Well-defined hydrocarbon soluble strontium fluoride and chloride complexes of composition [LSr(thf)(μ-F)$_2$Sr(thf)$_2$L] and [LSr(thf)(μ-Cl)$_2$Sr(thf)$_2$L]†‡

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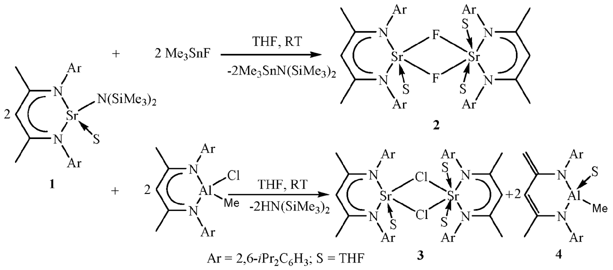
Reaction of LSrN(SiMe$_3$)$_2$(thf) 1 (L = CH(CMe-2,6-*i*-Pr$_2$C$_6$H$_3$N)$_2$) with Me$_3$SnF and LAlCl(Me), respectively, gave the first example of a strontium mono fluoride complex [LSr(thf)(μ-F)$_2$Sr(thf)$_2$L] 2 and the corresponding chloride derivative [LSr(thf)(μ-Cl)$_2$Sr(thf)$_2$L] 3.

There is a great deal of interest in the synthesis and characterization of novel group 2 halide complexes of the type RMX (M = an alkaline earth metal) due to their potential applications in synthetic chemistry and material science.[1] In view of these applications, various halide complexes of alkaline earth metals have been synthesized and structurally characterized.[2] Nevertheless, the organometallic halide chemistry with respect to heavier group 2 elements is still in its infancy. This is due to the percentage of ionic character in the M–X bond increasing from magnesium to strontium and also due to a fast ligand exchange.[3] In recent times, a calcium fluoride and a chloride were prepared as stable species by exploiting the unique electronic and steric effect offered by the β-diketiminato ligand L (L = CH(CMe-2,6-*i*-Pr$_2$C$_6$H$_3$N)$_2$).[1c,4] Another calcium fluoride was also reported by Hill and co-workers.[5] But the strontium analogs of its lighter congener were missing because of the non-availability of a suitable precursor until recently. For example a well-defined molecular strontium hydroxide was obtained by the controlled hydrolysis of a strontium amide. The realization of the strontium hydroxide initiated the study of the Sr–OH bond present in these complexes in hydrocarbon solvents.[6] Consequently it is anticipated that the synthesis of the well-defined halide complexes of strontium enables the investigation of the nature of the Sr–X bond. In view of these, herein, we report the first example of a hydrocarbon soluble molecular strontium mono fluoride [LSr(thf)(μ-F)$_2$Sr(thf)$_2$L] **2** and a mono chloride [LSr(thf)(μ-Cl)$_2$Sr(thf)$_2$L] **3** obtained from the reaction of strontium amide LSrN(SiMe$_3$)$_2$(thf) **1**[6] with Me$_3$SnF and LAlCl(Me), respectively.



Scheme 1 Preparation of the strontium fluoride **2** and chloride **3** complex.

The reaction of LSrN(SiMe$_3$)$_2$(thf) **1** and Me$_3$SnF in THF at room temperature for 15 h led to the formation of the strontium fluoride **2** as colorless crystals (Scheme 1)[7a] while **1** and LAlCl(Me) in THF at room temperature yielded strontium chloride **3** (Scheme 1).[7b] The formation of **3** proceeds under elimination of HN(SiMe$_3$)$_2$ and generation of L$_1$AlMe(thf) (L$_1$ = CH[C(CH$_2$)](CMe)(2,6-*i*-Pr$_2$C$_6$H$_3$N)$_2$) **4**.[7c] So far we have not been able to obtain single crystals of **4**. However to support the composition of **4** indirectly we treated **4** with water to generate LAlOH(Me), which was compared with an original sample.[8] Compounds **2** and **3** are soluble in toluene, benzene, and THF, respectively. They have been well characterized by mass spectrometry, NMR spectroscopy [^{1}H, ^{13}C and ^{19}F (for **2**)], single crystal X-ray diffraction, and elemental analysis.

The ^{1}H and ^{19}F NMR spectra of compound **2** show a singlet (4.51 ppm) for the γ-protons and a singlet (−59.97 ppm) for the fluorine atoms, respectively.

