NJC

PAPER

View Article Online
View Journal | View Issue

Cite this: *New J. Chem.*, 2015, **39**, 7633

A structural investigation of heteroleptic lanthanide substituted cyclopentadienyl complexes†‡

Fabrizio Ortu, Jonathan M. Fowler, Matthew Burton, Alasdair Formanuik and David P. Mills*

Received (in Victoria, Australia) 26th March 2015,
Accepted 11th May 2015

DOI: 10.1039/c5nj00761e

www.rsc.org/njc

The substituted cyclopentadienyl group 1 transfer agents KCp″, KCp‴ and KCp^{tt} (Cp″ = $\{C_5H_3(SiMe_3)_2\text{-}1,3\}^-$; Cp‴ = $\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}^-$; Cp^{tt} = $\{C_5H_3({}^tBu)_2\text{-}1,3\}^-$) were prepared by modification of established procedures and the structure of $[K(Cp'')(THF)]_\infty\cdot THF$ (**1**) was obtained. KCp″ and KCp^{tt} were reacted variously with $[Ln(I)_3(THF)_4]$ (Ln = La, Ce) in 2 : 1 stoichiometries to afford monomeric $[La(Cp'')_2(I)(THF)]$ (**2a·THF**) and the dimeric complexes $[La(Cp'')_2(\mu\text{-}I)]_2$ (**2a**), $[Ce(Cp'')_2(\mu\text{-}I)]_2$ (**2b**) and $[Ce(Cp^{tt})_2(\mu\text{-}I)]_2$ (**3**). KCp‴ was reacted with $[Ce(I)_3(THF)_4]$ to afford the mono-ring complex $[Ce(Cp''')(I)_2(THF)_2]$ (**4**), regardless of the stoichiometric ratio of the reagents. Complex **4** was reacted with $[KN(SiMe_3)_2]$ to yield $[Ce(Cp''')_2(I)(THF)]$ (**5**), $[Ce(Cp''')\{N(SiMe_3)_2\}_2]$ (**6**) and $[Ce\{N(SiMe_3)_2\}_3]$ by ligand scrambling. Complexes **1–6** have all been structurally authenticated and are variously characterised by other physical methods.

Introduction

Since the first reported synthesis of lanthanide (Ln) cyclopentadienyl (Cp) complexes in the 1950s,[1] substituted Cp ligands, Cp^R, in which up to five ring protons have been replaced by various R-groups, have been employed ubiquitously in f-element organometallic chemistry.[2] Cp^R ligands typically occupy three coordination sites and their steric demands are readily tunable. Bulky R-groups may be used to block undesired ligand scrambling and oligomerisation decomposition pathways. This, together with the electronically stabilising multihapto-donor properties of Cp^R ligands, has been exploited in the stabilisation of Ln Cp^R complexes that exhibit unusual Ln oxidation states and bonding modes.[3] Cp^R ligands have been shown to be particularly effective in stabilising heterobimetallic systems that contain Ln–transition metal (TM) bonds, in which the two fragments are supported by the metal–metal interaction.[4,5] There are currently very few examples of structurally characterised Ln–TM bonds,[6] and given that recent landmark metal–metal bonds have provided step changes in our understanding of chemical bonding[7] it would be considered prudent to explore novel Ln–TM systems.

A well-established synthetic route for the synthesis of heterobimetallic Ln–TM complexes is alkane elimination.[4c] However, alkali metal salt elimination pathways provide a useful synthetic alternative that can be less sluggish and produce fewer byproducts over alkane elimination in some cases.[4b,5b] It follows that novel heteroleptic $[Ln(Cp^R)_2(X)]$ (X = halide) complexes that offer significant kinetic stabilisation and are robust with respect to ligand exchange could be useful precursors for supporting novel Ln-element bonding motifs in the future. For the larger lanthanides (La, Ce, Pr, Nd) there is a surprising lack of reports on structurally authenticated $[Ln(Cp^R)_2(X)]$ complexes,[4b,8] and there are very few examples that contain bromide or iodide.[9] The employment of the heavier halides is particularly advantageous in salt elimination reactions, where they are less prone to ate complex formation and can offer facile reaction work-ups due to the insolubility of salts such as KI in most organic solvents.[5a,b]

To target the synthesis of novel $[Ln(Cp^R)_2(I)]$ complexes of the larger Ln, we focused our attention on a family of established Cp^R ligands: 1,3-bis(trimethylsilyl)cyclopentadienyl (Cp″, $\{C_5H_3(SiMe_3)_2\text{-}1,3\}^-$), 1,2,4-tris(trimethylsilyl)cyclopentadienyl (Cp‴, $\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}^-$) and 1,3-bis(*tert*-butyl)cyclopentadienyl (Cp^{tt}, $\{C_5H_3({}^tBu)_2\text{-}1,3\}^-$). These ligands have been previously utilised to prepare a variety of homoleptic and heteroleptic La and Ce complexes.[3d,8b–d,10] Herein we report the reactions of the group 1 ligand transfer agents KCp″, KCp‴ and KCp^{tt} in salt metathesis reactions with selected Ln triiodides, leading to the stabilisation and structural authentication of novel monomeric and dimeric $[Ln(Cp^R)_2(I)]$ (Ln = La, Ce) complexes that are robust towards ligand exchange side-reactions over typical experimental timescales.

School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. E-mail: david.mills@manchester.ac.uk

† This article is part of the '*Frontiers of Organo-f-element Chemistry*' themed issue.

