

Synthesis, Molecular Structure, and Reactivity of Organolanthanide Fluoride Complexes, $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{Ln}(\mu\text{-F})]_2$ (Ln = La, Nd, Sm, Gd) and $[(\text{C}_5\text{H}_5)_2\text{Ln}(\mu\text{-F})(\text{THF})]_2$ (Ln = Y, Yb)

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Treatment of Me_3NHF with 1 equiv of $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_3\text{Ln}$ or $(\text{C}_5\text{H}_5)_3\text{Ln}$ in THF gave $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{LnF}]_2$ (Ln = La (**1**), Nd (**2**), Sm (**3**), Gd (**4**)) or $[(\text{C}_5\text{H}_5)_2\text{LnF}(\text{THF})]_2$ (Ln = Y (**5**), Yb (**6**)) in moderate to good yield. All of them were fully characterized by elemental analyses, spectroscopy, and X-ray analyses. Compound **3** reacted with Na, AlCl_3 , $(\text{C}_6\text{H}_5)_3\text{SiOH}$, and 2,6- $\text{Pr}'_2\text{C}_6\text{H}_3\text{OH}$ to form $[(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3]_2\text{Sm}(\text{THF})$, $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{SmCl}]_2$, $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{Sm}(\text{THF})_3$ (**7**), and $[2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{O}]_3\text{Sm}(\text{THF})_3$ (**8**), respectively. The molecular structures of $[\{(\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3\}_2\text{SmCl}]_2$, **7**, and **8** were confirmed by X-ray diffraction study. The **3**/NaH system can convert $\text{C}_6\text{H}_5\text{Br}$ into C_6H_6 in 32% yield.

Introduction

Group 4 organometallic fluoride compounds have been shown to possess some unique properties as compared to the corresponding chlorides in very recent publications.^{1,2} For example, they can be used as versatile building blocks for generating various kinds of clusters¹ and can catalyze the defluorination of perfluorocarbons and the hydrosilylation of imines.² By contrast, the chemistry of organolanthanide fluoride is scarcely known although the corresponding chloride chemistry is extensively studied.³ The reason for this different development may be the lack of general procedures for the preparation of organolanthanide fluoride compounds. The commonly used metathesis methods for the preparation of organolanthanide chloride, bromide, or iodide are *not* applicable to the fluorides due to the extremely poor solubility of lanthanide trifluorides, even in highly polar organic solvents. As a matter of fact, none of organolanthanide fluorides had been prepared from LnF_3 . To date, only a few such fluorides are known,

including structurally characterized examples such as $\text{Cp}^*\text{Yb}(\mu\text{-F})\text{YbCp}^*$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$),⁴ $\text{Cp}^*\text{Yb}_4\text{F}_4$,⁵ $\text{Cp}^*\text{Yb}_5\text{F}_9$,⁶ $\text{Cp}^*\text{YbF}(\text{OEt}_2)$, $\text{Cp}^*\text{YbF}(\text{THF})$,⁶ and $[(\text{Bu}'\text{C}_5\text{H}_4)_2\text{Sm}(\mu\text{-F})]_3$.⁷ All of them were prepared from the corresponding divalent organolanthanide complexes. Since only three elements (Sm, Eu, and Yb) from the lanthanide series can form the stable divalent organometallic complexes,⁸ the above methodology is severely limited. Therefore, it is highly desirable to develop a general method for the preparation of organolanthanide fluorides. On the other hand, the reactivity of organolanthanide fluoride compounds is virtually unexplored, and the similarities and differences between organolanthanide chlorides and the corresponding fluorides are not clear. In view of these problems, a program to explore the organolanthanide fluorides has been initiated in our laboratory. We have recently described the synthesis of $[\text{Cp}''_2\text{Sm}(\mu\text{-F})]_2$ ($\text{Cp}'' = (\text{Me}_3\text{Si})_2\text{C}_5\text{H}_3$) from its trivalent organolanthanide complexes.⁹ We report here the systematic study of the chemistry of organolanthanide fluorides. A number of organolanthanide fluoride compounds have been prepared and structurally characterized. Their reactivities are examined. The similarities and differences among organolanthanide halides are also discussed.

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Experimental Section

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $\text{Cp}^*\text{Ln}^{10}$ and Cp_3Ln ($\text{Cp} = \text{C}_5\text{H}_5$)¹¹ were prepared according to the literature methods. Me_3NHF was prepared from the equimolar reaction of Me_3N with HF in aqueous solution, followed by recrystallization from acetone, and then dried at 50 °C under vacuum.⁹ All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from a KBr pellet prepared inside the glovebox on a Nicolet Magna 550 Fourier transform spectrometer. MS spectra were recorded on a Bruker APEX FTMS spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker 300 MHz DPX spectrometer at 300.13 and 75.47 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of deuterated solvent or external TMS (0.00 ppm) for proton and carbon chemical shifts. Complexometric metal analyses were conducted by titration with EDTA.

Preparation of $[\text{Cp}^*_2\text{LaF}]_2$ (1). To a mixture of Cp^*_3La (1.545 g, 2.00 mmol) and Me_3NHF (0.159 g, 2.00 mmol) was added 60 mL of THF at room temperature. The suspension was then stirred for 1 day. After removal of THF and remaining Me_3N under vacuum, the solid was extracted with hot hexane (3×20 mL). The hexane solution was then concentrated to give a white solid, which was recrystallized from hot hexane to afford **1** as colorless crystals (0.49 g, 42%). ¹H NMR (CD_2Cl_2): δ 6.87 (s, 1H), 6.76 (s, 2H), 0.41 (s, 18H). ¹H NMR ($\text{CD}_2\text{Cl}_2/\text{THF}$): δ 6.86 (s, 1H), 6.75 (s, 2H), 0.41 (s, 18H), 3.69 (m, 4H), 1.82 (m, 4H). ¹³C NMR (CD_2Cl_2): δ 130.9, 129.2, 125.2, 0.07. MS (EI, 70 eV): 944 ($[\text{M-Cp}^*]^+$, 49), 577 ($1/2\text{M}^+$, 8), 557 ($[\text{Cp}^*_2\text{La}]^+$, 100), 367 ($[\text{Cp}^*\text{LaF}]^+$, 27). IR (KBr, cm^{-1}): ν 3075 (w), 3044 (w), 2955 (s), 2897 (m), 1250 (s), 1079 (s), 921 (m), 828 (vs), 752 (s). Mp: 217–220 °C. Anal. Calcd for $\text{C}_{44}\text{H}_{84}\text{Si}_8\text{La}_2\text{F}_2$: C, 45.81; H, 7.34; La, 18.10. Found: C, 45.67; H, 7.22; La, 18.30.

Preparation of $[\text{Cp}^*_2\text{NdF}]_2$ (2). To a mixture of Cp^*_3Nd (0.39 g, 0.51 mmol) and Me_3NHF (0.040 g, 0.51 mmol) was added 20 mL of THF at room temperature. The mixture was then stirred at room temperature for 4 h, followed by procedures similar to those used in the synthesis of **1**, affording **2** as a blue solid (0.26 g, 89%). Recrystallization from hot hexane gave X-ray quality blue crystals. ¹H NMR (benzene-*d*₆): δ 29.48 (br, 1H), 15.11 (br, 2H), –8.65 (s, 18H). MS (EI, 70 eV): 949 ($[\text{M-Cp}^*]^+$, 2), 740 ($[\text{M-2Cp}^*]^+$, 2), 560 ($[\text{Cp}^*_2\text{Nd}]^+$, 2), 370 ($[\text{Cp}^*\text{NdF}]^+$, 5). IR (KBr, cm^{-1}): ν 3079 (w), 3054 (w), 2955 (s), 2897 (m), 1249 (m), 1078 (s), 921 (m), 823 (vs), 753 (s). Mp: 269–270 °C. Anal. Calcd for $\text{C}_{44}\text{H}_{84}\text{Si}_8\text{Nd}_2\text{F}_2$: C, 45.39; H, 7.27. Found: C, 44.78; H, 7.35.