The complete disappearance of the SiMe$_3$ resonance (0.14 ppm) of **1** in the ^{1}H NMR spectra of **2** and **3** clearly indicates the elimination of Me$_3$SnN(SiMe$_3$)$_2$ and HN(SiMe$_3$)$_2$, respectively. Compounds **2** and **3** are very sensitive to air and moisture and in non-coordinating hydrocarbon solvents both have a tendency slowly to rearrange to form L$_2$Sr.[9] The molecular ion peak corresponding to **2** and **3** was not observed in the EI mass spectra.

Single crystals of **2** and **3** suitable for structural analysis were obtained when a concentrated solution of **2** and **3**, respectively, in a mixture of THF–toluene was stored at −5 °C in a freezer. Compounds **2** and **3** crystallize in the triclinic $P\bar{1}$ and monoclinic $C2/c$ space group, respectively.§ The structures of **2** and **3** (Fig. 1 and 2) reveal the dimeric nature of the complexes and contain two six-membered

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† This paper is dedicated to Professor Martin Jansen on the occasion of his 65th birthday.

‡ Electronic supplementary information (ESI) available: General experimental details and X-ray crystallographic details for compounds **2** and **3**. CCDC 708838 and 708839. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b822148k

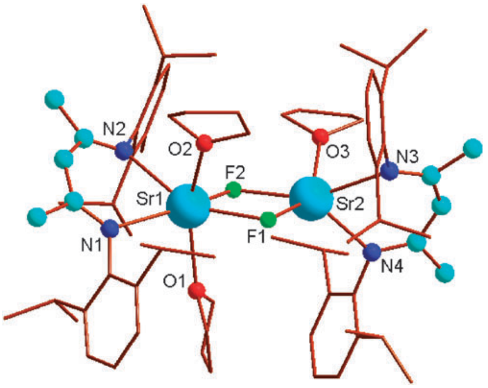

Fig. 1 Crystal structure of **2**·1.5C$_7$H$_8$. Selected bond distances (Å) and angles (°): Sr(1)–N(1) 2.605(2), Sr(1)–F(1) 2.397(1), Sr(1)–F(2) 2.345(1), Sr(1)–O(1) 2.581(2), Sr(1)–O(2) 2.581(2), Sr(2)–F(1) 2.317(1), Sr(2)–F(2) 2.333(1), Sr(2)–O(3) 2.554(2), Sr(1)–Sr(2) 3.739(1); Sr(1)–F(1)–Sr(2) 104.94(5), Sr(1)–F(2)–Sr(2) 106.09(5), F(1)–Sr(1)–F(2) 73.53(5), F(1)–Sr(2)–F(2) 75.23(5). All of the hydrogen atoms and toluene molecules have been omitted for clarity.

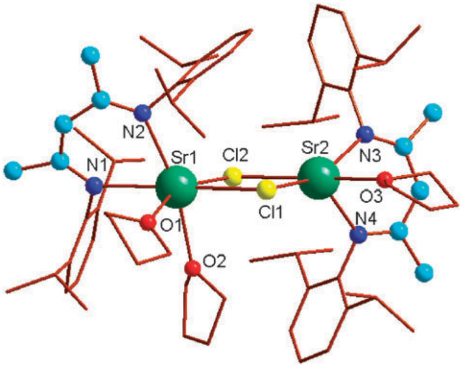

Fig. 2 Crystal structure of **3**·0.5C$_7$H$_8$. Selected bond distances (Å) and angles (°): Sr(1)–N(1) 2.618(3), Sr(1)–Cl(1) 2.954(1), Sr(1)–Cl(2) 2.898(1), Sr(1)–O(1A) 2.584(7), Sr(1)–O(2) 2.577(2), Sr(2)–Cl(1) 2.890(1), Sr(2)–Cl(2) 2.821(1), Sr(2)–O(3) 2.599(2), Sr(1)–Sr(2) 4.469(1); Sr(1)–Cl(1)–Sr(2) 99.76(3), Sr(1)–Cl(2)–Sr(2) 102.78(3), Cl(1)–Sr(1)–Cl(2) 77.58(2), Cl(1)–Sr(2)–Cl(2) 79.87(3). All of the hydrogen atoms and the toluene molecule have been omitted for clarity.

C_3N_2Sr rings. These six-membered rings are connected to each other by two μ-F or μ-Cl atoms, which result in the formation of a four-membered Sr_2F_2 ring in **2** and a corresponding Sr_2Cl_2 ring in **3**. The six-membered rings are not planar and are almost perpendicular to each other in **2** [81.3°] but exhibit an angle of 55.5° in **3**. The four-membered Sr_2Cl_2 and Sr_2F_2 rings are nearly planar and form angles with the two six-membered rings of 35.84° and 66.48° in compound **2**, and 67.67° and 82.91° in compound **3**.

