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Synthesis and structure of the lithium, zirconium and hafnium *N*-silyl-*N*'-benzyl-benzamidinates

Yong Zhang, Jian-Ren Xie, Jian-Ping Guo, Xue-Hong Wei, Shu-Ping Huang, Dian-Sheng Liu*

Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, PR China

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ABSTRACT

The interaction of LiN(SiMe₃)CH₂Ph with one equivalent of benzenitrile gave the *N*-silyl-*N*-benzyl-benzamidinato-lithium compound [{Me₃SiNC(Ph)N(CH₂Ph)}Li(Et₂O)]₂ (**1**). The derivative zirconium and hafnium compounds were produced by the treatment of **1** with ZrCl₄ or HfCl₄ in tetrahydrofuran or diethyl ether at ambient temperature, respectively, with the general formula [Me₃SiNC(Ph)N(CH₂Ph)]₃MCl (M = Zr (**2**), Hf (**3**)). Compounds **1**, **2** and **3** were also characterized by X-ray single crystal diffraction and NMR analysis.

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1. Introduction

Amidinates [RC(NR')₂]⁻ exhibit versatile, and flexible coordination properties and have received increasing attention as ancillary ligands for both main-group and transition-metal complexes [1-15]. The alkali-metal chemistry of bis(aryl)formamidinate ligands has also been active for the past 5 years [16]. These anions make attractive ligands because of their steric and electronic tenability through the programmed variation of the N and C substituents [17-20]. The transition metal amidinates have been used as ancillary ligands in olefin polymerization catalysts [21]. The applicability of these ligands could be enhanced considerably with the ability to introduce additional functionalities as pendant groups on the amidinate ligand framework. Recently, we reported a convenient route for the synthesis of silyl-linked bis(amidinate)ligands, group (I) metal derivatives [22] and the chelating diamido zirconium and hafnium compounds [23]. In this contribution we describe the synthesis of such a functionalized amidinate, [Me₃SiNC(Ph)N(CH₂Ph)]⁻, which has a pendant benzyl group attached to one of the amidinate nitrogens. The zirconium and hafnium compounds with this ligand were prepared and structurally characterized by X-ray single crystal diffraction.

* Corresponding author.

E-mail address: dsliu@sxu.edu.cn (D.-S. Liu).

2. Experimental

2.1. Materials and apparatus

All the reactions were carried out under nitrogen atmosphere in a flamed Schlenk-type glassware on a dual manifold Schlenk line. Solvents were pre-dried. All the chemicals used were of reagent grade, obtained from ACROS. ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-300 spectrometer. Elemental analyses were performed on a Vario EL-III instrument.

2.2. Synthesis

2.2.1. Li₂[Me₃SiNC(Ph)NCH₂Ph]₂(OEt₂)₂ (1)

A solution of LiBu^{*n*} in hexane (6.94 mmol) was added dropwise to a stirred solution of Me₃SiNHCH₂Ph (1.244 g, 6.94 mmol) in diethyl ether (30 ml) at 0 °C. The mixture was then warmed to room temperature and stirred for 12 h. PhCN (0.687 ml, 6.94 mmol) was added to the above reactant mixture dropwise at 0 °C. The reactant mixture was concentrated in vacuo to *ca*. 10 ml and stored at -15 °C, yielding colourless crystals of **1** (2.11 g, 84%). ¹H NMR (300 MHz, C₆D₆): δ 0.15 (s, SiMe₃), 1.11 (t, *J* = 6.9 Hz, CH₃ of Et₂O), 3.26 (q, *J* = 6.9 Hz, OCH₂ of Et₂O), 4.431 (s, CH₂), 7.170–7.379 (m, phenyls). ¹³C{¹H} NMR (75.5 MHz, C₆D₆): δ 2.28 (q, *J* = 131.8 Hz, CH₂), 65.7 (t, *J* = 139.8 Hz, OCH₂ of Et₂O), 125.3, 125.8, 126.4, 127.2, 129.3, 129.7, 141.5, 144.4



Note



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Scheme 1. Synthesis of compound 1, 2 and 3.

(phenyls), 179.6 (N–C–N). Anal. Calc. for $C_{42}H_{62}Li_2N_4O_2Si_2$: C, 69.57; H, 8.55; N, 7.72; O, 4.41. Found: C, 69.50; H, 8.62; N, 7.70; O, 4.36%.

2.2.2. $ZrCl[Me_3SiNC(Ph)NCH_2Ph]_3$ (2)

ZrCl₄ (0.343 g, 1.47 mmol) was added in small portions to a stirred solution of **1** (1.273 g, 4.42 mmol) in Et₂O (30 ml) at -78 °C. The solution was warmed to room temperature and stirred for 24 h. The solvent was removed in vacuo. The remaining solid was dissolved in dichloromethane (ca. 10 ml) and filtered. The filtrate was concentrated under vacuum and stored at -15 °C, yielding colorless crystals of compound **2** (2.51 g, 88%). ¹H NMR (300 MHz, CDCl₃): δ 0.05 (s, SiMe₃, 27H), 4.24 (d, *J* = 16.2 Hz, CH₂, 3H), 4.64 (d, *J* = 16.2 Hz, CH₂, 3H), 6.70–7.51 (m, phenyls, 30H). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 2.33 (q, *J* = 118.9 Hz, SiMe₃), 53.3 (t, *J* = 134.7 Hz, CH₂), 124.8, 126.2, 127.1, 128.4, 129.2, 130.4, 136.0, 142.4 (phenyls), 180.1 (N–C–N). Anal. Calc. for C₅₁H₆₃ClN₆Si₃Zr: C, 63.08; H, 6.49; N, 8.65. Found: C, 62.93; H, 6.52; N, 8.53%.

