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## Cerium–quinone redox couples put under scrutiny†

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Homoleptic cerous complexes  $\text{Ce}[\text{N}(\text{SiMe}_3)_2]_3$ ,  $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_2]_2$  and  $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_2]_2$  were employed as thermally robust, weakly nucleophilic precursors to assess their reactivity towards 1,4-quinones in non-aqueous solution. The strongly oxidizing quinones 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or tetrachloro-1,4-benzoquinone ( $\text{Cl}_4\text{BQ}$ ) readily form hydroquinolato-bridged ceric complexes of the composition  $[(\text{Ce}^{\text{IV}}\text{L}_3)_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)]$ . Less oxidising quinones like 2,5-di-*tert*-butyl-1,4-benzoquinone ( $\text{tBu}_2\text{BQ}$ ) tend to engage in redox equilibria with the ceric hydroquinolato-bridged form being stable only in the solid state. Even less oxidising quinones such as tetramethyl-1,4-benzoquinone ( $\text{Me}_4\text{BQ}$ ) afford cerous semiquinolates of the type  $[(\text{Ce}^{\text{III}}\text{L}_2(\text{thf})_2)(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)]_2$ . All complexes were characterised by X-ray diffraction,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{29}\text{Si}$  NMR spectroscopy, DRIFT spectroscopy, UV-Vis spectroscopy and CV measurements. The species putatively formed during the electrochemical reduction of  $[\text{Ce}^{\text{IV}}\{\text{N}(\text{SiMe}_3)_2\}_2]_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)$  could be mimicked by chemical reduction with  $\text{Co}^{\text{II}}\text{Cp}_2$  yielding  $[(\text{Ce}^{\text{III}}\{\text{N}(\text{SiMe}_3)_2\}_2)_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)][\text{Co}^{\text{III}}\text{Cp}_2]_2$ .

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## Introduction

Quinones are multifunctional organic molecules exhibiting intriguing redox behaviour.<sup>1,2</sup> Of particular note is their importance in biological electron-transfer processes (photosynthesis, respiration)<sup>3</sup> and in industrial catalysis (anthraquinone process for hydrogen peroxide production).<sup>4</sup> Quinones can engage in one or two electron redox processes involving the formation of either semiquinolates or hydroquinolates.<sup>5</sup> Strikingly, the reduction potential of 1,4-benzoquinones (*para*-benzoquinones) can easily be modified by introducing electron-withdrawing or donating substituents into the benzene ring.<sup>5,6</sup> As a consequence, tetrachloro-1,4-benzoquinone (chloranil,  $\text{Cl}_4\text{BQ}$ ) and even more so 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) emerged as efficient oxidants in organic synthesis.<sup>7</sup> DDQ has been further successfully applied in photoredox catalysis.<sup>8</sup> Moreover, anionic  $\eta^4$ -1,4-benzoquinone manganese tricarbonyl features a quinoid  $\pi$ -complex, broadly used for the fabrication of supramolecular metal–organometallic coordination networks.<sup>9</sup> Relatedly, deprotonated variants of 2,5-dihydroxy-1,4-benzoquinone (DHBQ) were shown to act

as rigid ditopic linkers,<sup>10</sup> e.g., to support the formation of pentagonal dodecahedral  $\text{Ce}_2(\text{H}_2\text{O})_{18}$  cages or in permanently porous aluminium frameworks.<sup>11</sup> DHBQ was also probed as a bridging redox-active ligand in bimetallic  $[\text{LnCl}_2(\text{thf})_3]_2(\mu\text{-bobq})$  ( $\text{Ln} = \text{Y}, \text{Dy}$ ;  $\text{bobq} = 2,5\text{-bisoxide-1,4-benzoquinolato}$ ) to build single-molecule magnets.<sup>12</sup> More recently, the related semiquinolato radical-bridged dimeric complexes  $[\text{LnCl}_2(\text{thf})_3(\mu\text{-Me}_4\text{sq})_2]_2$  ( $\text{Ln} = \text{Y}, \text{Gd}$ ) were obtained by oxidation of the corresponding *in situ* formed hydroquinolate complexes with  $\text{FeCl}_3$ .<sup>13</sup> Semiquinolato-bridged scandium(III) species were reported to promote self-organised electron transfer from d-transition metals (Ir, Fe) to 1,4-quinones.<sup>14,15</sup>