Interestingly, like the strontium hydroxide [LSr(thf)(μ-OH)$_2$-Sr(thf)$_2$L] the strontium atoms in **2** and **3** have different environments due to the number of coordinated THF molecules. Thus, one of the strontium atoms is penta-coordinate and has distorted trigonal bipyramidal geometry with two nitrogen atoms of the β-diketiminate ligand, one oxygen atom of the THF molecule and two fluorine or chlorine atoms. The other strontium atom in **2** and **3**, respectively, has an additional THF molecule in its coordination sphere that results in a hexa-coordinate environment. This makes **2** and **3** different from the magnesium and calcium analogs {[LMg(μ-F)(thf)]$_2$[2d] and [LCa(μ-X)(thf)]$_2$[1c,4] (X = F or Cl)}, where both of the alkaline earth metal centers have the same coordination geometry. As expected the average Sr–F (2.348(1)$_{av}$ Å) and Sr–Cl (2.891(1)$_{av}$ Å) bond distances are longer than those of the corresponding calcium [2.180(2)$_{av}$ Å and 2.680(1)$_{av}$ Å] analogs.

In conclusion we have shown the facile synthesis of well-defined strontium fluoride **2** and chloride **3** by utilizing strontium amide **1**, and the stability and good solubility of **2** and **3** have provided a chance to study the nature of the M–X bond present in these complexes.

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Notes and references

§ *Crystal data for* **2** *and* **3**. **2**·1.5C$_7$H$_8$: $C_{80.5}H_{118}F_2N_4O_3Sr_2$, M_r = 1403.03, triclinic, space group $P\bar{1}$, a = 12.5946(3), b = 14.3939(4), c = 24.1189(6) Å, α = 75.519(2)°, β = 84.178(2)°, γ = 64.647(2)°, V = 3825.68(17) Å^3, Z = 2, ρ_{calcd} = 1.218 Mg m^{-3}, $F(000)$ = 1494, T = 133(2) K, μ(Mo-Kα) = 1.447 mm^{-1}, 58 191 reflections measured, 15 932 independent (R_{int} = 0.0499). The final refinement converged to R_1 = 0.0440 for $I > 2\sigma(I)$, wR_2 = 0.0922 for all data. **3**·0.5C$_7$H$_8$: $C_{73.50}H_{110}Cl_2N_4O_3Sr_2$, M_r = 1343.80, monoclinic, space group $C2/c$, a = 53.0398(12), b = 12.2780(3), c = 22.2041(5) Å, β = 98.945(2)°, V = 14 284.0(6) Å^3, Z = 8, ρ_{calcd} = 1.250 Mg m^{-3}, $F(000)$ = 5704, T = 133(2) K, μ(Mo-Kα) = 1.616 mm^{-1}, 65 549 reflections measured, 14 872 independent (R_{int} = 0.0953). The final refinement converged to R_1 = 0.0590 for $I > 2\sigma(I)$, wR_2 = 0.0960 for all data.

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7 (*a*) *Synthesis of* **2**: a solution of LSrN(SiMe$_3$)$_2$(thf) **1**[6] (2.213 g, 3.00 mmol) in THF (25 mL) was added to a slurry of Me$_3$SnF (0.548 g, 3.00 mmol) in THF (40 mL) at room temperature and stirred for 15 h. The solvent was removed in vacuum and the residue was dissolved in a mixture of THF–toluene, concentrated and stored for crystallization at −5 °C in a freezer for 2 days. Compound **2** was obtained as colorless crystals. Yield (0.526 g, 0.416 mmol, 27.7%); mp 169–170 °C. ^{1}H NMR (500 MHz, THF-d_8): δ = 6.97–6.86 (m, 12H, *m*-, *p*-Ar-*H*); 4.51 (s, 2H, γ-C*H*), 3.08 (sept, 8H, C*H*(CH$_3$)$_2$), 1.49 (s, 12H, C*H*$_3$), 1.09–1.08 (d, 24H, CH(C*H*$_3$)$_2$), 1.06–1.05 (d, 24H, CH(C*H*$_3$)$_2$). ^{13}C NMR (125.77 MHz,