‡ Electronic supplementary information (ESI) available. CCDC 1056158–1056165 for **1**, **2a–b**, **2a·THF** and **3–6**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5nj00761e

Results and discussion

KCp″,[11] KCp‴[11] and KCp^{tt}[12] (Cp″ = $\{C_5H_3(SiMe_3)_2\text{-}1,3\}^-$; Cp‴ = $\{C_5H_2(SiMe_3)_3\text{-}1,2,4\}^-$; Cp^{tt} = $\{C_5H_3(^tBu)_2\text{-}1,3\}^-$) were prepared by slight modifications of published procedures by deprotonation of the pro-ligands with KH or $[KN(SiMe_3)_2]$. On one occasion, crystals of $[K(Cp'')(THF)]_\infty\cdot THF$ (**1**) were obtained, and these were subjected to a single crystal XRD study. The crystals were of poor quality and weakly diffracting, leading to a poor quality dataset. As a result no discussion is given of the metrical parameters although the connectivity is clear-cut (see ESI‡). KCp″ and KCp^{tt} were reacted separately in 2 : 1 stoichiometric ratios with $[La(I)_3(THF)_4]$ and $[Ce(I)_3(THF)_4]$ to afford $[La(Cp'')_2(\mu\text{-}I)]_2$ (**2a**), $[Ce(Cp'')_2(\mu\text{-}I)]_2$ (**2b**) and $[Ce(Cp^{tt})_2(\mu\text{-}I)]_2$ (**3**) (Scheme 1). The synthesis of $[La(Cp^{tt})_2(\mu\text{-}I)]_2$ was not attempted. Complexes **2a** and **2b** were obtained in fair crystalline yields but the yield of **3** was significantly lower. It is noteworthy that the syntheses of **2b** and **3** from CeI_3 were discussed previously by Andersen, although no characterisation data were reported.[10h]

The ^1H NMR spectra of **2a** and **2b** in d_6-benzene exhibit resonances for the $SiMe_3$ protons (**2a**: δ = 0.49 ppm; **2b**: δ = −3.23 and 0.29 ppm) and three signals for the Cp″ ring protons (**2a**: δ = 7.16, 7.22 and 7.27 ppm; **2b**: δ = −7.30, −6.88 and −0.04 ppm). The reason for the difference in the number of $SiMe_3$ group resonances in solution for **2a** and **2b** is unknown as they have similar solid state structures (see below). A single resonance was observed in the $^{29}Si\{^1H\}$ NMR spectrum of **2a** (δ = −9.69 ppm), but no resonance was observed in the $^{29}Si\{^1H\}$ NMR spectrum of **2b** due to paramagnetic broadening. The ^1H NMR spectrum of **3** displays one broad signal for the *tert*-butyl protons (δ = −1.71 ppm) and three resonances (δ = −5.86 ppm, 0.29 and 1.13 ppm) for the Cp^{tt} ring protons. Elemental analyses of all three complexes are in good agreement with donor solvent-free $[Ln(Cp^R)_2(\mu\text{-}I)]_2$ formulations.

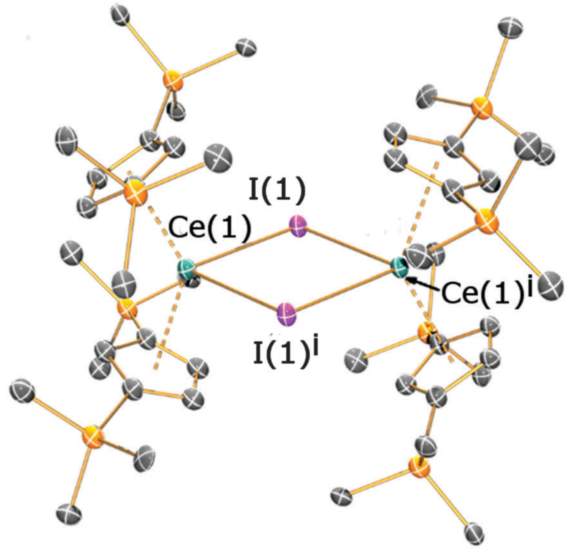


Fig. 1 Molecular structure of **2b** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Symmetry operation to generate equivalent atoms: i = 2 − x, −y, −z. Selected bond distances [Å] and angles [°] for **2b**: Ce(1)–I(1) 3.1943(6), Ce(1)–I(1i) 3.1973(6), Ce(1)···Cp$_{centroid}$(1) 2.511(3), Ce(1)···Cp$_{centroid}$(2) 2.499(3), Ce(1)···Ce(1i) 4.7342(9), I(1)–Ce(1)–I(1i) 84.422(15), Ce(1)–I(1)–Ce(1i) 95.578(15).

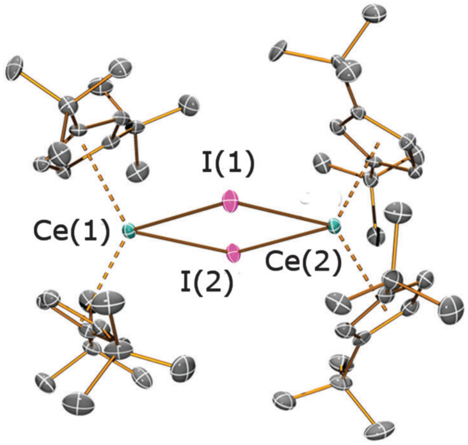
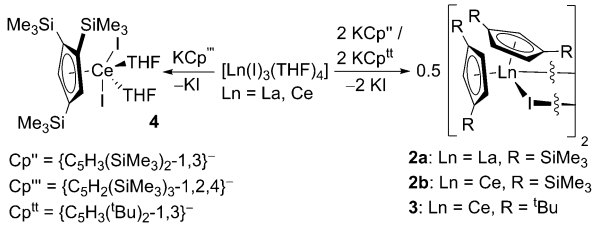


Fig. 2 Molecular structure of **3** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] for **3**: Ce(1)–I(1) 3.2238(5), Ce(1)–I(2) 3.2410(4), Ce(2)–I(1) 3.2157(4), Ce(2)–I(2) 3.2286(5), Ce(1)···Cp$_{centroid}$(1) 2.510(2), Ce(1)···Cp$_{centroid}$(2) 2.516(2), Ce(1)···Ce(2) 5.0121(4), I(1)–Ce(1)–I(2) 77.963(11), I(1)–Ce(2)–I(2) 78.259(11), Ce(1)–I(1)–Ce(2) 102.218(12), Ce(1)–I(2)–Ce(2) 101.560(12).

