Reactivity of Ce(IV) Imido Compounds with Heteroallenes

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Figure S1. The dimeric structure of carbamate **2** depicted at 30% probability level. Hydrogen atoms have been omitted for clarity. Pyridine molecules and *tert*-butyl groups are depicted using a wire model.



Figure S2. A fragment of the crystal structure of **3** shown at 30% probability level. Hydrogen atoms have been omitted for clarity, *tert*-butyl groups are depicted using a wire model.



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e S3. The dimeric unit of the crystal structure of **3** shown at 30% probability level. Hydrogen atoms have been omitted for clarity, *tert*-butyl groups are depicted using a wire model.

General Methods. All reactions and manipulations were performed under an inert atmosphere (N_2) using standard Schlenk techniques or in a drybox equipped with a molecular sieves 13X/Q5

Cu–0226S catalyst purifier system. Glassware was oven-dried for at least 3 h at 150 °C prior to use. ¹H and ¹⁹F NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer operating at 300 MHz for ¹H, 75.48 MHz for ¹³C and 282.2 MHz for ¹⁹F. ¹³³Cs NMR spectrum for **3** was recorded on a Bruker UNI 400 NMR spectrometer operating at 52.48 MHz for ¹³³Cs. ¹³C NMR spectra for complexes **3**, **4** and **5** were measured on Bruker UNI500 spectrometer working at 125.77 MHz for ¹³C. Chemical shifts were recorded in units of parts per million and referenced against residual proteo solvent peaks (¹H), characteristic solvent peaks (¹³C) or an external CFCl₃ standard (¹⁹F). Infrared spectra were measured on a PerkinElmer 1600 series spectrometer. UV-vis spectra were recorded on PerkinElmer Lamba 950 spectrometer. Elemental analyses were recorded on a Costech ECS 4010 analyzer.

Materials. THF, DME, pyridine, pentane, and hexanes were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina respectively (for pentane and hexanes). Deuterated toluene and benzene (Cambridge Isotopes) were stored over molecular sieves (4 Å) overnight prior to use. THF- d_8 (Cambridge Isotopes) was dried over sodium and distilled prior to use. Potassium bis(trimethylsilyl)amide (Sigma Aldrich) was used as received. 3,5bis(trifluoromethyl)aniline (Oakwood Chemicals) was distilled and dried over 4 Å sieves before use. 3,5-bis(trifluoromethyl)isocyanate (Acros) was used as received. Adamantyl isocyanate (Acros) was vacuum dried at room temperature for 1 hour prior to use. Carbon dioxide (Praxair, grade 3.0), was used as received. **1-K** ([K(DME)₂][Ce(TriNOx)N(3,5-(CF₃)₂C₆H₃)]),¹ **1-Cs** $([Cs(DME)_2][Ce(TriNOx)N(3,5-(CF_3)_2C_6H_3)])^{-1}$ 1-Rb ([Rb(DME)₂][Ce(TriNOx)N(3,5- $(CF_3)_2C_6H_3)$]),¹ [Ce(TriNOx)NH(3,5-(CF_3)_2C_6H_3)],¹ cesium bis(trimethylsilyl)amide², rubidium bis(trimethylsilyl)amide² and (3,5-(CF₃)₂C₆H₃NH)₂CO³ were prepared according to published reports.

Data for 2.

Synthetic procedure 1. A solution of $[Cs(DME)_2][Ce=N(3,5-(CF_3)_2C_6H_3)(TriNOx)]$ (1-Cs) (200 mg, 0.163 mmol) in pyridine (3 mL) was exposed to 1 atmosphere of carbon dioxide at room temperature for 5 minutes with stirring. The resulting red-brown solution was layered with pentane and stored at -5 °C for 3 hours, which afforded dark red crystals of $[Cs(pyr)_2][Ce(OC(O)N-(3,5-(CF_3)_2C_6H_3))(TriNOx)]$. Yield 65 mg, 0.051 mmol, 31 %.

