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Article

Oxidation in Nonclassical Organolanthanide Chemistry: Synthesis, Characterization, and X-ray Crystal Structures of Cerium(III) and -(IV) Amides

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$[Ce(NR_2)_3]$ (R = SiMe$_3$) with TeCl$_4$ in tetrahydrofuran solution gave a mixture of two major products in a combined yield of ca. 50% based on available metal: (i) the Ce(IV) amide $[CeCl(NR_2)_3]$ (**1**), which was isolated as purple needles and identified on the basis of ^{1}H NMR and mass spectra, microanalysis, and a single-crystal X-ray analysis $[C_{18}H_{54}CeClN_3Si_6$, rhombohedral, $R3c$ (No. 161), $a = b = 18.4508(7)$ Å, $c = 16.8934(7)$ Å, $Z = 6]$; (ii) unstable $[\{Ce(NR_2)_2(\mu\text{-Cl})(thf)\}_2]$ (**2**), as colorless blocks $[C_{32}H_{88}Ce_2Cl_2N_4O_2Si_8$, monoclinic, $P2_1/n$ (No. 14), $a = 14.506(3)$ Å, $b = 13.065(3)$ Å, $c = 16.779(3)$ Å, $\beta = 113.789(12)°$, $Z = 2]$, which readily disproportionated in solution. In toluene solution, the product **1** was obtained exclusively. The same cerium(III) amide starting material was oxidized by PBr$_2$Ph$_3$ in diethyl ether solution to give purple $[CeBr(NR_2)_3]$ (**3**) $[C_{18}H_{54}BrCeN_3Si_6$, rhombohedral, $R3c$ (No. 161), $a = b = 18.4113(12)$ Å, $c = 16.9631(17)$ Å, $Z = 6]$, along with presumed $[CeBr_3(OEt_2)_n]$, which has not been characterized but with thf, by displacement of the ether ligands, gave $[CeBr_3(thf)_4]$ (**4**) $[C_{16}H_{32}Br_3CeO_4$, triclinic, $P\bar{1}$ (No. 2), $a = 8.2536(7)$ Å, $b = 9.4157(5)$ Å, $c = 15.5935(14)$ Å, $\alpha = 79.009(5)$, $\beta = 87.290(3)°$, $\gamma = 74.835(5)°$, $Z = 2]$. TeBr$_4$ reacted with $[Ce(NR_2)_3]$ in thf to give small amounts of **3**; the major product (although only formed in 15% yield) was monomeric $[CeBr_2(NR_2)(thf)_3]$ (**5**) $[C_{18}H_{42}Br_2CeNO_3Si_2$, monoclinic, $P2_1/c$ (No. 14), $a = 14.9421(4)$ Å, $b = 11.8134(5)$ Å, $c = 15.8317(7)$ Å, $\alpha = \gamma = 120°$, $\beta = 92.185(3)°$, $Z = 4]$.

Introduction

It seems likely that while the Ln(III) (Ln = Sc, Y, La–Lu) oxidation state will continue to be of predominant interest in the inorganic and organometallic chemistry of the lanthanide elements, the more redox-active Ln(II) and Ln(IV) states offer greater promise of new and unforseen applications. The only brake on the development of these species stems from the considerable synthetic difficulties encountered during the synthesis and isolation of well-defined and fully characterized molecular compounds, although this is being slowly redressed. Thus, the synthesis[1–12] and applications of crystalline diiodides of neodymium, dysprosium, and thulium, such as $[LnI_2(dme)_3]$, $[LnI_2(thf)_3]$, and $[TmI_2(dme)_2(thf)]$ have been reported.[1–4] Some of these have proved to be useful reducing agents, both in inorganic[5–9] and organic[2,10,13,14] syntheses, and three organometallic compounds of Tm(II) have been prepared and X-ray characterized: $[Tm\{\eta^5\text{-}C_5H_3(SiMe_3)_2\text{-}1,3\}_2(thf)]$;[15] $[Tm\{\eta^5\text{-}EC_4(SiMe_3)_2$

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2,5-Me$_2$-3,4}$_2$(thf)] (E = P, As).[16] We have for some time been engaged in research into unusual lanthanide complexes and have concentrated on those elements of the 4f series with few or no known nonclassical molecular compounds: recent successes include the isolation and full characterization of lipophilic, bulky cyclopentadienyl complexes of La(II), Ce(II), Pr(II), and Nd(II), such as [K([18]-crown-6)(η^2-ArH)]-[(LnCp^x)$_2$(μ-ArH)] (Cp^x = η^5-C$_5$H$_3$(SiMe$_3$)$_2$-1,3 or η^5-C$_5$H$_3$-Bu$^t_2$-1,3 and ArH = C$_6$H$_6$ or C$_7$H$_8$).[17,18] For further details, see a recent review.[19]

While remaining with this aim broadly in mind, we present here a slight digression from the trail of truly nonclassical lanthanide chemistry, namely the synthesis of some Ce(IV) amido complexes derived oxidatively from [Ce(NR$_2$)$_3$] (R = SiMe$_3$) (**A**). There are three precedents for Ce(IV) amides, [Ce(NR$_2$)$_2$(OBu^t)$_2$] (reported at a conference),[20] [CeI-(NN′$_3$)] (**B**),[22] and [CeCl(NR$_2$)$_3$] reported in our preliminary communication.[23] The amide **A** had previously proved to be unexpectedly resistant to oxidation.[22]

Experimental Section

Materials and Procedures. All manipulations were carried out under argon using Schlenk techniques. Solvents were dried and distilled over sodium−potassium alloy under nitrogen gas prior to use. [Ce(NR$_2$)$_3$] (**A**) was prepared by known procedures and sublimed prior to use.[24] TeCl$_4$ and TeBr$_4$ were purchased from Aldrich Chemical Co. and used as received. Microanalyses were carried out by Medac Ltd. (Brunel University). The NMR spectra in C$_6$D$_6$ were recorded using a Bruker DPX 300 instrument (^{1}H, 300.1; ^{13}C 75.5 MHz) and referenced internally to residual solvent resonances (benzene-d_6, data in δ/ppm). EI mass spectra were obtained from solid samples using a Kratos MS 80 RF instrument; m/z values are reported for the most common isotope, and observed envelopes were compared with calculated patterns. Melting points were taken in sealed capillaries and are uncorrected.

