κ²- coordination of 18-crown-6 to Ce(III) cation: Solution dynamics and reactivity

Haolin Yin, Jerome R. Robinson, Patrick J. Carroll, Patrick J. Walsh and Eric J. Schelter*

P. Roy and Diana T. Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,
Philadelphia, PA 19104

E-mail: schelter@sas.upenn.edu

Supporting Information

Experimental Procedures

General Methods. Unless otherwise indicated all reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at 150 °C prior to use. ^{1}H, ^{19}F, and ^{13}C NMR spectra were obtained at room temperature on a Bruker DMX-300 Fourier transform NMR spectrometer operating at ^{1}H frequency of 300 MHz. ^{1}H and ^{19}F variable temperature NMR measurements were carried out at 300 MHz and 282 MHz. ^{1}H EXSY experiments were collected at room temperature on Bruker UNI-400 Fourier transform NMR spectrometer operating at ^{1}H frequency of 400 MHz over a range of mix times (0, 10, 25, 50, 100, 200 ms). Chemical shifts were recorded in units of parts per million referenced against residual proteo solvent peaks (^{1}H) deteuro solvent peaks (^{13}C) or fluorobenzene (^{19}F, -113.15 ppm). Elemental analyses were performed at the University of California, Berkeley, Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer.

Materials. Tetrahydrofuran, diethyl ether, dichloromethane, fluorobenzene, hexanes, and *n*-pentane were purchased from Fisher Scientific. The solvents were sparged for 20 min with dry N_2 and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for hexanes and *n*-pentane), or two columns of neutral alumina (for THF, Et_2O and toluene). Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc.. Prior to use, pyridine-*d*$_5$ and C_6D_6 were stored overnight over molecular sieves and potassium mirror, respectively. 4,4′-di-*tert*-butyl-2,2′-dipyridyl was purchased from Sigma-Aldrich and used as received. $Ce[N(SiMe_3)_2]_3$[1] and $HN(SiMe_3)Ph^{F}$[2] were prepared according to reported procedures.

X-Ray Crystallography. X-ray reflection intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT,[3] producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[4] program package for further processing and structure solution on a Dell Pentium 4 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS[5] or SADABS.[6] The structures were solved by direct methods (SHELXS-97).[7] Refinement was by full-matrix least squares based on F^2 using SHELXL-97.[7] All reflections were used during refinements. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0907P)^2 + 0.3133P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Synthetic Details and Characterization

Synthesis of $Ce^{III}[N(SiMe_3)Ph^F]_3$ (1). To a vial containing $Ce[N(SiMe_3)_2]_3$ (1.24 g, 2.00 mmol, 1.00 equiv) dissolved in 10 mL pentane, a pentane solution containing $HN(SiMe_3)Ph^F$ (1.690 g, 6.600 mmol, 3.30 equiv) was added. White solids gradually formed after stirring this mixture for 6 d. The precipitates were collected by filtration over a medium porosity fritted filter, washed with 3 × 3 mL pentane and dried under reduced pressure for 1 h. Yield: 1.49 g, 1.65 mmol, 83%. ^1H NMR (C_6D_6): δ –9.15 (s, 36H, $–SiMe_3$). ^{19}F NMR (C_6D_6): δ –163.47 (d, 6F, *m*-F, J = 23 Hz), –173.09 (br, 6F, *o*-F, FWHM 350 Hz), –173.42 (t, 3F, *p*-F, J = 23 Hz). Elemental analysis found (calculated) for $C_{27}H_{27}F_{15}N_3Si_3Ce$: C, 35.65 (35.92), H, 2.95 (3.01), N, 4.63 (4.65). Single crystals suitable for X-ray analysis were obtained by storing a saturated pentane solution at –21 °C overnight.

Synthesis of $Ce(\kappa^2\text{-18-crown-6})[N(SiMe_3)Ph^F]_3$ (2). To a vial containing $Ce[N(SiMe_3)Ph^F]_3$ (0.045 g, 0.050 mmol, 1.00 equiv) suspended in 5 mL pentane, a 1 mL pentane solution containing 18-crown-6 (0.013 g, 0.050 mmol, 1.00 equiv) was added. After stirring for 0.5 h, the mixture was filtered through Celite packed in a pipette, concentrated to 1 mL and stored at –21 °C overnight to yield colorless crystals. The crystals were collected by a filtration over a medium porosity fritted filter and dried under reduced pressure. Crystalline yield: 0.040 g, 0.034 mmol, 69 %. ^1H NMR (tol-d_8): –1.30 (br, 24H, 18-crown-6), –4.22 (s, 27H, $-SiMe_3$). ^{19}F NMR (tol-d_8): –151.80 (br, 6F, *o*-F, FWHM 105 Hz), –163.76 (d, 6F, *m*-F, J = 17 Hz), –168.42 (t, 3F, *p*-F, J = 20 Hz). Elemental analysis found (calculated) for $C_{39}H_{51}F_{15}N_3Si_3O_6Ce$: C, 39.80 (40.13), H, 4.24 (4.40), N, 3.57 (3.60). Single crystals suitable for X-ray analysis were obtained by storing a pentane solution at –21°C overnight. The same reaction performed on NMR scale (i.e. 0.014 g **1**) in toluene or Et_2O with addition of 18-crown-6 in corresponding solvent dropwise (1 ml in ~30 s) gave near quantitative conversion to **2** by NMR spectroscopy after stirring for 0.5 h.

Synthesis of $\{Ce(\kappa^6\text{-18-crown-6})[N(SiMe_3)Ph^F]_2\}^+\{Ce[N(SiMe_3)Ph^F]_4\}^-$ (3). To a vial containing $Ce[N(SiMe_3)Ph^F]_3$ (0.27 g, 0.30 mmol, 2.0 equiv) dissolved in 2 mL THF, a THF solution containing 18-crown-6 (0.040 g, 0.15 mmol, 1.0 equiv) was added. After stirring for 3 h, the conversion to **3** was near quantitative, as indicated by NMR spectroscopy (Figure S11-S12). The volatiles were removed under reduced pressure. The solid residue was triturated with pentane and collected by filtration over a medium porosity fritted filter. The white solids were further washed with 3 × 3 mL pentane and dried under reduced pressure for 1 h. Yield: 0.30 g, 0.15 mmol, 97%. ^{1}H NMR (thf-h_8): δ 5.92 (s, 18H, $\text{-SiMe}_{3\text{cation}}$), –3.54 (s, 24H, 18-crown-6), –5.32 (s, 36H, $\text{-SiMe}_{3\text{anion}}$). ^{19}F NMR (thf): δ –141.08 (d, 4F, *o*-F_{cation}, *J* = 21 Hz), –166.11 (t, 4F, *m*-F_{cation}, *J* = 20 Hz), –167.06 (br, 8F, *o*-F_{anion}), –166.90 (d, 8F, *m*-F_{anion}, *J* = 23 Hz), –167.77 (t, 2F, *p*-F_{cation}, *J* = 23 Hz), –175.21 (t, 4F, *p*-F_{anion}, *J* = 20 Hz). Elemental analysis found (calculated) for $C_{66}H_{78}F_{30}N_6Si_6O_6Ce_2$: C, 38.13 (38.29), H, 3.83 (3.80), N, 4.09 (4.06). Single crystals suitable for X-ray analysis were obtained by THF/pentane layering stored at –21 °C. The same reaction performed on NMR scale in dimethoxyethane, dichloromethane or pyridine similarly gave near quantitative conversion to **3**.

Transformation of 2 to 3: $Ce(\kappa^2\text{-18-crown-6})[N(SiMe_3)Ph^F]_3$ was generated quantitatively *in situ* by adding 18-crown-6 (0.006 g, 0.022 mmol, 1.10 equiv) into an Et_2O solution containing $Ce[N(SiMe_3)Ph^F]_3$ (0.018 g, 0.020 mmol, 1.00 equiv) following stirring for 1 h. The solvent was removed under reduced pressure and CH_2Cl_2 was added into the mixture. ^{19}F and ^{1}H NMR measurements confirmed its near quantitative conversion to $\{Ce(\kappa^6\text{-18-crown-}$

6)[N(SiMe$_3$)Ph^F$_2$]$_2$}$^+$ {Ce[N(SiMe$_3$)Ph^F]$_4$}$^-$. The same reaction performed on NMR scale in tetrahydrofuran, dimethoxyethane, or pyridine also gave **3** in near quantitative yield. Representative NMR was shown in Figure S13-S14.

Synthesis of Ce(^{t}Bu$_2$bipy)[N(SiMe$_3$)Ph^F]$_3$ (4). To a vial containing Ce[N(SiMe$_3$)Ph^F]$_3$ (0.045g, 0.050 mmol, 1.00 equiv) dissolved in suspended in 2 mL pentane, a 1 mL pentane solution containing 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.013 g, 0.050 mmol, 1.00 equiv) was added resulting in an orange clear solution. After stirring for 0.5 h, the solution was concentrated to 1 mL and stored at –21 °C overnight to yield orange crystals. The orange crystals were collected by filtration over a medium porosity fritted filter and dried under reduced pressure. Crystalline yield: 0.050 g, 0.043 mmol, 86 %. ^{1}H NMR (C_6D_6): 19.50 (br, 2H, py-H), 7.83 (s, 2H, py-H), 3.68 (s, 2H, py-H), 0.20 (s, 18H, -^{t}Bu), –3.69 (s, 27H, -SiMe$_3$). ^{19}F NMR (tol-d_8): –162.55 (br, 6F, *o*-F, FWHM 130 Hz), –166.04 (d, 6F, *m*-F, J = 23 Hz), –171.50 (t, 3F, *p*-F, J = 23 Hz). Elemental analysis found (calculated) for $C_{45}H_{51}F_{15}N_5Si_3Ce$: C, 46.07 (46.15), H, 4.21 (4.39), N, 5.77 (5.98). Single crystals suitable for X-ray analysis were obtained by storing a pentane solution of **4** at –21°C.

