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The First Cationic Complex of Tetravalent Cerium

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Abstract. The recently reported cerium(IV) tripodal Schiff-base complex (TRENDSAL)CeCl (TRENDSAL = $[N\{CH_2CH_2N{=}CH(C_6H_2tBu_2\text{-}3,5\text{-}O\text{-}2\}_3]^{3-}$) serves as excellent starting material for novel Ce^{4+} coordination compounds. The first cerium(IV) azide, (TRENDSAL)CeN_3 and the first cationic cerium(IV) complex, [(TRENDSAL)Ce][BPh_4] are both readily accessible from (TRENDSAL)CeCl via simple salt metathesis reaction.

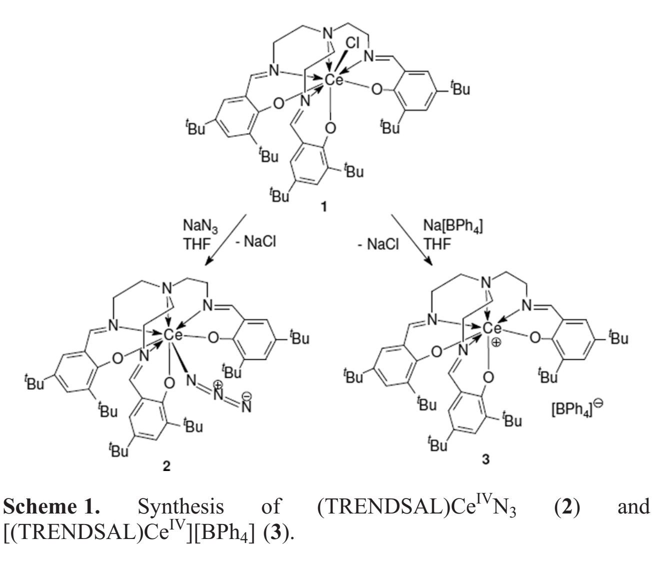
Introduction

Due to their high oxidation potential (E = 1.70 V in 1 m $HClO_4$), cerium(IV) compounds are widely used in various areas of chemistry and technology. Important fields of application include organic synthesis,[1] bioinorganic chemistry,[2] materials science,[3] and industrial catalysis (automotive three-way catalysts, oxygen storage etc.).[4] More recently, soluble cerium(IV) compounds are increasingly employed for the production of ceria nanoparticles.[5] The long known cerium(IV) alkoxides form a well-investigated class of compounds which are useful precursors for the MOCVD production of thin CeO_2 layers.[6] Thus there is a constant demand for new, well-defined cerium(IV) species. Cerium is the only lanthanide with an extensive chemistry in the +4 oxidation state. Its coordination chemistry is dominated by oxygen and nitrogen donor ligands.[7] Well-investigated neutral complexes besides the alkoxides include e.g. the β-diketonates,[8] amides,[9] as well as bis(porphyrin) and bis(phthalocyanine) complexes.[10] Then there is a number of anionic complexes like the familiar orange-red ceric ammonium nitrate (= CAN), $(NH_4)_2[Ce(NO_3)_6]$, as well as cerium(IV) halide complexes (e.g. $(NH_4)_2[CeF_8]$, $(NH_4)_3[CeF_7(H_2O)]$, and salts of $[CeCl_6]^{2-}$ with bulky cations).[7] In sharp contrast, cationic cerium(IV) complexes are completely unknown. We report here the synthesis of the first cationic coordination compound of tetravalent cerium as well as the first cerium(IV) azide species.

