Synthesis and characterization of N-silylated, C_1-symmetric benzamidinates of lithium, sodium, and tin(II)[1]

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Abstract: The synthesis and characterization of complexes obtained from the reactions between Li[*N*-*t*-Bu($SiMe_3$)] (**A**) or the sodium analogue Na[*N*-*t*-Bu($SiMe_3$)] (**B**) and the cyanoarene RCN (R = Ph or 4-$MeOC_6H_4$) are discussed. These are the THF adduct [Li{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(THF)]$_2$ (**1**), the TMEDA adduct Li[N(*t*-Bu)C(Ph)N($SiMe_3$)]-(TMEDA) (**2**), the neutral ligand-free lithium benzamidinate Li[N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)] (**3**), and the THF adduct Li[N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)](THF) (**3a**). The preparation and structure of the crystalline compound [Na{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(OEt_2)]$_2$ (**4**) is described. From the lithium benzamidinate **1** and Sn(II) chloride the tin(II) complex [Sn{N(*t*-Bu)C(Ph)N($SiMe_3$)}$_2$] (**5**) was obtained. The molecular structures of the crystalline compounds **1**, **4**, and **5** were established by X-ray diffraction. In **1** and **4** the benzamidinato ligand is both chelating and bridging, with the Me_3Si-substituted nitrogen atom as the bridging site. The central planar $(MN)_2$ four-membered ring is a rhombus in **1**, with almost equal Li—N bond lengths, whereas in **4** the bonds to Na(1) are significantly longer than those to Na(2). In **5**, the ligand is N,N′-chelating.

Key words: alkali metals, tin(II), benzamidinates, NMR spectra, X-ray structures.

Résumé : On discute de la synthèse et de la caractérisation de complexes obtenus par les réactions du Li[*N*-*t*-Bu($SiMe_3$)] (**A**) ou de analogue sodique Na[*N*-*t*-Bu($SiMe_3$)] (**B**) avec des cyanoarènes RCN (R = Ph ou 4-$MeOC_6H_4$) et isolés sous la forme de benzamidinate de lithium neutre, sans ligand, [Li[N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)] (**3**) ou sous la forme d'adduits avec le THF [Li{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(THF)]$_2$ (**1**) ou [Li[N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)]-(THF) (**3a**) et avec le TMEDA Li[N(*t*-Bu)C(Ph)N($SiMe_3$)](TMEDA) (**2**). On a aussi préparer le composé [Na{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(OEt_2)]$_2$ (**4**) dont on a déterminé la structure cristalline. La réaction du benzamidinate de lithium (**1**) avec le chlorure d'étain(II) permet d'obtenir le complexe d'étain(II) [Sn{N(*t*-Bu)C(Ph)N($SiMe_3$)}$_2$] (**5**). On a déterminé les structures moléculaires des composés cristallins **1**, **4** et **5** par diffraction des rayons X. Dans les composés **1** et **4**, le ligand benzamidinato agit à la fois comme pont et comme agent chélatant alors que l'atome d'azote substitué par un groupe Me_3Si agit comme pont. Le cycle central planaire à quatre chaînons $(MN)_2$ est rhombique dans le composé **1** et les longueurs de ses liaisons Li—N sont pratiquement égales alors que dans le composé **4** les longueurs des liaisons vers le Na(1) sont beaucoup plus longues que celles vers la Na(2). Dans le composé **5**, le ligand est N,N′-chélatant.

Mots clés : métaux alcalins, étain(II), benzamidinates, spectres RMN, structures déterminées par diffraction des rayons X.

[Traduit par la Rédaction]

Introduction

Amidines and amidinates are valuable reagents in organic synthesis (1). The amidinato ligand $[N(R^1)C(R^2)N(R^3)]^-$ (Am^-) is widely employed in coordination chemistry; there have already been more than 100 publications in the 21st century. Its role often is that of a spectator ligand. Attractive features are that (*i*) its steric and electronic properties can be widely varied by judicious selection of the substituents R^1, R^2, and R^3, (*ii*) it can display a diversity of bonding modes in its binding to the metal or metals, and (*iii*) it often is firmly bound to the latter. Reviews have dealt with transition metal amidinates (2*a*), s-, p-, d-, and f-block metal *N*,*N*′-bis(trimethylsilyl)benzamidinates (R^1 = $SiMe_3$ = R^3, R^2 = an aryl group) (2*b*), and "paddle-wheel" dinuclear formamidinates of formula $[M_2\{N(R^1)C(H)N(R^3)\}_4(L_{ax})_n]$ (M = Mo, Rh, Ni, or Ru; R^1 = an aryl group = R^3, L_{ax} is the axial ligand; n = 0–2) (2*c*).

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This paper is dedicated to Dr. Arthur J. Carty, in recognition of his many important contributions to organometallic chemistry, and as a mark of esteem and (by MFL) friendship.

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Some group 4 metal amidinates are catalysts for olefin polymerization, as summarized in a recent survey on advances in non-metallocene olefin polymerization (3). For example, isotactic polypropylene was obtained using tris(amidinato)zirconium(IV) complexes bearing a chiral N-substituted ligand (4); and C_1-symmetric amidinates, $[Zr(Am)_2Me_2]$ (Am: $R^1 \neq R^3$), were moderately active for formation of isotactic poly(1-hexene) (5). Cationic aluminium amidinates, such as $[Al\{(N\text{-}i\text{-}Pr)_2C\text{-}t\text{-}Bu\}Me][B(C_6F_5)_3Me]$, were shown to be active single site catalysts for the living polymerization of ethylene (6). Lanthanide metal amidinates, $[Ln\{(N(c\text{-}C_6H_{11}))_2CR^2\}_3]$ (Ln = Nd, Gd, Yb; R^2 = Me or Ph), were highly active catalysts for the ring-opening polymerization of ε-caprolactam (7).