Synthetic procedure 2. A solution of $[Ce(TriNOx)NH(3,5-(CF_3)_2C_6H_3)]$ (200 mg, 0.219 mmol) in pyridine was exposed to 1 atmosphere of carbon dioxide at room temperature for 10 minutes with stirring. Cesium bis(trimethylsilyl)amide (64 mg, 0.219 mmol, 1 equiv) was added to the reaction mixture. The resulting red-brown solution was filtered through a Celite-packed pipette. The filtrate was layered with pentane and stored at $-5^{\circ}C$ for 3 hours, yielding dark red crystals of **2**. Yield 98 mg, 35%. ¹H NMR (500 MHz, 298 K, THF-*d*₈) δ 8.72 (s, 2H, *ortho-H*-Ar^F), 8.53 (d, ³J_{HH} = 4.1 Hz, ~5H, Py), 7.65 (tt, ³J_{HH} = 7.6 Hz, ⁴J_{HH} = 2.0 Hz, 3H, Ar*H*), 7.44–7.22 (m, ~14H, Ar*H* + Py), 7.16 (t, ³J_{HH} = 7.3 Hz, 3H, Ar*H*), 6.96 (s, 1H, *para-H*-Ar^F), 4.59 (d, ²J_{HH} = 11.5 Hz, 3H, *CH*₂), 2.75 (d, ²J_{HH} = 11.5 Hz, 3H, *CH*₂), 0.73 (s, 27H, C(*CH*₃)₃).

¹³C NMR (126 MHz, THF- d_8) δ 170.1 (s, O₂CNAr^F), 156.1 (s, Ar), 151.8 (s, Ar), 150.8 (s, Py), 136.0 (s, Py), 134.1 (s, Ar), 132.7 (s, Ar), 129.8 (bq, ² $J_{CF} \sim 30$ Hz, *meta-C-*Ar^F), 129.3 (s, Ar), 128.3 (s, Ar), 126.6 (d, ³ $J_{CF} \sim 7$ Hz, *ortho-C-*Ar^F), 126.0 (q, ¹ $J_{CF} = 272$ Hz, *C*F₃), 124.9 (s, Py),

122.8 (bs, *ipso*-C-Ar^F), 108.5–108.1 (m, *para*-C-Ar^F), 65.3 (s, $C(CH_3)_3$), 61.8 (s, CH_2), 26.7 (s, $C(CH_3)_3$).

¹⁹F NMR (376 MHz, THF-*d*₈): δ –62.78.

¹³³Cs NMR (52 MHz, THF-*d*₈) δ 10.99.

UV-vis (THF, λ_{max}, nm): 258, 284, 421.

Anal. Calc'd for $(C_{52}H_{58}CeCsF_6N_7O_5) \cdot (C_5H_5N) : C, 51.56; H, 4.79; N, 8.45.$ Found: C, 51.88; H, 4.39; N, 8.39





Figure S5. ¹³C NMR spectrum for 2 in THF-*d*₈.

---62.29 ----62.78 ----63.60





*

Figure S7. ¹³³Cs NMR spectrum for 2 in THF-d8.







Figure S9. Stacked NMR spectra of (A) – independently prepared 2, (B) –solid residue from the reaction of **1-Cs** with CO₂ recrystallized from pyridine (in THF– d_8).



Figure S10. IR spectrum of 2 in a KBr pellet.

Data for 3. To the solution of **1-Rb** ([Rb(DME)₂][Ce=N(3,5-(CF₃)₂C₆H₃)(TriNOx)]) in 5 mL THF (134 mg, 0.113 mmol) was added adamantyl isocyanate (20.1 mg, 0.113 mmol, 1 equiv). The reaction mixture was stirred for 5 h at ambient temperature and the volatiles were removed at reduced pressure. The solid residue was dissolved in 1 mL DME and filtered through a plug of Celite. The resulting solution was layered with pentane and stored at -25° C for 12 h affording crystalline **3**. Yield 58 mg, 41%.

