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Synthesis, mechanism and ethylene polymerization catalysis of Ge(IV), Sn(II) and Zr(IV) complexes derived from substituted β-diketiminates†

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Insertion of $LiCH(SiMe_3)_2$ into the CN bond of the appropriate nitriles RCN afforded dimeric β-diketiminato lithium complexes $[Li\{N(SiMe_3)C(R)C(H)C(R')N(SiMe_3)\}]_2$ (**1a**, R = R′ = NMe_2; **1b**, R = Bu^t, R′ = *o*-C_5H_4N). Lithium salt **1a** was used as a precursor to react with $SnCl_2$ and $GeCl_4$, respectively, and complexes $[ClSn\{N(SiMe_3)C(NMe_2)C(H)C(NMe_2)N(SiMe_3)\}]$ (**2**) and $[Cl_2Ge\{NC(NMe_2)C(H)C(NMe_2)N(GeCl_3)\}]$ (**3**) were obtained in good yields. By β-diketiminato lithium **1b** ligand transfer, the cyclo-1,3-diazasilane heterocyclic complex $[\overline{N(R)C(Bu^t)C(H)C(o\text{-}C_5H_4N)N}SiMe_2]ZrCl_4$ (**4**) was prepared using **1b** and $ZrCl_4$. Unexpectedly, the chelating β-diketiminato backbone in **3** acts as a dianionic ligand, whereas in **4**, the ligand acts as a neutral cyclo-1,3-diazasilane heterocyclic ring to coordinate with the Zr center. The X-ray structures of **2**–**4** are presented, and reaction pathways for each complex are proposed. Upon activation with methylaluminoxane, complex **4** exhibits good activity for ethylene polymerization.

Introduction

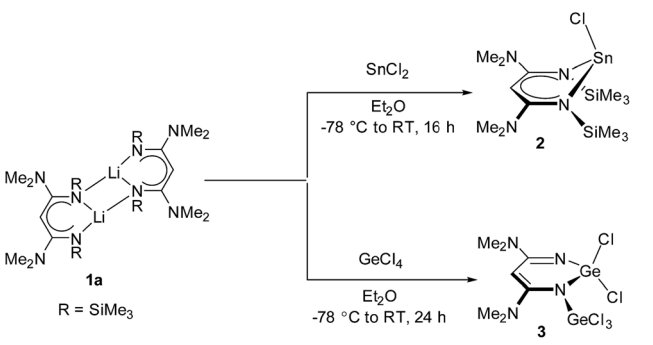
Metal complexes supported by monoanionic β-diketiminato ligands have been widely explored[1] mainly due to the modification in steric and electronic demands.[2] The steric bulk of β-diketiminato ligands can be easily tuned by substituents on the nitrogen atoms or on the carbon framework. However, the variation of substituents attached to the carbon backbone of the ligands is rather limited.[3] Thus, modification of the ligand skeleton can provide an opportunity to change their steric and electronic properties by coordination chemistry. In our former publications, we described the synthesis and structures of the β-diketiminato lithium compounds, in which the β-diketiminato ligands were prepared *via* insertion of various nitriles into the Li–C bond of $LiCH(SiMe_3)_2$.[4–6] These β-diketiminato lithium compounds were ligand-transfer reagents when reacted with metal halides.[7,8]

In this paper, we report the insertion products $[Li\{N(SiMe_3)C(R)C(H)C(R')N(SiMe_3)\}]_2$ (**1a**, R = R′ = NMe_2; **1b**, R = Bu^t, R′ = *o*-C_5H_4N) *via* $LiCH(SiMe_3)_2$ with nitriles,[4,5] were used as ligand transfer reagents to react with metal chlorides. The precursor complexes **1a** reacted with $SnCl_2$ and $GeCl_4$, respectively, to provide $[ClSn\{N(SiMe_3)C(NMe_2)C(H)C(NMe_2)N(SiMe_3)\}]$ (**2**) and $[Cl_2Ge\{NC(NMe_2)C(H)C(NMe_2)N(GeCl_3)\}]$ (**3**). The reaction of **1b** with $ZrCl_4$ afforded a cyclo-1,3-diazasilane Zr complex $[\overline{N(R)C(Bu^t)C(H)C(o\text{-}C_5H_4N)N}SiMe_2]ZrCl_4$ (**4**). Interestingly, complex **3** contains a novel dianionic β-diketiminato ligand and **4** has a neutral cyclo-1,3-diazasilane heterocyclic ring, which is a new type of stable silicon compound. Complex **4** can initiate ethylene polymerization. Herein, the detailed investigations and discussions are described.

