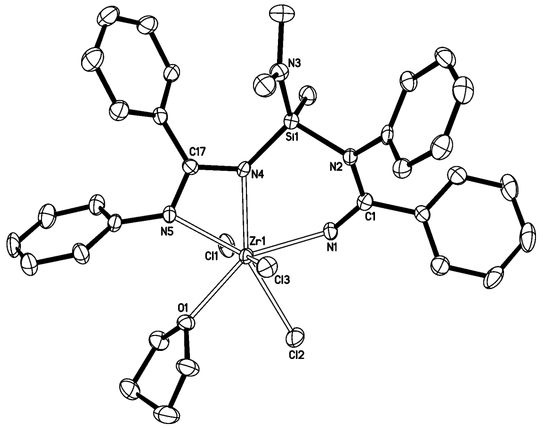


Fig. 4 ORTEP view of **4** with thermal ellipsoids at 30% probability level.

In order to select appropriate co-catalysts, four common co-catalysts ($AlEt_3$, $AlEt_2Cl$, MAO or MMAO) have been used at the same temperature (entries 1–4 in Table 5). As illustrated in Table 5, in the study of the compound **4** as catalyst at 1 atm of ethylene pressure (entries 1–4 in Table 5), almost no absorption of ethylene was observed with $AlEt_3$ and $AlEt_2Cl$ as co-catalysts using Al/Zr of 200 (entries 1 and 2 in Table 5); by using Al/Zr of 1000, MAO and MMAO were promising as activities increased to 0.21×10^4 g mol $(Zr)^{-1}$ h^{-1} with MMAO (entry 3 in Table 5) and to 0.32×10^4 g mol $(Zr)^{-1}$ h^{-1} (entry 4 in Table 5) with MAO, respectively.

In almost all cases, the best activities were observed with a 1000 Al/Zr molar ratio under 10 atm of ethylene at 70 °C.[34] Such temperatures are favored for commercially applicable catalysts (about 80 °C for the Ziegler–Natta catalytic system). Since the polymerisation is a highly exothermic reaction, the reaction temperature will rise and accelerate the formation of the active species.[34]

As illustrated in Table 5, in the study of complex **4** as catalyst at 10 atm of ethylene pressure in the presence of MAO as co-catalyst (entries 4–7 in Table 5), much higher catalytic activities were observed than those obtained at 1 atm (entries 1–4 in Table 5). Increasing the reaction temperature from 30 to 70 °C (entries 5–7 in Table 5) gave the highest activity of 80.8×10^4 g mol $(Zr)^{-1}$ h^{-1} with M_w value of 12.7×10^4 g mol^{-1} and molecular weight distribution (MWD) of 5.76 (entry 7 in Table 5). The obtained PEs possessed melting points (T_m) in the range 133–136 °C (entries 3–7 in Table 5), typical for high-density polyethylene (HDPE). The T_m

Table 5 Ethylene polymerization by complex **4**

Entry	Co-cat.	p/atm	T/°C	Al/Zr	Activity[a]	T_m[b]/°C	$10^{-4}M_w$[c]	M_w/M_n[c]
1	$AlEt_3$	1	30	200	None	—	—	—
2	$AlEt_2Cl$	1	30	200	None	—	—	—
3	MMAO	1	30	1000	0.21	136.5	—	—
4	MAO	1	30	1000	0.32	136.1	—	—
5	MAO	10	30	1000	0.91	134.9	—	—
6	MAO	10	50	1000	2.40	134.3	—	—
7	MAO	10	70	1000	80.8	133.2	12.7	5.76

Conditions: 5 μmol cat, 30 min, 30 ml toluene for 1 atm or 100 ml toluene for 10 atm. [a] 10^4 g mol $(Zr)^{-1}$ h^{-1}. [b] Determined by DSC. [c] Determined by GPC.

values of PEs gradually decreased with an increase in the reaction temperature (entries 3–7 in Table 5).

In a comparison with results by recently explored precatalysts,[33,34] compound **4** showed relatively higher activities for ethylene polymerisation at 10 atm of ethylene pressure, and produced similar high-density polyethylene (HDPE). However, compared with the most commonly used precatalyst Cp_2ZrCl_2 (about 10^5 g mol $(Zr)^{-1}$ h^{-1}),[35,36] the catalytic activity of compound **4** is relatively lower under similar conditions. In conclusion, compound **4** exhibited moderate activity for ethylene polymerization in the presence of methylalumoxane (MAO).

Conclusions

A synthetic pathway for the silyl-linked amidinate-amidine monoanion **3** had been developed. To the best of our knowledge it is the first example of a silyl-linked amidinate-amidine ligand. The processes of double addition of PhCN through bulky silyl shifts and an intramolecular Li/H metathesis were described. A related zirconium complex **4** with a structural rearrangement from its precursor had been obtained and showed moderate activity for ethylene polymerization in our primary tests.

Acknowledgements

We are grateful for the financial support from the Natural Science Foundation of China (20772074 to D.-S. Liu, 20702029 to S.-D. Bai) and the Natural Science Foundation of Shanxi Province (2009011059-1 to H.-B. Tong). We especially acknowledge Prof. W.-H. Sun for helpful advice.