Crystals suitable for X-ray diffraction studies were obtained for **2a**, **2b** and **3**, and their solid state structures were determined (Fig. 1 and 2; see ESI‡). Complexes **2a** and **2b** are structurally analogous, featuring the same open metallocene-type array, so only the structure of **2b** is depicted here (for a picture of **2a** see ESI‡). The two compounds display very similar metrical parameters, such as the Ln···Cp$_{centroid}$ [**2a**: La···Cp$_{centroid}$ = 2.519(7) Å mean; **2b**: Ce···Cp$_{centroid}$ = 2.505(3) Å mean] and Ln–I distances [**2a**: La–I = 3.2128(16) Å mean; **2b**: Ce–I = 3.1958(6) Å mean]. These values may be compared to $[La(Cp'')_2(\mu\text{-}F)]_2$,[8c] the only other structurally authenticated heteroleptic Cp″ La or Ce halide-bridged dimer, to the best of our knowledge. In $[La(Cp'')_2(\mu\text{-}F)]_2$ the La···Cp$_{centroid}$ distances [2.548(9) and 2.561(8) Å] are longer than the corresponding distances in **2a** and **2b**; also the Cp$_{centroid}$–Ln–Cp$_{centroid}$ angle in $[La(Cp'')_2(\mu\text{-}F)]_2$ [129.42(19)°] is smaller than the analogous angles in **2a** [132.8(3)°] and **2b** [132.19(10)°]. Such variations are consistent with previous observations on the flexibility of coordinated Cp^R ligands in Ln chemistry, as they are capable of interlocking with each other in various conformations in order to best accommodate the



Scheme 1 Synthesis of complexes **2–4**.

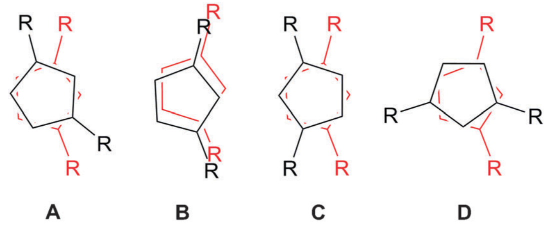


Fig. 3 Different conformations of La and Ce open metallocenes supported by 1,3-di-substituted Cp^R ligands.[8d,10i]

space required by co-ligands. This behaviour was reported for a series of heteroleptic Cp^{tt} cerium complexes, which exhibited three different Cp^{tt} ring orientations in the solid state (Fig. 3A–C).[8d,10i] Complexes **2a** and **2b** adopt orientation C in the solid state and the presence of two $SiMe_3$ resonances in the ^1H NMR spectra of **2a** and **2b** (see above) indicates that a low-symmetry orientation is maintained in solution.

On one occasion in an attempted synthesis of **2a** we were able to determine the molecular structure of the monomeric THF adduct $[La(Cp'')_2(I)(THF)]$, **2a·THF** (Fig. 4; see ESI‡), which resulted from incomplete removal of THF *in vacuo* prior to recrystallization from toluene. Complex **2a·THF** displays similar $La\cdots Cp_{centroid}$ distances to its dimeric counterpart $[La(1)\cdots Cp_{centroid}$ = 2.539(4) Å mean], however the $Cp_{centroid}$–La–$Cp_{centroid}$ angle in **2a·THF** [127.97(12)°] is smaller. This is due to the absence of a relatively rigid La_2I_2 rhomboid in **2a·THF**, which enables the two Cp'' rings to interlock in a staggered conformation (Fig. 3D). To the best of our knowledge, this has not previously been observed for heteroleptic Cp'' and Cp^{tt} lanthanum and cerium complexes, but it has been reported in Cp'' and Cp^{tt} U(IV) chemistry.[13]

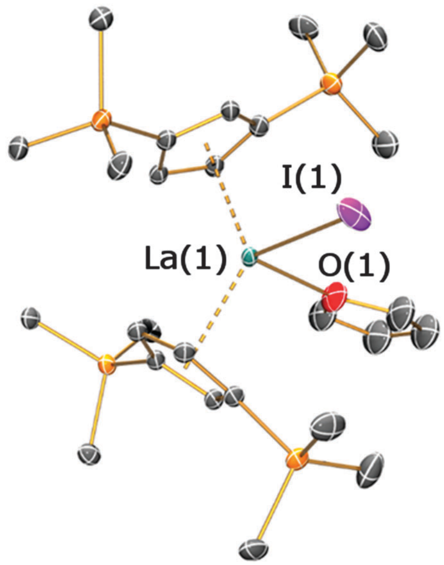


Fig. 4 Molecular structure of **2a·THF** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms and disorder components have been omitted for clarity. Selected bond distances [Å] and angles [°] for **2a·THF**: La(1)–I(1) 3.094(16), La(1)–O(1) 2.51(3), $La(1)\cdots Cp_{centroid}(1)$ 2.538(4), $La(1)\cdots Cp_{centroid}(2)$ 2.539(4), I(1)–La(1)–O(1) 93.0(7), $Cp_{centroid}(1)$–La(1)–$Cp_{centroid}(2)$ 127.97(12).

In the solid state **3** exhibits a dimeric structure, with $Ce\cdots Cp_{centroid}$ distances ranging between 2.510(2) and 2.528(2) Å. These distances are comparable to those observed for $[Ce(Cp^{tt})_2(\mu\text{-}Cl)]_2$ [2.523(10) Å mean] and $[Ce(Cp^{tt})_2(\mu\text{-}H)]_2$ [2.538(4) Å mean][8d,10i] but are longer than those observed in $[Ce(Cp^{t})_2(\mu\text{-}I)]_2$ [range $Ce\cdots Cp_{centroid}$ 2.492(5)–2.510(4) Å].[9a] Furthermore, the $Cp_{centroid}$–Ce–$Cp_{centroid}$ angles in **3** are relatively small [124.49(7)° and 125.29(7)°], bringing the Cp^{tt} rings closer to each other than the Cp'' rings in **2a** and **2b**. These angles are even smaller than those observed in **2a·THF**, in which a staggered conformation of the Cp^{tt} rings was observed in the solid state, yet **3** exhibits a pseudo-eclipsed configuration of the Cp^{tt} rings (Fig. 3B). It is noteworthy that the ^1H NMR spectrum of **3** exhibits only one signal for the *tert*-butyl protons (see above), indicating that this high symmetry environment is maintained in solution. In $[Ce(Cp^{tt})_2(\mu\text{-}Cl)]_2$ the two Cp^{tt} rings deviate even further from the ideal parallel sandwich configuration [$Cp_{centroid}$–Ce–$Cp_{centroid}$ = 121.0(2)°],[8d] highlighting the potentially large effect of crystal packing interactions on these configurations.[14]

