Organometallic Cerium Complexes from Tetravalent Coordination Complexes

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Dedicated to Professor *Jean-Claude Bünzli* on the occasion of his 65th birthday

The use of tetravalent cerium alkoxides, nitrates, and triflates was studied as a direct route to [Ce^{IV}(carbene)] complexes. Protonolysis reactions between 1H-imidazolium- or imidazoline (=4,5-dihydro-1H-imidazole)-containing alkoxide proligands HL (L = OCMe$_2$CH$_2$[1-C(NCHCHN^{i}Pr)]) and HL^S (L^S = OCMe$_2$CH$_2$[1-C(NCH$_2$CH$_2$N^{i}Pr)]) and Ce^{IV} *tert*-butoxide, triflate, and nitrate compounds were studied to target [Ce^{IV}(N-heterocyclic carbene)] complexes (of unsaturated and saturated carbenes, resp.). Instead, tetravalent cerium imidazolium [(O^{t}Bu)$_3$Ce(μ-O^{t}Bu)$_2$(μ-HL)Ce(O^{t}Bu)$_3$], or imidazolinium adducts [(O^{t}Bu)$_3$Ce(μ-O^{t}Bu)$_2$(μ-HL^S)Ce(O^{t}Bu)$_3$] were isolated. However, the salt metathesis of cerium triflate with KL provided a simple route to [CeL$_4$], which was significantly improved if an external oxidant, benzoquinone, was included in the mixture to maintain oxidation-state integrity. Likewise, the salt metathesis of cerium triiodide with KL and added benzoquinone provided a straightforward route to [CeL$_4$].
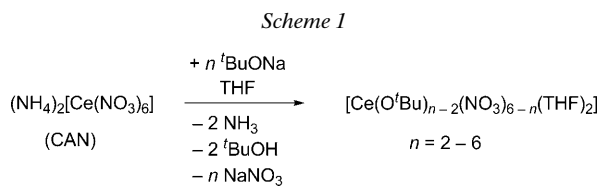
1. Introduction. – The lanthanides form predominantly trivalent complexes, as a consequence of the fourth ionisation energy being significantly larger than the first, second, and third ionisation energies combined. The most notable exception to this rule is cerium; however, as the Ce^{IV} ion possesses a more stable closed-shell electronic configuration, [Xe]4f^0, which, coupled with the high energy and, therefore, inherent instability of the 4f orbitals in the early lanthanides, renders Ce^{III} complexes vulnerable to the loss of the final electron. Predictably, tetravalent cerium complexes are strong oxidising agents, with numerous inorganic salts, among them ceric ammonium nitrate (CAN) and cerium(IV) sulfate having found myriad applications in both organic [1] and inorganic [2] oxidation reactions.

The most common tetravalent cerium coordination compounds are ceric ammonium nitrate (NH$_4$)$_2$[Ce(NO$_3$)$_6$] (CAN), ceric ammonium sulfate (NH$_4$)$_4$[Ce(SO$_4$)$_4$] (CAS), cerium sulfate [Ce(SO$_4$)$_2$], cerium acetate [Ce(OAc)$_4$] (AcO = MeCOO), and cerium triflate [Ce(OTf)$_4$] (TfO = CF$_3$SO$_3$) [3]. Of these reagents, CAN is by far the most synthetically useful as a precursor to other more soluble tetravalent cerium starting materials, particularly the alkoxides.

Authenticated examples of organometallic Ce^{IV} complexes are relatively sparse, and the outcome of oxidation reactions for all but a handful of porphyrin complexes [4] is capricious and highly dependant upon judicious choice of the ligand, solvent, and oxidant.

Since the first report by *Cesca* and co-workers in 1976 of the neutral cerium cycloocta-1,3,5,7-tetraenyl (cot) complex $[Ce(\eta^8\text{-}cot)_2]$, cerocene [5], there has been much academic debate as to the validity of the assignment of the Ce^{IV} oxidation state [6]. The synthesis and stability of cerocene has been noted as being quite remarkable, as the Ce^{IV} ion is a strong oxidising agent and the cyclooctatetraene dianion $(cot)^{2-}$ is a reducing agent [7].

Lanthanide alkoxides are widely used as molecular precursors in materials science [8]. Although Ce^{IV} alkoxides have been known for many years, their preparation was laborious and time consuming [9], until the readily available and cheap tetravalent cerium reagent, ceric ammonium nitrate $(NH_4)_2[Ce(NO_3)_6]$ (CAN), was utilised in their synthesis, originally by *Gradeff et al.* [10] and subsequently modified by *Evans et al.* (*Scheme 1*) [11].

$$(NH_4)_2[Ce(NO_3)_6] \xrightarrow[\substack{-2\,NH_3 \\ -2\,^tBuOH \\ -n\,NaNO_3}]{\substack{+\,n\,^tBuONa \\ THF}} [Ce(O^tBu)_{n-2}(NO_3)_{6-n}(THF)_2]$$

(CAN) $\qquad\qquad\qquad\qquad\qquad$ $n = 2 - 6$

Evans et al. demonstrated that it was possible to synthesise a range of Ce^{IV} nitrate, mixed nitrate – alkoxide, and alkoxide complexes by careful control of the reaction stoichiometry. The low cost, ease of synthesis, and control of the functionalities present rendered this an appealing route into further Ce^{IV} chemistry. The same group used $[Ce(O^tBu)(NO_3)_3(THF)_2]$ and three equiv. of $[Na(Cp)]$ in the synthesis of $[Ce(Cp)_3(O^tBu)]$ [12]. More recently, *Gun'ko*, *Lappert*, and co-workers reported the mixed-valence cerium trinuclear cluster $[Ce_3(O^tBu)_5(\mu_2\text{-}O^tBu)_3(\mu_3\text{-}O^tBu)_2(NO_3)]$, obtained by treatment of a mixture of $[Ce(O^tBu)_3(NO_3)]$ and two equiv. of $[Ce(O^tBu)_4(THF)_2]$ with three equiv. of $[Sn(1,3\text{-}^tBu_2C_5H_3)]$ [13]; structural characterisation and a computational analysis of model compounds revealed the oxidation states of the metal centers as $Ce^{III}Ce^{IV}Ce^{IV}$, in which the single f electron is localised on the NO_3-bearing Ce-atom.