Reaction of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ with 4,4′-di-*tert*-butyl-2,2′-dipyridyl: Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ was generated quantitatively *in situ* by adding 18-crown-6 (0.003 g, 0.011 mmol, 1.10 equiv) into a C_6D_6 solution containing Ce[N(SiMe$_3$)Ph^F]$_3$ (0.009 g, 0.010 mmol, 1.00 equiv). After stirring for 1 h, white solids of 4,4′-di-*tert*-butyl-2,2′-dipyridyl (0.003 g, 0.011 mmol, 1.10 equiv) were added to the mixture causing an immediate color change to orange, followed by stirring for 3 h. The quantitative conversion into Ce(^{t}Bu$_2$bipy)[N(SiMe$_3$)Ph^F]$_3$ was confirmed by NMR (Figure S15-16).

Synthesis of $KN(SiMe_3)Ph^F$. To a 20 mL colorless ethyl ether solution containing $HN(SiMe_3)Ph^F$ (2.530 g, 9.9 mmol, 1.00 equiv) in a 150 mL flask, a ethyl ether solution containing $KN(SiMe_3)_2$ (1.970 g, 9.9 mmol, 1.00 equiv) was added. The mixture turned slightly yellow and was stirred for 4 h and dried under vacuum. The resulting white solid were collected by filtration over medium porosity fritted filter and washed with 5 mL pentane three times. Drying for 3 h under reduced pressure yielded white powder identified by ^1H NMR as $KN(SiMe_3)Ph^F$ without solvation. Yield: 2.750 g, 9.4 mmol, 95 %. ^1H NMR (pyr-d_5): δ 0.49 (s, 9H, -$SiMe_3$). ^{19}F NMR (pyr-d_5): δ –164.67 (t, 2F, *o*-F, J = 17 Hz), –171.66 (t, 2F, *m*-F, J = 23 Hz), –195.08 (m, 2F, *p*-F). Elemental analysis found (calculated) for $C_9H_9F_5NSiK$: C, 36.82 (36.85), H, 3.12 (3.09), N, 5.00 (4.77). Single crystals of $KN(SiMe_3)Ph^F\cdot Et_2O$ suitable for X-ray analysis were obtained from Et_2O/pentane.

Reaction of $Ce(\kappa^2\text{-18-crown-6})[N(SiMe_3)Ph^F]_3$ with $KN(SiMe_3)Ph^F$: $Ce(\kappa^2\text{-18-crown-6})[N(SiMe_3)Ph^F]_3$ was generated quantitatively *in situ* by adding a Et_2O solution of 18-crown-6 (0.007 g, 0.026 mmol, 1.00 equiv) into a Et_2O solution containing $Ce[N(SiMe_3)Ph^F]_3$ (0.023 g, 0.026 mmol, 1.00 equiv). After stirring for 1 h, a Et_2O solution containing $KN(SiMe_3)Ph^F$ (0.008 g, 0.026 mmol, 1.00 equiv) was added to the mixture and further stirred for 3 h. NMR measurement confirmed the nearly quantitative conversion into $\{Ce[N(SiMe_3)Ph^F]_4\}^-$ (**3-anion**).

X-ray Crystal Structures

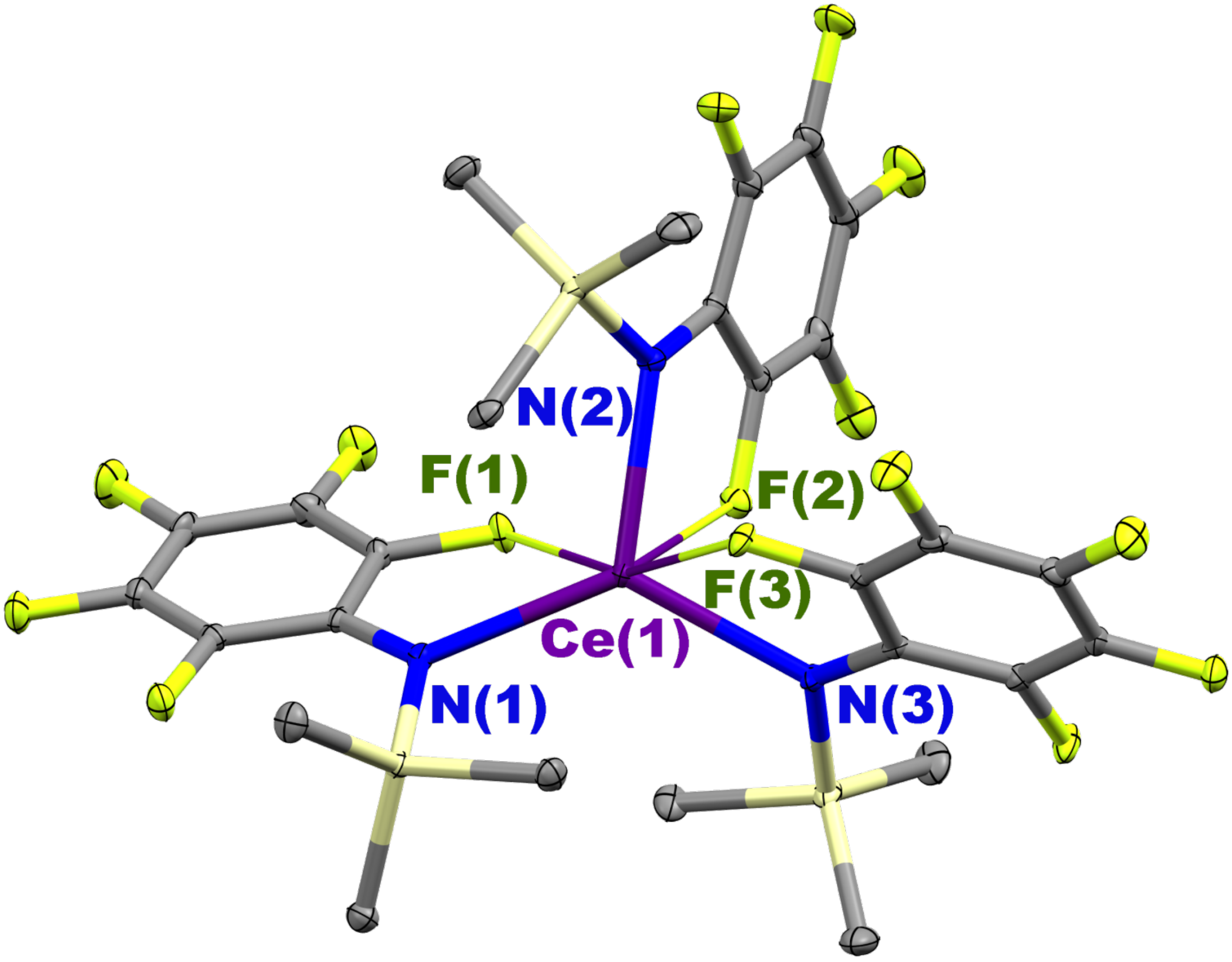


Figure S1. Thermal ellipsoid plot of **$Ce^{III}[N(SiMe_3)Ph^F]_3$ (1)** at 30% probability. Selected bond length (Å) and angles (deg): Ce(1)–N(1) 2.416(2), Ce(1)–N(2) 2.381(2), Ce(1)–N(3) 2.394(2), Ce(1)–F(1) 2.6140(16), Ce(1)–F(2) 2.6185(16), Ce(1)–F(3) 2.6418(16); N(1)–Ce(1)–N(2) 119.97(8), N(1)–Ce(1)–N(3) 128.92(8), N(2)–Ce(1)–N(3) 111.11(8).