Preparation of $[\text{Cp}^*_2\text{SmF}]_2$ (3). To a mixture of Cp^*_3Sm (2.00 g, 2.57 mmol) and Me_3NHF (0.204 g, 2.58 mmol) was added 100 mL of THF at room temperature. The mixture was then stirred at room temperature for 1 day, followed by procedures similar to those used in the synthesis of **1**, affording **3** as yellow crystals (1.10 g, 73%). ¹H NMR (benzene-*d*₆): δ 21.64 (s, 1H), 17.10 (s, 2H), –2.20 (s, 18H). MS (EI, 70 eV): 969 ($[\text{M-Cp}^*]^+$, 4), 589 ($1/2\text{M}^+$, 2), 570 ($[\text{Cp}^*_2\text{Sm}]^+$, 100), 361 ($[\text{Cp}^*\text{Sm}]^+$, 18). IR (KBr, cm^{-1}): ν 3082 (w), 2955 (s), 2898 (m), 1437 (m), 1318 (m), 1247 (s), 1077 (s), 921 (s), 832 (vs), 782 (s). Mp: 218–220 °C. Anal. Calcd for $\text{C}_{44}\text{H}_{84}\text{Si}_8\text{Sm}_2\text{F}_2$: C, 44.91; H, 7.20; Sm, 25.56. Found: C, 44.45; H, 7.19, Sm, 25.33.

Preparation of $[\text{Cp}^*_2\text{GdF}]_2$ (4). To a mixture of Cp^*_3Gd (0.237 g, 0.30 mmol) and Me_3NHF (0.024 g, 0.30 mmol) was added 20 mL of THF at room temperature. The mixture was then stirred at room temperature for 4 h, followed by procedures similar to those used in the synthesis of **1**, affording **4** as a white solid (0.13 g, 73%). Recrystallization from hot hexane gave X-ray quality colorless crystals. ¹H NMR (benzene-*d*₆): δ 6.65 (br, 2H), 1.01 (br, 1H), –0.04 (s, 18H). MS (EI, 70 eV): 981 ($[\text{M-Cp}^*]^+$, 36), 576 ($[\text{Cp}^*_2\text{Gd}]^+$, 56), 386 ($[\text{Cp}^*\text{GdF}]^+$, 9). IR (KBr, cm^{-1}): ν 3084 (w), 3063 (w), 3042 (w), 2956 (s), 2897 (m), 1248 (s), 1078 (s), 923 (m), 831 (vs), 752 (s). Mp: 327–330 °C. Anal. Calcd for $\text{C}_{44}\text{H}_{84}\text{Si}_8\text{Gd}_2\text{F}_2$: C, 44.39; H, 7.11. Found: C, 44.32; H, 7.25.

Attempt to Prepare $\text{Cp}^*_3\text{SmF}_2(\text{THF})_x$. To a mixture of Cp^*_3Sm (0.56 g, 0.71 mmol) and Me_3NHF (0.11 g, 1.40 mmol) was added 30 mL of THF at –30 °C with stirring. The suspension was allowed to warm to room temperature and stirred for 2 days. The white precipitate was filtered off (50 mg) and identified as SmF_3 by XPS. The pale yellow solution was then concentrated, and hexane vapor diffusion afforded a pale yellow solid. This solid was first extracted with hexane (3×10 mL) and then with THF (3×10 mL). The residue was identified as SmF_3 (80 mg). Concentration of the hexane solution gave a yellow solid (70 mg), identified as **3** by MS and ¹H NMR. Concentration of the THF solution and hexane vapor diffusion yielded a pale yellow solid again which is a mixture of SmF_3 , **3**, and other unidentified compounds.

Preparation of $[\text{Cp}_2\text{YF}(\text{THF})]_2$ (5). To a mixture of $\text{Cp}_3\text{Y}(\text{THF})$ (0.28 g, 0.79 mmol) and Me_3NHF (0.063 g, 0.79 mmol) was added 30 mL of THF at room temperature. The suspension was then stirred at room temperature for 4 days, at which time it became a homogeneous solution. Removal of half of the solvent and cooling to –30 °C gave **5** as colorless crystals after several days. The second crop of crystals was collected after further concentration of the mother liquor. The total yield of the colorless crystals was 0.17 g (69% yield). ¹H NMR (pyridine-*d*₅): δ 6.09 (s, 10H), 3.63 (t, 4H), 1.59 (m, 4H). ¹³C NMR (pyridine-*d*₅): δ 132.0, 67.6, 25.9. The MS of **5** showed the presence of THF in the early scans (<120 °C) and above 280 °C unsolvated ions with a maximum *m/z* of 649 ($\text{Cp}_5\text{Y}_3\text{F}_3^+$, 62), along with a series of fragments containing one, two, and three yttrium atoms, suggesting the formation of trimer $(\text{Cp}_2\text{YF})_3$ in the gas phase. MS (EI, 70 eV): 649 ($[(\text{Cp}_2\text{YF})_3 - \text{Cp}]^+$, 62), 476 ($[\text{M-2THF}]^+$, 5), 411 ($[\text{M-2THF} - \text{Cp}]^+$, 20), 219 ($[\text{Cp}_2\text{Y}]^+$, 100), 173 ($[\text{CpYF}]^+$, 10). IR (KBr, cm^{-1}): ν 3090 (m), 2965 (s), 2894 (s), 1639 (m), 1459 (m), 1261 (m), 1015 (s), 872 (m), 767 (vs). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{F}_2\text{OY}_2$ (**5** – THF): C, 52.57; H, 5.15. Found: C, 52.27; H, 5.91. The coordinated THF molecules can be removed under vacuum at 30 °C overnight. ¹H NMR (pyridine-*d*₅): δ 6.05 (s, 10H). The MS spectrum of this unsolvated compound is the same as that of **5** but with no THF fragments.

Preparation of $[\text{Cp}_2\text{YbF}(\text{THF})]_2$ (6). To a mixture of $\text{Cp}_3\text{Yb}(\text{THF})$ (0.19 g, 0.43 mmol) and Me_3NHF (0.034 g, 0.43 mmol) was added 30 mL of THF at room temperature. The suspension was then stirred at room temperature for several days, at which time it became a homogeneous solution. Filtration and slow evaporation of the clear THF solution gave **6** as yellow crystals (0.085 g, 53%). ¹H NMR (pyridine-*d*₅): δ 6.56 (s, 10H), 3.60 (br, 4H), 1.57 (br, 4H). MS (EI, 70 eV): 72 (THF^+ , 27), 66 (C_5H_6^+ , 100), 65 (C_5H_5^+ , 52); no fragments containing ytterbium atom were observed. IR (KBr, cm^{-1}): ν 3092 (m), 2977 (s), 2894 (s), 1651 (m), 1458 (m), 1013 (s), 872 (m), 776 (vs). Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{F}_2\text{Yb}_2$ (**6** – 2THF): C, 37.28; H, 3.13. Found: C, 36.72; H, 3.87.

Attempt To Prepare $[\text{Cp}_2\text{SmF}(\text{THF})]_2$. To a mixture of $\text{Cp}_3\text{Sm}(\text{THF})$ (0.35 g, 0.83 mmol) and Me_3NHF (0.065 g, 0.83 mmol) was added 30 mL of THF at room temperature. The suspension was then stirred for several days, at which time it became a homogeneous solution. Filtration and slow evaporation of the clear THF solution at room temperature gave a

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mixture of SmF_3 (25 mg) and $\text{Cp}_3\text{Sm}(\text{THF})$ (0.15 g). They can be separated by extracting with hot THF and identified by the spectroscopic analyses.

Under similar reaction conditions, reaction of $\text{Cp}_3\text{Er}(\text{THF})$ with 1 equiv of Me_3NHF in THF also resulted in the isolation of ErF_3 and $\text{Cp}_3\text{Er}(\text{THF})$. No pure $[\text{Cp}_2\text{ErF}(\text{THF})]_2$ was isolated.