Syntheses of [CeCl(NR$_2$)$_3$] (1) and [{Ce(NR$_2$)$_2$(μ-Cl)(thf)}$_2$] (2). [Ce(NR$_2$)$_3$] (1.0 g, 1.6 mmol) was dissolved in thf (25 mL) at room temperature, and TeCl$_4$ (0.11 g, 0.25 equiv) was added in one portion with vigorous stirring. The solution immediately turned purple, and stirring was continued for 2 h. The solution was reduced in volume under vacuum to ca. 2 mL, hexane (ca. 15 mL) was added, and the resulting deep purple mixture was filtered into a fresh, tared Schlenk vessel. Storage overnight at −30 °C produced well-formed purple/black needles of **1** (0.25 g, 24%), which were

isolated by filtration. ^{1}H NMR: δ 0.42. Anal. Calcd for C$_{18}$H$_{54}$-CeClN$_3$Si$_6$: C, 32.9; H, 8.29; N, 6.40. Found: C, 32.4; H, 8.2; N, 6.5. EI-MS: m/z 640 ([M − Me]$^+$, 4%), 620 ([Ce(NR$_2$)$_3$]$^+$, 54%), 605 ([Ce(NR$_2$)$_3$ − Me]$^+$, 14%), 495 ([CeCl(NR$_2$)]$^+$, 5%), 459 ([Ce-(NR$_2$)$_2$]$^+$, 78%), 444 ([Ce(NR$_2$)$_2$ − Me]$^+$, 24%), 430 ([Ce(NR$_2$)$_2$ − 2Me]$^+$, 19%), 299 ([Ce(NR$_2$)]$^+$, 73%), 284 ([Ce(NR$_2$) − Me]$^+$, 57%). Mp: 119−121 °C (dec). The filtrate was stored for another 1 week at −30 °C to furnish **2** as small, colorless blocks, contaminated by small amounts of **1** (0.25 g, 27%), which were separated manually and stored in a freezer due to their thermal instability. ^{1}H NMR: δ 3.6 (br, 4H, thf), 1.4 (br, 4H, thf), −2.2 (br, 36H, SiMe$_3$). EI-MS: m/z 992 ([{Ce(NR$_2$)$_2$Cl}$_2$]$^+$, 0.5%), 620 ([Ce(NR$_2$)$_3$]$^+$, 31%), 605 ([Ce(NR$_2$)$_3$ − Me]$^+$, 7%), 459 ([Ce(NR$_2$)$_2$]$^+$, 72%), 444 ([Ce(NR$_2$)$_2$ − Me]$^+$, 11%), 430 ([Ce-(NR$_2$)$_2$ − 2Me]$^+$, 8%), 299 ([Ce(NR$_2$)]$^+$, 55%), 284 ([Ce(NR$_2$) − Me]$^+$, 22%). Mp: dec > 25 °C.

Syntheses of [CeBr(NR$_2$)$_3$] (3) and [CeBr$_3$(thf)$_4$] (4). A solution of [Ce(NR$_2$)$_3$] (1.0 g, 1.6 mmol) in Et$_2$O (20 mL) was added via cannula to a suspension of PBr$_2$Ph$_3$ (formed in situ from 0.42 g PPh$_3$ and 0.25 g Br$_2$ in 30 mL Et$_2$O)[25] with stirring; the solid dissolved, and a purple coloration developed over the course of 3 h. Hexanes (100 mL) were added, and the solution was separated from the precipitated byproducts by filtration into another Schlenk vessel. Cooling of the filtrate overnight at −30 °C produced an oily precipitate. The supernatant layer was removed via cannula, hexanes (20 mL) were added, and then sufficient Et$_2$O (ca. 40 mL) was added to ensure complete dissolution of the purple solids at the boiling point of the mixture. The resulting solution was filtered while still warm into a clean, tared Schlenk vessel and stored overnight at −30 °C. The resulting purple/black needles of **3** (0.34 g, 30%), mp 128−131 °C, were isolated by filtration. ^{1}H NMR: δ 0.43. ^{13}C NMR: δ 5.43. Anal. Calcd for C$_{18}$H$_{54}$BrCeN$_3$Si$_6$: C, 30.8; H, 7.8; N, 5.99. Found: C, 30.4; H, 7.7; N, 6.1. EI-MS: 700 ([M]$^+$, 2%), 686 ([M − Me]$^+$, 14%), 671 ([M − 2Me]$^+$, 4%), 620 ([Ce-(NR$_2$)$_3$]$^+$, 95%), 605 ([Ce(NR$_2$)$_3$ − Me]$^+$, 91%), 541 ([CeBr-(NR$_2$)$_2$]$^+$, 60%), 525 ([CeBr(NR$_2$)$_2$ − Me]$^+$, 40%), 460 ([Ce-(NR$_2$)$_2$]$^+$, 100%), 444 ([Ce(NR$_2$)$_2$ − Me]$^+$, 58%), 430 ([Ce(NR$_2$)$_2$ − 2Me]$^+$, 43%), 299 ([Ce(NR$_2$)]$^+$, 74%), 284 ([Ce(NR$_2$) − Me]$^+$, 58%). Prolonged storage of the remaining solution gave colorless crystals which are presumed to have been [CeBr$_3$(OEt$_2$)$_4$] (**4**). On redissolution in thf and crystallization by addition of hexane, complex **4** (0.35 g, 33%) was isolated as colorless blocks by further cold storage and identified by X-ray crystallography.

Synthesis of [CeBr$_2$(NR$_2$) (thf)$_3$] (5). [Ce(NR$_2$)$_3$] (1.0 g, 1.6 mmol) was dissolved in thf (25 mL) at room temperature, and TeBr$_4$ (0.18 g, 0.25 equiv) was added in one portion with vigorous stirring. The solution immediately turned purple, stirring was continued for 1 h, and then was concentrated under vacuum to ca. 1 mL; hexane (ca. 5 mL) was added, and the resulting deep purple mixture was filtered into a clean, tared Schlenk vessel. Storage of the filtrate for 3 days at −30 °C produced a small amount of needles of **3**, along with colorless blocks of **5** (0.13 g, 12%), mp 100−120 °C (dec), which were separated manually and stored in a freezer due to their thermal instability. ^{1}H NMR: δ 4.0 (br, 12H, thf), 1.1 (br, 12H, thf), −2.9 (br, 18H, SiMe$_3$). EI-MS: m/z 1081 ([{CeBr$_2$(NR$_2$)}$_2$-NR$_2$]$^+$, 2.5%), 920 ([{CeBr$_2$(NR$_2$) }$_2$]$^+$, 1%), 620 ([Ce(NR$_2$)$_3$]$^+$, 20%), 605 ([Ce(NR$_2$)$_3$ − Me]$^+$, 7%), 541 ([CeBr(NR$_2$)$_2$]$^+$, 11%), 525 ([CeBr(NR$_2$)$_2$ − Me]$^+$, 9%), 460 ([Ce(NR$_2$)$_2$]$^+$, 93%), 299 ([Ce-(NR$_2$)]$^+$, 58%), 284 ([Ce(NR$_2$) − Me]$^+$, 25%).

