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Synthesis of New β-Diketiminato Complexes of Scandium(III): Unprecedented Formation of a Multicyclic Aggregate

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Summary: The reaction of $ScCl_3$ with LLi (L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$) yields the compound $LScCl_2$. The unique electronic and steric features of the ligand allow the formation of a very stable multicyclic aggregate by reaction of the new halogeno β-diketiminato complex $LScCl_2$ with $NaN(SiMe_3)_2$.

Due to their ability to take part in various catalytic processes involving C−H bond activation, the organo complexes of the early transition metals and lanthanides have been actively investigated over the past decade.[1−8] Although many of the studied complexes are metallocene derivatives, recent years have brought a strong tendency to develop the nonmetallocene chemistry of these metals, replacing at least one of the cyclopentadienyl groups with ligands of similar steric and electronic demand.[9−17] Herein, we report the synthesis and characterization of a new dichloro β-diketiminato complex of scandium, **1**, and the reaction of it with sodium bis(trimethylsilyl)amide to form the double-methylene-bridged dimeric compound **2**.

For the preparation of complex **1**[18] we used the β-diketiminato ligand L (L = $Et_2NCH_2CH_2NC(Me)CHC(Me)NCH_2CH_2NEt_2$), which was recently developed in our group.[19] The Lewis acid character of scandium is diminished due to the donor abilities of the ligand, so that the presence of basic solvent molecules in the coordination sphere of the metal is not necessary. This was confirmed by an X-ray structural investigation of $LScX_2$.

The structural analysis[18,20] shows **1** as a monomeric molecule in which the hexacoordinated scandium has a pseudooctahedral geometry with all four nitrogen atoms in the same plane and the two chlorine atoms in trans positions (Cl(1)−Sc(1)−Cl(2) = 166.71°). The Sc−Cl bond lengths are in the range of those for previously reported compounds[17,21−23] (Figure 1).

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(1) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem.* **1999**, *111*, 449; *Angew. Chem., Int. Ed.* **1999**, *38*, 428 and references therein.

(2) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587.

(3) (a) Carpentier, J.-F.; Maryin, V. P.; Luci, J.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 898. (b) Keaton, R. J.; Jayaratne, K. C.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 12909. (c) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499. (d) Tjaden, E. B.; Swenson, D. C.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1995**, *14*, 371.

(4) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(5) Evans, W. J.; Cano, D. A.; Greci, M. A.; Ziller, J. W. *Organometallics* **1999**, *18*, 1381.

(6) Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931.

(7) Arndt, S.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2001**, 73.

(8) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

(9) Hajela, S.; Schaefer, W. P.; Bercaw, J. E. *J. Organomet. Chem.* **1997**, *532*, 45.

(10) Edelmann, F. T. *Angew. Chem.* **1995**, *107*, 2647; *Angew. Chem., Int. Ed.* **1995**, *34*, 2466 and references therein.

(11) (a) Roesky, P. W.; Bürgstein, M. R. *Inorg. Chem.* **1999**, *38*, 5629. (b) Bürgstein, M. R.; Berberich, H.; Roesky, P. W. *Organometallics* **1998**, *17*, 1452.

(12) Schmidt, J. A. R.; Arnold, J. *Chem. Commun.* **1999**, 2149.

(13) (a) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720. (c) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197.

(14) Graf, D. D.; Davis, W. M.; Schrock, R. R. *Organometallics* **1998**, *17*, 5820.

(15) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923.

(16) Dawson, D. M.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2000**, 459.

(17) Hayes, P. G.; Piers, W. E.; Lee, L. W. M.; Knight, L. K.; Parvez, M.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **2001**, *20*, 2533.