The more important methods that have been used to prepare metal amidinates are (*i*) metallation of the amidine $HN(R^1)C(R^2)N(R^3)$, (*ii*) ligand transfer reactions from either an alkali metal (8) or trimethylsilyl (9) amidinate and a metal chloride, (*iii*) addition of a metal hydrocarbyl to a carbodiimide (e.g., LiR^2 to $R^1N{=}C{=}NR^3$, $R^1 = SiMe_3 = R^3$, R^2 = aryl), and (*iv*) the reaction between a metal bis(trimethylsilyl)amide and a cyanoarene. As for (*iv*), Sanger (in our laboratory) found in 1973 that $Li[N(SiMe_3)_2]$ and PhCN in Et_2O readily yielded $Li[\{N(SiMe_3)\}_2CPh]$, which was characterized by treatment with Me_3SiCl, yielding the benzamidine $N(SiMe_3)_2C(Ph){=}N(SiMe_3)$ (10); substantial extensions to this methodology up to 1990 have been summarized (5*b*). In the present paper are described reactions of the related, but C_1-symmetric, alkali metal amides $M[N\text{-}t\text{-}Bu(SiMe_3)]$ (M = Li (**A**) (11), M = Na (**B**) (12)) with PhCN or $4\text{-}MeOC_6H_4CN$.

Our prior publications in this area dealt with $[K\{N(SiMe_3)C(C_6H_3Me_2\text{-}2,5){=}C(H)SiMe_3\}]_2$ and $[\{UCl(\mu\text{-}Cl)(L)N(SiMe_3)\}_2][UCl_2(L)(Am)]_2$ (L = $\{N(SiMe_3)C(Ph)\}_2CH$, Am = $N(SiMe_3)C(Ph)NC(Ph){=}C(H)SiMe_3$) (13*a*), $M[\{N(CH{=}NSiMe_3)\}_2CH]_n$ [n = 3 and M = Li (13*b*), Na (13*c*); n = 4, Tl (13*c*)); $[Li(Am)(CNPh)]_2$ (13*d*), $[K(Am)]_2$, $[SnCl(Am)]$, $[Sn(Am)_2]$, and $[Hg(Am)_2]$ (Am = $N(SiMe_3)C(Ph)NC(Ph){=}C(SiMe_3)_2$) (13*e*); $Li[N(SiMe_3)C(Ar)NC(Ar){=}C(H)SiMe_3](D)$ (D = TMEDA or THF with Ar = Ph; or D = TMEDA, Ar = $4\text{-}MeC_6H_4$) (13*f*); $[Li(Am)]_2$, $[M(Am)Cl_2]$ (M = Al or Ga) and $[\{Ln(Am)_2(\mu\text{-}Cl)\}_2]$ (Am = $N(SiMe_3)C(Ph)N(CH_2)_3NMe_2$, Ln = La or Ce) (13*g*); $Li[N(SiMe_3)C(H)NC(H){=}C(H)C(t\text{-}Bu){=}NSiMe_3]$ (13*h*); and $Li[N(SiMe_2OMe)C(C_6H_3Me_2\text{-}2,5)NC(C_6H_3Me_2\text{-}2,5){=}C(H)SiMe_3](TMEDA)$ (13*i*).

Experimental

General remarks

All manipulations were performed under argon using standard Schlenk techniques. Hexane was dried and distilled over sodium–potassium alloy, THF and diethyl ether were dried and distilled over sodium–benzophenone and stored over a sodium mirror under argon. TMEDA (Aldrich) was distilled from CaH_2 prior use. Nitriles (Aldrich) were dried over molecular sieves. The alkali metal amides $M[N\text{-}t\text{-}Bu(SiMe_3)]$ (M = Li (**A**) (14), Na (**B**) (12)) were synthesized by published procedures. The NMR spectra were recorded on a Bruker DPX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C, and 116.6 MHz for ^7Li) or an AMX 500 (49.7 MHz for ^{29}Si) instrument, and referenced externally (^7Li, using LiCl; ^{29}Si, using $SiMe_4$) or internally to the residual solvent resonances. Unless otherwise stated, all NMR spectra were measured at 298 K and other than ^1H were proton-decoupled. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected. Elemental analyses were determined by Medac Ltd., Brunel University, Uxbridge, Middlesex, UK.

Preparations

[Li{μ-cis-N(t-Bu)C(Ph)N(SiMe$_3$)}(THF)]$_2$ (1)

A solution of PhCN (0.46 cm^3, 4.49 mmol) in diethyl ether (5 cm^3) was added slowly to a cooled (–78 °C) solution of **A** (1.01 g, 4.49 mmol) in diethyl ether (15 cm^3). The resulting yellow mixture was allowed to warm to room temperature and was stirred for 12 h. The slightly cloudy mixture was filtered and the filtrate was concentrated and stored at –25 °C for 24 h, yielding colorless crystals of the 1:1 ether adduct (0.58 g, 44.7%). As the diethyl ether was not strongly bonded to the molecule, during the drying in vacuo the complex gradually lost the coordinated solvent, compromising the credibility of the analysis. Thus, the diethyl ether adduct was recrystallized from a satd. THF solution and a few colorless crystals of compound **1** were obtained (mp 55–80 °C). ^1H NMR (C_6D_6) δ: 0.06 (s, 9H, $SiMe_3$), 1.26 (s, 9H, *t*-Bu), 1.35 (m, 4H, THF), 3.59 (m, 4H, THF), 7.09 (d, 1H, $^3J_{HH}$ = 7.20 Hz), 7.12 (m, 2H, Ph), 7.29 (d, 2H, $^3J_{HH}$ = 7.12 Hz). ^{13}C NMR (C_6D_6) δ: 2.91 ($SiMe_3$), 25.43 (THF), 33.49 (CMe_3), 51.38 (CMe_3), 68.11 (THF), 126.59, 127.49, and 127.83 (Ph), 145.37 (ipso-C), 175.65 (NCN). ^7Li NMR (C_6D_6) δ: –0.48. ^{29}Si NMR (C_6D_6) δ at 323 K: –8.08 and –10.65; at 298 K, δ –10.69. MS (M denotes the monomer) m/z (% and assignment): 508 (8%, $[M_2 - 2THF]^+$), 451 (72%, $[M_2 - 2THF - t\text{-}Bu]^+$), 395 (8%, $[M_2 - 2THF - 2t\text{-}Bu + H]^+$), 375 (48%, $[M_2 - 2THF - Ph + H]^+$).

