

Silylamine Elimination

Cerium(III/IV) Formamidinate Chemistry, and a Stable Cerium(IV) Diolate

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Abstract: Four new cerium(III) formamidinate complexes [Ce(*p*-TolForm)₃], comprising [Ce(DFForm)₃(thf)₂], [Ce(DFForm)₃], and [Ce(EtForm)₃] were synthesized by protonolysis reactions using [Ce{N(SiMe₃)₂}₃] and formamidines of varying functionality, namely N,N'-bis(4-methylphenyl)formamidine (p-TolFormH), N,N'-bis(2,6-difluorophenyl)formamidine (DFFormH), and the sterically more demanding N,N'bis(2,6-diethylphenyl)formamidine (EtFormH). The bimetallic cerium lithium complex [LiCe(DFForm)₄] was synthesized by treating a mixture of $[Ce\{N(SiHMe_2)_2\}_3(thf)_2]$ and [Li{N(SiHMe₂)₂}] with four equivalents of DFFormH in toluene. Oxidation of the trivalent cerium(III) formamidinate complexes by trityl chloride (Ph₃CCl) caused dramatic color

Introduction

Recent advances in cerium(IV) silylamide chemistry have shown that [Ce{N(SiMe₃)₂}] can be oxidized by TeCl₄,^[1] Ph₃CCl,^[2] and PhICl₂^[3] to give the heteroleptic cerium(IV) complex [Ce{N(SiMe₃)₂}₃Cl], in varying yields. Notably, oxidation of [Ce{N(SiMe₃)₂}₃] by Ph₃CCl appeared quantitative, with a good isolated yield (81%). When initially synthesized by Lappert and co-workers, [Ce{N(SiMe₃)₂}₃Cl] was described as unstable, decomposing after several hours at ambient temperature, producing small amounts of [Ce{N(SiMe₃)₂}₃] and a trivalent chloro-bridged species [Ce{N(SiMe₃)₂}₂(µ-Cl)(thf)]₂.^[1,4] Such instability of cerium(IV) species is not uncommon, with a multitude of products generated upon decomposition.^[1,2,4,5] Furthermore, in the case of heteroleptic chlorides, ligand redistribution is possible forming homoleptic species, and, if the coordination of four bulky ligands is too sterically demanding at the cerium(IV) center, spontaneous reduction may occur. The stability, or resistance of cerium(IV) compounds towards redis-

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changes, although the cerium(IV) species appeared transient and reformed cerium(III) complexes and *N'*-trityl-*N*,*N'*-diarylformamidines shortly after oxidation. The first structurally characterized homoleptic cerium(IV) formamidinate complex [Ce(*p*-ToIForm)₄] was obtained through a protonolysis reaction between [Ce{N(SiHMe₂)₂}₄] and four equivalents of *p*-ToI-FormH. [Ce{N(SiHMe₂)₂}₄] was also treated with DFFormH and EtFormH, but the resulting cerium(IV) complexes decomposed before isolation was possible. The new cerium(IV) silylamide complex [Ce{N(SiMe₃)₂}₃(bda)_{0.5}]₂ (bda = 1,4-benzenediolato) was synthesized by treatment of [Ce{N(SiMe₃)₂}₃] with half an equivalent of 1,4-benzoquinone, and showed remarkable resistance towards protonolysis or reduction.

tribution is highly dependent on ligand type, reaction environment, and solvent.^[2, 5-7] This is highlighted with the comparison between the cerium bis(trimethylsilyl)amide complex (above) and the slightly less bulky bis(dimethylsilyl)amide analogue. When [Ce{N(SiHMe₂)₂}₃(thf)₂] was oxidized by chlorinating agents PhICl₂, Ph₃CCl, or C₂Cl₆, the homoleptic species [Ce{N-(SiHMe₂)₂]₄] was isolated, in varying yields.^[7] Of the oxidants used, treatment with Ph₃CCl showed the highest yield (60% isolated) when compared with PhICl₂ (20% crystal yield) or C₂Cl₆, which reacted slowly compared with the other oxidants (45% crystal yield). Furthermore, [Ce{N(SiHMe₂)₂]₄] was produced by a redistribution process, making bulk purification difficult.^[7] The presence of donor solvents dramatically affected the synthesis of [Ce{N(SiHMe₂)₂}₄]. In the absence of THF, oxidation by the above chlorinating agents produced the cerium(III) chloride cluster $[Ce_5{N(SiHMe_2)_2}_8CI_7]$, instead of a tetravalent complex. Such a subtle change to the system highlights the many difficulties associated with the synthesis of organocerium(IV) complexes. Another example of the formation of a homoleptic complex occurred with the di(cyclohexyl)amido (NCy₂) ligand. The homoleptic cerium(IV) species [Ce(NCy)₄] was generated by exposure of the trivalent precursors [Ce(NCy₂)₃] (through redistribution) or [Li(thf)Ce(NCy₂)₄] to dry O₂, and the cerium(IV) complex generated showed stability in toluene.^[8]

Although monoanionic amido ligands have allowed Ce^{IV} stabilization to some degree, very few bidentate nitrogen-based donors have been employed as Ce^{IV} supports. The oxidation of cerium amidinates has not been widely studied, with [Ce(*p*-MeOC₆H₄C(NSiMe₃)₂)₃Cl] featuring as the only reported example of a tetravalent amidinate species, which was isolated from the

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oxidation of [Ce(p-MeOC₆H₄C(NSiMe₃)₂)₃] with half an equivalent of PhICl₂.^[3] Within the class of amidinato ligands, N,N'-diarylformamidinato derivatives are of potential interest in cerium(IV) chemistry as the proligands are readily prepared and can be electronically and sterically tuned. Such formamidinato ligands have been studied extensively in transition-metal^[9] and main-group chemistry.^[10] One focus of the more recently developed rare-earth metal-derived chemistry^[11] has been the modulation of steric effects of formamidinato ligands to induce C-F bond activation of a coordinating C_6F_5 group.^[11a,b,12] Oxidation studies of rare-earth metal formamidinate complexes have so far only involved reactions of divalent Yb^[11c] and Sm complexes.^[12,13] Currently there is only one example of a cerium formamidinate complex, namely the trivalent [Ce(DippForm)₂F-(thf)] (DippForm = N, N'-bis(2, 6-diisopropylphenyl)formamidinate), and its possible oxidation was not examined.^[11b] Thus, trivalent and tetravalent cerium formamidinate chemistry is still an unexplored area.

Herein we describe the synthesis of five new cerium(III) formamidinate complexes utilizing three formamidinato ligands of varying functionality, namely N,N'-bis(4-methylphenyl)formamidinato (p-TolForm), N,N'-bis(2,6-difluorophenyl)formamidinato (DFForm), and N,N'-bis(2,6-diethylphenyl)formamidinato (EtForm). The complexes have been treated with the oxidizing agent Ph₃CCI in an attempt to isolate cerium(IV) formamidinate complexes. Although oxidation was apparent, no stable cerium(IV) product was isolated with any ligand system, but some decomposition products of the cerium(IV) transient species were obtained, namely trityl-coupled formamidines and in some cases cerium(III) products

some cases cerium(III) products. In an alternative approach, [Ce{N(SiHMe₂)₂}₄] was synthesized by an improved route and was subsequently used as a protonolysis precursor for reactions with formamidines, thereby giving the cerium(IV) formamidinate complex $[Ce(p-TolForm)_4]$. A new cerium(IV) silylamide complex, $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2$ (bda = 1,2-benzenediolato), was synthesized by oxidation of [Ce{N(SiMe₃)₂}₃] with 1,4-benzoquinone, and shows remarkable stability towards reduction and protonolysis.

Results and Discussion

Synthesis and structural characterization of cerium(III) formamidinate complexes

All cerium(III) silylamide reagents were synthesized by salt metathesis reactions between $[CeCl_{3^{-1}}$ (thf)₂] and $[KN(SiMe_3)_2]$ or [LiN- $(SiHMe_2)_2$]. All cerium(III) formamidinate species $[Ce(p-Tol-Form)_3]$ (1), $[Ce(DFForm)_3(thf)_2]$ (2), $[Ce(DFForm)_3]$ (3), and $[Ce(EtForm)_3]$ (4; p-TolFormH: N,N'-bis(4-methylphenyl)formamidine, DFFormH: N,N'-bis(2,6-difluorophenyl)formamidine, EtFormH: N,N'-bis(2,6-diethylphenyl)formamidine) were synthesized by protonolysis reactions between $[Ce\{N(SiMe_3)_2\}_3]$ and the stoichiometric amount of the corresponding formamidine, whereas $[LiCe(DFForm)_4]$ (5) was synthesized by treating equivalent amounts of $[Ce\{N(SiHMe_2)_2\}_3(thf)_2]$ and $[LiN(SiHMe_2)_2]$ with four equivalents of DFFormH (Scheme 1).