(18) All operations were carried out under dry nitrogen using Schlenk and drybox techniques. The lithium salt was prepared according to literature procedures.[19] Other materials were purchased from Aldrich and used without purifying. Procedures for compound **1** are as follows. (a) A solution of LLi (2.70 g, 9 mmol) in THF (25 mL) was added to a suspension of $ScCl_3 \cdot 3THF$(3.33 g, 9 mmol) in THF (50 mL). The resulting yellow solution was stirred overnight at room temperature, and then the solvent was removed in vacuo and the solid material extracted with toluene (50 mL). The subsequent removal of the toluene led to 3.30 g (88.5%) of **1**. (b) A solution of LLi (2.04 g, 6.74 mmol) in toluene (25 mL) was added to a suspension of $ScCl_3$ (1.02 g, 6.74 mmol) in toluene (25 mL). The suspension was refluxed for 3 days, and then the hot solution was filtered; finally, the solvent was removed in vacuo. The resulting crude product was washed with hexane (25 mL) to yield 2.51 g (90.5%) of **1.** Mp: 159−161 °C. Anal. Calcd for $C_{17}H_{35}Cl_2N_4Sc$: C, 49.63; H, 8.57; N, 13.62. Found: C, 49.51; H, 8.43; N, 13.46. ^1H NMR (200 MHz, C_6D_6, 300 K): δ 4.82 (s, 1 H, CH), 3.08 (m, 16 H, $NCH_2CH_2N(CH_2)_2$), 1.6 (s, 6 H, $CHCCH_3$), 0.85 (t, 12 H, CH_2CH_3). ^{13}C NMR (125.75 MHz, C_6D_6, 300 K): δ 165.46 (CCHC), 99.56 (CH), 54.7 ($CNCH_2$), 47.67 (NCH_2CH_2), 30.16 (CH_2NCH_2), 22.34 ($CHCCH_3$), 8.64 (NCH_2CH_3). ^{45}Sc NMR (121.49 MHz, referenced to $[Sc(H_2O)_6]^{3+}$ in D_2O, C_6D_6, 300 K): δ 286.21. EI-MS (*m*/*z* (relative intensity, %)): 410 (M^+, 10), 324 ($M^+ - C_5H_{12}N$, 100).

(19) Neculai, D.; Roesky, H. W.; Neculai, A. M.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *J. Organomet. Chem.*, in press.

(20) It should be noted that **1** crystallizes in two different unit cells, depending on the orientation of the ethyl groups. Crystal data for **1**: $C_{17}H_{35}Cl_2N_4Sc$, $M_r = 411.35$, monoclinic, space group $P2_1/c$, $a = 15.3091(15)$ Å, $b = 10.9126(7)$ Å, $c = 13.0490$ Å, $\alpha = 90°$, $\beta = 107.156(8)°$, $\gamma = 90°$, $V = 2083.0(3)$ Å^3, $Z = 4$, $\sigma_{calcd} = 1.312$ g cm^{-3}, R1 = 0.0357 (wR2 = 0.0827) for 2580 observed reflections with $I > 2\sigma(I)$. Crystal data for **2**: $[C_{17}H_{34}N_4ScN(SiMe_3)_2]_2 \cdot 2C_7H_8$, $M_r = 1183.94$, monoclinic, space group $P2_1/n$, $a = 16.3133(7)$ Å, $b = 20.4752(9)$ Å, $c = 22.1557(10)$ Å, $\alpha = 90°$, $\beta = 108.290(3)°$, $\gamma = 90°$, $V = 7026.5(5)$ Å^3, $Z = 4$, $\sigma_{calcd} = 1.119$ g cm^{-3}, R1 = 0.0409 (wR2 = 0.0963) for 8127 observed reflections with $I > 2\sigma(I)$. See the Supporting Information.

(21) Hagadorn, J. R.; Arnold, J. *Organometallics* **1996**, *15*, 984.

(22) Lee, L. W. M.; Piers, W. E.; Elsegood, M. R. J.; Clegg, W.; Parvez, M. *Organometallics* **1999**, *18*, 2947.

(23) Arnold, J.; Hoffman, C. G.; Dawson, D. Y.; Hollander, F. J. *Organometallics* **1993**, *12*, 3645.