An increase in the number of sterically demanding R-groups around a Cp^R ring can have significant effects on its coordination to metal centres. It has previously been shown that salt metathesis reactions between group 1 salts of the more sterically encumbered Cp''' ligand with LaI_3 afford the mono-ring complex $[La(Cp''')(I)_2(py)_3]$ as the main product,[15] with the bis-Cp''' derivative $[La(Cp''')_2(I)(py)]$ isolated in poor yields.[8b] Germane to this, the mono-ring complex $[Ce(C_5Me_5)(I)_2(THF)_3]$ was synthesised from $[CeI_3(THF)_x]$ and KC_5Me_5, whilst $[Li(Et_2O)_2][Ce(C_5Me_5)_2(Cl)_2]$ was isolated when $CeCl_3$ and LiC_5Me_5 were employed as starting materials.[16] Similarly, the reaction of KCp''' with $[Ce(I)_3(THF)_4]$ yielded $[Ce(Cp''')(I)_2(THF)_2]$ (**4**), regardless of the stoichiometric ratio employed. The ^1H NMR spectrum of **4** exhibits two $SiMe_3$ proton resonances (δ = −3.74 and 0.27 ppm) and two signals are observed for the Cp''' ring protons (δ = −0.03 and 0.76 ppm). The elemental analysis of **4** was consistent with its formulation.

The solid state structure of **4** is depicted in Fig. 5 (see ESI‡). Complex **4** exhibits a four-legged piano stool coordination motif, with the two iodides and THF molecules mutually *trans*-with respect to each other [I(1)–Ce(1)–I(2) = 125.53(2)°; O(1)–Ce(1)–O(2) = 149.48(18)°]. The Cp''' ring is closer to the cerium centre $[Ce(1)\cdots Cp_{centroid}$ = 2.495(4) Å] than the Cp^R rings in **2b** and **3** and this parameter is shorter than the corresponding distance in $[La(Cp''')(I)_2(py)_3]$ $(La\cdots Cp_{centroid}$ = 2.557 Å).[15] As a mono-ring complex typically has reduced steric crowding around the metal centre compared with the corresponding open metallocene, the Ce–I bond lengths of **4** [3.0859(7) and 3.1209(6) Å] are shorter than those observed in **2b** and **3**. These distances are also shorter than those exhibited by $[Ce(C_5Me_5)(I)_2(THF)_3]$ [3.2269(12) and 3.1733(12) Å], although this complex contains an additional molecule of THF.[16]

In an attempt to prepare a heteroleptic Cp'''-silylamide cerium complex, "$[Ce(Cp''')(I)\{N(SiMe_3)_2\}]$", complex **4** was reacted with one equivalent of $[KN(SiMe_3)_2]$ (Scheme 2). An orange crystalline product was obtained from the reaction mixture, allowing the structural identification of $[Ce(Cp''')_2(I)(THF)]$ (**5**), which has formed by ligand scrambling (Fig. 6; see ESI‡). Complex **5** is

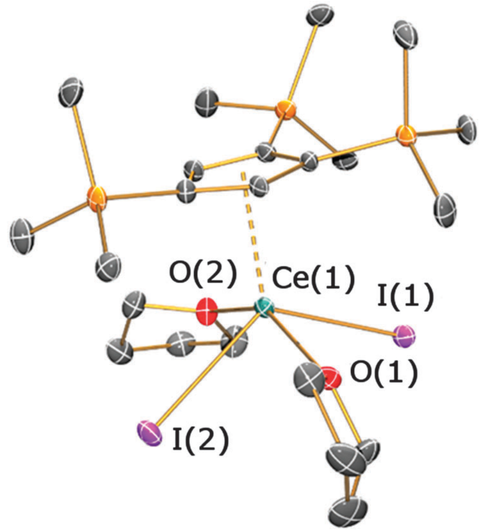


Fig. 5 Molecular structure of **4** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] for **4**: Ce(1)–I(1) 3.0859(7), Ce(1)–I(2) 3.1209(6), Ce(1)–O(1) 2.495(5), Ce(1)–O(2) 2.505(5), Ce(1)···$\mathrm{Cp_{centroid}}$(1) 2.495(4), I(1)–Ce(1)–I(2) 125.53(2), O(1)–Ce(1)–O(2) 149.48(18), I(1)–Ce(1)–O(1) 81.88(13), I(1)–Ce(1)–O(2) 89.39(13).

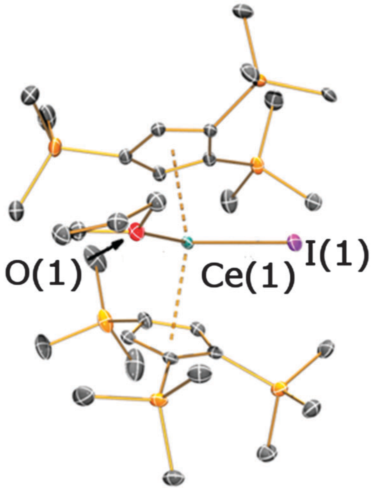


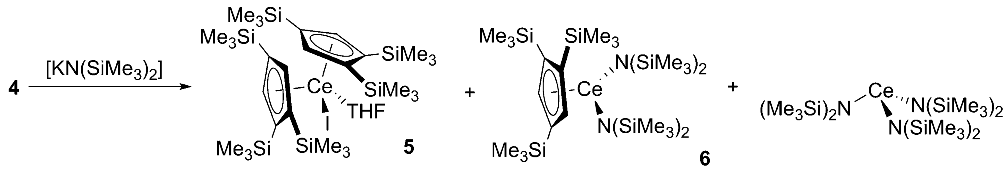
Fig. 6 Molecular structure of **5** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] for **5**: Ce(1)–I(1) 3.1000(4), Ce(1)–O(1) 2.490(3), Ce(1)···$\mathrm{Cp_{centroid}}$(1) 2.5416(16), Ce(1)···$\mathrm{Cp_{centroid}}$(2) 2.5259(19), I(1)–Ce(1)–O(1) 89.01(7), $\mathrm{Cp_{centroid}}$(1)–Ce(1)–$\mathrm{Cp_{centroid}}$(2) 133.77(6).

