Angewandte
Zuschriften

Multiple Bonding

DOI: 10.1002/ange.201306984

A Cerium(IV)–Carbon Multiple Bond**

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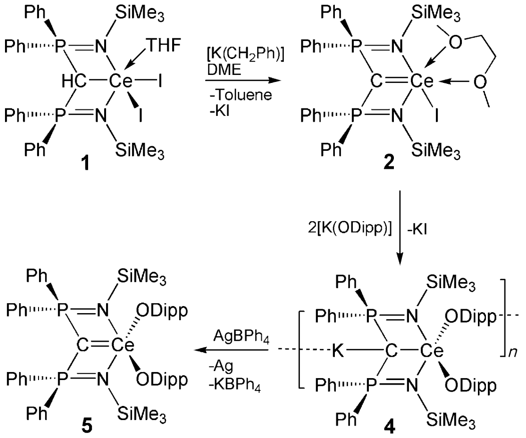
Metal–ligand multiple bonding is a central chemical concept,[1] but one area that is not well-developed is that of the lanthanides.[2] This has been rationalized on the basis that lanthanide 4f valence orbitals are "core-like" and thus chemically inaccessible. Also, lanthanide 5d orbitals are considered too high in energy to engage in bonding with ligand frontier orbitals. Thus, the bonding of lanthanides is characterized as principally ionic and highly polarized, rendering lanthanide–ligand multiple bonds labile and difficult to stabilize. Where lanthanide carbenes with formal covalent double bonds are concerned,[3] the most successful strategy has involved carbenes with chelating phosphorano arms, for example, $[C(PPh_2NR)_2]^{2-}$ (R = SiMe$_3$, BIPM^{TMS}) or $[C(PPh_2S)_2]^{2-}$, which provide electronic stabilization, steric protection, and pin the carbene to the metal through multidentate coordination. Where phosphorano-free lanthanide carbenes have been prepared- the carbon center bridges multiple metal ions to stabilize the charge accumulation.[4]

All lanthanide carbenes possessing a degree of covalency in a twofold bonding interaction utilize trivalent lanthanides.[3] One strategy not yet investigated is the use of tetravalent lanthanides. However, this approach suffers from the fact that accessing tetravalent lanthanides is far from trivial,[5] as the fourth ionization energy typically exceeds the sum of the first three ionization energies. Although a limited number of lanthanide tetrafluorides are known, the only lanthanide that it is realistic to obtain in the tetravalent oxidation state in a molecular context is cerium.[6] However, although cerium(IV) has many applications in materials science and industrial catalysis, and is well known in inorganic salts, for example CeO$_2$, CeF$_4$, and $[Ce(NO_3)_6][NH_4]_2$ (CAN), it is difficult to stabilize in a organometallic context because hydrocarbyl ligands are intrinsically reducing and cerium(IV) is oxidizing ($E^o(Ce^{IV/III}) = +1.7$ V (vs SHE) in 1 M HClO$_4$).[7] Also, attempts to oxidize neutral cerium(III) complexes are often plagued by unpredictable decomposition reactions that also afflict CAN-based syntheses.[8] To date, RO^-[9] or R_2N^-[10] ligands have been the overwhelming choice for stabilizing cerium(IV). For organometallics,[6] cyclopentadienyl and cerocene derivatives dominate, and the only examples of σ-bonded hydrocarbyls involve datively bound *N*-heterocyclic carbenes.[11] Thus, cerium(IV)–carbon multiple bonds are yet to be reported. Indeed, in a wider context there are no examples of any lanthanide(IV)–element multiple bonds.

Herein, we report a lanthanide(IV)–element multiple bond through the synthesis of a cerium(IV) carbene. Our strategy combined a heteroatom-stabilized carbene BIPM^{TMS} and sterically demanding aryloxide ligands, with a new approach of effecting one-electron oxidation of an electron-rich cerium(III) "ate" precursor (Scheme 1).



Scheme 1. Synthesis of compound **5**.

