# Facile formation of a homoleptic Ce(IV) amide *via* aerobic oxidation†

**Peter B. Hitchcock, Michael F. Lappert* and Andrey V. Protchenko***

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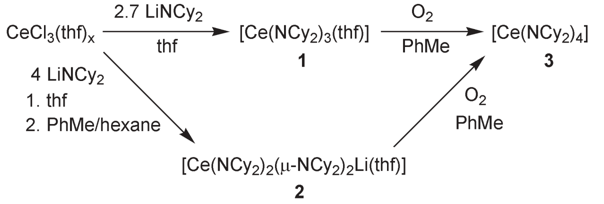
**Oxidation of $[\mathrm{Ce(NCy_2)_3(thf)}]$ or $[\mathrm{Ce(NCy_2)_4Li(thf)}]$ with dry air produced the first homoleptic Ce(IV) amide $[\mathrm{Ce(NCy_2)_4}]$.**

Cerium is often considered as an analogue of a group 4 metal due to its ability to form compounds in the oxidation state +4. However, homoleptic dialkyl amides, which are common and widely used for Zr and Hf,[1] are unknown for Ce. Related are Ce(IV) bis(trifluoromethanesulfonyl)amide[2] and porphyrinato- or phthalocyaninato-Ce complexes,[3] the latter often being considered as having the Ce atom in an intermediate (between +3 and +4) oxidation state due to the high redox activity of the ligands. Each of the three heteroleptic Ce(IV) amides reported up to date, $[\mathrm{CeI\{N(SiMe_2Bu^t)CH_2CH_2\}_3N}]$[4a] and $[\mathrm{Ce\{N(SiMe_3)_2\}_3X}]$ (X = Cl or Br),[4b,c] contain silyl substituents on the amido N atoms.

The initial attempts to prepare a Ce(IV) dialkylamido complex using $[\mathrm{Ce(TMP)_3}]$ (TMP = 2,2,6,6-tetramethylpiperidinate) failed,[5] apparently due to the high steric demands of the TMP ligand. Thus, dicyclohexylamide ($\mathrm{NCy_2}$) was chosen as a less bulky alternative to TMP for stabilisation of the Ce +4 oxidation state. Here we report the synthesis and characterisation of two new Ce(III) dicyclohexylamides and their oxidation to produce the first homoleptic Ce(IV) amide.

The starting Ce(III) amides $[\mathrm{Ce(NCy_2)_3(thf)}]$ (**1**) and $[\mathrm{Ce(NCy_2)_4Li(thf)}]$ (**2**) were prepared *via* the salt elimination route (Scheme 1) using 2.7 or 4 equivalents of Li amide, respectively.‡ Both compounds demonstrate paramagnetically shifted $^1$H NMR signals in $\mathrm{C_6D_6}$ with one set of the Cy group signals for **1** and two sets (terminal and bridging $\mathrm{NCy_2}$ ligands) for **2** (see ESI†). In a coordinating solvent (thf-$d_8$) complex **2** apparently dissociates into the tetrahedral anion $[\mathrm{Ce(NCy_2)_4}]^-$ (which gives only one set of slightly paramagnetically shifted Cy signals) and the $[\mathrm{Li(thf)}_x]^+$ cation (which gives a sharp signal in the $^7$Li NMR spectrum; no such signal was observed in $\mathrm{C_6D_6}$ solvent due to paramagnetic broadening).



**Scheme 1**

The thf-solvated cerium triamide **1** was stable in solution in hydrocarbon solvents and was thermally robust up to its melting point (*ca.* 235 °C) in contrast to the bulkier analogue $[\mathrm{Ce(TMP)_3(thf)}]$,[5] which can be desolvated at room temperature. The lithium tetraamidocerate(III) **2** decomposed slowly in aromatic solvents and much faster in thf, apparently due to thf C–O bond cleavage similar to that observed in the synthesis of $[\mathrm{Ce(TMP)_3}]$.[6]

Complexes **1** and **2** were extremely air-sensitive in solution and if the smallest amount of air was accidentally introduced during the work-up, a blue colouration appeared in the solution immediately, later yielding black microcrystals. When a measured amount of dry air was added to toluene or thf solutions of **1** or **2** the diamagnetic Ce(IV) amide $[\mathrm{Ce(NCy_2)_4}]$ (**3**)‡ was isolated in a moderate yield (Scheme 1).