[Li{N(t-Bu)C(Ph)N(SiMe$_3$)}(TMEDA)] (2)

A solution of PhCN (0.32 cm^3, 3.11 mmol) in hexane (5 cm^3), was added to a cooled (0 °C) solution of **A** (0.47 g, 3.11 mmol) in hexane (25 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for 4 h. TMEDA (0.61 cm^3, 4.04 mmol) was added to the mixture, which was stirred for 12 h. The mixture was filtered; the filtrate was concentrated and stored at 10 °C for 12 h. Being cloudy, it was again filtered; the filtrate was concentrated and stored at 10 °C for a further 12 h to furnish yellow crystals of compound **2** (0.71 g, 61.3%), mp 132–135 °C. ^1H NMR (C_6D_6) δ: 0.09 (s, 9H, $SiMe_3$), 1.25 (s, 9H, *t*-Bu), 1.78 (s, 4H, TMEDA), 2.02 (s, 12H, TMEDA), 7.06 (tt, 1H, *p*-H of Ph, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz), 7.15 (m, 2H, *m*-H of Ph), 7.35 (dd, 2H, *p*-H of Ph, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.2 Hz). ^{13}C NMR (C_6D_6) δ: 4.05 ($SiMe_3$), 34.32 (CMe_3), 50.67 (CMe_3), 125.80, 127.18 (CH of Ph), 146.47 (ipso-C), 174.56 (NCN). ^{29}Si NMR (C_6D_6) δ at 50 °C: –15.19. ^7Li NMR (C_6D_6) δ: –0.34. MS m/z (% and assignment): 375 (34%, $[M + Li - H]^+$), 262 (37%, $[M - TMEDA + Li + H]^+$), 247 (79%, $[M - Li - TMEDA]^+$), 191 (100%, $[247 - t\text{-}Bu]^+$).

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[Li{N(t-Bu)C(C_6H_4OMe-4)N($SiMe_3$)}] (3)

4-MeOC_6H_4CN (0.49 g, 3.62 mmol) was added in small portions to a cooled (–78 °C) solution of **A** (0.55 g, 3.63 mmol) in diethyl ether (45 cm^3). The reaction mixture was allowed to warm to room temperature and was stirred for 12 h. The cloudy mixture was filtered and the filtrate concentrated and stored at –25 °C for 12 h to afford an amorphous, ether-solvated product (Et_2O–benzamidinate, 1:2; calculated from the NMR integrals), recrystallized from a saturated hexane solution yielding compound **3** (0.29 g, 28%), as a yellow crystalline material (not suitable for X-ray analysis); mp 127–130 °C. ^{1}H NMR (C_6D_6) δ: 0.01 (s, 9H, $SiMe_3$), 1.25 (s, 9H, *t*-Bu), 3.30 (s, 3H, MeO), 6.75 (d, 2H, $^3J_{HH}$ = 8.37 Hz), 7.17 (d, 2H, $^3J_{HH}$ = 9.42 Hz). Anal. calcd. for $C_{15}H_{25}LiN_2OSi$ (%): C 63.5, H 9.41, N 9.83; found: C 62.5, H 8.49, N 9.81.

Variable temperature (V.T.) experiments

IR (cm^{-1}): 2246 ν(CN). ^{1}H NMR ($C_6D_5CD_3$ at ca. 231 K) δ: 0.09, 0.18, 0.23 (s, 9H, $SiMe_3$), 1.28, 1.32, 1.35 (s, 9H, *t*-Bu), 3.17, 3.22, 3.34 (s, 3H, MeO), 6.66 (m, 2H), 7.18 (d, 1H, $^3J_{HH}$ = 8.21 Hz), 7.30 (d, 1H, $^3J_{HH}$ = 7.95 Hz); at ca. 243 K δ: 0.08, 0.16, 0.21 (s, 9H, $SiMe_3$), 1.26, 1.31, 1.34 (s, 9H, *t*-Bu), 3.17, 3.22, 3.24, 3.30 (s, 3H, MeO), 6.65 (d, 1H, $^3J_{HH}$ = 7.93 Hz), 6.67 (d, 1H, $^3J_{HH}$ = 6.86 Hz), 7.16 (d, 1H, $^3J_{HH}$ = 8.24 Hz), 7.25 (d, 1H, $^3J_{HH}$ = 7.97 Hz); at ca. 253 K δ: 0.07, 0.14, 0.19 (s, 9H, $SiMe_3$), 1.24, 1.29, 1.34 (s, 9H, *t*-Bu), 3.17, 3.22, 3.24, 3.27 (s, 3H, MeO), 6.72 (m, 2H), 7.17 (m, 2H); at ca. 273 K δ: 0.90 (m, 9H, $SiMe_3$), 1.20 (s, 9H, *t*-Bu), 3.23, 3.25 (m, 3H, MeO), 6.67 (m, 3H, (d, 2H, $^3J_{HH}$ = 6.92 Hz)), 7.13 (d, 1H, $^3J_{HH}$ = 7.27 Hz); at ca. 298 K δ: 0.01 (s, 9H, $SiMe_3$), 1.18 (s, 9H, *t*-Bu), 3.26 (s, 3H, MeO), 6.66 (d, 2H, *o*-H, $^3J_{HH}$ = 7.44 Hz), 7.09 (m, 2H, *m*-H); at ca. 338 K δ: 0.09 (s, 9H, $SiMe_3$), 1.25 (s, 9H, *t*-Bu), 3.43 (s, 3H, MeO), 6.66 (d, 2H, $^3J_{HH}$ = 6.82 Hz), 7.25 (d, 2H, $^3J_{HH}$ = 8.52 Hz). ^{13}C NMR (C_6D_6 at ca. 298 K) δ: 2.78 ($SiMe_3$), 33.41 (C*Me*$_3$), 54.68 (*C*Me$_3$), 113.05 (MeO), 126.32, 128.40, 129.23 (Ph), 158.95 (CN). ^{7}Li NMR (C_6D_6 at ca. 298 K) δ: –0.24. ^{29}Si NMR (C_6D_6 at 338 K) δ: –9.92. MS *m*/*z* (% and assignment): 277 (85%, [*M* – Li]$^+$), 263 (38%, [*M* – Li – Me]$^+$), 221 (100%, [*M* – *t*-Bu – H]$^+$), 206 (65%, [*M* – *t*-Bu – Me – H]$^+$), 73 (100%, [$SiMe_3$]$^+$), 57 (12%, [*t*-Bu]$^+$).