Crystal Data and Refinement Details for 1−5. Diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer using

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Table 1. Crystal Data and Refinement Parameters for [CeCl(NR$_2$)$_3$] (**1**), [{Ce(NR$_2$)$_2$(μ-Cl)(thf)}$_2$] (**2**), [CeBr(NR$_2$)$_3$] (**3**), [CeBr$_3$(thf)$_4$] (**4**), and [CeBr$_2$(NR$_2$)(thf)$_3$] (**5**)

|	1	2	3	4	5
formula	C$_{18}$H$_{54}$CeClN$_3$Si$_6$	C$_{32}$H$_{88}$Ce$_2$Cl$_2$N$_4$O$_2$Si$_8$	C$_{18}$H$_{54}$BrCeN$_3$Si$_6$	C$_{16}$H$_{32}$Br$_3$CeO$_4$	C$_{18}$H$_{42}$Br$_2$CeNO$_3$Si$_2$
M_r	656.75	1136.92	701.21	668.3	676.65
cryst syst	rhombohedral	monoclinic	rhombohedral	triclinic	monoclinic
space group	$R3c$ (No. 161)	$P2_1/n$ (No. 14)	$R3c$ (No. 161)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
cryst size/mm	0.3 × 0.1 × 0.1	0.3 × 0.3 × 0.2	0.10 × 0.05 × 0.05	0.2 × 0.2 × 0.05	0.4 × 0.3 × 0.3
a/Å	18.4508(7)	14.506(3)	18.4113(12)	8.2536(7)	14.9421(4)
b/Å	18.4508(7)	13.065(3)	18.4113(12)	9.4157(5)	11.8134(5)
c/Å	16.8934(7)	16.779(3)	16.9631(17)	15.5935(14)	15.8317(7)
α/deg	90	90	90	79.009(5)	90
β/deg	90	113.789(12)	90	87.290(3)	92.185(3)
γ/deg	120	90	120	74.835(5)	90
V/Å^3	4980.6(3)	2909.8(10)	4979.7(7)	1148.2(2)	2792.5(2)
D_c/g cm^{-3}	1.31	1.30	1.40	1.93	1.61
μ(Mo Kα)/mm^{-1}	1.68	1.83	2.80	7.22	4.59
$F(000)$	2052	1172	2160	646	1348
reflcns collcd	6300	15 242	5901	9106	15 065
indpndt reflcns	1781	4858	1440	5428	4904
R_{int}	0.037	0.090	0.108	0.066	0.052
reflcns with $I > 2\sigma(I)$	1693	3376	1077	4224	4104
goodness-of-fit on F^2	1.047	0.824	1.056	1.042	1.039
R1, wR2 [$I > 2\sigma(I)$]	0.023, 0.056	0.054, 0.173	0.044, 0.081	0.060, 0.138	0.033, 0.071
R1, wR2 (all data)	0.025, 0.057	0.088, 0.220	0.070, 0.089	0.084, 0.153	0.045, 0.075

Scheme 1. Synthesis of a Mononuclear Ce(IV) Amide with R = SiMe$_2$^{t}Bu[22]
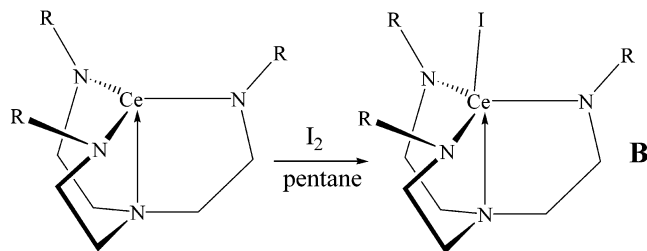
monochromated Mo Kα radiation, λ = 0.710 73 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The structures were refined on all F^2 using SHELXL-97.[26] Further details are found in Table 1.

Results and Discussion

It is paradoxical that while in any isoleptic series of lanthanide complexes the cerium analogue is generally by far the most sensitive to the presence of traces of oxygen gas (i.e. it provides an easily oxidizable metal center), oxidation of Ce(III) reliably yields molecular Ce(IV) products only when the coligands are porphyrins or similar hard macrocycles.[21] Indeed, to our knowledge there are only two other examples of successful oxidation of a CeX$_3$ species: (i) the reaction of [Ce(NN$'_3$)] [NN$'_3$ = N(CH$_2$CH$_2$NSiMe$_2$-Bu^t)$_3$] with iodine to give [CeI(NN$'_3$)] (**B**), as demonstrated by Scott and co-workers (see Scheme 1);[22] (ii) the reaction of Ce(OCBu$^t_3$)$_3$ with (Bu^{t}O)$_2$, [PhC(O)O]$_2$, or a quinone (giving inter alia the X-ray-characterized Ce(IV) complex **C**)[27] to give the Ce(IV) silsequioxane complex **D** (R = c-C$_6$H$_{11}$), obtained from **A** (or CeCl$_3$, thf) and 2 equiv of (c-C$_6$H$_{11}$)$_8$Si$_8$O$_{11}$(OH)$_2$ in Et$_2$O and an excess of pyridine.[28] Regarding **B**, that an oxidant as weak as molecular iodine is