Recently, several cerium(IV) complexes containing the very bulky tripodal Schiff-base ligand $N[CH_2CH_2N{=}CH(C_6H_2tBu_2\text{-}3,5\text{-}OH\text{-}2]_3$ (= H_3TRENDSAL) have been reported.[11] The dark purple compounds (TRENDSAL)CeCl (**1**) and (TRENDSAL)Ce(NO_3) were prepared in simple one-pot reactions via condensation of tris(2-aminoethyl)amine and 3,5-di-*tert*-butylsalicylaldehyde and the appropriate starting material $CeCl_3(H_2O)_6$ (in air) or $(NH_4)_2[Ce(NO_3)_6]$, respectively. In both cases, the anionic ligands are coordinated to the central cerium(4+) ion, resulting in eight- (Cl) or nine-coordinate (NO_3) species. In a continuation of this work, we now found that **1** can serve as excellent starting material for novel tetravalent cerium(IV) complexes, including the first cerium(IV) azide species and the first cationic cerium(IV) complex.

Results and Discussion

Treatment of blue-purple **1** with a large excess of NaN_3 afforded a dark red-purple solution, from which the cerium(IV)



Scheme 1. Synthesis of (TRENDSAL)$Ce^{IV}N_3$ (**2**) and [(TRENDSAL)Ce^{IV}][BPh_4] (**3**).

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azide (TRENDSAL)CeN_3 could be obtained in the form of black, block-like crystals in 53 % isolated yield (Scheme 1).

The air- and moisture-stable azide derivative **2** is moderately soluble in THF and acetonitrile, little soluble in toluene and insoluble in *n*-pentane. A strong IR band at 2044 cm^{-1} can be assigned to the asymmetric stretching vibration of the azido ligand. A mass spectrum of **2** showed the molecular ion with very low intensity. The presence of the first cerium(IV) azide species was verified by a single-crystal X-ray analysis (Figure 1). Crystallographic data for **2** and **3** are summarized in Table 1, whereas selected bond lengths and angles for **2** and **3** are listed in Table 2 and Table 3.

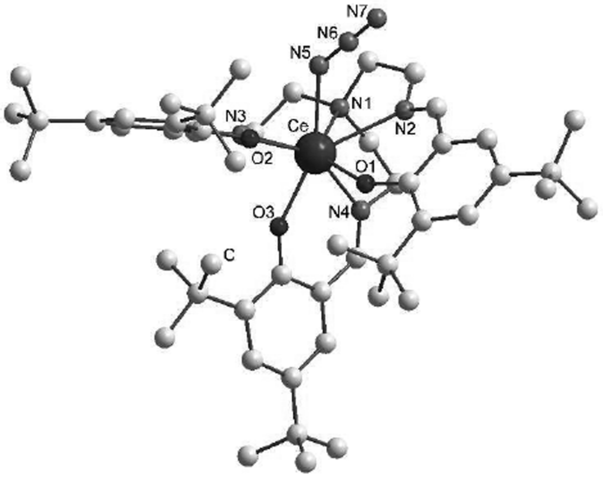

Figure 1. Molecular structure of (TRENDSAL)$Ce^{IV}N_3$ **2** in the solid state.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the unit cell. The coordination geometry around the eight-coordinate cerium can be described as distorted bicapped octahedral. Bond lengths and angles within the tripodal ligand do not differ significantly from those in **1**. With 2.437(3) and 2.423(2) Å the Ce–N(N3) distance is significantly longer than typical Ce^{IV}–N(amide) bond lengths (e.g. 2.217(3) in$[(Me_3Si)_2N]_3CeCl$).[9b]

Of even greater importance was the finding at the chlorido complex **1** can also serve as starting material in the preparation of the first cationic cerium(IV) complex. Chloride abstraction from **1** seemed feasible as the TRENDSAL is known to effectively encapsulate even the large lighter lanthanide ions.[12] A reaction of equimolar amounts of **1** and $Na[BPh_4]$ in THF (Scheme 1) led to formation of a red-purple solution, from which the salt-like product **3** could be isolated. Crystallization from acetonitrile afforded large black, block-like crystals of

Table 1. Crystallographic Data for (TRENDSAL)$Ce^{IV}N_3$ (**2**) and [(TRENDSAL)Ce][BPh_4] (**3**).

