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

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General Methods: All manipulations were carried out in an atmosphere of dry argon using standard Schlenk tube techniques or under vacuum in a sealed all-glass apparatus. Solvents were dried from the appropriate drying agent, distilled, degassed and stored over a potassium mirror. The NMR spectra were recorded on a DPX 300 spectrometer at 293 K with residual solvent signals as internal reference for ^{1}H while ^{13}C NMR spectra were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Elemental analyses were carried out at London Metropolitan University. Anhydrous $CeCl_3$ was prepared from commercial hydrate (Aldrich) by dehydration with NH_4Cl.[1] Dicyclohexylamine (Aldrich) was stored over molecular sieves. $LiNCy_2$ was prepared by the published procedure.[2]

*Synthesis of [Ce(NCy$_2$)$_3$(thf)] (**1**)*: $CeCl_3$ (0.453 g, 1.84 mmol) was stirred in thf (15 mL) at room temperature for 2 days when it transformed from a compact powder into a copious microcrystalline (needles) precipitate. To this suspension a solution of $LiNCy_2$ (0.945 g, 5.05 mol) in thf (20 mL) was slowly added at 0 °C. During the addition a colourless solution was formed first (indicating the absence of unreacted $CeCl_3$) turning yellow upon completion of the addition. 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), the LiCl precipitate (0.156 g, 73 %) was filtered off and discarded, and the combined toluene solution was concentrated to *ca.* 2 mL and covered with hexanes. Storing at −27 °C for 2 days gave 0.811 g (57%) of **1**ᵡPhMe as large yellow crystals; mp 235-240 °C (the tendency of **1** to form

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hollow crystals with mother solution inclusions and its high solubility prevented preparation of analytically pure samples). ^{1}H-NMR (C_6D_6): d 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 (Fig. 1S).

Synthesis of [Ce(NCy$_2$)$_4$Li(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 it 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 (larger crystals had red to orange colour depending on lighting conditions) suitable for X-ray crystallography; mp 146-148 °C (decomp.). Anal. Calc. for $C_{52}H_{96}N_4OCeLi$: C, 66.4; H, 10.29; N, 5.96. Found: C, 66.6, H, 10.18, N, 5.79%. ^{1}H-NMR (C_6D_6): d 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 (Fig. 2S). ^{1}H-NMR (thf-d_8): d 6.18 (br s, 16 H), 3.62 (m, thf), 3.08 (br s, 8 H), 1.78 (m, thf), 1.07 (br d, 16 H), 0.57 (br m, 24 H), –0.56 (br s, 8 H), –2.99 (br s, 16 H) (Fig. 3S).

Synthesis of [Ce(NCy$_2$)$_4$] (3): A Schlenk tube containing a degassed solution of **1**xPhMe (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, dried over P_2O_5). 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. Black crystals were washed by decantation with cold toluene and dried, yielding 0.108 g (35 %) of complex **3**. Melting point determination showed that complex **3** decomposed at 90-100 °C without melting. Anal. Calc. for $C_{48}H_{88}CeN_4$: C, 66.9; H, 10.30; N, 6.50. Found: C, 66.8; H, 10.43; N, 6.40%. ^{1}H-NMR (C_6D_6): d 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, d): 57.44 (NCH), 39.60 (CH_2), 27.22 (CH_2), 26.08 (CH).

Similarly, complex **3** was isolated (0.116 g, 28%) from **2** (0.455 g, 0.48 mmol) and dry air (12 mL).

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Crystallography: Data for the crystal structure determination of **1**, **2** and **3** were collected on a Nonius Kappa CCD diffractometer at 173(2) K with Mo-Kα X-rays (λ = 0.71073 Å). Crystal data and refinement details are listed in Table 1S. The structures were solved by direct method and refined using SHELXL-97.[3] Crystals of complex **3** obtained from toluene had significant disorder, which could not be modelled; good quality single crystals were obtained by crystallisation from hot thf. In the structure of **3** there are two independent molecules lying on $\bar{4}$ inversion centers and one lying on a two-fold rotation axis.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers: XXXXXXX (**1**), XXXXXXX (**2**) and XXXXXXX (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained online free of charge (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

1. M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.,* 1962, **24**, 387.
2. J. Jubb, P. Berno, S. Hao and S. Gambarotta, *Inorg. Chem.,* 1995, **34**, 3563.
3. G. M. Sheldrick, *SHELXL-97,* University of Göttingen, Göttingen, Germany, 1997.