Complex **3** was only sparingly soluble in hexane, benzene, toluene or thf, producing deep blue solutions, which were stored in a vacuum-sealed tube without decomposition for several months at room temperature (in contrast to the solution instability of $[\mathrm{Ce\{N(SiMe_3)_2\}_3X}]$ [X = Cl, Br][4c]). The solubility increased upon heating to 70 °C thus allowing recrystallisation of **3** without noticeable decomposition even at this temperature.

To confirm the oxidation state of Ce in these complexes the structures of **1**, **2** and **3** were determined by single crystal X-ray diffraction.§ The molecular structures of complexes **1** and **2** are similar to those of their Sm analogues;[7] details are given in ESI†. In the structure of complex **3** there are two independent molecules

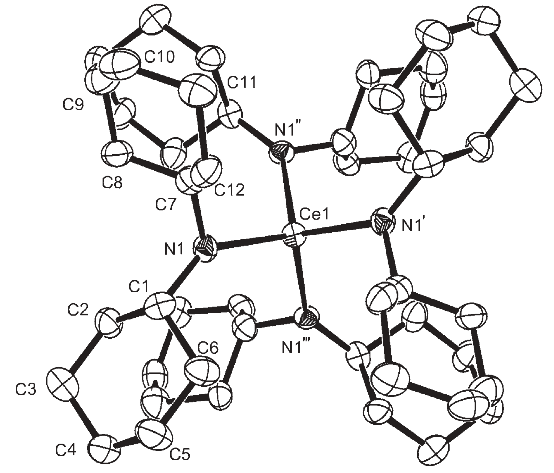


**Fig. 1** Molecular structure of $[\mathrm{Ce(NCy_2)_4}]$ (**3**) (50% probability ellipsoids) showing one of the three independent molecules in the crystal. Symmetry transformations used to generate equivalent atoms: ′ 1 − *y*, *x*, −*z*; ″ *y*, 1 − *x*, −*z*; ‴ 1 − *y*, 1 − *x*, *z*.

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*The Chemistry Department, University of Sussex, Brighton, UK BN1 9QJ E-mail: m.f.lappert@sussex.ac.uk; a.protchenko@sussex.ac.uk; Fax: 44 1273 677196; Tel: 44 1273 678316*

† Electronic supplementary information (ESI) available: details of synthesis, characterisation and crystallographic data for compounds **1**, **2** and **3**. See DOI: 10.1039/b607429d

**Table 1** Ce–N (terminal amido ligand) and Ce–O (thf) bond lengths (Å) in selected Ce(III) and Ce(IV) amides

| Compound | Ce–N | Ce–O |
|---|---|---|
| $[Ce(NCy_2)_3(thf)]$ (**1**) | 2.299(2), 2.317(2), 2.336(2) | 2.582(2) |
| $[Ce(NCy_2)_4Li(thf)]$ (**2**) | 2.320(2), 2.330(2) | |
| $[Ce(TMP)_3]$[6] | 2.332(7), 2.346(7), 2.291(7) | |
| $[Ce(TMP)_3(thf)]$[5] | 2.374(2), 2.346(2), 2.363(2) | 2.810(2) |
| $[Ce\{N(SiMe_3)_2\}_3]$[8] | 2.320(3) | |
| $[Ce(NCy_2)_4]$ (**3**)[a] | 2.247(6), 2.242(6), 2.238(5), 2.240(5) | |
| $[CeCl\{N(SiMe_3)_2\}_3]$[4b] | 2.217(3) | |
| $[CeBr\{N(SiMe_3)_2\}_3]$[4c] | 2.219(7) | |

[a] The four Ce–N bond lengths for **3** are due to the presence of 3 different molecules in the crystal.

lying on $\bar{4}$ inversion centers and one lying on a two-fold rotation axis. Fig. 1 shows a higher-symmetry molecule of **3**, and important bond lengths for these compounds (together with the data for selected Ce(III) and Ce(IV) complexes) are given in Table 1.

