Los Alamos NATIONAL LABORATORY EST.1943

LA-UR-15-29339 (Accepted Manuscript)

Synthesis and Characterization of Cerium(IV) Metallocenes

Sutton, Andrew
Gordon, John Cameron
Clark, David Lewis
Scott, Brian Lindley

Provided by the author(s) and the Los Alamos National Laboratory (2016-12-16).

To be published in: Inorganics

DOI to publisher's version: 10.3390/inorganics3040589

Permalink to record: http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-15-29339

Disclaimer:
Approved for public release. Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the Los Alamos National Security, LLC for the National Nuclear Security Administration of the U.S. Department of Energy under contract DE-AC52-06NA25396. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

RESEARCH LIBRARY

Inorganics **2015**, *3*, 589-596; doi:10.3390/inorganics3040589

OPEN ACCESS

inorganics

ISSN 2304-6740

www.mdpi.com/journal/inorganics

Communication

Synthesis and Characterization of Cerium(IV) Metallocenes

Andrew D. Sutton [1,*], David L. Clark [2,*], Brian L. Scott [3] and John C. Gordon [1,*]

[1] Chemistry Division—Inorganic, Isotope and Actinide Chemistry (C-IIAC), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[2] National Security Education Centre (NSEC), Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[3] Materials Synthesis and Integrated Devices (MPA-11), Los Alamos National Laboratory, Los Alamos, NM 87545, USA; E-Mail: bscott@lanl.gov

* Authors to whom correspondence should be addressed; E-Mails: adsutton@lanl.gov (A.D.S.); dlclark@lanl.gov (D.L.C.); jgordon@lanl.gov (J.C.G.); Tel.: +1-505-665-2931 (A.D.S.); +1-505-665-0983 (D.L.C.); +1-505-665-6962 (J.C.G.).

Academic Editors: Stephen Mansell and Steve Liddle

Received: 24 October 2015 / Accepted: 4 December 2015 / Published: 11 December 2015

Abstract: By applying a salt metathesis approach between $Ce(O^tBu_3)_2(NO_3)_2(THF)_2$ and the potassium salts of mono- and ditrimethylsilyl substituted cyclopentadienes, we were able to isolate two new Ce(IV) metallocenes, including to the best of our knowledge, the first structurally characterized bis-cyclopentadiene Ce(IV) compound.

Keywords: cerium; organometallic; cyclopentadiene; crystal structure

1. Introduction

Cerium(IV) is a strong one-electron oxidant and its use in areas such as organic synthesis [1–3], bioinorganic chemistry [4,5], materials science [6] and industrial catalysts such as automotive catalytic converters [7–13] is widespread. Soluble cerium(IV) complexes are also important precursors for the preparation of ceria nanoparticles [14] and this has increased the demand for well-characterized precursors for the development of this area. Ce(IV) alkoxides are well suited for this purpose and reports of Ce(IV) alkoxides exist where these have exhibited utility as precursors in CVD applications [15] and in ring-opening polymerization of lactide [16]. The synthesis of Ce(IV) organometallic complexes,