	2	**3**
Identification code	ip51a	ip43a
Empirical formula	$C_{51}H_{69}CeN_7O_3\cdot(CH_3CN)_2$	$C_{75}H_{95}BCeN_4O_3\cdot(CH_3CN)$
Formula weight	1050.37	1292.53
Temperature	150(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions	a = 15.9264(3) Å	a = 21.7685(4) Å
	b = 16.7188(3) Å	b = 14.3963(3) Å
	c = 22.7258(4) Å	c = 22.6783(3) Å
	α = 70.1880(10)°	α = 90°
	β = 70.2910(10)°	β = 90.99990(10)°
	γ = 84.9700(10)°	γ = 90°
Volume	5357.10(17) $Å^3$	7106.0(2) $Å^3$
Z	4	4
Density (calculated)	1.201 $Mg\cdot m^{-3}$	1.208 $Mg\cdot m^{-3}$
Absorption coefficient	0.893 mm^{-1}	0.689 mm^{-1}
F(000)	2024	2728
Crystal size	0.40 × 0.30 × 0.30 mm	0.40 × 0.20 × 0.20 mm
Theta range for data collection	1.94 to 28.28°	1.91 to 29.24°
Index ranges	$-21 \le h \le 21$	$-29 \le h \le 27$
	$-22 \le k \le 22$	$-19 \le k \le 19$
	$-30 \le l \le 30$	$-31 \le l \le 31$
Reflections collected	187447	96988
Independent reflections	26575 [*R*(int) = 0.0658]	19157 [*R*(int) = 0.0855]
Completeness to θ = 29.23°	99.9 %	99.9 %
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	26575 / 0 / 1148	19157 / 0 / 803
Goodness-of-fit on F2	1.083	1.059
Final *R* indices [$I > 2\sigma(I)$]	$R1$ = 0.0431, $wR2$ = 0.0981	$R1$ = 0.0555, $wR2$ = 0.0810
R indices (all data)	$R1$ = 0.0557, $wR2$ = 0.1035	$R1$ = 0.0755, $wR2$ = 0.0862
Largest diff. peak and hole	0.808 and –1.363 $e\cdot Å^{-3}$	0.836 and –1.312 $e\cdot Å^{-3}$

Table 2. Selected bond lengths /Å and angles /° for (TRENDSAL)$Ce^{IV}N_3$ (**2**). Compound **2** crystallizes with two molecules in the asymmetric unit.

Ce(1)–O(1)	2.159(2)	Ce(2)–O(5)	2.1542(19)
Ce(1)–O(2)	2.1888(19)	Ce(2)–O(6)	2.1870(19)
Ce(1)–O(3)	2.193(2)	Ce(2)–O(4)	2.197(2)
Ce(1)–N(1)	2.762(2)	Ce(2)–N(8)	2.773(2)
Ce(1)–N(2)	2.661(3)	Ce(2)–N(9)	2.510(2)
Ce(1)–N(3)	2.520(2)	Ce(2)–N(10)	2.630(2)
Ce(1)–N(4)	2.587(2)	Ce(2)–N(11)	2.603(2)
Ce(1)–N(5)	2.437(3)	Ce(2)–N(12)	2.423(2)
O(1)–Ce(1)–O(2)	99.61(7)	O(4)–Ce(2)–O(5)	94.90(8)
O(1)–Ce(1)–O(3)	90.24(8)	O(4)–Ce(2)–O(6	81.61(7)
O(2)–Ce(1)–O(3)	81.54(8)	O(5)–Ce(2)–O(6)	89.64(8)
N(2)–Ce(1)–N(3)	125.49(8)	N(9)–Ce(2)–N(10)	124.73(8)
N(2)–Ce(1)–N(4)	77.30(8)	N(9)–Ce(2)–N(11)	100.45(8)
N(3)–Ce(1)–N(4)	95.41(8)	N(10)–Ce(2)–N(11)	75.14(7)
N(1)–Ce(1)–N(2)	62.50(8)	N(8)–Ce(2)–N(9)	65.60(8)
N(1)–Ce(1)–N(3)	65.66(8)	N(8)–Ce(2)–N(10)	63.35(7)
N(1)–Ce(1)–N(4)	64.77(8)	N(8)–Ce(2)–N(11)	64.06(7)
N(1)–Ce(1)–N(5)	80.28(9)	N(8)–Ce(2)–N(12)	79.23(8)
O(1)–Ce(1)–N(1)	127.71(8)	O(4)–Ce(2)–N(8)	130.95(8)
O(2)–Ce(1)–N(1)	127.83(7)	O(5)–Ce(2)–N(8)	129.61(8)
O(3)–Ce(1)–N(1)	114.65(8)	O(6)–Ce(2)–N(8)	113.49(8)
O(1)–Ce(1)–N(2)	69.38(8)	O(4)–Ce(2)–N(9)	71.60(8)
O(3)–Ce(1)–N(4)	68.16(8)	O(6)–Ce(2)–N(11)	67.93(7)
O(2)–Ce(1)–N(3)	71.50(7)	O(5)–Ce(2)–N(10)	69.74(7)