able to produce and subsequently stabilize a Ce(IV) center clearly indicates that the coligands can have a decisive influence on the magnitude of the Ce$^{III/IV}$ couple and, by extension, the viability of any oxidation. As an illustration, we note that $E_{1/2}$ for [Ce(η^5-C$_5$H$_5$)$_3$(OPr^i)] in thf with [NBu$_4$]-[BF$_4$] as supporting electrolyte is + 0.32 V vs SSCE (i.e., it is an oxidant comparable to [FeCp$_2$]);[29] Ce(η^8-C$_8$H$_8$)$_2$] is much more resistant to reduction, $E_{1/2}$ = −1.52 V.[30] With these facts in mind it is surprising that [Ce(NR$_2$)$_3$] (R = SiMe$_3$) (**A**), containing as it does the prototypical hexamethyldisilazide ligand with its renowned stabilizing effects,[31] tenaciously retains its sole 4f electron, being unaffected by Cl$_2$[22] or (this work) Br$_2$ or I$_2$.
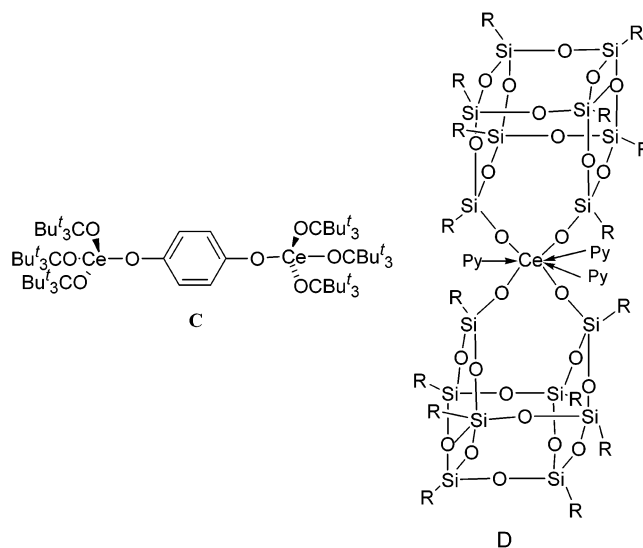
It is, then, initially even more surprising to find that oxidation may take place at the metal when utilizing even weaker (in an electrochemical sense) oxidants (Scheme 2).

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Scheme 2. Oxidation of [Ce(NR$_2$)$_3$] (**A**)^a
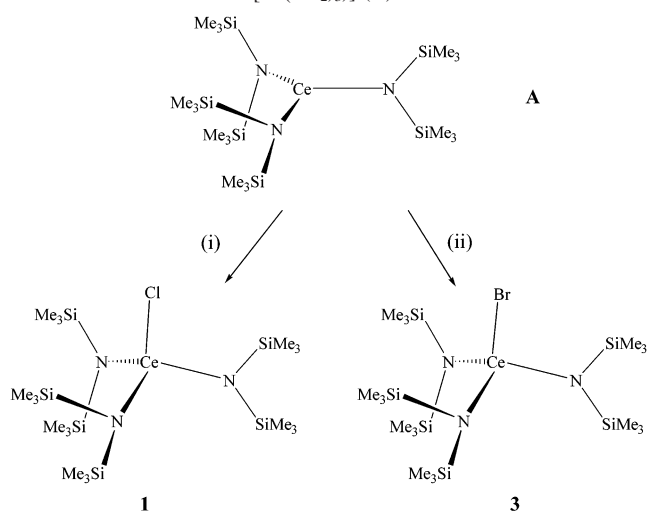
^{a} Reagents and conditions: (i) $^1/_4$ TeCl$_4$, thf, or PhMe, room temperature; (ii) PBr$_2$Ph$_3$, Et$_2$O, room temperature. For reaction byproducts, see text.

Our first resort was to use TeCl$_4$, a high-valent main-group compound which one of us has applied successfully in the past to oxidation of some transition metal complexes.[32] Addition of 0.25 equiv of the solid to solutions of [Ce(NR$_2$)$_3$] (**A**) in either thf or toluene at room temperature resulted in a color change from yellow to deep purple almost instantaneously. No advantage was gained by carrying out the reaction at lower temperatures or with an excess of the chloride; the yield of the product [CeCl(NR$_2$)$_3$] (**1**) was consistently around 25% and decreased markedly on scaling up the reaction beyond ca. 1 g of starting amide. Isolation of **1** was easily accomplished. It furnished well-formed purple/black needles, although the workup procedure had to be carried out promptly as delays resulted in the deposition of colorless blocks of [{Ce(NR$_2$)$_2$(μ-Cl)(thf)}$_2$] (**2**) as a coproduct in significant amounts. The isolation of this very unstable complex was unexpected, and its formulation was based on ^{1}H NMR and EI mass spectra, microanalytical data, and an X-ray crystallographic study.

The air-sensitivity of **1** was reduced in comparison to that of [Ce(NR$_2$)$_3$] (**A**), and this more user friendly behavior made its spectroscopic characterization straightforward: the ^{1}H NMR spectrum in C$_6$D$_6$ consisted of a sharp singlet which showed no paramagnetic shift (δ 0.45; cf., a broad peak centered at δ -3.5 for **A**). The mass spectrum showed [M $-$ Me]$^+$ as its heaviest ion. Compound **1** was, however, too unstable in any solvent other than thf for the accumulation of good quality ^{13}C NMR data.

The X-ray molecular structure of **1** has been determined and is shown in Figure 1, with selected bond lengths and angles collected in Table 2, which also includes data for the
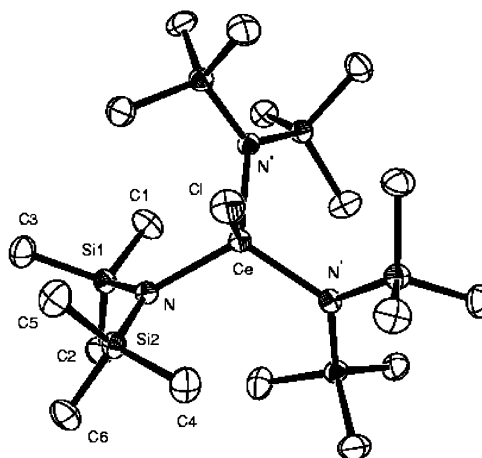
Figure 1. Molecular structure of [CeCl(NR$_2$)$_3$] (**1**).

Table 2. Selected Bond Lengths and Angles for [CeCl(NR$_2$)$_3$] (**1**) and Zr^{33} and Pb^{34} Analogues

	M = Ce	M = Zr^a	M = Pb
	Bond Lengths (Å)		
M−Cl	2.597(2)	2.394(2)	2.479(4)
M−N	2.217(3)	2.070(3)	2.13(2)
Si−N	1.751(3)	1.766(4)	1.777
Si−C	1.866	1.865	1.855
	Bond Angles (deg)		
N−M−N′^{b}	117.34(4)	114.1(1)	116.6(9)
N−M−Cl	99.48(7)	104.3(1)	100.7(5)
Si−N−M	119.9	121.8	120.5
Si−N−Si′	120.13(16)	116.6(1)	119(1)

^{a} Data for the isomorphous Ti and Hf compounds are available;[33] the isoleptic Th compound is also known.[35] ^{b} Symmetry transformations used to generate equivalent atoms: (′) $-x + y$, $-x$, z.

