Inorganic Chemistry

Small-Scale Metal-Based Syntheses of Lanthanide Iodide, Amide, and Cyclopentadienyl Complexes as Analogues for Transuranic Reactions

Cory J. Windorff,^{†,‡} Megan T. Dumas,[†][®] Joseph W. Ziller,[†] Andrew J. Gaunt,[‡][®] Stosh A. Kozimor,^{*,‡} and William J. Evans^{*,†}[®]

[†]Department of Chemistry, University of California, Irvine, California 92697, United States

[‡]Los Alamos National Laboratory, Los Alamos, New Mexico 87544, United States

Supporting Information

ABSTRACT: Small-scale reactions of the Pu analogues La, Ce, and Nd have been explored in order to optimize reaction conditions for milligram scale reactions of radioactive plutonium starting from the metal. Oxidation of these lanthanide metals with iodine in ether and pyridine has been studied, and $LnI_3(Et_2O)_x$ (1-Ln; x = 0.75-1.9) and $LnI_3(py)_4$ (2-Ln; py = pyridine, NC₃H₅) have been synthesized on scales ranging from 15 mg to 2 g. The THF adducts $LnI_3(THF)_4$ (3-Ln) were synthesized by dissolving 1-Ln in THF. The viability of these small-scale samples as starting materials for amide and



cyclopentadienyl f-element complexes was tested by reacting $KN(SiMe_3)_2$, KCp' ($Cp' = C_5H_4SiMe_3$), KCp'' ($Cp'' = C_5H_4SiMe_3$), and KC_5Me_4H with **1-Ln** generated in situ. These reactions produced $Ln[N(SiMe_3)_2]_3$ (**4-Ln**), Cp''_3Ln (**5-Ln**), Cp''_3Ln (**6-Ln**), and (C_5Me_4H)₃Ln (**7-Ln**), respectively. Small-scale samples of Cp'_3Ce (**5-Ce**) and Cp'_3Nd (**5-Nd**) were reduced with potassium graphite (KC_8) in the presence of 2.2.2-cryptand to check the viability of generating the crystallographically characterizable Ln^{2+} complexes [K(2.2.2-cryptand)][Cp'_3Ln] (**8-Ln**; Ln = Ce, Nd).

INTRODUCTION

Recent developments in reductive f-element chemistry have shown that the +2 oxidation state is available in isolable, crystallographically characterizable molecular complexes of La, Ce, Pr, Gd, Tb, Ho, Er, Lu, $^{1-7}$ U, 8,9 and Th 10 according to eq 1.



R = H; M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu, U

Following these discoveries, attempts to synthesize analogous $Np^{2+11,12}$ and Pu^{2+13} complexes were made. The results reported here were used to aid in the synthesis of the first complex of Pu^{2+} , $[K(2.2.2\text{-cryptand})][Cp''_{3}Pu]$ ($Cp'' = C_{s}H_{3}(SiMe_{3})_{2}$ -1,3), which was isolated according to eq 1.¹³

 $C_5H_3(SiMe_3)_2$ -1,3), which was isolated according to eq 1.¹³ The synthesis of complexes of ²³⁹Pu is challenging due to the radioactivity of this isotope (less radioactive ²⁴²Pu is occasionally utilized but is more scarcely available). Small-scale reactions are often required for both logistical and safety reasons. Most fundamental chemical studies with Pu are conducted in radiological (not nuclear) facilities, placing constraints on radioisotope inventory limits. Therefore, it is desirable to minimize the number of reactions run and conserve the amount of plutonium used. This requires that preoptimization of reaction conditions is important. Typically, individual reactions are performed on a scale of less than 50 mg of metal content $(0.21 \text{ mmol of }^{239}\text{Pu})$, and less than 20 mg $(0.084 \text{ mmol }^{239}\text{Pu})$ is commonplace. One method to determine optimum reaction conditions is to test analogous reactions with nonradioactive analogues. Since trivalent rare-earth metals are the closest analogs of trivalent transuranic elements, their small-scale reactions can provide insight on how to best handle the chemistry of the radioactive actinides.

To aid in the synthesis of new transuranic complexes, the synthesis of several classes of lanthanide complexes was examined on a small scale starting from the metal, since this is an available form of plutonium which was the starting material for the Pu²⁺ synthesis.¹³ Ce and Nd were selected as representative analogues for Pu due to their similar ionic radii (La³⁺ 1.03 Å, Np³⁺ 1.01 Å, Ce³⁺ 1.01 Å, Pu³⁺ 1.00 Å, and Nd³⁺ 0.983 Å for coordination number 6).¹⁴ Some La samples were also examined to facilitate characterization by NMR spectroscopy since La³⁺ is diamagnetic. The synthesis of lanthanide iodide complexes was pursued because metal iodide precursors are common in actinide chemistry^{15–29} with UI₃L_x, UI₄L_x, and ThI₄L_x being most commonly synthesized from their elemental forms.^{15–20} Small-scale syntheses of Ln[N(SiMe₃)₂]₃, Cp'₃Ln (Cp' = C₅H₄SiMe₃), Cp''₃Ln, and (C₅Me₄H)₃Ln were examined, since these are well established classes of f-element

Received: August 2, 2017

complexes and include precursors to complexes of new +2 ions. $^{1-10,12,13,30}$

The reactions and complexes reported here both have precedent in the literature. Lanthanide triiodides have been synthesized in many ways, both in solution and in the solid state.³¹ These include synthesis from Ln₂O₃ oxides with NH₄I at elevated temperature,³² from Ln_2O_3 or Ln metal with HI, followed by dehydration with $NH_4I_3^{33-36}$ from the metal and iodine, 37,38 diiodoethane, iodoform, ${}^{39-42}$ AlI₃, and HgI₂.^{21,31,43-45} Lanthanide triiodides can be dissolved in THF to form solvated species that crystallize in a variety of forms, including $LnI_3(THF)_4$ (Ln = La, Pr, Ce), 37,46,47 $[LnI_2(THF)_5][LnI_4(THF)_2]$ (Ln = Nd, Sm, Gd, Dy, Er, Tm, Yb, Y), ^{37,48-53} $[LnI_2THF_5][I]$, ⁵¹ and $[LnI_2(THF)_5][I_3]$ (Ln = La,⁵¹ Yb³⁸). While numerous THF solvates of LnI₃ have been characterized, there are fewer reports with pyridine and ether solvates: to our knowledge, these are limited to $[LnI_2(py)_5]$ - $[I]^{38}$ and the plutonium complex $[PuI_2(THF)_4(py)][I_3]^2$. LnI₂ dissolves in pyridine to form $LnI_3(py)_{xy}$ but only the characterization of SmI₃(py)₄ has been reported.⁵⁴⁻⁵⁸ Ln[N-(SiMe₃)₂]₃, Cp'₃Ln, Cp"₃Ln, and (C₅Me₄H)₃Ln are typically synthesized from LnCl₃(THF)_x and an alkali-metal salt of the ligand, though some syntheses have utilized $Ln(O_3SCF_3)_3$ (Ln = $La^{59}_{,59}$ Ce⁶⁰) or, in the case of cyclopentadienyl ligands, protonolysis from Ln[N(SiMe₃)₂]₃.^{61,62} Iodides have been used to synthesize $\{ [C_5H_3(EMe_3)_2]_2LnI \}_2$ (Ln = La, Ce; E = C, Si)⁶³ and Cp["]₂LaI(THF).⁶³

Herein we report the small-scale synthesis of LnI_3L_x solvates including $\text{LnI}_3(\text{OEt}_2)_x$ (1-Ln; x = 0.75-1.9) and $\text{LnI}_3(\text{py})_4$ (2-Ln), the dissolution of 1-Ln in THF to form $\text{LnI}_3(\text{THF})_4$ (3-Ln), and the use of 1-Ln to form common precursors such as $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ (4-Ln), $\text{Cp'}_3\text{Ln}$ (5-Ln), $\text{Cp''}_3\text{Ln}$ (6-Ln), and $(\text{C}_5\text{Me}_4\text{H})_3\text{Ln}$ (7-Ln) (Ln = La, Ce, Nd). The purpose of this study was to evaluate the yield and purity available from these reactions *on a small scale* and the viability of these small-scale samples as starting materials. This research supported the isolation of the first molecular example of a Pu^{2+} complex¹³ and should be applicable to other transuranic studies.⁶⁴⁻⁷⁵

EXPERIMENTAL SECTION

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques under an argon or dinitrogen atmosphere. Solvents (THF, Et₂O, toluene, hexane, and pentane) were sparged with UHP argon (Praxair) and dried by passage through columns containing Q-5 and molecular sieves prior to use. Pyridine was dried over sodium, degassed by three freeze-pump-thaw cycles, and distilled. All ethereal solvents and pyridine were stored over activated 4 Å molecular sieves. Deuterated NMR solvents (Cambridge Isotopes) were dried over sodium benzophenone ketyl, degassed by three freeze-pump-thaw cycles, and vacuum-transferred before use. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker GN500 MHz or CRYO500 spectrometer operating at 499.3 and 125 MHz, respectively, at 298 K unless otherwise stated. ¹H and ${}^{13}C{}^{1}H{}$ NMR spectra were referenced internally to solvent resonances. Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS elemental analyzer. Lanthanum powder under oil (99.9% REO, Strem), was pumped into the glovebox overnight, decanted, washed with hexane several times, and dried under vacuum. Ce and Nd metal (99.5% REO, Stanford Materials Corporation) were pumped into the glovebox, filed to remove any oxide layer, and filed further to form shavings. An Nd₂Fe₁₄B magnet (United Nuclear) was passed over the filings to remove any iron particles that detached from the file. Iodine (99.8%, Acros) was sublimed before use, and 2.2.2-cryptand (Sigma-Aldrich) was placed under vacuum (10^{-3} Torr) before use. KN(SiMe₃)₂ (Aldrich) was dissolved in toluene, centrifuged, decanted, and dried under reduced pressure. Cp'₃Pr,⁴ UI₃(py)₄ (2-U),¹⁶ KC₈,⁷⁶ and KC₅Me₄H¹⁸ were prepared according to the literature. KCp'' was prepared from KCp'₃ by following the literature preparation.⁷⁷ UI₃(py)₄ (2-U) was crystallized by diffusion of ether into a pyridine solution at ambient glovebox temperature.