The formamidinate complexes 1-5 were isolated in high yields (1, 96%; 2, 90%; 3, 95%; 4, 95%; 5, 72%). Considering also the initial synthesis of [Ce{N(SiMe₃)₂}₃], the yields are comparable with those of similar formamidinate complexes of other rare-earth metals ([Ln(Form)₃(thf)_n], n = 0-2), previously synthesized by the one-pot redox transmetalation protonolysis (RTP) using diarylmercury reagents.^[11a,b] Complex 1, when synthesized in Et₂O or toluene, precipitates as an insoluble powder allowing easier isolation compared with the synthesis in THF, from which, upon vacuum drying, a mixture of uncharacterized solvated and unsolvated species was obtained. Complex 1 is sparingly soluble in toluene and essentially insoluble in hexane or Et₂O at ambient temperature. When compared with the other more soluble mononuclear complexes 2-4, it is plausible that complex 1 is a multinuclear species. Once synthesized in THF, 2 can be dried and crystallized from a hexane solution as a solvated mononuclear complex: [Ce(DFForm)₃-(thf)₂] (Figure 1, top). The complex is soluble in toluene and is sparingly soluble in hexane at ambient temperature. The coor-



Scheme 1. Synthesis of complexes **1–4**, reaction time for each complex: 16 h. In each reaction three equivalents of $3 \text{ HN}(\text{SiMe}_3)_2$ were produced and removed by vacuum drying (2–5 h). a) 3 p-TolFormH, toluene or diethyl ether; b) 3 DFFormH, THF; c) 3 DFFormH, toluene; d) 3 EtFormH, THF; e) reaction time 24 h in toluene, Ar = (2,6-diffuorophenyl), four equivalents of HN(SiHMe}_2)_2 were removed by vacuum drying.

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Figure 1. Crystal structures of complexes $[Ce(DFForm)_3(thf)_2]$ (**2**, top) and $[Ce(DFForm)_3]$ (**3**, bottom). Ellipsoids shown at 50% probability. Lattice solvents and hydrogen atoms have been removed for clarity. Complex **2** crystallized with two independent molecules in the asymmetric unit, only one is depicted above.

dinating THF on complex 2 cannot be removed readily. When boiled in toluene and dried under vacuum, recrystallization from hexane yielded only 2 in good yields. The unsolvated DFForm complex 3 was prepared and isolated from a toluene solution. It has a lower solubility in toluene than complex 2, but much higher solubility than 1. From a toluene solution under partial vacuum, 3 crystallized as the monomeric homoleptic species [Ce(DFForm)₃]-PhMe (3-PhMe, Figure 1, bottom), with a toluene of crystallization that is partly lost upon extended drying giving a bulk solid with composition [Ce-(DFForm)₃]-0.5 PhMe as determined by elemental analysis and ¹H NMR spectroscopy. Complex 3 can be readily dissolved in THF forming the THF solvated species 2, but this process, as indicated above, appears irreversible (Scheme 1).

Because of the lack of solvent coordinating to cerium in complex **3** and the relatively low bulk of the ligand, coordination saturation of the cerium atom is accomplished by the interaction with four fluorine atoms, all weakly bonding at an

identical distance of 2.92 Å, well within the sum (3.29 Å) of the Ce metallic radius (1.82 Å)^[14] and fluorine van der Waals radius (1.47 Å).^[15] Thus, cerium has a formal coordination number of ten. The Ce–F distances in complex **3** are longer than those reported for other ligand systems which also show *o*-F–Ce coordination,^[16a,b] such as the eight-coordinate cerium diaminate complex tris(*N*,*N'*-diethyl-*N'*-2,3,5,6-tetrafluorophenylethane-1,2-diaminato)cerium(III), which displays three shorter Ce–F interactions at 2.686, 2.764, and 2.779 Å and has good thermal stability.^[16a] Investigations into a potential C–F bond activation of the coordinating fluorine atoms in complex **3** has not yet been undertaken. The Ce–N bond lengths for **3** are shorter than those observed in complex **2**, and are more comparable with those of the six-coordinate EtForm species **4**, consistent with weak *o*-F–Ce interactions (Table 1). The absence of THF in com-

Table 1. Selected interatomic distances [Å] for complexes 2, 3, and 4.									
Ce–X	2	3	4	Ce–X	2	3			
Ce-N(1)	2.576(3)	2.486(2)	2.507(2)	Ce-F(1)	-	2.9186(13)			
CeN(2)	2.599(4)	2.489(2)	2.526(2)	Ce-F(3)	-	2.9189(13)			
Ce-N(3)	2.546(3)	2.479(2)	2.480(2)	Ce-F(5)	-	2.9189(13)			
CeN(4)	2.602(3)	2.580(2)	2.476(2)	Ce-F(11)	-	2.9206(13)			
CeN(5)	2.566(3)	2.581(2)	2.501(2)	Ce-O(1)	2.515(3)	-			
Ce—N(6)	2.595(4)	2.479(2)	2.499(2)	Ce-O(2)	2.508(3)	-			

plex 3 allows closer Ce-N distances and, consequently, fluorine coordination. Although a weak interaction, the coordinating fluorine has an influence on the C_{ipso} -N-CH angle. For a phenyl group containing a fluorine atom coordinating to cerium in 3, the Cipso-N-CH angles are in the range 126.4(2)-128.3(2)°, whereas for those with non-coordinating fluorine atoms, they are in the range 121.68(19)-121.71(19)° (Figure 2). The corresponding angles in complex 2 are significantly smaller (116.1(4)–121.4(4)°). Furthermore, Ce–F interactions have a slight effect on the o-carbon fluorine bond length causing slight elongation: 1.376(2) Å, compared with the non-coordinating fluorine atoms (1.359(2) Å). Complex 2 has no Ce-F interactions, with the closest Ce-F distance (3.67 Å) far beyond the sum of the van der Waals radii. Therefore, cerium has a coordination number of eight and a geometry best described as distorted dodecahedral and the THF ligands have a transoid disposition $(O(1)-Ce(1)-O(2) = 153.60(11)^{\circ}$ O(3)-Ce(2)-O(4) =157.34(11)°). The transoid THF coordination in 2 is comparable to [La(o-TolForm)₃(thf)₂], which also displays transoid THF coor-



Figure 2. Increase in the C_{ioso}-N-CH bond angle due to Ce–F interactions.



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dination (O(1)-La(1)-O(1): 157.23(17)°).^[11b] Complex **4**, using the bulkier EtForm ligand, crystallizes from toluene to afford the six-coordinate homoleptic species [Ce(EtForm)₃]·PhMe (**4**·PhMe, not shown), mirroring the La, Nd, Sm, Ho and Yb species previously reported.^[11b]

The cerium–lithium bimetallic complex **5** is the first reported trivalent rare-earth complex with *four* coordinating formamidinato ligands, with all previous derivatives having only two or three (Figure 3). The cerium atom is ten-coordinate, with eight



Figure 3. Crystal structure of $[LiCe(DFForm)_4]$ (5); ellipsoids shown at 50% probability; hydrogen atoms removed for clarity. See Scheme 1 for a simplified drawing. Relevant interatomic distances [Å]: Ce–N(1) 2.694(2), Ce–N(3) 2.805(3), Ce–N(5) 2.900(2), Ce–N(2) 2.498(3), Ce–N(4) 2.543(3), Ce–N(6) 2.528(2), Ce–N(7) 2.490(2), Ce–N(8) 2.731(2), Ce–F(3) 2.962(2), Ce–F(7) 3.276(2), ^[a] Ce–F(11) 3.127(2), ^[a] Ce–F(13) 3.009(2), Li–N(1) 2.199(6), Li–N(3) 2.136(6), Li–N(5) 2.128(6), Li–F(1) 2.053(6), Li–F(5) 2.012(6), Li–F(9) 2.023(6). [a] Non-bonding.

nitrogen and two fluorine donor atoms. The Ce–F distances are somewhat longer than for complex ${\bf 3}$ but still well within

the sum of the appropriate radii (above). Longer Ce-F(7) and Ce-F(11) distances have less significance. The encapsulated lithium atom is six-coordinate, with closer lithium fluorine interactions than the bridging lithium nitrogen bond lengths. The preferential interaction with fluorine over nitrogen is in contrast to the N,N'-bis(2-fluorophenyl)formamidinate (FForm) derivative $[Li(FForm)(Et_2O)]_{2}$ which shows closer Li-N bonding than Li-F. The inability of the lithium metal to bind to the nitrogen atoms at a closer distance is probably due to the bridging of the ligands to the larger, higher charged cerium atom. The

cerium nitrogen bonding brings three fluorine atoms into close proximity to lithium. Complex 5 shows one terminal formamidinato ligand bound to cerium and three formamidinato ligands bridging between cerium and lithium. The bridging formamidinato ligands have one μ - κ^1 , κ^1 nitrogen atom and one κ^1 . One of the bridging ligands is tetradentate, with four sites of coordination (F, N, N', F'), and two are tridentate (F, N, N') whereas the terminal ligand shows F, N, N' chelation. The structure is the first crystallographically characterized rareearth metal-lithium bimetallic amidinate complex, showing unsolvated six-coordinate lithium encapsulation (three N and three F donor atoms). Despite the close Li-F interactions, the complex appeared stable at ambient temperature, with no signs of C–F bond activation (compare with ref. [16]). In C₆D₆, the ¹⁹F NMR spectrum of the complex shows only a single ligand environment, indicating rapid formamidinato ligand (or Li⁺) exchange at ambient temperature.

The trivalent formamidinate complexes showed typical paramagnetic shifting in their NMR spectra and with complexes 1 and 2 no coherent ¹H NMR spectra could be obtained. In this regard, the contrast between 2 with THF coordination and unsolvated 3 is noteworthy. However, both gave clear but differing ¹⁹F NMR spectra. Elemental analyses for complexes 1–5 were obtained from the bulk material, after hexane washing and drying, and all values are within acceptable limits for airsensitive rare-earth metal complexes.