Targeted metal-redox chemistry with quinones has been a recurring issue for the rare-earth-metal couples  $\text{Ln}(\text{II})/\text{Ln}(\text{III})$ <sup>16</sup> and  $\text{Ce}(\text{III})/\text{Ce}(\text{IV})$ .<sup>17</sup> Especially in the case of molecular cerium chemistry,<sup>17</sup> its unique single-electron-transfer (SET) pathway has recently been extended beyond the traditional application of ceric ammonium nitrate (CAN; redox potential of 1.61 V vs. NHE) in organic synthesis<sup>18</sup> to photoredox catalysis.<sup>19</sup> On the other hand, redox protocols are known to provide efficient access to metalorganic  $\text{Ce}^{\text{IV}}$  complexes. Typically, such  $\text{Ce}^{\text{III}} \rightarrow \text{Ce}^{\text{IV}}$  transformations are promoted by halogenating oxidants (e.g.  $\text{C}_2\text{Cl}_6$ ,  $\text{Ph}_3\text{CCl}$ ,  $\text{PhICl}_2$ ,  $\text{TeCl}_4$ ,  $\text{FcPF}_6$ ,  $\text{FcBF}_4$ ,  $\text{Ph}_3\text{CBF}_4$ ,  $\text{Ph}_3\text{CPF}_6$ ,  $\text{I}_2$ ),<sup>20</sup> silver salts ( $\text{AgX}$ ,  $\text{X} = \text{F}, \text{I}, \text{BF}_4, \text{OTf}$ )<sup>21</sup> or dioxygen.<sup>20b,22</sup>

Archetypical 1,4-benzoquinone (BQ) has been established as a versatile oxidant for the synthesis of homoleptic ceric complexes  $\text{CeL}_4$  from cerous ate complexes  $[\text{CeL}_4\text{M}(\text{do})_x]$  via tandem oxidation-ligand redistribution protocols ( $\text{L} =$

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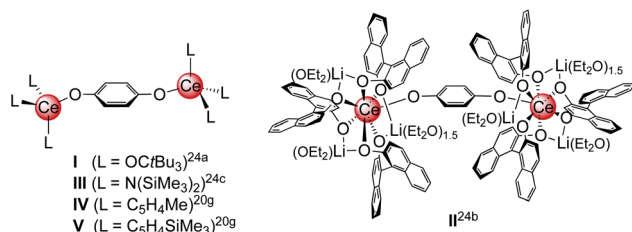


Chart 1 Structurally characterised dicerium(IV) hydroquinolate complexes (I–V),<sup>20g,24</sup> obtained *via* oxidation of cerous precursor with BQ.