Preparation of $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{Sm}(\text{THF})_3$ (7). To a THF solution (15 mL) of **3** (0.19 g, 0.16 mmol) was slowly added the solution of $(\text{C}_6\text{H}_5)_3\text{SiOH}$ (0.087 g, 0.32 mmol) in 5 mL of THF at 0 °C. The mixture was then stirred at room temperature for 2 days. The solution turned from yellow to almost colorless during the course of the reaction. Concentration of the colorless solution and cooling to -30 °C gave **7** as colorless crystals (0.059 g, 46% based on $(\text{C}_6\text{H}_5)_3\text{SiOH}$). ^1H NMR (pyridine- d_5): δ 8.26 (br, 6H, ortho H), 7.96 (br, 3H, para H), 7.34 (br, 6H, meta H), 3.63 (m, 4H), 1.59 (m, 4H). ^{13}C NMR (pyridine- d_5): δ 142.9, 136.5, 128.8, 127.9 (C_6H_5), 67.9, 25.8 (THF). IR (KBr, cm^{-1}): ν 3134 (w), 3061 (s), 3043 (s), 2991 (s, br), 2880 (s), 1958 (w), 1891 (w), 1830 (w), 1777 (w), 1426 (s), 1109 (s), 1032 (s), 970 (s), 704 (s), 519 (s). Anal. Calcd for $\text{C}_{66}\text{H}_{69}\text{O}_6\text{Si}_3\text{Sm}$: C, 66.45; H, 5.83. Found: C, 65.30; H, 5.91.

Preparation of $(2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{O})_3\text{Sm}(\text{THF})_3$ (8). A solution of $2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{OH}$ (0.055 g, 0.30 mmol) in 5 mL of THF was slowly added to a THF solution (30 mL) of **3** (0.18 g, 0.15 mmol) at 0 °C. The mixture was then stirred at room temperature for 2 days. The solution turned from yellow to almost colorless during the course of the reaction. After removal of the THF, crystallization of the white solid from the mixture of THF/hexane at -30 °C gave **8** as colorless crystals (0.046 g, 50% based on $2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{OH}$). ^1H NMR (pyridine- d_5): δ 7.34 (d, $J = 8$ Hz, 2H, meta H), 7.23 (t, $J = 8$ Hz, 1H, para H), 3.75 (septet, $J = 7$ Hz, 2H, CHMe_2), 3.63 (br, 4H), 1.59 (br, 4H), 1.30 (d, $J = 7$ Hz, 12H, CHMe_2). ^{13}C NMR (pyridine- d_5): δ 160.5, 138.7, 131.0, 117.7 (C_6H_3), 69.3, 27.3 (THF), 29.1, 25.6 (Pr'). IR (KBr, cm^{-1}): ν 3057 (w), 3020 (w), 2959 (s), 2886 (m), 1587 (w), 1429 (s), 1329 (s), 1265 (s), 1207 (m), 859 (s), 753 (m). Anal. Calcd for $\text{C}_{48}\text{H}_{75}\text{O}_6\text{Sm}$: C, 64.17; H, 8.42. Found: C, 63.50; H, 8.10.

Reaction of **3 with AlCl_3 .** To a mixture of **3** (0.13 g, 0.11 mmol) and AlCl_3 (0.030 g, 0.22 mmol) was added 15 mL of toluene at room temperature with stirring, and the mixture was stirred overnight. The solution turned from yellow to orange-yellow during the course of the reaction. The suspension was filtered, and the clear filtrate was then concentrated to give a orange-yellow solid which was recrystallized from toluene to yield orange-yellow crystals (0.12 g, 86%), identified as $[\text{Cp}''_2\text{SmCl}]_2$ by MS spectroscopy,^{12a-c} and X-ray analysis. Anal (complexometric). Calcd for $\text{C}_{44}\text{H}_{84}\text{Cl}_2\text{Si}_8\text{Sm}_2$: Sm, 24.86. Found, 24.51.

Reaction of **3 with Na.** A mixture of **3** (0.13 g, 0.11 mmol), Na (0.049 g, 2.13 mmol), and 15 mL of THF was stirred at room temperature for 1 week. The solution turned gradually from yellow to dark red during this time. Removal of the white precipitate (NaF) and concentration of the clear filtrate gave a dark red solid which was recrystallized from hot hexane as a dark green solid (0.078 g, 90%), identified as $\text{Cp}''_2\text{Sm}(\text{THF})$ by ^1H NMR and MS spectroscopy.¹³

Reaction of **3 with $2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{ONa}$.** To a solution of **3** (0.23 g, 0.20 mmol) in 20 mL of THF was added a THF solution (8 mL) of $2,6\text{-Pr}'_2\text{C}_6\text{H}_3\text{ONa}$ (0.078 g, 0.39 mmol) at 0 °C with stirring. The mixture was stirred overnight, resulting in a pale yellow solution. Removal of the solvent and extraction of the

residue with *n*-hexane gave a light yellow solution and a white solid (42 mg). The latter was identified as $\text{Cp}''\text{Na}$ by ^1H NMR^{12d} ($(\text{CDCl}_3/\text{H}^+)$: δ 6.68 (m, 2H), 6.50 (m, 2H), 0.13 (s, 3H), -0.05 (s, 15H)). The light yellow solution was concentrated and cooled to -30 °C to yield colorless crystals (~20 mg), identified as **8** by ^1H and ^{13}C NMR spectroscopy. Further concentration of the mother liquor gave yellow solid (~20 mg), identified as **3** by ^1H , ^{13}C NMR and MS spectroscopy.

Reaction of **3 with $\text{Cp}''\text{Na}$.** To a THF solution (10 mL) of **3** (0.13 g, 0.11 mmol) was added a THF solution (5 mL) of $\text{Cp}''\text{Na}$ (0.18 g, 0.78 mmol) at room temperature with stirring, and the mixture was stirred for 2 days. Removal of the THF and extraction of the residue with hexane gave **3** (0.12 g). The residue (0.15 g) was identified as $\text{Cp}''\text{Na}$. No $\text{Cp}''_3\text{Sm}$ was isolated from this reaction. Refluxing in THF or toluene did not yield $\text{Cp}''_3\text{Sm}$ either.

Reaction of **3/NaH with $\text{C}_6\text{H}_5\text{Br}$.** A mixture of **3** (14.2 mg, 0.012 mmol) and NaH (14.0 mg, 0.56 mmol) in 2 mL of THF was stirred at room temperature to give a purple suspension in 5 min. To this solution was added $\text{C}_6\text{H}_5\text{Br}$ (25.0 μL , 0.24 mmol) by a microsyringe. The purple color disappeared immediately, and the reaction mixture was refluxed. Samples were then taken from this mixture after refluxing for 8, 24, and 48 h, respectively, and were analyzed by GC/MS spectroscopy, showing that $\text{C}_6\text{H}_5\text{Br}$ was converted into C_6H_6 in 13, 30, and 32% yield, respectively.

X-ray Structure Determination of **1, **2**, **4-8**, and $[\text{Cp}''_2\text{SmCl}]_2$.** All single crystals were sealed under N_2 in a thin-walled glass capillary. For those solvated compounds, it is essential to put a little drop of mother liquor inside the glass capillary. Data were collected at 294 K either on a MSC/Rigaku RAXIS-IIC imaging plate using Mo $\text{K}\alpha$ radiation (0.710 73 Å) from a Rigaku rotating-anode X-ray generator operating at 50 kV and 90 mA or on a Rigaku AFC7R diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation and a 12 kW rotating anode generator. Absorption was corrected by either correlation of symmetry-equivalent reflections using the ABSCOR program¹⁴ or an empirical absorption correction based on azimuthal scans of several reflections.¹⁵ All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least squares, on F^2 using the Siemens SHELXTL V 5.03 program package (PC version)^{16a} or the teXsan program package,¹⁵ and on F for **1** and **2** using the Siemens SHELXTL V 4.1 program package (PC version).^{16b} All hydrogen atoms were geometrically fixed using the riding model. Crystal data and details of data collection and structure refinement are given in Tables 1 and 2. Further details are included with the Supporting Information.