[Li{μ-cis-N(t-Bu)C(C_6H_4OMe-4)N($SiMe_3$)}(THF)] (3a)

Evaporation of a THF solution of **3** produced the amorphous complex **3a**. ^{1}H NMR (C_6D_6) δ: 0.11 (s, 9H, $SiMe_3$), 1.29 (s, 9H, *t*-Bu), 1.39 (m, 4H, CH_2 of THF), 3.33 (s, 3H, MeO), 3.64 (m, 4H, OCH_2 of THF), 6.78 (d, 2H, *m*-H of C_6H_4, $^3J_{HH}$ = 8.65 Hz), 7.22 (d, 2H, *o*-H of C_6H_4, $^3J_{HH}$ = 8.48 Hz). ^{13}C NMR (C_6D_6) δ: 3.22 ($SiMe_3$), 25.51 (THF), 33.65 (C*Me*$_3$), 51.35 (*C*Me$_3$), 54.63 (MeO), 68.16 (THF), 112.90 (*m*-C of C_6H_4), 129.05 (*o*-C of C_6H_4), 138.07 (ipso-C of C_6H_4), 158.75 (*p*-C of C_6H_4), 175.58 (NCN). ^{7}Li NMR (C_6D_6) δ: 1.86. ^{29}Si NMR (inverse gated, d_1 = 25 s, C_6D_6) δ: –11.30. ^{1}H NOE (C_6D_6, η, %) irradiation of MeO: 5.7 (*m*-H of C_6H_4). ^{1}H{^{7}Li} NOE (C_6D_6, – η, %): 0.08 ($SiMe_3$), 0.12 (OCH_2 of THF), 0.15 (*o*-H of C_6H_4).

[Na{μ-cis-N(t-Bu)C(Ph)N($SiMe_3$)}(OEt_2)]$_2$ (4)

A solution of PhCN (0.98 cm^3, 9.56 mmol) in diethyl ether (5 cm^3) was added slowly to a cooled (0 °C) solution of **B** (1.60 g, 9.56 mmol) in diethyl ether (50 cm^3). The resulting solution was allowed to warm to room temperature, stirred for 12 h, concentrated and stored at –25 °C for 24 h, yielding colorless crystals of compound **4** (2.24 g, 69%). ^{1}H NMR (C_6D_6) δ: 0.04 (s, 9H, $SiMe_3$), 1.20 (t, 6H, Et_2O), 1.25 (s, 9H, *t*-Bu), 3.24 (q, 4H, Et_2O), 7.00–7.25 (m, 5H, Ph). ^{13}C NMR (333 K, C_6D_6) δ: 3.70 ($SiMe_3$), 15.30 (C*Me*$_3$), 34.12 (Et_2O), 51.38 (*C*Me$_3$), 65.91 (Et_2O), 126.28, 127.49, 129.08 (Ph), 146.23 (ipso-C), 175.10 (NCN). ^{23}Na NMR (C_6D_6) δ: 8.54 ($\Delta\nu_{1/2} \approx$ 2.6 kHz). ^{29}Si NMR (ineptrd, C_6D_6) δ: –13.37. Anal. calcd. for $C_{18}H_{33}N_2NaOSi$ (%): C 62.8, H 9.65, N 8.13; found: C 62.3, H 9.38, N 8.09.

[Sn{N-t-BuC(Ph)N($SiMe_3$)}$_2$] (5)

$SnCl_2$ (0.481 g, 2.54 mmol) was added to a cooled (0 °C) solution of **1** (1.48 g, 5.08 mmol) in diethyl ether (40 cm^3). The mixture was warmed to room temperature and stirred for 12 h. The volatiles were removed at 30 °C and 10^{-2} Torr (1 Torr = 133.3224 Pa). The residue was extracted into diethyl ether. The extract was filtered and the filtrate concentrated and stored at –25 °C for 4 months to furnish pale yellow crystals of compound **5** (1.0 g, 64%), mp 73–80 °C. ^{1}H NMR (C_6D_6) δ: 0.11 (s, 9H, $SiMe_3$), 1.24 (s, 9H, *t*-Bu), 7.01 (m, 5H, Ph). ^{13}C NMR (C_6D_6) δ: 2.86 ($SiMe_3$), 33.22 (C*Me*$_3$), 53.94 (*C*Me$_3$), 126.88, 128.32, 128.99 (Ph), 142.15 (ipso-C), 170.01 (NCN). ^{29}Si NMR (C_6D_6) δ: –1.75. ^{119}Sn NMR (C_6D_6) δ: –258.5. MS *m*/*z* (% and assignment): 614 (25%, [*M*]$^+$), 557 (6%, [*M* – *t*-Bu]$^+$), 367 (27%, [*M* – (*N*-*t*-Bu)C(Ph)N$SiMe_3$)]$^+$), 247 (48%, [(*N*-*t*-Bu)C(Ph)(N$SiMe_3$)]$^+$), 233 (50%, [(*N*-*t*-Bu)C(Ph)(N$SiMe_3$) – *t*-Bu]$^+$), 191 (100%, [$SiMe_3$N=CPh]$^+$). Anal. calcd. for $C_{28}H_{46}N_4Si_2Sn$ (%): C 54.8, H 6.59, N 9.11; found: C 54.0, H 7.57, N 9.13.

X-ray crystallographic analysis of [Li{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(THF)]$_2$ (1), [Na{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(OEt_2)]$_2$ (4), and [Sn{η^3-N(*t*-Bu)C(Ph)N($SiMe_3$)}$_2$] (5)

Diffraction data for compound **1** were collected on a Nonius CAD4 and for **4** and **5** on a Nonius Kappa-CCD diffractometer using monochromated Mo Kα radiation (λ = 0.710 73 Å). Crystals were directly mounted on the diffractometer under a stream of cold nitrogen gas. In complex **4** there was unresolved end-for-end disorder in one ligand giving rise to partial Si/C occupancy for the sites labeled Si(2) and C(25) and some unrealistic ADPs for this ligand. DELU restraints were applied. Dimensions in the disordered ligand are unreliable. In both ligands of complex **5** there was unresolved end-for-end disorder of the $SiMe_3$ and *t*-Bu groups; 0.86:0.14 for Si1 and C8, and 0.65:0.35 for Si2 and C22. Bonds and angles involving these atoms are therefore unreliable. The structures were refined on all F^2 using SHELXL 97 (15). Further details are in Table 1.