Table 3. Selected bond lengths /Å and angles /° for [(TRENDSAL)Ce][BPh_4] (**3**).

Ce–O(1)	2.1438(16)	Ce–N(1)	2.6548(19)
Ce–O(2)	2.1427(16)	Ce–N(2)	2.472(2)
Ce–O(3)	2.1376(15)	Ce–N(3)	2.4857(19)
		Ce–N(4)	2.492(2)
O(3)–Ce–O(2)	98.91(6)		
O(3)–Ce–O(1)	94.64(6)	N(2)–Ce–N(3)	105.78(6)
O(2)–Ce–O(1)	99.69(6)	N(2)–Ce–N(4)	103.99(7)
		N(3)–Ce–N(4)	110.54(6)
O(1)–Ce–N(1)	120.37(6)		
O(3)–Ce–N(1)	121.08(6)	N(2)–Ce–N(1)	68.09(6)
O(2)–Ce–N(1)	117.30(6)	N(4)–Ce–N(1)	68.13(6)
		N(3)–Ce–N(1)	67.72(6)
O(1)–Ce–N(2)	71.26(6)		
O(2)–Ce–N(3)	71.36(6)		
O(3)–Ce–N(4)	70.86(6)		

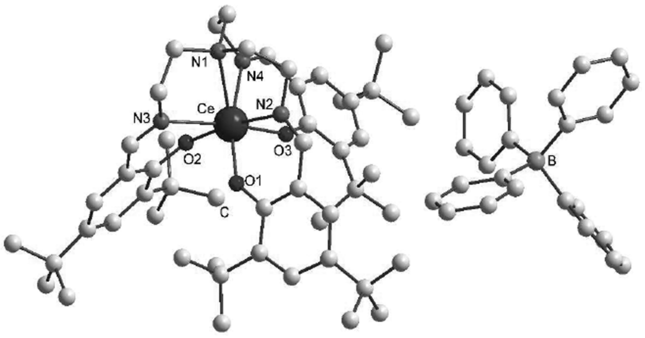

Figure 2. Structure of [(TRENDSAL)Ce][BPh_4] (**3**) in the solid state.

the mono-acetonitrile solvate in 89 % yield which were suitable for X-ray diffraction (Figure 2).

In accordance with its salt-like nature the product is insoluble in hydrocarbons and only moderately soluble in THF, acetone, DME, or acetonitrile. An X-ray diffraction study confirmed the presence of the first cationic coordination compound of tetravalent cerium. In the solid state, compound **3** exists as separated ion pairs. The coordination polyhedron around the Ce^{4+} ion in the cation can be best described as a distorted capped octahedron with the amine nitrogen atom forming the cap. Due to the formal positive charge at the cerium atom, there is a significant shortening of the Ce–N(imine) distances (*av.* 2.482 Å in **3**) as compared to the azido complex **2** (*av.* 2.581 Å). The N(imine)–Ce–N(imine) (103.99(7)–110.54(6)°) and O–Ce–O angles (94.64(6)–99.69(9)°) fall in relatively narrow ranges, indicating a quite symmetrical overall coordination of the tripodal Schiff-base ligand.