Results and Discussion

Syntheses. Synthesis of $[\text{Cp}''_2\text{LnF}]_2$. To prepare compounds containing a Ln-F bond, it is highly desirable to have a suitable fluorinating reagent. We recently found that Me_3NHF is a very useful fluorinating reagent for organometallic compounds.⁹ It can be conveniently prepared from the reaction of Me_3N with HF in aqueous solution, followed by recrystallization from acetone. It can be viewed as a substitute for anhydrous HF to some extent. Treatment of $\text{Cp}''_3\text{Ln}$ with 1 equiv of Me_3NHF in THF at room temperature gave organolanthanide

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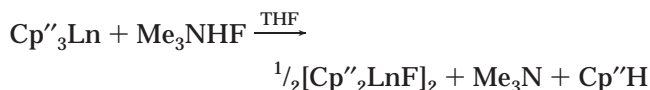
Table 1. Crystal Data and Summary of Data Collection and Refinement for 1, 2, 4, 5, and 6

	1	2	4	5	6
formula	C ₄₄ H ₈₄ F ₂ La ₂ Si ₈	C ₄₄ H ₈₄ F ₂ Nd ₂ Si ₈	C ₄₄ H ₈₄ F ₂ Gd ₂ Si ₈	C ₂₈ H ₃₆ F ₂ Y ₂ O ₂	C ₂₈ H ₃₆ F ₂ Yb ₂ O ₂
crystal size (mm)	0.30 × 0.32 × 0.40	0.08 × 0.25 × 0.42	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30
fw	1153.7	1164.3	1190.3	620.4	788.7
crystal class	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	<i>P</i> (-1)	<i>P</i> (-1)	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	11.598(2)	11.613(1)	12.167(4)	13.606(2)	7.939(7)
<i>b</i> , Å	12.082(2)	12.048(1)	15.907(4)	9.879(4)	20.396(4)
<i>c</i> , Å	13.000(2)	12.930(1)	15.574(4)	20.423(5)	8.589(4)
α, deg	62.88(1)	63.28(1)			
β, deg	73.69(1)	73.56(1)	99.72(2)	100.83(2)	104.34(5)
γ, deg	88.63(1)	89.34(1)			
<i>V</i> , Å ³	1544.5(8)	1535.7(8)	2970(1)	2696(1)	1347(1)
<i>Z</i>	1	1	2	4	2
<i>D</i> _{calcd} , Mg/m ³	1.240	1.259	1.330	1.528	1.944
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer	Rigaku RAXIS IIC	Rigaku RAXIS IIC	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R
2θ range, deg	3.0–55.0	3.0–55.0	3.0–50.0	3.0–50.0	3.0–50.0
μ, mm ⁻¹	1.550	1.859	2.412	4.324	6.933
<i>F</i> (000)	592	598	1212	1264	756
<i>T</i> , K	294	294	293	293	293
no. of indep reflns	5366	5423	5139	2516	2462
no. of obsd reflns (<i>I</i> > 3σ(<i>I</i>))	3161	5100	3283	1581	1605
no. of params refnd	245	364	253	154	155
goodness of fit	2.30	2.49	1.39	2.08	1.86
<i>R</i> _F	0.079	0.039	0.039	0.058	0.046
<i>R</i> _w	0.126	0.045	0.045	0.066	0.053
Δρ _{max} , Δρ _{min} , e/Å ³	1.31, -0.90	0.58, -1.05	1.07, -0.86	0.94, -0.80	0.78, -2.71

Table 2. Crystal Data and Summary of Data Collection and Refinement for 7, 8, and [Cp''₂SmCl]₂

	7	8	[Cp'' ₂ SmCl] ₂
formula	C ₆₆ H ₆₉ O ₆ Si ₃ Sm	C ₄₈ H ₇₅ O ₆ Sm	C ₄₄ H ₈₄ Cl ₂ Si ₈ Sm ₂
crystal size (mm)	0.10 × 0.35 × 0.40	0.20 × 0.22 × 0.34	0.20 × 0.20 × 0.30
fw	1192.8	898.4	1209.5
crystal class	monoclinic	trigonal	triclinic
space group	<i>P</i> 2 ₁	<i>P</i> (-3) <i>c</i> 1	<i>P</i> (-1)
<i>a</i> , Å	14.661(1)	18.083(1)	11.828(5)
<i>b</i> , Å	16.699(1)	18.083(1)	13.237(7)
<i>c</i> , Å	15.123(1)	22.593(1)	10.549(5)
α, deg	90.00	90.00	99.43(4)
β, deg	115.79(1)	90.00	95.94(4)
γ, deg	90.00	120.00	109.25(3)
<i>V</i> , Å ³	3333.7(3)	6398.0(4)	1515(1)
<i>Z</i>	2	4	1
<i>D</i> _{calcd} , Mg/m ³	1.188	0.933	1.325
radiation (λ), Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
diffractometer	Rigaku RAXIS IIC	Rigaku RAXIS IIC	Rigaku AFC7R
2θ range, deg	3.0–50.0	3.0–50.0	3.0–50.0
μ, mm ⁻¹	0.980	0.950	2.194
<i>F</i> (000)	1234	1892	618
<i>T</i> , K	294	294	293
no. of indep reflns	10 116	3486	4359
no. of obsd reflns (<i>I</i> > <i>X</i> σ(<i>I</i>))	10 046 (<i>X</i> = 2)	3421 (<i>X</i> = 2)	3300 (<i>X</i> = 3)
no. of params refnd	686	167	253
goodness of fit	1.015	0.902	1.58
<i>R</i> _F	0.058	0.090	0.041
<i>R</i> _w	0.065	0.119	0.050
Δρ _{max} , Δρ _{min} , e/Å ³	0.71, -0.68	1.27, -1.27	0.90, -1.10

fluoride compounds of the general formula [Cp''₂LnF]₂ in good yield (eq 1). These compounds were fully



characterized by elemental analyses, MS, IR, and NMR spectroscopy as well as X-ray analyses. They are soluble in most organic solvents, sensitive to moisture, but thermally stable.

MS spectroscopic analyses indicate the dimeric structures of these fluoride compounds in the gas phase. This

type of structure may be retained in CD₂Cl₂ solution based on the analysis of ¹H NMR spectra of **1**.²⁵ The doubly bridging La₂F₂ unit does not dissociate into the terminal La–F in the CD₂Cl₂/THF mixture, probably due to the strong interaction between La and F and/or

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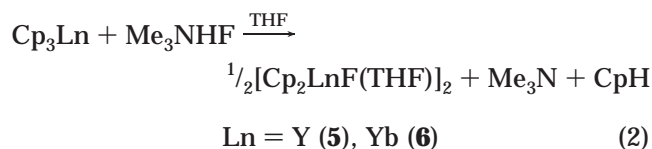
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steric reasons. Single-crystal X-ray analyses confirm the dimeric structures of these compounds in the solid state as well.