There is only one reported instance of a Ce^{IV} alkoxide being formed *via* an oxidation reaction, from the reaction of cerium tris[tri(*tert*-butyl)methoxide] with either an organic peroxide or benzoquinone [14]. The complex $[\{(Bu^t_3CO)_3Ce\}_2(\mu\text{-}OC_6H_4O)]$ formed immediately but decomposed over time, highlighting the instability of the Ce^{IV} state [15].
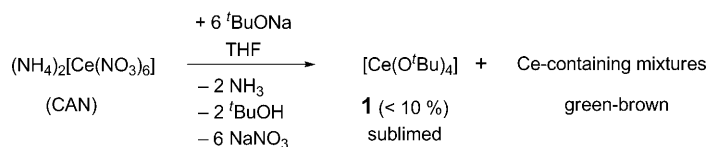
N-Heterocyclic carbenes (NHCs) act as excellent σ-donor ligands to metals, and currently receive much attention as ligands in organometallic catalysis [16]. Many fewer complexes with more electropositive metals exist [17], but anionic-functionalised NHC ligands have allowed this area to expand rapidly over the last few years [18]. The first $[Ce(NHC)]$ complexes, reported by our group in 2005 [19], contained an anionic, amido-functionalised NHC ligand.

We recently reported the synthesis of a trivalent (alkoxycarbene)cerium complex $[CeL_3]$ ($L = OCMe_2CH_2[1\text{-}C(NCHCHN^iPr)]$), and its oxidation to $[CeL_4]$, a compound that contains σ-bound cerium(IV) – carbene groups [20]. Herein, we describe

the use of tetravalent cerium coordination compounds to provide a simple, direct route to organometallic Ce^{IV} complexes. We also report the reactivity of the saturated carbene analogue HL^S (L^S = OCMe$_2$CH$_2$[1-C(NCH$_2$CH$_2$NMes)]) in this chemistry (Mes = 2,4,6-trimethylphenyl).

2. Results and Discussion. – 2.1. *Synthesis of [Ce(O^{t}Bu)$_4$] and [Ce$_3$(μ_3-O^{t}Bu)$_2$(μ-O^{t}Bu)$_3$(O^{t}Bu)$_6$].* We considered that the reported high-yielding route to [Ce(O^{t}Bu)$_4$-(THF)$_2$] might provide a good entry point into [Ce^{IV}(NHC)] chemistry. However, in our hands, this reaction proved difficult to reproduce. Complex product mixtures were obtained with many reaction mixtures becoming green or brown after a few hours (*Scheme 2*). However, sublimation of the crude reaction product (120°/10^{-5} mbar) yielded a yellow crystalline solid in low yield (<10%). The complex [Ce(O^{t}Bu)$_4$-(THF)$_2$] is reported to be a yellow solid, but the ^{1}H-NMR spectrum of the sublimate contains a resonance at δ(H) 1.58 consistent with the formation of an unsolvated complex [Ce(O^{t}Bu)$_4$] (**1**). Unfortunately, elemental analysis of the material is significantly low in both C- and H-atom content. This could be due to the presence of unidentified μ-oxo clusters in the sublimed product arising from further decomposition over time, but the compound behaves as the suggested empirical formula in further studies (*vide infra*).

Scheme 2

(NH$_4$)$_2$[Ce(NO$_3$)$_6$]
(CAN)

+ 6 ^{t}BuONa
THF
— 2 NH$_3$
— 2 ^{t}BuOH
— 6 NaNO$_3$

[Ce(O^{t}Bu)$_4$] + Ce-containing mixtures

1 (< 10 %)   green-brown
sublimed

On one occasion, the green-brown solution which formed during the reaction was isolated by filtration, and dried (*Scheme 3*). The dark green solution obtained by hot hexane extraction of this powder was allowed to cool slowly, upon which single crystals suitable for an X-ray diffraction study grew. This showed the identity of **2** to be [Ce$_3$(μ_3-O^{t}Bu)$_2$(μ-O^{t}Bu)$_3$(O^{t}Bu)$_6$]. An ORTEP drawing of the molecular structure is shown in *Fig. 1*, but the low quality of the data means that only connectivity can be ascertained. The ^{1}H-NMR spectrum of the crystals of **2** contains three broad *s* at δ(H) 3.58, 0.54, and − 5.09, which, based on the integral ratios of 6:2:3, can be assigned as terminal

Scheme 3

(NH$_4$)$_2$[Ce(NO$_3$)$_6$]

+ 6 ^{t}BuONa
THF, 25°, 3 h
— 6 NaNO$_3$
— 2 ^{t}BuOH
— 2 NH$_3$
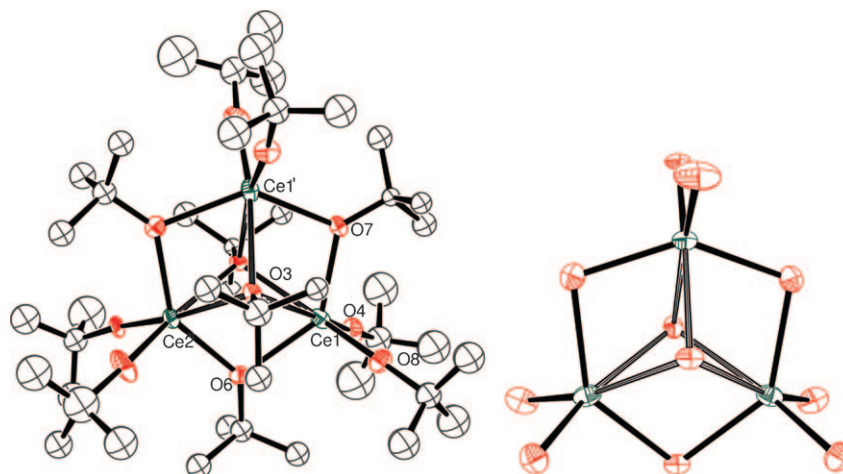
1/3