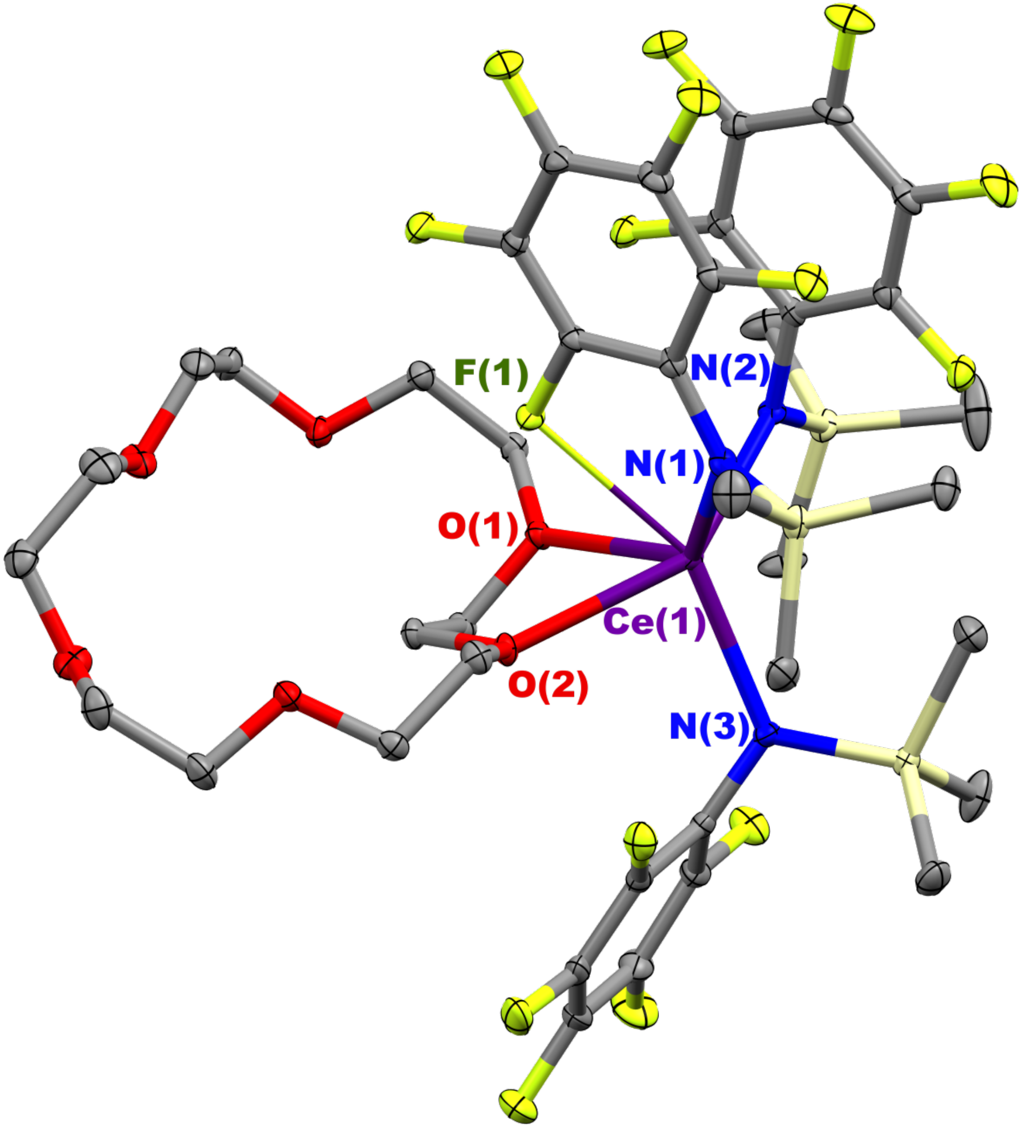


Figure S2. Thermal ellipsoid plot of **Ce^{III}(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ (2)** at 30% probability. Selected bond length (Å) and angles (deg): Ce(1)–N(1) 2.4595(17), Ce(1)–N(2) 2.3785(17), Ce(1)–N(3) 2.4057(17), Ce(1)–F(1) 2.7545(12), Ce(1)–O(1) 2.5201(14), Ce(1)–O(2) 2.6050(15); N(1)–Ce(1)–N(2) 92.15(6), N(1)–Ce(1)–N(3) 123.64(6), N(2)–Ce(1)–N(3) 113.57(6), O(1)–Ce(1)–O(2) 64.63(4), F(1)–Ce(1)–N(1) 62.84(5).

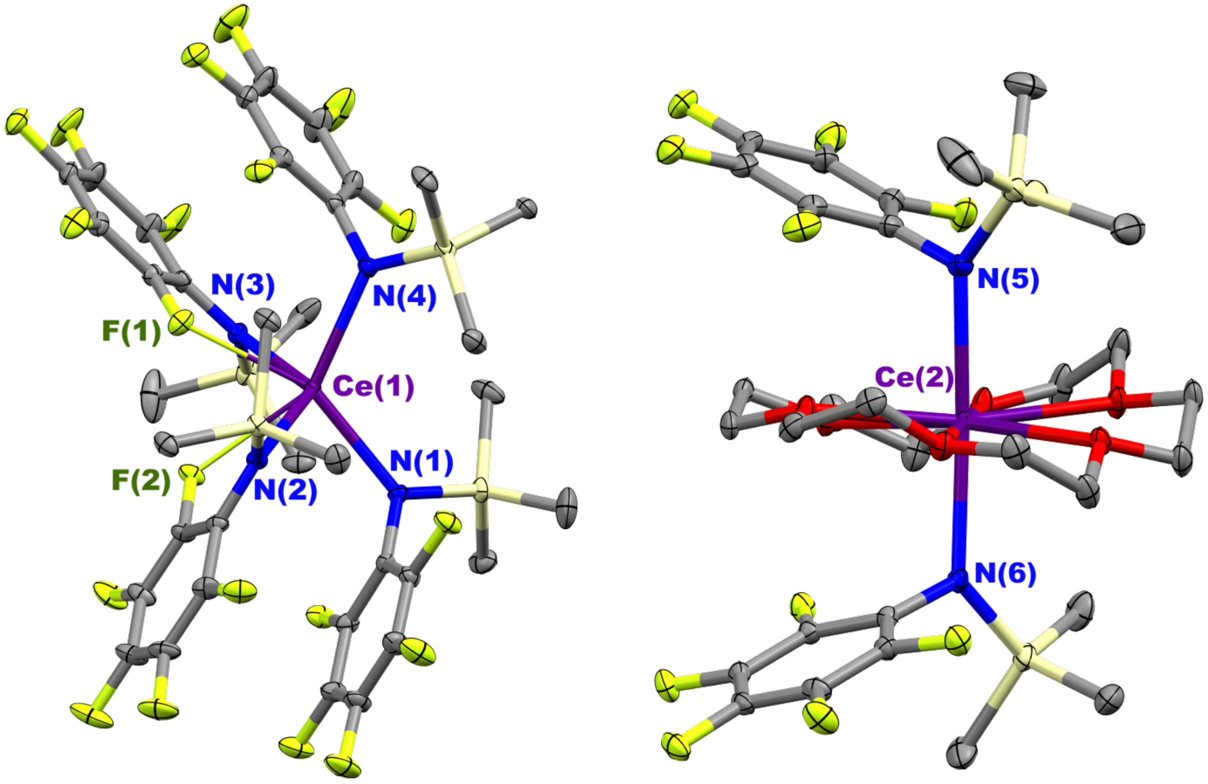


Figure S3. Thermal ellipsoid plot of **{Ce(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+${Ce[N(SiMe$_3$)Ph^F]$_4$}$^-$ (3)** at 30% probability (Left: Ce^{III}[N(SiMe$_3$)Ph^F]$_4^-$, right: Ce(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2^+$; interstitial THF molecule is omitted for clarity). Selected bond length (Å) and angles (deg): Ce(1)–N(1) 2.409(3), Ce(1)–N(2) 2.489(3), Ce(1)–N(3) 2.527(3), Ce(1)–N(4) 2.402(3), Ce(2)–N(5) 2.472(3), Ce(2)–N(6) 2.454(3), Ce(1)–F(1) 2.678(2), Ce(1)–F(2) 2.681(2), Ce(2)–Oave 2.614(3); N(1)–Ce(1)–N(2) 86.51(10), N(1)–Ce(1)–N(3) 123.42(10), N(1)–Ce(1)–N(4) 116.99(10), N(2)–Ce(1)–N(4) 118.43(10), N(3)–Ce(1)–N(4) 89.89(10), N(3)–Ce(1)–F(1) 63.33(8), N(2)–Ce(1)–F(2) 63.87(8), N(5)–Ce(2)–N(6) 168.31(11).

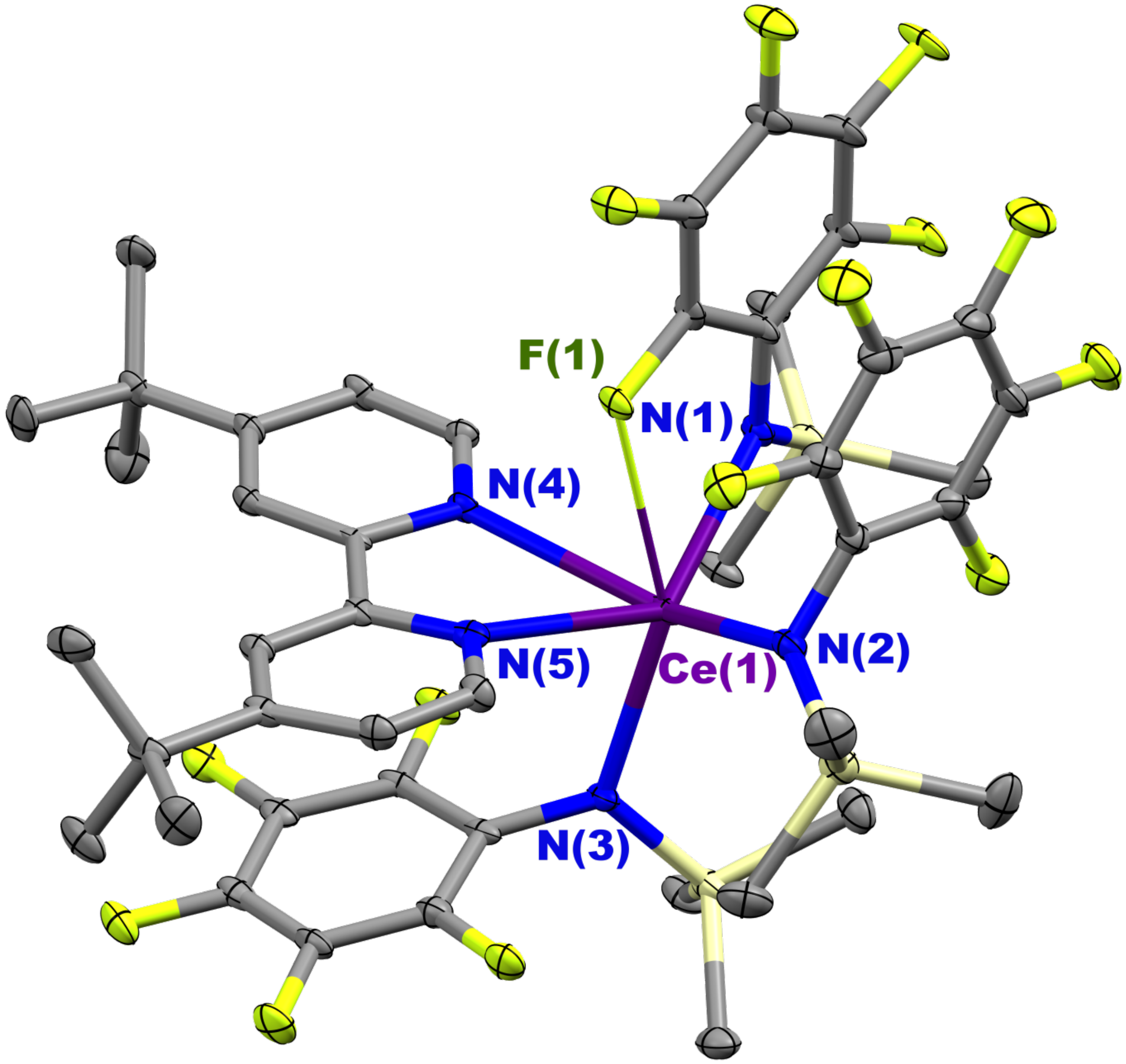


Figure S4. Thermal ellipsoid plot of **Ce^{III}(^{t}Bu$_2$bipy)[N(SiMe$_3$)Ph^F]$_3$ (4)** at 30% probability. Selected bond length (Å) and angles (deg): Ce(1)–N(1) 2.491(6), Ce(1)–N(2) 2.407(7), Ce(1)–N(3) 2.402(6), Ce(1)–N(4) 2.662(6), Ce(1)–N(5) 2.613(7), Ce(1)–F(1) 2.673(4); N(1)–Ce(1)–N(2) 102.8(2), N(1)–Ce(1)–N(3) 130.5(2), N(2)–Ce(1)–N(3) 110.7(2).