Results and discussion

Synthesis and characterization of complexes 2 and 3

The β-diketiminato lithium salt (**1a**) was synthesized following the procedure reported in our previous publication.[4] The reaction mechanism involves two consecutive nucleophilic attacks on a nitrile molecule, and each one is followed by a 1,3-shift of a trimethylsilyl group. Reaction of $SnCl_2$ and $GeCl_4$ with an equivalent of **1a** in diethyl ether at −78 °C afforded the



Scheme 1 Synthetic pathway of complexes **2** and **3**.

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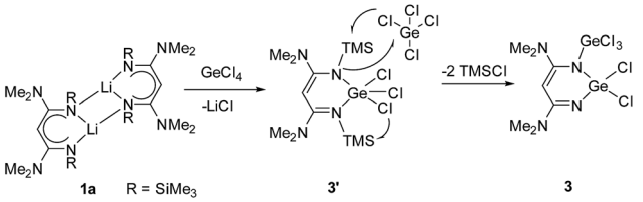


Scheme 2 Possible mechanism for the formation of **3**.

corresponding complex **2** (86%) as a white solid and **3** (65%) as a red solid, respectively. Complexes **2** and **3** are soluble in THF and Et_2O but show poor solubility in hexanes (Scheme 1).

We noticed that the reaction of **1a** with $GeCl_4$ afforded an unanticipated β-diketiminate **3**, in which the end groups at the nitrogen atoms are not trimethylsilyl substituents. It was suggested that the silyl group is quite labile in the presence of Lewis acid $GeCl_4$. Scheme 2 depicts a possible mechanism for the formation of **3**. We hypothesized two steps to the formation of **3** from reactant **1a**: (i) the Li compound **1a** reacted with $GeCl_4$ to form the corresponding β-diketiminate **3′** *via* a metathesis reaction; (ii) in the presence of excess $GeCl_4$, an intermolecular reaction between **3′** and $GeCl_4$ yields **3** *via* elimination of 2 equiv. Me_3SiCl due to the Si–N bond being weaker than the Ge–N bond. For the elimination reaction of the chlorotrimethylsilane, it has been reported that the reaction of lithium amidinate $[Me_3SiNC(Ph)N(CH_2)_3N(Me)SiMe_3]Li(THF)$ with $TiCl_4(THF)_2$ gave titanium amidinato amide dichloride complex $[\eta^2,\eta^1\text{-}Me_3SiNC(Ph)N(CH_2)_3NMe]TiCl_2$ by the elimination of LiCl and Me_3SiCl.[9] Our group demonstrated that lithium silylquinolylamide reacted with $(MeC_5H_4)TiCl_3$ to afford titanium(IV) complex $[\{8\text{-}(C_9H_6N)NC(NMe_2)N\}Ti(MeC_5H_4)Cl]_2$ *via* a metathesis reaction and the elimination of $SiMe_3Cl$.[10] Apparently, in the presence of a stronger Lewis acid, the formation of a new metal–amido bond was thermodynamically favored by elimination of $SiMe_3Cl$.

Crystals of **2** and **3** suitable for X-ray diffraction study were grown from a concentrated diethyl ether solution at −30 °C. The structures of **2** and **3**, along with selected bond lengths and angles, are depicted in Fig. 1 and 2, respectively; the crystal and structural refinement data are summarized in Table 2.