We began[12] by preparing the colorless cerium(III)-methanide $[Ce(BIPM^{TMS}H)(I)_2(THF)]$ (**1**) from $[Ce(I)_3(THF)_4]$ and $[Rb(BIPM^{TMS}H)]$ (89% yield), and treated it with benzyl potassium to afford the cerium(III)–carbene $[Ce(BIPM^{TMS})(I)(DME)]$ (**2**) as a colorless powder (72% yield). Treatment of **2** with one equivalent of [K(ODipp)] (Dipp = 2,6-diisopropylphenyl) affords the yellow cerium(III) carbene aryloxide $[Ce(BIPM^{TMS})(ODipp)(THF)]$ (**3**, 35% yield), which when treated with a further equivalent of [K(ODipp)] affords the "ate" cerium(III) carbene bis(aryloxide) $[\{Ce(BIPM^{TMS})(ODipp)_2K(THF)\}_\infty]$ (**4**) as yellow crystals (70% yield). Complex **4** can more conveniently be prepared directly from **2** and two equivalents of [K(ODipp)], because **3** is unstable in solution and decomposes surprisingly easily. The solid-state structure of **4** is itself notable because infinite polymeric chains are constructed through multihapto potassium···arene interactions, and the central carbon adopts a highly unusual distorted planar four-coordinate geometry.[12,13] With **4** in hand, we reasoned that the electron-rich "ate" formulation would promote straightforward removal of

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[**] We thank the Royal Society, the Engineering and Physical Sciences Research Council, the European Research Council, and the University of Nottingham for generously supporting this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306984.

the 4f-electron, thereby avoiding the unpredictable side-reactions of neutral cerium(III)-compound oxidations.[8]

Treatment of **4** with one equivalent of $AgBPh_4$ resulted in elimination of Ag^0 and $KBPh_4$ to give, after work-up and recrystallization, dark purple crystals of the cerium(IV) carbene bis(aryloxide) $[Ce(BIPM^{TMS})(ODipp)_2]$ (**5**, 28% yield).[12] To enable comparison of cerium(III)–carbene and cerium(IV)–carbene bond lengths in a $BIPM^{TMS}$-bis(aryloxide) environment, we prepared colorless $[Ce(BIPM^{TMS}H)(ODipp)_2(THF)]$ (**6**) from **1** and two equivalents of $[K(ODipp)]$ (19% crystalline yield).[12]

The ^1H NMR spectrum of **5** spans the range $\delta = +0.4$ to $+7.5$ ppm and exhibits eight sharp resonances consistent with C_s symmetry on the NMR timescale. The carbene center, located definitively by a ^{13}C–^{31}P 2D NMR correlation experiment, appears in the ^{13}C NMR spectrum as a triplet at $\delta = 324.6$ ppm ($J_{PC} = 148.7$ Hz). The carbene nature is thus confirmed by this downfield chemical shift, which is well within the 200–400 ppm range of covalent transition-metal carbenes[14] and at much higher frequency than ionic yttrium(III) analogues ($\delta = 10$–40 ppm).[3e] The ^{31}P and ^{29}Si NMR spectra exhibit sharp resonances at $\delta = -10.2$ and -3.5 ppm, respectively. These data are in line with the diamagnetic formulation of **5**.

The molecular structure of **5** is shown in Figure 1.[15] The salient feature of **5** is a monomeric formulation with a terminal M=C bond. The remaining coordination sphere of cerium is composed of the two $BIPM^{TMS}$ imino chelate arms and the two aryloxide oxygen centers, which enforce a pseudo square-based pyramidal geometry that is distorted principally by the bite angle of the $BIPM^{TMS}$ ligand (ca. 121°). In **5**, the cerium(IV)–carbene distance was determined to be 2.441(5) Å, which is one of the shortest molecular cerium–carbon distances on record. This is equaled only in the special case of cerium confined in an endohedral fullerene with a Ce–C distance of 2.436(6) Å.[16] Indeed, the Ce=C bond distance in **5** is shorter than all the other cerium–carbon bond distances in this study (Ce–C: 2.539(2)–2.810(2) Å), is about 0.3 Å shorter than dative cerium(IV)–*N*-heterocyclic carbene distances,[11] and shorter than Ce^{III}–C_{alkyl} distances, which average 2.6 Å.[17] In the context of $BIPM^{TMS}$, a cerium(III)–carbene bond distance of 2.472(4) Å has been reported in $[Ce(BIPM^{TMS})(BIPM^{TMS}H)]$,[18] but here the carbene is planar whereas in **5** the carbene is pyramidalized ($\Sigma\angle = 322.7(3)°$), which accounts for the only marginally shorter Ce=C distance in **5**. Theoretically, a Ce=C distance of 2.127 Å was computed for $[Ce(CH_2)(\eta^5\text{-}C_5H_5)_2]$,[19] but this complex is sterically unencumbered and is not experimentally validated.