THF-d_8): δ = 163.99, 149.47, 142.14, 123.73, 123.50, 93.35, 28.34, 25.38, 24.83, 24.73 ppm. ^{19}F NMR (188.3 MHz, THF-d_8): δ = −59. 97 ppm (s, 2F, Sr*F*). MS (70 eV): *m*/*z* (%): 403.2 (100) [L^+ − Me]. Anal. calc. for $C_{70}H_{106}F_2N_4O_3Sr_2$ (1264.85): C, 66.5; H, 8.5; N 4.4. Found: C, 65.6; H, 8.4; N 4.5%; (*b*) *Synthesis of* **3**: a solution of LAlCl(Me) (1.485 g, 3 mmol) in THF (25 mL) was added to a clear solution of LSrN(SiMe$_3$)$_2$(thf) **1**[6] (2.213 g, 3 mmol) in THF (40 mL) at room temperature under stirring and after the completion of addition the stirring was continued for 1 day. All volatiles were removed in vacuum and the residue was dissolved in THF–toluene mixture. The solution was concentrated and stored for crystallization at −5 °C in a freezer. Compound **3** was obtained as pale yellow crystals. Yield: (0.974 g, 0.751 mmol, 49.59%); mp 155–157 °C. ^{1}H NMR (500.13 MHz, C_6D_6): δ = 7.13–7.10 (m, 12 H, *m*-, *p*-Ar-*H*), 4.77 (s, 2H, γ-C*H*), 3.53 (m, 12H, O-C*H*$_2$-CH$_2$), 3.26 (sept, 8H, C*H*(CH$_3$)$_2$), 1.67 (s, 12H, C*H*$_3$), 1.33 (m, 12H, O-CH$_2$-C*H*$_2$), 1.25–1.24 (d, 48H, CH(C*H*$_3$)$_2$). ^{13}C {1H} NMR(125.77 MHz, C_6D_6): δ = 164.33, 147.36, 141.95, 124.02, 123.73, 93.88, 68.72, 28.15, 25.40, 25.37, 24.71 ppm. MS (70 eV): *m*/*z* (%): 403 (100) [L^+ − Me]. Anal. calc. for $C_{70}H_{106}Cl_2N_4O_3Sr_2$, (1297.76): C, 64.8; H, 8.2; N, 4.3. Found: C, 64.3; H, 8.2; N, 4.2%; (*c*) *Isolation of* **4**: after the separation of compound **3** as crystals, the solvent was removed and the residue was dissolved in toluene–*n*-pentane mixture, filtered, dried and washed with a minimum amount of *n*-pentane. Again dried in vacuum to yield compound **4** as a pale yellow solid. ^{1}H NMR (500.131 MHz, C_6D_6): δ = 7.28–7.26, 7.19–7.18, 7.09–7.08 (m, 6 H, *m*-, *p*-Ar-*H*), 5.38 (s, 1H, γ-C*H*), 4.05 (sept, 1H, C*H*(CH$_3$)$_2$), 3.91 (sept, 1H, C*H*(CH$_3$)$_2$), 3.90 (s, 1H, NCC*H*$_2$), 3.84 (m, 2H, O-C*H*$_2$-CH$_2$), 3.77 (m, 2H, O-C*H*$_2$-CH$_2$), 3.33 (sept, 1H, C*H*(CH$_3$)$_2$), 3.21 (sept, 1H, C*H*(CH$_3$)$_2$), 3.18 (s, 1H, NCC*H*$_2$),1.59–1.58 (d, 3H, CH(C*H*$_3$)$_2$), 1.58 (s, 3H, CH$_3$), 1.52–1.50 (d, 3H, CH(CH$_3$)$_2$), 1.44–1.41 (3d (merged together), 9H, CH(C*H*$_3$)$_2$), 1.20 (m, 4H, O-C*H*$_2$-CH$_2$), 1.18–1.16 (d, 3H, CH(C*H*$_3$)$_2$), 1.07–1.06 (d, 3H, CH(C*H*$_3$)$_2$), 1.00–0.99 (d, 3H, CH(C*H*$_3$)$_2$), −0.99 (s, 3H, Al*Me*). ^{13}C {1H} NMR (125.77 MHz, C_6D_6): δ = 155.21, 148.66, 147. 59, 147.01, 145.47, 145.46, 143.14, 143.01, 125.71, 125.51, 124.67, 124.45, 123.74, 123.14, 104.88, 81.30, 72.48, 29.03, 28.55, 27.69, 27.15, 26.53, 26.09, 26.06, 25.75, 25.30, 25.10, 24.65, 24.63, 24.37, 23.34, −15.13 ppm. Anal. calc. for $C_{34}H_{51}AlN_2O$, (530.76): N, 5.3. Found: N, 4.8%.

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