Lal₃(OEt₂)_x (1-La). Solid iodine (1.400 g, 5.500 mmol) was added to a suspension of lanthanum powder (0.500 g, 3.60 mmol) in Et₂O (40 mL) in a 100 mL round-bottom flask and stirred for 4 days. Over the course of the reaction, a gray powder precipitated, a pale orange color persisted in solution, and there was no evidence of remaining metal. The mixture was filtered on a 350 mL medium frit and washed with Et₂O (2 × 20 mL) and hexane (2 × 20 mL) until the filtrate was colorless. The gray solids were transferred to a tared scintillation vial and held under reduced pressure (10^{-3} Torr) for 4 h to yield a gray powder characterized as LaI₃(OEt₂)_{1.6} (1.75 g, 76%, based on La) by elemental analysis. Anal. Calcd for LaI₃(OEt₂)_{1.6}: C, 12.45; H, 2.61. Found: C, 12.39; H, 2.46. A sample placed under 10^{-6} Torr for 60 h analyzed as LaI₃(OEt₂)_{0.88}. Anal. Calcd for LaI₃(OEt₂)_{0.88}: C, 7.29; H, 1.53. Found: C, 7.24; H, 1.29.

 $\text{Cel}_3(\text{OEt}_2)_{\text{X}}$ (1-Ce). Following the procedure for 1-La, iodine (1.240 g 4.886 mmol) was combined with Ce shavings (0.450 g, 3.22 mmol) to yield a gray powder characterized as $\text{Cel}_3(\text{OEt}_2)_{1.9}$ (1.82 g, 89%, based on Ce) by elemental analysis. Anal. Calcd for $\text{Cel}_3(\text{OEt}_2)_{1.9}$: C, 13.80; H, 2.89. Found: C, 13.93; H, 2.63. A sample placed under 10^{-6} Torr for 60 h analyzed as $\text{Cel}_3(\text{OEt}_2)_{0.75}$. Anal. Calcd for Cela(for CeI_3(OEt_2)_{0.75}: C, 6.25; H, 1.31. Found: C, 6.23; H, 1.05.

 $Ndl_3(OEt_2)_x$ (1-Nd). Following the procedure for 1-La, iodine (0.752 g, 2.96 mmol) was combined with Nd shavings (0.284 g, 1.97 mmol) to yield a pale blue powder characterized as $NdI_3(OEt_2)_{1.5}$ (860 mg, 69%, based on Nd) as determined by elemental analysis. Anal. Calcd for $NdI_3(OEt_2)_{1.5}$: C, 11.33; H, 2.38. Found: C, 11.23; H, 2.04. A sample placed under 10^{-6} Torr for 60 h was analyzed as $NdI_3(OEt_2)_{0.87}$. Anal. Calcd for $NdI_3(OEt_2)_{0.87}$: C, 7.07; H, 1.48. Found: C, 7.24; H, 1.29.

Lal₃(py)₄ (2-La). When a solution of iodine (141 mg, 0.554 mmol) in pyridine (4 mL) was added to a suspension of La powder (51 mg, 0.37 mmol) in pyridine (2 mL), the mixture quickly turned black and was stirred for 2 days. The mixture was centrifuged to remove a small amount of black material, and the volatiles were removed under reduced pressure to yield a brown oil. The oil was triturated with Et₂O, and the supernatant was decanted and dried under reduced pressure to yield LaI₃(py)₄ (2-La) as a brown solid (265 mg, 86%). Colorless X-ray-quality crystals were grown by diffusion of Et₂O into a concentrated pyridine solution at -15 °C. ¹H NMR (C₆D₆): δ 9.06 (br s, *o-py*, 8H), 6.79 (t, $J_{\rm H} = 7.0$ Hz, *p-py*, 4H), 6.51 (m, *m-py*, 8H). ¹³C{¹H} NMR (C₆D₆): δ 150.63 (*o-py*), 136.61 (*p-py*), 123.78 (*m-py*). Anal. Calcd for LaI₃(py)_{3.5}: C, 26.39; H, 2.21; N, 6.16. Found: C, 26.64; H, 2.41; N, 6.12.

Cel₃(**py**)₄ (**2-Ce**). Following the procedure for **2-La**, iodine (254 mg, 1.08 mmol) was combined with Ce shavings (100 mg, 0.714 mmol) to yield CeI₃(py)₄ (**2-Ce**; 512 mg, 57%) as a brown solid. ¹H NMR (C₆D₆): δ 9.49 (br s, *o-py*, 8H), 7.54 (br s, *p-py*, 4H), 7.39 (br s, *m-py*, 8H). Anal. Calcd for C₁₅H₁₅N₃I₃Ce: C, 23.76; H, 1.99; N, 5.54. Found: C, 24.07; H, 1.98; N, 5.22.

Ndl₃(**py**)₄ (**2-Nd**). Following the procedure for **2-La**, iodine (135 mg, 0.530 mmol) was combined with Nd shavings (49 mg 0.34 mmol) to yield NdI₃(py)₄ (259 mg 91%) as a brown solid. ¹H NMR (C₆D₆): δ 9.7 (br s, *p*-*py*, 4H) 7.7 (br s, *py*, 8H). Only two of the expected resonances were observed due to the paramagnetism of the Nd³⁺ ion. Anal. Calcd for C₁₅H₁₅N₃I₃Nd: C, 23.64; H, 1.98; N, 5.51. Found: C, 23.71; H, 2.26; N, 5.16.

Lal₃(THF)₄ (3-La). As an alternative to the published procedures for 3-La, 37,41,78,79 LaI₃(OEt₂)_{1.6} (12 mg, 0.019 mmol) was dissolved in THF (3 mL) to give a colorless solution. This was filtered, and the volatiles were removed under reduced pressure to give LaI₃(THF)₄ (15 mg, quantitative) as a white solid. Colorless X-ray-quality crystals of 3-La were grown over 2 weeks from a hot THF solution cooled to -30 °C, which matched the unit cell of LaI₃(THF)₄, 47 ¹H NMR (C₆D₆): δ 3.77 (s, *THF*), 1.40 (s, *THF*). ¹³C{¹H} NMR (C₆D₆): δ

69.50 (*THF*), 25.65 (*THF*). When **3-La** was crystallized from hot toluene cooled to ambient glovebox temperature, colorless crystals of $[LaI_2(THF)_5][LaI_4(THF)_2]$ (**3-La**') were isolated after 1 week and characterized by X-ray crystallography.

Cel₃(THF)₄ (3-Ce). As an alternative to the published procedures, ^{37,45,46,78,79} following the procedure for **3-La**, Cel₃(OEt₂)_{0.66} (13 mg, 0.023 mmol) was dissolved in THF (3 mL) to give Cel₃(THF)₄ (18 mg, 95%) as a white solid. Colorless X-ray-quality crystals of **3-Ce** were grown over 2 weeks from a hot THF solution cooled to $-30 \,^{\circ}$ C, which matched the unit cell of Cel₃(THF)₄.⁴⁶ ¹H NMR (C₆D₆): δ 68.23 (*THF*), 26.06 (*THF*).

NdI₃(THF)₄ (3-Nd). As an alternative to the published procedure^{42,80} following the procedure for **3-La**, NdI₃(OEt₂)_{0.66} (13 mg, 0.023 mmol) was dissolved in THF (3 mL) to give NdI₃(THF)₄ (16 mg, quantitative) as a pale blue solid. Pale blue X-ray-quality crystals of **3-Nd** were grown over 2 weeks from a hot THF solution cooled to -30 °C, which matched the unit cell of NdI₃(THF)₄.⁸¹ ¹H NMR (C₆D₆): δ 3.78 (s, br $\nu_{1/2}$ 115 Hz, *THF*), 1.60 (s, br $\nu_{1/2}$ 100 Hz, *THF*).

La[N(SiMe₃)₂]₃ (4-La). As an alternative to the published procedure,⁸² a toluene (2 mL) solution of KN(SiMe₃)₂ (60 mg, 0.30 mmol) was added to a suspension of LaI₃(OEt₂)_{1.6} (48 mg 0.075 mmol) in toluene (1 mL). The solution was stirred overnight, volatiles were removed under reduced pressure, and the product was extracted in pentane. Removal of the volatiles under reduced pressure yielded La[N(SiMe₃)₂]₃ as a white solid (44 mg, 95%) as confirmed by ¹H NMR analysis.⁸² ¹H NMR (C₆D₆): δ 0.28 (s, SiMe₃, 54H). ¹³C{¹H} (C₆D₆): δ 3.67 (SiMe₃).

Ce[N(SiMe₃)₂]₃ (4-Ce). As an alternative to the published procedure, ⁸² KN(SiMe₃)₂ (44 mg, 0.22 mmol) was added to a stirred slurry of CeI₃(OEt₂)_{0.66} (40 mg, 0.071 mmol) in toluene (2 mL); the solution quickly turned bright yellow and was stirred overnight. Volatiles were removed under reduced pressure, and the product was extracted into pentane and dried under reduced pressure to yield a yellow solid identified as Ce[N(SiMe₃)₂]₃ (30 mg, 70%) by ¹H NMR spectroscopy.⁸² ¹H NMR (C₆D₆): δ –3.3 (s, SiMe₃, 54H).