monomeric in the solid state, analogous to the related La Cp′′′ complex [La(Cp′′′)$_2$(I)(py)].[8b] The Ce–O distance in **5** [Ce(1)–O(1) = 2.490(3) Å] is consistent with those measured for **4** (see above) and the Ce···$\mathrm{Cp_{centroid}}$ distances of **5** [2.534(2) Å mean] are longer than those in the mono-ring complex **4**, as would be expected from the increased steric demands of two Cp′′′ ligands in **5**. The $\mathrm{Cp_{centroid}}$–Ce–$\mathrm{Cp_{centroid}}$ angle in **5** [133.77(6)°] is comparable to the $\mathrm{Cp_{centroid}}$–La–$\mathrm{Cp_{centroid}}$ angle observed for [La(Cp′′′)$_2$(I)(py)] [134.50(7)°],[8b] though it is noteworthy that [Ce(Cp^R)$_2$(X)]$_n$ (X = anionic ligand) complexes with larger $\mathrm{Cp_{centroid}}$–Ce–$\mathrm{Cp_{centroid}}$ angles have been previously reported in the literature.[8a,9b,c]

Further evidence of the steric repulsion in **5** is given by the SiMe$_3$ substituents, which are pushed away from the cerium centre in comparison to **4** [range of $\mathrm{Cp_{centroid}}$–C–Si angles, **5**: 157.4(3)–169.4(4)°; **4**: 168.1(6)–168.9(5)°] and are similar to the corresponding angles observed for [La(Cp′′′)$_2$(I)(py)] [156.5(4)–167.4(4)°].[8b] Complex **5** was further characterised by ^{1}H NMR spectroscopy, giving a simple spectrum with two resonances for the SiMe$_3$ protons (δ = 0.30 and 0.90 ppm) and two signals for the Cp′′′ protons (δ = −5.75 and −5.34 ppm). The elemental analysis of **5** was in good agreement with the proposed formulation.

In order to better understand the ligand scrambling process which led to the formation of **5**, several crystals obtained from the third crop of **5** were screened by single crystal XRD. Two additional crystal types were observed: orange needles and dark orange blocks. The needles were identified as [Ce{N(SiMe$_3$)$_2$}$_3$] and the blocks were found to be the heteroleptic complex [Ce(Cp′′′){N(SiMe$_3$)$_2$}$_2$] (**6**) (Fig. 7; see ESI‡). The structure of **6** is based on a two-legged piano stool motif and is comparable to [Ce(C$_5$Me$_5$){N(SiMe$_3$)$_2$}$_2$],[17] which exhibits similar Ce–N distances [2.353(7) Å mean] to **6** [2.353(8) Å mean]. The Ce···$\mathrm{Cp_{centroid}}$ distance in **6** [2.551(5) Å] is comparable to that observed for **4** and all other metrical parameters of **6** are unremarkable. It was not possible to fractionally crystallise analytically pure **6** under the conditions employed due to the similar solubility of [Ce{N(SiMe$_3$)$_2$}$_3$] in hexanes/toluene, therefore no further analytical data were obtained. The global yield of **5** from this reaction was 50%, however, reaction conditions were not optimised as such ligand scrambling mechanisms can be difficult to control. It has been reported that mono-ring C$_5$Me$_5$ cerium complexes can undergo ligand scrambling in solution (Scheme 3),[17] and if similar processes are occurring during the synthesis of **5** this would affect the yields of all the products.

The Evans method was employed to determine the room temperature solution magnetic moments of all isolated cerium complexes.[18] The values obtained for **2b** (μ_{eff} = 2.79 μ_{B}), **3** (2.23 μ_{B}), **4** (2.41 μ_{B}) and **5** (2.22 μ_{B}) are in good agreement with the



Scheme 2 Synthesis of **5**–**6**.

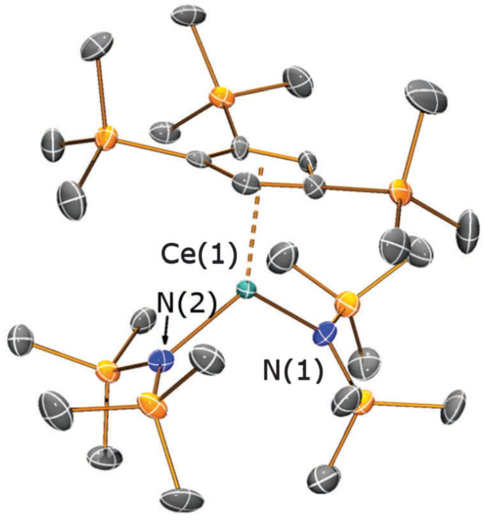


Fig. 7 Molecular structure of **6** with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] for **6**: Ce(1)–N(1) 2.355(8), Ce(1)–N(2) 2.350(7), Ce(1)···Cp$_{centroid}$(1) 2.551(5), N(1)–Ce(1)–N(2) 119.0(3).

predicted magnetic moment for a Ce(III) $4f^1$ $^2F_{5/2}$ ground state (2.54 μ_B)[19] and previously reported magnetic moments of Ce(III) complexes in the literature (range 1.88–2.75 μ_B).[20]

