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Synthesis of Heteroleptic Cerium(III) Anionic Amido-Tethered N-Heterocyclic Carbene Complexes

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The in situ low-temperature (−78 °C) reaction of the amine N-heterocyclic carbene t-BuNHCH$_2$CH$_2$[C{t-BuN(CHCH)N}] (**3**, HL^1), KMe, and $^1/_2$ equiv of [CeI$_3$THF$_4$] (**6**) in DME/diethyl ether solutions does not afford [(L^1)$_2$CeI] (**7a**); instead, **6** and H$_2$L^{1}I (**8**) are isolated in low yields. H$_2$L^{1}Cp (**11**) is the only isolable product from the reaction of LiL^1 (**9**) and TlCp. The *N*-methyl analogue proligand t-BuNH$_2$CH$_2$CH$_2$[HC{MeN(CHCH)N}]2Br (**12**, H$_3$L^{2}Br$_2$) and the amine−N-heterocyclic carbene t-BuNHCH$_2$CH$_2$[C{MeN(CHCH)N}] (**13**, HL^2) have been synthesized. However, attempts to prepare and isolate the lithium amido−N-heterocyclic carbene t-BuNLiCH$_2$CH$_2$[C{MeN(CHCH)N}] (**14**, LiL^2) were unsuccessful. Transamination of [(HL^1)LiBr] (**2**) with [Ce{N(SiMe$_3$)$_2$}$_3$] successfully affords the compounds [{(L^1)Ce(N[SiMe$_3$]$_2$)(μ-Br)}$_2$] (**15**) and [(L^1)Ce{N(SiMe$_3$)$_2$}$_2$] (**16**), the former being a product of ligand exchange of **16** with the LiBr byproduct. The complex [{(L^1)Ce(N[SiMe$_3$]$_2$)(μ-I)}$_2$] (**17**) is obtained by a ligand exchange reaction between **16** and LiI. Compounds **6**, **8**, **11**, **12**, and **15**−**17** have been characterized by X-ray crystallography and, variously, by NMR spectroscopy and CHN microanalysis.

Introduction

Nucleophilic imidazol-2-ylidenes, which are more popularly referred to as N-heterocyclic carbenes (NHCs), have become extremely popular in recent years due to their many applications as ancillary ligands in homogeneous catalysis.[1] Unsurprisingly, given the analogy between NHCs and phosphines, the majority of NHC literature is concerned with their use in late-transition-metal systems for catalysis.[2] Until recently, NHC complexes of the f block were synthesized only as “curiosity” compounds in which the NHC binds as a simple dative donor solvent molecule.[3] In addition, the overwhelming majority of NHCs are symmetrical (with respect to the N and N′ substituents) and/or neutral, incorporating donor groups such as pyridyl, phosphine, and NHC.[4] In recent years, we have been investigating the binding of asymmetric NHC ligands to early metals, where the NHC is pendant to an anionic tether;[5] others are currently pursuing similar strategies.[6] This approach allows for variations of the nature of the tether (amide or alkoxide) and the substituents on the tether and NHC (which can impart chirality to the NHC ligand), and since the anionic tether will be anchored to a metal center, the strength of the NHC−metal bond and the noninnocence/reactivity of the NHC group in reactions can be monitored. This latter point is important, since NHCs are increasingly being used as additives in Lewis acid catalyzed reactions, such as Cu(II)-,[5c,7] Al(III)-,[8] and Zn(II)-mediated[9] organic trans-

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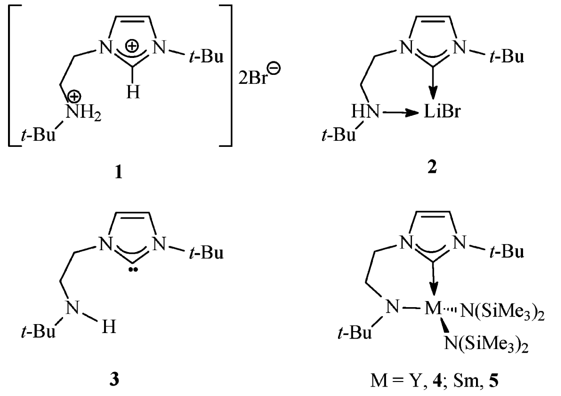
Chart 1 [5d]



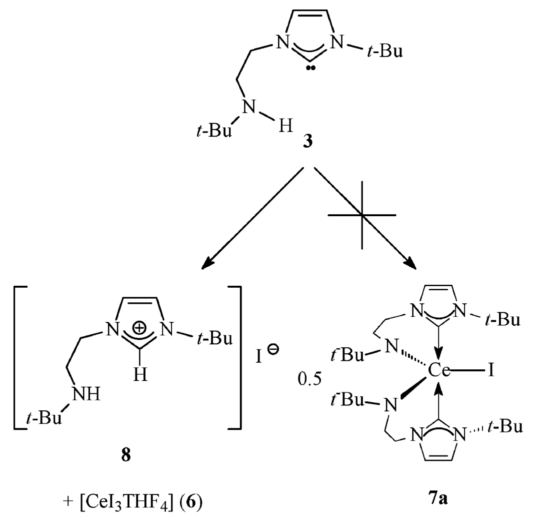
formations, and a Sm(II)−NHC complex has been used as a precatalyst for the polymerization of MMA,[10] but the role of the NHC is unclear. It has been demonstrated that NHCs can form strong dative bonds to late transition metals such as ruthenium and palladium, with little, or no, back-bonding.[11] More recently, we have provided evidence that in complexes where NHCs are bound to electropositive closed-shell early metals such as lithium, magnesium, and uranyl, the metal−carbene bond is primarily electrostatic, displaying no angular dependence on bond distance or measurable bond strength.[5a] However, it has been suggested NHCs can engage in "cis-ligand back-bonding", where a ligand cis to the NHC back-donates a lone pair to the essentially vacant carbene-based p orbital in the NHC.[12]

In a prior communication (Chart 1) we reported the synthesis of the alkylammonium−imidazolium dibromide proligand $t\text{-BuNH}_2\text{CH}_2\text{CH}_2[\text{HC}\{t\text{-BuN(CHCH)N}\}]\text{-}2\text{Br}$ (**1**, $\text{H}_3\text{L}^1\text{Br}_2$), the amine−NHC lithium bromide adduct $[\{t\text{-BuNHCH}_2\text{CH}_2(\text{C}[t\text{-BuN(CHCH)N}])\}\text{LiBr}]$ (**2**, $[(\text{HL}^1)\text{LiBr}]$), the amine−NHC $t\text{-BuNHCH}_2\text{CH}_2[\text{C}\{t\text{-BuN(CHCH)N}\}]$ (**3**, HL^1), and the early-metal amido−NHC complexes $[(\text{L}^1)\text{M}\{\text{N(SiMe}_3)_2\}_2]$ (M = Y (**4**), Sm (**5**); $\text{L}^1 = t\text{-BuNCH}_2\text{CH}_2[\text{C}\{t\text{-BuN(CHCH)N}\}]$), and assessed the strength of the M-NHC bond by competition reactions with potential Lewis base donor ligands.[5d] We were keen to extend this chemistry to cerium, since no Ce(III)−NHC complexes have yet been reported, and such chemistry would potentially open the door to Ce(IV)−NHC organometallic chemistry. Furthermore, we were interested in pursuing this chemistry, and complexes of the type $[(\text{L}^1)_2\text{CeX}]$ (X = halide), to explore the metathesis chemistry of such species. Herein, we report the results of our endeavors in this area.