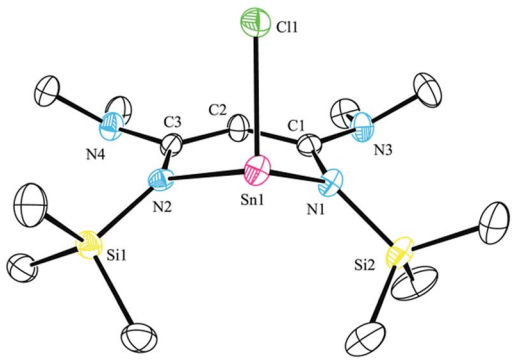


Fig. 1 ORTEP (30% probability) diagram of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–N(1) 2.154(6), Sn(1)–N(2) 2.187(6), Sn(1)–Cl(1) 2.471(2), N(1)–C(1) 1.362(9), N(2)–C(3) 1.350(9), C(1)–C(2) 1.408(9), C(2)–C(3) 1.396(9), N(1)–Sn(1)–N(2) 87.5(2), N(1)–Sn(1)–Cl(1) 95.51(17), N(2)–Sn(1)–Cl(1) 93.24(14).

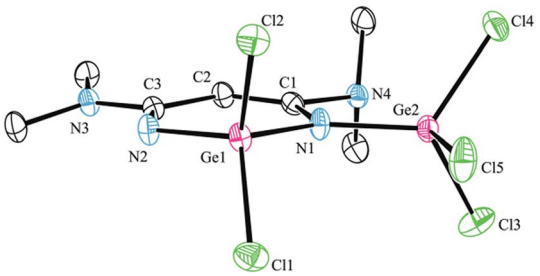


Fig. 2 ORTEP (30% probability) diagram of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–N(2) 1.765(3), Ge(1)–N(1) 1.844(3), Ge(2)–N(1) 1.838(3), N(1)–C(1) 1.371(5), N(2)–C(3) 1.297(5), C(1)–C(2) 1.329(6), C(2)–C(3) 1.472(5), N(2)–Ge(1)–N(1) 106.03(15), N(2)–Ge(1)–Cl(1) 112.23(12), N(1)–Ge(1)–Cl(1) 111.77(11), N(2)–Ge(1)–Cl(2) 112.81(12), N(1)–Ge(1)–Cl(2) 108.78(12), Cl(1)–Ge(1)–Cl(2) 105.30(5).

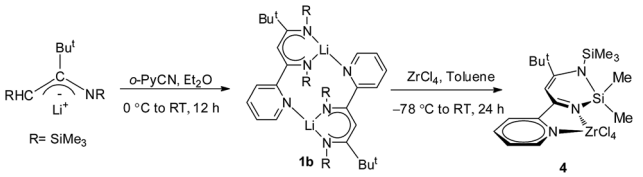
In complex **2**, the backbone of the chelating ligand (N1C1C2C3N2) is essentially planar (mean deviation: 0.0139 Å) and the tin atom is out of the plane (1.0601 Å); whereas the skeletal atoms including Ge (N1C1C2C3N2Ge six-membered ring) in complex **3**, are almost coplanar with a mean deviation of 0.0282 Å. For β-diketiminato N1C1C2C3N2 moieties: in **2**, the distances of C1–C2 and C2–C3 [1.408(9) and 1.396(9) Å] are rather the same, and the distances of N1–C1 and N2–C3 [1.362(9) and 1.350(9) Å] are between the bond lengths of C–N and C=N bonds, indicating that a significant π-electron delocalization present as a η^5 anion; in **3**, the distances of C1–C2 and C2–C3 are 1.329(6) and 1.472(5) Å, and the distances of N(1)–C(1) and N(2)–C(3) are 1.371(5) and 1.297(5), which is consistent with localized β-diketiminate bonding over these atoms.

Analogues of **2** are reported in the following compounds: $[HC(CMeNAr)_2]SnCl$ (Ar = 2,6-i-$Pr_2C_6H_3$),[11] $[HC\{CPhN(SiMe_3)\}_2]SnCl$,[12] $[(Mes)_2DAP]SnCl$ (where $[(Mes)_2DAP]$ = 2,4-dimethyl-*N*,1-*N*′-bis(2,4,6-trimethylphenyl)-1,5-diazapentadienyl),[13] $[\{N(C_6H_3Pr^i_2\text{-}2,6)C(H)\}_2CPh]SnCl$,[14] which were obtained from $SnCl_2$ and the appropriate Li β-diketiminate. The fragment ClSnNN in **2** is similar to those analogues and the Sn–N bond lengths [2.154(6) and 2.187(6) Å] are in the normal range (2.121–2.397 Å).[15]