Attempts to prepare organolanthanide difluoride of the type $\text{Cp}''\text{LnF}_2(\text{THF})_x$ by the reaction of $\text{Cp}''_3\text{Ln}$ with 2 equiv of Me_3NHF in THF failed. The reason for this is probably that $\text{Cp}''\text{LnF}_2$ disproportionates to $[\text{Cp}''_2\text{LnF}]_2$ and LnF_3 . In one case, that of samarium, small amounts of $[\text{Cp}''_2\text{SmF}]_2$ and SmF_3 were isolated during crystallization. By contrast, the corresponding organolanthanide dichloride compounds are well known.³

Synthesis of $[\text{Cp}_2\text{LnF}(\text{THF})]_2$. To investigate the effect of substituents on the Cp ring on the formation and molecular structure of organolanthanide fluoride compounds, and to explore the generality of the methodology, compounds of the type $[\text{Cp}_2\text{LnF}(\text{THF})]_2$ were prepared as shown in eq 2. These two compounds were



fully characterized by elemental analyses and various spectroscopic and X-ray analyses. They are soluble in polar organic solvents such as THF and DME, slightly soluble in aromatic solvents, but insoluble in nonpolar organic solvents such as hexane. The solvated THF molecules in **5** can be removed under vacuum at 30 °C overnight, generating a solvent-free organoyttrium fluoride compound. Its MS spectrum shows the presence of unsolvated ions with a maximum m/z of 649 ($[(\text{Cp}_2\text{YF})_3 - \text{Cp}]^+$), along with a series of fragments containing one, two, or three yttrium atoms, a fragmentation pattern that is similar to those observed in the MS spectra of $[(\text{C}_5\text{H}_4\text{Bu}^t)_2\text{SmF}]_3$ ⁷ and $[\text{Cp}_2\text{ScF}]_3$,¹⁷ indicating that this unsolvated organoyttrium fluoride may have a trimeric structure similar to those of $[(\text{C}_5\text{H}_4\text{Bu}^t)_2\text{SmF}]_3$ ⁷ and $[\text{Cp}_2\text{ScF}]_3$.¹⁷ For those lanthanide metals larger than yttrium, no pure fluoride compounds were isolated, probably due to the disproportionation of $[\text{Cp}_2\text{LnF}(\text{THF})]_2$. For instance, treatment of Cp_3Sm or Cp_3Er with 1 equiv of Me_3NHF in THF at room tempera-

ture resulted in the isolation of SmF_3 and Cp_3Sm , or ErF_3 and Cp_3Er , respectively. Like the Cp'' case, attempts to prepare compounds of the type $[\text{Cp}\text{LnF}_2(\text{THF})_x]$ failed. These results clearly show that disproportionation is important, and this is probably due to the greater stability of LnF_3 relative to LnCl_3 . The sterically bulky ligands play a critical role in stabilizing the organolanthanide fluoride compounds.

Reactivity. The chemical reactions of organolanthanide fluoride compounds are largely unexplored. Since the fluorine atom has the highest electronegativity and very small size, these features have resulted in some unique properties of fluoride compounds.^{1,2,18} We have chosen to study the reactions of $[\text{Cp}''_2\text{SmF}]_2$ (**3**) with various reagents.

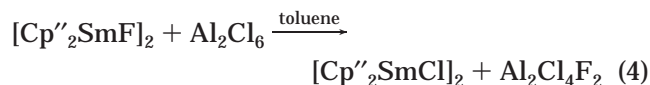
Like other $\text{Sm}(\text{III})$ compounds,³ **3** can be reduced by sodium to $\text{Cp}''_2\text{Sm}^{\text{II}}(\text{THF})$ in THF at room temperature in high yield (eq 3). Unlike group 4 organometallic



fluoride compounds,^{1a,b,d} however, no NaF-containing organolanthanide cluster was isolated.

Treatment of **3** with an excess amount of $\text{Cp}''\text{Na}$ in THF or toluene at room temperature or under reflux for 3 days gave unreacted **3** and $\text{Cp}''\text{Na}$ in >90% yield, respectively. No $\text{Cp}''_3\text{Sm}$ was isolated. This reactivity pattern differs from that of $[\text{Cp}''_2\text{SmCl}]_2$ with $\text{Cp}''\text{Na}$, since this reaction afforded $\text{Cp}''_3\text{Sm}$ in 75% isolated yield.¹⁰

Reaction of **3** with 1 equiv of anhydrous AlCl_3 in dry toluene gave $[\text{Cp}''_2\text{SmCl}]_2$ in 86% yield (eq 4). The



bimetallic compound $\text{Cp}''_2\text{Sm}(\mu\text{-F})(\mu\text{-Cl})\text{AlCl}_2$ was not isolated, but it might serve as an intermediate.^{1e} The driving force for the reaction shown in eq 4 may lie in the higher fluorophilicity of Al.¹⁹ Such high fluorophilicity was also reflected in the Me-F exchange reaction between Me_3Al and $\text{Cp}''\text{ZrF}_3$.^{1c,e} However, **3** does not react with $\text{B}(\text{C}_6\text{F}_5)_3$, which is one of the strongest Lewis acid known, although the B-F bond strength is very high (147 kcal mol⁻¹).¹⁹ These results indicate that bond strengths are not the sole factor in the above reactions; steric factors also play an important role, at least with respect to the $\text{B}(\text{C}_6\text{F}_5)_3$ reaction.

Treatment of **3** with 1 equiv of $(\text{C}_6\text{H}_5)_3\text{SiOH}$ or 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3\text{OH}$ in THF at room temperature gave an unexpected product, $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{Sm}(\text{THF})_3$ (**7**, Figure 3), or $(2,6\text{-Pr}^i_2\text{C}_6\text{H}_3\text{O})_3\text{Sm}(\text{THF})_3$ (**8**, Figure 4), respectively. These alkoxides or silyl oxides are usually prepared by metathesis or acid-base reactions via employing slightly excess amounts of RO^- , R_3SiO^- or ROH , R_3SiOH .²⁰ It has been known that the reaction of Cp_3Ln with ROH yielded $\text{Cp}_2\text{Ln}(\text{OR})$ or $\text{CpLn}(\text{OR})_2$, depending on the molar ratio of the reactants.²¹ Such stepwise protonolysis is a useful method for the preparation of mono- or dialkoxylorganolanthanide compounds. Thus, it may be suggested that, in the above reactions, $(\text{C}_6\text{H}_5)_3\text{SiOH}$ or 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3\text{OH}$ first protonates one Cp'' ligand rather than the fluoro group to generate the intermediate, $[\text{Cp}''\text{SmF}(\text{OR})(\text{THF})_x]$, which

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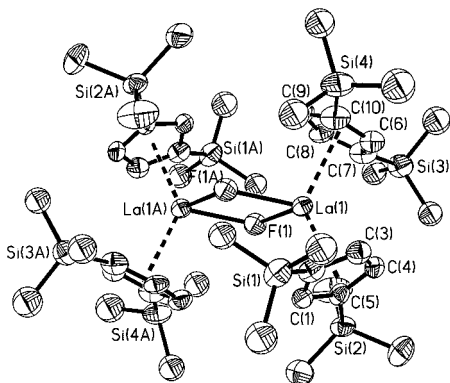


Figure 1. Molecular structure of $[\text{Cp}^*_2\text{LaF}]_2$ (**1**) (thermal ellipsoids drawn at the 35% probability level). All hydrogen atoms are omitted for clarity.

is kinetically unstable and undergoes ligand redistribution to produce the thermodynamically more stable compound **7** or **8**.

Reaction of **3** with 1 equiv of 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3\text{ONa}$ in THF does not give the expected compound $\text{Cp}^*_2\text{Sm}[\text{OC}_6\text{H}_3\text{Pr}^i_2\text{-2,6}]$; instead, small amounts of **8**, Cp^*_2Na , and **3** were isolated from the reaction mixture. This result implies that 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3\text{O}^-$ replaces one Cp^* ligand rather than F^- during the reaction to form an intermediate, $[\text{Cp}^*_2\text{SmF}(\text{OR})(\text{THF})_x]$, which undergoes ligand redistribution, yielding **8**. Again, the very strong $\text{Sm}-\text{F}$ bond dominates, in contrast to the other halides. Thus, $(\text{ArO})_2\text{SmI}(\text{THF})_2$ and $[(\text{ArO})_2\text{SmCl}(\text{THF})]_2$ are isolable compounds.²²

It has been reported that $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]\text{LnCl}$ can catalyze the dehalogenation of organic bromide or organic iodide compounds in the presence of NaH .²³ Under similar reaction conditions, the **3**/ NaH system can convert $\text{C}_6\text{H}_5\text{Br}$ into C_6H_6 in 13, 30, and 32% yield after 8, 24, and 48 h, respectively. This reaction is very slow and is not catalytic, which suggests that no organosamarium hydride was produced in the **3**/ NaH system; otherwise, a much faster and catalytic reaction should be observed. Unlike the $[\text{O}(\text{CH}_2\text{CH}_2\text{C}_5\text{H}_4)_2]\text{LnCl}/\text{NaH}$ system,²³ **3**/ NaH does not show any activity toward 1-hexene. These results indicate that the $\text{Ln}-\text{F}$ bond is probably not substituted by NaH under the above reaction conditions, a result which differs from the $\text{Ln}-\text{Cl}/\text{Br}$ bonds.