+   other products

2
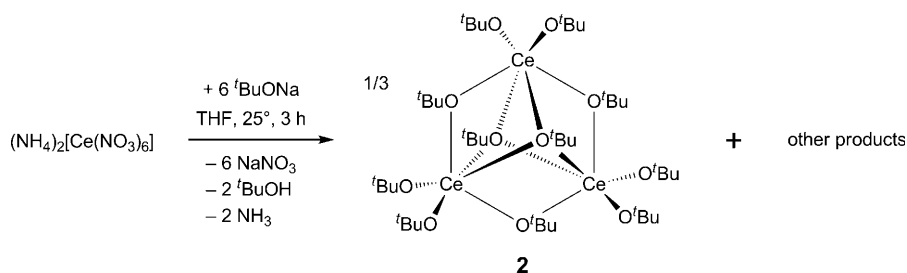
Fig. 1. *ORTEP Drawing of* **2** (left: 50% probability displacement ellipsoids, with H-atoms omitted; right, Ce-O core only)

*t*BuO, triply bridging μ_3-*t*BuO, and doubly bridging μ_2-*t*BuO ligands, respectively. The product **2** can be isolated pure by washing the blocks with hexane. Two crystal morphologies were observed; emerald blocks and semi-crystalline green needles, present in an approximate 1:1 ratio. Manual separation of these two components and ^{1}H-NMR spectroscopic analysis of each showed that they are essentially the same material, although the needles contain a higher proportion of an unidentified diamagnetic product, observed in each sample.

The cluster **2** has D_{3h} symmetry and contains a trinuclear central core consisting of three Ce-atoms, arranged in an almost equilateral triangle. Each Ce-atom is six-coordinate with distorted octahedral geometry, a consequence of the bridging alkoxide ligands forming the central Ce_3O_3 core, and is bound by two terminal, two bridging, and two triply bridging *t*BuO ligands. *Lewis* base solvated analogues of this trinuclear cluster are the most commonly structurally characterised species isolated for trivalent lanthanide alkoxides. The two most closely related examples are shown in *Fig. 2* alongside **2**, which is drawn as a mixed-valent $Ce^{III}Ce^{IV}Ce^{IV}$ trimeric cluster. Compound **A** is the mixed-valent trinuclear cluster $[Ce_3(O^tBu)_{10}NO_3]$ described above [13], and **B** is the Ce^{III} trimer $[Ce_3(\mu_3\text{-}O^tBu)_2(\mu\text{-}O^tBu)_3(O^tBu)_4(^tBuOH)_2]$, recently reported by *Boyle et al.* [21], which is isostructural with the Y, La, Nd, Dy, and Er congeners [8]. Complex **B** was synthesised by treatment of CeN''_3 ($N'' = N(SiMe_3)_2$) with an excess of *t*BuOH, and although coordinated *t*BuOH was not identified in the solid state, its presence was inferred by charge balance with the three Ce^{III} cations.

In toluene solution, complex $[Ce(O^tBu)_4(THF)_2]$ is reported to convert to a yellow trimetallic Ce^{IV} oxo-alkoxide, $[Ce_3(O)(O^tBu)_{10}]$ (**C** in *Fig. 2*), over a period of 2–3 days at room temperature. The reaction pathway is not known but the oxidation state of the metal cations is maintained. The trimeric uranium analogue of **C** was reported by *Cotton et al.* in 1984, and it was noted that the reaction conditions, and in particular the temperature during the workup procedure, strongly influenced the
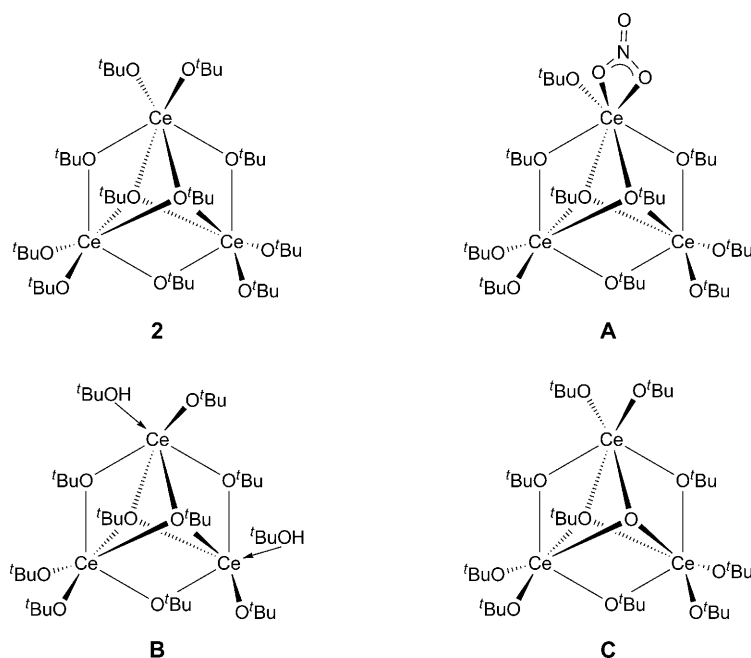
Fig. 2. *Trimetallic cerium* tert-*butoxide clusters*

nature of the products isolated [22]. Conversely, the solvated cluster **B** contains exclusively trivalent Ce-atoms, and was isolated as a colourless crystalline solid. Complex **2** was isolated as dark green crystals, confirming the difference to **C**. Considering the paramagnetic nature of **2**, the cluster most likely contains either one or two Ce^{IV} cations, and the rest is Ce^{III}. The $Ce^{III}Ce^{IV}Ce^{IV}$ cluster **A** is a green-brown crystalline solid.