Results and Discussion

Metalation and Metathesis Chemistry of HL^1 (3). The in situ reaction at low temperature (−78 °C) of KMe with **3**, followed by addition to $^1/_2$ equiv of $[\text{CeI}_3\text{THF}_4]$ (**6**) in diethyl ether/DME, was carried out (Scheme 1) with the aim of preparing $[(\text{L}^1)_2\text{CeI}]$ (**7a**). Following workup a dark red solution was obtained which gave a small crop of colorless crystals of **6**, as determined by an X-ray diffraction study, in very low yield (<10%). The molecular structure is illustrated in Figure 1, and selected bond lengths and angles are given in Table 1. Compound **6** crystallizes as a discrete molecular species which is isostructural with the previously reported La,[13] Pr,[14] and U[15] analogues; the Ce−I bond lengths compare well with literature examples.[16−18]

Scheme 1[a]



[a] Reagents and conditions: KMe, 0.5 CeI_3THF_4, $\text{DME/Et}_2\text{O}$, −78 °C.

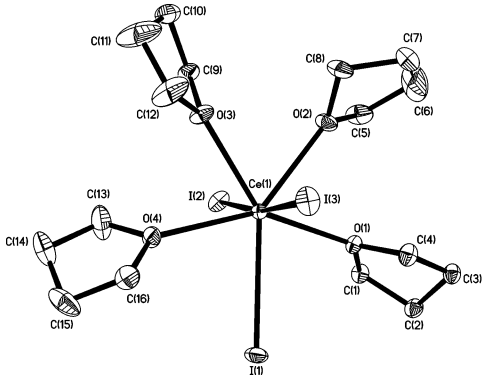


Figure 1. Molecular structure of **6** with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

A second crop of colorless crystals were obtained from the mother liquor from the above reaction (Scheme 1) by storage at −30 °C, which were identified as $t\text{-BuNHCH}_2\text{CH}_2[\text{HC}\{t\text{-BuN(CHCH)N}\}]\text{I}$ (**8**, $\text{H}_2\text{L}^1\text{I}$). The asymmetric unit is shown in Figure 2, and selected bond lengths and angles are given in Table 1.

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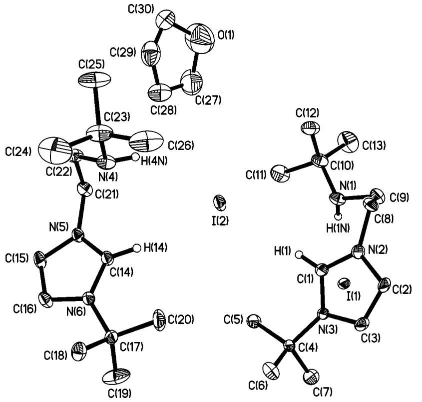


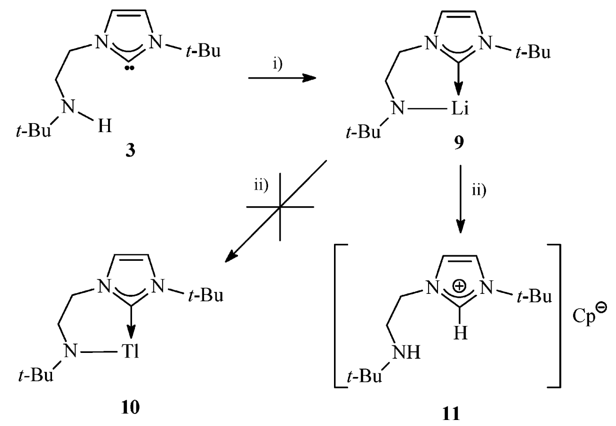
Figure 2. The molecular asymmetric unit of **8** with thermal ellipsoids at 50% probability. Carbon-bound hydrogen atoms (except for C(1) and C(14)) are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 6, 8, 11, and 12

Compound **6**			
Ce(1)–I(1)	3.180(2)	Ce(1)–I(2)	3.112(2)
Ce(1)–I(3)	3.132(2)	Ce(1)–O(1)	2.480(3)
Ce(1)–O(2)	2.550(3)	Ce(1)–O(3)	2.520(3)
Ce(1)–O(4)	2.509(3)		
O(1)–Ce(1)–O(2)	70.11(10)	O(1)–Ce(1)–O(3)	140.38(10)
O(1)–Ce(1)–O(4)	149.09(10)	O(2)–Ce(1)–O(3)	70.51(10)
O(2)–Ce(1)–O(4)	140.65(10)	O(3)–Ce(1)–O(4)	70.14(11)
O(1)–Ce(1)–I(1)	73.50(7)	O(2)–Ce(1)–I(1)	143.24(7)
O(3)–Ce(1)–I(1)	146.10(8)	O(4)–Ce(1)–I(1)	76.04(8)
O(1)–Ce(1)–I(2)	87.07(6)	O(2)–Ce(1)–I(2)	88.73(8)
O(3)–Ce(1)–I(2)	87.92(7)	O(4)–Ce(1)–I(2)	90.18(7)
O(1)–Ce(1)–I(3)	96.22(6)	O(2)–Ce(1)–I(3)	85.07(8)
O(3)–Ce(1)–I(3)	84.57(7)	O(4)–Ce(1)–I(3)	90.95(7)
I(1)–Ce(1)–I(2)	94.486(11)	I(2)–Ce(1)–I(3)	93.937(11)
I(2)–Ce(1)–I(3)	171.525(12)		
Compound **8**			
C(1)–N(2)	1.328(5)	C(1)–N(3)	1.341(5)
N(2)–C(2)	1.367(5)	N(3)–C(3)	1.375(5)
C(2)–C(3)	1.346(6)	C(14)–N(5)	1.333(5)
C(14)–N(6)	1.328(5)	N(5)–C(15)	1.369(5)
N(6)–C(16)	1.381(5)	C(15)–C(16)	1.351(6)
N(2)–C(1)–N(3)	109.0(3)	N(5)–C(14)–N(6)	108.7(3)
Compound **11**			
C(1)–N(2)	1.325(2)	C(1)–N(3)	1.326(2)
N(2)–C(2)	1.362(2)	N(3)–C(3)	1.376(2)
C(2)–C(3)	1.338(2)	C(14)–C(15)	1.383(3)
C(15)–C(16)	1.389(3)	C(16)–C(17)	1.386(3)
C(17)–C(18)	1.385(3)	C(18)–C(14)	1.384(3)
N(2)–C(1)–N(3)	109.05(13)	C(15)–C(14)–C(18)	108.14(19)
C(14)–C(15)–C(16)	108.0(2)	C(17)–C(16)–C(15)	107.74(19)
C(18)–C(17)–C(16)	108.16(19)	C(14)–C(18)–C(17)	107.93(19)
Compound **12**			
C(1)–N(2)	1.330(3)	C(1)–N(3)	1.327(3)
N(2)–C(2)	1.381(3)	N(3)–C(3)	1.376(3)
C(2)–C(3)	1.346(3)		
N(2)–C(1)–N(3)	108.5(2)		

Preparations of $[(L^1)_2CeI]$ (**7a**) and $[(L^1)_2CeCl]$ (**7b**) by salt metathesis reactions between 2 equiv of *t*-BuNLiCH$_2$CH$_2$[C{*t*-BuN(CHCH)N}] (**9**, LiL^1) and **6** or CeCl$_3$, respectively, in ethereal or aromatic solvents were attempted. However, in all instances only variable quantities of **3** were recovered, along with intractable halide-containing products.

Scheme 2[a]



[a] Reagents and conditions: (i) *n*-BuLi, THF, −78 °C, −*n*BuH; (ii) CpTl, THF, −78 °C, −CpLi.