however, is limited by the lack of available starting materials and this has constrained the growth and development of traditional organometallic chemistry and reactivity using this high-oxidation state lanthanide [17]. Two main approaches exist as entry points into Ce(IV) chemistry; the oxidation of Ce(III) compounds and the use of materials such as $Ce(OPr^i)_4$, $Ce(OTf)_4$, cerium ammonium nitrate (CAN) derived $[Ce(O^tBu)_2(NO_3)_2(THF)_2]$ [18] and most recently, the amide complex, $Ce[(N^iPr_2)_4]$ [19]. The oxidation of Ce(III) is challenging and the results are often unpredictable due to ligand redistribution reactions. For example, $CeX[N(SiMe_3)_2]_3$ can be prepared from $Ce[N(SiMe_3)_2]_3$ using $TeCl_4$ or PBr_2Ph_3 as oxidants for X = Cl, Br respectively in low yields (Cl: 24%, Br: 30%) [20,21] but these are unstable is solvents other than THF. In contrast, $TeCl_4$ was ineffective in the oxidation of $Ce[(OCMe_2CH_2(1\text{-}C\{NCHCHNPr^i\})]$, while benzoquinone readily oxidized it to the tetravalent cerium carbene $Ce[(OCMe_2CH_2(1\text{-}C\{NCHCHNPr^i\})]_4$ [22]. Benzoquinone was also used effectively to oxidize $[Ce\{N(SiMe_3)_2\}_3]$ to form the new cerium(IV) silylamide complex $[Ce\{N(SiMe_3)_2\}_3(bda)_{0.5}]_2$ (bda = 1,4-benzenediolato) [23]. While cyclopentadienyl Ce(IV) complexes have been characterized spectroscopically [24,25] or even claimed [26] and refuted [27], to the best of our knowledge and with the aid of the Cambridge Crystallographic Database (CCDC), we are only aware of two reports of structurally characterized Ce(IV) metallocene complexes. The first was reported by Evans *et al.* in 1989 and was prepared from $Ce(O^tBu_3)_n(NO_3)_m(THF)_2$ (m = 2 or 3; $n + m = 4$) and mNaCp to give $Cp_2Ce(O^tBu_3)_2$ and $Cp_3Ce(O^tBu_3)$, the latter being crystallographically characterized [28]. These complexes utilized a soluble Ce(IV) alkoxide nitrate species which is readily prepared from cerium ammonium nitrate (CAN) [18]. Following this in 2010, Anwander and Edelmann reported the oxidation of $CeCp_3$ with $PhICl_2$ to form Cp_3CeCl [29]. Herein we present further expansion of known cyclopentadiene Ce(IV) complexes, with the first structurally characterized biscyclopentadiene Ce(IV) compound, and we will briefly discuss attempts to perform subsequent transformations of these relatively rare compounds.

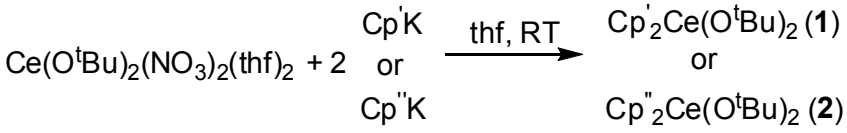
2. Results and Discussion

2.1. Preparation of Cerium(IV) Metallocenes

Our initial goal was to access a system containing sterically demanding ligands that would direct chemistry to the ancillary ligand sites. To this end we decided to utilize –$SiMe_3$-substituted cyclopentadienyl ligands. We added two equivalents of KCp′ (Cp′ = $C_5H_4SiMe_3$) to a solution of $Ce(O^tBu_3)_2(NO_3)_2(THF)_2$ in THF and observed an immediate color change from orange to deep red. The solution was allowed to stir overnight and the solvent was removed. The solid was extracted with HMDSO, filtered and a microcrystalline purple solid was obtained after storage at −20 °C for several days. This was analyzed by ^{1}H- and $^{13}C\{^1H\}$-NMR spectroscopy which permitted the characterization of **1** as $(Cp')_2Ce(OCMe_3)_2$, produced in reasonable yield (Scheme 1). Despite numerous attempts using various solvents and solvent combinations, single crystals for X-ray crystallography could not be obtained.

The same methodology was applied to the 1,3-substituted cyclopentadiene, KCp″, (Cp″ = $C_5H_4(SiMe_3)_2$-1,3) (Scheme 1) and when extracted with hexamethyldisiloxane (HMDSO) this afforded red single crystals which enabled us to crystallographically characterize **2** as $(Cp'')_2Ce(O^tBu_3)_2$ (Figure 1). The structure of **2** was solved in monoclinic $P2_1/c$ and exhibits a pseudo-tetrahedral

geometry with two coordinated Cp″ ligands and two coordinated O^{t}Bu ligands. Selected bond lengths and angles are provided in Table 1. Due to the steric bulk associated with the TMS groups, the angle between the rings is more obtuse causing a deviation from true T_d geometry with respect to the O–Ce–O angle between the two O^{t}Bu groups (103.9°). The Ce-centroid distances in **2** (2.511 Å average) are comparable to those in $Cp_3Ce(O^tBu_3)$ (2.509 Å average) [28] but significantly longer than those reported for Cp_3CeCl (2.460 Å average) [29] presumably due to the added steric congestion closer to the metal center resulting from the O^{t}Bu groups. The Ce–O bond lengths in **2** (2.077(5) and 2.097(6) Å) are slightly elongated compared to that in $Cp_3Ce(O^tBu_3)$ (2.045(6) Å) [28] which is most likely a steric effect rather than an electronic effect due to the comparable Ce-centroid distance between substituted and unsubstituted ring systems.