The FT-IR spectrum of **2** does not contain an OH stretch attributable to an alcohol, which supports the suggested unsolvated $Ce^{III}Ce^{IV}Ce^{IV}$ structure drawn in *Fig. 2*. The EI-MS contains a peak at m/z 1093 (15%), assigned to $[\{Ce(O^tBu)_3\}_3O]^+$. This mass fragment was observed also for **B**, but at a higher relative intensity, and the fragmentation patterns for the two differ. The UV/VIS spectrum of a solution of **2** in toluene contains strong absorptions at λ 219, 229, 241, 258, and 278 nm, comparable to those reported for **A**.

The precise mechanism by which **2** is formed remains unclear, but it would seem that the reaction conditions and workup procedure are likely to play a pivotal role in the product isolated from this reaction.

2.2. *Alkoxycarbene Precursors HL and HL^S, Crystal Structure of HL^{SMes}.* We recently reported the synthesis of the saturated carbene-analogue precursor of HL, HL^S. The backbone CH_2 ring H-atoms of this carbene should no longer be susceptible to unwanted deprotonation or rearrangements that has been demonstrated for other early metal adducts of L [23]. The compound HL^S forms a bicyclic structure rather than the zwitterionic structure shown by HL (*Fig. 3*) as evidenced by ^{1}H-NMR spectroscopy,
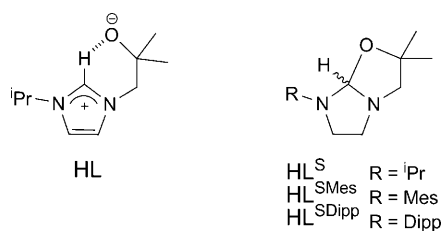
Fig. 3. *Proligands HL and HL^S.* Mes = 2,4,6-Me₃C₆H₂, Dipp = 2,6-ⁱPr₂C₆H₃.

and now confirmed here by a single-crystal X-ray diffraction study of the related HL^SMes (*Fig. 4*). The solid-state structure of the mesityl-substituted saturated proligand HL^SMes was obtained from single crystals grown from the product after storage of the oily solid for 3 months. The molecular structure is drawn in *Fig. 4*. The expected asymmetric, bicyclic adduct structure is confirmed in the solid state and can be compared with the methanol adduct $(MeO)(H)C(NMesCH_2)_2$, reported by *Waymouth*, *Hedrick* and co-workers [24]. The imidazolidine C-atom C(1) is essentially tetrahedral with a range of angles between 105.71(14) and 114.08(14)°; the $N-C-N$ bond angle of 105.71(14)° is more acute than in the imidazolinium proligand starting material (110–114°), as expected. The heterocyclic $C-N$ bond lengths are different, at 1.459(2) and 1.438(2) Å, and the $C-O$ bond length is 1.432(2) Å.
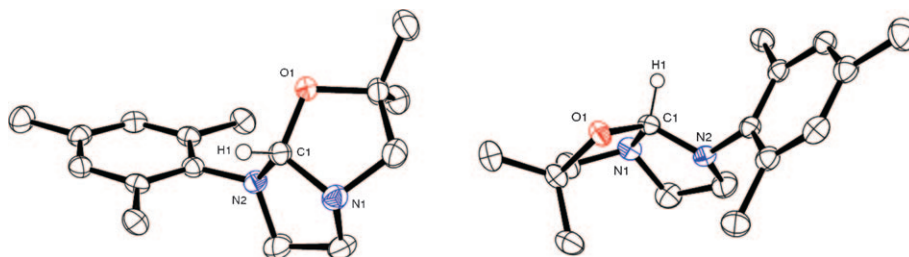

Fig. 4. *ORTEP Drawing of the molecular structure of HL^SMes* (50% probability displacement ellipsoids). H-Atoms omitted for clarity (except for $H-C(1)$). Selected bond lengths [Å] and angles [°]: $C(1)-O(1)$ 1.432(2), $C(1)-N(1)$ 1.459(2), $C(1)-N(2)$ 1.438(2); $N(1)-C(1)-N(2)$ 105.71(14), $N(1)-C(1)-O(1)$ 108.23(13), $N(2)-C(1)-O(1)$ 114.08(14).

2.3. *Protonolysis Reaction of [Ce(OᵗBu)₄] with Alkoxycarbene Precursors HL and HL^S.* Despite the contrasting structures of the unsaturated and saturated proligands HL and HL^S, their reaction chemistry is very similar. Treatment of [Ce(OᵗBu)₄] with either half or one equiv. of the unsaturated zwitterion HL in THF at −78° afforded a yellow solution which was stirred at room temperature overnight, during which time it darkened to a brown solution. After workup, in each case a brown solid was isolated in 25% yield, formulated as the dinuclear [(1*H*-imidazolium-1-yl)alkoxy]cerium complex **3** (*Scheme 4*). The ¹H-NMR spectrum of **3** contains a single set of ligand resonances with the characteristic imidazolium CH resonance at $\delta(H)$ 9.84. There are three ᵗBuO resonances at $\delta(H)$ 2.05, 1.75, and 1.53, which integrate in a 1:1:2 ratio and can be assigned to the two bridging μ-ᵗBuO, two terminal ᵗBuO on the same face as the [(1*H*-