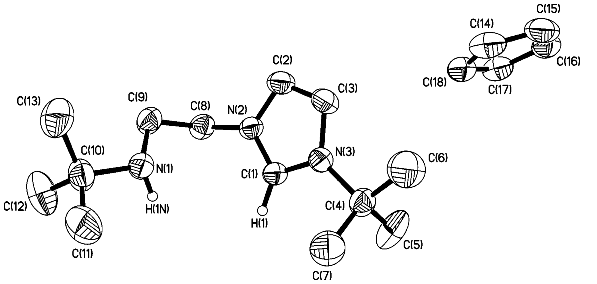


Figure 3. Molecular structure of **11** with 50% probability thermal ellipsoids. Carbon-bound hydrogen atoms (except for C(1) and those bound to N(1)) are omitted for clarity.

We also investigated (Scheme 2) the synthesis of the thallium amido–NHC complex *t*-BuNTlCH$_2$CH$_2$[C{*t*-BuN(CHCH)N}] (**10**, TlL^1), as thallium ligand transfer reagents have previously proven effective in preparative lanthanide chemistry[19] and thallium alkoxy–NHCs have precedent.[5b] However, the reaction of CpTl with **9** in THF did not afford the anticipated precipitate of CpLi. Instead, a cube of thallium metal was deposited, and after workup, the new separated ion pair compound *t*-BuNHCH$_2$CH$_2$[HC{*t*-BuN(CHCH)N}]Cp (**11**, H$_2$L^{1}Cp) was isolated. The molecular structure of **11** is illustrated in Figure 3, and selected bond lengths and angles are listed in Table 1.

Preparation and Metalation Reactions of HL^2 (13). Given that we were unable to prepare **7a** or **7b**, we undertook the synthesis of the new proligand *t*-BuNH$_2$CH$_2$CH$_2$CH$_2$[HC{MeN(CHCH)N}]2Br (**12**, H$_3$L^{2}Br$_2$) as an alternative to **3** (Scheme 3). Thus, analogously to **3**,[5d] reaction of *t*-BuNH$_2$CH$_2$CH$_2$CH$_2$Br·Br with [HC{MeN(CHCH)N}] in refluxing acetonitrile afforded **12** in good yield. In d_6-DMSO, the high-frequency signal at 9.26 ppm in the ^{1}H NMR spectrum and the three signals at 122.51, 123.63, and 137.30 ppm in the ^{13}C{^{1}H} NMR spectrum are diagnostic of an imidazolium group. X-ray diffraction quality crystals were obtained by slow evaporation of a solution of **12** in acetonitrile. The molecular structure is illustrated in Figure 4, and selected bond lengths and angles are listed in Table 1. The C(1)–N(2) and C(1)–N(3) bond lengths of 1.330(3) and 1.327(3) Å, respectively, and the N(2)–C(1)–N(3) angle of 108.5(2)° are comparable to those observed in **8** and **11**. The bromide anions form a hydrogen-bonded

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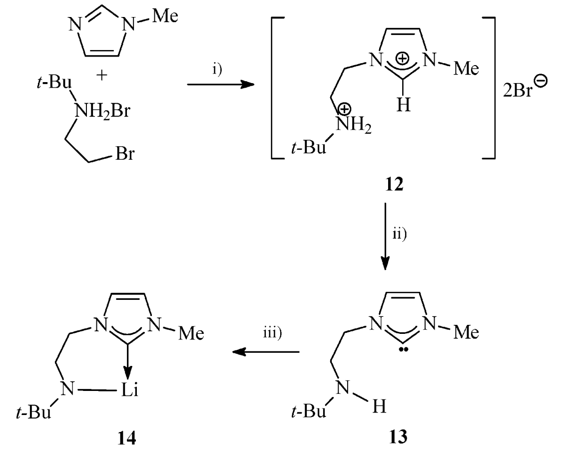
Scheme 3[a]



[a] Reagents and conditions: (i) acetonitrile, reflux, 2 days; (ii) 2 KH, THF, reflux, 2 days, $-H_2$; (iii) *n*-BuLi, THF, −78 °C, −*n*-BuH.

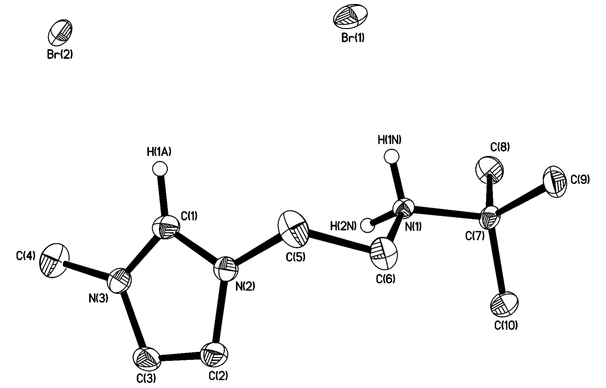


Figure 4. Molecular structure of **12** with 50% probability thermal ellipsoids . Carbon-bound hydrogen atoms (except for C(1)) are omitted for clarity.

network with the ammonium NH and imidazolium CH protons in a manner similar to that for **1**.[5d]

Reaction of 2 equiv of KH with **12** in refluxing THF (Scheme 3) over 2 days affords, after workup and distillation, the amine−NHC *t*-$BuNHCH_2CH_2[C\{MeN(CHCH)N\}]$ (**13**, HL^2) as an orange oil. However, yields are consistently half of those routinely obtained for **3** (∼42%), which we attribute to the lower degree of steric protection afforded to the carbene by the *N*-methyl substituent, and the oil obtained is always contaminated with a variety of species (∼5−10%) which we are unable to remove by any other method. The $^{13}C\{^1H\}$ NMR spectrum exhibits a signal at 212.5 ppm characteristic of an NHC.

Addition of 1 equiv of *n*-BuLi to a cold (−78 °C) solution of **13** in THF (Scheme 3) results in a rapid color change to dark red, but despite repeated recrystallization attempts, with a variety of Lewis base donors (THF, Et_2O, DME, TMEDA), only a dark red oil could be isolated, which we propose is *t*-$BuNLiCH_2CH_2[C\{MeN(CHCH)N\}]$ (**14**, LiL^2). However, the oily nature of **14** and the extremely broad NMR spectra obtained prevented satisfactory characterization.

Preparation of Ce(III)−NHC Complexes by Transamination. Previously, we demonstrated that lanthanide amido−NHCs, such as **4** and **5**, could be prepared by transamination reactions.[5d] Consequently, we have explored the transamination chemistry of **2**[5d] with the homoleptic cerium amide $[Ce\{N(SiMe_3)_2\}_3]$,[20] since this should afford a convenient entry point to cerium(III)−NHC chemistry and the further possibility of Ce(IV)−NHC chemistry.

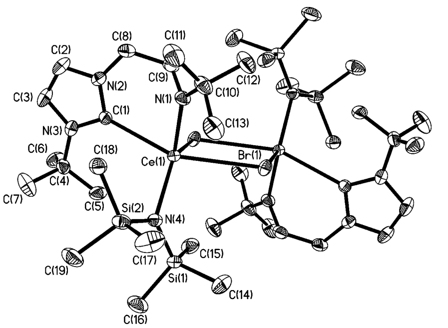


Figure 5. Molecular structure of **15** with 50% probability thermal ellipsoids and labeling of symmetry-unique atoms only. Carbon-bound hydrogen atoms are omitted for clarity.

Reaction of 1 equiv of **2** with $[Ce\{N(SiMe_3)_2\}_3]$ in toluene (Scheme 4) affords a sticky yellow solid after workup. In the first batch that was prepared, a bright yellow microcrystalline solid was obtained after washing with diethyl ether (in which it is insoluble), which is soluble in warm toluene. X-ray diffraction quality crystals were obtained by slow cooling to room temperature. However, unexpectedly the resulting compound was shown to be $[\{(L^1)Ce(N[SiMe_3]_2)(\mu\text{-}Br)\}_2]\cdot{}^1/_2C_6H_5CH_3$ ($\mathbf{15}\cdot{}^1/_2C_6H_5CH_3$), the product of a ligand exchange reaction between the LiBr from **2** and the targeted compound $[(L^1)Ce\{N(SiMe_3)_2\}_2]$ (**16**). The isolation of **15** is notable on two counts: first, in our laboratory we have prepared **4** and **5**,[5d] and the Nd and Eu analogues,[21] but have never observed any evidence for ligand exchange reactions, and yields are typically excellent (>85%). Presumably the Lewis acidity of Ce, which is less than that of Y, Nd, Sm, and Eu, is such that Li, which is exceptionally Lewis acidic, can compete for the amide ligand; second, heteroleptic lanthanide complexes of the type LnLL′L″ are far rarer than complexes of the type $LnLL'_2$[22] and, as recently pointed out,[23] are usually restricted to the heavier, and smaller, lanthanides.