Complex **3** consists of two germanium atoms, both of them are in a distorted tetrahedral environment. It was worth noting that the distances of Ge(IV) to the amido nitrogen atom N1 [Ge(1)–N(1) = 1.844(3) and Ge(2)–N(1) = 1.838(3) Å] are longer than the distance of germanium to the imino nitrogen atom [Ge(1)–N(2) = 1.765(3) Å]; however, both of them are shorter than those of the corresponding Ge(II)–N_{av} in $[CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2]GeCl$ (1.993 Å)[16] or $[CH\{(CMe)(2,4,6\text{-}Me_3C_6H_2N)\}_2]GeCl$ (1.993 Å).[17]

Synthesis and catalytic behavior of complex 4

The aza-allyl lithium starting material was obtained by the insertion of Bu^tCN into $LiCH(SiMe_3)_2$.[8,18–20] The synthetic procedure for zirconium complex **4** is illustrated in Scheme 3.



Scheme 3 Synthetic pathway for complex **4**.

The β-diketiminato lithium $[Li\{N(R)C(Bu^t)C(H)C(o\text{-}C_5H_4N)N(R)\}]_2$ (R = $SiMe_3$) (**1b**) is prepared from treatment of aza-allyl lithium with *o*-PyCN in a 1 : 1 molar ratio in diethyl ether.[5]

Treatment of lithium precursor **1b** (ref. 5) with an equimolar amount of $ZrCl_4$ in toluene at −78 °C to room temperature for 24 h unexpectedly yielded the cyclo-1,3-diazasilane product $[\overline{N(R)C(Bu^t)C(H)C(o\text{-}C_5H_4N)NSiMe_2}]ZrCl_4$ (**4**) instead of the β-diketiminato zirconium. Zr compound **4** was isolated in good yield (59%) as an orange solid by filtration of the resulting mixture to remove insoluble residue followed by recrystallization from toluene.

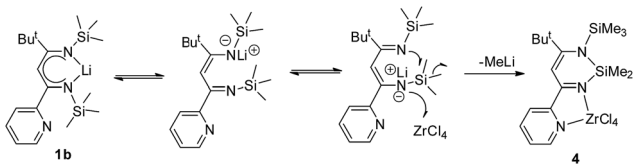
The formation of the silicon heterocyclic complex **4** involved Lewis-acid assisted cleavage of a Si–C bond and the formation of a new Si–N bond. The similar reaction was also reported by Leung and co-workers, in which the reaction of 2,3-pyrazyl-linked bis(1-aza-allyl) dilithium complex $[Li_2\text{-}\{\{N(SiMe_3)C(Bu^t)C(H)\}_2C_4H_2N_2\text{-}2,3\}(THF)_2]_2$ with $CdCl_2$ afforded the silicon cyclized product $[\{Me_2\overline{Si\{NC(Bu^t)C(H)\}}\}_2C_4H_2\overline{N}_2\text{-}2,3]$.[21] The Lewis-acid assisted Si–C bond cleavage reaction was also applied in a methyl/chlorine exchange reaction triggered by the action of $GaCl_3$.[22] Herein, the unexpected formation of **4** in the reaction of **1b** with $ZrCl_4$ is presumably that of an intermolecular interaction of the weak acceptor, zirconium, with the anionic imido-nitrogen leading to the cleavage of an Si–C bond and the formation of a new Si–N bond with concomitant elimination of MeLi, which is a possible pathway to form the cyclized compound **4** (Scheme 4).

The ^{1}H NMR spectrum of **4** shows that the silylic CH_3 protons are diastereotopic, appearing as two singlets at δ 0.05 and 0.91 ppm. As expected, the proton signals for SiMe_2 are more deshielded than SiMe_3. Likewise, the ^{13}C NMR spectrum of **2** also indicates that the carbon chemical shift of SiMe_2 (δ 3.81) is substantially more deshielded than SiMe_3 (δ 3.30).