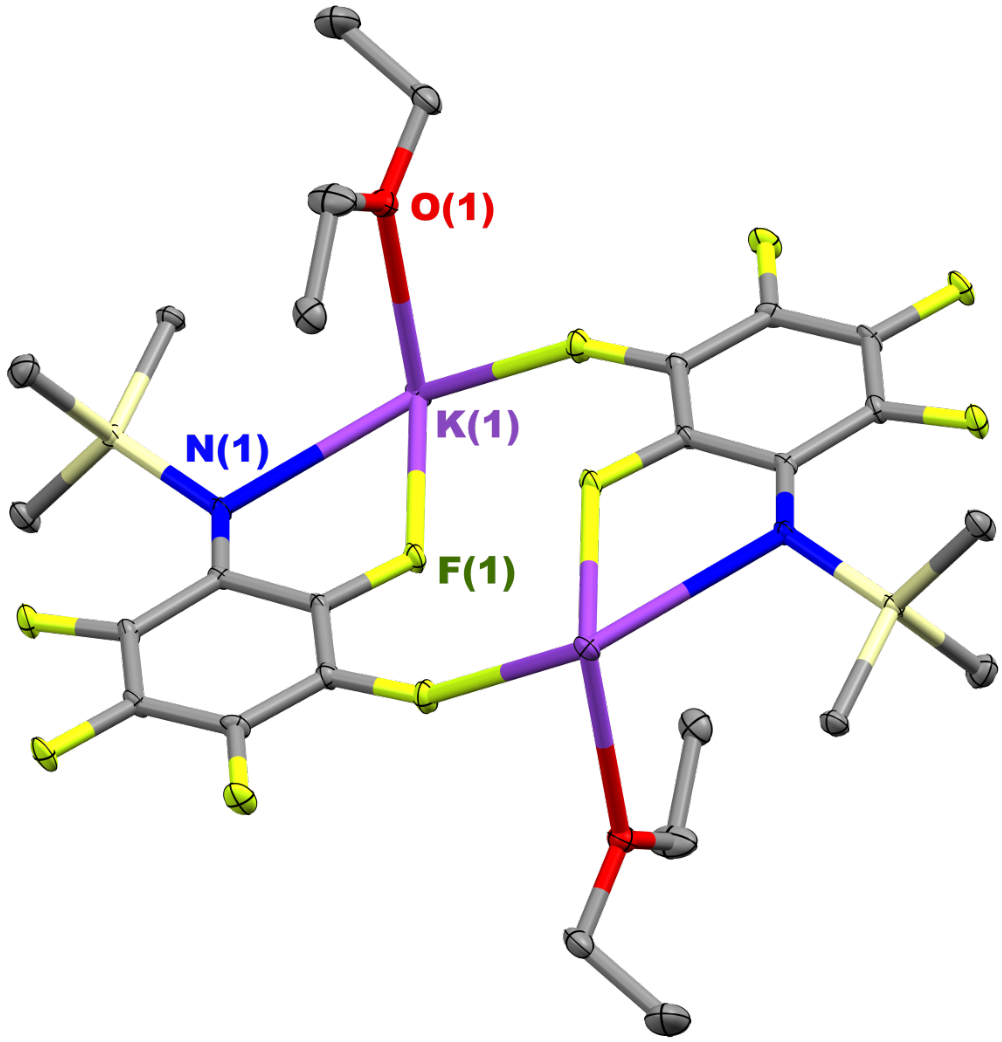


Figure S5. Thermal ellipsoid plot of **KN(SiMe$_3$)Ph^F·Et$_2$O** at 30% probability.

VT NMR Spectra

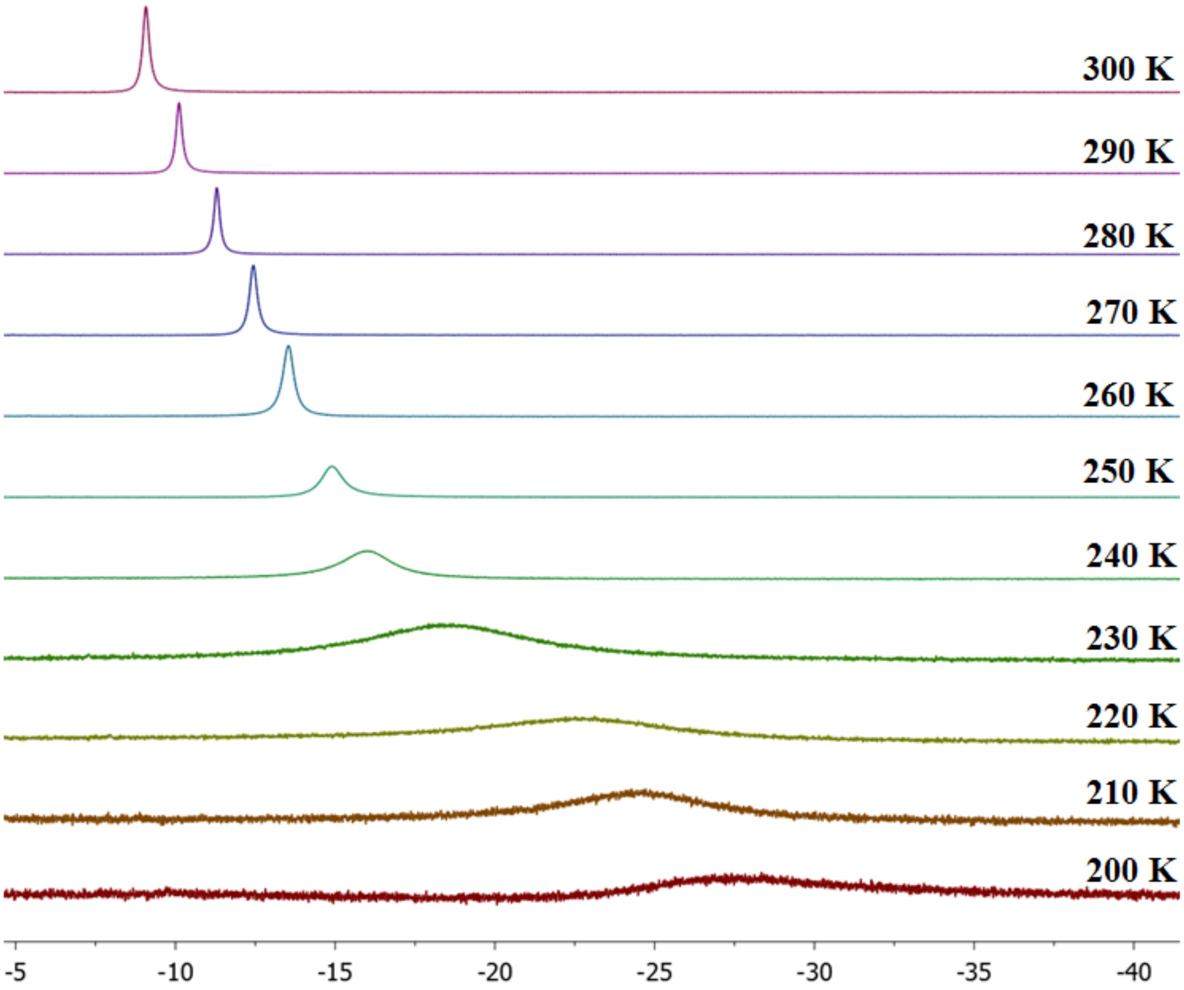


Figure S6. ^{1}H VT NMR data for **Ce^{III}[N(SiMe$_3$)Ph^F]$_3$ (1)** in toluene-*d*$_8$ between 200–300 K. Peaks downfield of -5 ppm were attributed solely to solvent impurities, so this region of the spectrum was omitted for clarity.