Nd[N(SiMe₃)₂]₃ (4-Nd). As an alternative to the published procedure, ⁸² following the procedure for 4-Ce, KN(SiMe₃)₂ (40 mg, 0.20 mmol) was combined with NdI₃(OEt₂)_{0.66} (40 mg, 0.068 mmol) to give a blue solid identified as Nd[N(SiMe₃)₂]₃ (30 mg, 71%) by ¹H NMR spectroscopy. ⁸² ¹H NMR (C₆D₆): δ -6.1 (s, SiMe₃, 54H).

 $Cp'_{3}Ce$ (5-Ce). A solution of KCp' (71 mg, 0.40 mmol) in Et₂O (2 mL) was added to a stirred slurry of CeI₃(OEt₂)_{1.5} (70 mg, 0.134 mmol). The solution quickly turned bright blue, and a white precipitate was observed. The blue mixture was stirred overnight and centrifuged to remove white insoluble material, presumably KI. The supernatant was dried under reduced pressure, extracted into pentane, filtered, and dried under reduced pressure to give a royal blue solid, identified as Cp'₃Ce (29 mg, 39%) by ¹H NMR spectroscopy.⁶¹

In Situ Synthesis of 5-Ce. Iodine (30 mg, 0.12 mmol) was added to an Et₂O (3 mL) suspension of Ce shavings (11 mg, 0.082 mmol). After the mixture was stirred for 24 h, the solution was colorless and a pale white precipitate was present. The volume was reduced to 0.5 mL under reduced pressure, and a solution of KCp' (46 mg, 0.26 mmol) in Et₂O (2 mL) was added. A blue solution quickly formed along with white insoluble material. The mixture was stirred overnight and centrifuged to remove the white insoluble material, presumably KI. The filtrate was dried under reduced pressure, extracted into pentane, filtered, and dried under reduced pressure to give a blue solid, identified as Cp'₃Ce (17 mg, 38% based on Ce metal) by ¹H NMR spectroscopy.⁶¹

 Cp'_3Nd (5-Nd). Iodine (36 mg, 0.14 mmol) was added to a suspension of Nd shavings (15 mg, 0.10 mmol) in Et₂O (3 mL). After the mixture was stirred for 24 h, the solution was colorless and a pale blue precipitate was present. The volume was reduced to 0.5 mL under reduced pressure, and a solution of KCp' (55 mg, 0.31 mmol) in Et₂O (2 mL) was added. A blue solution quickly formed, which turned to mint green after approximately 3 h with the formation of white insoluble material, presumably KI. The mixture was stirred overnight

and centrifuged to remove the white insoluble material. The filtrate was dried under reduced pressure, extracted into pentane, filtered, and dried under reduced pressure to give a mint green solid, identified as Cp'₃Nd (40 mg, 72%) by ¹H NMR spectroscopy.⁸³

Cp["] **3Ce** (6- \overline{Ce}). As an alternative to the published procedure, ^{60,61,84} iodine (30 mg, 0.12 mmol) was added to a stirred suspension of Ce shavings (11 mg, 0.082 mmol) in Et₂O (2 mL) and stirred for 2 days, during which time a colorless solid precipitated. Volatiles were removed under reduced pressure, washed with several portions of hexane, and dried under reduced pressure. After the addition of a solution of KCp^{''} (65 mg, 0.26 mmol) in Et₂O (3 mL), the solution quickly became green. Within 15 min the solution turned dark blue and a white solid precipitated, presumably KI. The mixture was stirred overnight, and the volatiles were removed under reduced pressure. The product was extracted into hexane, filtered, and dried under reduced pressure to give a royal blue solid identified as Cp["]₃Ce (35 mg, 55%) by ¹H NMR spectroscopy.⁶¹

 $Cp''_{3}Nd$ (6-Nd). As an alternative to the published procedure, ^{62,84,85} following the procedure for 6-Ce solid iodine (41 mg, 0.162 mmol) was combined with Nd shavings (13 mg 0.090 mmol) and KCp'' (70 mg, 0.28 mmol) to give a green solid identified as Cp''_{3}Nd (55 mg, 80%) by ¹H NMR spectroscopy.^{29,62,84}.

 $(C_5Me_4H)_3La$ (7-La). As an alternative to the published procedure, ⁸⁶ solid KC₅Me₄H (51 mg, 0.32 mmol) was added to a toluene (5 mL) suspension of LaI₃(OEt₂)_{1.66} (49 mg, 0.076 mmol); the mixture quickly turned yellow and was stirred overnight. The mixture was then centrifuged to remove white solids (presumably KI and excess KC₅Me₄H) and was dried under reduced pressure to give a yellow solid identified as (C₅Me₄H)₃La (36 mg 94%) by ¹H NMR spectroscopy.⁸⁶

 $(C_5Me_4H)_3Ce$ (7-Ce). As an alternative to the published procedure,⁸⁷ following the procedure for 7-La, KC₅Me₄H (51 mg, 0.32 mmol) was combined with CeI₃(OEt₂)_{1.5} (49 mg, 0.078 mmol), to give a blue solid identified as (C₃Me₄H)₃Ce (30 mg, 76%) by ¹H NMR spectroscopy.⁸⁸

 $(C_5Me_4H)_3Nd$ (7-Nd). As an alternative to the published procedure,⁸⁹ following the procedure for 7-La, KC_5Me_4H (35 mg, 0.22 mmol) was combined with $NdI_3(OEt_2)_{0.66}$ (40 mg, 0.070 mmol) to give a green solid identified as $(C_5Me_4H)_3Nd$ (25 mg, 71%) by ¹H NMR spectroscopy.⁸⁹ X-ray-quality crystals were grown from a hot toluene solution cooled to -30 °C.

[K(2.2.2-cryptand)][Cp'₃Ce]·THF (8-Ce). This synthesis follows the published procedure.⁵ THF (0.5 mL) was added to a blue Et₂O (1.5 mL) solution of Cp'₃Ce (20 mg, 0.036 mmol) and crypt (16 mg, 0.042 mmol). This immediately formed a yellow solution consistent with the formation of Cp'₃Ce(THF).⁹⁰ A pipet was packed with a glass fiber circle and KC_8 (40 mg, 30 mmol) to form a flash reduction column. The yellow solution, KC8 reduction column, THF, Et2O, an empty 20 mL glass scintillation vial, and several glass pipettes were cooled to -30 °C for 2 h. The cold solution was quickly passed through the reduction column into the new vial, causing an instant color change to dark purple. The column was washed with cold THF until the effluent was colorless (1.5 mL), and the solution was returned to a-30 °C freezer. After 2 h, the solution was carefully layered with cold Et₂O (4 mL) and returned to a -30 °C freezer. Within 1 day, dark purple-black X-ray-quality crystals formed. A sample was separated for unit cell analysis, the colorless mother liquor was decanted, and the sample was washed with pentane $(3 \times 1 \text{ mL})$ and dried under reduced pressure. The purple crystals were identified as [K(2.2.2-cryptand)][Cp'₃Ce]·THF (24 mg, 65% crystalline yield) by unit cell analysis.

[K(2.2.2-cryptand)][Cp'₃Nd]·THF (8-Nd). Similar to the published procedures⁵ and following the procedure for **8-Ce**, Cp'_3Nd (25 mg, 0.046 mmol) and crypt (18 mg, 0.048 mmol) were dissolved in Et₂O and THF, which caused a color change from green to pale blue. Following the reduction protocol above, dark purple-black crystals were isolated and identified as [K(2.2.2-cryptand)][Cp'₃Nd]·THF (35 mg, 73% crystalline yield) by unit cell analysis.⁵

[K(2.2.2-cryptand)][Cp'₃Pr]·THF (8-Pr). Similar to the published procedures⁴ and following the procedure for 8-Ce, $Cp'_{3}Pr$ (19 mg,

Inorganic Chemistry

0.035 mmol) and crypt (13 mg, 0.036 mmol) were dissolved in Et₂O and THF, which caused a color change from bright yellow to pale yellow. Following the reduction protocol above, dark purple-black crystals were isolated and identified as [K(2.2.2-cryptand)][Cp'_3Pr]·THF (24 mg, 65% crystalline yield) by unit cell analysis.⁴

X-ray Data Collection, Structure Determination, and Refinement. Crystallographic details for compounds (CCDC number) 2-La (1559160), 2-U (1559168), 3-La' (1559161), and 7-Nd (1559169) are summarized in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis. Lnl₃(Et₂O), (1-Ln). Addition of iodine, either as a solid or in solution, to a suspension of lanthanide metal shavings in diethyl ether deposited solvated lanthanide triiodides, $LnI_3(Et_2O)_r$ [1-Ln; Ln = La, Ce (colorless) Nd (blue)] as powders over the course of 1-4 days depending on the scale. Elemental analysis was used to quantify the average level of solvation in the powders, which varied in the range x =1.5–1.9. After these solids were exposed to high vacuum (10^{-6}) Torr) for 60 h, the solvation level was reduced to x = 0.75 - 0.88as determined by elemental analysis. The complexes were isolated in 70-80% yields and are easily isolable by centrifugation or can be used in situ (see below). A slight excess of iodine was used, which can be removed by washing with hexane or pentane. Reactions could also be performed with a deficiency of iodine, in which case unreacted metal was present within the lanthanide triiodide product. The excess metal could be removed with tweezers or later after reaction with either a potassium amide or cyclopentadienyl reagent during the filtration step which removes KI.