Single crystals of **4** suitable for X-ray diffraction were obtained at −30 °C after two weeks. In compound **2**, the neutral ligand is coordinated to the metal in a κ^2-fashion with the two nitrogen atoms from the cyclo-1,3-diazasilane and pyridyl (Fig. 3). The zirconium atom exhibits a distorted octahedral geometry furnished with two N atoms of ligand and four chlorine atoms. Both dative Zr1–N1 and Zr1–N2 bond distances of 2.328(4) and 2.283(4) Å, respectively, are comparable to those dative Zr–N interactions in bis{3-(2-pyridyl)-1-azaallyl} zirconium system $[Zr\{N(SiMe_3)C(Bu^t)C(H)(C_5H_4N\text{-}2)\}_2Cl_2]$ (2.322(3) Å) and $[Zr\{N(SiMe_3)C(Ph)C(SiMe_3)(C_5H_4N\text{-}2)\}_2Cl_2]$ (2.354(3) Å),[23] and pyridyl imido zirconium complexes $[Zr\{(2\text{-}C_5H_4N)C\text{-}(CH_3)\{CH_2NSi(CH_3)_2{}^tBu\}_2(=N^{DIPP})(Py)\}]$ ($Zr\text{–}N_{Py}$ = 2.315(2) Å) and $[Zr\{(2\text{-}C_5H_4N)C\text{-}(CH_3)\{CH_2NSi(CH_3)_2\text{-}{}^tBu\}_2(N^{Mes}N_2N(Ph))\}]$ ($Zr\text{–}N_{Py}$ = 2.338(2) Å).[24] These dative bond distances are significantly longer than the Zr–N covalent bond in the pyridyl imido zirconium complexes ($Zr\text{–}N_{imido}$ = 2.096(2) and 2.104(2) Å),[23] and amido complex ($Zr\text{–}N_{amido}$ = 2.141(2)–2.231(3) Å).[22] For the cyclo-1,3-diazasilane skeleton, the bond lengths of N(2)–C(6) [1.309(6) Å] and C(7)–C(8) [1.362(6) Å] are significantly shorter than N(3)–C(8) [1.407(6) Å] and C(6)–C(7) [1.441(6) Å], indicating the presence of localized C=C and C=N double bonds; a similar phenomenon is also found in $[\{Me_2\overline{Si\{NC(Bu^t)C(H)\}}\}_2C_4H_2\overline{N}_2\text{-}2,3]$.[21]

Compound **4** was investigated for its catalytic behavior of ethylene polymerization with methylaluminoxane (MAO) as a co-catalyst under atmospheric pressure. The results of the optimization conditions are summarized in Table 1.

At the temperature of 25 °C, with an increase of the molar ratios of Al to Zr from 200 to 1000 (entries 1–3), the catalytic ability of **4** achieved the maximum activity of 2.58×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1} at a Al/Zr molar ratio of 500 (entry 2) and then decreased to a lower value of 1.52×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1} at a Al/Zr molar ratio of 1000 (entry 3). At different times (0.5 to 1 h, entries 2 and 4), the yield increased with the increase of polymerization time. This behavior indicated that the catalyst had a catalytic lifetime of at least 1 h. The reaction temperature also influenced the catalytic performance



Scheme 4 Plausible mechanism for the formation of **4**.