monoanionic ligand, M = alkali metal and do = donor solvent; separation of an alkali-metal hydro-/semiquinolato).<sup>23</sup> In the presence of sterically demanding ligands L, BQ was also shown to form hydroquinolato (hq)–bridged ceric complexes of the general composition [L<sub>3</sub>Ce–OC<sub>6</sub>H<sub>4</sub>O–CeL<sub>3</sub>].<sup>20g,24</sup> This very Ce<sup>III</sup> → Ce<sup>IV</sup> transformation was pioneered by Sen *et al.* in 1992, resulting in the isolation of [(*t*Bu<sub>3</sub>CO)<sub>3</sub>Ce(OC<sub>6</sub>H<sub>4</sub>O)Ce(OC*t*Bu<sub>3</sub>)<sub>3</sub>] (Chart 1, I).<sup>24a</sup> In the same paper, the oxidation of Ce(OC*t*Bu<sub>3</sub>)<sub>3</sub> with 2,6-di-*tert*-butyl-1,4-benzoquinone to the terminal Ce<sup>IV</sup>-semiquinolato radical (*t*Bu<sub>3</sub>CO)<sub>3</sub>Ce(O<sub>2</sub>C<sub>6</sub>H<sub>2</sub>*t*Bu<sub>2</sub>) was described as evidenced by <sup>1</sup>H NMR and EPR spectroscopic measurements.<sup>24a</sup> More recently, Schelter *et al.* reported on hq-bridged complex II resulting from the oxidation of cerous Ce(BINolate)<sub>3</sub>(thf)Li<sub>3</sub>(thf)<sub>4</sub> with 0.5 equivalents of BQ.<sup>24b</sup> Similarly, our group synthesized [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>3</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)<sup>24c</sup> (III) and (CeCp<sup>R</sup>)<sub>3</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (Cp<sup>R</sup> = C<sub>5</sub>H<sub>4</sub>Me (IV) and C<sub>5</sub>H<sub>4</sub>(SiMe<sub>3</sub>) (V)).<sup>20g</sup> In contrast, the reaction of BQ with [Ce(Me<sub>2</sub>pz)<sub>3</sub>]<sub>x</sub> featuring the sterically less demanding and increasingly nucleophilic 3,5-dimethylpyrazolato ligand (Me<sub>2</sub>pz) led in fact to a transient Ce<sup>IV</sup> hydroquinolate species (as indicated by the characteristic colour change), which, however, at ambient temperature was converted into the isolable trimetallic Ce<sup>III</sup>

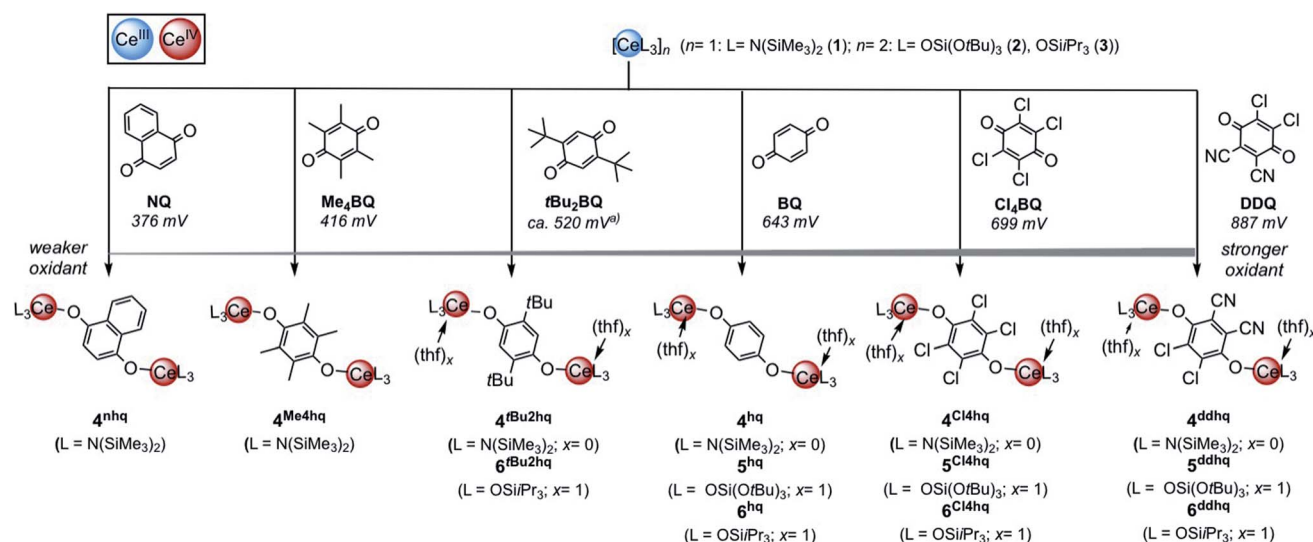
complex Ce<sub>3</sub>(pchd)<sub>2</sub>(Me<sub>2</sub>pz)<sub>5</sub>(thf)<sub>2</sub> (pchd = 1,4-bis(3,5-dimethylpyrazol-1-yl)cyclohex-2,5-diene-1,4-diolato).<sup>23c</sup> Apparently, the new pchd ligand formed *via* 1,4-nucleophilic attack at bq by two adjacent Me<sub>2</sub>pz ligands. This nucleophilic reaction pathway could be prevented by using bulky *t*Bu groups on the pz ligand, but homoleptic Ce(*t*Bu<sub>2</sub>pz)<sub>4</sub> was formed as the main ceric product *via* irreversible ligand rearrangement.<sup>23c</sup>