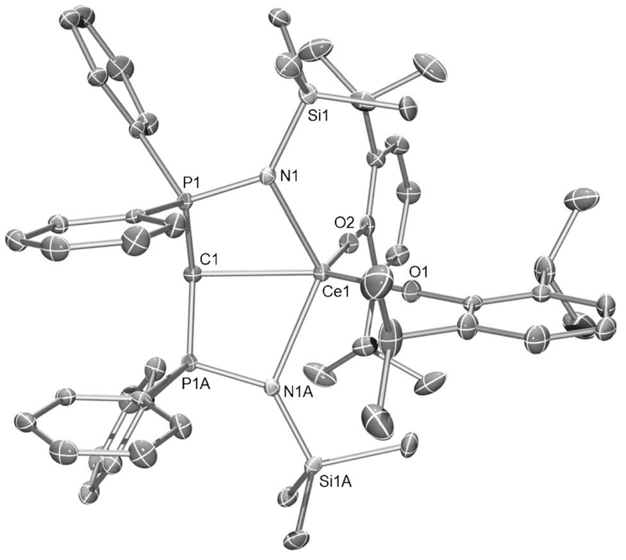

Figure 1. Molecular structure of $[Ce(BIPM^{TMS})(ODipp)_2]$ (**5**) with ellipsoids set at 40% probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å]: Ce1–C1 2.441(5), Ce1–N1 2.374(3), Ce1–N1A 2.374(3), Ce1–O1 2.137(4), Ce1–O2 2.130(4), C1–P1 1.692(2), C1–P1A 1.692(2), P1–N1 1.626(3), P1A–N1A 1.626(3).

The UV/Vis/NIR electronic absorption spectrum of **5** was examined in the range 5000–53000 cm^{-1}.[12] The NIR region is featureless and thus void of f→f transitions, as expected for a $4f^0$ cerium(IV) center. The visible region is dominated by minor and major absorptions centered at 23000 and 18500 cm^{-1} ($\varepsilon = 4560$ and 5365 $L\,mol^{-1}\,cm^{-1}$); the latter band is principally responsible for the purple color of **5**, as it falls in the green range of the electromagnetic spectrum. To understand the electronic transitions responsible for the purple color of **5**, we modeled the spectrum using TD-DFT calculations at the SAOP/ZORA/TZP level. The profile of the experimental spectrum is reproduced well by the TD-DFT calculations. The absorption band at 23000 cm^{-1} arises principally from LMCT from the *N*-imino lone pairs to cerium 4f orbitals. The broad absorption band at 18500 cm^{-1} is a composite of several transitions principally derived from LMCT from the Ce=C π- and σ-combinations to cerium(IV) 4f-orbitals.

A preliminary reactivity study of **5** shows that it reacts with 9-anthracene carboxaldehyde and benzaldehyde to afford the metallo-Wittig alkene products $RC(H)=C(PPh_2NSiMe_3)_2$ (R = phenyl or 9-anthracene).[20] This reaction is presumably accompanied by the formation of "$[Ce(O)(ODipp)_2]$", but we could not isolate the cerium byproduct. Metallo-Wittig reactivity provides experimental support for the carbene formulation of **5** with some covalent character; yttrium(III) $BIPM^{TMS}$ analogues, which are known to be highly ionic,[3d] engage in C–H activation reactions with aryl–carbonyl compounds, whereas uranium $BIPM^{TMS}$ analogues, which are known to be more covalent,[20b,c] engage exclusively in metallo-Wittig reactivity.

As the experimental data suggest some covalency in the Ce=C linkage of **5**, we computationally probed the ground-state electronic nature of **5**. The DFT geometry-optimized structure agrees well with experiment, with bond lengths and angles computed to within 0.03 Å and 2° of experiment. The overlap population density of states (DOS) diagram for **5** shows maximum overlap populations between the cerium and carbene center of about 0.04 per orbital. For comparison, the calculated maximum overlap populations per orbital between the carbon atoms in ethene are about 0.2 for those orbitals involved in the C=C bond.[12] Thus, the overlap populations in **5** suggest that the cerium–carbon interaction is predominantly electrostatic and that covalent interactions contribute only modestly to the cerium–carbon interaction. For **5**, HOMO and HOMO−1 are primarily centered on the aryloxide