The molecular structure of **15** is illustrated in Figure 5, and selected bond lengths and angles are listed in Table 2. The structure is dimeric, constructed around a transoid Ce_2Br_2 four-membered ring, which is strictly planar, as a consequence of residing over a crystallographic inversion center. Each cerium center is coordinated to two *μ*-Br atoms, the N(4) atom of the $N(SiMe_3)_2$ ligand, and the N(1) and C(1) atoms of the amido−NHC ligand, adopting a distorted-trigonal-bipyramidal geometry such that C(1) and Br(1) are axial. The Ce(1)−C(1) bond length is 2.699(2) Å; there are no structurally characterized Ce−carbene bond lengths for comparison in the literature, but this value compares with values of 2.501(5) and 2.588(2) Å for **4** and **5**, respectively.[5d] The Ce(1)−Br(1) and Ce(1)−Br(1)A bond lengths of 3.026(2) and 3.056 (2) Å, respectively, are

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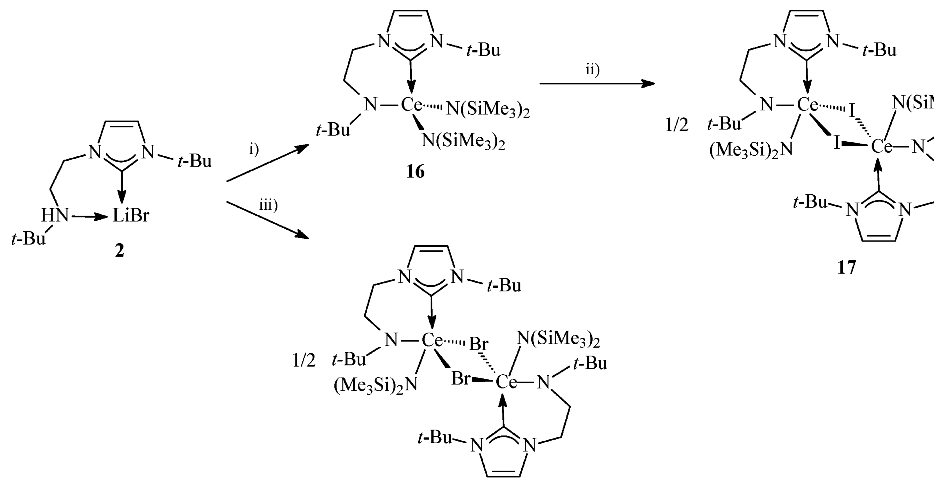
[20] Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

[21] Liddle, S. T.; Mungur, S. A.; Arnold, P. L. Unpublished results.

[22] For a recent review see: Piers, W. E.; Emslie, D. J. H. *Coord. Chem. Rev.* **2002**, *233−234*, 131.

[23] Bonnet, F.; Visseaux, M.; Barbier-Baudry, D.; Vigier, E.; Kubicki, M. M. *Chem. Eur. J.* **2004**, *10*, 2428.

Scheme 4[a]



[a] Reagents and conditions: (i) $[Ce\{N(SiMe_3)_2\}_3]$, toluene, $-LiBr$, $-HN(SiMe_3)_2$; (ii) $[Ce\{N(SiMe_3)_2\}_3]$, toluene, $-LiN(SiMe_3)_2$, $-HN(SiMe_3)_2$; (iii) LiI, 80 °C, $-LiN(SiMe_3)_2$.

long, as befits their bridging nature; terminal Ce−Br bond lengths of 2.912(5)/2.885(2) and 2.874(2)-2.912(2) Å have been reported for $[CeBr_2\{N(SiMe_3)_2\}(THF)_2]$ and $[CeBr_3THF_4]$.[24] The Ce(1)−N(1) bond length of 2.239(2) Å is shorter than the Ce(1)−N(4) bond length of 2.376(2) Å, as befits the nature of the more electron rich dialkyl amide−NHC compared to the silicon-substituted amide. The $Ce-N_{silylamide}$ bond is toward the higher end of reported $Ce-N_{silylamide}$ bonds, due to the sterically crowded coordination sphere at cerium; $Ce-N_{silylamide}$ bond lengths of 2.320(3) and 2.349(7)/2.357(7) Å have been reported for $[Ce\{N(SiMe_3)_2\}_3]$[25] and $[Cp^*Ce\{N(SiMe_3)_2\}_2]$,[26] respectively. Structural changes are apparent in the NHC group; as expected, the C(1)−N(2) and C(1)−N(3) bond lengths of 1.357(3) and 1.368(3) Å, respectively, are lengthened compared to those in **8**, **11**, and **12**, and the N(2)−C(1)−N(3) bond angle is contracted to 103.3(2)°, reflecting the diminished s character of the NHC N−C bonds. Ce(1)···Si(1) and Ce(1)···C(9) distances of 3.498 and 2.999 Å, respectively, are suggestive of close contacts.

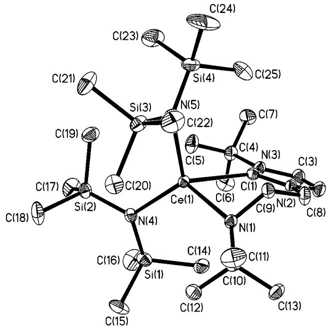


Figure 6. Molecular structure of **16** with 50% probability thermal ellipsoids. Carbon-bound hydrogen atoms are omitted for clarity.

The isolation of **15** was unexpected; however, attempts to repeat the reaction have thus far proved unsuccessful, despite varied reaction conditions, and all subsequent attempts have generated the initially desired compound **16** (Scheme 4). We note, also, that reaction of 2 equiv of **2** with $[Ce\{N(SiMe_3)_2\}_3]$ gives **16** as the only isolable compound. Crystals of **16**, which are isomorphous with **4** and **5**, suitable for an X-ray diffraction study were grown from cold (−30 °C) diethyl ether. The molecular structure of **16** is illustrated in Figure 6, and selected bond lengths and angles are listed in Table 2. The geometry at cerium is distorted tetrahedral, with cerium bonded to the N(1) and C(1) atoms of the amido−NHC and two N atoms of the $N(SiMe_3)_2$ ligands. As in **15**, close contacts of Ce(1) to Si(3) and C(9) are suggested by distances of 3.393 and 2.934 Å, respectively. The Ce(1)−C(1) bond distance is 2.670(2) Å, slightly shorter than that observed in **15**. The Ce(1)−N(1) bond length of 2.278(2) Å is shorter than the corresponding bond length in **15** and shorter than the two $Ce(1)-N_{silylamide}$ bond lengths (Ce(1)−N(4) = 2.418(2) Å, Ce(1)−N(5) = 2.404(2) Å); however, the $Ce(1)-N_{silylamide}$ bond lengths are long, reflecting the congested coordination sphere at cerium. Bond lengths and angles within the N(2)−C(1)−N(3) unit are in agreement with those observed in **15**.