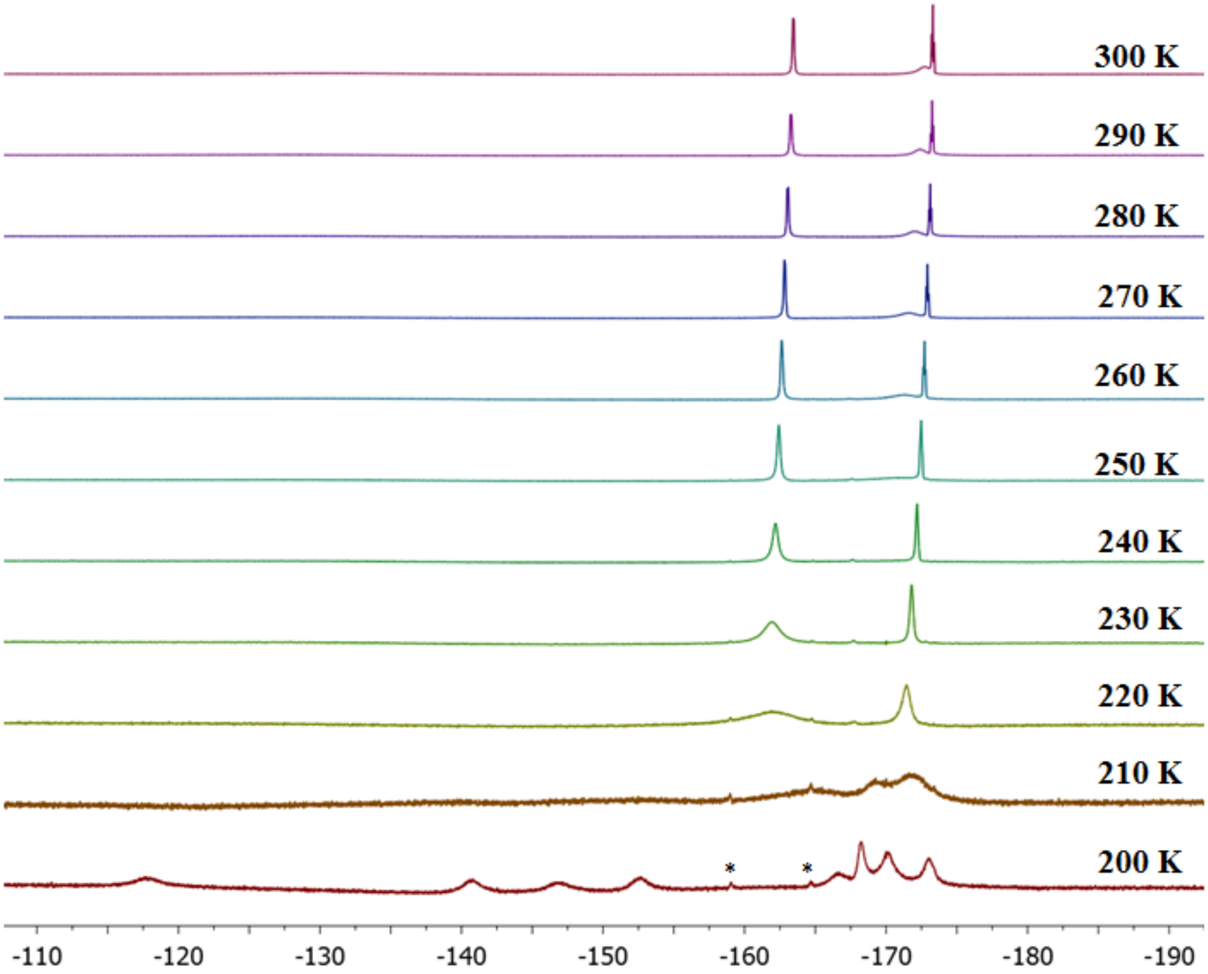


Figure S7. ^{19}F VT NMR data for **Ce^{III}[N(SiMe$_3$)Ph^F]$_3$ (1)** in toluene-d_8 between 200–300 K. Minor impurity HN(SiMe$_3$)Ph^F is visible as a minor impurity in some spectra, indicated by *.

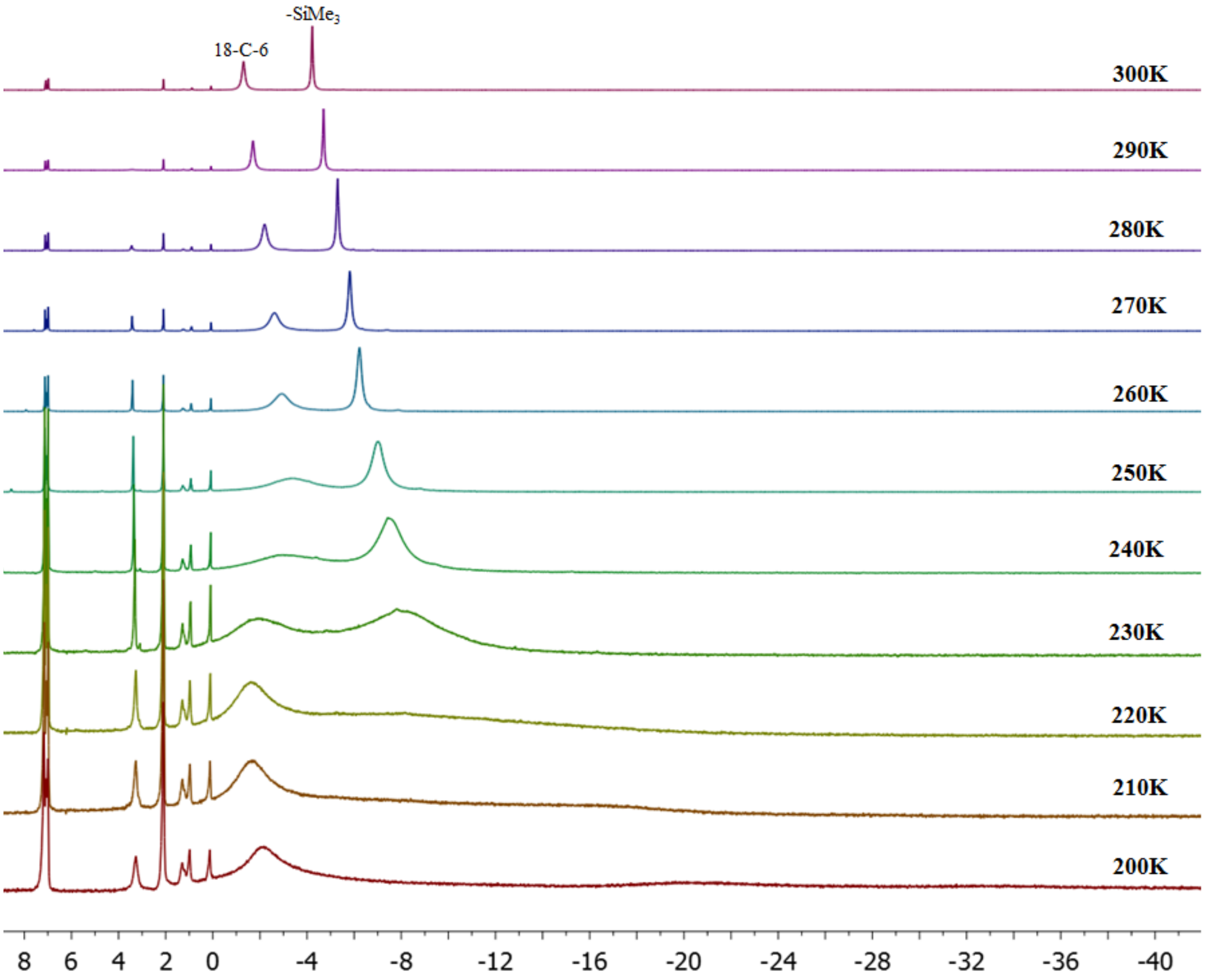


Figure S8. ^{1}H VT NMR data for **Ce^{III}(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ (2)** in toluene-*d$_8$* between 200–300 K. Resonances downfield of 0 ppm can be solely attributed to solvent residue(pentane and toluene), a minor amount of HN(SiMe$_3$)Ph^F and free 18-crown-6.