 $LnI_3(py)_4$ (2-Ln). When oxidations were performed in pyridine (py), the solutions quickly became brown. After the mixtures were stirred for 2-4 days and filtered or centrifuged, the products were isolated as brown oils that could be triturated with Et_2O to yield $LnI_3(py)_4$ (2-Ln; Ln = La, Ce, Nd), as brown powders. These materials were characterized by ¹H and ¹³C NMR spectroscopy where possible, along with elemental analysis and X-ray crystallography. The ¹H and ¹³C NMR resonances in 2-La were shifted from their free pyridine values in C₆D₆.⁹¹ The ¹H and ¹³C NMR resonances of **2-Ce** and **2-Nd** were shifted and broadened due to the paramagnetism of the metals. As in the Et₂O reactions, a small excess of I₂ was used, which was subsequently washed away with hexane. Excess iodine has the potential to form triiodide products like those observed for $[PuI_2(THF)_4(py)][I_3]^{11}$ and $[LnI_2(THF)_5][I_3]$ $(Ln = La, {}^{30} Yb^{29})$; however, no evidence of such products was observed here. The 2-Ln complexes are slightly soluble in benzene and toluene. If the synthesis is conducted with a deficiency of iodine, the excess metal can be removed by filtration from a solution of 2-Ln.

Diffusion of Et₂O into concentrated pyridine solutions allowed the isolation of single crystals of **2-La** and **2-U**^{16,92} suitable for X-ray crystallography. Crystals of the uranium analogue were also obtained to confirm the synthesis and the method of crystallization with the structure.⁹² These crystallizations were performed with less than 30 mg of material to better mimic the conditions of transuranic chemistry.

Complex 2-La adopts a seven-coordinate pentagonalbipyramidal geometry with two iodide ligands in the axial positions and one in the equatorial position. The pyridine ligands occupy the other equatorial positions (Figure 1). This is a typical structure for f-element trihalide tetrasolvates.^{36,37,46,47,58,92–96} The La–I bond distances in 2-La are similar to those in LaI₃(THF)₄,⁴⁷ while the 2.689(4) Å average



Figure 1. Thermal ellipsoid plot of LaI₃(py)₄ (**2-La**) drawn at the 50% probability level. The corresponding uranium complex **2-U** is isomorphous. Selected bond distances (Å) and angles (deg): **2-La**, La–I_{ax} 3.1543(3), 3.1522(3), La–I_{equ} 3.1943(3), La–N_{avg} 2.689(4), I_{ax}–La–I_{ax} 177.168(9), I_{ax}–La–I_{equ} 86.938(8), 95.088(9); **2-U**, U–I_{ax} 3.1311(5), 3.1317(5), U–I_{equ} 3.1718(4), U–N_{avg} 2.653(4), I_{ax}–U–I_{ax} 177.313(8), I_{ax}–U–I_{equ} 86.75(1), 95.574(1).

La–N(py) distance is larger than the 2.54(1) Å average La– O(THF) distance in LaI₃(THF)₄ (Table S1 in the Supporting Information). The La–N(py) average distance in **2-La** is longer than the analogous 2.605(8) Å distance in LaCl₃(py)₄,⁹⁴ which is consistent with the larger size of iodide vs chloride.

The corresponding uranium complex synthesized here, $UI_3(py)_4$ (2-U), crystallized in the $P2_1/n$ space group and is isomorphous with 2-La. A *Pbca* structure of 2-U was previously deposited in the Cambridge Structural Database⁹² and has two independent molecules in the unit cell with metrical parameters similar to the $P2_1/n$ structure (Table S2 in the Supporting Information). Comparison of 2-U with $UI_3(THF)_4^{-16,97}$ (Table S2) is similar to the comparison of 2-La with $LaI_3(THF)_4$; the iodide distances are similar, and the U–N(py) distances are longer than the U–O(THF) distances.

 $LnI_3(THF)_4$ (3-Ln). The etherate materials 1-Ln could be converted to their THF adducts by dissolution in THF and removal of the volatiles under reduced pressure to give $LnI_3(THF)_4$ (3-Ln; Ln = La, Ce, Nd) in high yield. This method produced materials with a consistent level of solvation in contrast to the isolation of 1-Ln, which had varying numbers of associated solvent molecules. The compounds were identified through unit cell determination and comparison with the published structures. $^{46,47,81,98}_{}$ Their $^1\!H$ and $^{13}\!C$ NMR spectra were recorded in $C_6 D_6$ and displayed a single set of resonances shifted from the value for free THF in $C_6 D_6$.⁹¹ In the La case, crystallization of 3-La from hot toluene instead of hot THF gave colorless crystals of $[LaI_2(THF)_5][LaI_4(THF)_2]$. This salt is isomorphous with the Nd,^{37,99} Sm,⁴⁸ Gd,³⁷ Yb,⁴⁹ and Y³⁷ analogues and has structural parameters as expected on the basis of the lanthanide contraction (Table S3 in the Supporting Information). Formation of such salts is not uncommon for lanthanide trihalides, depending on crystal-lization conditions.^{37,48,49,51–53,100}

 $Ln[N(SiMe_3)_2]_3$ (4-Ln). Although many methods have been developed for the synthesis of tris(amide) lanthanide

complexes, the most common preparations use lanthanide trichloride starting materials.⁸² As described below, lanthanide triiodides **1-Ln**, prepared from the metal, are also viable starting materials for the synthesis of these compounds.^{101,102}

Addition of a toluene solution of $KN(SiMe_3)_2$ to a toluene suspension of **1-Ln** forms $Ln[N(SiMe_3)_2]_3$ (**4-Ln**) in 70–95% yields after workup as confirmed by ¹H NMR spectroscopy.⁸² Tris(amide) plutonium complexes have been prepared from the metal following this protocol in ether⁶⁶ and could be examined for reduction to +2 complexes.³⁰

 $Cp'_{3}Ln$ (5-Ln). The Cp' ligand was chosen as a representative ligand, since its complexes recently led to the isolation of the lanthanides and uranium in the formal +2 oxidation state (eq 1).^{2-5,8,103} The Cp'_{3}Ln complexes 5-Ln are typically prepared from LnCl₃ with 3.1 equiv of KCp'.^{2-5,61,77,85,104} A similar protocol with 1-Ln in ether provides 5-Ln in 40% yield (Ln = Ce, Nd). In addition, 5-Ln can be prepared in 40–70% yields from 1-Ln generated in situ, and single crystals of 5-Ln could be obtained in small-scale reactions done with 11–15 mg of metal (Ln = Ce, Nd). The samples of 5-Ln prepared in this way could be reduced to form the Ln²⁺ complexes [K(2.2.2-cryptand)][Cp'_{3}Ln] (8-Ln), as confirmed by unit cell analysis, in greater than 60% yield (Ln = Ce, Pr, Nd).

 $Cp''_{3}Ln$ (6-Ln). Since the Cp'' ligand was used to prepare Th²⁺¹⁰ and $(Cp''_{3}U)^{-}$ is more stable than $(Cp'_{3}U)^{-,9}$ the preparation of Cp''_{3}Ln (6-Ln)^{59-62,84,85} on a small scale was also examined. This proved to be the protocol for preparing the starting material used to isolate Pu^{2+,13} Similar to the preparation of 5-Ln, addition of 3.1 equiv of KCp'' to either isolated 1-Ln or in situ generated 1-Ln gave Cp''_{3}Ln (6-Ln) in 55-80% yields (Ln = Ce, Nd).

 $(C_5Me_4H)_3La$ (**7-La**). Preparation of tris(cyclopentadienyl) complexes of the $(C_{s}Me_{4}H)^{-}$ ligand was also examined. The 7-Ln series can be made from 1-Ln in 70-90% yields, again showing the viability of 1-Ln generated from the elemental metal for organometallic synthesis. Despite its use in spectroscopy and reactivity, $^{105-111'}$ the structure of $(C_5Me_4H)_3Nd$ (7-Nd) to our knowledge, has not been reported. Cooling a hot toluene solution of 7-Nd to -30 °C afforded green single crystals suitable for X-ray crystallography (Figure 2). 7-Nd crystallizes in the $R\overline{3}$ space group and is isomorphous with the other members of the $(C_5Me_4H)_3M$ series $(La,^{89} Ce,^{88} Pr,^{88} Sm,^{89} Tb,^{86} Yb,^{112} Lu,^{113} Y,^{114} Th,^{115} U^{116})$, which crystallize in either the $R\overline{3}$ or $R\overline{3}r$ space group. The metrical parameters for 7-Nd match those of the analogues on the basis of the lanthanide contraction (Table S4 in the Supporting Information) and are comparable to those for other tris-(cyclopentadienyl) neodymium complexes (Table S5 in the Supporting Information).

CONCLUSION

Small-scale reactions of the elemental lanthanide metals Ce and Nd, with sizes similar to that of plutonium, have been found to provide viable routes to inorganic and organometallic complexes that can function as starting materials for new transuranic syntheses. These reactions provide protocols for developing other transuranic chemistry starting from the elemental metal or triiodides. Oxidation of the lanthanide metals with iodine in Et_2O provides the triiodides $[LnI_3(OEt_2)_x]$ (1-Ln), which can be used directly as starting materials for Ln[N(SiMe_3)_2]_3 (4-Ln), Cp'_3Ln (5-Ln), Cp''_3Ln (6-Ln), and (C₅Me_4H)_3Ln (7-Ln) or can be converted to the



Figure 2. Thermal ellipsoid plot of $(C_5Me_4H)_3Nd$ (7-Nd) plotted at the 50% probability level with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Nd-C(C_5Me_4H) range 2.719(1)-2.852(2), Nd-(centroid) 2.518, (centroid)-Nd-(centroid) 120.

THF adducts $LaI_3(THF)_4$ (3-Ln). Oxidation of the lanthanide metals with iodine in pyridine forms the tetrakis(pyridine) adducts $LnI_3(py)_4$ (2-Ln). The syntheses were extended to isolate the new Ln^{2+} complexes [K(2.2.2-cryptand)][Cp'_3Ln] (8-Ln) on a small scale.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01968.