Unlike Cp_2TiCl_2 ^{2b} or $\text{Cp}^*_2\text{SmCH}(\text{SiMe}_3)_2$,²⁴ **3** and $(\text{C}_6\text{H}_5)_3\text{SiH}_3$ do not react. On the other hand, the reaction of **3** with MeLi or $(\text{C}_6\text{H}_5\text{CH}_2)\text{MgCl}$ gave a mixture of products on the basis of ^1H NMR analyses, and no pure products were isolated.

Structures. Crystal Structure of $[\text{Cp}^*_2\text{LnF}]_2$ ($\text{Ln} = \text{La}$ (1**), Nd (**2**), and Gd (**4**)).** The solid-state structures of **1**, **2**, **3**,⁹ and **4** as derived from the single-crystal X-ray diffraction studies reveal that they are all centrosymmetric fluoride-bridging dimer with pseudotetrahedral geometry around the central metal, typical of the structures of $[\text{Cp}_2\text{LnX}]_2$ dimeric organolanthanide complexes.³ Since they are isostructural, only the representative structure of **1** is shown in Figure 1. Table 3 lists the selected interatomic distances and angles. The similarity of these structures is also indicated by examining the compilation of values of the four angles (ring centroid)–metal–(ring centroid), (ring centroid)–metal–fluoride, (ring centroid)–metal–fluoride (A), fluoride–metal–fluoride (A). It is noteworthy

that bis[1,3-bis(trimethylsilyl)cyclopentadienyl]lanthanide fluoride, chloride,^{12,25} and bromide²⁶ all have similar dimeric structures.

Comparing the mean $\text{Ln}-\text{C}$ (ring) distances (Table 4), we find that the decreases of the above values on going from **1** to **6** are those expected from the decrease in the eight-coordinate (**1–4**) or nine-coordinate (**5**, **6**) metals' ionic radii,²⁷ suggesting ionic interactions between metal and C_5 ring.^{12b,28} For instance, a change of neodymium for lanthanum makes the average metal–C distances shorter by 0.051 Å, which is identical to the 0.051-Å difference in the Shannon's ionic radii of Nd^{3+} (1.109 Å) and La^{3+} (1.160 Å).²⁷ The variations in the metal–fluoride distances are, however, not as predictable. The $\text{La}-\text{F}$ distance differs from the $\text{Nd}-\text{F}$ distance by 0.001 Å, which is significantly smaller than the 0.051 Å difference in the metals' ionic radii. The $\text{Nd}-\text{F}$ distance is 0.034 Å longer than that of $\text{Sm}-\text{F}$,⁹ which is very close to the 0.030 Å difference between their ionic radii. The difference between $\text{Sm}-\text{F}$ and $\text{Gd}-\text{F}$ is 0.043 Å, which is larger than the 0.026 Å difference between their ionic radii. These results indicate that the $\text{Ln}-\text{F}$ distances are not as predictable as the $\text{Ln}-\text{C}$ (Cp ring) distances by such an ionic model. Except for Sm , Eu , and Yb ,³ no other organolanthanide fluoride compounds are mentioned in the literature. Therefore, no other data on $\text{Ln}-\text{F}$ bond distances are available for further comparison.

Crystal Structure of $[\text{Cp}_2\text{LnF}(\text{THF})]_2$ ($\text{Ln} = \text{Y}$ (5**), Yb (**6**)).** Figure 2 represents the typical molecular structure of **5** and **6**. They are centrosymmetric fluoride-bridging dimers with distorted trigonal bipyramidal geometry around the central metal typical of $[\text{Cp}_2\text{LnCl}(\text{THF})]_2$ complexes.²⁹ On changing from Cp^* to Cp , the molecular structure of the complex shifts from the formally eight-coordinate monomer ($\text{Cp}^*_2\text{YbF}(\text{THF})_6$) to the formally eight-coordinate dimer ($[\text{Cp}^*_2\text{LnF}]_2$) to the nine-coordinate dimer ($[\text{Cp}_2\text{LnF}(\text{THF})]_2$) in order to achieve steric saturation.

The average $\text{Yb}-\text{F}$ distance of 2.193(8) Å in **6** can be compared with the value of 2.258 Å which would be expected by adding the difference, 0.057 Å, between Shannon's ionic radii²⁷ of nine-coordinate Yb^{3+} (1.042 Å) and eight-coordinate Yb^{3+} (0.985 Å) to a doubly bridging $\text{Yb}-\text{F}$ distance, 2.201(2) Å, in $\text{Cp}^*_6\text{Yb}_5\text{F}_9$.⁶ The difference between these two values may be due to steric effects. No organoyttrium fluoride compounds is reported in the literature to date. The bond distances of $\text{Y}-\text{F}$ found here in **5** are 2.233(5) and 2.217(5) Å with an average value of 2.225(5) Å. This measured value is 0.032 Å longer than the $\text{Yb}-\text{F}$ distance, which is consistent with the difference of their ionic radii.²⁷

Crystal Structure of $[(\text{C}_6\text{H}_5)_3\text{SiO}]_3\text{Sm}(\text{THF})_3$ (7**).** As shown in Figure 3, **7** is similar in structure to the yttrium^{20a} and cerium^{20d} analogues which were prepared in the reaction of $\text{Y}[\text{N}(\text{SiMe}_3)_2]_3$ with 3 equiv of $(\text{C}_6\text{H}_5)_3\text{SiOH}$ or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_5$ with 5 equiv of $(\text{C}_6\text{H}_5)_3\text{SiONa}$, respectively. The six oxygen atoms roughly define an octahedron, with the two sets of ligands

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Table 3. Selected Interatomic Distances (Å) and Angles (deg)^a