isoleptic compounds [MCl(NR$_2$)$_3$] (M = Zr,[33] Pb[34]) (analogues with M = Ti,[33] Hf,[33] and Th[35] are also known). Unlike the parent amide **A** and its lanthanide analogues, also found for each of the above M(IV) chloro amides, there was no inclusion of solvent in the lattice of **1**. The molecule is C_3-symmetric about the Ce−Cl axis, the hexamethyldisilazido ligands being arranged in a propeller-like conformation. While this renders each individual molecule chiral, the bulk material comprises a 50:50 mixture of isomers, a characteristic shared with [Ce(NR$_2$)$_3$] (**A**).[36] The observed Ce−N distance of 2.217(3) Å is contracted by ca. 0.1 Å relative to the value of 2.320(3) Å found for **A** and is broadly comparable to those found for analogous Ce(IV)−N bonds in [CeI(NN′$_3$)] (**B**).[22] The reduction in Ce−N bond lengths from Ce(III) to Ce(IV) is accompanied by an increase in the N−Si distance from 1.702 Å in **A** to around 1.751(3) Å in **1**. Current theory cannot unequivocally confirm or deny the presence of significant π-bonding in the case of nitrogen and silicon atoms, and so there are two plausible interpretations which may be applied to the aforementioned changes. Either

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the methyl groups rigidly envelope the cerium, nitrogen, and silicon atoms to form a fixed shell in a variation of the ligand polyhedron model[37] (hence a decrease in the Ce−N distance must be accompanied by an increase in the N−Si bond length for steric reasons) or enhanced donation from N to Ce removes electron density which would otherwise be shared between the nitrogen and silicon atoms. The matter has recently been addressed directly by Maron and Eisenstein, who suggested the presence of $p\pi-d\pi$ bonding in the NR_2 fragment for the model compound $[Ln\{N(SiH_3)_2\}_3]$.[38] They concluded that SiH_3 is not an adequate substitute for $SiMe_3$; their calculation for Ln = Ce, which for computational reasons utilized a Ce^{4+} ion, predicted a Ce−N bond length of 2.22 Å.[23] Such close agreement with the experimental value imparts considerable validity to their model and suggests that the presence of the chloride ligand influences the metal center to a negligible degree. The general similarity in the trends of the geometric parameters of the Ce (**1**), Zr, and Pb complexes of Table 2 is also consistent with the π-bonding hypothesis.

The Ce−Cl separation of 2.597(2) Å in **1** is the shortest recorded for a mononuclear cerium chloride {cf., 2.763(3)−2.792(3) Å in $[CeCl_3(OAsPh_3)_3]$};[39] this is likely to be simply a result of the decreased effective ionic radius ($Ce^{4+} < Ce^{3+}$) and the low metal coordination number in **1**. The absence of close Ce−Si contacts in **1**, of the kind found in the structure of $[Ce(NR_2)_3]$,[36] is reflected in the regularity of the three bond angles around nitrogen [120.13(16), 121.35(14), and 118.47(13)°; sum of angles around N = 359°], while the Cl−Ce−N−Si torsion angle decreases by around 6° in **1** from its equivalent in **A** to 38°, again presumably in response to increased crowding between the trimethylsilyl groups.

The coordination environment around the central metal in $[MCl\{N(SiMe_3)_2\}_3]$ complexes is closely similar for M = Ce (**1**) and M = Pb[34] but differs substantially from that for M = Zr (and indeed for M = Ti or Hf),[33] as evident by comparing the difference between the N−M−N′ and N−M-Cl angles in Table 2. The failure of **1** to adopt an apparently easily accessible tetrahedral geometry leads us to suggest that it is more appropriate to view the Ce (**1**) and Pb complexes as incipient trigonal pyramidal species undergoing a tetrahedral distortion prompted by the presence of a fourth ligand in the apical site.

The effective ionic radii of the lanthanides show a marked dependence on coordination number, and so it is difficult to make precise comparisons between the structure of **1** and those of similar species. No structural data are available for the only directly comparable complex, $[Ce(NR_2)_2(OBu^t)_2]$ (**E**),[20] so a rough estimate of 0.76 Å for the radius of four-coordinate Ce^{4+} may be made from our data, given a radius of ca. 1.46 Å for the NR_2 ligand. This may in turn be compared with the radii of Y^{3+} and Yb^{3+} (both around

0.77 Å for four-coordination) as found in $[Li(thf)_4][YCl-(NR_2)_3]$ (**F**)[40] and $[Na([12]\text{-crown-}4)_2][Yb(NR_2)_3(OSiMe_3)]$ (**G**),[41] and by so doing the electronic effects that the high-valent cerium ion has on the structure may be separated from any distortions imposed by the hexamethyldisilazido ligands. The ytterbate(III) ion in **G** shows a distorted tetrahedral geometry due to the overriding steric effect of its much more bulky siloxide ligand; the yttrate ion in **F** appears to be quite similar in structure to **1**, although, due to a poor refinement, full data are not available. What is apparent from the available information is that the metal ion resides 0.42 Å above the N_3 plane in the Y(III) complex, while in its neutral Ce(IV) counterpart **1** this projection is reduced to 0.36 Å. This suggests that an increase in the charge/radius ratio (i.e., the Lewis acidity) of the metal center, as found for Ce^{4+}, polarizes the chloride ligand, effectively decreasing its size and allowing a flatter structure to be adopted. The driving force behind the adoption of this ligand arrangement in **1** is likely to be an enhancement in the Ce−N bond energy associated with the shorter bond length, a necessary consequence of the metal ion's descent into the plane of the three amido nitrogen atoms. We have not been able to isolate a complex of Ce(III) analogous to **G**, for instance by direct addition of [cation]X (cation = PPh_4, NMe_4, NBu_4) to the neutral tris(amide) **A**, to study these structural effects further.