Photographs of compounds and details of crystallographic data collection, structure solution, and refinement (PDF)

Accession Codes

CCDC 1559160–1559161 and 1559168–1559169 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

*E-mail for S.A.K.: stosh@lanl.gov.

*E-mail for W.J.E.: wevans@uci.edu.

ORCID 0

Megan T. Dumas: 0000-0001-7000-2130

Andrew J. Gaunt: 0000-0001-9679-6020

William J. Evans: 0000-0002-0651-418X

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy for supporting the research (W.J.E., DE-SC0004739; A.J.G., S.A.K., DE-AC52-06NA25396) and the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists, Office of Science Graduate Student Research (SCGSR) program for a fellowship (C.J.W.). The SCGSR program is administered by the Oak Ridge Institute for Science and Education (ORISE) for the DOE. ORISE is managed by ORAU under contract number DE-AC05-06OR23100. We thank Dr. Jason R. Jones and Michael K. Wojnar for assistance with the X-ray crystallog-raphy.

REFERENCES

(1) Hitchcock, P. B.; Lappert, M. F.; Maron, L.; Protchenko, A. V. Lanthanum Does Form Stable Molecular Compounds in the +2 Oxidation State. *Angew. Chem., Int. Ed.* **2008**, 47 (8), 1488–1491.

(2) MacDonald, M. R.; Ziller, J. W.; Evans, W. J. Synthesis of a Crystalline Molecular Complex of Y^{2+} , [(18-crown-6)K]-[($C_{3}H_{4}SiMe_{3})_{3}Y$]. J. Am. Chem. Soc. **2011**, 133 (40), 15914–15917.

(3) MacDonald, M. R.; Bates, J. E.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Expanding Rare-Earth Oxidation State Chemistry to Molecular Complexes of Holmium(II) and Erbium(II). *J. Am. Chem. Soc.* **2012**, *134* (20), 8420–8423.

(4) MacDonald, M. R.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Completing the Series of +2 Ions for the Lanthanide Elements: Synthesis of Molecular Complexes of Pr^{2+} , Gd^{2+} , Tb^{2+} , and Lu^{2+} . *J. Am. Chem. Soc.* **2013**, *135* (26), 9857–9868.

(5) Fieser, M. E.; MacDonald, M. R.; Krull, B. T.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Structural, Spectroscopic, and Theoretical Comparison of Traditional vs Recently Discovered Ln^{2+} Ions in the $[K(2.2.2\text{-cryptand})][(C_5H_4\text{SiMe}_3)_3\text{Ln}]$ Complexes: The Variable Nature of Dy^{2+} and Nd^{2+} . J. Am. Chem. Soc. **2015**, 137 (1), 369–382.

(6) Evans, W. J. Tutorial on the Role of Cyclopentadienyl Ligands in the Discovery of Molecular Complexes of the Rare-Earth and Actinide Metals in New Oxidation States. *Organometallics* **2016**, *35* (18), 3088–3100.

(7) Woen, D. H.; Evans, W. J. Expanding the +2 Oxidation State of the Rare-Earth Metals, Uranium, and Thorium in Molecular Complexes. In *Handbook on the Physics and Chemistry of Rare Earths,* Jean-Claude, G. B.; Vitalij, K. P., Eds.; Elsevier: Amsterdam, 2016; Vol. 50, pp 337–394.

(8) MacDonald, M. R.; Fieser, M. E.; Bates, J. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Identification of the +2 Oxidation State for Uranium in a Crystalline Molecular Complex, [K(2.2.2-Cryptand)]- $[(C_3H_4SiMe_3)_3U]$. J. Am. Chem. Soc. **2013**, 135 (36), 13310–13313.

(9) Windorff, C. J.; MacDonald, M. R.; Meihaus, K. R.; Ziller, J. W.; Long, J. R.; Evans, W. J. Expanding the Chemistry of Molecular U^{2+} Complexes: Synthesis, Characterization, and Reactivity of the {[C₄H₃(SiMe₃)₂]U}¹⁻ Anion. *Chem. - Eur. J.* **2016**, *22*, 772–782.

(10) Langeslay, R. R.; Fieser, M. E.; Ziller, J. W.; Furche, F.; Evans, W. J. Synthesis, structure, and reactivity of crystalline molecular complexes of the $\{[C_5H_3(SiMe_3)_2]_3Th\}^{1-}$ anion containing thorium in the formal +2 oxidation state. *Chem. Sci.* **2015**, *6* (1), 517–521.

(11) Dutkiewicz, M. S.; Farnaby, J. H.; Apostolidis, C.; Colineau, E.; Walter, O.; Magnani, N.; Gardiner, M. G.; Love, J. B.; Kaltsoyannis, N.; Caciuffo, R.; Arnold, P. L. Organometallic neptunium(III) complexes. *Nat. Chem.* **2016**, *8* (8), 797–802.

(12) Dutkiewicz, M. S.; Apostolidis, C.; Walter, O.; Arnold, P. L. Reduction chemistry of neptunium cyclopentadienide complexes: from structure to understanding. *Chem. Sci.* **2017**, *8* (4), 2553–2561.

(13) Windorff, C. J.; Chen, G. P.; Cross, J. N.; Evans, W. J.; Furche, F.; Gaunt, A. J.; Janicke, M. T.; Kozimor, S. A.; Scott, B. L. Identification of the Formal +2 Oxidation State of Plutonium: Synthesis and Characterization of $\{Pu^{II}[C_5H_3(SiMe_3)_2]_3\}^-$. J. Am. Chem. Soc. **2017**, 139, 3970.

(14) Shannon, R. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, 32 (5), 751–767.

(15) Clark, D. L.; Frankcom, T. M.; Miller, M. M.; Watkin, J. G. Facile solution routes to hydrocarbon-soluble Lewis base adducts of thorium tetrahalides. Synthesis, characterization, and x-ray structure of $ThBr_4(THF)_4$. *Inorg. Chem.* **1992**, *31* (9), 1628–1633.

(16) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. A Convenient Entry into Trivalent Actinide Chemistry: Synthesis and Characterization of $AnI_3(THF)_4$ and $An[N(SiMe_3)_2]_3$ (An = U, Np, Pu). *Inorg. Chem.* **1994**, 33 (10), 2248–2256.

(17) Clark, D. L.; Sattelberger, A. P.; Andersen, R. A. Lewis Base Adducts of Uranium Triiodide and Tris[Bis(Trimethylsilyl)Amido]-Uranium. *Inorg. Synth.* **1996**, *31*, 307–315.

(18) Evans, W. J.; Kozimor, S. A.; Ziller, J. W.; Fagin, A. A.; Bochkarev, M. N. Facile Syntheses of Unsolvated UI_3 and Tetramethylcyclopentadienyl Uranium Halides. *Inorg. Chem.* **2005**, 44 (11), 3993–4000.

(19) Carmichael, C. D.; Jones, N. A.; Arnold, P. L. Low-Valent Uranium Iodides: Straightforward Solution Syntheses of UI_3 and UI_4 Etherates. *Inorg. Chem.* **2008**, 47 (19), 8577–8579.

(20) Monreal, M. J.; Thomson, R. K.; Cantat, T.; Travia, N. E.; Scott, B. L.; Kiplinger, J. L. $UI_4(1,4\text{-dioxane})_2$, $[UCl_4(1,4\text{-dioxane})]_2$, and $UI_3(1,4\text{-dioxane})_{1.5}$: Stable and Versatile Starting Materials for Lowand High-Valent Uranium Chemistry. *Organometallics* **2011**, *30* (7), 2031–2038.

(21) Asprey, L. B.; Keenan, T. K.; Kruse, F. H. Preparation and Crystal Data for Lanthanide and Actinide Triiodides. *Inorg. Chem.* **1964**, 3 (8), 1137–1141.

(22) Bagnall, K. W.; Brown, D.; Jones, P. J.; Du Preez, J. G. H. 52. Iodo-complexes of thorium(IV) and uranium(IV). *J. Chem. Soc.* **1965**, 350–353.

(23) Brown, D.; Edwards, J. Preparation and crystallographic properties of the trichlorides, tribromides, and tri-iodides of uranium, neptunium, and plutonium. *J. Chem. Soc., Dalton Trans.* **1972**, 1757–1762.

(24) Karraker, D. G. The reaction of diiodoethane with neptunium and plutonium metals. *Inorg. Chim. Acta* **1987**, *139* (1), 189–191.

(25) Cloke, F. G. N.; Hitchcock, P. B. Reversible Binding and Reduction of Dinitrogen by a Uranium(III) Pentalene Complex. *J. Am. Chem. Soc.* **2002**, *124* (32), 9352–9353.

(26) Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. New Efficient Synthesis of $[UI_4(MeCN)_4]$. X-ray Crystal Structures of $[UI_2(MeCN)_7][UI_6]$, $[UI_4(py)_3]$, and $[U(dmf)_9]I_4$. Inorg. Chem. 2005, 44 (4), 1142–1146.

(27) Schnaars, D. D.; Wu, G.; Hayton, T. W. Reactivity of UH_3 with mild oxidants. *Dalton Trans.* **2008**, No. 44, 6121–6126.

(28) Gaunt, A. J.; Reilly, S. D.; Enriquez, A. E.; Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Neu, M. P. Low-Valent Molecular Plutonium Halide Complexes. *Inorg. Chem.* **2008**, 47 (18), 8412– 8419.

(29) Reilly, S. D.; Brown, J. L.; Scott, B. L.; Gaunt, A. J. Synthesis and characterization of $NpCl_4(DME)_2$ and $PuCl_4(DME)_2$ neutral transuranic An(IV) starting materials. *Dalton Trans.* **2014**, 43 (4), 1498–1501.