Results and discussion

Reactions between Li[*N*-*t*-Bu($SiMe_3$)] (A) and the nitrile RCN (R = Ph or 4-MeOC_6H_4)

The initial targets in the nitrile reactions were lithium amidinates derived from Li[*N*-*t*-Bu($SiMe_3$)] (**A**) (11). This was based on an analogy with reactions of Li[N($SiMe_3$)$_2$] (14) with a cyanoarene (10, 2*b*). The results of treating **A** with PhCN and 4-MeOC_6H_4CN are summarized in Scheme 1.

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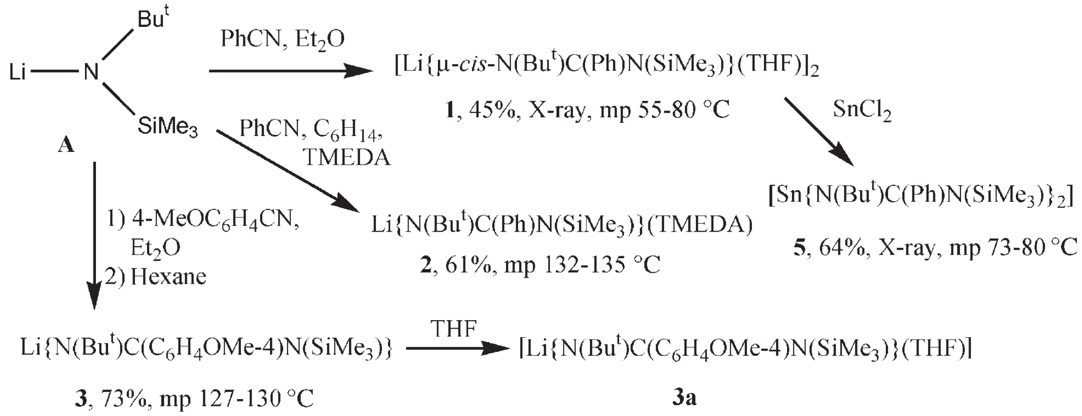
Table 1. Crystal data and structure refinements for **1**, **4**, and **5**.

Compound	**1**	**4**	**5**
Empirical formula	$C_{36}H_{62}Li_2N_4O_2Si_2$	$C_{36}H_{66}N_4Na_2O_2Si_2$	$C_{28}H_{46}N_4Si_2Sn$
Formula weight	652.96	689.09	613.56
Crystal system	Monoclinic	Tetragonal	Triclinic
Space group	$C2/c$ (No. 15)	$P4_3$ (No. 78)	$P\bar{1}$ (No. 2)
a (Å)	11.413(2)	12.0845(4)	10.7754(2)
b (Å)	17.370(3)	12.0845(4)	11.9247(3)
c (Å)	20.526(4)	29.6425(6)	14.0436(4)
α (°)	90	90	67.740(1)
β (°)	99.27(2)	90	73.941(1)
γ (°)	90	90	86.438(2)
V (Å^3)	4016.3(13)	4 328.8(2)	1 603.01(7)
Z	4	4	2
D_c (Mg m^{-3})	1.08	1.06	1.27
μ(Mo Kα) (mm^{-1})	0.12	0.13	0.89
Reflections collected	3712	12 138	25 339
Independent reflections	3533 [R(int) = 0.029]	7 216 [R(int) = 0.043]	9 307 [R(int) = 0.035]
Reflections with $I > 2\sigma(I)$	2376	5 783	7 955
Data/restraints/parameters	3533/0/208	7 216/209/416	9 307/0/318
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.057$, $wR2 = 0.120$	$R1 = 0.062$, $wR2 = 0.148$	$R1 = 0.033$, $wR2 = 0.072$
R indices (all data)	$R1 = 0.098$, $wR2 = 0.139$	$R1 = 0.084$, $wR2 = 0.164$	$R1 = 0.044$, $wR2 = 0.077$

Scheme 1. Synthesis of complexes **1**–**3** and **5**.



The colorless, crystalline, binuclear THF-bound lithium benzamidinate [Li{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(THF)]$_2$ (**1**) was obtained after crystallizing the initially formed weakly bound diethyl ether adduct from THF. Alternatively, by carrying out the reaction between **A** and PhCN in hexane, followed by addition of TMEDA, the product was the yellow, crystalline, and probably (MS) mononuclear TMEDA adduct, Li[N(*t*-Bu)C(Ph)N($SiMe_3$)](TMEDA) (**2**), as in the X-ray-characterized compounds, [Li{N($SiMe_3$)C(Ph)N($SiMe_3$)}-(TMEDA)] (16), [Li{N(myrtanyl)C(Ph)N($SiMe_3$)}(TMEDA)] (4), and [Li{N(*i*-Pr)C(terpenyl)N(*i*-Pr)}(TMEDA)] (17).

The reaction between **A** and 4-$MeOC_6H_4CN$ in diethyl ether yielded the expected lithium benzamidinate as an amorphous powder containing weakly bound diethyl ether; crystallization from hexane afforded the neutral donor-free, pale-yellow, crystalline compound [Li{N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)}] (**3**), which in THF solution yielded the adduct [Li{N(*t*-Bu)C(C_6H_4OMe-4)N($SiMe_3$)}(THF)] (**3a**).

Compounds **1**, **2**, and **3** gave satisfactory multinuclear (^{1}H, ^{13}C, ^{7}Li and ^{29}Si) NMR and mass (EI) spectra, as well as microanalysis for **3**. Complex **1** was further authenticated by its molecular structure determination by single crystal X-ray diffraction; X-ray quality crystals were not obtained for **2**, **3**, and **3**·THF. Whereas the mass spectrum of **3** was consistent with it being a mononuclear complex, the ^{1}H NMR spectrum in $C_6D_5CD_3$ at ambient temperature gave broad signals, which sharpened only upon heating. In the 231–338 K range, there appeared to be three species present. The heteronuclear ^{1}H{^{7}Li} NOE experiment of the THF adduct **3a** suggests that in benzene solution the compound has the cis-dimeric structure, as found in the crystalline THF adduct **1** (Fig. 1).