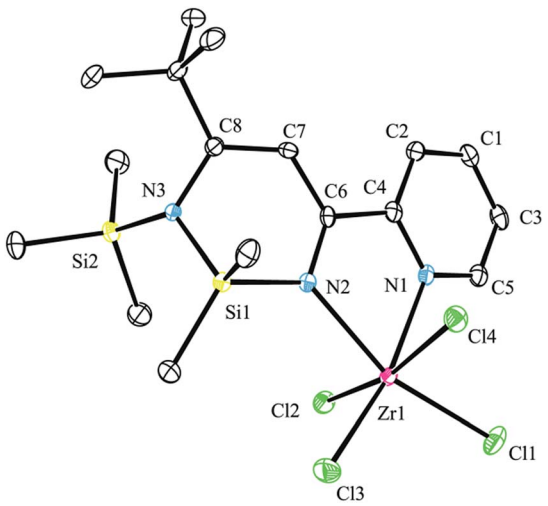


Fig. 3 ORTEP (30% probability) diagram of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–N(1) 2.328(4), Zr(1)–N(2) 2.283(4), N(1)–C(4) 1.355(6), N(2)–C(6) 1.309(6), C(4)–C(6) 1.494(6), C(6)–C(7) 1.441(6), C(7)–C(8) 1.362(6), N(3)–C(8) 1.407(6), Si(1)–N(2) 1.810(4), Si(1)–N(3) 1.756(4), N(2)–Zr(1)–N(1) 70.25(13), Cl(1)–Zr(1)–Cl(4) 92.05(5), N(2)–Zr(1)–Cl(1) 160.33(10), N(1)–Zr(1)–Cl(3) 168.24(9), Cl(2)–Zr(1)–Cl(4) 167.43(5), N(1)–Zr(1)–Cl(1) 90.33(11), N(2)–Zr(1)–Cl(3) 98.00(11).

Table 1 Ethylene polymerization with complex **4**/MAO[a]

Entry	Al/Zr	Cat. (μmol)	T (°C)	Time (h)	Yield (mg PE)	Activity[b]	T_m[h] (°C)	$10^5 M_w$[i]	M_w/M_n
1	200	5	25	0.5	43.1	1.72	138.2	8.78	3.17
2	500	5	25	0.5	64.5	2.58	138.0	10.5	3.6
3	1000	5	25	0.5	38.2	1.52	136.2	9.28	5.7
4	500	5	25	1.0	108	2.16	138.8	11.5	5.7
5	500	5	50	0.5	560	22.4	137.8	12.4	6.7
6[c]	500	10	50	1.0	950	0.37	n.d.	n.d.	
7[d]	500	10	50	0.5	1100	22.0	140.6	12.3	5.9
8[e]	500	10	50	0.5	1200	24.0	142.8	13.8	5.9
9[f]	500	10	50	1.0	4500	45.8	137.5	n.d.	
10[g]	1000	2.0	25	1.0	560	4.51	138.1	n.d.	

[a] Conditions: complex, 5 μmol; solvent, toluene; $V_{total} = 100$ mL; ethylene pressure, 1 atm. [b] Activity in units of 10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}. [c] The complex is $ZrCl_4$. 5 atm of ethylene pressure.[25] [d] The complex is $ZrCl_4(THF)_2$.[25] [e] The complex is $ZrCl_4(Et_2O)_2$.[25] [f] The complex is $Cp_2Zr_2Cl_2$.[26] [g] The complex is dimethyl-β-IAM–$ZrCl_3$. 6.8 atm of ethylene pressure.[27] [h] Determined by DSC. [i] Determined by GPC.

Table 2 Details of the X-ray structure determination of complexes **2**, **3**, **4**

Complex	**2**	**3**	**4**
Formula	$C_{13}H_{31}ClN_4Si_2Sn$	$C_7H_{13}Cl_5Ge_2N_4$	$C_{17}H_{29}Cl_4N_3Si_2Zr$
M_w (g mol^{-1})	455.75	475.64	564.63
T (K)	183(2) K	456(2) K	293(2) K
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P21/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	11.7137(17)	8.7293(16)	10.139(2)
b (Å)	15.426(2)	9.6018(18)	12.050(2)
c (Å)	11.7657(17)	10.0436(19)	12.659(3)
α (°)	90	91.651(2)	118.34(3)
β (°)	91.121(2)	98.999(2)	110.25(3)
γ (°)	90	102.452(2)	91.62(3)
V (Å^3)	2125.6(5)	810.2(3)	1241.9(4)
Z, D_{calcd} (g cm^{-3})	4, 1.424	2, 1.950	2, 1.510
μ (mm^{-1})	1.441	4.522	0.978
F(000)	936	464	576
Reflections collected	8605	3339	5135
Independent (R_{int}) reflections	3697(0.0427)	2782(0.0166)	4291(0.0255)
Goodness of fit on F^2	1.015	1.010	1.048
Final R indices [$I > 2\sigma(I)$] R_1, wR_2	0.0517, 0.1577	0.0326, 0.0780	0.0545, 0.1120
R indices (all data) R_1, wR_2	0.0626, 0.1745	0.0402, 0.0803	0.0674, 0.1181
Largest diff. peak and hole [e Å^{-3}]	0.580 and −1.024	0.580 and −1.024	1.064 and −0.411

significantly, the activities were increased from 2.58×10^4 to 22.4×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1} at 50 °C (entry 5). This result showed that raising the temperature could accelerate the formation of the active species.