Scheme 1. Reaction scheme for the preparation of **1** and **2**.

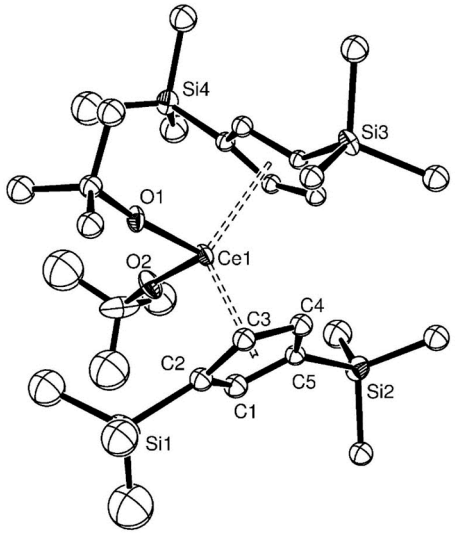


Figure 1. Thermal ellipsoid plot of the structure of **2** (hydrogen atoms omitted ellipsoids at 30% probability).

Table 1. Selected bond lengths (Å) and angles (°) of **2**.

Ce(1)–O(1)	2.077(5)	Ce(1)–Cn(1)	2.508(7)
Ce(1)–O(2)	2.097(6)	Ce(1)–C(12)	2.798(8)
Ce(1)–C(1)	2.799(9)	Ce(1)–C(13)	2.791(8)
Ce(1)–C(2)	2.811(9)	Ce(1)–C(14)	2.764(8)
Ce(1)–C(3)	2.743(9)	Ce(1)–C(15)	2.774(8)
Ce(1)–C(4)	2.733(9)	Ce(1)–C(16)	2.812(9)
Ce(1)–C(5)	2.810(8)	Ce(1)–Cn(2)	2.514(7)
O(1)–Ce(1)–Cn(1)	108.7(4)	O(1)–Ce(1)–Cn(2)	109.9(8)
O(1)–Ce(1)–Cn(2)	105.8(2)	O(1)–Ce(1)–O(2)	103.9(2)
O(2)–Ce(1)–Cn(1)	105.6(4)	Cn(1)–Ce(1)–Cn(2)	121.7(2)

2.2. Attempted Reactivity of **1** *and* **2**

In order to probe the reactivity of **1** and **2**, and synthesize additional cyclopentadienyl compounds of Ce(IV), each was reacted in tetrahydrofuran or toluene with one and two equivalents of KOTf, TMS-Cl, Ph_3SiOH, $MeNH_2$, Et_3N, MeMgBr, Bu_2Mg with no reaction observed by NMR spectroscopy. Reaction with dilute HCl as a solution in Et_2O led to reduction of both **1** and **2** as evidence by paramagnetic NMR spectra although no tractable product could be isolated and characterized.

3. Experimental Section

Unless otherwise noted, all reactions were performed using standard Schlenk-line techniques or in a Vacuum Atmosphere glove box. All glassware and Celite were stored in an oven at *ca.* 425 K. Hexamethyldisiloxane was distilled and degassed before use. Hexane, toluene, and THF were freshly distilled from sodium and degassed with nitrogen prior to use. C_6D_6 was vacuum transferred from sodium/benzophenone. NMR spectra were recorded at ambient temperature on Bruker AV-400. ^1H and $^{13}C\{^1H\}$ chemical shifts are given relative to residual protic solvent peaks and coupling constants (*J*) are given in Hz. Infra-red samples were prepared as Nujol mulls and taken between KBr plates. Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected. Unless otherwise noted, all reagents were acquired from commercial sources and used as received.

A crystal of **2** was mounted in a nylon cryoloop from Paratone-N oil. The data were collected on a Bruker D8 diffractometer, with an APEX II charge-coupled-device (CCD) detector, and a Bruker Kryoflex liquid nitrogen low temperature device (140 K). The instrument was equipped with a graphite monochromatized MoKα X-ray source (λ = 0.71073 Å), and a 0.5 mm monocapillary. A hemisphere of data was collected using ω scans, with 10-s frame exposures and 0.5° frame widths. Data collection and initial indexing and cell refinement were handled using APEX II [30] software. Frame integration, including Lorentz-polarization corrections, and final cell parameter calculations were carried out using SAINT+ [31] software. The data were corrected for absorption using redundant reflections and the SADABS [32] program. Decay of reflection intensity was not observed as monitored via analysis of redundant frames. The structure was solved using Direct methods and difference Fourier techniques. One t-butyl group was disordered, and the methyl groups were refined in two positions (C28/C28′, C29/C29′, and C30/C30′). Site occupancy factors for disordered pairs were tied to 1.0. A total of 31 bond distance and temperature factor restraints were used to force convergence of the disordered group. All hydrogen atom positions were idealized, and rode on the atom they were attached to. The final refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL [33] software. Additional details can be found in crystallographic information file (CCDC No. 1433004) and in the Supplementary Information.