Apparently the key to the successful isolation of the cationic complex **3** is the combination of high steric bulk and significant flexibility of the tripodal TRENDSAL ligand. In order to illustrate this coordinative flexibility, Figure 3 shows an overlay of the structure cores of the azide derivative **2** (bold bonds) and the cation in **3** (dotted bonds). It is clearly seen how upon removal of the additional ligand (Cl or N_3) two of the chelating arms of the tripodal Schiff-base ligand move in to fill the empty cavity in the coordination sphere around the cerium atom.

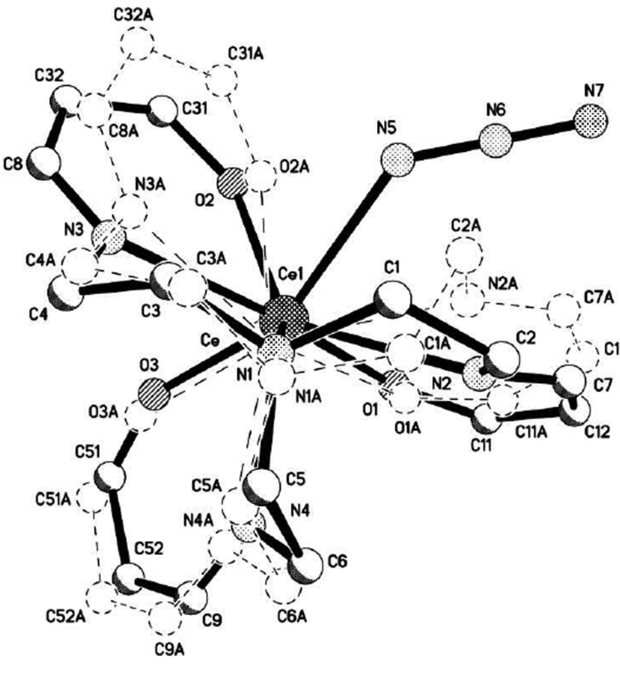

Figure 3. Overlay of the structure cores of **2** and **3**.

In summarizing the results reported here, we established the readily accessible cerium(IV) tripodal Schiff-base complex

(TRENDSAL)CeCl (**1**) as an excellent starting material for novel cerium(IV) coordination compounds. Simple salt metathesis reactions not only afforded the first Ce^{IV} azido complex (**2**), but also the first structurally authenticated cationic cerium(IV) complex, [(TRENDSAL)Ce][BPh$_4$] (**3**), which might find interesting future applications e.g. in oxidation catalysis.

Experimental Section

All operations could be performed without any special precautions as the starting materials and the products are all air- and moisture-stable. The starting materials NaN$_3$ and Na[BPh$_4$] were obtained from commercial sources and used as received. Compound **1** was prepared according to the literature procedure.[11] The NMR spectra were recorded in [D$_8$]THF or [D$_6$]acetone solutions with a Bruker-AVANCE-DMX400 spectrometer (5 mm BB, ^{1}H: 400.13 Hz; ^{13}C: 100.62 MHz). ^{1}H and ^{13}C shifts are referenced to internal solvent resonances and reported in parts per million relative to TMS. IR spectra were recorded using KBr pellets with a Perkin–Elmer FT-IR spectrometer system 2000 between 4000 cm^{-1} and 400 cm^{-1} with dry KBr/sample mixtures and KBr windows. Mass spectra (EI, 70 eV) were run with a MAT 95 apparatus. Microanalyses of the compounds were performed using a Leco CHNS 923 apparatus. Melting points: Büchi Melting Point B-540. The intensity data of **2** and **3** were collected with a Stoe IPDS 2T diffractometer with Mo-K_α radiation. The data were collected with the Stoe XAREA[13] program using ω-scans. The space groups were determined with the XRED32[13] program. The reflections were merged. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods on F^2 using SHELXL-97.[14] Data collection parameters as well as bond lengths and angles are given in Table 1, Table 2, and Table 3.