Each of **1**, **2** and **3** has the four-coordinate Ce atom in a distorted tetrahedral environment, which facilitates the following bond length comparisons. In complex **1** the three Ce–N distances are very similar to those in $[Ce(TMP)_3]$[6] but slightly shorter than in the overcrowded thf solvate $[Ce(TMP)_3(thf)]$,[5] while the Ce–O distance is much shorter than in the latter (Table 1) paralleling the difference in the thermal stability of these complexes.

In complex **2**, two Ce–N distances to the terminal ligands are close to those in **1** and in the silylamide $[Ce\{N(SiMe_3)_2\}_3]$,[8] while the two bridging Ce–N distances are longer at 2.472(2) and 2.497(2) Å. The $Ce^{IV}$–N distances in **3** are shorter than the terminal $Ce^{III}$–N distances in **1** or **2** by *ca.* 0.1 Å, but are slightly longer than the $Ce^{IV}$–N bonds in the less sterically hindered heteroleptic compounds $[Ce\{N(SiMe_3)_2\}_3X]$ (X = Cl or Br).[4b,c] Thus the structural study (along with the NMR data) confirms the +4 cerium oxidation state in the homoleptic amide **3**.

Possible intermediates along the route to complex **3** may include $Ce^{IV}$ superoxo-, peroxo- and oxo-complexes; the latter would disproportionate into **3** and a polymeric amido-oxo-compound of the type $\{Ce(\mu\text{-}O)(NCy_2)_2\}_x$. While organolanthanides and low-valent Ln compounds with *N*-centred ligands are generally considered as decomposing completely on exposure to air, some examples of oxygen-containing products resulting from aerial oxidation have been reported, including superoxo- $[Sm\{HB(3,5\text{-}Me_2pz)_3\}_2(\eta^2\text{-}O_2)]$,[9] peroxo- $[\{Yb(C_5H_9C_5H_4)_2(thf)\}_2(\mu\text{-}O_2)]$[10] and $[\{Yb(N(SiMe_3)_2)_2(thf)\}_2(\mu\text{-}O_2)]$,[11] and complexes with oxygenated ligands.[12] The present study has demonstrated the suitability of this approach to the synthesis of oxygen-free organoamides of high-valent cerium. This oxidative route to complex **3** parallels that reported for the aerial oxidation of $Ce(\kappa^2\text{-}S_2CNEt_2)_3$ to $[Ce(\kappa^2\text{-}S_2CNEt_2)_4]$.[13]

In conclusion, two new $Ce^{III}$ amides **1** and **2** containing bulky dicyclohexylamido ligand were prepared by the salt metathesis reaction; their oxidation by air provided a route to the remarkably stable homoleptic $Ce^{IV}$ amide $[Ce(NCy_2)_4]$ (**3**).

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## Notes and references

‡ *Synthesis of [Ce(NCy₂)₃(thf)] (**1**):* $CeCl_3$ (0.453 g, 1.84 mmol) was stirred in thf (15 mL) at room temperature for 2 days to give a copious microcrystalline solvate. To this suspension a solution of $LiNCy_2$ (0.945 g, 5.05 mol) in thf (20 mL) was slowly added at 0 °C producing a yellow solution. The mixture was stirred for 1 h at room temperature and the solvent was removed in a vacuum. The residue was extracted with toluene (2 × 10 mL), filtered, and the filtrate was concentrated to *ca.* 2 mL and covered with hexanes. Storing at −27 °C for 2 days gave 0.811 g (57%) of **1**·PhMe as large yellow crystals; mp 235–240 °C. $^1H$-NMR ($C_6D_6$): $\delta$ 13.33, 7.00–7.13 (aromatic CH, toluene), 2.47, 2.11 (sharp s, $CH_3$ toluene), 1.71, 1.49 (and 1.47 sh), 1.19, 1.05, 0.27, −4.07, −7.83.