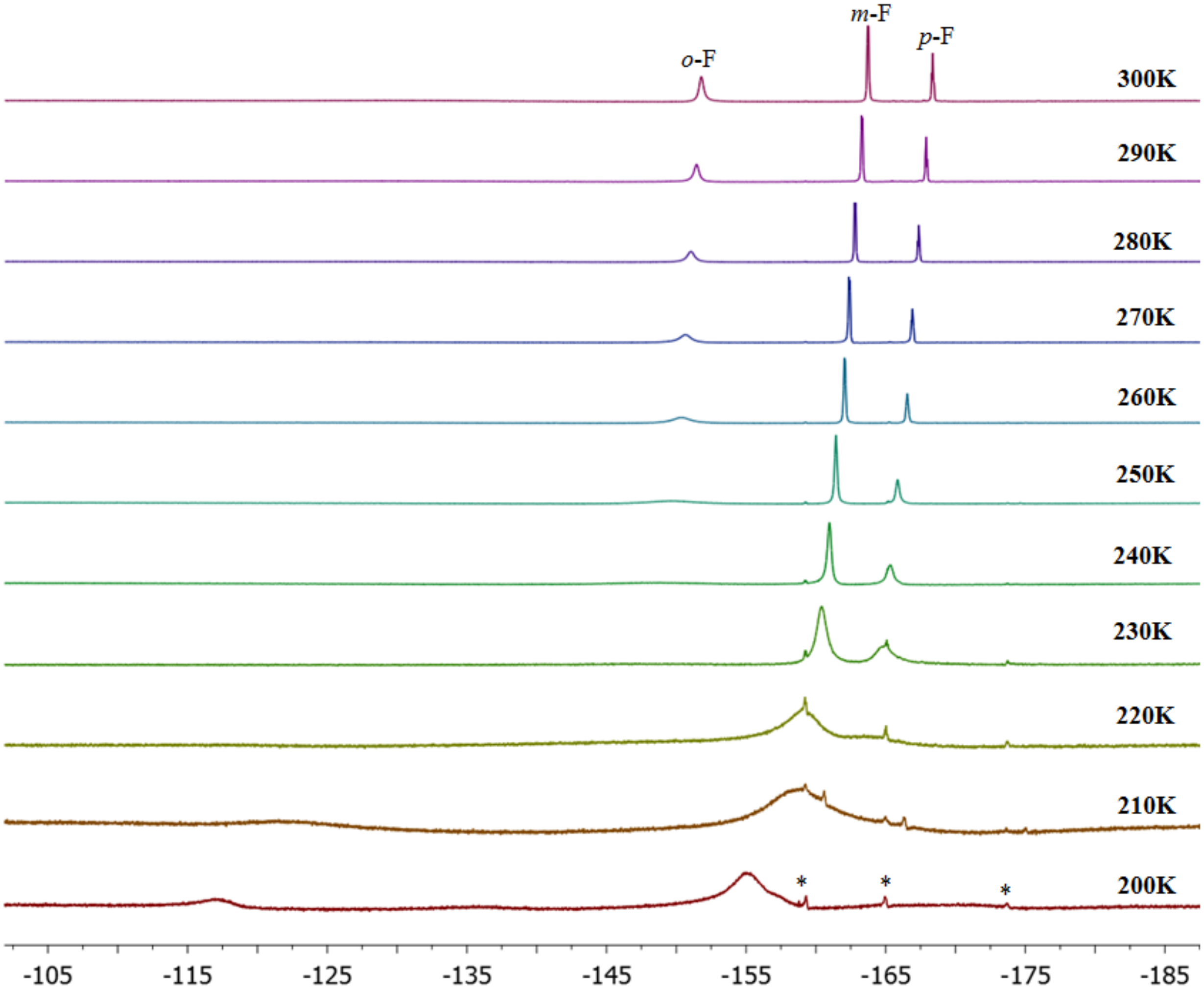


Figure S9. ^{19}F VT NMR data for **Ce^{III}(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ (2)** in toluene-*d$_8$* between 200–300 K. Minor impurity HN(SiMe$_3$)Ph^F is visible in some spectra, indicated by *.

NMR Spectra

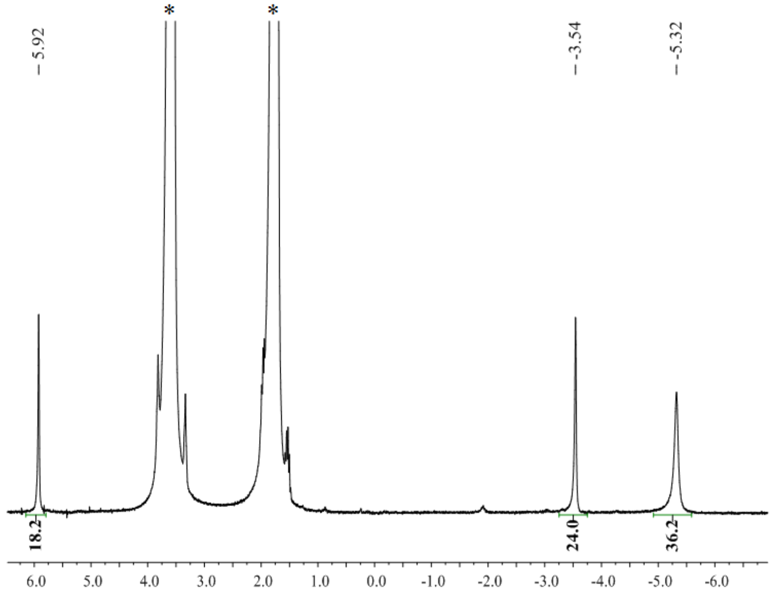


Figure S10. ^{1}H NMR of reaction aliquots of Ce[N(SiMe$_3$)Ph^F]$_3$ **(1)** with 18-crown-6 in thf-*h$_8$*. Quantitative conversion to {Ce^{III}(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+${Ce^{III}[N(SiMe$_3$)Ph^F]$_4$}$^-$ **(3)** was observed. Proteo-solvent (thf) resonances are indicated by *.

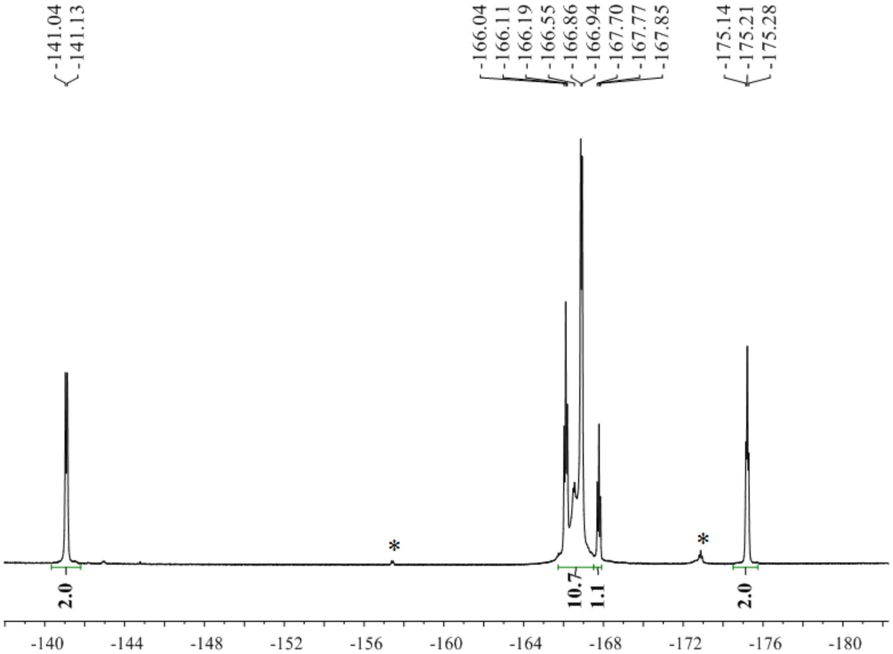


Figure S11. ^{19}F NMR of reaction aliquots of Ce[N(SiMe$_3$)Ph^F]$_3$ **(1)** with 18-crown-6 in thf-*h$_8$*. Quantitative conversion to {Ce^{III}(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+$ {Ce^{III}[N(SiMe$_3$)Ph^F]$_4$}$^-$ **(3)** was observed. Minor impurity of HN(SiMe$_3$)Ph^F was also noted in the spectrum, indicated by *.

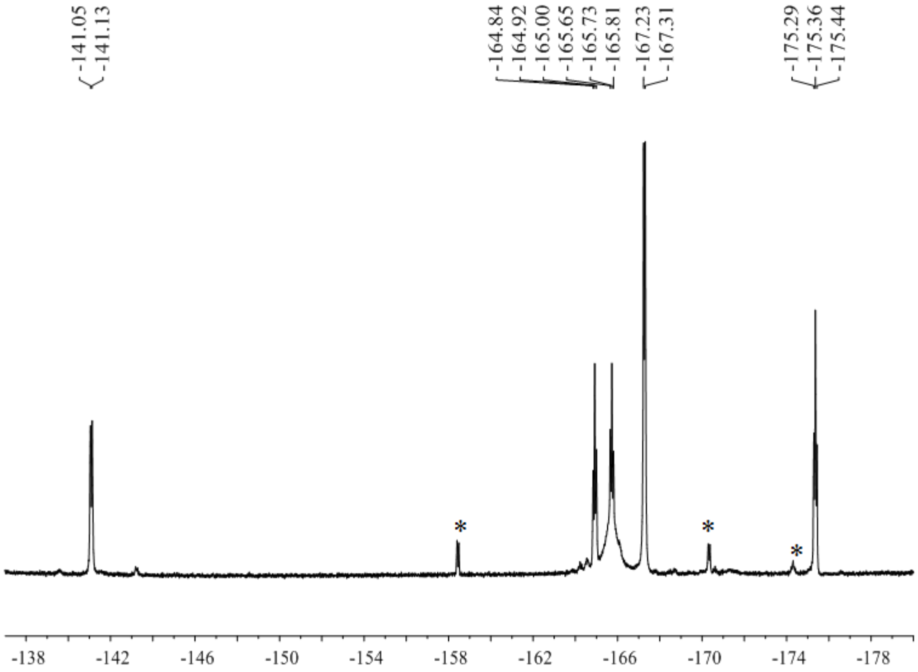


Figure S12. ^{19}F NMR of reaction aliquots of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ **(2)** in CH_2Cl_2. Near quantitative conversion to {Ce^{III}(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+$ {Ce^{III}[N(SiMe$_3$)Ph^F]$_4$}$^-$ **(3)** was observed. A minor impurity of HN(SiMe$_3$)Ph^F was also noted in the spectrum, indicated by *.

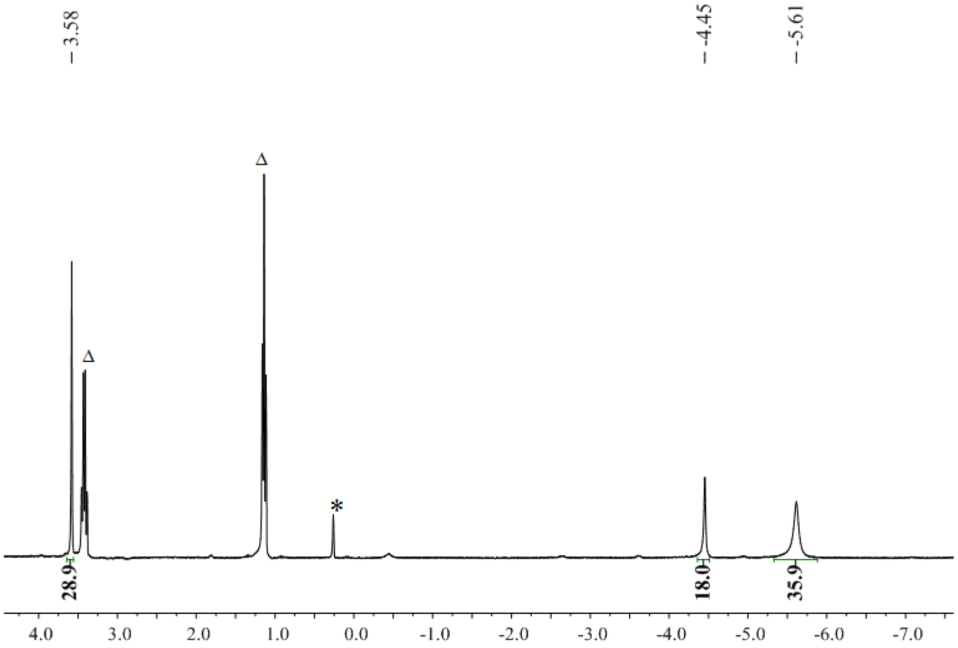


Figure S13. ^{1}H NMR of reaction aliquots of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ **(2)** in CH_2Cl_2. Near quantitative conversion to {Ce^{III}(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+$ {Ce^{III}[N(SiMe$_3$)Ph^F]$_4$}$^-$ **(3)** and free 18-crown-6 was observed. Minor amount of HN(SiMe$_3$)Ph^F (*), residue solvent Et_2O (Δ) were also noted in the spectrum.