E

$[Li(thf)_4]^{+}$

F

$[Na([12]\text{-crown-}4)_2]^{+}$

G
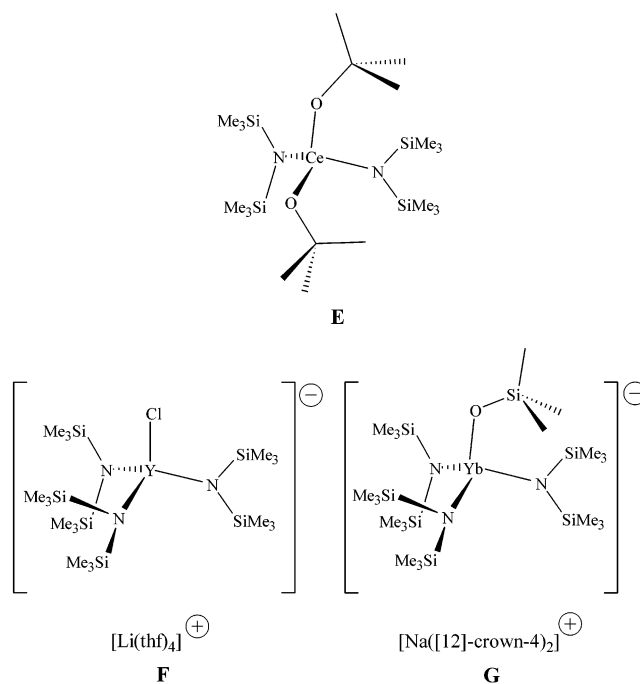
The complicating presence of **2** as a coproduct with **1** from the $[Ce(NR_2)_3]$−$TeCl_4$ system was not entirely unwelcome, as it is the lightest member of its isoleptic series to be thus far isolated, and indeed was thought to be too unstable for its successful synthesis;[42a] thus, $[\{Eu(NR_2)_2(\mu\text{-Cl})(thf)\}_2]$ (**H**)

(37) Johnson, B. F. G.; Lewis, J. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 225 (see p 245).
(38) Maron, L.; Eisenstein, O. *New J. Chem.* **2001**, *25*, 255.
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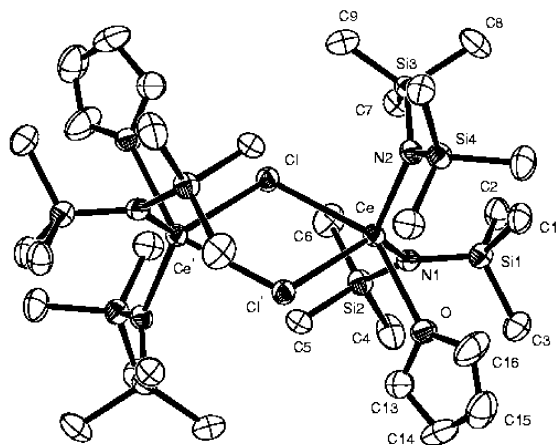
Figure 2. Molecular structure of [{Ce(NR$_2$)$_2$(μ-Cl)(thf)}$_2$] (**2**).

was reported to redistribute into [Eu(NR$_2$)$_3$] and EuCl$_3$ in solution,[42a] with only the smaller, heavier isoleptic lanthanides being stable.[42a, b] While this was not entirely the case for the cerium example **2**, adequate characterizing data were difficult to obtain as the dimer readily disproportionated, both in solution (although it is possible to assign a broad resonance at δ −2.2 in the ^{1}H NMR spectrum in C$_6$D$_6$ to the NR$_2$ ligands, along with similarly broadened features at δ 3.6 and δ 1.4 to the thf ligand) and in the gas phase; the heaviest peak in the EI MS is assigned as [M − 2(thf)]$^+$. The thermal instability of the solid **2** also precluded the obtaining of accurate microanalytical data, and so the first resort method of characterization for **2** was by X-ray crystallography.
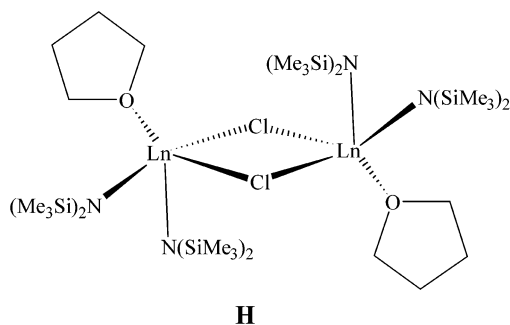
H

The X-ray crystal structure of **2** (see Figure 2) shows it to be isostructural with its Yb and Gd analogues,[42a] comprising a slightly asymmetrically chloride-bridged dimer. The geometry about the cerium atom is again highly irregular but may be most accurately described as square pyramidal. Periodic trends caused by increasing ionic radius, as implied by the published data for ytterbium and gadolinium,[42a] are continued in the cerium analogue **1** (see Table 3 for selected values).

It is worth emphasizing that **2** has the status of a contaminant in the reaction medium, but its appearance can easily be avoided by carrying out the synthesis of **1** in toluene

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(42) (a) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623. (b) The equivalent species with dicyclohexylamido ligands is stable for Ln = Sm: Minhas, R. K.; Ma, Y.; Song, J.-I.; Gambarotta, S. *Inorg. Chem.* **1996**, *35*, 1866.

Table 3. Bond Lengths and Angles for [{Ce(NR$_2$)$_2$(μ-Cl)(thf)}$_2$] (**2**)

Bond Lengths (Å)			
Ce−N(1)	2.342(7)	Ce−N(2)	2.320(7)
Ce−O	2.570(6)	Ce−Cl	2.843(2)
Ce−Cl'^{a}	2.859(2)	N(1)−Si(1)	1.716(7)
N(1)−Si(2)	1.719(8)	N(2)−Si(3)	1.715(7)
N(2)−Si(4)	1.721(7)		

Bond Angles (deg)			
N(1)−Ce−N(2)	119.1(2)	N(2)−Ce−Cl	92.93(18)
N(1)−Ce−O	84.4(2)	N(1)−Ce−Cl'	128.27(18)
N(2)−Ce−O	113.5(2)	N(2)−Ce−Cl'	112.55(17)
N(1)−Ce−Cl	101.20(18)	O−Ce−Cl	146.23(15)

^{a} Symmetry transformations used to generate equivalent atoms: (') $-x + 2$, $-y + 2$, $-z$.

solution rather than thf, the workup being identical in all other respects.

Having established the stability of the Ce(IV) amide **1**, we next investigated the syntheses of other halide congeners, albeit with mixed success. The synthesis of [CeBr(NR$_2$)$_3$] (**3**) proved to be straightforward, but the isolation of its fluoride and iodide counterparts posed significant problems.