Although the isolation of **15** was unexpected, it is a synthetically more desirable compound than **16**, since it contains a bromide which may allow further metathesis chemistry to be explored. However, as stated above, we were unable to prepare **15** subsequently. Since the source of the bromide is the lithium bromide incorporated in **2**, we reasoned that addition of lithium iodide to a solution of **16** should generate the compound $[\{(L^1)Ce(N[SiMe_3]_2)(\mu\text{-}I)\}_2]$ (**17**), since it should be more favorable for lithium to exchange iodide, as compared to bromide, for an amide in a ligand exchange reaction, and iodide is a more attractive halide than bromide from a metathesis chemistry standpoint. Thus, reaction of LiI with **16** (Scheme 4) in hot (80 °C) toluene affords, after workup, a bright yellow microcrystalline solid which, as for **15**, is insoluble in diethyl ether but soluble in toluene. X-ray diffraction quality crystals were obtained from a cold (−30 °C) solution in toluene. The molecular structure of **17**, which is isomorphous with **15**, is

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[24] Hitchcock, P. B.; Hulkes, A. G.; Lappert, M. F. *Inorg. Chem.* **2004**, *43*, 1031.

[25] Rees, W. S., Jr.; Just, O.; Van Derveer, D. S. *J. Mater. Chem.* **1999**, *9*, 249.

[26] Heeres, H. J.; Meetsma, A.; Teuben, J. H.; Rogers, R. D. *Organometallics* **1989**, *8*, 2637.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 15−17 and 17a

Compound **15**			
Ce(1)−C(1)	2.699(2)	Ce(1)−N(1)	2.239(2)
Ce(1)−N(4)	2.376(2)	Ce(1)−Br(1)	3.056(2)
Ce(1)−Br(1A)	3.026(2)	C(1)−N(2)	1.357(3)
C(1)−N(3)	1.368(3)	N(2)−C(2)	1.385(4)
N(3)−C(3)	1.381(3)	C(2)−C(3)	1.336(5)
N(4)−Si(1)	1.710(2)	N(4)−Si(2)	1.704(2)
N(1)−Ce(1)−N(4)	122.04(8)	N(1)−Ce(1)−C(1)	80.80(8)
N(4)−Ce(1)−C(1)	106.92(7)	N(1)−Ce(1)−Br(1A)	108.91(6)
N(4)−Ce(1)−Br(1A)	128.89(5)	C(1)−Ce(1)−Br(1A)	83.58(5)
N(1)−Ce(1)−Br(1)	89.35(6)	N(4)−Ce(1)−Br(1)	98.39(5)
C(1)−Ce(1)−Br(1)	154.37(5)	Br(1)−Ce(1)−Br(1A)	77.302(8)
Ce(1)−Br(1)−Ce(1A)	102.698(8)	N(2)−C(1)−N(3)	103.3(2)
Compound **16**			
Ce(1)−C(1)	2.670(2)	Ce(1)−N(1)	2.278(2)
Ce(1)−N(4)	2.418(2)	Ce(1)−N(5)	2.404(2)
C(1)−N(2)	1.360(3)	C(1)−N(3)	1.360(3)
N(2)−C(2)	1.373(3)	N(3)−C(3)	1.384(3)
C(2)−C(3)	1.341(3)	N(4)−Si(1)	1.702(2)
N(4)−Si(2)	1.7106(19)	N(5)−Si(3)	1.701(2)
N(5)−Si(4)	1.708(2)		
N(1)−Ce(1)−N(4)	120.46(6)	N(1)−Ce(1)−N(5)	103.16(6)
N(4)−Ce(1)−N(5)	123.64(6)	N(1)−Ce(1)−C(1)	80.47(6)
N(5)−Ce(1)−C(1)	109.07(7)	N(4)−Ce(1)−C(1)	111.65(6)
N(2)−C(1)−N(3)	103.41(18)		
Compound **17**			
Ce(1)−C(1)	2.700(3)	Ce(1)−N(1)	2.244(2)
Ce(1)−N(4)	2.361(2)	Ce(1)−I(1)	3.311(2)
Ce(1)−I(1A)	3.250(2)	C(1)−N(2)	1.359(3)
C(1)−N(3)	1.369(3)	N(2)−C(2)	1.376(4)
N(3)−C(3)	1.386(3)	C(2)−C(3)	1.332(4)
N(4)−Si(1)	1.713(2)	N(4)−Si(2)	1.713(2)
N(1)−Ce(1)−N(4)	123.87(8)	N(1)−Ce(1)−C(1)	80.75(8)
N(4)−Ce(1)−C(1)	108.36(7)	N(1)−Ce(1)−I(1A)	107.69(6)
N(4)−Ce(1)−I(1A)	128.16(5)	C(1)−Ce(1)−I(1A)	83.17(5)
N(1)−Ce(1)−I(1)	89.10(6)	N(4)−Ce(1)−I(1)	94.53(5)
C(1)−Ce(1)−I(1)	156.92(5)	I(1)−Ce(1)−I(1A)	80.254(6)
Ce(1)−I(1)−Ce(1A)	99.746(6)	N(2)−C(1)−N(3)	103.5(2)
Compound **17a**			
Ce(1)−C(1)	2.697(8)	Ce(1)−N(1)	2.249(7)
Ce(1)−N(4)	2.352(8)	Ce(1)−I(1)	3.255(2)
Ce(1)−I(1A)	3.343(2)	C(1)−N(2)	1.361(11)
C(1)−N(3)	1.346(11)	N(2)−C(2)	1.371(11)
N(3)−C(3)	1.384(11)	C(2)−C(3)	1.347(13)
N(4)−Si(1)	1.700(8)	N(4)−Si(2)	1.719(9)
N(1)−Ce(1)−N(4)	121.8(3)	N(1)−Ce(1)−C(1)	81.2(3)
N(4)−Ce(1)−C(1)	107.0(3)	N(1)−Ce(1)−I(1A)	110.3(2)
N(4)−Ce(1)−I(1A)	127.7(2)	C(1)−Ce(1)−I(1A)	83.9(2)
N(1)−Ce(1)−I(1)	88.53(19)	N(4)−Ce(1)−I(1)	94.9(2)
C(1)−Ce(1)−I(1)	158.0(2)	I(1)−Ce(1)−I(1A)	81.547(18)
Ce(1)−I(1)−Ce(1A)	98.453(18)	N(2)−C(1)−N(3)	103.3(7)

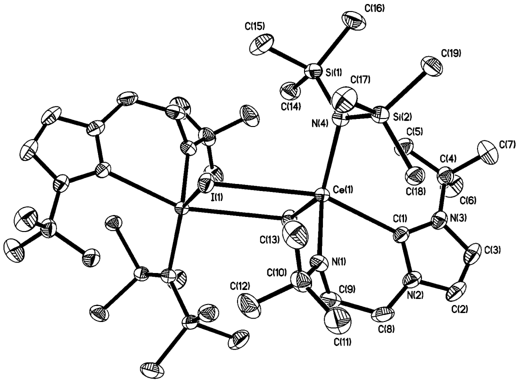
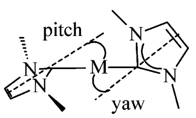


Figure 7. Molecular structure of **17** with 50% probability thermal ellipsoids and labeling of symmetry-unique atoms only. Carbon-bound hydrogen atoms are omitted for clarity.