Conclusions

We have reported the synthesis and structural characterisation of a novel series of heteroleptic substituted Cp Ln complexes using salt metathesis methodologies. These include bis-substituted Cp^R Ln dimeric complexes with bridging iodides (**2**–**3**) and for the bulky Cp′′′ ligand we were able to isolate a mono-ring Ce complex **4**, as disubstitution was not possible for this ligand under the conditions employed. The monomeric Ce complex **5** was prepared by the reaction of **4** with [KN(SiMe$_3$)$_2$], triggering a ligand scrambling process which gave **5** in fair yield together with the mixed substituted Cp′′′ silylamide Ce complex **6** and [Ce{N(SiMe$_3$)$_2$}$_3$]. Although the yield of **5** is only moderate, it is considerable when compared to the previously reported low-yielding synthesis of the closely related La complex, [La(Cp′′′)$_2$(I)(py)].[8b] Solid state characterisation of **2**–**6** provides in-depth knowledge of the structural features of these systems and this will help us to predict their reactivity profile. In our hands, complexes **2a**–**b** and **5** have not shown any tendency to ligand scramble in both coordinating and non-coordinating solvents over experimental timescales. As such, we envisage that they will be useful precursors for the preparation and stabilisation of novel La/Ce-element bonding motifs, including the preparation of heterobimetallic species, by salt metathesis methodologies.

$$2\,[\mathrm{Ce(Cp^R)(X)_2}] \rightleftharpoons [\mathrm{Ce(Cp^R)_2(X)}] + \mathrm{CeX_3}$$

$$\mathrm{Cp^R} = \text{substituted Cp; X = Halide}$$

Scheme 3 Ligand scrambling of heteroleptic mono-ring Ce complexes.[17]

Experimental

Materials and methods

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and were degassed before use. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles, and stored under argon. KCp′′,[11] KCp′′′,[11] KCp^{tt},[12] [Ln(I)$_3$(THF)$_4$] (Ln = La, Ce)[21] and [KN(SiMe$_3$)$_2$][22] were prepared according to published procedures. KH was obtained as a suspension in mineral oil and was washed three times with hexane and dried *in vacuo*. ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra were recorded on a spectrometer operating at 400.2, 100.6 and 79.5 MHz respectively; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded as Nujol mulls in KBr discs on a PerkinElmer Spectrum RX1 spectrometer. Elemental microanalyses were carried out by Stephen Boyer at the Microanalysis Service, London Metropolitan University, UK.

Synthetic procedures

[La(Cp′′)$_2$(μ-I)]$_2$ (2a). A Schlenk flask was charged with KCp′′ (1.74 g, 7 mmol) and [La(I)$_3$(THF)$_4$] (2.83 g, 3.5 mmol). The flask was cooled to −78 °C and THF (15 ml) was added dropwise with stirring. The yellow reaction mixture was allowed to warm slowly and stirred for 72 h, during which time a suspension formed. The mixture was allowed to settle for 2 hours and the suspension was filtered. The solvent was removed *in vacuo* (10^{-2} mbar) and the solid residue extracted with toluene (10 ml). The solution was concentrated to approximately 3 ml and stored at −30 °C to afford **2a** as colourless crystals (1.16 g, 48%). On one occasion crystals of **2a·THF** were found. Anal. calcd (%) for $C_{44}H_{84}La_2I_2Si_8$: C, 38.59; H, 6.18. Found: C, 38.47; H, 6.28. ^{1}H NMR (d_6-benzene, 298 K): δ = 0.49 (s, 72H, Si(C*H*$_3$)$_3$), 7.16 (m, 4H, Cp′′-C*H*), 7.22 (m, 4H, Cp′′-C*H*), 7.27 (m, 4H, Cp′′-C*H*). ^{13}C{^{1}H} NMR (d_6-benzene, 298 K): δ = 1.51 (Si(*C*H$_3$)$_3$), 123.32 (Cp′′-*C*), 126.27 (Cp′′-*C*H), 132.28 (Cp′′-*C*H). ^{29}Si{^{1}H} NMR (d_6-benzene, 298 K): δ = −9.69 (s, Si(CH$_3$)$_3$). FTIR (Nujol, cm^{-1}): ν = 1318 (m), 1249 (br s), 1077 (s), 919 (s), 833 (br s), 752 (s), 690 (m).

[Ce(Cp′′)$_2$(μ-I)]$_2$ (2b). A Schlenk flask was charged with KCp′′ (4.97 g, 20 mmol) and [Ce(I)$_3$(THF)$_4$] (8.01 g, 10 mmol). The flask was cooled to −30 °C and THF (20 ml) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and then stirred for a further 16 hours. The mixture was allowed to settle for 2 hours and the suspension was filtered, giving a clear yellow solution. Volatiles were removed *in vacuo* (10^{-2} mbar), affording a bright pink solid. Recrystallisation from toluene (30 ml) afforded **2b** as a crystalline product (2.85 g, 42%). ^{1}H NMR (d_6-benzene, 298 K): δ = −7.30 (s, 4H, Cp′′-C*H*), −6.88, (s, 4H, Cp′′-C*H*), −3.23 (s, 36H, Si(C*H*$_3$)$_3$), −0.04 (s, 4H, Cp′′-C*H*), 0.29 (s, 36H, Si(C*H*$_3$)$_3$). Anal calcd (%) for $C_{44}H_{84}Ce_2I_2Si_8$: C, 38.39; H, 6.23. Found (%): C, 38.52; H, 6.18. μ_{eff} (Evans method, 298 K, d_6-benzene): 2.79 μ_B. FTIR (Nujol, cm^{-1}): ν = 1260 (s), 1078 (br s), 919 (m), 836 (br m), 800 (br m).