Scheme 4

1   **HL**   **3**
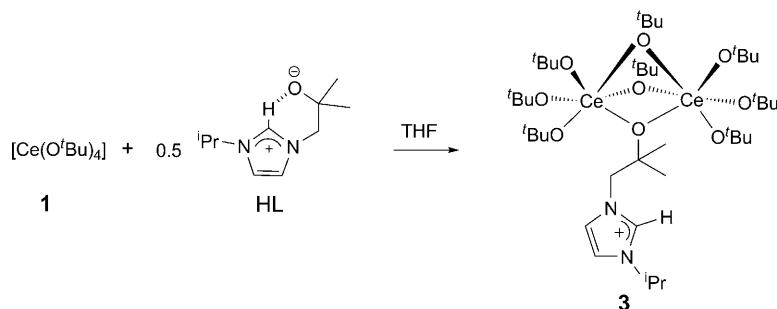
imidazolium-1-yl)alkoxy] ligand, and the remaining four terminal ^{t}BuO ligands. The ^{13}C-NMR spectrum is commensurate with this and displays an imidazolium C-atom resonance at δ(C) 137.3. As for **1**, the elemental-analysis data for **3** were significantly low in both C- and H-atoms content although the value for the N-atom content was correct. Single crystals of **3** suitable for an X-ray diffraction study were grown from a THF solution stored at $-30°$, although again the data were of poor quality. So it is only possible to establish connectivity that supports the structure of **3** as drawn in *Scheme 4*. To account for charge balance, and for the diamagnetic NMR spectra, both metals are assigned as Ce^{IV} cations. This again supports the formulation of the starting material **1** as $[Ce(O^tBu)_4]$.

The saturated analogue of **3**, the (imidazoliniumylalkoxy) complex **4** (see *Scheme 5*) was synthesised by treatment of a hexane solution of **1** with half an equiv. of the proligand HL^S in hexanes. A pale yellow precipitate formed from the yellow solution after standing at room temperature overnight, and was isolated in 20% yield. The ^{1}H-NMR spectrum displays an imidazolinium CH resonance at δ(H) 9.22, as well as a simplified set of ligand resonances which are reminiscent of breaking the bicyclic ring structure. As observed for **3**, three ^{t}BuO resonances are present at δ(H) 2.02, 1.76, and 1.63 in a ratio of 1:1:2. The ^{13}C-NMR spectrum is in agreement with these assignments, and contains an imidazolinium CH resonance at δ(C) 159.0.

Scheme 5. *Addition of HL^S to $[Ce(O^tBu)_4]$*

$[Ce(O^tBu)_4] + 0.5$ HL^S **4**
1
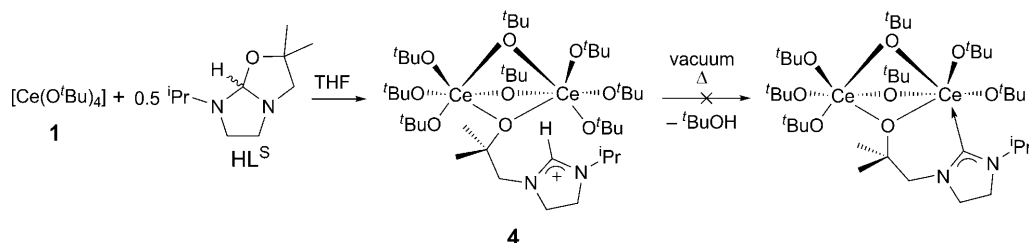
The isolation of **3** and **4** indicate that the elimination of ^{t}BuOH from these complexes to form the corresponding $[Ce^{IV}(NHC)]$ complexes, is not a favourable process. In an attempt to force the elimination of ^{t}BuOH, and concomitant formation of the M−NHC bond, a sample of **4** was heated in a sublimation apparatus at $100°/$

10^{-5} mbar (*Scheme 5*). The ^{1}H-NMR spectrum of the resulting pale yellow solid contains predominantly starting material **4** with decomposition products that could not be assigned.

2.4. *Salt Metathesis Reactivity between Ce^{IV} Salts and KL*. 2.4.1. *Cerium Ammonium Nitrate* (CAN). The direct synthesis of mixed [Ce^{IV}(NHC)(nitrate)] complexes was attempted *via* treatment of CAN with three or five equiv. of KL in THF at room temperature (*Scheme 6*). The evolution of NH$_3$ and precipitation of KNO$_3$ were observed, although the resulting yellow and brown residues, respectively, proved intractable to all attempts at further analysis.
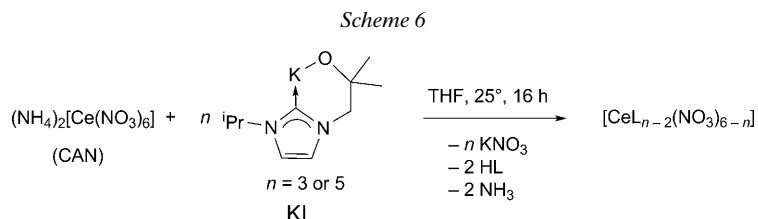
Scheme 6

2.4.2. *Cerium Triflate*. In contrast, treatment of [Ce(OTf)$_4$] with four equiv. of KL in THF resulted in the formation of a dark orange solution which afforded an orange solid after filtration and removal of the volatiles (*Scheme 7*). ^{1}H-NMR Spectroscopic