Compound 1							
La(1)–C(1)	2.856 (18)	La(1)–C(4)	2.826 (15)	La(1)–C(7)	2.842 (18)	La(1)–C(10)	2.804 (16)
La(1)–C(2)	2.834 (20)	La(1)–C(5)	2.812 (14)	La(1)–C(8)	2.835 (20)	La(1)–F(1)	2.324 (9)
La(1)–C(3)	2.823 (18)	La(1)–C(6)	2.804 (16)	La(1)–C(9)	2.808 (19)	La(1)–F(1A)	2.349 (7)
La(1)–F(1)–La(1A)	112.3 (4)	F(1)–La(1)–F(1A)	67.7 (4)	Cent(1)–La(1)–Cent(2)	129.4 (4)	Cent(1)–La(1)–F(1)	114.2 (4)
Cent(2)–La(1)–F(1)	107.3 (4)						
Compound 2							
Nd(1)–C(1)	2.793 (3)	Nd(1)–C(4)	2.778 (2)	Nd(1)–C(7)	2.787 (2)	Nd(1)–C(10)	2.760 (2)
Nd(1)–C(2)	2.766 (2)	Nd(1)–C(5)	2.822 (3)	Nd(1)–C(8)	2.763 (3)	Nd(1)–F(1A)	2.337 (1)
Nd(1)–C(3)	2.753 (2)	Nd(1)–C(6)	2.771 (2)	Nd(1)–C(9)	2.737 (2)	Nd(1)–F(1)	2.335 (2)
Nd(1)–F(1)–Nd(1A)	107.9 (1)	F(1)–Nd(1)–F(1A)	72.1 (1)	Cent(1)–Nd(1)–Cent(2)	128.3 (1)	Cent(1)–Nd(1)–F(1)	114.3 (1)
Cent(2)–Nd(1)–F(1)	107.2 (1)						
Compound 4							
Gd(1)–C(1)	2.709(7)	Gd(1)–C(4)	2.670(7)	Gd(1)–C(13)	2.700(8)	Gd(1)–C(16)	2.657(8)
Gd(1)–C(2)	2.715(8)	Gd(1)–C(5)	2.670(7)	Gd(1)–C(14)	2.706(8)	Gd(1)–F(1)	2.259(4)
Gd(1)–C(3)	2.719(8)	Gd(1)–C(12)	2.724(8)	Gd(1)–C(15)	2.676(8)	Gd(1)–F(1A)	2.259(4)
Gd(1)–F(1)–Gd(1A)	108.9 (2)	F(1)–Gd(1)–F(1A)	71.1 (2)	Cent(1)–Gd(1)–Cent(2)	129.4 (2)	Cent(1)–Gd(1)–F(1)	113.5 (2)
Cent(2)–Gd(1)–F(1)	107.0 (2)						
Compound 5							
Y(1)–C(1)	2.66(1)	Y(1)–C(4)	2.66(1)	Y(1)–C(7)	2.66(1)	Y(1)–C(10)	2.69(1)
Y(1)–C(2)	2.68(1)	Y(1)–C(5)	2.69(1)	Y(1)–C(8)	2.66(1)	Y(1)–F(1)	2.217(5)
Y(1)–C(3)	2.66(1)	Y(1)–C(6)	2.67(1)	Y(1)–C(9)	2.66(1)	Y(1)–F(1A)	2.233(5)
Y(1)–O(1)	2.467(6)						
Y(1)–F(1)–Y(1A)	112.0 (2)	F(1)–Y(1)–F(1A)	68.0 (2)	Cent(1)–Y(1)–Cent(2)	125.5 (2)	Cent(1)–Y(1)–F(1)	118.6 (2)
F(1)–Y(1)–O(1)	73.7 (2)	F(1A)–Y(1)–O(1)	141.6 (2)	Cent(2)–Y(1)–F(1)	115.8 (2)		
Compound 6							
Yb(1)–C(1)	2.63(2)	Yb(1)–C(4)	2.64(2)	Yb(1)–C(7)	2.62(2)	Yb(1)–C(10)	2.64(2)
Yb(1)–C(2)	2.64(2)	Yb(1)–C(5)	2.64(2)	Yb(1)–C(8)	2.61(1)	Yb(1)–F(1)	2.166(8)
Yb(1)–C(3)	2.61(2)	Yb(1)–C(6)	2.64(2)	Yb(1)–C(9)	2.62(1)	Yb(1)–F(1A)	2.219(7)
Yb(1)–O(1)	2.42(1)						
Yb(1)–F(1)–Yb(1A)	112.7 (3)	F(1)–Yb(1)–F(1A)	67.3 (3)	Cent(1)–Yb(1)–Cent(2)	123.9 (3)	Cent(1)–Yb(1)–F(1)	120.2 (3)
F(1)–Yb(1)–O(1)	73.2 (3)	F(1A)–Yb(1)–O(1)	140.4 (3)	Cent(2)–Yb(1)–F(1)	115.9 (3)		
Compound 7							
Sm(1)–O(1)	2.186(2)	Sm(1)–O(3)	2.152(2)	Sm(1)–O(5)	2.518(2)	O(1)–Si(1)	1.582(2)
Sm(1)–O(2)	2.171(2)	Sm(1)–O(4)	2.513(2)	Sm(1)–O(6)	2.557(2)	O(2)–Si(2)	1.584(2)
O(3)–Si(3)	1.606(2)						
O(3)–Sm(1)–O(2)	100.80(8)	O(2)–Sm(1)–O(4)	165.06(7)	O(1)–Sm(1)–O(6)	87.87(8)	O(5)–Sm(1)–O(6)	77.22(8)
O(3)–Sm(1)–O(1)	103.28(7)	O(2)–Sm(1)–O(6)	86.51(8)	O(1)–Sm(1)–O(4)	86.12(8)	O(6)–Sm(1)–O(3)	164.88(8)
O(3)–Sm(1)–O(5)	89.65(8)	O(2)–S(1)–O(5)	88.60(8)	O(1)–Sm(1)–O(5)	161.09(8)	Si(1)–O(1)–Sm(1)	170.22(13)
O(3)–Sm(1)–O(4)	89.15(8)	O(2)–Sm(1)–O(1)	102.19(8)	O(4)–Sm(1)–O(5)	80.26(7)	Si(2)–O(2)–Sm(1)	175.37(12)
O(4)–Sm(1)–O(6)	81.35(8)	Si(3)–O(3)–Sm(1)	178.04(12)				
Compound 8							
Sm(1)–O(1)	2.158(2)	O(1)#1–Sm(1)–O(1)	102.29(6)	O(1)#1–Sm(1)–O(2)	83.96(7)	O(2)#1–Sm(1)–O(2)	79.33(6)
Sm(1)–O(2)	2.542(2)	O(1)–Sm(1)–O(2)#1	162.40(7)	O(1)–Sm(1)–O(2)	92.25(7)	O(2)–Sm(1)–O(2)#2	79.33(6)
Sm(1)–O(1)–C(1)	163.9 (2)						
[Cp'' ₂ SmCl] ₂							
Sm(1)–C(1)	2.721(8)	Sm(1)–C(4)	2.710(8)	Sm(1)–C(7)	2.722(8)	Sm(1)–C(10)	2.692(8)
Sm(1)–C(2)	2.710(8)	Sm(1)–C(5)	2.683(8)	Sm(1)–C(8)	2.709(8)	Sm(1)–Cl(1)	2.758(2)
Sm(1)–C(3)	2.737(8)	Sm(1)–C(6)	2.736(8)	Sm(1)–C(9)	2.679(9)	Sm(1)–Cl(1A)	2.771(2)
Sm(1)–Cl(1)–Sm(1A)	101.84 (7)	Cl(1)–Sm(1)–Cl(1A)	78.16 (7)	Cent(1)–Sm(1)–Cent(2)	129.6(1)	Cent(1)–Sm(1)–Cl(1)	111.2 (1)
Cent(2)–Sm(1)–Cl(1)	107.3 (1)						

^a Cent: the centroid of the cyclopentadienyl ring. Symmetry transformations: #1, $-x+y+1, -x+1, z$; #2, $-y+1, x-y, z$.

Table 4. Summary of Bond Distances (Å) and Angles (deg) for 1–6

	av Cent–Ln	av Ln–C	Cent– Ln–Cent	av Ln–F	Ln...Ln	ionic radius (Ln ³⁺) ^a
1	2.555(15)	2.824(19)	129.4(4)	2.337(8)	3.882	1.160
2	2.498(2)	2.773(3)	128.3(1)	2.336(2)	3.778	1.109
3^b	2.440(5)	2.721(6)	129.6(1)	2.302(2)	3.750	1.079
4	2.409(8)	2.695(8)	129.4(2)	2.259(4)	3.675	1.053
5	2.41(1)	2.67(1)	125.5(2)	2.225(5)	3.689	1.075
6	2.35(2)	2.63(2)	123.9(3)	2.193(8)	3.650	1.042

^a See ref 27. ^b See ref 9.

oriented in a facial arrangement. The average Sm–O(Si) distance of 2.170(2) Å can be compared with the 2.13(2) Å average Y–O(Si) length in [(C₆H₅)₃SiO]₃Y–(THF)₃^{20a} and the 2.222(4) Å average Ce–O(Si) length in [(C₆H₅)₃SiO]₃Ce(THF)₃.^{20b} The differences in the above distances are close to those in their six-coordinate ionic radii.²⁷ The 174.5(1)° average value for Sm–O–Si angles is close to the 174.4(3)° and 171.0(1)° average

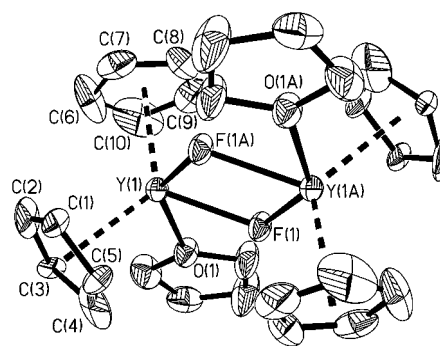


Figure 2. Molecular structure of [Cp''₂YF(THF)]₂ (**5**) (thermal ellipsoids drawn at the 35% probability level). All hydrogen atoms are omitted for clarity.

in [(C₆H₅)₃SiO]₃Ce(THF)₃ and [(C₆H₅)₃SiO]₃Y(THF)₃, respectively.