Addition of a diethyl ether solution of [Ce(NR$_2$)$_3$] (**A**) to a preformed suspension of PBr$_2$Ph$_3$, also in ether, resulted in a color change to purple, in this case taking around 3 h. The workup method was slightly more complicated than for **1**, but purple/black needles, indistinguishable externally from those formed by **1**, were isolated in low yield from the mixture. Mass and NMR spectral, microanalytical and X-ray data all confirmed its formulation as [CeBr(NR$_2$)$_3$] (**3**). The stability of **3** is enhanced relative to that of **1**, with several prominent bromine-containing peaks being visible in the EI mass spectrum, including a parent ion at $m/z = 700$. In addition, its stability in C$_6$D$_6$ solution allowed for the accumulation of ^{13}C NMR spectral data, which showed a singlet at δ 5.43 for the methyl groups; the ^{1}H NMR spectrum was virtually identical with that of **1**, comprising a singlet at δ 0.43. As with **1**, the major product of the reaction, was a Ce(III) species, this time [CeBr$_3$(OEt$_2$)$_n$]. This formulation rests solely on the isolation of the product of its reaction with thf, namely [CeBr$_3$(thf)$_4$] (**4**), which is very similar to several known lanthanide trichloride/thf complexes,[43] and was here characterized exclusively by X-ray crystallography due to its inherent insolubility, involatility, and instability (see Experimental Section and Supporting Information).

The molecular structure of **3** (as determined by X-ray crystallography), depicted in Figure 3 with selected bond lengths and angles collected in Table 4, reveals it to be exactly isostructural with the chloride **1**. Thus, its sole distinguishing feature is the terminal Ce(IV)−Br bond, which at 2.766(2) Å has no precedent and exhibits the expected bond contraction associated with the presence of a more Lewis acidic, coordinatively unsaturated center. The lack of structural differences between the two Ce(IV) halide complexes is probably a reflection both of the predominantly ionic nature of their bonding and of the similarity of ligand cone angles for each of the halogens.

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(43) Zhang, X.-W.; Li, X.-F.; Benetollo, F.; Bombieri, G. *Inorg. Chim. Acta* **1987**, *139*, 103.
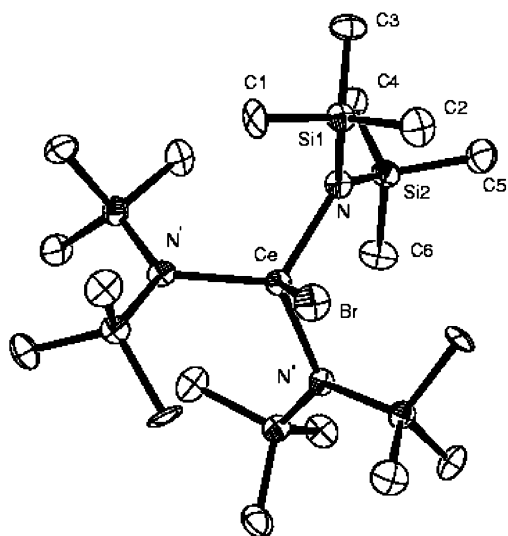
Figure 3. Molecular structure of [CeBr(NR$_2$)$_3$] (**3**).

Table 4. Bond Lengths and Angles for [CeBr(NR$_2$)$_3$] (**3**)

Bond Lengths (Å)			
Ce–N	2.219(7)	Ce–Br	2.766(2)
Si(1)–N	1.757(8)	Si(2)–N	1.745(8)
Si(1)–C(1)	1.884(9)	Si(1)–C(2)	1.845(11)
Si(1)–C(3)	1.859(9)	Si(2)–C(4)	1.865(10)
Si(2)–C(5)	1.878(10)	Si(2)–C(6)	1.862(10)
Bond Angles (deg)			
N–Ce–N′^{a}	117.25(12)	N–Ce–Br	99.7(2)
Si(1)–N–Si(2)	120.0(4)	Si(1)–N–Ce	118.4(4)
Si(2)–N–Ce	121.5(4)		

^{a} Symmetry transformations used to generate equivalent atoms: (′) −y, x − y, z.

We did not initially use TeBr$_4$, the most obvious oxidant as the reagent of choice for the synthesis of **3**, as it is prohibitively expensive. We have, however, investigated its chemistry and found that it too will oxidize [Ce(NR$_2$)$_3$] (**A**) to **3**. However, with the Te(IV) reagent isolation of the product was very much more complicated; the yields were lower than was the case with the P(V) oxidant, and so this is not an effective method for the synthesis of **3**. Its use is associated with some unusual reactivity, and we have repeatedly isolated one byproduct which is apparently not produced in the previous system, this being the monomeric, mono(amido)cerium(III) complex [CeBr$_2$(NR$_2$)(thf)$_3$] (**5**). Considering the instability of diamide [{Ce(NR$_2$)$_2$(μ-Cl)- (thf)}$_2$] (**2**), the isolation of a mono(amide) was unexpected and shows that the nature of the halide plays a decisive role in determining the stability of related systems. While, as with **2**, the bromide complex **5** was not really adequately stable for full spectroscopic characterization due to the ever-present problem of redistribution, its identity was firmly established by X-ray crystallography (see Figure 4 and Table 5).

The trivalent cerium ion in **5** is surrounded by a very irregular shell of six ligands and one close contact with the C(6) atom of a methyl group of the amido ligand, which together comprise what may loosely be described as a pentagonal bipyramid, N and Br(1) being axial. The agostic interaction is betrayed by five indicators: the otherwise vacant space in the idealized coordination sphere; a relatively
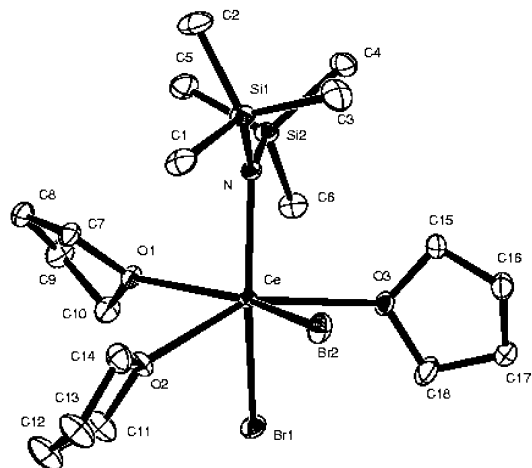

Figure 4. Molecular structure of [CeBr$_2$(NR$_2$)(thf)$_3$] (**5**).