3.1. Preparation of $(Cp')_2Ce(O^tBu)_2$ (**1**)

KCp′ (0.352 g, 2.0 mmol) was dissolved in THF (2.5 mL) and added to a suspension of $Ce(O^tBu)_2(NO_3)_2(THF)_2$ (0.555 g, 1.0 mmol) in THF (2.5 mL), resulting in an immediate color change to deep red. The reaction was allowed to stir overnight and the solvent removed *in vacuo*. The resultant

solid was extracted with HMDSO (10 mL) and stored at −20 °C to afford a microcrystalline purple solid (0.305 g, 54%). ^{1}H-NMR (400 MHz, C_6D_6): δ 0.48 (s, 18 H, Si(C*H*$_3$)$_3$); 1.32 (s, 18 H, C(C*H*$_3$)$_3$); 6.26 (m, 4 H); 6.65 (m, 4 H). ^{13}C{^{1}H}-NMR (100.6 MHz, C_6D_6): 0.73, 33.56, 84.56, 123.95, 127.55, 127.79. IR (cm^{-1}): 1622 (m); 1377 (s); 1314 (w); 1287 (w), 1268 (m); 1195 (w); 1099 (m); 1085 (w); 1042 (w); 1015 (m); 980 (w); 930 (s); 846 (w); 814 (w); 800 (w); 746 (w); 665 (w). m.p. > 260 °C (dec.). CHO for $C_{24}H_{44}CeO_2Si_2$ Calc. % (found) C 51.39 (51.61), H 7.91 (7.86), O 5.70 (5.44).

*3.2. Preparation of (Cp″)$_2$Ce(O^{t}Bu)$_2$ (**2**)*

KCp″ (0.497 g, 2.0 mmol) was dissolved in THF (2.5 mL) and added to a suspension of Ce(O^{t}Bu)$_2$(NO$_3$)$_2$(THF)$_2$ (0.555 g, 1.0 mmol) in THF (2.5 mL) resulting in an immediate color change to deep red. The reaction was allowed to stir overnight and the solvent was removed *in vacuo*. The resultant solid was extracted with HMDSO (20 mL) and stored at −20 °C for two days to afford X-ray quality crystals (0.474 g, 67%). ^{1}H-NMR (300 MHz, C_6D_6): δ 0.45 (s, 36 H, Si(C*H*$_3$)$_3$); 1.39 (s, 18 H, C(C*H*$_3$)$_3$); 6.20 (m, 4 H); 6.59 (m, 4 H). ^{13}C{^{1}H}-NMR (100.6 MHz, C_6D_6): 0.77, 34.87, 85.77, 125.23, 128.11, 129.02. IR (cm^{-1}): 1620 (m); 1381 (s); 1373 (s); 1322 (w); 1292 (w), 1258 (m); 1204 (w); 1123 (w); 1103 (m); 1074 (w); 1057 (w); 1035 (w); 1012 (m); 976 (w); 924 (s); 849 (w); 817 (w); 796 (w); 777 (m); 743 (w); 722 (w); 690 (w); 639 (w). m.p. > 260 °C (dec.). CHO for $C_{30}H_{60}CeO_2Si_4$ Calc. % (found) C 51.09 (51.18), H 8.58 (8.41), O 4.54 (4.38).