As such, cerium-1,4-benzoquinone couples have revealed distinct redox chemistry, we became curious about as to what extent such redox transformations are affected by both the type of 1,4-benzoquinone oxidant and the molecular Ce<sup>III</sup> precursor. The present study uncovers some unexpected correlation between Ce<sup>IV</sup>–hydroquinolato stabilisation and quinone oxidant strength, as well as a new path to *p*-semiquinolato-radical-bridged rare-earth-metal complexes.

## Results and discussion

### Molecular redox precursors

The quinones used in this study comprise 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), tetrachloro-1,4-benzoquinone (Cl<sub>4</sub>BQ), 1,4-benzoquinone (BQ), tetramethyl-1,4-benzoquinone (Me<sub>4</sub>BQ), 2,5-di-*tert*-butyl-1,4-benzoquinone (*t*Bu<sub>2</sub>BQ), 1,4-naphthoquinone (NQ), and 9,10-anthraquinone (AQ). All are commercially available and were selected according to their reduction potentials spanning a *E*<sup>0</sup> range of 89 to 887 mV (2e<sup>−</sup>/2H<sup>+</sup>, *vs.* NHE, *cf.*, Scheme 1).<sup>5,25</sup> The cerous precursors were chosen according to the criteria solubility, weak nucleophilicity, proven access to the tetravalent state, and a stabilizing effect on the latter. Furthermore, the use of sterically bulky ligands was assumed to minimise the occurrence of ligand redistribution reactions. Accordingly, homoleptic Ce [N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (1) appeared to be an ideal benchmark system.<sup>24c</sup> After additional investigations into the respective pyrazolate



Scheme 1 Oxidation of trivalent cerium complexes with 1,4-quinone derivatives under formation of hydroquinolato-bridged ceric complexes. To enable better assessment of the relative oxidation ability 2e<sup>−</sup>/2H<sup>+</sup> reductions potentials are given in mV *versus* NHE according to ref. 5. (a) Calculated value.

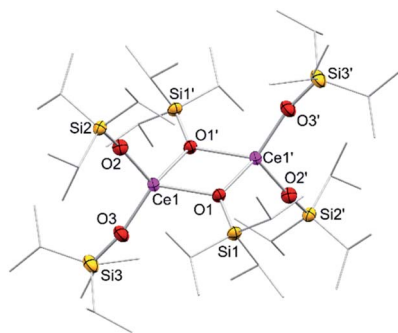


Fig. 1 Crystal structure of  $[\text{Ce}(\text{OSiPr}_3)_3]_2$  (**3**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ce1–O1 2.3951(12), Ce1–O2 2.1659(14), Ce1–O3 2.1671(14); Ce1–O2–Si2 163.03(9), Ce1–O3–Si3 167.40(10).