Oxidation of trivalent cerium formamidinate complexes 1-5

The cerium(III) complexes **1–5** were tested as precursors for cerium(IV) formamidinate complexes. Initially each complex was treated with either TeCl_{4r} Hg(C₆F₅)₂, perfluorodecalin or C₂Cl₆, but showed no signs of oxidation upon reagent addition. When trityl chloride was added, each complex **1–5** showed signs of oxidation by dramatic color changes, typically from light yellow to darker colors (dark brown/deep green). Each cerium(IV) species was short lived decomposing soon after for-



Scheme 2. Attempted synthesis of $Ce^{|V|}$ formamidinate complexes from trivalent formamidinate complexes by oxidation with trityl chloride: a) $[Ce(p-TolForm)_3]$ (1), THF; b) $[Ce(DFForm)_3(thf)_2]$ (2), THF; c) $[Ce(DFForm)_3]$ (3), toluene; d) $[Ce(EtForm)_3]$ (4), THF; e) $[LiCe(DFForm)_4]$ (5), THF, -LiCl.

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mation (from near instantaneous to several hours, see the Experimental Section), with no cerium(IV) products isolated before decomposition (Scheme 2). It appears that when trityl chloride is used as an oxidant for **1**, the initially formed cerium(IV) complex is reduced by the trityl radical co-product, producing *N*,*N'*-bis(4-methylphenyl),*N'*-(triphenylmethyl)-formamidine (**6a**, Scheme 2, a; Figure 4, top). Likewise *N*,*N'*-bis(2,6-difluorophenyl),*N'*-(triphenylmethyl)formamidine (**6b**) was obtained from oxidation of complexes **2**, **3**, and **5** (Scheme 2, b, c, e; Figure 4, middle). All reactions appear to follow the reaction pathway: $[Ce^{III}(Form)_3] + Ph_3CCI \rightarrow "[Ce^{IV}(Form)_3CI] +$



Figure 4. Crystal structures of compounds **6a** (top), **6b** (middle), and **6c** (bottom). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvent were removed for clarity.

 $Ph_3C'' \rightarrow [Ce^{III}(Form)_2CI] + Form(CPh_3)$. Cerium(III) products then arise from the degradation of $[Ce^{III}(Form)_2CI]$.

With the oxidation of complexes 1 and 3, isolation of the cerium-containing product was not possible. The trimetallic pentachloride complex $[Ce_3Cl_5(DFForm)_4(thf)_4]$ (7 a) was obtained from the oxidation of complex 2, and identified by X-ray crystallography of very small crystals (Figure 5). However 7 a was not the sole product of decomposition, and the presence of other species caused difficulty in characterizing the product by other means. Complex 4, with the bulky EtForm ligand, was the least stable transient cerium(IV) complex, discoloring from dark green to light gold within seconds after formation. Small crystals were grown from the reaction mixture revealing the formation of the formamidinatocerium dichloride species $[Ce(EtForm)Cl_2(thf)_3]$ (7 b, Figure 5, bottom). A small



Figure 5. Crystal structures of [Ce₃Cl₅(DFForm)₄(thf)₄]·4 THF (7 a, top) and [Ce-(EtForm)Cl₂(thf)₃] (7 b, bottom). Ellipsoids shown at 50% probability. Lattice solvents (7 a), and hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: 7a: Ce1-Cl1 2.8323(15), Ce1-Cl2 2.9870(15), Ce1-Cl3 2.9585(14), Ce1-Cl4 2.8027(13), Ce1-N1 2.521(5), Ce1-N2 2.547(5), Ce1-O1 2.482(5), Ce1-O2 2.496(4), Ce2-Cl1 2.8526(15), Ce2-Cl2 3.0053(14), Ce2-Cl3 2.9151(14), Ce2-Cl5 2.8075(14), Ce2-N3 2.525(5), Ce2-N4 2.549(5), Ce2-O3 2.472(4), Ce2-O4 2.518(5), Ce3-Cl2 2.9191(14), Ce3-Cl3 3.0527(14), Ce3-Cl4 2.8990(14), Ce3-Cl5 2.9095(14), Ce3-N5 2.565(5), Ce3-N6 2.534(4), Ce3-N7 2.563(5), Ce3-N8 2.566(5); Ce1-Cl1-Ce2 97.28(4), Ce1-Cl2-Ce2 90.81(4), Ce1-Cl3-Ce2 93.81(4), Ce1-Cl4-Ce3 97.46(4), Ce2-Cl2-Ce3 92.76(4), Ce2-Cl3-Ce3 91.87(4), Ce2-Cl5-Ce3 97.21(4). 7 b: Ce1-Cl1 2.7224(12), Ce1-Cl2 2.7308(12), Ce1-N1 2.500(3), Ce1-N2 2.523(3), Ce1-O1 2.488(3), Ce1-O2 2.551(3), Ce1-O3 2.518(3); Cl1-Ce1-Cl2 165.68(4), Cl1-Ce1-O1 95.69(8), Cl1-Ce1-O2 80.55(8), Cl1-Ce1-O3 87.14(8), Cl2-Ce1-O1 83.46(8), Cl2-Ce1-O2 85.44(9), Cl2-Ce1-O3 86.60(8).

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amount of reaction mixture was hydrolyzed by D₂O in C₆D₆ and analyzed by ¹H NMR spectroscopy, indicating the presence of *N,N'*-bis(2,6-diethylphenyl),*N'*-(triphenylmethyl)formamidine (**6 c**) by the chemical shift of the N=CH–N backbone (8.54 ppm) distinctive from that of EtFormH (6.92 ppm, N=CH– N). Crystals of **6 c** were not obtained directly from the reaction mixture. However, treatment of the residue from evaporation of the reaction mixture with hot acetonitrile gave small crystals of **6 c**-CH₃CN (Figure 4, bottom). Treatment of complex **5** with Ph₃CCl gave a deep red solution within hours of stirring. However, upon evaporation and addition of hexane only crystals of

complex **2** and compound **6b** were obtained. The ¹⁹F NMR spectrum of a reaction mixture showed the presence of only **2** and **6b**.

Complex **7a** has two different cerium coordination environments. Ce(3) is ligated by two formamidinato ligands and four chloro anions, whereas Ce(1) and Ce(2) are coordinated by one formamidinato ligand, two THF molecules and four chloro anions. Thus, each cerium atom is eight-coordinate. The complex crystallized with four THF molecules within the lattice. This pentachloro bridging motif is known for other rare-earth metal com-

plexes, with similar examples for diketiminate^[17] and cyclopentadienyl complexes.^[18] Other similar motifs have four bridging chloro ligands and another bridging species, such as $[N(SiHMe_2)_2]$ or $[CH_2]$.^[19] A similar fluoro-bridged moiety is known in the bulky aryloxide complex $[Er_3F_5(thf)_4(OArOMe)_4]$ (OArOMe=2,6-di-tert-butyl-4-methoxy-phenolato),^[20] which has the same asymmetry of ligand attachment, but each erbium atom is six- or seven-coordinate, opposed to the eight-coordinate cerium atoms in complex **7a**. Complex **7b** contains two terminal chloro anions coordinating *trans* to each other with bond lengths of Ce–Cl(1)=2.7224(12) and Ce–Cl(2)= 2.7308(12), which, as expected, are shorter than the bridging Ce–Cl bonds of complex **7a**. The closest Ce–Cl interaction in **7a** is 2.8027(13) between Ce(1) and Cl(4), with the other Ce–Cl distances ranging between 2.8075 (14) and 3.0527 (14).

Other reagents were examined for cerium(III) formamidinate oxidation, such as dry O_2 , benzoquinone, and $PhICI_2$. Each oxidant showed signs of oxidizing the trivalent cerium complexes 1–5, as indicated by a dramatic color change, but each species decomposed to lighter colored species, with NMR analyses showing paramagnetic peak broadening, all indicative of the formation of trivalent cerium complexes. Currently no products have been isolated. It should also be noted that treatment of complex 2 with Ph_3SiCI showed no signs of reactivity, even with extended heating.

$[Ce\{N(SiHMe_2)_2\}_4]$ as a precursor for cerium(IV) formamidinates

The homoleptic Ce^{IV} bis(dimethylsilyl)amide (**9**) has formerly been synthesized from a redistribution process (see the Introduction).^[7] Therefore, a new synthesis route that eliminated the redistribution step was sought.^[21] A trivalent cerium–lithium bimetallic complex with four silylamido ligands, [Li-(thf)Ce{N(SiHMe₂)₂}] (**8**), was synthesized by treatment of [CeCl₃(thf)₂] with four equivalents of [Li{N(SiHMe₂)₂}] in toluene (Scheme 3). The crystal structure of complex **8** mirrors the



Scheme 3. Synthesis of homoleptic complex $[Ce{N{SiHMe}_2}_2]_4]$ (9) from Ce^{III} bis(dimethylsilyl)amide ate complex 8 and formamidine-promoted protonolysis reactions.

cerium di(cyclohexyl)amide complex $[Ce(NCy_2)_4Li(thf)]$.^[8] Two terminal bis(dimethylsilyl)amido ligands coordinate to cerium while the remaining two bridge between the Ce and Li metal atoms (Figure 6). The presence of THF impacts the solubility and reactivity of **8** dramatically.