References

1 J. Barker and M. Kilner, *Coord. Chem. Rev.*, 1994, **133**, 219.
2 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.
3 D. A. Kissounko, M. V. Zabalov, G. P. Brusova and D. A. Lemenovskii, *Russ. Chem. Rev.*, 2006, **75**(5), 351–374.
4 J.-F. Li, L.-H. Weng, X.-H. Wei and D.-S. Liu, *J. Chem. Soc., Dalton Trans.*, 2002, 1401.
5 J.-F. Li, S.-P. Huang, L.-H. Weng and D.-S. Liu, *Eur. J. Inorg. Chem.*, 2003, 810.
6 S.-D. Bai, J.-P. Guo and D.-S. Liu, *Dalton Trans.*, 2006, 2244.
7 S.-D. Bai, H.-B Tong, J.-P Guo, M.-S Zhou and D.-S Liu, *Inorg. Chim. Acta*, 2009, **362**, 1143.
8 S.-D. Bai, J.-P. Guo, D.-S. Liu and W.-Y. Wong, *Eur. J. Inorg. Chem.*, 2006, 4903.
9 S.-D. Bai, H.-B Tong, J.-P Guo and D.-S Liu, *Inorg. Chim. Acta*, 2009, **362**, 114.
10 C. Matthes, M. Noltemeyer and U. Klingebiel, *Organometallics*, 2007, **26**, 838–845.
11 *Bruker SMART (Version 5.0) and SAINT (Version 6.02)*, Bruker AXS Inc., Madison, WI, 2000.
12 G. M. Sheldrick, *SADABS, SHELXS97 and SHELXL97*, University of Göttingen, Germany, 1997.
13 G. M. Sheldrick, *SHELXTL/PC. Version, 6.10*, Bruker AXS Inc., Madison, WI, 1999.
14 H. Braunschweig and F. M. Breitling, *Coord. Chem. Rev.*, 2006, **250**, 2691.
15 W. A. Chomitz and J. Arnold, *Chem. Commun.*, 2007, 4797.
16 H. Ferreira, A. R. Dias, M. T. Duarte, J. R. Ascenso and A. M. Martins, *Inorg. Chem.*, 2007, **46**, 750.
17 V. Passarelli, F. Benetollo and P. Zanella, *Eur. J. Inorg. Chem.*, 2004, 1714.
18 S. Bambirra, A. Meetsma and B. Hessen, *Organometallics*, 2006, **25**, 3486.
19 L. Morello, P. H. Yu, C. D. Carmichael, B. O. Patrick and M. D. Fryzuk, *J. Am. Chem. Soc.*, 2005, **127**, 12796.
20 S.-J. Kim, I. N. Jung, B. R. Yoo, S. Cho, J. Ko, S. H. Kim and S. O. Kang, *Organometallics*, 2001, **20**, 1501.
21 S.-J. Kim, I. N. Jung, B. R. Yoo, S. H. Kim, J. Ko, D. Byun and S. O. Kang, *Organometallics*, 2001, **20**, 2136.
22 S.-J. Kim, Y.-J. Lee, S. H. Kim, J. Ko, S. Cho and S. O. Kang, *Organometallics*, 2002, **21**, 5358.
23 S. Barroso, J. L. Cui, A. R. Dias, M. T. Duarte, H. Ferreira, R. T. Henriques, M. C. Oliveira, J. R. Ascenso and A. M. Martins, *Inorg. Chem.*, 2006, **45**, 3532.
24 V. Passarelli, F. Benetollo, P. Zanella, G. Carta and G. Rossetto, *Dalton Trans.*, 2003, 1411.
25 W. A. Chomitz, S. G. Minasian, A. D. Sutton and J. Arnold, *Inorg. Chem.*, 2007, **46**, 7199.
26 M. S. Hill and P. B. Hitchcock, *Organometallics*, 2002, **21**, 3258.
27 M. Lamberti, M. Mazzeo, D. Pappalardo and C. Pellecchi, *Coord. Chem. Rev.*, 2009, **253**, 2082–2097.
28 R. Murugavel, N. Palanisami and R. J. Butcher, *J. Organomet. Chem.*, 2003, **675**, 65.
29 M. S. Hill and P. B. Hitchcock, *Organometallics*, 2002, **21**, 3258.
30 V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams and P. Howard, *Chem. Commun.*, 1998, 313.
31 M. Veith, W. Frank, H. Töller and H. Lange, *J. Organomet. Chem.*, 1987, **326**, 315.
32 D. J. Brauer, H. Burger, B. R. Liewald and J. Wilke, *J. Organomet. Chem.*, 1986, **310**, 317.
33 S.-F. Yuan, S.-D. Bai, D.-S Liu and W.-H. Sun, *Organometallics*, 2010, **29**, 213.
34 S.-F. Yuan, X.-H. Wei, H.-B Tong, L.-P. Zhang, D.-S Liu and W.-H. Sun, *Organometallics*, 2010, **29**, 2085.
35 Petra C. Möhring and Neil J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
36 K. Soga and T. Shiono, *Prog. Polym. Sci.*, 1997, **22**, 1503.