*Synthesis of [Ce(NCy₂)₄Li(thf)] (**2**):* $CeCl_3$ (0.383 g, 1.55 mmol) was solvated with thf as described above and a solution of $LiNCy_2$ (1.132 g, 6.05 mol) in thf (20 mL) was slowly added at 0 °C. The mixture was stirred for 1 h at room temperature and the solvent was removed in a vacuum (if it was left as the THF solution overnight, the yield of crystalline products decreased significantly). The residue was extracted with toluene (2 × 10 mL), the combined toluene solution was concentrated to *ca.* 5 mL and covered with hexanes. Storing at 5 °C overnight gave 0.892 g (61%) of **2** as bright pink crystals; mp 146–148 °C (decomp.). $^1H$-NMR ($C_6D_6$): $\delta$ 12.73, 11.75, 6.05, 5.50, 3.34, 1.50, 0.29, −0.35, −0.87, −1.38, −2.06, −3.44, −4.85, −6.58, −10.52, −29.74.

*Synthesis of [Ce(NCy₂)₄] (**3**):* A Schlenk tube containing a degassed solution of **1**·PhMe (0.303 g, 0.36 mmol) in toluene (30 mL) was connected *via* a short rubber tubing to an ampoule containing dry air (10 mL, 0.093 mmol of $O_2$). After stirring for 30 min at 25 °C a dark blue-violet solution was formed; the Schlenk tube was closed and stored at 5 °C overnight yielding a greenish-yellow solution with black crystals and some light brown amorphous precipitate. The crystals were washed by decantation with cold toluene and dried, yielding 0.108 g (35% based on Ce) of **3**. Complex **3** decomposed at 90–100 °C without melting. $^1H$-NMR ($C_6D_6$): $\delta$ 4.13 (m, 1 H, NCH), 2.04 (d, 2 H), 1.88 (m, 2 H), 1.79 (m, 1 H), 1.70 (m, 2 H), 1.55 (m, 2 H), 1.30 (m, 1 H). $^{13}C$-NMR ($C_6D_6$): $\delta$ 57.44 (NCH), 39.60 ($CH_2$), 27.22 ($CH_2$), 26.08 (CH).

§ *Crystal data.* For **1**·PhMe (yellow prism 0.25 × 0.20 × 0.20 mm³): $[C_{40}H_{74}CeN_3O]\cdot(C_7H_8)$, $M = 845.28$, monoclinic, space group $P2_1/c$, $a = 10.3004(2)$, $b = 23.4770(4)$, $c = 19.3077(3)$ Å, $\beta = 101.189(1)$, $V = 4580.29(14)$ Å³, $Z = 4$, $T = 173(2)$ K, $\mu = 1.03$ mm$^{-1}$, 8044 independent reflections [$R_{int} = 0.060$], final $R1 = 0.032$ [for 6438 reflections with $I > 2\sigma(I)$], $wR2 = 0.069$ (all data). For **2** (pink prism 0.25 × 0.25 × 0.20 mm³): $[C_{52}H_{96}CeLiN_4O]$, $M = 940.39$, monoclinic, space group $P2_1/n$, $a = 15.1681(3)$, $b = 19.1024(4)$, $c = 18.1727(3)$ Å, $\beta = 96.822(1)$, $V = 5228.21(17)$ Å³, $Z = 4$, $T = 173(2)$ K, $\mu = 0.91$ mm$^{-1}$, 10277 independent reflections [$R_{int} = 0.078$], final $R1 = 0.035$ [for 7866 reflections with $I > 2\sigma(I)$], $wR2 = 0.073$ (all data). For **3** (black needle 0.10 × 0.05 × 0.05 mm³): $[C_{48}H_{88}CeN_4]$, $M = 861.34$, tetragonal, space group $P\bar{4}$, $a = b = 21.1876(5)$, $c = 10.3198(3)$ Å, $V = 4632.7(2)$ Å³, $Z = 4$, $T = 173(2)$ K, $\mu = 1.02$ mm$^{-1}$, 8991 independent reflections [$R_{int} = 0.054$], final $R1 = 0.048$ [for 7005 reflections with $I > 2\sigma(I)$], $wR2 = 0.106$ (all data). CCDC numbers: **1**·PhMe 609099, **2** 609100, **3** 609101. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b607429d

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