Preparation of (TRENDSAL)Ce^{IV}N$_3$ (2): In a 300 mL Erlenmeyer flask, (TRENDSAL)CeCl (**1**, 0.60 g, 0.62 mmol) was dissolved in THF (200 mL), solid NaN$_3$ (0.08 g, 1.24 mmol, 100 % excess) was added, and the mixture was stirred at room temp. for 10 h. The resulting red-purple solution was filtered and the solvents were evaporated to dryness (50 °C/350 mbar). The residue was redissolved in hot acetonitrile (120 mL). Cooling to 5 °C for 24 h afforded the bis-acetonitrile adduct of **2** as black, block-like single-crystals that were suitable for X-ray diffraction. Thorough drying under vacuum (oil pump) afforded the unsolvated material, which was subsequently analyzed. Yield: 0.32 g (53 %), m.p. 201 °C. $C_{51}H_{75}CeN_7O_3$ (*M*r = 974.3 g·mol^{-1}): C, 62.87; H, 7.76; N, 10.06. Found: C, 62.82; H, 7.84; N, 9.90 %. **^{1}H NMR** (400 MHz, [D$_8$]THF, 25 °C): δ = 8.63 (s$_{br}$, 3 H, –N=C***H***–Ar), 7.43 (s$_{br}$, 3 H, Ar–***H***), 7.13 (s$_{br}$, 3 H, Ar–***H***), 4.24 (s$_{br}$, 6, N–C***H***$_2$–CH$_2$–), 3.07 (s$_{br}$, 6, N–CH$_2$–C***H***$_2$–), 1.27 (s, 54 H, –C(C***H***$_3$)$_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, [D$_8$]THF, 25 °C): δ = 168.2 (–CH$_2$–N=***C***H–Ar), 139.9 (*t*Bu–***C***$_{Ar}$), 137.9 (*t*Bu–***C***$_{Ar}$), 129.9 (H–***C***$_{Ar}$), 126.8 (H–***C***$_{Ar}$), 65.8 (–***C***H$_2$–), 64.2 (–***C***H$_2$–), 36.5 (Ar–***C***Me$_3$), 35.3 (Ar–***C***Me$_3$), 32.8 (–C(***C***H$_3$)), 31.8 (–C(***C***H$_3$)). **IR** (KBr): $\tilde{\nu}_{max}$ = 3437 (m), 2956 (vs, ν_s CH$_3$), 2907 (m, ν_s CH$_2$), 2868 (m, ν_{as} CH$_3$), 2044 (vs, ν_{as} N$_3$), 1618 (vs, C=N), 1551 (m, C=C ring), 1460 (m), 1435 (m), 1412 (m), 1391 (m), 1361 (m), 1336 (w), 1298 (m), 1272 (st), 1254 (vs), 1203 (m), 1174 (m), 836 (st, CH ring), 811 (w), 779 (w), 746 (m), 526 (w) cm^{-1}. **MS** (EI): *m/z* (%) 972.9 (0.02) [M]$^+$, 945.0 (1) [M – N$_2$]$^+$, 931.9 (100) [M – N$_3$]$^+$.