Figure 6. Crystal structure of [Li(thf)Ce{N(SiHMe₂)₂}₄] (**8**). Ellipsoids shown at 35% probability. Hydrogen atoms and atom disorder removed for clarity. Selected bond (Å) lengths and angles (°) for (**8**): Ce1–N1 2.388(5), Ce1–N2 2.386(4), Ce1–N3 2.523(4), Ce1–N4 2.532(5), Li1–N3 2.087(11), Li1–N4 2.094(12), Li1–O1B 1.83(3); N1-Ce1-N2 98.19(16), N1-Ce1-N3 110.76(15), N1-Ce1-N4 134.64(16), N2-Ce1-N3 131.98(15), N2-Ce1-N4 107.21(15), Ce1-N3-Li1 90.04(3), Ce1-N4-Li1 90.0(3), O1B-Li1-Ce1 167.1(7), N3-Li-O1B 134.9(10), N3-Li-N4 100.3, N4-Li-O1B 124.1(9).

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Ate complex **8** proved to be an excellent precursor for $[Ce\{N(SiHMe_2)_2\}_4]$ (**9**), when treated with half an equivalent of C_2Cl_6 in toluene. The ¹H NMR analysis of the reaction mixture indicated quantitative oxidation. Complex **9** was separated from LiCl by filtration and was isolated as sticky red crystals by evaporation of solvent and C_2Cl_4 under vacuum. The oxidation of **8** was repeated several times under different conditions and the major factors which adversely affected reaction times were (determined by time taken for color change) 1) oxidation in THF instead of toluene and 2) the use of stronger oxidants, such as PhICl₂ or TeCl₄ (caused the sample to fume and form a black viscous oil in toluene). The first cerium(IV) formamidinate complex was then synthesized by treating **9** with four equivalents of *p*-ToIFormH producing $[Ce(p-ToIForm)_4]$ (**10**) in high isolated yield (72%; Scheme 3).

When **9** was treated with DFFormH in THF or toluene, the solution initially remained dark red, but completely discolored to white after 16 h of stirring. Clear colorless crystals were grown from a THF/hexane mixture, with X-ray crystallography revealing the formation of the trivalent complex **2**. When Et-FormH was added to **9** in toluene the solution turned dark green but discolored completely to a golden yellow after minutes of stirring. Crystals of complex **4** were grown from the reaction solution. The formation of the trivalent derivatives indicates that the corresponding cerium(IV) formamidinate complexes are unstable. Similarly, Lappert's [Ce{N(SiMe₃)₂}₃CI] also reformed [Ce{N(SiMe₃)₂}₃] upon decomposition.^[4] Evidently, steric effects govern the stability of cerium(IV) formamidinates, as stability declines in the series *p*-TolForm > DFForm > EtForm, namely, in the order of increasing steric bulk.

Complex **10**, unlike the trivalent derivative, is dark green in color and readily soluble in toluene, C_6D_6 , Et_2O , and THF (Figure 7). The ¹H NMR spectrum of **10** showed no indication of a paramagnetic species or impurities upon synthesis. The ¹H NMR resonance (9.83 ppm) of the N=CH–N backbone of **10** is comparable with that of the diamagnetic potassium complex [K(*p*-TolForm)(18-crown-6)] (9.15 ppm)^[10e] notably shifted from the *p*-TolFormH value: (7.88 ppm). Typically for paramagnetic systems, the backbone hydrogen resonance is shifted extensively, as shown by the paramagnetic complexes **3**, **4**, and **5** (20.82, 14.38, 12.76 ppm, respectively).

Complex 10 is the first cerium(IV) formamidinate complex and only the second cerium(IV) amidinate complex known (see the Introduction). The coordination number of cerium in 10 is eight, showing stereochemistry best described as distorted dodecahedral. The Ce-N bond lengths average 2.44 Å, with a range of 2.407(2) (N3)-2.477(2) Å (N6). As expected these are shorter on average than those of the cerium(III) formamidinate precursors (Table 1 and Figure 3, caption), such differences owing to the larger ionic radii of Ce³⁺. The bond lengths of **10** are comparable with those of the bulky N,N'-bis(trimethylsilyl)-4-methoxybenzeneimidamide complex [Ce(p-MeOC₆H₄C-(NSiMe₃)₂)₃Cl], which has Ce-N bond lengths averaging 2.43 Å with a wider range of 2.3583(19)-2.5019(19) Å.^[3] Although isolated, 10 was still unstable, completely decomposing within days of formation, thereby explaining the somewhat deviant microanalysis. The decomposition of 10 occurred quicker in



Figure 7. Crystal structure of $[Ce(p-TolForm)_4]$ (10). Ellipsoids shown at 50% probability, hydrogen atoms removed for clarity. Selected bond distances and angles (°): Ce1–N1 2.452(2), Ce1–N2 2.456(2), Ce1–N3 2.407(2), Ce1–N4 2.462(2), Ce1–N5 2.427(2), Ce1–N6 2.477(2), Ce1–N7 2.434(2), Ce1–N8 2.459(2); C8-Ce1-C23 119.30(8), C8-Ce1-C38 90.81(7), C8-Ce1-C53 117.46(7).

 Et_2O or THF than in toluene or hexane, from which a brown colored solution was obtained, but no products could be identified.

Despite the shielding of the cerium(IV) center by the $[N(SiHMe_2)_2]$ ligands, complex **9** underwent protonolysis reactions with each formamidine, affording Ce^{IV} formamidinates of differing stabilities. In the following, another cerium(IV) silylamide species was generated which showed a complete contrast in protonolysis reactivity. $[Ce{N(SiMe_3)_2}_3]$ was treated with half an equivalent of 1,4-benzoquinone forming the dinuclear cerium(IV) complex $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2$ (**11**, bda = 1,4-benzenediolato, Scheme 4). A similar redox protocol was previously applied for the synthesis of Ce^{IV} alk(aryl)oxide complexes of type $[\{(tBu_3CO)_3Ce\}_2(\mu_2-O_2C_6H_4)]^{[22]}$ and $[\{Li_3(Et_2O)_{3.5}\}_{(BINOLate)_6Ce}_2(\mu_2-O_2C_6H_4)]$ -Et₂O.^[23]

Complex **11** was isolated from toluene as dark brown crystals. The crystal structure shows $[Ce\{N(SiMe_3)_2\}_3(bda)_{0.5}]$ in the asymmetric unit, with Ce–N bond lengths ranging from 2.2386(14) to 2.2486(14) Å (average: 2.24 Å), values slightly



Scheme 4. Synthesis of heteroleptic Ce^{IV} complex $[Ce\{N(SiMe_3)_2\}_3(bda)_{0.5}]_2$ (11, bda = 1,4-benzenediolato).

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longer than those of $[Ce{N(SiMe_3)_2}_3CI]$ (2.22 Å),^[1] and comparable with $[Ce{N(SiHMe_2)_2}_4]$ (2.25 Å; Figure 8).^[7] The Ce–N bond lengths in **11** are much shorter than in **10**, which has a much higher coordination number. The benzoquinone reagent upon reduction becomes aromatized, which is evident in the crystal structure parameters. The bda ligand coordinates in a near



Figure 8. Crystal structure of $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2$ (**11**, bda = 1,4-benzenediolato). Ellipsoids shown at 50% probability, hydrogen atoms and lattice solvents removed for clarity. Selected bond distances (Å) and angles (°): Ce1-N1 2.2388(14), Ce1-N2 2.2398(15), Ce1-N3 2.2487(14), Ce1-O1 2.0895(13), O1-C19 1.356(2), C19-C20 1.399(2), C20-C21 1.387(3); N1-Ce1-O1 97.19(5), N2-Ce1-O1 99.58(5), N3-Ce1-O1) 105.69(5), Ce1-O1-C19 173.13(11), O1-C19-C20 120.55(16), O1-C19-C21' 120.93(16).

linear fashion to the cerium atom, (Ce-O-C(19) 173.14°, Ce-O 2.0895(13) Å. The C-C bond distances within the reduced bda ring are C(19)-C(20) = 1.399(2), C(19)-C(21)' = 1.396(3), and C(20)–C(21) = 1.388(3) Å, all indicating aromaticity. The cerium(IV) atom is four-coordinate and the stereochemistry is best described as distorted tetrahedral. The ¹H NMR spectrum also supports the aromaticity of the benzene-1,4-diolato ligand, with one resonance in the aromatic region (7.28 ppm) and one signal for the $\{N(SiMe_3)_2\}$ ligands at 0.43 ppm (-3.39 ppm for [Ce{N(SiMe₃)₂}₃]). The dark color, aromaticity of the bda, and the ¹H NMR spectrum all support the successful formation of a cerium(IV) species. Complex 11 shows remarkable stability, with no signs of decomposition weeks after formation unlike the other cerium(IV) silylamide or formamidinate complexes. This stability, however, made 11 a poor reagent as a protonolysis precursor. When one or three equivalents of DFFormH, p-TolFormH, or EtFormH were added to 11, no color change occurred, even after several days of stirring. Large crystals of both the protonated ligand (FormH) and 11 were isolated from all reaction mixtures. Complex 11 also showed no reactivity towards AIMe₃, HAIMe₂, and HN(SiHMe₂)₂, even when excess amounts were used. Complex 11 also resisted reduction when treated with Sml₂(thf)₂, showing no sign of reaction after days of stirring. The inert behavior of 11 can be related to the markedly decreased reactivity of [Ln-{N(SiMe₃)₂}] moieties, as compared to [Ln-{N(SiHMe₂)₂}] (steric effect)—complex 9 readily reacts with formamidines, even with the bulky EtFormH—^[24] or to the presence of the aromatic bda ligand. For comparison, when [Ce{N(SiHMe₂)₂}₃(thf)₂] was treated with half an equivalent of benzoquinone, instead of putative $[Ce{N(SiHMe_2)_2}_3-(bda)_{0.5}]$ only crystals of **9** were isolated with the other species of redistribution unidentified.