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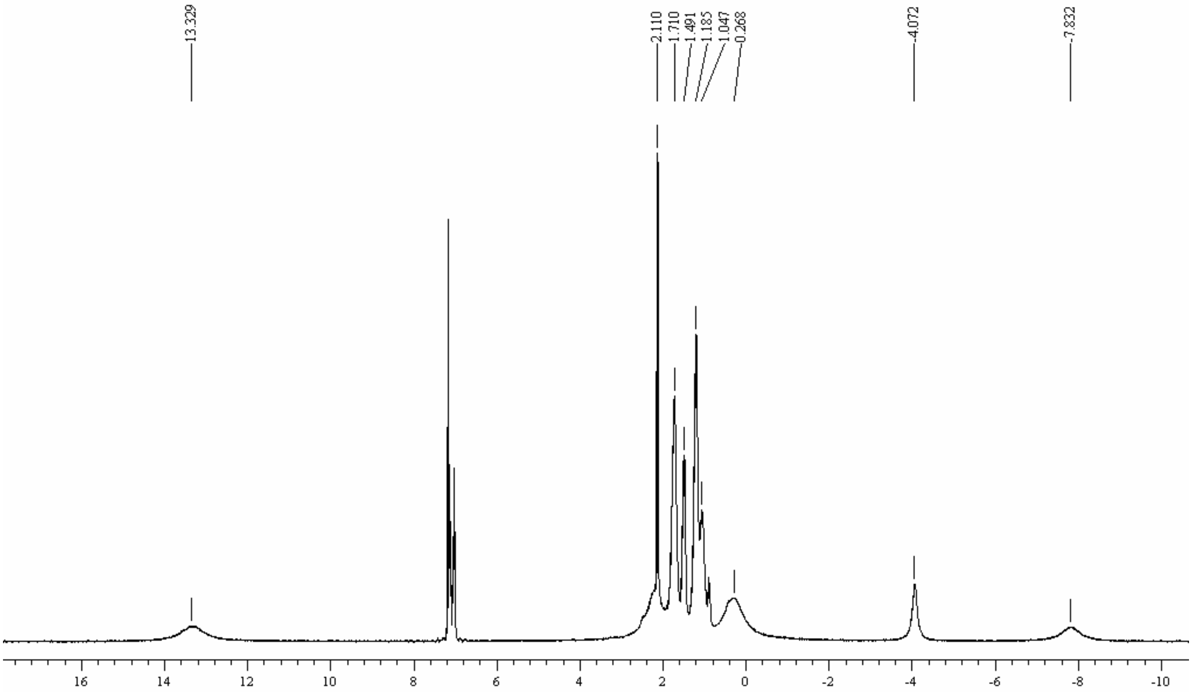

Fig. 1S. The ^{1}H NMR spectrum of complex **1**xPhMe in C_6D_6.

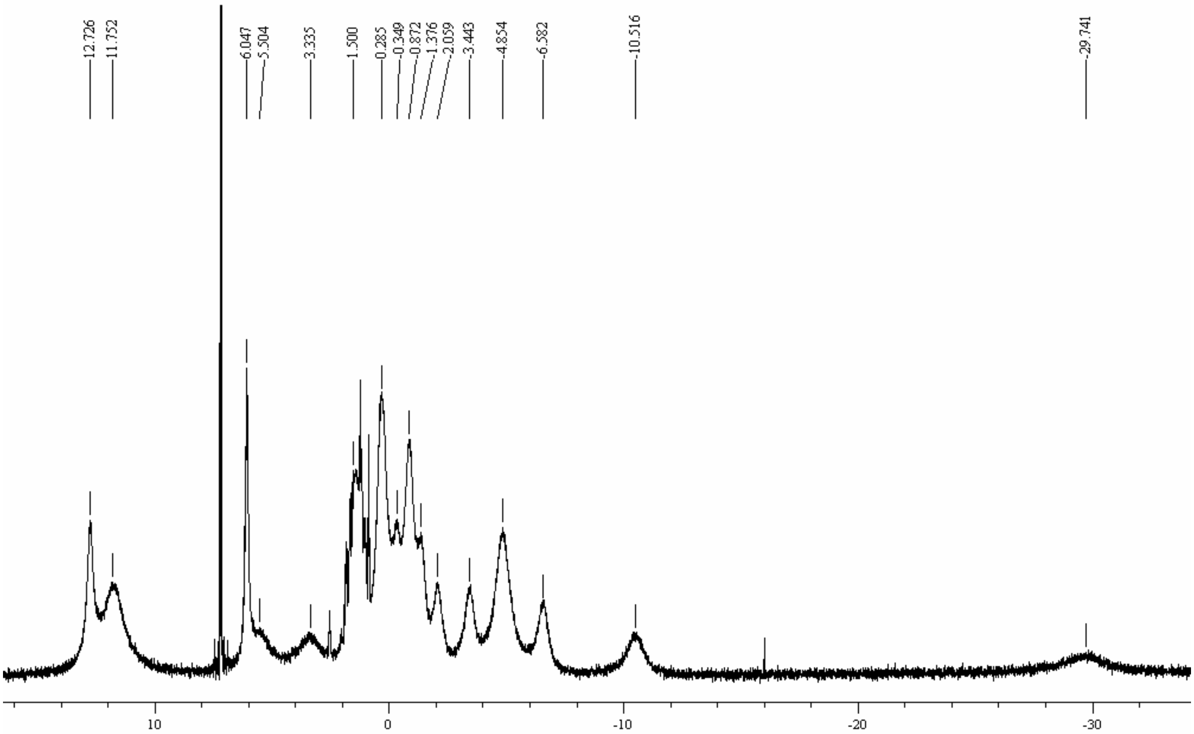

Fig. 2S. The ^{1}H NMR spectrum of complex **2** in C_6D_6 (a group of sharp peaks in the δ 2.5 – 0.5 range belongs to $HNCy_2$ as a decomposition product of **2** in solution)