Chart 2



illustrated in Figure 7, and selected bond lengths and angles are listed in Table 2. The structure is dimeric, constructed around a transoid Ce_2I_2 four-membered ring, which is strictly planar as a consequence of residing over a crystallographic inversion center. Each cerium center is coordinated to two μ-I atoms, the N(4) atom of the $N(SiMe_3)_2$ ligand, and the N(1) and C(1) atoms of the amido−NHC ligand, adopting a distorted-trigonal-bipyramidal geometry such that C(1) and I(1) are axial. The Ce(1)−C(1) bond length of 2.700(3) Å is statistically invariant with that observed in **15**. The Ce(1)−I(1) and Ce(1)−I(1)A bond lengths of 3.111(3) and 3.250(3) Å, respectively, are comparable to those observed in **6** and in $[CeI_3(OH\text{-}i\text{-}Pr)_4]$,[16] $[CeI_3(2,2'\text{-bipyridyl})_2]$,[17] and $[CeI_2(2,2',6',2''\text{-terpyridine})][I]$.[18] The Ce(1)−N(1) bond length of 2.244(2) Å is shorter than the Ce(1)−N(4) bond length of 2.361(2) Å, essentially unchanged from the corresponding bond lengths in **15**. Bond lengths and angles within the N(2)−C(1)−N(3) unit are essentially the same as those in **15** and **16**. Again, Ce(1)···Si(2) and Ce(1)···C(9) distances of 3.472 and 2.978 Å, respectively, are suggestive of close contacts. **17** crystallizes without solvent; however, we have also obtained a second crystalline modification of **17**, **17a**, which is essentially identical with **17**, albeit with minor variations of bond lengths and angles, except for cocrystallization of three highly disordered molecules of toluene. Further details of **17a** are in Table 2 and the Supporting Information.

Recently, we reported amido−NHC lithium and uranyl complexes,[5a] which exhibited large deviations from the anticipated trigonal-planar geometry at the carbene center. Two angles may be used to describe these deviations, namely the pitch and yaw (Chart 2); deviations of up to 23 and 22°, respectively, were observed in the lithium and uranyl complexes.[5a] Compounds **15**−**17** and **17a** all display deviations, although to a much lesser extent; the pitch and yaw values for **15**−**17** and **17a** are respectively as follows: 3.2 and 7.8°, 1.0 and 7.6°, 6.9 and 8.2°, and 7.5 and 8.3°. These low values suggest the amido−NHC is well suited to bind cerium(III).

Conclusions

Attempts to prepare bis-ligand complexes of Ce(III) resulted in isolation of $[CeI_3THF_4]$ (**6**) and the alkyl−imidazolium compound H_2L^1I (**8**). Attempted preparation of the thallium amido−NHC **10** results in reductive elimination of thallium and isolation of the amine−imidazolium Cp salt H_2L^1Cp (**11**) in low yield. The new alkylammonium−imidazolium proligand $H_3L^2Br_2$ (**12**) and amine−NHC HL^2 (**13**) were prepared, but no tractable product could be isolated from the oily solids that resulted from syntheses to prepare the corresponding lithium salt LiL^2 (**14**). A transamination strategy enabled the preparation of the bis-silylamido cerium amido−NHC complex $[(L^1)Ce\{N(SiMe_3)_2\}_2]$ (**16**) and the amido cerium amido−NHC bromide complex $[\{(L^1)Ce(N[SiMe_3]_2)(\mu\text{-}Br)\}_2]$ (**15**), the latter being the product of a ligand exchange reaction. Reaction of **16** with LiI affords the amido cerium amido−NHC iodide complex $[\{(L^1)Ce(N[SiMe_3]_2)(\mu\text{-}I)\}_2]$ (**17**). We are currently working to improve the preparative yield of **17** and are investigating its metathesis chemistry.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk techniques, or an MBraun UniLab glovebox, under an atmosphere of dry nitrogen. Pentane, hexane, toluene, diethyl ether, and THF were dried by passage through activated alumina towers and degassed before use. DME was distilled from potassium under an atmosphere of dry nitrogen. All solvents were stored over potassium mirrors (with the exception of THF and DME, which were stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze−pump−thaw cycles, and stored under nitrogen. Acetonitrile was used as supplied. *n*-Butyllithium (2.5 M solution in hexanes), methyllithium (1.6 M solution in diethyl ether), hexamethyldisilazane, $CeCl_3$, 1-methylimidazole, and potassium hydride were purchased from Aldrich and used without any further purification. CpTl was sublimed prior to use. *t*-BuOK was purchased from Aldrich and baked at 120 °C in vacuo for 3 h prior to use. The compounds $[CeI_3(THF)_4]$ (**6**),[14] $[Ce\{N(SiMe_3)_2\}_3]$,[20] $t\text{-}BuNH_2CH_2CH_2Br{\cdot}Br$,[27] $H_3L^1Br_2$ (**1**),[5d] $[(HL^1)LiBr]$ (**2**),[5d] HL^1 (**3**),[5d] LiL^1 (**9**),[5a] and KMe[28] were prepared by published literature procedures. With the exception of compound **12**, yields for all compounds were not optimized.

^1H, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 300 spectrometer operating at 300.1 and 75.5 MHz, respectively; chemical shifts are quoted in ppm and are relative to $SiMe_4$. Elemental microanalyses were carried out by Mr. Stephen Boyer at the Microanalysis Service, London Metropolitan University, London, U.K.

Attempted Preparation of $[(L^1)_2CeI]$ (7a) and Isolation of $[CeI_3THF_4]$ (6) and $H_2L^1I{\cdot}{}^1/_2THF$ ($8{\cdot}{}^1/_2THF$). **3** (1.31 g, 5.86 mmol) in cold (−10 °C) DME (15 mL) was added to a cold (−78 °C) slurry of KMe (0.31 g, 5.86 mmol) in diethyl ether (20 mL) and stirred for 3 h, during which time the initially yellow solution became red. The solution was then added to a cold (−78 °C) slurry of **6** (2.37 g, 2.93 mmol) in diethyl ether (15 mL) to afford a yellow solution. The mixture was stirred for 16 h, during which time it was warmed slowly to room temperature. Volatiles were removed in vacuo to give a sticky red solid. Extraction into THF (3 × 15 mL), filtration, and removal of volatiles in vacuo gave a sticky orange solid. This was dissolved in THF (3 mL), filtered, and stored at 5 °C for 4 days to afford a colorless crop of crystals of **6** suitable for an X-ray diffraction study; storage of the mother liquor at −30 °C overnight afforded a crop of colorless crystals of $\mathbf{8}{\cdot}{}^1/_2THF$ suitable for an X-ray diffraction study. Crystals of $\mathbf{8}{\cdot}{}^1/_2THF$ placed under vacuum lose lattice THF, as evidenced by NMR spectroscopy and CHN microanalysis. Yield: 0.38 g, 19%. Anal. Calcd for $C_{13}H_{26}N_3I$: C, 44.45; H, 7.46; N, 11.96. Found: C, 44.29; H, 7.40; N, 11.86. ^1H NMR (d_6-DMSO, 295 K): δ 0.92 (s, 9H, *t*-Bu), 1.58 (s, 9H, *t*-Bu), 2.82 (m, 2H, CH_2), 4.12 (m, 2H, CH_2), 7.82 (s, 1H, CH), 7.99 (s, 1H, CH), 9.25 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 29.26 (*t*-Bu), 29.61 (*t*-Bu), 42.12 (CH_2), 50.18 (C), 50.83 (C), 59.74 (CH_2), 120.16 (CH), 123.40 (CH), 135.22 (CH). Analysis of the mother liquor by ^1H NMR spectroscopy shows the remainder of the product to be predominantly **8** and minor impurities.