Conclusion

Utilizing three formamidinato ligands of varying steric bulk and functionality five new cerium(III) formamidinate complexes were prepared. Each species was treated with various oxidants, mainly with Ph₃CCl and showed evidence of successful oxidation. However, rapid reductive decomposition was prevalent giving trityl formamidines and chlorinated trivalent cerium complexes with the two isolated examples [Ce₃Cl₅(DFForm)₄- $(thf)_{4}$ and $[Ce(EtForm)Cl_{2}(thf)_{3}]$ (DFForm = N,N'-bis(2,6-difluorophenyl)formamidinato and EtForm = N,N'-bis(2,6-diethylphenyl)formamidinato) revealing the structural variety of such heteroleptic complexes. The synthesis of homoleptic [Ce{N-(SiHMe₂)₂]₄] was improved by treating ate complex [Li(thf)Ce{N- $(SiHMe_2)_2_4$] with C_2Cl_6 in toluene. Crucially, $[Ce\{N(SiHMe_2)_2\}_4]$ can be used successfully as a precursor in $Ce^{IV} \rightarrow Ce^{IV}$ transformations as shown for the synthesis, via protonolysis, of the first cerium(IV) formamidinate species [Ce(p-TolForm)₄] (p-Tol-Form = N, N'-bis(4-methylphenyl)formamidinato). The stability of such tetravalent formamidinate species, however, seems to be quite sensitive to the type of formamidinato ligand. Tetravalent $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2$ (bda = 1,4-benzenediolato) was synthesized by oxidation of [Ce{N(SiMe₃)₂}₃] with 1,4-benzoquinone, but unlike $[Ce\{N(SiHMe_2)_2\}_4]$, $[Ce\{N(SiMe_3)_2\}_3(bda)_{0.5}]_2$ did not engage in protonolysis reactions.

Experimental Section

General

All manipulations were performed using glovebox (MBraun 200B; $< 0.1 \text{ ppm O}_{21} < 0.1 \text{ ppm H}_{2}$ O) or Schlenk line techniques under an atmosphere of purified argon gas or nitrogen, in oven-dried glassware. Formamidine proligands (DFFormH, p-TolFormH, and Et-FormH) were synthesized according to a published procedure.^[26] Anhydrous CeCl₃ was purchased from ABRC chemicals and was activated by Soxhlet extraction with THF, giving [CeCl₃(thf)₂]. [K{N(SiMe₃)₂}] was purchased from Sigma–Aldrich and purified by high-vacuum sublimation before use. [Li{N(SiHMe₂)₂}] was synthesized according to published procedures.^[27] Cerium(III) silylamide complexes were synthesized by treatment of [CeCl₃(thf)₂] with three equivalents of [Li{N(SiHMe₂)₂}] or [K{N(SiMe₃)₂}] in hexane and were purified by filtration, evaporation to dryness and crystallization from fresh hexane. [Li(p-TolForm)] was synthesized by treatment of *p*-TolFormH with [Li{N(SiHMe₂)₂}]. Benzoquinone, perfluorodecalin, Cl₂Cl₆, Ph₃CCl, Ph₃SiCl, and TeCl₄ were purchased from Sigma-Aldrich, whereas $C_6H_5ICI_2$ was synthesized according to a published procedure.^[28] Solvents used (THF, Et₂O, hexane, and toluene) were purified with Grubbs columns (MBraun SPS, solvent purification system) and stored in a glovebox. Acetonitrile was purified by distillation over CaH₂ and stored over molecular sieves (3 Å). C₆D₆ was purchased from Sigma-Aldrich, degassed, and dried by being stirred over Na metal for 12 h. The NMR spectra of air and moisture-sensitive compounds in C₆D₆ were recorded with J. Young valve NMR spectroscopy tubes at 25 °C with a Bruker 266 Avance DMX400 (1H: 400.13 MHz; 19F: 282.0 MHz) spectrometer. In-



frared spectra were recorded on either: a Nicolet 6700 FTIR spectrometer (\tilde{v} =4000-400 cm⁻¹) by using a DRIFT chamber with dry KBr/sample mixtures and KBr windows or a Perkin–Elmer 1600 Fourier transform infrared spectrometer (\tilde{v} =4000-500 cm⁻¹) as a Nujol mull. Micro-elemental analysis (C, H, N) was performed with an Elementar Vario Micro cube by Mr. S. Bock (Tübingen University), with the exception of complex **8b**, which was analyzed by the elemental analysis service of London Metropolitan University.

General synthesis of cerium(III) formamidinate complexes 1– 4

[Ce{N(SiMe₃)₂}₃] (0.16 g, 0.26 mmol) and 3 equivalents of formamidine (0.77 mmol) were added to a preweighed sample vial and dissolved in a solvent: (1: Et₂O or toluene, **2**: THF, **3**: toluene, **4**: THF, 3–6 mL). The solution was stirred for 16 h then evaporated in vacuo. Each complex was washed with small amounts of cold hexane, redried, and weighed. Elemental analysis, infrared, and ¹H NMR and ¹⁹F NMR spectra were determined on the bulk sample. ¹H NMR spectra of complexes **1** and **2** were examined but due to paramagnetism, no interpretable spectra were obtained at ambient temperature or on heating.

[**Ce(p-TolForm**]₃] (1): Yield: 0.20 g (96%); DRIFT (KBr): $\bar{v} = 3026$ (m), 2918 (m), 2860 (m), 2729 (vw), 1653 (m), 1608 (w), 1513 (vs), 1506 (vs), 1456 (w), 1419 (w), 1375 (vw), 1302 (s), 1218 (m), 1177 (w), 1112 (vw), 1036 (vw), 1015 (vw), 993 (w), 943 (m), 818 (s), 731 (vw), 711 (w), 644 (vw), 586 (w), 519 (w), 464 cm⁻¹ (w); elemental analysis calcd (%) for C₄₅H₄₅CeN₆ (810.01): C 66.72, H 5.59, N 10.37; found: C 67.19, H 5.54, N 10.11.

[Ce(DFForm)₃(thf)₂] (2): Yield: 0.25 g (90%); ¹⁹F(¹H) NMR (C₆D₆, 300 K): δ = −135.9 ppm (brs); ¹⁹F(¹H) NMR (THF, 300 K): δ = −129.0 ppm (brs); IR (Nujol): \tilde{v} = 1667 (w), 1617 (s), 1576 (vs), 1545 (vs), 1315 (vs), 1269 (s), 1214 (vs), 1149 (w), 1098 (w), 1063 (s), 1000 (vs), 942 (m), 871 (s), 830 (m), 804 (vw), 774 (vs), 742 cm⁻¹ (m); elemental analysis calcd (%) for C₄₇H₃₇CeF₁₂N₆O₂ (1085.93): C 51.98, H 3.43, N 7.74; found: C 51.55, H 3.08, N 7.81. Small amounts of THF and 2 mL of hexane were added to **2**. Colorless block crystals formed at ambient temperature suitable for X-ray diffraction. Boiling **2** in toluene and evaporation to dryness whilst hot (under vacuum) did not remove coordinating THF but, after crystallization from hexane, yielded complex **2**.

[Ce(DFForm)₃]·0.5 PhMe (3): Yield: 0.23 g (95%); ¹H NMR (C₆D₆, 300 K): δ = 2.11 (s, 1.5 H; CH₃, PhMe), 5.58 (m, 12 H; H 3,5, DFForm), 5.77 (m, 6H; H 4, DFForm) 7.03 (m, 2.5 H; Ar-H, PhMe), 20.82 ppm (s, 3 H, NC(H)N); ¹⁹F{¹H} NMR (C₆D₆, 300 K): δ = −138.2 ppm (br s); IR (Nujol): \tilde{v} = 2722 (m), 1652 (s), 1616 (s), 1582 (vs), 1540 (vs), 1309 (vs), 1261 (s), 1234 (m), 1209 (s), 1148 (m), 1060 (s), 989 (s), 937 (m), 825 (w), 769 (m), 715 (m), 688 cm⁻¹ (vw); elemental analysis calcd (%) for C_{42.5}H₂₅CeF₁₂N₆ (3·0.5 PhMe, 987.79): C 51.68, H 2.55, N 8.50; found: C 51.58, H 2.34, N 7.70. Toluene (5 mL) was added to the sample and the mixture was stirred until completely dissolved. The solution was concentrated in vacuo (1–2 mL) and allowed to stand affording colorless block crystals of [Ce(DFForm)₃]·PhMe (3·PhMe) suitable for X-ray diffraction.

[Ce(EtForm)₃] **(4)**: Yield: 0.26 g (95%); ¹H NMR (C₆D₆, 300 K): δ = −14.82 (brs, 3 H; NC(H)N), 0.36 (brs, 24 H; CH₂), 0.71 (brs, 36 H; CH₃), 6.56 (m, 6 H; H4-Ar), 6.72 ppm (m, 12 H; 3,5H-Ar); IR (DRIFT): \bar{v} = 3063 (w), 3063 (w), 2965 (s), 2931 (m), 2872 (m), 1592 (w), 1521 (vs), 1448 (vs), 1375 (w), 1321 (w), 1290 (vs), 1234 (vw), 1195 (s), 1106 (w), 1059 (vw), 1011 (vw), 940 (m), 869 (vw), 808 (w), 767 (m) 756 cm⁻¹ (m); elemental analysis calcd (%) for C₆₃H₈₁CeN₆ (1062.47): C 71.22, H 7.68, N 7.91; found: C 71.03, H 7.20, N 7.85. The sample was redissolved in a toluene/hexane mixture, concent

trated (1 mL), then stored at -30 °C affording large light yellow block crystals of [Ce(EtForm)₃]-PhMe (4-PhMe).