Scheme 7. *Synthesis of [CeL$_4$] from Ce(OTf)$_4$ and [CeI$_3$(THF)$_4$]*
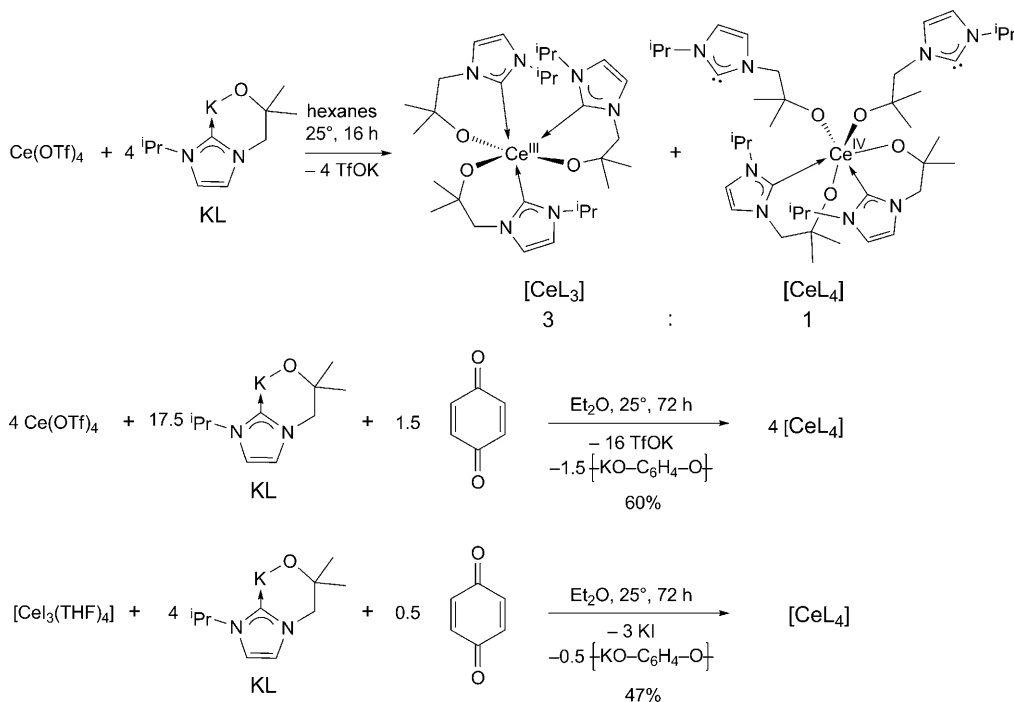
analysis of the product mixture confirmed the presence of paramagnetic [CeL$_3$] and diamagnetic [CeL$_4$] in a 3:1 ratio and a total yield of 57%.

Since cerium triflate is a readily available Ce^{IV} reagent, this still represents a straightforward route to these homoleptic complexes. We previously reported the stoichiometric reaction of [CeL$_3$] with benzoquinone and KL to afford [CeL$_4$]. These reagents are both compatible with Ce(OTf)$_4$, so it was reasoned that the addition of benzoquinone to the reaction mixture could maintain oxidation-state integrity and allow the direct conversion of cerium triflate to [CeL$_4$] in high yields. Pleasingly, this proved correct (*Scheme 7*). Since [CeL$_3$] was originally made from CeI$_3$, we have also now tested the feasibility of incorporation of benzoquinone into the reaction mixture of [CeI$_3$(THF)$_4$] and KL, and found that this too afforded [CeL$_4$] as the only isolable product, in 47% yield (*Scheme 7*).

3. Conclusions. – A mixed-valence trinuclear [Ce(alkoxide)] cluster was isolated from reactions of CAN with ^{t}BuOK. The [Ce^{IV}(*tert*-butoxide)] complexes themselves could not be used to access [Ce^{IV}(NHC)] complexes *via* protonolysis reactions in our systems. However, the tetravalent triflate salt Ce(OTf)$_4$ could be used to make [CeL$_4$] directly if benzoquinone was added to the reaction.

Experimental Part

1. *General.* All manipulations were carried out under a dry, O$_2$-free N$_2$ with standard *Schlenk* techniques, or in an *MBraun Unilab* or vacuum atmospheres *Omni-Lab* glovebox unless otherwise stated. The solvents used were degassed and dried either by refluxing over K or by passage through activated alumina towers prior to use. All deuterated solvents were refluxed over K, vacuum-transferred and freeze-pump-thaw degassed three times prior to use. Benzoquinone was sublimed prior to use. The compounds CeN$_3''$ [25] and KL [26] were synthesised according to literature procedures. All other reagents were used as received without further purification. UV/VIS/NIR: *Perkin-Elmer-Lambda-900* UV/VIS/NIR spectrometer: solns. were made in the glovebox and recorded in a *Young*-tap-topped 10 mm quartz cell. IR Spectra: *Nicolet-210* and *Jasco-410* spectrophotometers; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker-Arx-250*, *-Avance-360*, or *-Ava-500* spectrometers, ^{1}H at 250, 360, or 500 MHz, resp., ^{13}C at 63, 90, and 125 MHz, resp.; at 300 K unless otherwise stated; δ in ppm referenced internally to residual proton solvent, J in Hz. MS: *VG-Autospec* instrument or *Agilent-1100* LC/MS instrument; in m/z (rel. %). Elemental analyses were determined by Mr. *Stephen Boyer* at London Metropolitan University.

2. *Syntheses.* *[Ce(O^{t}Bu)$_4$]* (**1**). To a stirred slurry of CAN (2.00 g, 3.64 mmol) in THF (10 ml) was added portionwise a soln. of ^{t}BuONa (2.10 g, 21.89 mmol) in THF (10 ml) at r.t. A yellow soln. formed immediately with concomitant production of a colourless precipitate and evolution of NH$_3$. The soln. was stirred at r.t. for 2 h and after filtration and evaporation of the volatiles, the crude product was isolated as a yellow solid (1.50 g). Sublimation at 120°/10^{-5} mbar yielded **1** (150 mg, 9.5%). Yellow crystalline solid. ^{1}H-NMR (C$_6$D$_6$): 1.58 (*s*, ^{t}Bu). Anal. calc. for C$_{16}$H$_{36}$CeO$_4$: C 44.42, H 8.40; found: C 30.06, H 5.79.