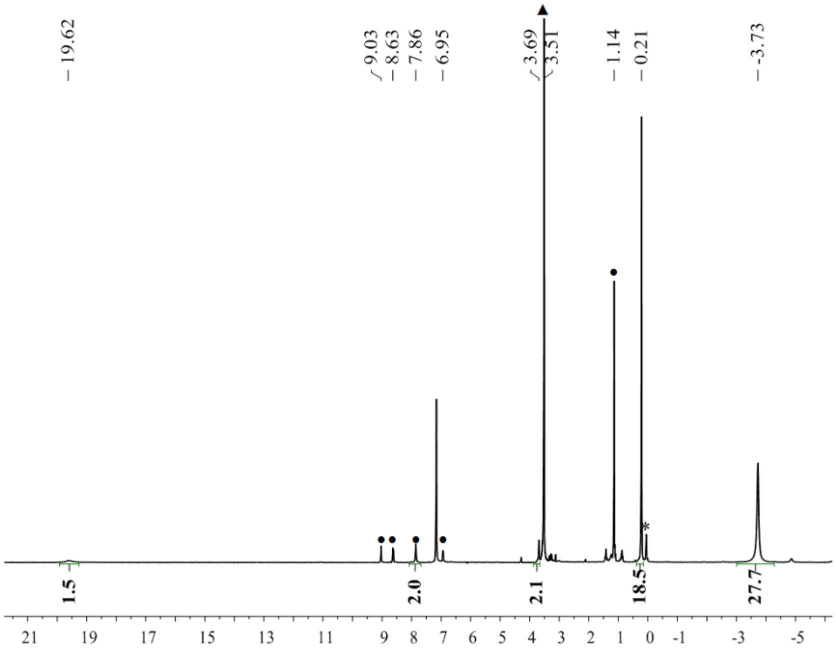


Figure S14. ^{1}H NMR of reaction aliquots of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ **(2)** with 4,4'-di-tert-butyl-2,2'-dipyridyl. NMR obtained in C_6D_6 shows near quantitative conversion to Ce^{III}(^{t}Bu$_2$bipy)[N(SiMe$_3$)Ph^F]$_3$ **(4)**, excessive 4,4'-di-tert-butyl-2,2'-dipyridyl (indicated by ●), byproduct 18-crown-6 (indicated by ▲) and a minor impurity HN(SiMe$_3$)Ph^F (*) is also evident in the spectra.

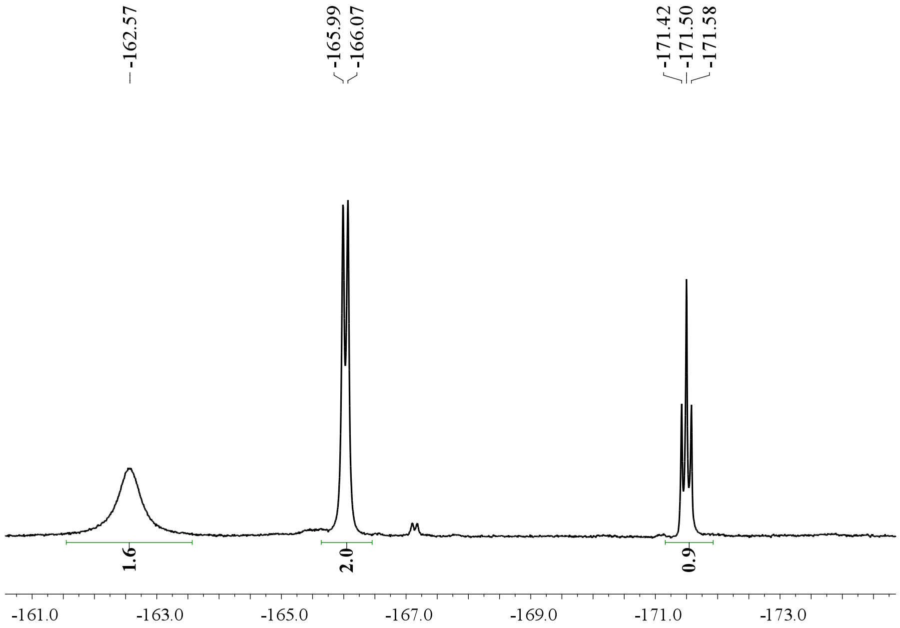


Figure S15. ^{19}F NMR of reaction aliquots of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ **(2)** with 4,4'-di-tert-butyl-2,2'-dipyridyl. NMR obtained in C_6D_6 shows near quantitative conversion to Ce^{III}(^{t}Bu$_2$bipy)[N(SiMe$_3$)Ph^F]$_3$ **(4)**.

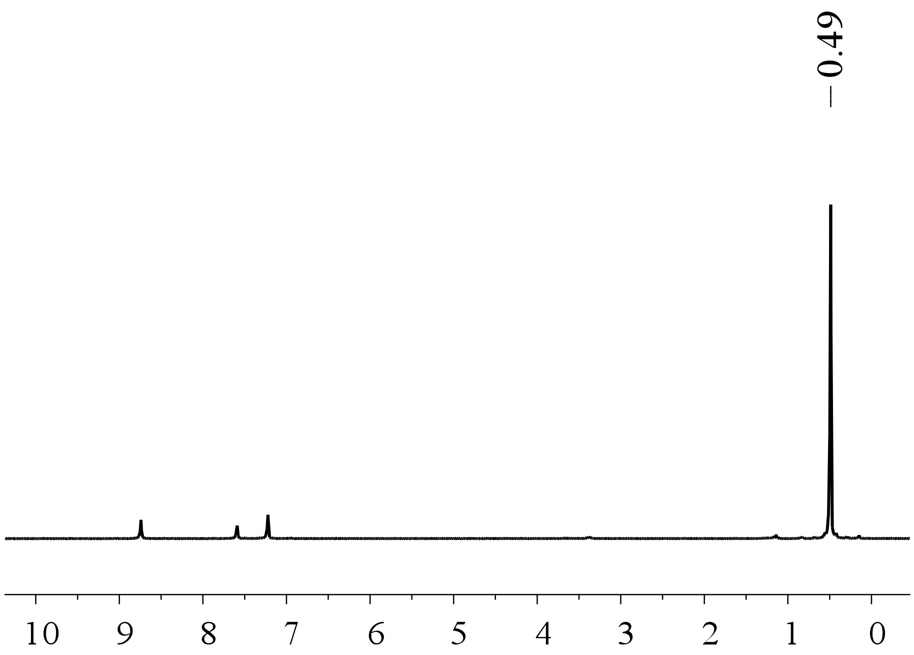


Figure S16. ^{1}H NMR of KN(SiMe$_3$)Ph^F in pyr-d_5. The lack of Et$_2$O resonances suggests the compound is obtained with no solvation.

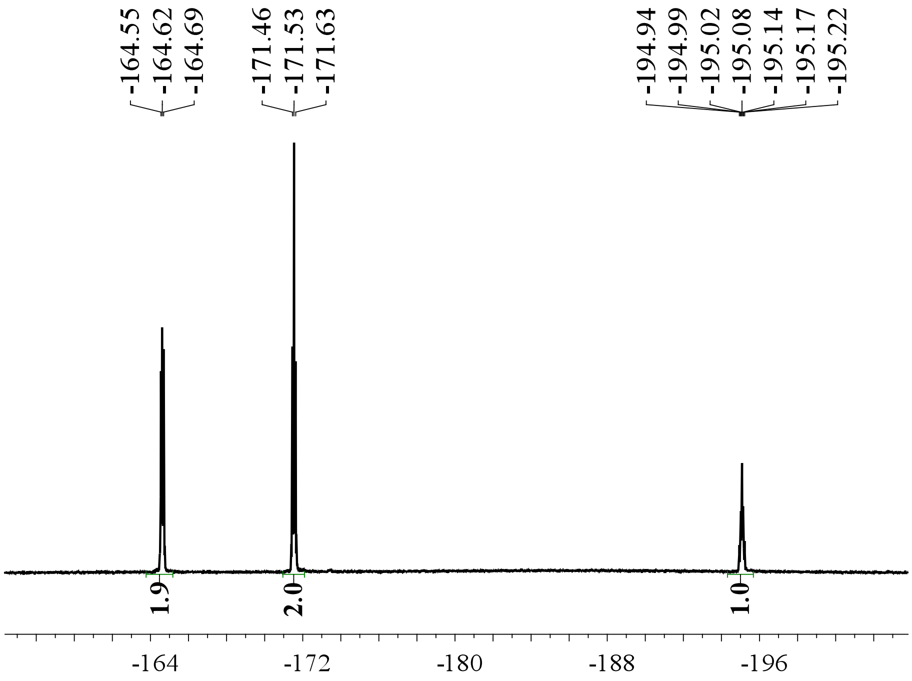
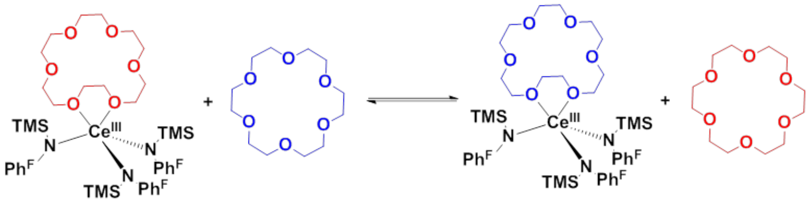


Figure S17. ^{19}F NMR of KN(SiMe$_3$)Ph^F in pyr-d_5.