4. Conclusions

By applying a salt metathesis approach between Ce(O^{t}Bu$_3$)$_2$(NO$_3$)$_2$(THF)$_2$ and the potassium salts of mono- and ditrimethylsilyl substituted cyclopentadienes, we were able to isolate two new Ce(IV) metallocenes, including to the best of our knowledge, the first structurally characterized dicyclopentadiene Ce(IV) compound. With these two compounds in hand, we attempted to exploit the reactivity of these, but to no avail. The Ce–O bonds were inert to all our attempts to substitute the O^{t}Bu ligands, highlighting the oxophilic nature of the (higher valent) lanthanides. Due to this lack of reactivity, we believe that Ce(O^{t}Bu$_3$)$_2$(NO$_3$)$_2$(THF)$_2$ is not well suited as a starting material due to the resilience of the resultant Ce–O bonds to further substitution. It is our opinion that future efforts should be focused on more amenable starting compounds such as Ce(OTf)$_4$ and Ce(N^{i}Pr$_2$)$_4$ [19] and using oxidation strategies from Ce(III) to Ce(IV) [20–22,29].

Supplementary Materials

Supplementary materials can be found at http://www.mdpi.com/2304-6740/3/4/0589/s1.

Acknowledgments

Andrew D. Sutton acknowledges the Seaborg Institute at Los Alamos National Laboratory for funding a Postdoctoral Fellowship.

Author Contributions

Andrew D. Sutton designed and performed the experimental work and wrote the manuscript, David L. Clark designed the experiments, Brian L. Scott performed the X-ray crystallography and structural determination and John C. Gordon, designed the experiments and wrote the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Das, A.K. Kinetic and mechanistic aspects of metal ion catalysis in cerium(IV) oxidation. *Coord. Chem. Rev.* **2001**, *213*, 307–325.
2. Dziegiec, J.; Domagala, S. The oxidation activity of cerium(IV) ions toward some of the organic compounds. *Trends Inorg. Chem.* **2005**, *8*, 43–64.
3. Nair, V.; Balagopal, L.; Rajan, R.; Mathew, J. Recent advances in synthetic transformations mediated by cerium(IV) ammonium nitrate. *Acc. Chem. Res.* **2004**, *37*, 21–30.
4. Komiyama, M. Sequence-selective scission of DNA and RNA by lanthanide ions and their complexes. *Met. Ions Biol. Syst.* **2003**, *40*, 463–475.
5. Yamamoto, Y.; Komiyama, M. Development of new biotechnology by cerium(IV)-based artificial restriction enzyme. *Mater. Integr.* **2005**, *19*, 55–59.
6. Jian, H.-O.; Zhou, X.-R.; Zhao, D.-F. Recent progress of synthetic methods and applications of cerium β-diketones. *Huaxue Shiji* **2006**, *28*, 279–282.
7. Duprez, D.; Descorme, C. Oxygen storage/redox capacity and related phenomena on ceria-based catalysts. *Catal. Sci. Ser.* **2002**, *2*, 243–280.
8. Imamura, S. Ceria-based wet-oxidation catalysts. *Catal. Sci. Ser.* **2002**, *2*, 431–452.
9. Kaspar, J.; Fornasiero, P. Nanostructured materials for advanced automotive de-pollution catalysts. *J. Solid State Chem.* **2003**, *171*, 19–29.
10. Kaspar, J.; Fornasiero, P.; Graziani, M. Use of CeO_2-based oxides in the three-way catalysis. *Catal. Today* **1999**, *50*, 285–298.
11. Primet, M.; Garbowski, E. Fundamentals and applications of ceria in combustion reactions. *Catal. Sci. Ser.* **2002**, *2*, 407–429.
12. Shelef, M.; Graham, G.W.; McCabe, R.W. Ceria and other oxygen storage components in automotive catalysts. *Catal. Sci. Ser.* **2002**, *2*, 343–375.
13. Trovarelli, A.; de Leitenburg, C.; Boaro, M.; Dolcetti, G. The utilization of ceria in industrial catalysis. *Catal. Today* **1999**, *50*, 353–367.
14. Droese, P.; Gottfriedsen, J.; Hrib, C.G.; Jones, P.G.; Hilfert, L.; Edelmann, F.T. The first cationic complex of tetravalent cerium. *Z. Anorg. Allg. Chem.* **2011**, *637*, 369–373.
15. Aspinall, H.C.; Bacsa, J.; Jones, A.C.; Wrench, J.S.; Black, K.; Chalker, P.R.; King, P.J.; Marshall, P.; Werner, M.; Davies, H.O.; *et al*. Ce(IV) complexes with donor-functionalized alkoxide ligands: Improved precursors for chemical vapor deposition of CeO_2. *Inorg. Chem.* **2011**, *50*, 11644–11652.