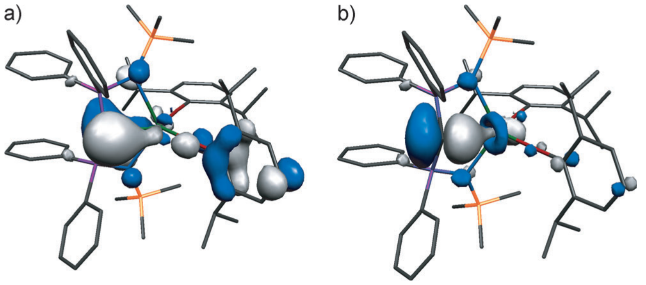

Figure 2. Selected Kohn Sham orbitals for [Ce(BIPM^{TMS})(ODipp)$_2$] (**5**). a) HOMO−2 (272, −5.011 eV); b) HOMO−3 (271, −5.189 eV).

aromatic rings. HOMO−2 and HOMO−3 correspond to the principal π- and σ-interactions in the Ce=C unit (Figure 2).[12] The Ce=C interaction is polarized as evidenced by a Nalewajski–Mrozek bond order of 1.1, which compares to bond orders of 1.2–1.5 for BIPM-uranium carbenes,[20] whereas ionic yttrium(III)–BIPM complexes return bond indices of about 0.7.[3e] Noting that calculated charges are difficult to partition, donation of ligand electron density to cerium in **5** is suggested by charges of +1.91 and −1.47 for the cerium and carbene atoms.

We also performed NBO analyses as this method is suited to assessing covalency in molecules.[21] For **5**, NBO analysis reveals a σ-combination composed of 13 % cerium and 87 % carbon character. The carbon σ-component contains 12 % 2s and 88 % 2p character, whereas the cerium component is constructed from 3 % 6s, 21 % 5d, and 76 % 4f character. The π-component is composed of 12 % cerium and 88 % carbon character; the latter is predominantly 2p-character (98 %), with only a minor 2s (2 %) contribution reflecting the π-nature of this interaction. The cerium component of the π-combination comprises 1 % 6p, 19 % 5d, and 80 % 4f character.

To further analyze the Ce=C bond in **5** we employed Bader's atoms in molecules to analyze the topological electron density [$\rho(\mathbf{r})$], the Laplacian of the electron density [$\nabla^2\rho(\mathbf{r})$], and the electronic energy density $H(\mathbf{r})$ of the charge distribution (defined as $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$, where $G(\mathbf{r})$ is the kinetic energy density and $V(\mathbf{r})$ is the potential energy). For **5**, the Ce=C bond critical point (BCP) values for $\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, $G(\mathbf{r})$, $V(\mathbf{r})$, and $H(\mathbf{r})$ are 0.074, 0.155, 0.046, −0.054, and −0.008, respectively. These BCP values support the predominantly ionic bonding picture as suggested by the DOS analysis but hint at a bond with a minor covalent component as suggested by the DFT and NBO analyses. Importantly, the calculated ellipticity parameter for the Ce=C bond is 0.32. For a cylindrical σ-bond the ellipticity is 0, and for a bond with a π-contribution the ellipticity is >0. For example, the ellipticity values for the C−C bonds in ethane, benzene, and ethene are calculated to be 0.0, 0.23, and 0.45, respectively.[22] Thus, the ellipticity value for **5** is intermediate to that of benzene and ethene and suggests that the bonding between the cerium(IV) and carbene centers in **5** is composed of σ- *and* π-components, and therefore a two-fold multiple bonding interaction involving two electron pairs.

Previous studies have focused on cerium(IV) amide and aryl/alkoxide linkages, and our isolation of **5** is the first example of a cerium(IV) compound that may demonstrate cerium(IV)–carbon σ- and π-multiple bonding character. Our calculations suggest that cerium(IV) may employ its 4f-orbitals to engage in multiple bonding interactions with carbon, with only modest d contributions. This can be rationalized on the basis that whilst the 5d-orbitals are too high in energy to engage in bonding with ligand frontier orbitals, donation of electron density from the carbene, a strongly nucleophilic entity,[3] to empty 4f-orbitals will raise their energies resulting in 4f radial expansion and better metal–ligand orbital overlap.[19] The apparent use of predominantly f- instead of d-orbitals accounts for the mainly electrostatic nature of cerium(IV)–ligand linkages compared to transition metals,because 4f-orbitals are highly angular and therefore usually do not achieve as effective spatial overlap with ligand frontier orbitals when compared to d-orbitals. Thus, a two-fold multiple bonding interaction involving two electron pairs between cerium(IV) and carbon results in a bond order that deviates substantially below two,[23] and a polarized linkage that is commensurate with the previous paucity of tetravalent lanthanide–element multiple bonds.