Table 5. Bond Lengths and Angles for [CeBr$_2$(NR$_2$)(thf)$_3$] (**5**)

Bond Lengths (Å)			
Ce–N	2.331(3)	Ce–O(1)	2.566(3)
Ce–O(2)	2.546(3)	Ce–O(3)	2.523(3)
Ce–Br(1)	2.9115(5)	Ce–Br(2)	2.8854(5)
N–Si(1)	1.720(3)	N–Si(2)	1.710(4)
Bond Angles (deg)			
N–Ce–O(1)	82.14(11)	O(2)–Ce–O(3)	145.16(10)
N–Ce–O(2)	118.04(11)	O(1)–Ce–Br(1)	80.25(6)
N–Ce–O(3)	90.05(11)	O(1)–Ce–Br(2)	149.98(7)
N–Ce–Br(1)	142.99(8)	O(2)–Ce–Br(1)	87.88(7)
N–Ce–Br(2)	99.16(8)	O(2)–Ce–Br(2)	78.90(7)
Br(1)–Ce–Br(2)	112.202(18)	O(3)–Ce–Br(1)	79.21(7)
O(1)–Ce–O(2)	74.26(10)	O(3)-Ce-Br(2)	76.43(7)
O(1)–Ce–O(3)	133.57(10)		

short contact between Ce and C(6) of 3.38 Å; the very slight elongation of Si(2)–C(6); the closing of the N–Si(2)–C(6) angle to 110.2(2)°; the coplanarity of the atoms Ce, N, Si-(2), and C(6). This last observation ameliorates to some extent the lack of significant differences between the geometry around C(1) and C(6), especially when the Ce–C(1) distance of 3.81 Å (the second closest metal–methyl contact) is taken in comparison. Similar, although significantly stronger, agostic interactions have been detected in the crystal structure of [Ce(η^5-C$_5$Me$_5$)(NR$_2$)$_2$], where the closest methyl–cerium contacts are 2.972(9) and 2.952(9) Å.[44] The tenuous grasp that Ce has on C(6) in **5** results in the adjacent ligands' donor atoms O(1), O(3), and Br(1) folding in toward the partially vacant site, this being the major source of distortions from the ideal. Somewhat surprisingly, no Ce(III)–Br bond lengths are available for comparison with those found here, although at 2.8854(5) and 2.9115(5) Å they are practically identical with those [2.8738-(9), 2.8963(9), 2.9119(8) Å] found for the more straightforward tribromide [CeBr$_3$(thf)$_4$] (**4**) (see Figure 5, and Table 6) and represent simply the sum of the ionic radii of the respective elements.

The question of why exactly the reagents reported here are capable of oxidizing **A**, while the nominally more powerfully oxidizing elemental halogens fail in this role, is difficult to answer satisfactorily. A clue may be garnered

(44) Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637.
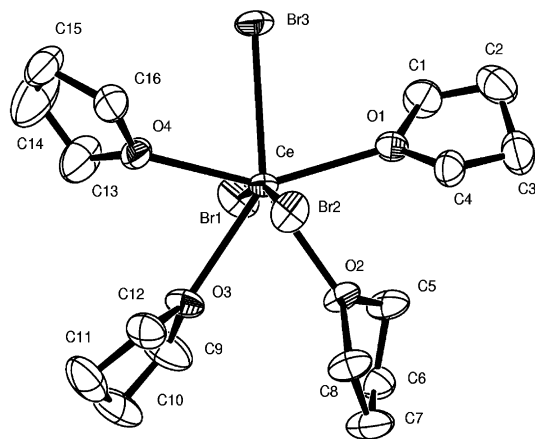
Figure 5. Molecular structure of [CeBr₃(thf)₄] (**4**).

Table 6. Selected Bond Lengths and Angles for [CeBr₃(thf)₄] (**4**)

	Bond Lengths (Å)		
Ce−Br1	2.8963(9)	Ce−O2	2.527(5)
Ce−Br2	2.8738(9)	Ce−O3	2.572(5)
Ce−Br3	2.9119(8)	Ce−O4	2.514(6)
Ce−O1	2.499(6)		
	Bond Angles (deg)		
Br1−Ce−Br2	166.11(3)	O1−Ce−O2	69.71(8)
Br1−Ce−Br3	89.58(3)	O1−Ce−O3	140.77(18)
Br2−Ce−Br3	104.30(3)	O1−Ce−O4	148.45(18)
O1−Ce−Br1	96.87(14)	O1−Ce−Br2	86.82(13)
O1−Ce−Br3	77.02(12)		

when it is noted that both $TeCl_4$ and PBr_2Ph_3 dissociate in solution to form halogenonium ions, specifically $[TeCl_3]^+$ and $[PBrPh_3]^+$. Thus, they display enhanced electrophilicity in coordinating solvents, and this may lower the barrier to electron transfer from the metal to the main group center. Of course, this is likely to be only one aspect of a more complicated overall picture.

While $TeCl_4$ is commercially available, as is PBr_2Ph_3 which is also readily synthesized,[25] attempts to make a fluoride analogue of **1** and **3** were hampered by a lack of suitable starting materials, as sources of electrophilic fluorine are rather rare. We found, however, that CoF_3 was capable of oxidizing [Ce(NR₂)₃] (the oxidation in this case being initiated by the metal ion itself) although isolation of products was exceptionally difficult and, more importantly, unreliable. On the one occasion that we isolated crystalline material from

the reaction mixture, its external appearance was indistingusihable from those of **1** and **3**. Its stability was marginal, decomposing above 30 °C or on dissolution in any solvent. The mass spectrum of the solid revealed only peaks for the precursor complex **A**; no fluoride-containing peaks were observed, and the existence of [CeF(NR₂)₃] therefore remains unconfirmed. In contrast, we found no evidence for Ce(IV) products in the reaction of [Ce(NR₂)₃] with PI_2Ph_3, although a transient purple coloration was observed. No starting materials were recovered, suggesting that an oxidation had taken place but also that the putative intermediate "[CeI-(NR₂)₃]" was too unstable for isolation. This parallels observations on the [U(C₅Me₅)₃X] (X = F, Cl, Br, I) system, where the iodide was the least stable.[45]

Conclusions

While we found that it is possible to oxidize [Ce(NR₂)₃] to give well-defined molecular cerium(IV) amides in the case of the chloride and bromide species, there is an apparent lack of generality in this system. The list of failed alternative oxidants that we have compiled for this cerium amide is quite lengthy: Br_2, I_2, NBS, NCS, $AgBF_4$, AgCN, $Hg(C_6F_5)_2$, $PbCl_2$, and *t*BuOO*t*Bu were all tried and in all cases only unreacted [Ce(NR₂)₃] was recovered. When taken as a whole, however, the present results must be judged to be encouraging; we are continuing work in this area to widen the available range of oxidants and substrates. In addition, those reactions which led to the isolation of Ce(III) species while circuitous have allowed the isolation of otherwise unavailable classical cerium complexes, namely the mono- and bis-(amido)cerium(III) halides.

Supporting Information Available: Tables of crystal data, refinement details, atomic displacement parameters for all non-hydrogen atoms, and bond angles and distance in CIF format for structures of the compounds **1−5**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC035100V

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