(30) Woen, D. H.; Chen, G. P.; Ziller, J. W.; Boyle, T. J.; Furche, F.; Evans, W. J. Solution Synthesis, Structure, and CO_2 Reduction Reactivity of a Scandium(II) Complex, $\{Sc[N(SiMe_3)_2]_3\}^-$. Angew. Chem., Int. Ed. 2017, 56 (8), 2050–2053.

(31) Meyer, G. In Synthesis of lanthanide and actinide compounds; Meyer, G., Morss, L. R., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1991.

(32) Young, R. C.; Hastings, J. L. Reaction of Lanthanum Oxide with Ammonium Iodide. J. Am. Chem. Soc. 1937, 59 (4), 765–766.

(33) Hohmann, E.; Bommer, H. Zur Thermochemie der seltenen Erden. III. Die Lösungs- und Bildungswärmen der wasserfreien Jodide der seltenen Erden. Z. Anorg. Allg. Chem. **1941**, 248 (4), 383–396.

(34) Taylor, M. D.; Carter, C. P. Preparation of anhydrous lanthanide halides, especially iodides. J. Inorg. Nucl. Chem. **1962**, 24 (4), 387–391.

(35) Kutscher, J.; Schneider, A. Notiz zur Präparation von wasserfreien Lanthaniden-Haloge-niden, Insbesondere von Jodiden. *Inorg. Nucl. Chem. Lett.* **1971**, 7 (9), 815–819.

(36) Boyle, T. J.; Ottley, L. A. M.; Alam, T. M.; Rodriguez, M. A.; Yang, P.; McIntyre, S. K. Structural characterization of methanol substituted lanthanum halides. *Polyhedron* **2010**, *29* (7), 1784–1795.

(37) Izod, K.; Liddle, S. T.; Clegg, W. A Convenient Route to Lanthanide Triiodide THF Solvates. Crystal Structures of $LnI_3(THF)_4$ [Ln = Pr] and $LnI_3(THF)_{3.5}$ [Ln = Nd, Gd, Y]. *Inorg. Chem.* **2004**, 43 (1), 214–218.

(38) Huebner, L.; Kornienko, A.; Emge, T. J.; Brennan, J. G. Heterometallic Lanthanide Group 12 Metal Iodides. *Inorg. Chem.* **2004**, 43 (18), 5659–5664.

(39) Bruno, G.; Ciliberto, E.; Fischer, R. D.; Fragala, I.; Spiegl, A. W. Photoelectron spectroscopy of f-element organometallic complexes. V. Comparative study of ring-substituted uranocenes. *Organometallics* **1982**, *1* (8), 1060–1062.

(40) Kunze, M. R.; Steinborn, D.; Merzweiler, K.; Wagner, C.; Sieler, J.; Taube, R. Synthese, Struktur und Reaktivität von Tris-, Bis- und Mono(2,4-dimethylpentadienyl)-Komplexen des Neodyms, Lanthans und des Yttriums. *Z. Anorg. Allg. Chem.* **2007**, *633* (9), 1451–1463.

(41) Deacon, G. B.; Feng, T.; Junk, P. C.; Meyer, G.; Scott, N. M.; Skelton, B. W.; White, A. H. Structural Variety in Solvated Lanthanoid(III) Halide Complexes. *Aust. J. Chem.* **2000**, *53* (10), 853–865.

(42) Lannou, M.-I.; Hélion, F.; Namy, J.-L. Some uses of mischmetall in organic synthesis. *Tetrahedron* **2003**, *59* (52), 10551–10565.

(43) Carter, F. L.; Murray, J. F. Preparation of the anhydrous rare earth trichlorides, tribromides, and triiodides. *Mater. Res. Bull.* **1972**, 7 (6), 519–523.

(44) Corbett, J. D.; Simon, A. Lanthanum Triiodide (and Other Rare Earth Metal Triiodides). *Inorg. Synth.* **1984**, *22*, 31–36.

(45) Voskoboynikov, A. Z.; Beletskaya, I. P. Lanthanide silanolates: Development of new procedures for the modification of silicones with rare-earth metals. *Appl. Organomet. Chem.* **1995**, *9* (5–6), 479–482.

(46) Liddle, S. T.; Arnold, P. L. Synthesis of Heteroleptic Cerium(III) Anionic Amido-Tethered N-Heterocyclic Carbene Complexes. Organometallics 2005, 24 (11), 2597–2605.

(47) Trifonov, A. A.; Weghe, P. V. d.; Collin, J.; Domingos, A.; Santos, I. Synthesis of lanthanide complexes coordinated by an asymmetric cyclopentadienyl ligand. *J. Organomet. Chem.* **1997**, 527 (1–2), 225–237.

(48) Xie, Z.; Chiu, K.-y.; Wu, B.; Mak, T. C. W. Autoionization of SmI_3 in Tetrahydrofuran. X-ray Crystal Structure of the Ionic Complex $[SmI_2(THF)_5][SmI_4(THF)_2]$. *Inorg. Chem.* **1996**, 35 (20), 5957–5958.

(49) Niemeyer, M. trans-Diiodopentakis(tetrahydrofuran)ytterbium(III) tetraiodo-trans-bis(tetrahydrofuran)ytterbium(III). *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2001**, 57 (8), m363–m364.

(50) Brown, J. L.; Davis, B. L.; Scott, B. L.; Gaunt, A. J. Early-Lanthanide(III) Acetonitrile-Solvento Adducts with Iodide and Noncoordinating Anions. *Inorg. Chem.* **2015**, *54* (24), 11958–11968.

(51) Anfang, S.; Karl, M.; Faza, N.; Massa, W.; Dehnicke, K.; Magull, J. Synthese und Kristallstrukturen der Seltenerd-Komplexe $[LaI_2(THF)_5]^+I_3^-$, $[SmCl_3(THF)_4]$, $[ErCl_2(THF)_5]^+$ $[ErCl_4(THF)_2]^-$, $[ErCl_3(DME)_2]$ und $[Na(18-Krone-6)(THF)_2]^+$ $[YbBr_4(THF)_2]^-$. Z. Anorg. Allg. Chem. **1997**, 623 (9), 1425–1432.

(52) Evans, W. J.; Shreeve, J. L.; Ziller, J. W.; Doedens, R. J. Structural Diversity in Solvated Lanthanide Halide Complexes. *Inorg. Chem.* **1995**, *34* (3), 576–585.

(53) Yuan Fu-Gen, S. Q. Sun Jie Reaction of Divalent Samarium Complexes with Phenyl Isocyanate Synthesis, Molecular Structure and Catalytic Activity of $[(CH_3C_5H_4)_2(THF)Sm]_2[\mu-\eta^4-(PhN)OCCO-(NPh)]\cdot 2THF. Chin. J. Struct. Chem. 2001, 22 (9), 1501–1505.$

(54) Wietzke, R.; Mazzanti, M.; Latour, J.-M.; Pecaut, J. Solution and solid state structures of uranium(III) and lanthanum(III) iodide complexes of tetradentate tripodal neutral N-donor ligands. *Dalton Trans.* **2000**, 4167–4173.

(55) Rivière, C.; Nierlich, M.; Ephritikhine, M.; Madic, C. Complexation Studies of Iodides of Trivalent Uranium and Lanthanides (Ce and Nd) with 2,2'-Bipyridine in Anhydrous Pyridine Solutions. *Inorg. Chem.* **2001**, *40* (17), 4428–4435.

(56) Berthet, J.-C.; Rivière, C.; Miquel, Y.; Nierlich, M.; Madic, C.; Ephritikhine, M. Selective Complexation of Uranium(III) over Cerium(III) and Neodymium(III) by 2,2':6',2"-Terpyridine – X-ray Crystallographic Evidence for Uranium-to-Ligand π Back-Bonding. *Eur. J. Inorg. Chem.* **2002**, 2002 (6), 1439–1446.

(57) Berthet, J.-C.; Nierlich, M.; Ephritikhine, M. A comparison of analogous 4f- and 5f-element compounds: syntheses and crystal structures of triphenylphosphine oxide complexes of lanthanide(III) and uranium(III) triflates and iodides $[MX_2(OPPh_3)_4][X]$ (X = OTf and M = Ce or U; X = I and M = Nd, Ce, La, U). *Polyhedron* **2003**, 22 (27), 3475–3482.

(58) Siffredi, G.; Berthet, J. C.; Thuery, P.; Ephritikhine, M. triiodotetrakis(pyridine)-samarium. Private Communication to CSD, 2013, CCDC Deposit number 958358, Code ZIXTEH.

(59) Cassani, M. C.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F.; Laschi, F. Synthesis and Characterization of Organolanthanidocene-(III) (Ln = La, Ce, Pr, Nd) Complexes Containing the 1,4-Cyclohexa-2,5-dienyl Ligand (Benzene 1,4-Dianion): Structures of [K([18]crown-6)][Ln{ η^{5} -C₅H₃(SiMe₃)₂-1,3}₂(C₆H₆)] [Cp'' = η^{5} -C₅H₃(SiMe₃)₂-1,3; Ln = La, Ce, Nd]. Organometallics **1999**, 18 (26), 5539–5547.

(60) Sofield, C. D.; Andersen, R. A. A general synthesis and crystal structure of $[(Me_3C)_2C_5H_3]_3$ Ce. J. Organomet. Chem. 1995, 501 (1), 271–276.

(61) Stults, S. D.; Andersen, R. A.; Zalkin, A. Structural studies on cyclopentadienyl compounds of trivalent cerium: tetrameric $(Me_{C_5}H_4)_3Ce$ and monomeric $(Me_3SiC_5H_4)_3Ce$ and $[(Me_3Si)_2C_5H_3]_3Ce$ and their coordination chemistry. *Organometallics* **1990**, *9* (1), 115–122.