2.2.3. $HfCl[Me_3SiNC(Ph)NCH_2Ph]_3$ (3)

This compound was synthesized using the similar procedure of compound **2**, yield 82%. ¹H NMR (300 MHz, CDCl₃): δ 0.01 (s, SiMe₃, 27h), 4.27 (d, *J* = 16.2 Hz, CH₂, 3H), 4.62 (d, *J* = 16.2 Hz, CH₂, 3H), 6.67–7.42 (m, phenyls, 30H). ¹³C{¹H} NMR (75.5 MHz, CDCl₃): δ 2.29 (q, *J* = 118.8 Hz, SiMe₃), 52.5 (t, *J* = 134.8 Hz, CH₂), 124.7, 126.0, 126.9, 128.1, 129.0, 130.2, 136.4, 142.1 (phenyls), 179.6 (N–C–N). *Anal.* Calc. for C₅₁H₆₃ClHfN₆Si₃: C, 57.83; H, 5.95; N, 7.93. Found: C, 57.92; H, 5.85; N, 7.89%.

2.3. X-ray crystal structure determination for 1-3

The intensity data were collected with a Bruker SMART APEX CCD area-detector diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 293 K. The collected frames were processed with the proprietary software sAINT [24] and an absorption correction was applied (sADABS [25]) to the collected reflections. The structures of these molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL [26]. Structure refinements were made on F^2 using the full-matrix least-squares technique. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective parent atoms. Pertinent crystallographic data and other experimental details are summarized in Table 2.

3. Results and discussion

3.1. Synthesis of complexes

The reaction of $Me_3SiNHCH_2Ph$ with *n*-butyllithium and then with PhCN gave [{ $Me_3SiNC(Ph)NCH_2Ph$ }Li(Et_2O)]₂ (1) in 84.0%

yield, as shown in Scheme 1. Treatment of **1** with ZiCl₄ or HfCl₄ in diethyl ether gave a pendant benzyl group amidinate zirconium **2** or hafnium **3** in good yield, 88% and 82%, respectively. The three products are colorless crystals and air sensitive. Compounds **1–3**



Fig. 1. Molecular structure of compound 1.



Fig. 2. Molecular structure of compound 2.

were characterized by NMR (¹H NMR and¹³C NMR), elemental analysis and X-ray diffraction determination.

3.2. X-ray structure of 1-3

3.2.1. X-ray structure of 1

Fig. 1 shows the molecular structure of lithium compound 1. The molecule is a centro-symmetric dimer with the center of parallelogram Li1–N1–Li1'–N1'. Each lithium of the dimer is coordinated by three nitrogen atoms, two of these belong to one amidinate anion and the third belongs to another, and one oxygen atom of diethyl ether. The four coordination atoms adopt the tetragonal geometry with Li–N distances of 2.145(6) (Li1–N1), 2.049(6) (Li1–N1') and 2.018(6) Å (Li1–N2).

3.2.2. X-ray structure of 2 and 3

Structural analyses of **2** and **3** reveal that their molecular structures are very similar. Both **2** and **3** adopt a C_3 rotational symmetry along the zirconium(IV)–Cl or hafnium(IV)–Cl. The metal(IV)–Cl axis is located at the center defined by the six nitrogen atoms of the three amidinato ligands. In **2**, with Zr–N distances of 2.2905(18) (Zr1–N1) and 2.2265(19) (Zr1–N2) Å. Each bidentate amidinato ligand forms a four-membered metallacycle with zirco-



Fig. 3. Molecular structure of compound 3.

Table 1	
Selected bond lengths (Å) and angles (°) of compound 1-3	;

nium. The four-membered ring is almost planar, with a mean deviation of 0.0673 Å from the plane. Within the amidinato ligand, the similarity between the N1–C8A [1.328(3) Å] and C8–N2 [1.335(3) Å] distances shows complete delocalization within the N–C–N framework. The N–Zr–N bond angle of amidinato with zirconium is 59.08(7)°. The attached phenyl ring forms a 60.1° dihedral angle with the four-membered ring (Fig. 2).

In **3** (see Fig. 3), similar to **2**, the bidentate amidinato ligand forms a nearly planar four-membered metallacycle with the metal ion. The Hf–N distances are 2.272(3) (Hf1–N1) and 2.208(3) (Hf1–N2) Å, respectively. The similar C–N distances, N1–C8 [1.318(6) Å] and C8–N2 [1.330(6) Å], indicate complete delocalization within the N–C–N framework. The four-membered ring forms a 60.2° dihedral angle with the attached phenyl. Selected bond lengths and angles of compounds **1–3** are listed in Table 1.