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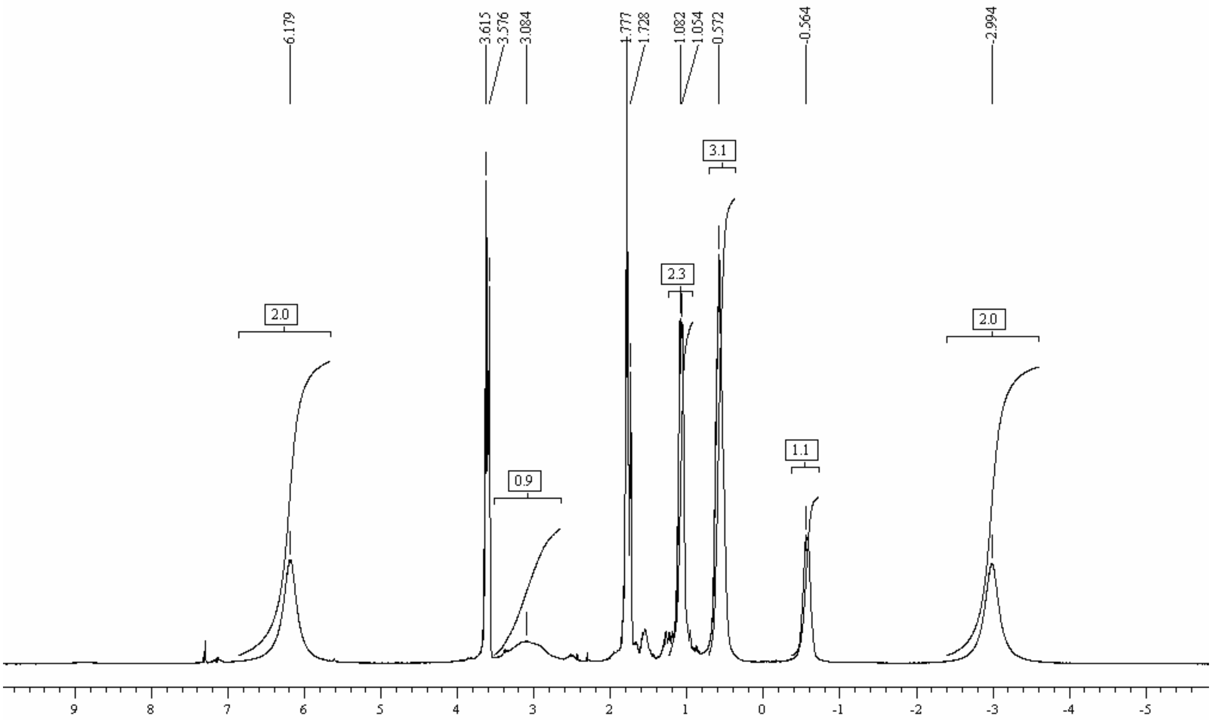

Fig. 3S. The ^{1}H NMR spectrum of complex **2** in thf-d_8 (integral values correspond to a number of protons in one cyclohexyl substituent)

Table 1S Crystal data and structure refinement for **1**, **2** and **3**

Compound	**1**	**2**	**3**
Empirical formula	$C_{40}H_{74}CeN_3O\cdot(C_7H_8)$	$C_{52}H_{96}CeLiN_4O$	$C_{48}H_{88}CeN_4$
Formula weight	845.28	940.39	861.34
Crystal system	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$ (No.14)	$P2_1/c$ (No.14)	$P\bar{4}$ (No.81)
a/Å	10.3004(2)	15.1681(3)	21.1876(5)
b/Å	23.4770(4)	19.1024(4)	21.1876(5)
c/Å	19.3077(3)	18.1727(3)	10.3198(3)
α/°	90	90	90
β/°	101.189(1)	96.822(1)	90
γ/°	90	90	90
V/Å^3	4580.29(14)	5228.21(17)	4632.7(2)
Z	4	4	4
D_c/Mg m^{-3}	1.23	1.20	1.24
μ(Mo-Kα)/mm^{-1}	1.03	0.91	1.02
F(000)			
Reflections collected	39309	60421	20827
Independent reflections	8044 [R(int) = 0.060]	10277 [R(int) = 0.078]	8991 [R(int) = 0.054]
Reflections with $I > 2\sigma(I)$	6438	7866	7005
Data/restraints/parameters	8044/0/469	10277/0/532	8991/0/478
Goodness-of-fit on F^2	1.031	0.997	1.006
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.032$, $wR2 = 0.063$	$R1 = 0.035$, $wR2 = 0.066$	$R1 = 0.048$, $wR2 = 0.096$
R indices (all data)	$R1 = 0.049$, $wR2 = 0.069$	$R1 = 0.059$, $wR2 = 0.073$	$R1 = 0.075$, $wR2 = 0.106$
Largest diff. peak and hole/ e A^{-3}	0.51 and –0.47	0.39 and –0.43	1.63 and –1.15 (near Ce)

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