[Ce$_3$(μ_3-O^{t}Bu)$_2$(μ-O^{t}Bu)$_3$(O^{t}Bu)$_6$] (**2**). Into a *Schlenk* tube were added CAN (3.0 g, 5.47 mmol) and ^{t}BuONa (3.16 g, 32.83 mmol), followed by THF (50 ml), with stirring at r.t. After 2–3 h, a yellow soln. and colourless precipitate formed, which was accompanied by the evolution of NH$_3$. The mixture was stirred overnight and the green/brown soln. filtered, followed by evaporation of the volatiles. The residue was dissolved in hexane and placed in a $-30°$ freezer, from which **2** was isolated (1.24 g, 55.6%). Green solid. X-Ray-quality single crystals were grown by slow cooling of a hot hexane soln. to r.t. overnight, and

formed as dark green blocks and light green needles. After manual separation, the blocks were washed with hexane and dried before further characterisation. IR (nujol): 1225m, 1188s, 1022w, 984m, 969s, 942s, 912s, 876m, 770m, 747m, 722m, 503m, 478m, 417m. ^{1}H-NMR (C$_6$D$_6$): 3.58 (br. s, 36 H, terminal ^{t}Bu); 0.54 (br. s, 18 H, μ_3-O^{t}Bu); -5.09 (br. s, 36 H, μ-O^{t}Bu). EI-MS: 1093 (15, [$M - {}^tBu$]$^+$), 1020 (30, [$M - {}^tBu - {}^tBuO$]$^+$), 963 (22, [$M - {}^tBu - {}^tBuO - {}^tBu$]$^+$), 874 (9, [$M - {}^tBu - 3\,{}^tBuO$]$^+$), 791 (65, [$M - {}^tBu - OCe(O^tBu)_2$]$^+$), 718 (41, [$M - {}^tBu - OCe(O^tBu)_3$]$^+$), 661 (29, [$M - {}^tBu - Ce(O^tBu)_4$]$^+$), 588 (21, [$M - {}^tBu - Ce(O^tBu)_5$]$^+$), 531 (10, [$M - {}^tBu - Ce(O^tBu)_5 - {}^tBu$]$^+$), 359 (78, [Ce(O^{t}Bu)$_3$]$^+$), 286 (58, [Ce(O^{t}Bu)$_2$]$^+$), 214 (59, [CeO^{t}Bu]$^+$), 156 (98, [CeO]$^+$), 57 (100, ^{t}Bu$^+$). Anal. calc. for C$_{44}H_{99}Ce_3O_{11}$: C 43.15, H 8.16; found: C 43.12, H 8.05.

[{Ce(μ-O^{t}Bu)(^{t}BuO)$_3$}$_2$(μ-HL)] (**3**). To a mixture of **1** (0.60 g, 1.51 mmol) and HL (138 mg, 0.76 mmol) at $-78°$ was added cooled ($-78°$) THF (15 ml) with stirring. A yellow soln. formed and was allowed to slowly warm to r.t. with stirring for 12 h. The resulting pale brown mixture was concentrated and stored at $-30°$ overnight. Filtration and evaporation of the volatiles from the filtrate afforded **3** (198 mg, 25.0%). Brown solid. X-Ray-quality single crystals were grown by slow cooling of a THF soln. to $-30°$. ^{1}H-NMR (C$_6$D$_6$): 9.84 (s, NCHN); 6.17 (s, NC*H*CHN); 5.76 (s, NCHC*H*N); 4.29 (*sept.*, ^3J(H,H) = 6, Me$_2$C*H*); 3.97 (s, NC*H*$_2$C); 2.05 (s, 18 H, ^{t}Bu); 1.75 (s, 18 H, ^{t}Bu); 1.53 (s, 36 H, ^{t}Bu); 0.85 (d, 6 H, ^3J(H,H) = 6, *Me$_2$*CH). ^{13}C-NMR: 137.3 (NCHN); 124.6 (N*C*HCHN); 114.6 (NCH*C*HN); 81.3, 79.4, 75.6 (Me$_3$*C*O); 74.1 (Me$_2$*C*O); 64.8 (*C*H$_2$N); 52.0 (Me$_2$*C*H); 35.9, 34.8, 34.6 (*Me$_3$*CO); 30.00 (*Me$_2$*CH); 22.5 (*Me$_2$*CO). Anal. calc. for C$_{42}$H$_{90}$Ce$_2$N$_2$O$_9$: C 48.15, H 8.68, N 2.67; found: C 33.72, H 6.13, N 2.69.

[{Ce(μ-O^{t}Bu)(^{t}BuO)$_3$}$_2$(μ-HL^S)] (**4**). To a soln. of **1** (85 mg, 0.20 mmol) in hexane (5 ml) was added a soln. of HL^S (18.1 mg, 0.1 mmol) in hexane. The yellow soln. was mixed well and stored under N$_2$ at r.t. overnight. A pale yellow precipitate formed, which was isolated by filtration, washed with hexane (2×2 ml), and dried under reduced pressure: **4** (35 mg, 19.6%). ^{1}H-NMR (C$_6$D$_6$): 9.22 (s, NCHN); 3.85 (*sept.*, ^3J(H,H) = 6.6, Me$_2$C*H*); 3.25 (br. s, NC*H*$_2$CMe$_2$); 2.89 (br. m, NCH$_2$C*H*$_2$N); 2.34 (*m*, NCH$_2$C*H*$_2$N); 2.02 (s, 18 H, ^{t}Bu); 1.83 (s, *Me$_2$*CO); 1.76 (s, 18 H, ^{t}Bu); 1.63 (s, 36 H, ^{t}Bu); 0.71 (d, ^3J(H,H) = 6.6, *Me$_2$*CH). ^{13}C-NMR: 159.0 (NCHN); 82.2, 80.2, 76.5 (Me$_3$*C*); 75.8 (Me$_2$*C*O); 62.5, 51.9, 41.5 (*C*H$_2$N); 50.3 (Me$_2$*C*H); 36.6, 35.7, 35.6 (*Me$_3$*CO); 30.9 (*Me$_2$*CO); 20.8 (*Me$_2$*CH). Anal. calc. for C$_{42}$H$_{91}$Ce$_2$N$_2$O$_9$: C 27.70, H 5.05, N 1.54; found: C 27.81, H 5.05, N 1.70.

Reaction of Ce(OTf)$_4$ with KL: [CeL$_4$] and [CeL$_3$]. To a mixture of Ce(OTf)$_4$ (750 mg, 1.02 mmol) and KL (900 mg, 4.08 mmol) cooled to $-78°$ was added THF (30 ml). The yellow suspension was allowed to warm to r.t. overnight with stirring. The resultant mixture of an orange soln. and colourless precipitate that had formed was concentrated and the residue extracted with Et$_2$O. After filtration to remove the colourless precipitate, the orange filtrate was concentrated and the residue dried under reduced pressure to afford a yellow-orange solid (0.43 g). The product mixture was analysed by ^{1}H-NMR: [CeL$_3$]/[CeL$_4$] 3 : 1, representing a yield of 58% assuming an effective molecular mass of 729 for the mixture.