¹H NMR (500 MHz, 298 K, THF- d_8) δ 8.81 (s, 1H, Ar^F), δ 7.28 (m, ~10H, A*r*-H + Ar^F), 7.09 (t, ³J_{HH} = 7.1 Hz, 3H, ArH), δ 6.76 (s, 1H, Ar^F), 4.72 (d, ²J_{HH} = 11.2 Hz, 3H, CH₂), 3.44 (s, ~7H, CH₂ (DME)), 3.28 (s, 10H, CH₃ (DME)), 2.81 (d, ²J_{HH} = 11.4 Hz, 3H, CH₂), 2.07 (m, 10H, Ad), 1.70 (s, 5H, Ad), 0.75 (s, 27H, C(CH₃)₃).

¹⁹F NMR (376 MHz, THF-*d*₈): δ -64.77 (s, Ar^F).

¹³C NMR (126 MHz, benzene-*d*₆): δ 166.6 (s, O₂*C*(NAr_F)₂), 157.0 (s, Ar), 150.8 (s, Ar), 133.1 (s, Ar), 131.6 (s, Ar), 130.0 (q, m, *meta*-C-Ar_F), 129.0 (s, Ar), 127.2 (s, Ar), 125.9 (m, CF₃), 72.0 (s, CH₂, DME), 65.1 (s, *C*(CH₃)₃), 61.5 (s, CH₂), 58.5 (s, CH₃, DME), 45.6 (CH₂, Ad), 37.3 (CH₂, Ad), 30.6 (CH, Ad), 29.5 (*C*, Ad), 26.0 (s, C(CH₃)₃).

Anal. Calc'd for $(C_{104}H_{114}O_8N_{12}Ce_2F_{12}Rb_2) \cdot (C_4H_{10}O_2) \cdot (C_5H_{12})$: C, 54.25; H, 5.48; N, 6.72. Found: C, 53.81; H, 5.74; N, 6.55.



Figure S11. ¹H NMR spectrum for 3 in THF-*d*₈. # - proteo solvent signals.



-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 f1(ppm)

Figure S12. ¹⁹F NMR spectrum for 3 in THF-*d*₈.



Figure S13. ¹³C NMR spectrum for **3** in benzene- d_6 , * - trace pentane, # - unidentified decomposition products.

Data for 4. Reaction of 1-K with 3,5-bis(trifluoromethyl)phenyl isocyanate. To the solution of **1-K** ([K(DME)₂][Ce=N(3,5-(CF₃)₂C₆H₃)(TriNOx)]) in 5 mL THF (95 mg, 0.084 mmol, 1 eq.) was added 3,5-bis(trifluoromethyl)phenyl isocyanate (21.4 mg, 0.084 mmol, 1 equiv). The reaction mixture was stirred for 4 h at ambient temperature and the volatiles were removed at reduced pressure. NMR investigation of the solid residue allowed detection of **4** as the main reaction product.

Independent synthesis. To the solution of $(3,5-(CF_3)_2C_6H_3NH)_2CO^3$ (217 mg, 0.448 mmol, 1 equiv) in THF was added potassium bis(trimethylsilyl)amide (179 mg, 0.896 mmol, 2 equiv). The resulting yellow solution was stirred for 1 h, and the volatiles were removed at reduced pressure. Then a suspension of [Cel(TriNOx)] (400 mg, 0.493 mmol, 1.1 eq) in THF (2 mL) was added to the yellow solid. The resulting solution was stirred for 1 h at ambient temperature and filtered through a Celite-packed pipette. The volatiles were removed at reduced pressure, and the solid residue was redissolved in DME (2 mL) and layered with pentane (15 mL). Storing the solution at $-25^{\circ}C$ afforded dark brown crystals of **4**. Yield 330 mg, 53%.