[Ce(Cp^{tt})$_2$(μ-I)]$_2$ (3). A Schlenk flask was charged with KCp^{tt} (0.82 g, 4 mmol) and [Ce(I)$_3$(THF)$_4$] (1.62 g, 2 mmol). The flask was cooled to −78 °C and THF (15 ml) was added dropwise with stirring. The yellow reaction mixture was allowed to slowly warm to room temperature and then stirred for a further 16 hours. The mixture was allowed to settle for 2 hours and the suspension was filtered. Volatiles were removed *in vacuo* (10^{-2} mbar), affording a bright orange solid. The solid residue was extracted with toluene (8 ml) and stored at room temperature, affording **3** as an orange crystalline product (0.30 g, 24%). ^{1}H NMR (d_6-benzene, 298 K): $\delta = -5.86$ (br m, 6H, Cp^{tt}-C*H*), −1.71, (br s, 72H, C(CH_3)$_3$), 0.29 (s, 2H, Cp^{tt}-C*H*), 1.13 (s, 4H, Cp^{tt}-C*H*). Anal calcd (%) for $C_{52}H_{84}Ce_2I_2$: C, 50.24; H, 6.81. Found (%): C, 49.88; H, 6.68. μ_{eff} (Evans method, 298 K, d_6-benzene): 2.23 μ_B. FTIR (Nujol, cm^{-1}): $\nu = 1250$ (m), 1201 (w), 1165 (m), 1089 (w), 1054 (br m), 1021 (m), 819 (s), 810 (s), 767 (m).

[Ce(Cp$'''$)(I)$_2$(THF)$_2$] (4). A THF (20 ml) solution of KCp$'''$ (1.60 g, 5 mmol) was added dropwise to a THF (15 ml) slurry of [Ce(I)$_3$(THF)$_4$] (4.05 g, 5 mmol) at −4 °C with stirring. A colour change to yellow with a white precipitate was observed, and the mixture was slowly warmed to room temperature and stirred for 72 hours. Volatiles were removed *in vacuo*, yielding a bright yellow powder. The solid was extracted with hexane (20 ml) and volatiles were removed *in vacuo* (10^{-2} mbar), affording **4** as a yellow powder (2.39 g, 58%). A small crop of crystals were grown from hexanes (2 ml) at −25 °C. ^{1}H NMR (d_6-benzene, 298 K): $\delta = -3.74$ (s, 18H, Si(CH_3)$_3$), −0.03 (s, 1H, Cp$'''$-C*H*), 0.27 (s, 1H, Cp$'''$-C*H*), 0.76 (s, 9H, Si(CH_3)$_3$), 2.25 (br m, 16H, THF). Anal calcd (%) for $C_{22}H_{45}CeI_2O_2Si_3$: C, 32.23; H, 5.53. Found (%): C, 32.08; H, 5.61. μ_{eff} (Evans method, 298 K, d_6-benzene): 2.41 μ_B. FTIR (Nujol, cm^{-1}): $\nu = 1260$ (m), 1249 (m), 1092 (br m), 1019 (br m), 934 (w), 837 (br s), 723 (w).

[Ce(Cp$'''$)$_2$(I)(THF)] (5) and [Ce(Cp$'''$){N(SiMe$_3$)$_2$}$_2$] (6). A toluene (20 ml) solution of [KN(SiMe$_3$)$_2$] (1.00 g, 5 mmol) was added dropwise to a toluene (20 ml) solution of **4** (4.10 g, 5 mmol) at −20 °C with stirring. The reaction mixture was warmed to room temperature and stirred for 16 hours, forming a dark orange mixture with a white precipitate. The suspension was filtered, the solution concentrated to 5 ml and cooled to 4 °C, yielding orange crystals of **5**. More crops of **5** were obtained from the supernatant liquid of the first crystallisation (2.36 g, 50%). From the third recrystallization several crystals with different morphologies were observed. These were identified as [Ce(N{SiMe$_3$}$_2$)$_3$] (orange needles) and **6** (orange blocks) *via* single crystal X-ray studies. Data for **5**: ^{1}H NMR (d_6-benzene, 298 K) $\delta = -5.75$ (s, 2H, Cp$'''$-C*H*), −5.34 (br s, 2H, Cp$'''$-C*H*), 0.30 (s, 36H, Si(CH_3)$_3$), 0.90 (s, 18H, Si(CH_3)$_3$). μ_{eff} (Evans method, 298 K, d_6-benzene): 2.22 μ_B. Anal calcd (%) for $C_{28}H_{58}CeISi_6$: C, 42.64; H, 7.27. Found: C, 42.72; H, 7.38 (%). FTIR (Nujol, cm^{-1}): $\nu = 1249$ (s), 1090 (s), 986 (s), 935 (m), 837 (br s), 753 (m).

Acknowledgements

We thank the EPSRC and The University of Manchester for generously supporting this work. This work was funded by the Engineering and Physical Sciences Research Council (grant numbers EP/K039547/1 and EP/L014416/1).

Notes and references

1 G. Wilkinson and J. M. Birmingham, *J. Am. Chem. Soc.*, 1954, **76**, 6210.

2 (*a*) S. Arndt and J. Okuda, *Chem. Rev.*, 2002, **102**, 1953; (*b*) F. T. Edelmann and V. Lorenz, *Coord. Chem. Rev.*, 2000, **209**, 99.

3 (*a*) M. R. MacDonald, J. E. Bates, J. W. Ziller, F. Furche and W. J. Evans, *J. Am. Chem. Soc.*, 2013, **135**, 9857; (*b*) W. J. Evans, *J. Alloys Compd.*, 2009, **488**, 493; (*c*) W. J. Evans, *Inorg. Chem.*, 2007, **46**, 3435; (*d*) M. C. Cassani, D. J. Duncalf and M. F. Lappert, *J. Am. Chem. Soc.*, 1998, **120**, 12958; (*e*) W. J. Evans, S. L. Gonzales and J. W. Ziller, *J. Am. Chem. Soc.*, 1991, **113**, 7423.