Table 2 Crystallographic data for compound 1

Compound	1	2	3
Empirical formula	C ₂₁ H ₃₁ LiN ₂ SiO	C51H63Cl1ZrN6Si3	C51H63ClHfN6Si3
Crystal system, space	triclinic, P1	cubic, I43d	cubic, I43d
group			
Unit cell dimensions			
a (Å)	10.202(4)	27.460(3)	27.377(2)
b (Å)	10.833(5)	27.460(3)	27.377(2)
c (Å)	12.278(5)	27.460(3)	27.377(2)
α (°)	108.612(5)	90	90
β (°)	114.169(6)	90	90
γ(°)	100.183(5)	90	90
V (Å ³)	1096.6(8)	20707(4)	20519(3)
Ζ	2	16	16
D_{calc} (mg mm ⁻³)	1.098	1.246	1.370
Absorption coefficient (mm ⁻¹)	0.118	0.373	2.195
F (000)	392	8160	8672
Crystal size (mm ³)	$0.30 \times 0.20 \times 0.20$	$0.50 \times 0.40 \times 0.30$	$0.40 \times 0.35 \times 0.35$
θ Range for data collection (°)	1.87–25.01	1.82-25.98	1.82-25.00
Limiting indices	$-11 \leq h \leq 12$	$-33 \leq h \leq 30$	$-32 \leq h \leq 29$
0	$-12 \leq k \leq 12$	$-33 \leqslant k \leqslant 29$	$-32 \leq k \leq 14$
	$-14 \leqslant l \leqslant 11$	$-25 \leqslant l \leqslant 33$	$-32 \leqslant l \leqslant 32$
Reflections collected	4551	52123	39315
Independent reflections (R)	3792 (0.0946)	3401 (0.0363)	3018 (0.0864)
Completeness to $\theta = 25^{\circ}$ (%)	97.9	100	100
GOF	1.034	1.106	1.049
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0827,$ $wR_2 = 0.2037$	$R_1 = 0.0280,$ $wR_2 = 0.0687$	$R_1 = 0.0268,$ $wR_2 = 0.0612$
R indices (all data)	$R_1 = 0.1020,$ $wR_2 = 0.2189$	$R_1 = 0.0316,$ $wR_2 = 0.0723$	$R_1 = 0.0295,$ $wR_2 = 0.0623$

Compound 1		Compound 2		Compound 3	
Li1–N1	2.145(6)	Zr1-N1	2.2905(18)	Hf1–N1	2.272(3)
Li1–N2	2.018(6)	Zr1-N2	2.2265(19)	Hf1–N2	2.208(3)
Li1–N1A	2.049(6)	Zr1–Cl1	2.4779(10)	Hf1–Cl1	2.4570(19)
Li1-01	1.932(6)	N1-C1	1.452(3)	N1-C1	1.442(5)
Li1–Li1A	2.500(11)	N1-C8A	1.328(3)	N1-C8	1.318(6)
N1-C1	1.468(4)	N2-C8	1.335(3)	N2-C8	1.330(6)
N1-C8	1.323(4)	N2-Si1	1.7493(19)	N2-Si1	1.751(3)
N2-C8	1.321(4)	N1B-C8-N2	113.52(19)	N1-C8-N2	113.9(4)
N2-Si1	1.707(3)	N1-Zr1-N2A	59.08(7)	N1-Hf1-N2	59.39(12)
N1-C8-N2	118.0(3)	N1-Zr1-N1A	87.14(7)	N1-Hf1-N1A	87.95(12)
N1-Li1-N2	65.9(2)	N2-Zr1-N2A	119.320(14)	N2-Hf1-N2A	119.16(3)
N1-Li1-N1A	106.9(2)	Cl1–Zr1–N1	127.26(5)	Cl1-Hf1-N1	126.70(8)
Li1–N1–Li1A	73.1(2)	Cl1-Zr1-N2	85.25(5)	Cl1-Hf1-N2	84.71(9)

3.2.3. The interaction of zirconium or hafnium with hydrogen of methene

In the molecular structure of compounds **2** and **3**, the distances between the two hydrogens of methene and metal are remarkably different. In **2**, the distance between Zr1 and H4A is 3.470 Å, which is shorter than the sum of their Van der Waals radii [27] and it is considered as the weak β agostic interaction. While the corresponding value of H4B is 4.106 Å and nonagostic. The interactions result in the different chemical environments for hydrogens of methene. It is consistent with the ¹H NMR spectrum, in which the chemical shifts of H4A and H4B are 4.6 and 4.2 ppm, respectively. The low field shift of H4A is due to the β agostic interaction [28]. Meanwhile, the different chemical environments for the two hydrogens on the same carbon lead to hydrogen–hydrogen coupling and give the separated two doublet peaks. The same phenomena could be observed in compound **3**.

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Appendix A. Supplementary material

CCDC 610328, 610326 and 610330 contain the supplementary crystallographic data for compounds **1**, **2** and **3**. 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 on-line version, at doi:10.1016/j.ica.2008.03.112.

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