Attempted Preparation of $[TlL^1]$ (10) and Isolation of H_2L^1Cp (11). THF (10 mL) was added to a cold (−78 °C) Schlenk tube, wrapped in tin foil, containing CpTl (0.56 g, 2.06 mmol) and **9** (0.47 g, 2.06 mmol) to give a turbid green solution. The solution was warmed to room temperature and stirred for 18 h. The brown-yellow solution was filtered from a solid block of metal, and volatiles were removed in vacuo to give a sticky brown-red solid. Diethyl ether (5 mL) was added, the solution filtered from the resulting brown precipitate, and the solution stored at 5 °C for 5 months to give a small crop of colorless crystals of **11** suitable for an X-ray diffraction study. Yield: 0.08 g, 13%. The low yield precluded CHN microanalysis. ^1H NMR (d_5-pyridine, 295 K): δ 0.95 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 2.82 (m, 2H, CH_2), 4.19 (m, 2H, CH_2), 6.49 (s, 5H, Cp), 7.34 (s, 1H, CH), 7.46 (s, 1H, CH), 7.92 (s, br, 1H, CH). $^{13}C\{^1H\}$ NMR (d_5-pyridine, 295 K): δ 28.80 (*t*-Bu), 29.46 (*t*-Bu), 42.46 (C), 49.83 (C), 51.2 (CH_2), 58.6 (CH_2), 105.94 (Cp), 118.79 (CH), 145.39 (CH). One CH signal is obscured by solvent resonances. NMR spectra of the mother liquor were consistent with a mixture of **3** and **11**.

Preparation of $H_3L^2Br_2$ (12). 1-Methylimidazole (5.04 g, 61.37 mmol) was added dropwise to a slurry of $t\text{-}BuNH_2CH_2CH_2Br{\cdot}Br$ (16.00 g, 61.37 mmol) in acetonitrile (80 mL) to give a turbid brown mixture, which was then refluxed for 2 days. The mixture was cooled to room temperature and the mother liquor removed by filtration to give an off-white powder. The powder was dissolved in hot DMSO (40 mL), and this solution was filtered, diluted with acetonitrile (260 mL), and filtered to give **12** as a white powder. Yield: 13.21 g, 63%. Colorless crystals of **12** suitable for an X-ray diffraction study were grown by slow evaporation of a solution of **12** in acetonitrile. Anal. Calcd for $C_{10}H_{21}N_3Br_2$: C, 35.01; H, 6.17; N, 12.25. Found: C, 35.06; H, 6.20; N, 12.19. ^1H NMR (d_6-DMSO, 295 K): δ 1.32 (s, 9H, *t*-Bu), 3.48 (m, 2H, CH_2), 3.87 (s, 3H, CH_3), 4.58 (m, 2H, CH_2), 7.76 (s, 1H, CH), 7.88 (s, 1H, CH), 8.92 (s, br, 2H, NH_2), 9.26 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (d_6-DMSO, 295 K): δ 25.04 (*t*-Bu), 30.67 (C), 35.80 (CH_3), 45.26 (CH_2), 57.31 (CH_2), 122.51 (CH), 123.63 (CH), 137.30 (CH).

Preparation of HL^2 (13). THF (100 mL) was added to a pressure ampule charged with KH (3.50 g, 87.5 mmol) and **12** (15 g, 43.76 mmol). The pressure was reduced and the mixture heated at 100 °C for 2 days. The mixture was cooled to room temperature, the pressure was vented slowly, then the mixture was filtered to give a red solution. Volatiles were removed in vacuo to afford a dark red viscous oil. Distillation at 100 °C (0.01 mmHg) afforded **13** as an orange oil. Yield: 3.34 g, 42%. ^1H NMR (d_6-benzene, 295 K): δ 1.05 (s, 9H, *t*-Bu), 2.91 (m, 2H, CH_2), 3.49 (s, 3H, CH_3), 4.03 (m, 2H, CH_2), 6.51 (d, $^3J_{HH}$ = 1.5 H, CH), 6.73 (d, $^3J_{HH}$ = 1.5 H, CH). $^{13}C\{^1H\}$ NMR (d_6-benzene, 295 K): δ 28.99 (*t*-Bu), 37.35 (*t*-Bu), 44.09 (CH_3), 49.82 (CH_2), 52.08 (CH_2), 119.29 (CH), 119.66 (CH), 212.52 (carbene). NMR spectra of **13** invariably contain minor signals (∼5−10%) of unidentified impurities, which we believe to be decomposition products of **13**. This is attributed to the lower degree of steric protection afforded by the methyl substituent to the NHC and is commensurate with the consistently poorer yield of **13** compared to **3**. Consequently, CHN microanalyses were not obtained.

Preparation of $[\{(L^1)Ce(N[SiMe_3]_2)(\mu\text{-}Br)\}_2]{\cdot}{}^1/_2C_6H_5CH_3$ ($15{\cdot}{}^1/_2C_6H_5CH_3$). $[Ce\{N(SiMe_3)_2\}_3]$ (1.92 g, 3.09 mmol) in toluene (20 mL) was added dropwise to a solution of **2** (0.96 g, 3.09 mmol) in toluene (10 mL) and stirred for 18 h. The cloudy yellow solution was filtered, and volatiles were removed in vacuo to give a sticky yellow solid, which was gently warmed in vacuo to remove residual $HN(SiMe_3)_2$. The yellow solid was washed with diethyl ether (5 mL), and the resulting bright yellow microcrystalline solid was isolated by filtration. The solid was extracted into hot toluene (5 mL), and the extract was filtered and cooled slowly to room temperature to give a crop of bright yellow crystals of $\mathbf{15}{\cdot}{}^1/_2C_6H_5CH_3$ suitable for an X-ray diffraction study. Yield (based on Ce): 0.37 g, 20%. Anal. Calcd for $C_{38}H_{84}Br_2Ce_2N_8Si_4{\cdot}{}^1/_2C_6H_5CH_3$: C, 39.83; H, 7.09; N, 8.95. Found: C, 40.03; H, 7.18; N, 8.95. ^1H NMR (d_6-benzene, 295 K): δ −6.49 (s, br, 2H, CH_2), −4.44 (s, br, 18H, *t*-Bu), −2.46

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Table 3. Crystallographic Data for 6, 8, 11, and 12

	6	**8**	**11**	**12**
formula	$C_{16}H_{32}CeI_3O_4$	$C_{15}H_{30}IN_3O_{0.50}$	$C_{18}H_{31}N_3$	$C_{10}H_{21}Br_2N_3$
fw	809.24	387.32	289.46	343.12
cryst size, mm	0.27 × 0.37 × 0.39	0.42 × 0.42 × 0.68	0.25 × 0.26 × 0.72	0.20 × 0.21 × 0.72
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1$
a, Å	8.7062(13)	22.939(2)	14.040(4)	5.9163(4)
b, Å	17.339(3)	7.6231(8)	9.176(2)	11.0261(8)
c, Å	16.627(2)	24.024(3)	15.583(4)	11.0801(8)
β, deg	92.716(2)	115.851(2)	110.878(4)	94.608(2)
V, Å^3	2507.1(6)	3780.6(7)	1875.8(8)	720.46(9)
Z	4	8	4	2
ρ_{calcd}, g cm^{-3}	2.144	1.361	1.025	1.582
μ, mm^{-1}	5.524	1.692	0.061	5.604
no. of rflns measd	27 944	10 434	17 775	5078
no. of unique rflns, R_{int}	5762, 0.0384	8629, 0.0480	3301, 0.0233	2486, 0.018
no. of rflns with $F^2 > 2\sigma(F^2)$	5072	6383	2359	2430
transmissn coeff range	0.222−0.317	0.392−0.537	0.958−0.985	0.107−0.400
R, R_w^{a} ($F^2 > 2\sigma$)	0.0313, 0.0785	0.0395, 0.0892	0.0413, 0.1016	0.0159, 0.0164
R, R_w^{a} (all data)	0.0372, 0.0824	0.0615, 0.0975	0.0645, 0.1170	0.0396, 0.0397
S^a	1.059	1.054	1.030	0.890
no. of params	217	372	200	146
max, min diff map, e Å^{-3}	1.446, −2.223	1.175, −0.620	0.155, −0.123	0.31, −0.42

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, and $S = [\sum w(F_o^2 - F_c^2)^2/((\text{no. of data}) - (\text{no. of params}))]^{1/2}$ for all data.