16. Broderick, E.M.; Diaconescu, P.L. Cerium(IV) catalysts for the ring-opening polymerization of lactide. *Inorg. Chem.* **2009**, *48*, 4701–4706.
17. Arnold, P.L.; Casely, I.J.; Zlatogorsky, S.; Wilson, C. Organometallic cerium complexes from tetravalent coordination complexes. *Helv. Chim. Acta* **2009**, *92*, 2291–2303.
18. Evans, W.J.; Deming, T.J.; Olofson, J.M.; Ziller, J.W. Synthetic and structural studies of a series of soluble cerium(IV) alkoxide and alkoxide nitrate complexes. *Inorg. Chem.* **1989**, *28*, 4027–4034.
19. Schneider, D.; Spallek, T.; Maichle-Moessmer, C.; Toernroos, K.W.; Anwander, R. Cerium tetrakis(diisopropylamide)—A useful precursor for cerium(IV) chemistry. *Chem. Commun.* **2014**, *50*, 14763–14766.
20. Eisenstein, O.; Hitchcock, P.B.; Hulkes, A.G.; Lappert, M.F.; Maron, L. Cerium masquerading as a group 4 element: Synthesis, structure and computational characterisation of [CeCl{N(SiMe$_2$)$_3$}]. *Chem. Commun.* **2001**, 1560–1561.
21. Hitchcock, P.B.; Hulkes, A.G.; Lappert, M.F. Oxidation in nonclassical organolanthanide chemistry: Synthesis, characterization, and X-ray crystal structures of cerium(III) and -(IV) amides. *Inorg. Chem.* **2004**, *43*, 1031–1038.
22. Casely, I.J.; Liddle, S.T.; Blake, A.J.; Wilson, C.; Arnold, P.L. Tetravalent cerium carbene complexes. *Chem. Commun.* **2007**, 5037–5039, doi:10.1039/B713041D.
23. Werner, D.; Deacon, G.B.; Junk, P.C.; Anwander, R. Cerium(III/IV) formamidinate chemistry, and a stable cerium(IV) diolate. *Chemistry* **2014**, *20*, 4426–4438.
24. Greco, A.; Cesca, S.; Bertolini, W. New 7r-cyclooctate′I′raenyl and iT-cyclopentadienyl complexes of cerium. *J. Organomet. Chem.* **1976**, *113*, 321–330.
25. Gulino, A.; Casarin, M.; Conticello, V.P.; Gaudiello, J.G.; Mauermann, H.; Fragala, I.; Marks, T.J. Efficient synthesis, redox characteristics, and electronic structure of a tetravalent tris(cyclopentadienyl)cerium alkoxide complex. *Organometallics* **1988**, *7*, 2360–2364.
26. Kalsotra, B.L.; Multani, R.K.; Jain, B.D. Preparation and properties of tricyclopentadienyl cerium(IV) chloride and bisindenyl cerium(IV) dichloride. *Isr. J. Chem.* **1971**, *9*, 569–572.
27. Deacon, G.B.; Tuong, T.D.; Vince, D.G. Refutation of the synthesis of tetrakis(cyclopentadienyl) cerium(IV). *Polyhedron* **1983**, *2*, 969–970.
28. Evans, W.J.; Deming, T.J.; Ziller, J.W. The utility of ceric ammonium nitrate-derived alkoxide complexes in the synthesis of organometallic cerium(IV) complexes. Synthesis and first X-ray crystallographic detrmination of a tetravalent cerium cyclopentadienide complex, (C$_5$H$_5$)$_3$Ce(OCMe$_3$). *Organometallics* **1989**, *8*, 1581–1583.
29. Dröse, P.; Crozier, A.R.; Lashkari, S.; Gottfriedsen, J.; Blaurock, S.; Hrib, C.G.; Maichle-Mössmer, C.; Schädle, C.; Anwander, R.; Edelmann, F.T. Facile access to tetravalent cerium compounds: One-electron oxidation using iodine(III) reagents. *J. Am. Chem. Soc.* **2010**, *132*, 14046–14047.
30. *APEX II 1.08*; Bruker AXS, Inc.: Madison, WI, USA, 2004.
31. *SAINT+ 7.06*; Bruker AXS, Inc.: Madison, WI, USA, 2003.

32. Sheldrick, G. *SADABS 2.03*; University of Göttingen: Göttingen, Germany, 2001.
33. *SHELXTL 5.10*; Bruker AXS, Inc.: Madison, WI, USA, 1997.

© 2015 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).