4 (*a*) M. V. Butovskii, B. Oelkers, T. Bauer, J. M. Bakker, V. Bezugly, F. R. Wagner and R. Kempe, *Chem. – Eur. J.*, 2014, **20**, 2804; (*b*) M. V. Butovskii, C. Döring, V. Bezugly, F. R. Wagner, Y. Grin and R. Kempe, *Nat. Chem.*, 2010, **2**, 741; (*c*) M. V. Butovskii, O. L. Tok, F. R. Wagner and R. Kempe, *Angew. Chem., Int. Ed.*, 2008, **47**, 6469; (*d*) I. P. Beletskaya, A. Z. Voskoboynikov, E. B. Chuklanova, N. I. Kirillova, A. K. Shestakova, I. N. Parshina, A. I. Gusev and G. K. I. Magomedov, *J. Am. Chem. Soc.*, 1993, **115**, 3156.

5 For other ligand systems see: (*a*) M. P. Blake, N. Kaltsoyannis and P. Mountford, *Chem. Commun.*, 2013, **49**, 3315; (*b*) P. L. Arnold, J. Mc Master and S. T. Liddle, *Chem. Commun.*, 2009, 818; (*c*) S. T. Liddle, *Proc. R. Soc. A*, 2009, **465**, 1673.

6 (*a*) D. Patel and S. T. Liddle, *Rev. Inorg. Chem.*, 2012, **32**, 1; (*b*) S. T. Liddle and D. P. Mills, *Dalton Trans.*, 2009, 5592.

7 See, for example: (*a*) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 844; (*b*) T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science*, 2005, **310**, 1754; (*c*) I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136.

8 (*a*) L. Maron, E. L. Werkema, L. Perrin, O. Esienstein and R. A. Andersen, *J. Am. Chem. Soc.*, 2005, **127**, 2792; (*b*) G. R. Giesbrecht, G. E. Collis, J. C. Gordon, D. L. Clark, B. L. Scott and N. J. Hardman, *J. Organomet. Chem.*, 2004, **689**, 2177; (*c*) Z. Xie, K. Chui, Q. Yang, T. C. W. Mak and J. Sun, *Organometallics*, 1998, **17**, 3937; (*d*) E. B. Lobkovsky, Yu. K. Gun'ko, B. M. Bulychev, V. K. Belsky, G. L. Soloveichik and M. Yu. Antipin, *J. Organomet. Chem.*, 1991, **406**, 343; (*e*) W. J. Evans, J. M. Olofson, H. Zhang and J. L. Atwood, *Organometallics*, 1988, **7**, 629.

9 (*a*) T. Mehdoui, J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Dalton Trans.*, 2005, 1263; (*b*) T. Mehdoui, J.-C. Berthet, P. Thuéry and M. Ephritikhine, *Chem. Commun.*, 2005, 2860; (*c*) P. N. Hazin, C. Lakshminarayan, L. S. Brinen, J. L. Knee, J. W. Bruno, W. E. Streib and K. Folting, *Inorg. Chem.*, 1988, **27**, 1393; (*d*) M. D. Walter, D. Bentz, F. Weber, O. Schmitt, G. Wolmershäuser and H. Sitzmann, *New J. Chem.*, 2007, **31**, 305.

10 (*a*) M. P. Coles, P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *Organometallics*, 2012, **31**, 2682;

(*b*) P. B. Hitchcock, M. F. Lappert, L. Maron and A. V. Protchenko, *Angew. Chem., Int. Ed.*, 2008, **47**, 1488; (*c*) Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *Organometallics*, 2000, **19**, 2832; (*d*) M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock, M. F. Lappert and F. Laschi, *Organometallics*, 1999, **18**, 5539; (*e*) Z. Xie, K. Chui, Z. Liu, F. Xue, Z. Zhang, T. C. W. Mak and J. Sun, *J. Organomet. Chem.*, 1997, **16**, 239; (*f*) M. C. Cassani, Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *Chem. Commun.*, 1996, 1987; (*g*) Y. K. Gun'ko, P. B. Hitchcock and M. F. Lappert, *J. Organomet. Chem.*, 1995, **499**, 213; (*h*) C. D. Sofield and R. A. Andersen, *J. Organomet. Chem.*, 1995, **501**, 271; (*i*) Y. K. Gun'ko, B. M. Bulychev, G. L. Soloveichik and V. K. Belsky, *J. Organomet. Chem.*, 1992, **424**, 289; (*j*) S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 115; (*k*) P. N. Hazin, J. W. Bruno and G. K. Schulte, *Organometallics*, 1990, **9**, 416.

11 M. J. Harvey, T. P. Hanusa and M. Pink, *J. Chem. Soc., Dalton Trans.*, 2001, 1128.

12 F. Jaroschik, F. Nief, X.-F. Le Goff and L. Ricard, *Organometallics*, 2007, **26**, 3552.

13 W. W. Lukens Jr., S. M. Beshouri, L. L. Blosch, A. L. Stuart and R. A. Andersen, *Organometallics*, 1999, **18**, 1235.

14 A. Gavezzotti, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1996, **52**, 201.

15 G. R. Giesbrecht, D. L. Clark, J. C. Gordon and B. L. Scott, *Appl. Organomet. Chem.*, 2003, **17**, 473.

16 (*a*) P. N. Hazin, J. C. Huffman and J. W. Bruno, *Organometallics*, 1987, **6**, 23; (*b*) M. D. Rausch, K. J. Moriarty, J. L. Atwood, J. A. Weeks, W. E. Hunter and H. G. Brittain, *Organometallics*, 1986, **5**, 1281.

17 H. J. Heeres, A. Meetsma, J. H. Teuben and R. D. Rogers, *Organometallics*, 1989, **8**, 2637.

18 (*a*) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (*b*) S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169; (*c*) D. H. Grant, *J. Chem. Educ.*, 1995, **72**, 39.

19 J. H. van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, UK, 1932.

20 See, for example: (*a*) A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake and S. T. Liddle, *Dalton Trans.*, 2010, **39**, 500; (*b*) G. Marshall, A. J. Wooles, D. P. Mills, W. Lewis, A. J. Blake and S. T. Liddle, *Inorganics*, 2013, **1**, 46.

21 K. Izod, S. T. Liddle and W. Clegg, *Inorg. Chem.*, 2004, **43**, 214.

22 K. F. Tesh, T. P. Hanusa and J. C. Huffman, *Inorg. Chem.*, 1990, **29**, 1584.