(62) Lukens, W. W.; Speldrich, M.; Yang, P.; Duignan, T. J.; Autschbach, J.; Kogerler, P. The roles of 4f- and 5f-orbitals in bonding: a magnetochemical, crystal field, density functional theory, and multireference wavefunction study. *Dalton Trans.* **2016**, *45* (28), 11508–21.

(63) Ortu, F.; Fowler, J. M.; Burton, M.; Formanuik, A.; Mills, D. P. A structural investigation of heteroleptic lanthanide substituted cyclopentadienyl complexes. *New J. Chem.* **2015**, *39* (10), 7633–7639.

(64) Gaunt, A. J.; Scott, B. L.; Neu, M. P. Homoleptic uranium(III) imidodiphosphinochalcogenides including the first structurally characterised molecular trivalent actinide-Se bond. *Chem. Commun.* **2005**, 3215–3217.

(65) Sykora, R. E.; Assefa, Z.; Haire, R. G.; Albrecht-Schmitt, T. E. First Structural Determination of a Trivalent Californium Compound with Oxygen Coordination. *Inorg. Chem.* **2006**, *45* (2), 475–477.

(66) Gaunt, A. J.; Enriquez, A. E.; Reilly, S. D.; Scott, B. L.; Neu, M. P. Structural Characterization of $Pu[N(SiMe_3)_2]_3$, a Synthetically Useful Nonaqueous Plutonium(III) Precursor. *Inorg. Chem.* **2008**, 47 (1), 26–28.

(67) Ingram, K. I. M.; Tassell, M. J.; Gaunt, A. J.; Kaltsoyannis, N. Covalency in the f Element–Chalcogen Bond. Computational Studies of $M[N(EPR_2)_2]_3$ (M = La, Ce, Pr, Pm, Eu, U, Np, Pu, Am, Cm; E = O, S, Se, Te; R = H, ⁱPr, Ph). *Inorg. Chem.* **2008**, 47 (17), 7824–7833. (68) Minasian, S. G.; Boland, K. S.; Feller, R. K.; Gaunt, A. J.; Kozimor, S. A.; May, I.; Reilly, S. D.; Scott, B. L.; Shuh, D. K. Synthesis and Structure of $(Ph_4P)_2MCl_6$ (M = Ti, Zr, Hf, Th, U, Np, Pu). *Inorg. Chem.* **2012**, *S1* (10), 5728–5736.

(69) Cross, J. N.; Villa, E. M.; Wang, S.; Diwu, J.; Polinski, M. J.; Albrecht-Schmitt, T. E. Syntheses, Structures, and Spectroscopic Properties of Plutonium and Americium Phosphites and the Redetermination of the Ionic Radii of Pu(III) and Am(III). *Inorg. Chem.* **2012**, *51* (15), 8419–8424.

(70) Cary, S. K.; Silver, M. A.; Liu, G.; Wang, J. C.; Bogart, J. A.; Stritzinger, J. T.; Arico, A. A.; Hanson, K.; Schelter, E. J.; Albrecht-Schmitt, T. E. Spontaneous Partitioning of Californium from Curium: Curious Cases from the Crystallization of Curium Coordination Complexes. *Inorg. Chem.* **2015**, *54* (23), 11399–11404. (71) Macor, J. A.; Brown, J. L.; Cross, J. N.; Daly, S. R.; Gaunt, A. J.; Girolami, G. S.; Janicke, M. T.; Kozimor, S. A.; Neu, M. P.; Olson, A. C.; Reilly, S. D.; Scott, B. L. Coordination chemistry of 2,2'biphenylenedithiophosphinate and diphenyldithiophosphinate with U, Np, and Pu. *Dalton Trans.* **2015**, *44* (43), 18923–18936.

(72) Brown, J. L.; Batista, E. R.; Boncella, J. M.; Gaunt, A. J.; Reilly, S. D.; Scott, B. L.; Tomson, N. C. A Linear trans-Bis(imido) Neptunium(V) Actinyl Analog: $Np^{V}(NDipp)_{2}({}^{f}Bu_{2}bipy)_{2}Cl$ (Dipp = 2,6- ${}^{i}Pr_{2}C_{6}H_{3}$). J. Am. Chem. Soc. **2015**, 137 (30), 9583–9586.

(73) Cary, S. K.; Ferrier, M. G.; Baumbach, R. E.; Silver, M. A.; Lezama Pacheco, J.; Kozimor, S. A.; La Pierre, H. S.; Stein, B. W.; Arico, A. A.; Gray, D. L.; Albrecht-Schmitt, T. E. Monomers, Dimers, and Helices: Complexities of Cerium and Plutonium Phenanthrolinecarboxylates. *Inorg. Chem.* **2016**, 55 (9), 4373–4380.

(74) Silver, M. A.; Cary, S. K.; Stritzinger, J. T.; Parker, T. G.; Maron, L.; Albrecht-Schmitt, T. E. Covalency-Driven Dimerization of Plutonium(IV) in a Hydroxamate Complex. *Inorg. Chem.* **2016**, *55* (11), 5092–5094.

(75) Brown, J. L.; Gaunt, A. J.; King, D. M.; Liddle, S. T.; Reilly, S. D.; Scott, B. L.; Wooles, A. J. Neptunium and plutonium complexes with a sterically encumbered triamidoamine (TREN) scaffold. *Chem. Commun.* **2016**, *52* (31), 5428–5431.

(76) Bergbreiter, D. E.; Killough, J. M. Reactions of potassiumgraphite. J. Am. Chem. Soc. 1978, 100 (7), 2126–2134.

(77) Peterson, J. K.; MacDonald, M. R.; Ziller, J. W.; Evans, W. J. Synthetic Aspects of $(C_5H_4SiMe_3)_3Ln$ Rare-Earth Chemistry: Formation of $(C_5H_4SiMe_3)_3Lu$ via $[(C_5H_4SiMe_3)_2Ln]^+$ Metallocene Precursors. Organometallics **2013**, 32 (9), 2625–2631.

(78) Rossmanith, K. Preparation of tetrahydrofuran compounds of cerium earth iodides. *Monatsh. Chem.* **1995**, *126* (8), *897–900*.

(79) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. Synthetic and structural studies of pentamethylcyclopentadienyl complexes of lanthanum and cerium. *Organometallics* **1987**, *6* (1), 23–27.

(80) Clark, D. L.; Gordon, J. C.; Scott, B. L.; Watkin, J. G. Synthesis and characterization of a mixed-ring bis-cyclopentadienyl derivative of neodymium. X-ray crystal structures of $(\eta$ -C₅Me₅)NdI₂(py)₃ and $(\eta$ -C₅Me₅)(η -C₅H₄SiMe₃)NdI(py). *Polyhedron* **1999**, *18* (10), 1389–1396.

(81) Balashova, T. V.; Kusyaev, D. M.; Kulikova, T. I.; Kuznetsova, O. N.; Edelmann, F. T.; Gießmann, S.; Blaurock, S.; Bochkarev, M. N. Use of Neodymium Diiodide in the Synthesis of Organosilicon, -Germanium and -Tin Compounds. *Z. Anorg. Allg. Chem.* **2007**, 633 (2), 256–260.

(82) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. Low co-ordination numbers in lanthanide and actinide compounds. Part I. The preparation and characterization of tris{bis(trimethylsilyl)-amido}lanthanides. J. Chem. Soc., Dalton Trans. **1973**, 1021–1023.

(83) Minasian, S. G.; Krinsky, J. L.; Rinehart, J. D.; Copping, R.; Tyliszczak, T.; Janousch, M.; Shuh, D. K.; Arnold, J. A Comparison of 4f vs 5f Metal–Metal Bonds in $(CpSiMe_3)_3M$ – ECp^* (M = Nd, U; E = Al, Ga; $Cp^* = C_5Me_5$): Synthesis, Thermodynamics, Magnetism, and Electronic Structure. *J. Am. Chem. Soc.* **2009**, *131* (38), 13767– 13783.

(84) Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. Activation of a C-O bond by reaction of a tris(cyclopentadienyl)lanthanide complex with an alkali metal in dimethoxyethane (DME); crystal structures of $[Nd\{\eta-C_5H_3(SiMe_3)_2-1,3\}_2(\mu-OMe)_2Li(DME)]$ and $[\{Ce(\eta-C_5H_3'Bu_2-1,3)_2(\mu-OMe)\}_2]$. J. Organomet. Chem. **1995**, 499 (1–2), 213–219.

(85) Xie, Z.; Chui, K.; Liu, Z.; Xue, F.; Zhang, Z.; Mak, T. C. W.; Sun, J. Systematic studies on the reactions of lanthanide trichlorides with Na[1,3-bis(trimethylsilyl) cyclopentadienyl]. Crystal structures of $[1,3-(Me_3Si)_2C_5H_3]_3Ln$ (Ln = La, Nd, Gd, Dy). J. Organomet. Chem. **1997**, 549 (1–2), 239–244.

(86) Schumann, H.; Glanz, M.; Hemling, H. Metallorganische verbindungen der Lanthanoide. *J. Organomet. Chem.* **1993**, 445 (1), C1–C3.

(87) Evans, W. J.; Rego, D. B.; Ziller, J. W. Lanthanum and Alkali Metal Coordination Chemistry of the Bis(dimethylphenylsilyl)amide Ligand. *Inorg. Chem.* **2006**, *45* (8), 3437–3443.

(88) Evans, W. J.; Rego, D. B.; Ziller, J. W. Synthesis, Structure, and ¹⁵N NMR Studies of Paramagnetic Lanthanide Complexes Obtained by Reduction of Dinitrogen. *Inorg. Chem.* **2006**, *45* (26), 10790–10798.

(89) Schumann, H.; Glanz, M.; Hemling, H.; Ekkehard Hahn, F. Metallorganische Verbindungen der Lanthanoide. 93 [1]. Tetramethylcyclopentadienyl-Komplexe ausgewählter 4f-Elemente. Z. Anorg. Allg. Chem. 1995, 621 (3), 341–345.