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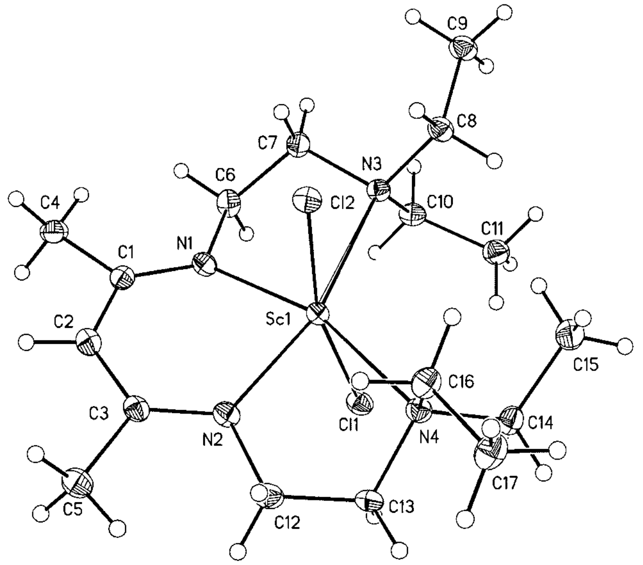


Figure 1. Molecular structure of **1**. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) = 2.151(2), Sc(1)−N(2) = 2.174(2), Sc(1)−Cl(1) = 2.453(1), Sc(1)−Cl(2) = 2.440(1); N(1)−Sc(1)−N(2) = 84.66(8), N(1)−Sc(1)−N(4) = 160.76(8), N(3)−Sc(1)−N(2) = 163.91(8), N(3)−Sc(1)−N(4) = 76.12(8), Cl(1)−Sc(1)−Cl(2) = 166.71(3).

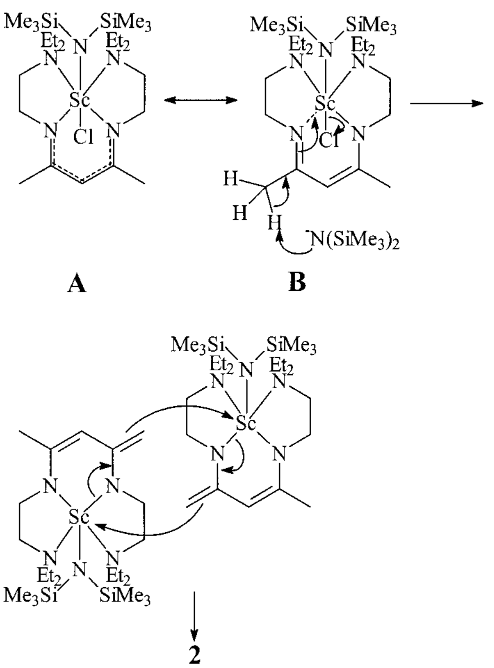
Compound **1** is quite resistant to metathesis reactions using alkyllithium reagents but reacts with NaN(SiMe$_3$)$_2$ in a 1:2 molar ratio to yield the dimeric compound **2** with two scandium ring systems connected by two methylene bridges (eq 1).

$$\underset{\mathbf{1}}{2C_{17}H_{35}N_4ScCl_2} + 4NaN(SiMe_3)_2 \xrightarrow[-2HN(SiMe_3)_2]{-4NaCl} \underset{\mathbf{2}}{[C_{17}H_{34}N_4ScN(SiMe_3)_2]_2} \quad (1)$$

For the formation of compound **2**, a multistep mechanism can be proposed. The first step is the monosubstitution (**A**) of one of the chlorine atoms in **1** followed by C−H bond-breaking and a dimerization step (Scheme 1). This assumption can be regarded as a result of both the high nucleophilicity of (Me$_3$Si)$_2$N$^-$ and the strong electrophilicity of scandium. Indeed, the β-diketiminato ligand possesses hydrogen atoms of low electron density on the methyl groups by virtue of the localized bond resonance form **B** (see Scheme 1). Nevertheless, the C−H bonds are even more polarized by the withdrawal effect of scandium and the highly hindered base ((Me$_3$Si)$_2$N$^-$) can easily deprotonate the ketiminato fragment to form a scandium "enolate" that then undergoes subsequent dimerization.