The activity of **4** (entry 5) is about a hundred times higher than $ZrCl_4$ (entry 6), but comparable to those complexes of $ZrCl_4$ incorporating donor reagents such as $ZrCl_4(THF)_2$ (entry 7) or $ZrCl_4(Et_2O)_2$ (entry 8).[25] As can be noted, **4**/MAO is only two times less active than metallocene pre-catalyst Cp_2ZrCl_2 (entries 5 and 9) under similar conditions;[26] therefore, this catalyst mixture can be described as high activity according to the Gibson classification.[27a] Comparison with β-diketiminate Zr complexes, such as dimethyl-β-iminoaminate (IAM)–$ZrCl_3$ [4.51 × 104 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}, entry 10][27b] and [(2-Pyr)C(H)C(Bu^t)N(SiMe$_3$)]$ZrCl_3$ [7.50×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1} atm^{-1}],[27a] the activity of complex **4** is an order of magnitude higher than those of β-diketiminates. The PEs produced by **4**/MAO have high melting temperatures in the range of 136.2–138.8 °C, typical for high-density polyethylene, which are lower than those of the polyethylenes obtained by $ZrCl_4(THF)_2$ and $ZrCl_4(Et_2O)_2$ (entries 7 and 8),[25] and comparable to those of the polyethylenes formed with zirconocenes (entries 9 and 10). The GPC analyses show a wide molecular weight distribution because of the formation of more than one active species in the reaction of **4** with MAO.

Conclusion

In summary, the unusual X-ray characterized crystalline Sn(II), Ge(IV) and Zr(IV) complexes have been prepared *via* a salt metathesis and elimination reaction. Their novelty lies in the phenomenon that a β-diketiminato ligand in each complex is

very different: (i) for the Sn(II) compound, the β-diketiminato ligand is monoanionic in η^5-fashion; (ii) for the Ge(IV) compound, the β-diketiminato ligand is dianionic with localized bonding over these atoms of backbone. And (iii) for the Zr(IV) compound, the ligand is a neutral cyclo-1,3-diazasilane heterocyclic ring, which represents a new type of silicon-bridged compound. The possible mechanistic pathways for the formation of complexes **3** and **4** have been proposed. The catalytic behavior of complex **4** was investigated in the presence of MAO as a co-catalyst, and the results showed that pre-catalyst **4** has high activity for ethylene polymerization up to 22.4×10^4 g of PE (mol of Zr)$^{-1}$ h^{-1}.

Experimental section

Materials and procedures

All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk techniques. Solvents were dried with sodium, distilled from sodium/potassium alloy (toluene), sodium/benzophenone (diethyl ether) and stored over molecular sieves (4 Å). Deuterated C_6D_6 was dried over activated molecular sieves (4 Å). All solvents were degassed prior to use. Chemicals were purified by distillation before use. The β-diketiminato lithium $[Li\{N(SiMe_3)C(NMe_2)C(H)C(NMe_2)N(SiMe_3)\}]_2$ (**1a**)[4] and $[Li\{N(SiMe_3)C(Bu^t)C(H)C(o\text{-}C_5H_4N)N(SiMe_3)\}]_2$ (**1b**)[5] were prepared according to the reported procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300. Elemental analyses were carried out with a Vario EL-III instrument. The molecular weights of polyethylene were measured by a PL-GPC at 150 °C using 1,2,4-trichlorobenzene as the eluent and calibrated by polystyrene standards. Transition melting temperatures (T_m) were measured on a Perkin-Elmer DSC-7 differential scanning calorimeter, measured upon reheating the polymer sample to 180 °C at a heating rate of 20 °C min^{-1}.