Crystal Structure of (2,6-Prⁱ₂C₆H₃O)₃Sm(THF)₃ (8**).** The overall structure of **8** is similar to that of **7**

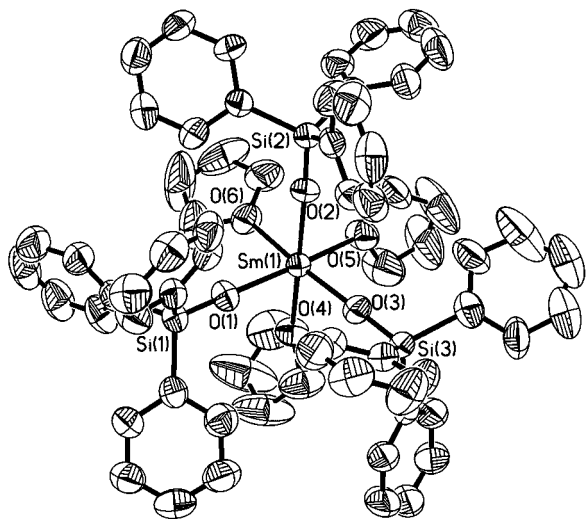


Figure 3. Molecular structure of $[(C_6H_5)_3SiO]_3Sm(THF)_3$ (**7**) (thermal ellipsoids drawn at the 35% probability level). All hydrogen atoms are omitted for clarity.

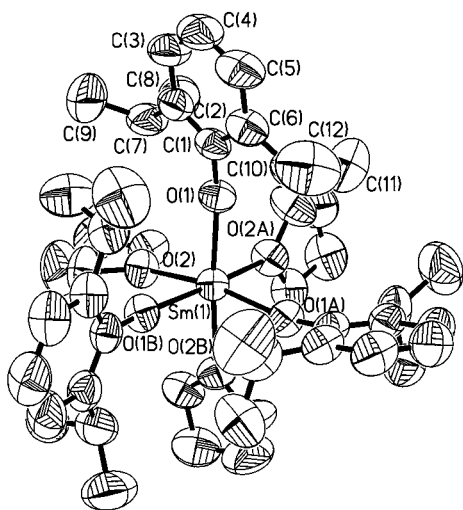


Figure 4. Molecular structure of $(2,6-Pr^{1/2}C_6H_3O)_3Sm(THF)_3$ (**8**) (thermal ellipsoids drawn at the 35% probability level). All hydrogen atoms are omitted for clarity.

(Figure 4). Three THF molecules and three 2,6- $Pr^{1/2}C_6H_3O$ groups are coordinated to Sm in a distorted octahedral geometry with a facial arrangement. Both the composition and the molecular structure of **8** are, however, different from its analogues, which have the general formula of $(2,6-Pr^{1/2}C_6H_3O)_3Ln(THF)_2$ and have a distorted trigonal bipyramidal fashion with three equatorial aryl oxide and two axial THF ligands.^{20e,f} The reasons for this difference are not clear.

The 2.158(2) Å Sm–O(Ar) distance can be compared with those values found in $(2,6-Pr^{1/2}C_6H_3O)_3Ln(THF)_2$, 2.21(1) Å for Ln = La,^{20f} 2.172(9) Å for Ln = Pr, and 2.130(9) for Ln = Gd.^{20e} The Sm–O(1)–C(1) angle of 163.9(2)° falls in the range of 162.5–167.2° normally observed for $(2,6-Pr^{1/2}C_6H_3O)_3Ln(THF)_2$ compounds.

Crystal Structure of $[Cp^*_2SmCl]_2$. As shown in Figure 5, the overall molecular structure of $[Cp^*_2SmCl]_2$ in the solid state is isostructural with that previously reported for $[Cp^*_2LnCl]_2$ (Ln = Pr,^{12a} Lu²⁵) and $[Cp^*_2LnF]_2$. The average Sm–C distance of 2.710(8) Å compares with the average values of 2.76 Å in $[Cp^*_2PrCl]_2$ and 2.603(6) Å in $[Cp^*_2LuCl]_2$. The differences

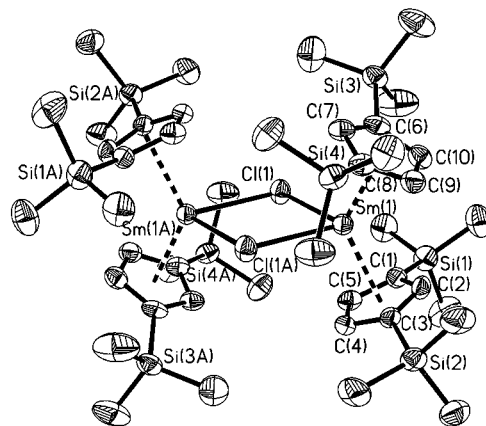


Figure 5. Molecular structure of $[Cp^*_2SmCl]_2$ (thermal ellipsoids drawn at the 35% probability level). All hydrogen atoms are omitted for clarity.

of the above values are those expected from the differences in the eight-coordinate metals' ionic radii.²⁷ The average Sm–Cl bond length is 2.765(2) Å, which can be compared with the 2.81 Å in $[Cp^*_2PrCl]_2$ and 2.628–(1) Å in $[Cp^*_2LuCl]_2$. The Cl–Sm–Cl angle (78.16(7)°), the Sm–Cl–Sm angle (101.84(7)°), and the Cent(1)–Sm–Cent(2) angle (129.6°) are similar to those found in Pr and Lu analogues.

Conclusions

By using Me_3NHF as a fluorinating reagent, a number of organolanthanide fluoride compounds have been successfully prepared and structurally characterized. All of them (except samarium) are the first example in the series. The main feature of this methodology is the use of readily available trivalent organolanthanide complexes rather than divalent complexes as the starting materials. This is the first general method known in the literature for the preparation of organolanthanide fluoride compounds.

Overall, the solid-state structures of organolanthanide fluoride compounds are similar to those of corresponding chloride compounds. On the other hand, due to the very small size of the fluorine atom and the very strong Ln–F bond, the reactivity pattern of organolanthanide fluoride differs significantly from the corresponding chloride compounds in certain reactions. The kinetic stability of organolanthanide difluoride compounds is much less than that of the corresponding dichloride compounds. Therefore, steric factors play a very important role in the stabilization of organolanthanide fluoride compounds.³⁰

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Supporting Information Available: Tables of crystallographic data collection information, atomic coordinates, bond distances and angles, anisotropic thermal parameters, hydrogen atom coordinates and atom-numbering schemes for **1**, **2**, **4–8**, and $[Cp^*_2SmCl]_2$ (97 pages). See any current masthead page for ordering information and Internet access instructions.

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(30) Added in proof. Compound $[Cp_2YbF(THF)]_2$ was very recently reported; see: Deacon, G. B.; Harris, S. C.; Meyer, G.; Stellfeldt, D.; Wilkinson, D. L.; Zelesny, G. *J. Organomet. Chem.* **1998**, 552, 165.