To summarize, by oxidizing an anionic "ate" precursor we have effected facile access to the first example of a formal cerium(IV)–ligand multiple bond interaction, thus avoiding the deleterious side-reactions that plague the oxidations of neutral cerium(III) compounds. Whilst the bonding is clearly predominantly electrostatic in this cerium(IV)–carbene, which contains the first examples of formal polarized-covalent cerium(IV)-carbon σ- and π-multiple bond interactions, theoretical calculations suggest a modest covalent component in the Ce=C bond in a model that is consistent with the spectroscopic and reactivity data.

Experimental Section

5: Toluene (15 mL) was added to a precooled (−78 °C) mixture of **4** (0.58 g, 0.5 mmol) and $AgBPh_4$ (0.21 g, 0.5 mmol). The yellow suspension was allowed to warm to room temperature with stirring over 16 h to give a purple suspension. The suspension was filtered and volatiles were removed in vacuo to afford a sticky purple solid. Recrystallisation from Et_2O (2 mL) at −30 °C afforded **5**·Et_2O as purple crystals. Yield: 0.16 g, 28 %. Anal. calcd (%) for $C_{59}H_{82}CeN_2O_3P_2Si_2$: C 62.95, H 7.35, N, 2.49 %; found: C 63.09, H 6.99, N 2.72 %. ^{1}H NMR (C_6D_6): $\delta = 0.43$ (18 H, s, NSi(CH_3)$_3$), 1.23 (6 H, t, $^3J_{HH} = 7.20$ Hz, OCH$_2$CH_3), 1.48 (24 H, d, $^3J_{HH} = 6.80$ Hz, CH(CH_3)$_2$), 3.38 (4 H, q, $^3J_{HH} = 7.20$ Hz, OCH_2CH$_3$), 4.00 (4 H, spt, $^3J_{HH} = 6.80$ Hz, CH(CH$_3$)$_2$), 7.00 (2 H, t, $^3J_{HH} = 7.60$ Hz, *p*-Dipp-*H*), 7.05 (4 H, d, *p*-Ar-*H*), 7.07 (8 H, s, *o*-Ar-H), 7.40 (4 H, d, $^3J_{HH} = 8.00$ Hz, *p*-Dipp-*H*), 7.53 ppm (8 H, m, *o*-Ar-H). ^{13}C NMR (C_6D_6): $\delta = 3.74$ (NSi(CH$_3$)$_3$), 15.34 (OCH$_2$$CH_3$), 24.30 (CH($CH_3$)$_2$), 27.45 ($C$H(CH$_3$)$_2$), 65.65 (O$CH_2CH_3$), 120.36 (*p*-Dipp), 122.52 (*m*-Dipp), 127.95 (*m*-Ar-*C*), 130.38 *o*-Ar-*C*), 132.04 (*p*-Ar-*C*), 137.17 (*o*-Dipp), 138.36 (*i*-Ar-*C*), 166.26 (*i*-Dipp), 324.63 ppm (t, $J_{PC} = 148.7$ Hz, CeCP$_2$). ^{31}P{^{1}H} NMR (C_6D_6): $\delta = -10.15$ ppm (CeCP_2). ^{29}Si{^{1}H} NMR (C_6D_6): $\delta = -3.47$ ppm (NSi(CH$_3$)$_3$). FTIR (Nujol): $\tilde{\nu} = 2360$ (w), 2341 (w), 1589 (w), 1403 (w), 1325 (w), 1198 (s), 855 (w), 748 cm^{-1} (w).

Received: August 8, 2013

Keywords: carbenes · cerium · density functional theory · lanthanides · multiple bonding

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[15] Crystal data for **5**: $C_{59}H_{82}CeN_2O_3P_2Si_2$, $M_r = 1125.5$, space group *Pnma*, $a = 18.505(2)$, $b = 17.021(2)$, $c = 19.022(2)$, $V = 5991.5(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.248\ g\,cm^{-3}$; $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 0.895\ mm^{-1}$, $T = 90$ K. 61651 data (7211 unique, $R_{int} = 0.052$, $\theta < 55.9°$). Data were collected on a Bruker SMART APEX CCD diffractometer and were corrected for absorption (transmission 0.16–0.43). The structure was solved by direct methods and refined by full-matrix least-squares on all F^2 values to give $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1158$, conventional $R = 0.0523$ for F values of 7211 with $F_o^2 > 2\sigma(F_o^2)$, $S = 1.089$ for 349 parameters. Residual electron density extrema were 2.77 and $-1.27\ e\,$Å^{-3}. CCDC 938903 (**5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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