The THF-solvated lithium benzamidinate [Li{μ-*cis*-N(*t*-Bu)C(Ph)N($SiMe_3$)}(THF)]$_2$ (**1**) was crystallized after storage for 1 day at –25 °C. An ORTEP representation of complex **1** is depicted in Fig. 1. Selected bond distances (Å) and angles (°) are reported, together with data for the related

Fig. 1. Molecular structure of $[\mathrm{Li}\{\mu\text{-}cis\text{-N}(t\text{-Bu})\mathrm{C(Ph)N(SiMe_3)}\}(\mathrm{THF})]_2$ (**1**) (20% ellipsoids, H atoms are omitted for clarity).

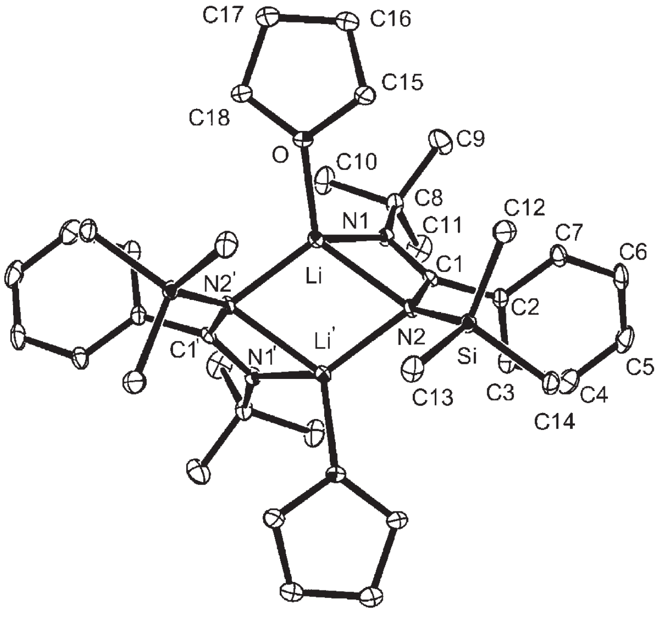


Table 2. Selected bond distances (Å) and angles (°) for compounds **1** and $[\mathrm{Li}\{\mu\text{-N(SiMe_3)C(C_6H_4OMe\text{-}4)N(SiMe_3)_2}\}(\mathrm{THF})]_2$ (**6**) (19).

Compounds	**1**	**6** (19)
Bond distances (Å)		
Li—N(1)	2.035(5)	2.099(9)
Li—N(2)	2.199(5)	2.145(8)
Li—N(2)′	2.063(5)	2.073(8)
Bond angles (°)		
N(1)-C(1)-N(2)	117.5(2)	120.1(4)
N(1)-Li-N(2)	65.2(2)	65.5(3)

compound, $[\mathrm{Li}\{\mu\text{-N(SiMe_3)C(C_6H_4OMe\text{-}4)N(SiMe_3)_2}\}(\mathrm{THF})]_2$ (**6**) (18, 19), in Table 2.

A fused array of three, four-membered rings forms the core of molecule **1**. The dihedral angles between each of the outer rings and the central are 129.85° and 112.19°. The central [LiN(2)Li′N(2)′] rhomboid core is puckered, being folded by 13.7° around the Li(1)-Li(2) vector. The presence of a *tert*-butyl group imposes a distinct asymmetry on the N-C-N system (N(1)—C(1) = 1.302(3) Å and C(1)—N(2) = 1.370(3) Å). This corresponds to differences in the Li—N(1) and Li—N(2) bond lengths. The two nitrogen atoms of each benzamidinate ligand differ in that the *tert*-butyl-bound N is three-coordinate, whereas the four-coordinated trimethylsilyl-bound N atom bridges the two lithium atoms; thus, each ligand is N,N′-chelating, but also $\mathrm{N(SiMe_3)}$-bridging. Due to steric impediments, the *tert*-butyl groups in complex **1** are arranged in a cis fashion. This creates narrower folding angles of the ladder structure core (112.89° and 129.85°) than in **6** (130.4° and 145.3°) (19). Thus, compound **1** exhibits a more compact architecture than that of **6**, evident also in the narrower N(1)-C(1)-N(2) angle in **1** than in **6** (19). A further structural detail concerns the orientation of the phenyl rings. The steric influence of the $\mathrm{SiMe_3}$ and *t*-Bu groups imposes, at the aromatic substituents, a nearly orthogonal orientation (80.5° for one phenyl group and 78.2° for the other) with respect to the N-C-N heteroallylic units, which precludes any significant conjugation between the two π systems.

Other examples of dimeric crystalline N-silylated lithium benzamidinates include $[\mathrm{Li}\{\mu\text{-N}(n\text{-Pr})\mathrm{C(Ph)N(SiMe_3)}\}(\mathrm{OEt_2})]_2$ (20*a*), $[\mathrm{Li(Am)}]_2$ (Am = $\mathrm{N(SiMe_3)C(Ph)N(CH_2)}_n\mathrm{NMe_2}$, n = 2 (20*b*) or 3 (13*g*)), $[\mathrm{Li}\{\mathrm{N(SiMe_3)C(Ph)NC(Ph){=}C(SiMe_3)_2}\}(\mathrm{NCPh})]_2$ (13*d*), $[\mathrm{Li}\{\mathrm{N(SiMe_3)C(Ph)NC(Ph){=}C(H)SiMe_3}\}(\mathrm{THF})]_2$ (13*f*), $[\mathrm{Li}\{\mathrm{N}((1R,2R)\text{-}(-)\text{-2-(trimethylsilylamino)-cyclohexyl)propyl)C(Ph)N(SiMe_3)}\}]_2$ (20*c*), several phenyl-fluorinated benzamidinates (20*d*), $[\mathrm{Li}\{\mathrm{N(SiMe_3)C(4\text{-}MeC_6H_4)N(SiMe_3)}\}(\mathrm{NCC_6H_4Me\text{-}4})]_2$ (20*e*), and $[\mathrm{Li}\{\mathrm{N(SiMe_3)C(Ph)N(SiMe_3)}\}(\mathrm{NCPh})]_2$ (20*f*).