Preparation of [(TRENDSAL)Ce][BPh$_4$] (3): In a 250 mL round-bottom flask, (TRENDSAL)CeCl (**1**, 0.78 g, 0.81 mmol) was dissolved in THF (70 mL), solid Na[BPh$_4$] (0.28 g, 0.81 mmol) was added, and the mixture was stirred at room temp. for 30 min. The resulting red-purple solution was filtered and the solvents were evaporated to dryness (50 °C/350 mbar). The residue was redissolved in hot acetonitrile (120 mL). Cooling to 5 °C for 24 h afforded the mono-acetonitrile solvate of **3** as black, block-like single-crystals that were suitable for X-ray diffraction. Thorough drying under vacuum (oil pump) afforded the unsolvated material, which was subsequently analyzed. Yield: 0.90 g (89 %), m.p. > 260 °C. $C_{75}H_{95}BCeN_4O_3$ (*M*r = 1250.66 g·mol^{-1}): C, 71.98; H, 7.65; N, 4.48. Found: C, 71.60; H, 7.71; N, 5.33 %. **^{1}H NMR** (400 MHz, [D$_6$]acetone, 25 °C): δ = 9.07 (s, 3 H, –N=C***H***–Ar), 7.62 (d, ^4J = 2.4 Hz, 3 H, Ar–*H*), 7.46 (d, ^4J = 2.4 Hz, 3 H, Ar–***H***), 7.35 (d$_{br}$, 8 H, B{C$_6$***H***$_5$}$_4$), 6.92 (t, ^3J = 7.3 Hz, 8 H, B{C$_6$***H***$_5$}$_4$), 6.77 (t, ^3J = 7.1 Hz, 4 H, B{C$_6$***H***$_5$}$_4$), 4.56 (t$_{br}$, 3 H, N{CH$_2$–C***H***$_2$–N=CH–Ar}$_3$Ce), 3.87 (d$_{br}$, 3 H, N{CH$_2$–C***H***$_2$–N=CH–Ar}$_3$Ce), 3.50 (t$_{br}$, 3 H, N{C***H***$_2$–CH$_2$–N=CH–Ar}$_3$Ce), 3.36 (d$_{br}$, 3 H, N{C***H***$_2$–CH$_2$–N=CH–Ar}$_3$Ce), 1.32 (s, 27 H, –C(C***H***$_3$)$_3$), 1.16 (s, 27 H, –C(C***H***$_3$)$_3$). **^{13}C{^{1}H} NMR** (100.6 MHz, [D$_6$]acetone, 25 °C): δ = 168.8 (N{CH$_2$–CH$_2$–N=***C***H–Ar}$_3$Ce), 165.7 (–O–***C***$_{Ar}$), 142.9 (*t*Bu–***C***$_{Ar}$), 137.0 (B{***C***$_6$H$_5$}$_4$), 136.0 (*t*Bu–***C***$_{Ar}$), 130.5 ({H–***C***$_{Ar}$}Ce$^+$), 129.7({H–***C***$_{Ar}$}Ce), 126.0 (B{***C***$_6$H$_5$}$_4$), 125.8 (–N=CH–***C***$_{Ar}$), 122.3 (B{***C***$_6$H$_5$}$_4$), 62.2 (N{***C***H$_2$–CH$_2$–N=CH–Ar}$_3$Ce), 56.0 (N{CH$_2$–***C***H$_2$–N=CH–Ar}$_3$Ce), 35.4 (–***C***Me$_3$), 34.7 (–***C***Me$_3$), 31.8 (–C(***C***H$_3$)), 30.3 (–C(***C***H$_3$)). **IR** (KBr): $\tilde{\nu}_{max}$ = 3432 (w), 3056 (m), 3036 (w), 2960 (st, ν_s CH$_3$), 2906 (m, ν_s CH$_2$), 2868 (m, ν_{as} CH$_3$), 1615 (vs, C=N), 1580 (w), 1558 (m, C=C ring), 1544 (m), 1478 (m), 1459 (m), 1435 (m), 1412 (m), 1391 (m), 1362 (m), 1333 (m), 1270 (st), 1252 (vs), 1200 (m), 1177 (m), 1135 (w), 1062 (w), 1033 (w), 979 (w), 908 (w), 879 (w), 837 (st, CH ring), 811 (w), 776 (w), 745 (st), 734 (m), 706 (m), 613 (w), 531 (m), 453 (w), 416 (w) cm^{-1}. **MS** (EI, 140Ce): *m/z* (%) 931.7 (100) [M – BPh$_4$]$^+$.

Supporting Information (see footnote on the first page of this article): ORTEP drawings and X-ray structural data as well as complete CIF files for **2** and **3**. Crystallographic data for the crystal structures reported in this paper can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/) by referring to the CIF deposition codes CCDC-793139 (**2**) and 793138 (**3**).

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