¹H NMR (400 MHz, 298 K, toluene-*d*₈): δ 7.72 (s, 3H), 7.43–7.23 (m, ~15H, Ar*H* + Ar^F-*H*), 4.63 (d, ²*J*_{HH} = 11.8 Hz, 3H, C*H*₂), 3.50 (s, 8H, DME, C*H*₂), 3.35 (s, 12 H, DME, C*H*₃), 2.57 (d, ²*J*_{HH} = 11.6 Hz, 3H, C*H*₂), 0.82 (s, 27H, C(C*H*₃)₃).

¹⁹F NMR (376 MHz, toluene-*d*₈) δ –62.71.

¹³C NMR (126 MHz, benzene-*d*₆): δ 170.8 (s, O₂*C*(NAr_F)₂), 154.3 (s, Ar), 150.3 (s, Ar), 133.0 (s, Ar), 132.2 (s, Ar), 130.9 (q, ₂*J*_{CF} = 32 Hz, *meta*-*C*-Ar_F), 128.5 (s, Ar), 126.9 (s, Ar), 125.1 (q, ₁*J*_{CF} = 273 Hz, *C*F₃), 123.4 (bs, *ortho*-*C*-Ar_F), 120.6 (bs, *ipso*-*C*-Ar_F), 110.7 (bs, *para*-*C*-Ar_F), 72.0 (s, *C*H₂, DME), 65.6 (s, *C*(CH₃)₃), 61.4 (s, *C*H₂), 58.7 (s, *C*H₃, DME), 26.1 (s, *C*(*C*H₃)₃).

Anal. Calc'd for $C_{58}H_{71}CeF_{12}KN_6O_8$: C, 50.19; H, 5.16; N, 6.06. Found: C, 50.44; H, 5.12; N, 6.14



Figure S14. ¹H NMR spectrum for **4** in toluene-*d*₈. # - proteo solvent signals.



Figure S15. ¹³C NMR spectrum for **4** in benzene- d_6 , * - trace pentane.



Figure S16. ¹⁹F NMR spectrum for **4** (in toluene- d_{θ} , * - trace decomposition products).



Figure S17. Stacked NMR spectra of (A) – independently prepared 4, (B) – crude reaction mixture of **1-K** with 3,5-bis(trifluoromethyl)phenyl isocyanate (in toluene– d_8).



Figure S18. IR spectrum of 4 in a KBr pellet.

X-ray Crystallography.

X-ray intensity data were collected on a Bruker APEXII⁴ CCD area detector or a Bruker APEXIII⁵ D8QUEST CMOS area detector, both employing graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 100(1) K. Rotation frames were integrated using SAINT,⁶ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXT program package⁷ for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS or TWINABS.⁸ Refinement was performed by full-matrix least squares based on F^2 using SHELXL-2015.⁹ All of the reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Computational details

All molecules were calculated in full with no simplification of the ligands. The Stuttgart-Dresden-Bonn Relativistic large Effective Core Potential (RECP) was used to represent the inner shells of Ce.^{10, 11} The associated basis set¹² augmented by an f-polarization function (α = 1.000) was used to represent the valence orbitals. Fluorine has also been represented by an RECP,¹³ with the associated basis set augmented by a d-polarization Gaussian function (α = 0.421). The atoms C, O, N and H were represented by an all-electron 6-31G(d,p) basis set.¹⁴⁻¹⁶ Calculations were carried out at the DFT(B3PW91) level¹⁷ with Gaussian 09.¹⁸ The nature of the extrema (minimum or transition state) was established with analytical frequencies calculations and the intrinsic reaction coordinate (IRC) was followed to confirm that the transition states connect to reactants and products. The NBO analysis¹⁹ was also carried out. The cartesian coordinates for the optimized structures are reported below and in an appended .xyz file.



Figure S19. DFT-optimized bimetallic reaction pathway for the formation of 4⁻ from 1⁻.

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