[LiCe(DFForm)₄] (5): DFFormH (0.20 g, 0.75 mmol) was added to [Ce{N(SiHMe₂)₂}₃(thf)₂] (0.11 g, 0.16 mmol) and [Li{N(SiHMe₂)₂}] (0.025 g, 0.18 mmol) and stirred in toluene (5 mL) for 1 day. The solvent was removed in vacuo. The resulting white powder was washed with cold toluene, redissolved in toluene (4 mL) and concentrated in vacuo producing crystals of **5**. Yield: 0.15 g, (76%); ¹H NMR (C₆D₆, 300 K): δ = 6.43 (brs, 8H; H4-Ar), 6.64 (brs, 16H; H3,5-Ar), 12.76 ppm (s, 4H; NC(H)N); ¹⁹F{¹H} NMR(C₆D₆, 300 K): δ = −133.7 ppm (brs); IR (DRIFT): $\bar{\nu}$ = 2934 (vw), 1622 (m), 1541 (vs), 1480 (s), 1471 (vs), 1394 (vw), 1312 (vs), 1262 (w), 1234 (vs), 1210 (vs), 1149 (w), 1062 (w), 1016 (vw), 998 (s), 933 (w), 826 (w), 771 (s), 743 (s), 732 (m), 714 (m), 687 (vw), 618 cm⁻¹ (m); elemental analysis calcd (%) for C₅₂H₂₈CeF₁₆LiN₈ (1215.86): C 51.37, H 2.32, N 9.22; found: C 51.25, H 2.39, N 9.02.

Oxidations

Oxidations of 1: a) Oxidation in THF: 1 (0.10 g, 0.12 mmol) was stirred in THF (3-5 mL) until dissolved. Trityl chloride (0.033 g, 0.12 mmol) was added and the mixture turned dark brown almost immediately. The solution discolored to a light orange/gold color after 20 min of stirring. The solvent was removed and the residue was analyzed by ¹H NMR spectroscopy showing no identifiable single species. The experiment was repeated with the addition of 1 equivalent of Li(p-TolForm) (0.027 g, 0.12 mmol). The solution turned a dark brown/green on addition of Ph₃CCl, but discolored to red after minutes of stirring. The solvent was removed in vacuo, toluene (2 mL) was added, and the sample was quickly filtered producing a light red solution and yellow precipitate. Once filtered from the precipitate (light yellow insoluble unidentified products), the solution was concentrated (1 mL) in vacuo affording small yellow block crystals of N,N'-bis(4-methylphenyl)-N'-(triphenylmethyl)formamidine (6a), identified by X-ray crystallography. ¹H NMR (C₆D₆, 300 K): $\delta = 1.73 - 1.95$ (brm, 6H, CH₃), 6.58-6.99 (brm, 23H, Ar-H), 8.11 ppm (s, 1 H, NC(H)N). b) Oxidation in toluene: 1 (0.10 g, 0.12 mmol) was added and rapidly stirred in toluene (5 mL). Ph₃CCl (0.033 g, 0.12 mmol) was added with stirring and the mixture slowly turned dark green. The compound decomposed after 30 min of stirring. No species was conclusively identified in the decomposed sample.

Oxidation of 2: a) Oxidation in THF: 2 (0.10 g, 0.18 mmol) was dissolved in THF (3 mL) and Ph₃CCI (0.05 g, 0.18 mmol) was added slowly with stirring. The solution slowly changed color to dark red/ brown. The solution completely discolored after 12 h, forming a white precipitate and a colorless solution. Small amounts of the solution were extracted and analyzed by ¹⁹F NMR spectroscopy. The spectrum indicated the formation of several species. ¹⁹F{¹H} NMR (THF, 300 K): $\delta = -128.8$ (brs, 6F), -127.6 (brs, 4F), -127.0 (s, 2F, F2,6-Ar(N), 6b), -113.8 ppm (s, 2F, F2,6-Ar(N'), 6b). The sample was dried in vacuo leaving a white powder. THF was added to the powder and the solution was filtered and concentrated under vacuum producing small crystals of [Ce₃Cl₅(DFForm)₄-(thf)₄]·4THF (7 a) identified by X-ray crystallography, elemental analysis was tried from three separate samples all giving similar but unsatisfactory results. The filtrate was refiltered and concentrated, producing small yellow crystals of N,N'-bis(2,6-difluorophenyl)-N'-(triphenylmethyl)formamidine (6b), identified by X-ray crystallography. The sample mixture was dried and C₆D₆ was added, producing a slightly yellow solution and a white precipitate. The ¹⁹F NMR spectrum showed only two peaks, identified as compound 6b; ¹⁹F{¹H} NMR (C₆D₆, 300 K): $\delta = -125.19$ (s, 2 F, F2,6-Ar(N)),

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−112.05 ppm (s, 2F, F2,6-Ar(N')). No cerium complexes could be identified by NMR spectroscopy. b) *Oxidation in toluene*: **2** (0.056 g, 0.052 mmol) was dissolved in toluene (3 mL). Ph₃CCl (0.013 g, 0.052 mmol) was added and the sample turned dark brown after 5 min of stirring. The solution discolored after 2 h and a small amount of sample was examined by NMR spectroscopy: ¹⁹F{¹H} NMR (toluene, 300 K): δ = −139.2−136.2 (brs, 10 F), −130.5 (s, 1F), −128.6 (s, 1F), −126.6 (s, 2F, F2,6-Ar(N), **6b**), −113.5 ppm (s, 2F, F2,6-Ar(N') **6b**). An additional 2 equivalents of Ph₃CCl (0.023 g, 0.10 mmol) were added to the NMR tube, forming a white precipitate and yellow solution. Further analysis by ¹⁹F NMR spectroscopy indicated only the presence of **6b**. ¹⁹F{¹H} NMR (toluene, 300 K): δ = −126.0 (s, 2F, F2,6-Ar(N)), −112.8 ppm (s, 2F, F2,6-Ar(N')).

Oxidation of 3: Complex **3** (0.02 g, 0.02 mmol), was dissolved in toluene (2 mL) and transferred to an NMR tube, Ph_3CCI (0.006 g, 0.02 mmol) was added and the white solution turned bright yellow and produced a white powder immediately. A small amount of solution was extracted and analyzed by ¹⁹F NMR spectroscopy, which showed only the presence of **6b**; ¹⁹F{¹H} NMR (toluene, 300 K): $\delta = -125.2$ (s, 2 F, F2,6-Ar(N)), -112.01 ppm (s, 2 F, F2,6-Ar(N')).

Oxidation of 4: Complex **4** (0.14 g, 0.13 mmol) was dissolved in THF (3 mL), Ph₃CCI (0.037 g, 0.13 mmol) and was added with stirring producing a dark green solution immediately on addition. Within a minute of stirring the sample completely changed to light gold. The sample mixture was concentrated (0.5 mL), and hexane was added (1 mL) producing a thick off white oil and small crystals of [Ce(EtForm)Cl₂(thf)₃] (**7b**), overnight (0.02 g, 20%). Elemental analysis calcd (%) for: C₃₃H₅₁CeCl₂N₂O₃ (734.79): C 53.94, H 7.00, N 3.81; found: C 54.16, H 6.89, N 3.94. The mixture was heated to 60 °C and cooled producing small white crystals of *N,N'*-bis(2,6-diethylphenyl)-*N'*-(triphenylmethyl)formamidine as the acetonitrile solvate **6**c·CH₃CN (0.03 g, 41%), as identified by X-ray crystallography.

Oxidation of 5: Complex **5** (0.10 g, 0.080 mmol) was dissolved in THF. Ph_3CCI (0.022 g, 0.080 mmol) was added slowly and the solution turned a dark gold color immediately. The color changed to red over several hours of stirring. The solution was filtered from the precipitated LiCl and the THF removed in vacuo. Hexane (4 mL) was added to the mixture and two small sets of crystals were grown and hand-picked for analysis by X-ray crystallography. Small cube crystals of complex **2** and block crystals of **6b**, were identified by unit cell comparisons with the authentic compounds. ¹⁹F NMR analysis of an NMR scale reaction mixture indicated the presence of only **6b** and **2** after 2 h of reaction.

Synthesis of 8-11

[Li(thf)Ce{N(SiHMe₂)₂}₄] (8): [Li{N(SiHMe₂)₂] (0.17 g,1.23 mmol) was added to [CeCl₃(thf)₂] (0.12 g, 0.31 mmol) in toluene (4 mL). The mixture was stirred for 16 h and then centrifuged, filtered and the solvent was removed in vacuo yielding a light yellow oil; yield: 0.19 g. The complex was redissolved in toluene (3 mL) and, after one day, small yellow block crystals were grown in vacuo. The *supernatant* solution was decanted from the crystals (yield: 0.10 g, 43%). (Note: in situ yield appears quantitative. Once separated from insoluble products, 8 can be treated with C₂Cl₆ without prior isolation to give 9.) ¹H NMR (C₆D₆, 300 K): $\delta = -17.70$ (br s, 6H; SiH), -0.04 (br s, 48H; Me), 2.71 (s, 2H; SiH), 5.73 (br s, 4H; THF), 12.18 ppm (br s, 4H; THF); IR (DRIFT): \bar{v} =2951 (s), 2896 (m), 2046 (vs, vSi-H), 1943 (vs, vSi-H), 1504 (w), 1417 (w), 1246 (vs), 1019 (s), 1019 (vs), 836 (vs), 787 (vs), 765 (vs), 700 (s), 683 (m), 624 cm⁻¹ (w);

elemental analysis calcd (%) for $C_{20}H_{64}$ CeLiN₄OSi₈ (748.49): C 32.18, H 8.56, N 7.49; found: C 31.98, H 7.91, N 7.18.