(90) Schneider, D.; Harmgarth, N.; Edelmann, F. T.; Anwander, R. Ceric Cyclopentadienides Bearing Alkoxy, Aryloxy, Chlorido, or Iodido Co-Ligands. *Chem. - Eur. J.* **2017**, *23*, 12243.

(91) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.

(92) Berthet, J. C.; Thuery, P.; Ephritikhine, M. tris(Iodo)tetrakis(pyridine)-uranium. Private Communication to CSD, 2013, CCDC Deposit number 959293, Code XIMWEX.

(93) Ninghai, H.; Yonghua, L.; Qi, S.; Yan, X.; Endong, S. Crystal structure of europium trichloride tetrapyridine. *Acta Chim. Sinica* **1986**, 44 (4), 388–391.

(94) Li, J.-S.; Neumüller, B.; Dehnicke, K. Pyridin-Komplexe von Seltenerd-Trichloriden. Synthese und Kristallstrukturen von $[YCl_3(Py)_4]$ und $[LnCl_3(Py)_4]$ ·0,5 Py mit Ln = La und Er. Z. Anorg. Allg. Chem. 2002, 628 (1), 45–50.

(95) Deacon, G. B.; Scott, N. M.; Skelton, B. W.; White, A. H. Synthesis and Structure of 'mer'-Trichlorotetrakis(pyridine)ytterbium-(III) Hemipyridine Solvate. *Z. Anorg. Allg. Chem.* **2006**, *632* (12–13), 1945–1946.

(96) Vasudevan, K. V.; Smith, N. A.; Scott, B. L.; McKigney, E. A.; Blair, M. W.; Gordon, J. C.; Muenchausen, R. E. An Ionic Liquid-Mediated Route to Cerium(III) Bromide Solvates. *Inorg. Chem.* **2011**, *50* (10), 4627–4631.

(97) Clark, D. L.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. Lewis base adducts of uranium triiodide: a new class of synthetically useful precursors for trivalent uranium chemistry. *Inorg. Chem.* **1989**, *28* (10), 1771–1773.

(98) Berthet, J. C.; Thuery, P.; Ephritikhine, M. tris(Iodo)tetrakis(tetrahydrofuran)-cerium. Private Communication to CSD, 2013, CCDC Deposit number 959292, Code NARFUI01.

(99) Khoroshen'kov, G. V.; Fagin, A. A.; Bochkarev, M. N.; Dechert, S.; Schumann, H. Reactions of neodymium(II), dysprosium(II), and thulium(II) diiodides with cyclopentadiene. Molecular structures of complexes $CpTmI_2(THF)_3$ and $[NdI_2(THF)_5]^+[NdI_4(THF)_2]^-$. Russ. Chem. Bull. 2003, 52 (8), 1715–1719.

(100) Evans, W. J.; Giarikos, D. G.; Ziller, J. W. Lanthanide Carboxylate Precursors for Diene Polymerization Catalysis: Syntheses, Structures, and Reactivity with Et_2AlCl . *Organometallics* **2001**, *20*, 5751–5758.

(101) Goodwin, C. A. P.; Joslin, K. C.; Lockyer, S. J.; Formanuik, A.; Morris, G. A.; Ortu, F.; Vitorica-Yrezabal, I. J.; Mills, D. P. Homoleptic Trigonal Planar Lanthanide Complexes Stabilized by Superbulky Silylamide Ligands. *Organometallics* **2015**, *34* (11), 2314–2325.

(102) Herrmann, W. A.; Anwander, R.; Kleine, M.; Scherer, W. Lanthanoiden-Komplexe, I Solvensfreie Alkoxid-Komplexe des Neodyms und Dysprosiums. Kristall- und Molekülstruktur von trans-Bis(acetonitril)tris(tri-tert-butylmethoxy)neodym. *Chem. Ber.* **1992**, *125*, 1971–1979.

(103) Kotyk, C. M.; MacDonald, M. R.; Ziller, J. W.; Evans, W. J. Reactivity of the Ln^{2+} Complexes [K(2.2.2-cryptand)]-[(C₃H₄SiMe₃)₃Ln]: Reduction of Naphthalene and Biphenyl. *Organometallics* **2015**, 34 (11), 2287–2295.

(104) Krinsky, J. L.; Minasian, S. G.; Arnold, J. Covalent Lanthanide Chemistry Near the Limit of Weak Bonding: Observation of $(CpSiMe_3)_3Ce-ECp^*$ and a Comprehensive Density Functional

Inorganic Chemistry

Theory Analysis of Cp_3Ln –ECp (E = Al, Ga). *Inorg. Chem.* 2011, 50 (1), 345–357.

(105) Reddmann, H.; Karbowiak, M.; Amberger, H.-D.; Drożdżyński, J. Electronic Structures of Organometallic Complexes of f Elements. 62 Parametric Analysis of the Crystal Field Splitting Pattern of Pseudo Trigonal Planar Nd($\eta^{\rm S}$ -C₅Me₄H)₃. *Z. Anorg. Allg. Chem.* **2006**, 632 (12–13), 1953–1955.

(106) Amberger, H.-D.; Reddmann, H. Zur Elektronenstruktur metallorganischer Komplexe der f-Elemente. 65 Erstmalige Beobachtung des linearen Dichroismus bei einem homoleptischen metallorganischen π -Komplex der f-Elemente: Tris(η 5-tetramethylcyclopenta-dienyl)neodym(III). Z. Anorg. Allg. Chem. 2007, 633 (3), 443–452.

(107) Amberger, H.-D.; Reddmann, H. Zur Elektronenstruktur metallorganischer Komplexe der f-Elemente. 70, Optische und Ramanspektroskopische Polarisationsmessungen an einem orientierten Tris- $(\eta^{5}$ -tetramethylcyclopentadienyl)neodym(III)-(Nd(C₅Me₄H)₃) sowie erstmalige Beobachtung "polarisierter" elektronischer Raman-Effekte an einem orientierten metallorganischen Einkristall: Pr(C₅Me₄H)₃. *Z. Anorg. Allg. Chem.* **2009**, 635 (2), 291–296.

(108) Amberger, H.-D.; Reddmann, H.; Mueller, T. J.; Evans, W. J. Electronic structures of organometallic complexes of f elements LXXV. *J. Organomet. Chem.* **2011**, *696* (15), 2829–2836.

(109) Evans, W. J.; Lee, D. S.; Lie, C.; Ziller, J. W. Expanding the LnZ_3 /Alkali-Metal Reduction System to Organometallic and Heteroleptic Precursors: Formation of Dinitrogen Derivatives of Lanthanum. *Angew. Chem., Int. Ed.* **2004**, *43* (41), 5517–5519.

(110) Evans, W. J.; Rego, D. B.; Ziller, J. W.; DiPasquale, A. G.; Rheingold, A. L. Facile Insertion of CO_2 into Tetra- and Pentamethylcyclopentadienyl Lanthanide Moieties To Form $(C_5Me_4RCO_2)^-$ Carboxylate Ligands (R = H, Me). Organometallics **2007**, 26 (19), 4737–4745.

(111) Ababei, R.; Massa, W.; Weinert, B.; Pollak, P.; Xie, X.; Clerac, R.; Weigend, F.; Dehnen, S. Ionic-radius-driven selection of the maingroup-metal cage for intermetalloid clusters $[Ln@Pb_x Bi_{14x}]^{q}$ and $[Ln@Pb_y Bi_{13-y}]^{q}$ (x/q = 7/4, 6/3; y/q = 4/4, 3/3). *Chem. - Eur. J.* **2015**, 21 (1), 386–94.

(112) Shestakov, B. G.; Mahrova, T. V.; Larionova, J.; Long, J.; Cherkasov, A. V.; Fukin, G. K.; Lyssenko, K. A.; Scherer, W.; Hauf, C.; Magdesieva, T. V.; Levitskiy, O. A.; Trifonov, A. A. Ytterbium(III) Complexes Coordinated by Dianionic 1,4-Diazabutadiene Ligands. *Organometallics* **2015**, *34* (7), 1177–1185.

(113) Evans, W. J.; Lee, D. S.; Johnston, M. A.; Ziller, J. W. The Elusive $(C_5Me_4H)_3Lu$: Its Synthesis and $LnZ_3/K/N_2$ Reactivity. Organometallics **2005**, 24 (26), 6393–6397.

(114) Soller, B. S.; Sun, Q.; Salzinger, S.; Jandl, C.; Pöthig, A.; Rieger, B. Ligand Induced Steric Crowding in Rare Earth Metal-Mediated Group Transfer Polymerization of Vinylphosphonates: Does Enthalpy Matter? *Macromolecules* **2016**, *49* (5), 1582–1589.

(115) Siladke, N. A.; Webster, C. L.; Walensky, J. R.; Takase, M. K.; Ziller, J. W.; Grant, D. J.; Gagliardi, L.; Evans, W. J. Actinide Metallocene Hydride Chemistry: C–H Activation in Tetramethylcyclopentadienyl Ligands to Form $[\mu$ - η^{5} -C₅Me₃H(CH₂)- κ C]^{2–} Tuckover Ligands in a Tetrathorium Octahydride Complex. *Organometallics* **2013**, 32 (21), 6522–6531.

(116) del Mar Conejo, M.; Parry, J. S.; Carmona, E.; Schultz, M.; Brennann, J. G.; Beshouri, S. M.; Andersen, R. A.; Rogers, R. D.; Coles, S.; Hursthouse, M. B. Carbon Monoxide and Isocyanide Complexes of Trivalent Uranium Metallocenes. *Chem. - Eur. J.* **1999**, 5 (10), 3000–3009. Article