Data of [CeL$_3$]: ^{1}H-NMR (C$_6$D$_6$): 11.71 (br. s, NC*H*$_2$C); 9.64 (br. s, *Me$_2$*CH); 6.05 (br. s, NC*H*CHN); 3.22 (br. s, NCHC*H*N); -2.94 (br. s, *Me$_2$*CHO); -5.56 (br. s, Me$_2$C*H*).

Data of [CeL$_4$]: ^{1}H-NMR (C$_6$D$_6$): 7.01 (s, NC*H*CHN); 6.50 (s, NCHC*H*N); 5.28 (*sept.*, ^3J(H,H) = 6, Me$_2$C*H*); 4.03 (s, CH$_2$N); 1.29 (s, *Me$_2$*CO); 1.23 (d, ^3J(H,H) = 6, *Me$_2$*CH).

Direct Synthesis of [CeL$_4$]: Reaction of Ce(OTf)$_4$ with KL and Benzoquinone. To a mixture of Ce(OTf)$_4$ (80 mg, 0.11 mmol), KL (104.5 mg, 0.475 mmol), and benzoquinone (4.05 mg, 0.037 mmol), Et$_2$O (10 ml) was added, and the dark-green suspension was stirred overnight at r.t. The resultant mixture was filtered to remove a dark-green solid. Evaporation of the yellow filtrate afforded a yellow solid (105.7 mg), which was identified as impure [CeL$_4$]. The impurities were the same as those identified in the conventional synthesis of [CeL$_4$] and easily removed by washing with cold hexane. No paramagnetic product was found. Yield (from integration of the NMR spectra) 55–60% of [CeL$_4$].

Direct Synthesis of [CeL$_4$]: Reaction of [CeI$_3$(THF)$_4$] with KL and Benzoquinone. To a mixture of [CeI$_3$(THF)$_4$] (400 mg, 0.49 mmol), KL (436 mg, 1.98 mmol), and benzoquinone (26.7 mg, 0.25 mmol), Et$_2$O (30 ml) was added, and the emerald-green suspension was stirred over the weekend at r.t. The resultant mixture was filtered to remove a dark-green solid, which was washed with an additional portion of Et$_2$O (10 ml). Evaporation of the combined yellow filtrates afforded a yellow solid, which was washed

with cold ($-78°$) hexane (5 ml) and finally dried *in vacuo* to give [CeL$_4$] (200 mg, 47.2%). Yellow powder. Identification by ^{1}H-NMR.

3. *X-Ray Crystallography*[1]. Crystallographic X-ray data were collected with MoK_α radiation ($\lambda = 0.71073$ Å) and a *Bruker-Smart-APEX-CCD* area detector diffractometer by means of ω scans (*Table*). Absorption correction: multi-scan (based on symmetry-related multiscan measurements). Structure solution and refinement was carried out with the SIR program and the SHELXTL suite of programs and

Table. *Crystallographic Data for Mesityl-Substituted Proligand HL^{SMes} and Complex [Ce$_3$(μ_3-O^{t}Bu)$_2$-(μ-O^{t}Bu)$_3$(O^{t}Bu)$_6$] (2)*

	Proligand HL^{SMes}	Complex **2**
Empirical formula	C$_{16}$H$_{24}$N$_2$O	C$_{44}$H$_{96}$Ce$_3$O$_{11}$
M_r	260.38	1221.57
Crystal form, colour	block, colourless	block, green
Crystal dimensions [mm]	$0.3 \times 0.27 \times 0.16$	$0.20 \times 0.20 \times 0.20$
Temperature [K]	150(2)	125(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Cmc2_1$
Z	4	4
Unit cell parameters:		
a [Å]	8.5230(2)	17.807
b [Å]	17.2780(5)	32.196
c [Å]	10.0850(3)	10.902
β [°]	91.125(2)	90
V [Å^3]	1484.83(7)	6250.3
D_x [Mg m^{-3}]	1.165	1.298
Radiation type	MoK_α	MoK_α
μ [mm^{-1}]	0.07	2.19
Data collection method	ω scans	ω scans
T_{min} [°]	0.832	0.668
T_{max} [°]	0.992	0.668
No. of measured, independent, and observed reflections	18663, 3951, 3387	4885, 4885, 4703
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.041	0.000
θ_{max} [°]	29.7	25.0
Refinement on	F^2	F^2
$R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, S	0.068, 0.159, 1.12	0.041, 0.103, 1.05
No. of relections	3951 reflections	3951 reflections
No. of parameters	177	218
H-Atom treatment	riding	riding
Weighting scheme	calculated $w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 1.1529P]$ where $P = (F_o^2 + 2F_c^2)/3$	calculated $w = 1/[\sigma^2(F_o^2) + (0.0499P)^2 + 0.537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	> 0.0001	0.001
$\Delta\rho$(max; min) [e Å^{-3}]	0.30, -0.25	0.25, -0.29
Flack parameter		0.18 (6) [27]

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[1] CCDC-751586 and -751587 contain the supplementary crystallographic data for proligand hexahydro-2,2-dimethyl-7-(2,4,6-trimethylphenyl)imidazo[2,1-*b*]oxazole (HL^{SMes}) and complex bis[μ_3-(1,1-dimethylethoxy)]tris[μ_2-(1,1-dimethylethoxy)]hexatris(1,1-dimethylethoxy)tricerium (**2**). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

graphics generated by ORTEP-3. Computer programs: SMART (*Siemens*, 1993), SAINT (*Siemens*, 1995), SIR-92 (*Giacovazzo*, 1994), SHELXL-97 (*Sheldrick*, 1997), and ORTEP (*Farrugia*, 1997).

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