Table 4. Crystallographic Data for 15−17 and 17a

	15	**16**	**17**	**17a**
formula	$C_{41.50}H_{88}Br_2Ce_2N_8Si_4$	$C_{25}H_{60}CeN_5Si_4$	$C_{38}H_{84}Ce_2I_2N_8Si_4$	$C_{59}H_{108}Ce_2I_2N_8Si_4$
fw	1251.62	683.26	1299.53	1575.93
cryst size, mm	0.19 × 0.30 × 0.76	0.43 × 0.46 × 0.51	0.10 × 0.11 × 0.18	0.27 × 0.36 × 0.38
cryst syst	triclinic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$
a, Å	11.0360(6)	12.431(2)	11.1998(7)	24.287(4)
b, Å	12.3745(7)	16.307(3)	11.5465(8)	21.230(4)
c, Å	13.0400(7)	19.037(4)	12.7282(8)	14.748(2)
α, deg	67.205(2)		70.256(2)	
β, deg	69.663(2)	106.456(3)	83.553(2)	104.499(4)
γ, deg	84.149(2)		64.661(2)	
V, Å^3	1538.28(15)	3701.2(12)	1399.17(16)	7362(2)
Z	1	4	1	4
ρ_{calcd}, g cm^{-3}	1.351	1.226	1.542	1.422
μ, mm^{-1}	2.869	1.379	2.826	2.163
no. of rflns measd	10 022	12 068	10 058	27 212
no. of unique rflns, R_{int}	7009, 0.0180	8569, 0.0358	4914, 0.0123	6486, 0.0402
no. of rflns with $F^2 > 2\sigma(F^2)$	6333	7638	4472	5576
transmissn coeff range	0.219−0.6112	0.540−0.589	0.630−0.765	0.494−0.593
R, R_w^{a} ($F^2 > 2\sigma$)	0.0272, 0.0675	0.0289, 0.0658	0.0199, 0.0470	0.0587, 0.1299
R, R_w^{a} (all data)	0.0309, 0.0688	0.0342, 0.0680	0.0229, 0.0485	0.0663, 0.1330
S^a	1.084	1.066	1.047	1.088
no. of params	256	334	256	244
max, min diff map, e Å^{-3}	3.298, −0.564	0.869, −0.480	0.866, −0.293	2.313, −2.321

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, and $S = [\sum w(F_o^2 - F_c^2)^2/((\text{no. of data}) - (\text{no. of params}))]^{1/2}$ for all data.

(s, br, 18H, $SiMe_3$), −1.89 (s, br, 2H, CH_2), 1.28 (s, br, 2H, CH), 1.63 (s, br, 2H, CH), 2.21 (s, 1.5H, *toluene*-CH_3), 5.20 (s, br, 18H, $SiMe_3$), 5.99 (s, br, 18H, *t*Bu), 7.52 (m, 2.5H, *toluene*-CH), 10.42 (s, br, 4H, CH_2).

Preparation of [(L^1)Ce{N($SiMe_3$)$_2$}$_2$] (16). Toluene (20 mL) was added to a Schlenk tube containing [Ce{N($SiMe_3$)$_2$}$_3$] (1.95 g, 3.14 mmol) and **2** (0.97 g, 3.14 mmol) and the mixture stirred for 18 h. The cloudy yellow solution was filtered, and volatiles were removed in vacuo to give a sticky yellow solid, which was gently warmed in vacuo to remove residual HN($SiMe_3$)$_2$. The resulting yellow solid was extracted with diethyl ether (20 mL), the extract was filtered, and volatiles were removed in vacuo to afford a yellow oil. The oil was dissolved in diethyl ether (2 mL) and stored at −30 °C for 7 days to yield a crop of yellow crystals of **16** suitable for an X-ray diffraction study. Yield: 0.55 g, 26%. Anal. Calcd for $C_{25}H_{60}CeN_5Si_4$: C, 43.95; H, 8.85; N, 10.25. Found: C, 43.74; H, 8.72; N, 10.30. ^{1}H NMR (d_6-benzene, 295 K): δ −6.35 (s, br, 9H, *t*-Bu), −3.08 (s, br, 9H, *t*-Bu), −2.52 (s, br, 1H, CH_2), −1.85 (s, br, 36H, $SiMe_3$), 1.15 (s, br, 1H, CH_2), 1.96 (s, 1H, CH), 5.02 (s, 1H, CH), 14.07 (s, br, 1H, CH_2), 57.50 (s, br, 1H, CH_2).

Preparation of [{(L^1)Ce(N[$SiMe_3$]$_2$)(μ-I)}$_2$] (17). [Ce{N($SiMe_3$)$_2$}$_3$] (1.86 g, 3.00 mmol) in toluene (40 mL) was added dropwise to a solution of **2** (0.93 g, 3.00 mmol) in toluene (10 mL) and the mixture stirred for 50 h. The cloudy yellow solution was filtered, and volatiles were removed in vacuo to afford a sticky yellow solid, which was gently warmed in vacuo to remove residual HN($SiMe_3$)$_2$. The resulting yellow solid was extracted with diethyl ether (20 mL) and the extract added to LiI (0.4 g, 3.00 mmol). Volatiles were removed in vacuo, and the solid was dissolved in toluene (20 mL). The mixture was then heated at 80 °C for 7 days. The solution was filtered, and volatiles were removed in vacuo to give a yellow solid. This was washed with diethyl ether (3 mL), and the resulting bright yellow microcrystalline solid was isolated by filtration. The solid was extracted into hot toluene (3 mL) and stored at −30

°C for 2 days to give a crop of bright yellow crystals of **17** suitable for an X-ray diffraction study. Yield (based on Ce): 0.36 g, 18%. Anal. Calcd for $C_{38}H_{84}Ce_2I_2N_8Si_4$: C, 35.12; H, 6.52; N, 8.62. Found: C, 35.03; H, 6.48; N, 8.62. ^{1}H NMR (d_6-benzene, 295 K): δ −6.42 (s, br, 2H, CH_2), −3.81 (s, br, 18H, *t*-Bu), −2.39 (s, br, 18H, $SiMe_3$), −1.90 (s, br, 2H, CH_2), 1.19 (s, br, 2H, CH), 1.64 (s, br, 2H, CH), 5.11 (s, br, 18H, $SiMe_3$), 5.91 (s, br, 18H, *t*Bu) and 14.01 (s, br, 4H, CH_2).

X-ray Crystallography. Crystal data for compounds **6**, **8**, **11**, **12**, **15**−**17**, and **17a** are given in Tables 3 and 4, and further details of the structure determinations are given in the Supporting Information. Bond lengths and angles are listed in Tables 1 and 2. Crystals were examined on a Bruker AXS 1000 or APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensities were integrated from a sphere of data recorded on narrow (0.3°) frames by ω rotation. Cell parameters were refined from the observed positions of all strong reflections in each data set. Semiempirical absorption corrections were applied, on the basis of symmetry-equivalent and repeat reflections. The structures were solved variously by heavy-atom and direct methods and were refined by least-squares methods on all unique F^2 values, with anisotropic displacement parameters and with constrained riding hydrogen geometries (except amine and ammonium hydrogens, which were freely refined); U(H) was set at 1.2 (1.5 for methyl groups) times the U_{eq} value for the parent atom. The largest features in final difference syntheses were close to heavy atoms. The absolute structure of **12** was determined by refinement of the Flack parameter.[29] Crystals of **15** and **17a** contained highly disordered toluene solvent molecules, which were treated by the PLATON SQUEEZE procedure.[30] Programs used were Bruker AXS SMART (control) and SAINT (integration)[31] and SHELXTL for structure solution, refinement, and molecular graphics.[32]

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Supporting Information Available: For **6**, **8**, **11**, **12**, **15**−**17**, and **17a**, CIF files giving details of the structure determination, atomic coordinates, bond lengths and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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