Monitoring the reaction on the NMR time scale was not successful, due to the rapid formation of **2**. Reaction of LScCl$_2$ with NaN(SiMe$_3$)$_2$ in a 1:1 molar ratio, using the same procedure for obtaining **2**, led to formation of a yellow substance whose MS spectrum presents a signal at *m*/*z* 520, which could be assigned to [LScClN(SiMe$_3$)(SiMe$_2$)]$^+$. This finding supports the proposed reaction pathway.

Scheme 1



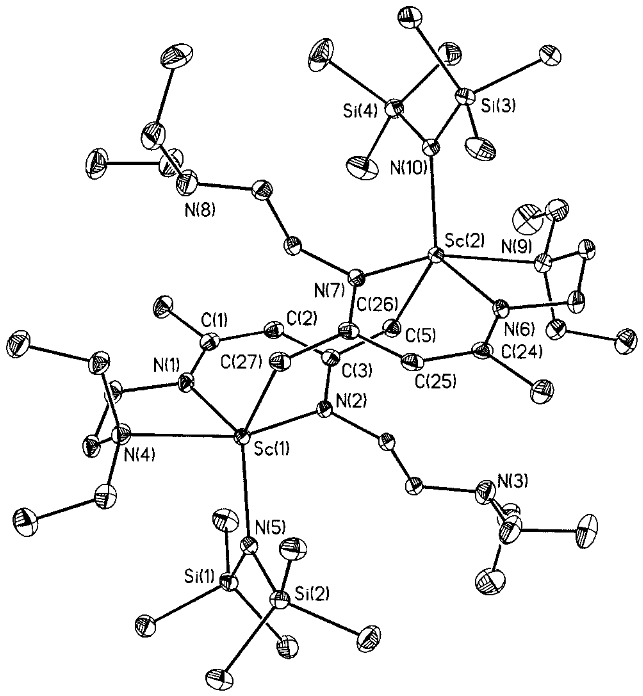


Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Sc(1)−N(1) = 2.130(2), Sc(1)−N(2) = 2.121(2), Sc(1)−N(5) = 2.124(2), Sc(1)−N(4) = 2.468(2), Sc(1)−C(27) = 2.397(2); N(1)−Sc(1)−C(27) = 111.88(8), N(1)−Sc(1)−N(5) = 120.12(7), N(5)−Sc(1)−C(27) = 127.26(8), N(4)−Sc(1)−N(2) = 158.67(7).

The X-ray single-crystal structural analysis[20] shows that **2** is a dimer with two toluene molecules retained in the asymmetric unit. The Sc atoms in **2** are pentacoordinated with a distorted-trigonal-bipyramidal geometry, where N(4) and N(2) (N(9) and N(7), respectively) are arranged in approximately apical positions (Figure 2). The toluene molecules can be partly removed when compound **2** is subjected to vacuum. This is confirmed by the elemental analysis and the NMR spectra. One of the characteristics of **2** is the unique arrangement of the scandium atoms, which are each part of five cycles: an eight-membered ring (in a chair conformation), two six-membered rings, and two five-membered rings. The thermodynamically favored formation of **2** and the conservation of its structure in solution are indicated by the NMR spectrum in toluene. In the temperature range 300−373 K we do not observe any changes of the resonances. The Sc−C(bridge) bond lengths are typical of those in other organoscandium complexes.[17,21−23,25] The Sc−N(SiMe$_3$) distance is greater than those in the tricoordinated Sc(N(SiMe$_3$)$_2$)$_3$[26] but is equal to the Sc−N(β-diketiminato) bond lengths of **2**. The ligand L is not symmetrically coordinated toward Sc, with one dangling NEt$_2$ group on each Sc atom in the solid state as well as in solution. The ^{1}H NMR spectrum of **2** exhibits eight resonances (in the 2.4−4.15 ppm region) whose overall intensities render the anticipated number of hydrogen atoms for the methylene groups, except those of the bridges, which cannot be assigned due to multiple interactions.[27] Moreover, the molecular asymmetry allows for observation of two different resonances in the ^{1}H NMR spectrum of the bridging methylene groups; in the ^{29}Si NMR spectrum two resonances for silicon atoms are observed. The Sc resonance in the NMR spectrum is shifted upfield in comparison with **1** (423.6 to 286.2 ppm) as a result of a lower coordination number and higher electron density at Sc in **2**.