Reactions between $\mathrm{Na}[N\text{-}t\text{-Bu(SiMe_3)}]$ (B) and PhCN

It had previously been shown that the sodium benzamidinate, $[\mathrm{Na}\{\mu\text{-N(SiMe_3)C(Ph)N(SiMe_3)}\}(\mathrm{OEt_2})]_2(\mathrm{OEt_2})$, had been obtained from the reaction of $\mathrm{Na[N(SiMe_3)_2]}$ with PhCN (21). Hence, $\mathrm{Na}[N\text{-}t\text{-Bu(SiMe_3)}]$ (**B**) was treated with PhCN in $\mathrm{Et_2O}$–hexane at low temperature; an inseparable mixture of starting materials and insertion products was formed. Various attempts to isolate the sodium benzamidinate (the presence of which was inferred by means of ^{13}C NMR spectroscopy of the reaction mixture (δ 174.8 NCN)) failed. It may be that some of the unidentified products consisted of oligomerized PhCN, as in the case of treating PhCN with Li-*n*-Bu (10, 22). In contrast, when the reaction was carried out in $\mathrm{Et_2O}$, the expected product, $[\mathrm{Na}\{\mu\text{-}cis\text{-N}(t\text{-Bu})\mathrm{C(Ph)N(SiMe_3)}\}(\mathrm{OEt_2})]_2$ (**4**), was obtained (eq. [1]).

$$[1]\qquad [\mathrm{Na}\{N\text{-}t\text{-Bu(SiMe_3)}\}]_3 + 3\mathrm{PhCN} \xrightarrow{\mathrm{Et_2O}} 3/2[\mathrm{Na}\{\mu\text{-}cis\text{-N}(t\text{-Bu})\mathrm{C(Ph)N(SiMe_3)}\}(\mathrm{OEt_2})]_2$$

(**4**, 69%, X-ray)

The sodium benzamidinate **4** was crystallized from the reaction mixture at –25 °C. An ORTEP representation of its molecular structure is shown in Fig. 2. Selected bond distances (Å) and angles (°), together with data for the related compound, $[\mathrm{Na}\{\mu\text{-N(SiMe_3)C(Ph)N(SiMe_3)}\}(\mathrm{OEt_2})]_2(\mathrm{OEt_2})$ (**7**) (21), are listed in Table 3.

There is disorder between the silicon and carbon atoms (Si2 and C25) attached to N3 and N4, respectively, of one of the benzamidinato ligands. The N-silylated, four-coordinate nitrogen atom N1 bridges the sodium atoms Na1 and Na2, whereas the *tert*-butyl-bound nitrogen atom N2 is in a three-coordinate environment. Thus, the ligand is both N1,N2-chelating and N1-bridging. The difference between the Na1—N bond lengths of the bridging (N1) and terminal (N2) atoms is 0.38 Å, whereas the corresponding value for compound **7** is 0.19 Å (21). While the angle N1-Na1-N2 is similar in **4** and **7**, the angle N1-C1-N2 is slightly smaller in **4** than in **7** (21). The dihedral angle between the C2-C7 phenyl ring plane and the N1-C1-N2 plane is 78.1°.

Synthesis and characterization of $[\mathrm{Sn}\{N(t\text{-Bu})\mathrm{C(Ph)N(SiMe_3)}\}_2]$ (5)

As indicated in Scheme 1, the reaction between **1** and $\mathrm{SnCl_2}$ in diethyl ether yielded crystalline $[\mathrm{Sn}\{\mathrm{N}(t\text{-Bu})\mathrm{C(Ph)N(SiMe_3)}\}_2]$ (**5**), which was characterized by ele-

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Fig. 2. Molecular structure of $\mathrm{[Na\{\mu\text{-}\mathit{cis}\text{-}N(\mathit{t}\text{-}Bu)C(Ph)N(SiMe_3)\}(OEt_2)]_2}$ (**4**) (20% ellipsoids, H atoms are omitted for clarity).

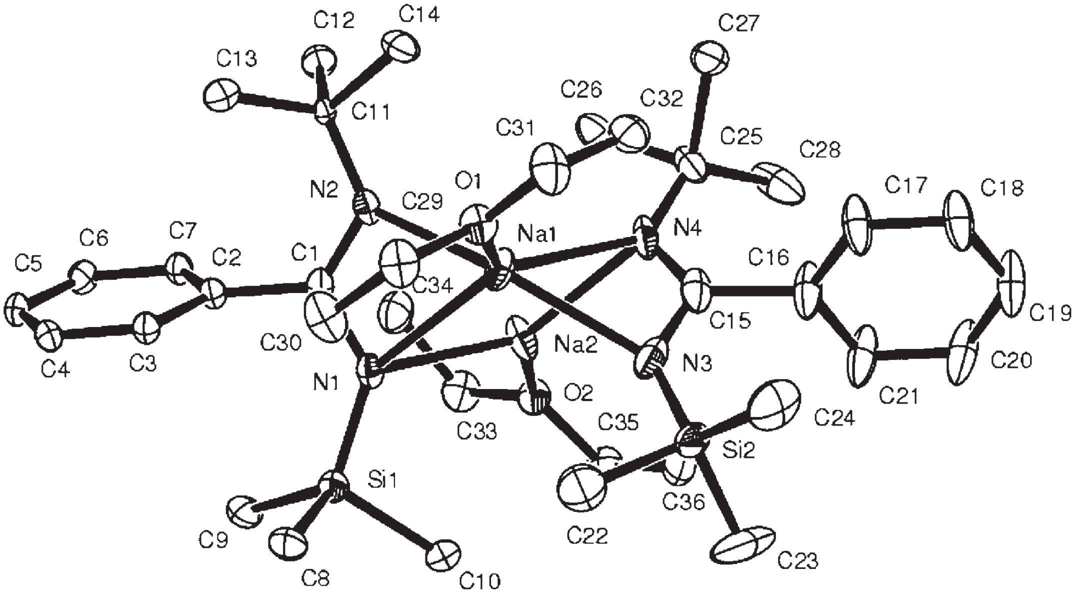


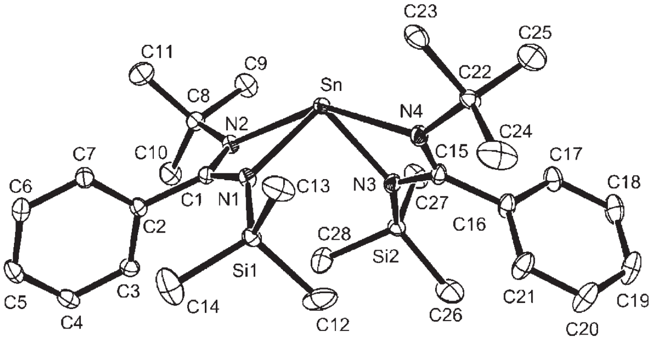
Table 3. Selected bond distances (Å) and angles (°) for compounds **4** and $\mathrm{[Na\{\mu\text{-}N(SiMe_3)C(Ph)N(SiMe_3)\}(OEt_2)]_2(OEt_2)}$ (**7**) (21).