[Ce{N(SiHMe₂)₂]₄] (9): a) Synthesis in toluene: hexachloroethane (0.023 g, 0.10 mmol) was added to a Schlenk flask charged with 8 (0.15 g, 0.20 mmol). Toluene (5 mL) was added and the mixture reacted immediately producing a dark red color. The solution was sonicated for 6 h leaving a deep red solution and white precipitate of LiCl. The solution was centrifuged and filtered from the insoluble LiCl (LiCl was washed, dried and weighed: ~0.0060 g, ~75 %). The dark red solution was dried under vacuum removing C₂Cl₄ and excess solvent leaving 9 as sticky red crystals (0.12 g, 92%). The ¹H NMR spectrum of the bulk sample gave data consistent with the literature.^[7] b) Attempted synthesis in THF: Upon addition of THF (5 mL) to 8 (0.15 g, 0.20 mmol) and C₂Cl₆ (0.023 g, 0.10 mmol) the mixture slowly changed color to dark red after 72 h of stirring, with no observable precipitate. c) Treating 8 with TeCl₄ or PhICl₂ in toluene caused violent oxidation, causing the sample to fume in the drybox, leaving a thick black oil..

[**Ce(***p***-TolForm)**₄] **(10)**: *p*-TolFormH (0.17 g, 0.75 mmol) was added with stirring to **9** (0.12 g, 0.18 mmol) dissolved in toluene (5 mL). The solution turned dark green within seconds and a light yellow precipitate slowly formed. The solution was filtered, concentrated, and hexane was added (1 mL) producing dark green block crystals of [Ce(*p*-TolForm)₄] **(10**), formula identified by X-ray crystallography. Crystal yield: 0.050 g, 25%. Total yield of dried sample: 0.14 g, 72%; ¹H NMR (C₆D₆, 300 K): δ = 2.28(s, 24 H; -C(H)₃), 6.96 (s, 32 H; Ar-H), 9.77 ppm (s, 4 H; NC(H)N),; IR (DRIFT): \tilde{v} = 3022 (w), 2917 (w), 1652 (w), 1607 (w), 1534 (v s), 1521 (v s), 1285 (s), 1217 (m), 1109 (v w), 981 (w), 942 (m), 810 cm^{−1} (m); elemental analysis (bulk product) calcd (%) for C₆₀H₆₀CeN₈ (1033.29): C 69.74, H 5.85, N 10.84; found: C 67.33, H 6.26, N 9.65. Repeated analyses were also deviant. The sample decomposed completely upon storage at −30 °C with no identified products from decomposition.

 $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2$ (11): $[Ce{N(SiMe_3)_2}_3]$ (0.22 g, 0.35 mmol) was dissolved in toluene (3 mL) and benzoquinone (0.02 g, 0.17 mmol) was added with stirring. The solution turned dark purple immediately. After being stirred for 2 h the solution was concentrated (1–2 mL) and stored at -30 °C for 2 weeks. Large dark brown block crystals suitable for X-ray analysis were isolated, yielding: $[Ce{N(SiMe_3)_2}_3(bda)_{0.5}]_2 \cdot 2 PhMe$ (11·2PhMe). The sample was dried under vacuum, removing toluene of crystallization; yield: 0.23 g (96%). ¹H NMR (C_6D_6 , 300 K): $\delta = 0.10$ (s, 14H; {N(SiMe₃)₂}), 0.43 (s, 94H; {N(SiMe₃)₂}), 7.28 ppm (s, 4H; bda); IR (DRIFT): $\tilde{v} = 2925$ (m), 2898 (w), 1486 (s), 1249 (vs), 1212 (s), 913 (vs), 836 (vs), 770 (s), 654 (s), 604 cm⁻¹ (vs); elemental analysis (%) calcd for C₄₂H₁₁₂Ce₂N₆O₂Si₁₂ (1350.64): C 37.34, H 8.36, N 6.22; found: C 37.35, H 8.40, N 5.96. Complex 11 was treated separately with one equivalent of DFFormH, p-TolFormH, AIMe₃, HAIMe₂, and EtFormH and no color change was observed after several days of stirring when treated in either THF or toluene. Two additional equivalents of reagents were added, and in each case the sample was stirred for 2 days without showing any signs of reaction, and crystals of 11.2 PhMe were isolated from concentrated toluene solutions. When an excess of Sml₂(thf)₂ was added to 11, the reaction mixture was stirred for 4 days showing no color change or indication of any reaction.

Attempted synthesis of [Ce(DFForm)₄] and [Ce(EtForm)₄]

a) DFForm/DFFormH (0.11 g, 0.40 mmol) was added with stirring to **9** (0.07 g 0.10 mmol) dissolved in THF (5 mL). The solution remained red upon addition but slowly discolored with stirring. After 16 h of stirring the solution completely discolored to colorless. The

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sample was dried and large colorless block crystals of complex **2** (identified by unit cell comparison), were isolated from a hexane solution. b) EtForm/EtFormH (0.13 g, 0.41 mmol) was added with stirring to **9** (0.07 g, 0.10 mmol) in toluene (3 mL). The solution turned dark green immediately on addition of EtFormH. The color completely dissipated to light gold after 3 min of stirring. Crystallization from concentrated toluene yielded crystals of **4**-PhMe identified by unit cell determination; other products of decomposition were not identified.

Reactions of benzoquinone and [Ce{N(SiHMe₂)₂}₃(thf)₂]

Compound [Ce{N(SiHMe₂)₂]₃(thf)₂] (0.10 g, 0.15 mmol) and benzoquinone (0.010 g, 0.10 mmol) were dissolved in THF (5 mL) producing a dark red colored complex immediately. Crystallization from hexane at -30 °C, produced small red crystals matching the unit cell of **9**. Upon storage of the filtrate for several days, small white crystals of another material formed. However, the crystals melted in paratone crystallography oil, silicon grease and solvents C₆D₆, Et₂O, and toluene. When exposed to air the material fumed. The material also decomposed in the cryo-stream of the diffractometer, producing highly twinned diffraction data with poor intensity, no unit cell could be determined.

X-ray crystallography

Compounds 2, 5, 6a, 6b, and 11 were examined on a Bruker APEX-II CCD diffractometer at 100.15 K, mounted on a fiber loop in paratone crystallography oil. Complexes 3, 4, 7 a, 8, and 10 were examined on a Bruker P4 diffractometer at 100.15 K, mounted on a glass fiber in viscous paratone crystallography oil. Compounds 6b and 7b were examined on an Oxford Gemini ultra diffractometer at 100.15 K, the crystals were mounted on a fiber loop in viscous paratone oil. Absorption corrections were completed using SADABS,^[29] or for complexes **6b** and **7b** SORTAV^[30] was used. Data for complexes 2–11 were obtained with $Mo_{K\alpha}$ radiation ($\!\lambda\!=\!$ 0.71073 Å). CCDC 973018 (10), 973019 (11), 973020 (2), 973021 (3), 973022 (4), 973023 (5), 973024 (6a), 973025 (6b), 973026 (6c), 973027 (7 a), 973028 (7 b), and 973029 (8) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Ce(DFForm)₃(thf)₂] (2): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₄₇H₃₇CeF₁₂N₆O₂ (*M*_r= 1085.94): triclinic, space group *P*1 (no. 2), *a*=12.7538(3), *b*= 18.9692(4), *c*=20.3546(5) Å, *a*=111.8920(10)°, *β*=103.2860(10)°, *γ*=94.5130(10)°, *V*=4372.69(18) Å³, *Z*=4, *T*=100.15 K, μ (Mo_{Kα})= 1.140 mm⁻¹, ρ_{calcd} =1.650 gmm⁻³, 63787 reflections measured (2.246 $\leq 2\theta \leq$ 61.428), 26142 unique (*R*_{int}=0.0295) which were used in all calculations. The final *R*₁ was 0.0504 (*I* > 2*σ*(*I*)) and *wR*₂ was 0.1625 (all data). Refinement remarks: disordered coordinating THF molecules were modeled with PART (50:50) refinement where applicable.

[Ce(DFForm)₃]-PhMe (3-PhMe): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₄₆H₂₉CeF₁₂N₆ (M_r =1033.86): monoclinic, space group P_2 /n (no. 14), a=13.1454(2), b= 13.4738(2), c=23.3893(4) Å, β =90.0280(10)°, V=4142.68(11) Å³, Z=4, T=100.15 K, μ (Mo_{Ka})=1.195 mm⁻¹, ρ_{calcd} =1.645 g mm⁻³, 67194 reflections measured (3.488 $\leq 2\theta \leq$ 58.828), 11408 unique (R_{int} =0.0254) which were used in all calculations. The final R_1 was

0.0287 ($l > 2\sigma(l)$) and wR_2 was 0.0642 (all data). Refinement details: toluene solvate was disordered over two positions, and refined with PART (50:50) refinement. The hydrogen atoms on the disordered toluene were not assigned.