^{1}H EXSY Spectra



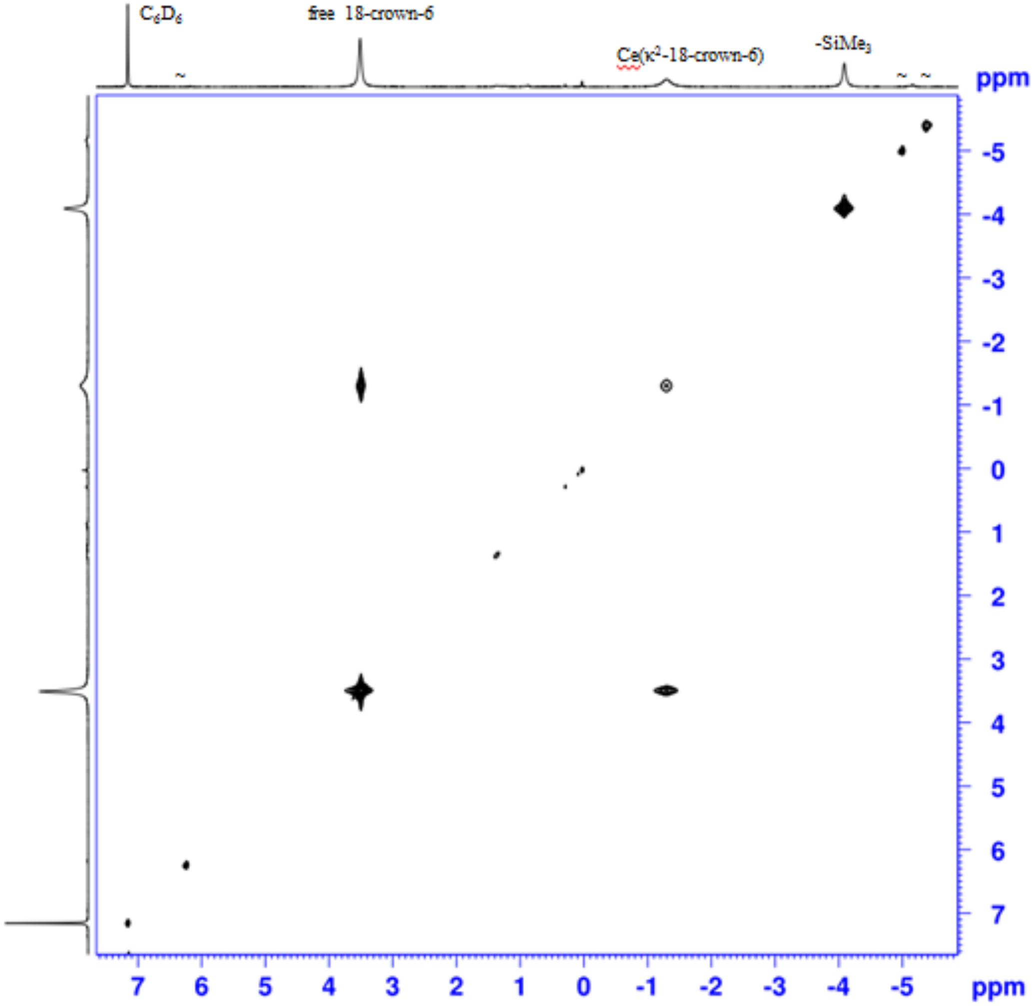


Figure S18. ^{1}H EXSY experiment of Ce(κ^2-18-crown-6)[N(SiMe$_3$)Ph^F]$_3$ **(2)** with free 18-crown-6 in C_6D_6 (each with a concentration of 1.5×10^{-2} mol•L^{-1}). The spectrum was collected with a mix time of 10 ms. The presence of off-diagonal peaks suggests a facile exchange between free and bound 18-crown-6 molecules. Note: Trace amounts of compound **3** are formed during the course of data collection (noted by ~).

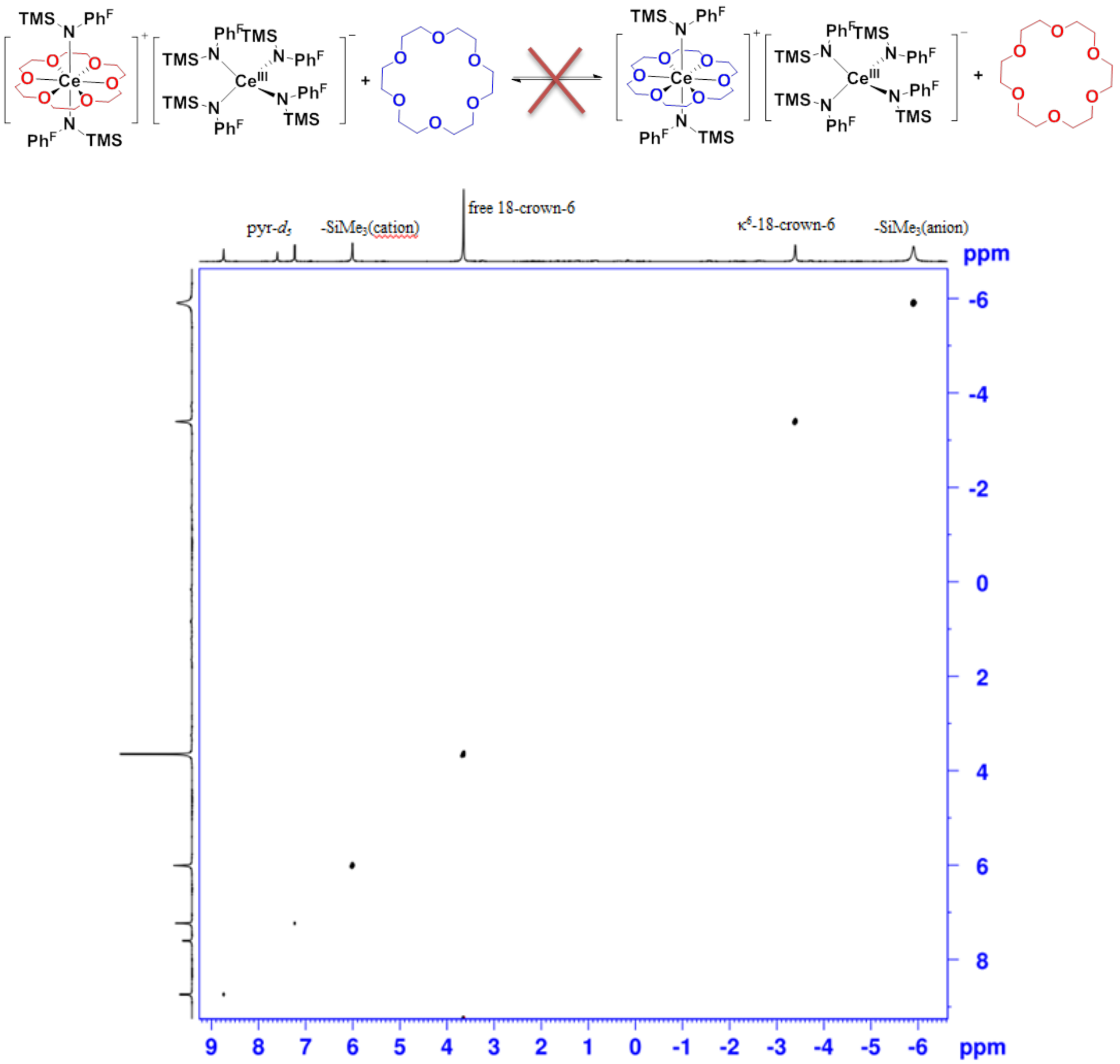


Figure S19. ^{1}H EXSY experiment of {Ce(κ^6-18-crown-6)[N(SiMe$_3$)Ph^F]$_2$}$^+${Ce[N(SiMe$_3$)Ph^F]$_4$}$^-$ **(3)** with free 18-crown-6 in pyr-d_5 (each with a concentration of 1.5×10^{-2} mol•L^{-1}). The spectrum was collected with mix time of 10 ms. Resonances are assigned in 1D spectrum. No off-diagonal peaks were observed at any of the mix times measured (0, 10, 25, 50 100, 200 ms), indicating no exchange occurring between the rigidly bound κ^6-18-crown-6 and free 18-crown-6.

References

(1) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.
(2) Oliver, A. J.; Graham, W. A. G. *J. Organomet. Chem.* **1969**, *19*, 17.
(3) *SAINT*; Bruker AXS Inc.: Madison, WI, 2009.
(4) *SHELXTL*; Bruker AXS Inc.: Madison, WI, 2009.
(5) Scheldrick, G. *TWINABS*; University of Gottingen: Gottingen, Germany, 2008.
(6) Scheldrick, G. *SADABS*; University of Gottingen: Gottingen, Germany, 2007.
(7) Sheldrick, G. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.
(8) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; Wiley, 2005; p 305-333.