$[ClSn\{N(SiMe_3)C(NMe_2)C(H)C(NMe_2)N(SiMe_3)\}]$ (2). $SnCl_2$ (0.73 g, 3.86 mmol) was added to a solution of complex **1a** (1.18 g, 3.86 mmol) in Et_2O (20 mL) at −78 °C. The resulting mixture was warmed to room temperature and stirred for a further 16 h. The resulting pale yellow solution was filtered and concentrated to approximately 10 mL. The product was isolated by crystallization from diethyl ether for 3 d at −30 °C to give colorless crystals **2**. Yield: 1.51 g (86%). ^{1}H NMR (C_6D_6, 300 MHz): δ 4.43 (s, 1H, *CH*), 2.81 (s, 12H, N(C*H*$_3$)$_2$), 0.17 (s, 18H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 173.3, 83.4, 41.3, −3.4. Anal. calcd for $C_{13}H_{31}ClN_4Si_2Sn$: C, 34.41; H, 6.89; N, 12.35. Found: C, 34.18; H, 7.17; N, 12.34.

$[Cl_2Ge\{NC(NMe_2)C(H)C(NMe_2)N(GeCl_3)\}]$ (3). $GeCl_4$ (0.75 g, 3.5 mmol) was added to a solution of complex **1a** (0.56 g, 2.3 mmol) in Et_2O (20 mL) at −78 °C. The mixture was warmed to room temperature and stirred for a further 16 h. The resulting solution was filtered and concentrated. The product was isolated by crystallization from diethyl ether for 7 d at −30 °C to give red crystals **3**. Yield: 1.21 g (65%). ^{1}H NMR (C_6D_6, 300 MHz): δ 5.33 (s, 1H, C*H*), 3.30 (s, 6H, N(C*H*$_3$)$_2$), 2.84 (s, 6H, N(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 170.3, 162.9, 83.4, 41.3. Anal. calcd for $C_7H_{13}Cl_5Ge_2N_4$: C, 17.67; H, 2.75; N, 11.78. Found: C, 17.53; H, 2.80; N, 11.69.

$[N(R)C(Bu^t)C(H)C(o\text{-pyridyl})NSiMe_2]_2ZrCl_4$ (4). $ZrCl_4$ (0.71 g, 3.03 mmol) was added to a solution of **1b** (1.12 g, 3.02 mmol) in toluene at −78 °C. The mixture was warmed to room temperature and stirred for a further 24 h. Then, the solution was filtered off and concentrated. The product was isolated by crystallization from toluene for 7 d at −30 °C to give yellow crystals **4**. Yield: 1.01 g (59%). ^{1}H NMR (C_6D_6, 300 MHz): δ 9.58 (s, 1H, *o*-py), 8.17 (d, 1H, $J = 8.7$ Hz, *o*-py), 7.93 (s, 1H, *o*-py), 7.09 (s, 1H, *o*-py), 2.34 (s, 1H, C*H*), 1.47 (s, 9H, C(C*H*$_3$)$_3$), 0.91 (s, 6H, Si(C*H*$_3$)$_2$), 0.05 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz): δ 181.1, 161.5, 149.7, 138.7, 122.8, 96.8, 99.7, 98.6, 44.5, 29.4, 3.8, 3.3. Anal. calcd for $C_{17}H_{29}Cl_4N_3Si_2Zr$: C, 36.16; H, 5.18; N, 7.44. Found: C, 36.08; H, 5.08; N, 7.40.

General procedure for ethylene polymerization

Ethylene polymerization. A 250 mL flask was equipped with an ethylene inlet, a magnetic stirrer, and a Schlenk line. The flask was filled with 50 mL of freshly distilled toluene, MAO (10 wt% in toluene) was added, and the flask was placed in a bath at the desired polymerization temperature for 10 min. The polymerization reaction was started by adding a toluene solution of the desired catalyst precursor with a syringe. Then, the solvent toluene was added to bring the total volume of the solution to 100 mL. The polymerization was carried out for the desired time and temperature and then quenched with 5% HCl in ethanol (250 mL). The precipitated polymer was filtered and dried overnight in a vacuum oven at 50 °C.

X-ray crystallography

Data collection of **2**, **3** and **4** was performed with Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer. The structures were solved by direct methods (SHELXS-97)[28] and refined against F^2 by full-matrix least squares using SHELXL-97.[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in Table 2.

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