[Ce(EtForm)₃]-PhMe (4-PhMe): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₇₀H₈₉CeN₆ (M_r =1154.59): monoclinic, space group P_2_1/c (no. 14), a=12.4367(4), b=23.7877(8), c=21.8256(8) Å, β =105.336(2)°, V=6227.0(4) Å³, Z=4, T=100.15 K, μ (Mo_{Kα})=0.776 mm⁻¹, ρ_{calcd} =1.232 g mm⁻³, 147 942 reflections measured (3.4 $\leq 2\theta \leq 57.64$), 16 126 unique (R_{int} =0.0554) which were used in all calculations. The final R_1 was 0.0370 (l>2 σ (l)) and wR_2 was 0.0792 (all data). Refinement details: toluene disordered over two positions, and was refined with PART (50:50) refinement. Disordered ethyl groups on EtForm were modeled with PART refinement (FVAR).

[LiCe(DFForm)₄**]** (5): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Patterson method and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₅₂H₂₈CeF₁₆LiN₈ (M_r = 1215.88): monoclinic, space group P_{2_1}/n (no. 14), a = 13.1871(3), b = 18.7513(5), c = 19.3773(4) Å, β = 98.8570(10)°, V = 4734.39(19) Å³, Z = 4, T = 100.15 K, μ (Mo_{Ka}) = 1.073 mm⁻¹, ρ_{calcd} = 1.706 g mm⁻³, 64.875 reflections measured (3.04 $\leq 2\theta \leq$ 56.724), 11.727 unique (R_{int} = 0.0342) which were used in all calculations. The final R_1 was 0.0275 (l>2 σ (l)) and wR_2 was 0.1188 (all data).

[p-TolForm(CPh₃)] (6a): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₃₄H₃₀N₂ (*M*_r=466.60): monoclinic, space group *P*2₁/*c* (no. 14), *a* = 9.6383(3), *b* = 13.1289(4), *c* = 20.3550(6) Å, β = 98.5740(10)°, *V* = 2546.94(13) Å³, *Z* = 4, *T* = 100.15 K, μ (Mo_{Kα}) = 0.071 mm⁻¹, ρ_{calcd} = 1.217 g mm⁻³, 21622 reflections measured (3.704 $\leq 2\theta \leq 52.756$), 5197 unique (R_{int} =0.0447) which were used in all calculations. The final R_1 was 0.0432 (*l*>2 σ (*l*)) and *w* R_2 was 0.1328 (all data).

[DFForm(CPh₃)] (6 b): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the olex2.refine^[32] refinement package using Gauss–Newton minimization. Crystal data for C₃₂H₂₂F₄N₂ (M_r =511.52): monoclinic, space group P₂/n (no. 14), a=9.7606(1), b= 21.0993(3), c=13.2290(2) Å, β =92.882(1)°, V=2720.96(6) Å³, Z=4, T=100.15 K, μ (Mo_{Kα})=0.092 mm⁻¹, ρ_{calcd} =1.2462 g mm⁻³, 26041 reflections measured ($4.94 \le 2\theta \le 56.9$), 6770 unique (R_{int} =0.0209) which were used in all calculations. The final R_1 was 0.0843 ($I > 2\sigma(I)$) and wR_2 was 0.2720 (all data). Refinement details: unaccounted for electron density within crystal lattice, could be modeled as disordered THF or disordered hexane with no conclusive preference, therefore density left unassigned.

[EtForm(CPh₃)]-CH₃CN (6c-CH₃CN): Using Olex2,^[31] the structure was solved with the olex2.solve^[32] structure solution program using Charge Flipping^[32] and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₄₂H₄₅N₃ (M_r =591.81): monoclinic, space group *Pc* (no. 7), *a*=11.0933(5), *b*=9.6838(4), *c*=15.8730(8) Å, *β*=103.798(5)°, *V*=1655.97(13) Å³, *Z*=2, *T*=123.00(16) K, μ (Mo_{Kα})=0.069 mm⁻¹, ρ_{calcd} =1.187 gmm⁻³, 10302 reflections measured (4.968 $\leq 2\theta \leq$ 61.886), 6439 unique (R_{int} =0.0218) which were used in all calculations. The final R_1 was 0.0372 (*I* > 2 σ (*I*)) and *w* R_2 was 0.0927 (all data).

 $[Ce_3(DFForm)_4Cl_5(thf)_4]$ -4THF (7 a): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using

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Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₈₄H₉₂Ce₃Cl₅F₁₆N₈O₈ (M_r =2243.26): monoclinic, space group *Cc* (no. 9), *a* = 13.6723(5), *b* = 34.9623(11), *c* = 19.2700(6) Å, β = 103.694(2)°, *V*=8949.5(5) Å³, *Z*=4, *T*=100.15 K, μ (Mo_{Ka}) = 1.741 mm⁻¹, ρ_{calcd} = 1.665 g mm⁻³, 77968 reflections measured (3.188 $\leq 2\theta \leq 58.91$), 22076 unique (R_{int} =0.0463) which were used in all calculations. The final R_1 was 0.0354 (*I* > 2 σ (*I*) and *w* R_2 was 0.0743 (all data). Refinement details: THF solvates indicated slight disorder, left unmodeled.

[Ce(EtForm)Cl₂(thf)₃] (7 b): Using Olex2,^[31] the structure was solved with the olex2.solve^[32] structure solution program using Charge Flipping^[32] and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₃₃H₅₁CeCl₂N₂O₃ (*M*_r = 734.79): tetragonal, space group *I*4₁/*a* (no. 88), *a* = 17.1407(4), *c* = 48.323(2), *V* = 14197.4(10) Å³, *Z* = 16, *T* = 123.01(14) K, μ (Mo_{Ka}) = 1.465 mm⁻¹, ρ_{calcd} = 1.373 gmm⁻³, 62412 reflections measured (3.76 ≤ 2 θ ≤ 54.994), 8145 unique (*R*_{int} = 0.1114) which were used in all calculations. The final *R*₁ was 0.0470 (*I* > 2 σ (*I*)) and *wR*₂ was 0.1037 (all data).

[Li(thf)Ce{N(SiHMe₂)₂}₄] (8): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₂₀H₆₄CeLiN₄OSi₈ (*M*_r = 748.49): monoclinic, space group *P*2₁/*c* (no. 14), *a* = 19.1228(5), *b* = 11.4421(3), *c* = 37.2808(11) Å, β = 92.328(2)°, *V* = 8150.5(4) Å³, *Z* = 8, *T* = 100.15 K, μ (Mo_{Kd}) = 1.370 mm⁻¹, ρ_{calcd} = 1.207 g mm⁻³, 55.375 reflections measured (3.116 $\leq 2\theta \leq 52.816$), 16.592 unique (*R*_{int} = 0.0555) which were used in all calculations. The final *R*₁ was 0.0499 (*I* > 2 σ (*I*)) and *wR*₂ was 0.1141 (all data). Refinement details: disordered SiH(CH₃)₂ groups were modeled with PART disorder (50:50, or FVAR), coordinating THF appeared disordered to several positions and was modeled to two, NPD were restrained with the ISOR command. Due to disorder Si–H atoms were not assigned.

[Ce(p-TolForm)_4] (10): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Direct Methods and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₆₀H₆₀CeN₈ (M_r =1033.28): monoclinic, space group P_2 /n (no. 14), a=16.5452(2), b= 18.3467(2), c=16.9889(2) Å, β =96.7900(10)°, V=5120.81(10) Å³, Z=4, T=100.15 K, μ (Mo_{Ka})=0.936 mm⁻¹, ρ_{calcd} =1.340 g mm⁻³, 43509 reflections measured (3.28 $\leq 2\theta \leq$ 52.944), 10562 unique (R_{int} =0.0498) which were used in all calculations. The final R_1 was 0.0338 ($I > 2\sigma(I)$) and wR_2 was 0.1104 (all data).

[Ce{N(SiMe₃)₂}₃(bda)_{0.5}]₂·2 PhMe (11·2 PhMe): Using Olex2,^[31] the structure was solved with the ShelXS^[32] structure solution program using Patterson method and refined with the XL^[32] refinement package using least squares minimization. Crystal data for C₅₆H₁₂₈Ce₂N₆O₂Si₁₂ (*M*_r=1534.96): triclinic, space group *P*[†] (no. 2), *a*=11.1102(6), *b*=11.5965(6), *c*=18.6253(10) Å, *α*=72.7870(10)°, β =75.1860(10)°, γ =63.9770(10)°, *V*=2037.55(19) Å³, *Z*=1, *T*= 100.15 K, μ (Mo_{Kα})=1.317 mm⁻¹, ρ_{calcd} =1.251 g mm⁻³, 41571 reflections measured (4 ≤ 2 θ ≤ 58.296), 10955 unique (*R*_{int}=0.0345) which were used in all calculations. The final *R*₁ was 0.0248 (*l*>2 σ (*l*)) and *wR*₂ was 0.0569 (all data).

Acknowledgements

We gratefully acknowledge support from the German Science Foundation (Grant AN 238/16-1) and the Australian Research Council (ARC Discovery: DP 130100152) and an Australian Postgraduate Award to D.W.

Keywords: cerium \cdot formamidinate \cdot oxidation \cdot protonolysis \cdot silylamide

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Received: November 22, 2013 Revised: January 30, 2014 Published online on March 18, 2014