Compounds	**4**	**7** (21)
Bond distances (Å)		
Na(1)—N(1)	2.752(4)	2.671(5)
Na(1)—N(2)	2.376(4)	2.482(5)
Na(1)—N(3)	2.412(4)	2.426(5)
Na(1)—N(4)	2.758(5)	2.725(5)
Na(2)—N(1)	2.380(4)	2.459(5)
Na(2)—N(4)	2.336(4)	2.397(5)
Bond angles (°)		
N(1)-Na(1)-N(2)	52.07(12)	52.8(2)
N(3)-Na(1)-N(4)	51.02(19)	52.8(2)
N(1)-Na(1)-N(4)	100.02(12)	105.9(2)
N(1)-Na(2)-N(4)	127.07(16)	124.9(2)
N(1)-C(1)-N(2)	118.3(3)	121.0(5)
N(3)-C(15)-N(4)	118.8(5)	121.0(5)

mental analysis, multinuclear NMR spectra in C_6D_6, and its EI mass spectrum. The ^{119}Sn NMR chemical shift value of δ –258.5 for **5** may be compared with the δ –387 for the tin(II) azaallyl $\mathrm{Sn[N(SiMe_3)C(\mathit{t}\text{-}Bu)C(H)SiMe_3]_2}$, which like **5** has a four-coordinate tin(II) atom at the spiro junction of two strained four-membered rings (23).

An ORTEP representation of complex **5** is depicted in Fig. 3. A list of selected bond distances (Å) and angles (°), together with complementary data on $\mathrm{[Sn\{N(SiMe_3)C(Ph)N(SiMe_3)\}_2]}$ (**8**) (24), is presented in Table 4.

Fig. 3. Molecular structure of $\mathrm{[Sn\{\mathit{N}\text{-}\mathit{t}\text{-}BuC(Ph)N(SiMe_3)\}_2]}$ (**5**) (20% ellipsoids, H atoms are omitted for clarity).



Crystalline **5** is a monomer with N,N′-chelating benzamidinato ligands. In each of the latter, there is unresolved end-for-end disorder of the $\mathrm{SiMe_3}$ and $\mathrm{CMe_3}$ groups: 0.86:0.14 for Si1 and C8, and 0.65:0.35 for Si2 and C22; bond lengths and angles involving these atoms are therefore unreliable. The structure of **5** is closely similar to that of **8** (24). The geometric parameters of each of the two Sn-N-C-N′ rings in both **5** and **8** are almost identical. The dihedral angle between the N1-Sn-N2 and N3-Sn-N4 planes in **5** is 86°, while that between each N-C-N plane and the attached aromatic C_6 plane is ca. 78°. There clearly is a stereochemically active lone pair of electrons at the Sn atom.

Other Sn(II) benzamidinates related to **5** and **8** (24) that have been reported include $\mathrm{[Sn\{N(SiMe_3)C(Ph)NC(Ph){=}C(SiMe_3)_2\}_2]}$ (13*d*), $\mathrm{[Sn\{N(SiMe_2Ph)C(Ph)N(SiMe_2Ph)\}_2]}$ (24), $\mathrm{[Sn\{N(SiMe_3)C(Me)N(SiMe_3)\}_2]}$ (25), and $\mathrm{[Sn\{N(SiMe_3)C(C_6H_4Ph\text{-}4)N(Ph)\}_2]}$ (26).[3]

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[3] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5000. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 273350–273352 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Table 4. Selected bond distances (Å) and angles (°) for **5** and [Sn{N($SiMe_3$)C(Ph)N($SiMe_3$)}$_2$] (**8**) (24).

Compounds	**5**	**8** (24)
Bond distances (Å)		
Sn—N(1,3)	2.224(2), 2.229(2)	2.239(2), 2.245(2)
Sn—N(2,4)	2.384(2), 2.382(2)	2.375(2), 2.374(4)
Bond angles (°)		
N(1)-Sn-N(3)	94.9(1)	93.3(1)
N(2)-Sn-N(3)	97.5(1)	95.3(1)
N(2)-Sn-N(4)	146.3(1)	143.1(1)
N(1)-Sn-N(4)	98.1(1)	94.2(1)
N(1,3)-Sn-N(2,4)	58.2(1)	58.7 (1) and 58.9(1)
N(1)-C(1)-N(2) [N(4)-C(15)-N(3)]	115.1(2)	117.2(2) [117.4(2)]

Conclusions

Five new crystalline benzamidinates bearing the C_1 symmetric [N(*t*-Bu)C(R)N($SiMe_3$)]$^-$ ligand (Am$^-$) have been prepared and characterized: [Li(Am)(THF)]$_2$ (**1**), Li(Am)(TMEDA) (**2**), Li(Am) (**3**), [Na(Am)(OEt_2)]$_2$ (**4**), and [Sn(Am)$_2$] (**5**) (R = Ph in **1**, **2**, **4**, and **5**; R = 4-MeOC_6H_4 in **3**). The X-ray structures of **1**, **4**, and **5** are reported. The Am$^-$ ligand in **1** and **4** is both chelating and via N($SiMe_3$) is also bridging. The two structures differ in that the core of the planar M-N-CN′-M′ ring is rhomboidal in **1** (M = Li), but C_2 symmetric with unequal contiguous Na—N bond lengths in **4**. The Am$^-$ ligand in **5** functions as a chelate.

Acknowledgments

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