In conclusion, new heteroleptic scandium(III) complexes have been obtained. The discussion of the mechanism for the formation of **2** remains open; for instance, the metathesis of the C−H bond and the Sc−N bond of a Sc−N(SiMe$_3$)$_2$ unit can be invoked. Investigations of the reactivity of **2** are in progress.

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Supporting Information Available: Tables of crystal data, atomic coordinates and isotopic thermal parameters, and bond lengths and angles for compounds **1** and **2** and for the second polymorphic form of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Synthesis of **2**: toluene (25 mL) was added to a mixture of **1** (1 g, 2.43 mmol) and NaN(SiMe$_3$)$_2$ (0.9 g, 4.87 mmol). The resulting red solution was stirred overnight and then filtered, concentrated, and kept at −26 °C. After 3 days, crystals of **2** can be filtered off and dried under a nitrogen stream. Yield: 0.2 g (19.1%) of **2**·0.74C$_7$H$_8$ (the composition is due to the drying procedure). Mp: 193−195 °C. Anal. Calcd for C$_{46}$H$_{104}$N$_{10}$Sc$_2$Si$_4$·0.74C$_7$H$_8$: C, 57.37; H, 10.37; N, 13.11. Found: C, 57.37; H, 9.98; N, 12.77. ^{1}H NMR (200 MHz, C$_6$D$_6$, 300 K): δ 5.16 (s, 2 H, CH), 4.15 (m), 3.3 (m), 3.09 (m), 2.92 (broad signal), 2.81 (m), 2.65 (m), 2.55 (t), 2.4 (m), 2.24 and 1.93 (d, 1 H, CH$_2$ bridge, overlapping with toluene signal), 1.82 (s, 12 H, CHCCH$_3$), 0.96 (t, 12 H, NCH$_2$CH$_3$), 0.85 (broad signal, 12 H, NCH$_2$CH$_3$), 0.59, 0.40 (2 s, 18 H, N(SiMe$_3$)$_2$). ^{13}C NMR (125.75 MHz, C$_6$D$_6$, 300 K): δ 156.19(CCH), 137.83 (CHCCH$_2$), 101.34 (C), 55.12, 50.16, 47.00, 46.59, 22.37 (CCH$_3$), 21.36 (CH$_2$ bridge overlapping with toluene signal), 12.26 (NCH$_2$CH$_3$), 6.69, 6.26 (N(SiMe$_3$)$_2$). ^{45}Sc NMR (121.49 MHz, referenced to [Sc(H$_2$O)$_6$]$^{3+}$ in D$_2$O, C$_6$D$_6$, 300 K): δ 423.64. ^{29}Si NMR (100 MHz, referenced to TMS, C$_6$D$_6$, 300 K): δ −7.93, −10.83. EI-MS (*m/z* (relative intensity, %)): 499 (C$_{17}$H$_{34}$N$_4$ScN(SiMe$_3$)$_2$, 7), 146 (NSi$_2$Me$_5$, 100).

(25) Thomson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santasiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203.

(26) Ghotra, J. G.; Hursthouse, M. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1973**, 669.

(27) Even the 2D-COSY experiments allow no reliable assignments.