chemistry, the abovementioned  $[\text{Ce}(\text{R}_2\text{pz})_3]$  ( $\text{R} = \text{Me}, t\text{Bu}$ ) were discarded because of persisting alternative reaction pathways like 1,4-nucleophilic attack of BQ by  $\text{Me}_2\text{pz}$  and ligand redistribution (formation of  $\text{Ce}(t\text{Bu}_2\text{pz})_4$ ).<sup>23c</sup> The new pyrazolate studies clearly confirmed that steric hindrance of both the pyrazolato ligand and the 1,4-benzoquinone can minimise/counteract such undesired reactions, but the formation of product mixtures seems inevitable. Products crystallised from these reactions include minor amounts of ceric  $[\text{Ce}(t\text{Bu}_2\text{pz})_3(\text{thf})]_2(\text{Me}_4\text{hq})$  or a cerous product of partial pyrazolyl-promoted nucleophilic attack  $\text{Ce}_3(\text{bpad})(\text{pasq})(\text{Me}_2\text{pz})_6(\text{thf})$  ( $\text{bpad} = 1,4\text{-bis}(3,5\text{-dimethylpyrazol-1-yl})\text{anthra-1,4-diolato}$ ;  $\text{pasq} = 1\text{-(3,5-dimethylpyrazol-1-yl)anthra-1,4-semiquinolato}$ ) (84%) mixed with semiquinolato  $[\text{Ce}(\text{Me}_2\text{pz})_2(\text{thf})_2(\text{asq})]_2$  ( $\text{asq} = \text{anthra-semiquinolato}$ ; cf. ESI† for structural details). The use of  $\text{Ce}^{\text{III}}$  halides was discarded mainly for solubility issues.

In addition to silylamide **1**, the siloxide derivatives  $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_2]$  (**2**)<sup>21d,26</sup> and  $[\text{Ce}(\text{OSi}^i\text{Pr}_3)_3]_2$  (**3**) were assessed as suitable cerous precursors. Complexes **2** and **3**, with and without intramolecular donor site, respectively, were readily obtained in pure form *via* protonolysis of **1** with the corresponding silanol.<sup>26</sup> The crystal structure of the new complex **3** revealed a dimeric arrangement with two  $\mu_2$ -bridging and four terminal siloxy groups (Fig. 1), similar to that found for tris(*tert*-butoxy)siloxy congener **2** or  $[\text{Ce}(\text{OSiPh}_3)_3]_2$ <sup>27</sup> or  $[\text{Ce}(\text{OCH}t\text{Bu}_2)_3]_2$ .<sup>28</sup> The Ce–O<sub>terminal</sub> (2.1659(14) and 2.1671(14) Å) and the Ce–O <sub>$\mu_2$</sub>  distances (2.3951(12) and 2.4030(12) Å) of **3** are slightly shorter than those in **2** (Ce–O<sub>terminal</sub> 2.202(3), 2.186(3) Å; Ce–O <sub>$\mu_2$</sub>  2.532(2) Å) and  $[\text{Ce}(\text{OSiPh}_3)_3]_2$  (Ce–O<sub>terminal</sub> 2.141(7), 2.185(6) Å; Ce–O <sub>$\mu_2$</sub>  2.345(6), 2.583(5) Å) reflecting the lower coordination number (CN 4 vs. 5), but slightly longer than in  $[\text{Ce}(\text{OCH}t\text{Bu}_2)_3]_2$  (Ce–O<sub>terminal</sub> 2.142(2), 2.152(3) Å; Ce–O <sub>$\mu_2$</sub>  2.363(3) Å).<sup>28</sup> The <sup>1</sup>H NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  shows two singlets at –28.82 and –17.23 ppm for the  $\mu_2$ -OSi<sup>*i*</sup>Pr<sub>3</sub> groups and two singlets at 6.46 and 9.09 ppm for the terminal siloxy ligands indicating a non-fluxional dimeric species in non-coordinating solvents. When recorded in  $\text{THF-}d_8$ , only two signals for the OSi<sup>*i*</sup>Pr<sub>3</sub> groups appeared, in accordance with the formation of a monomeric adduct  $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf-}d_8)_x]$ .

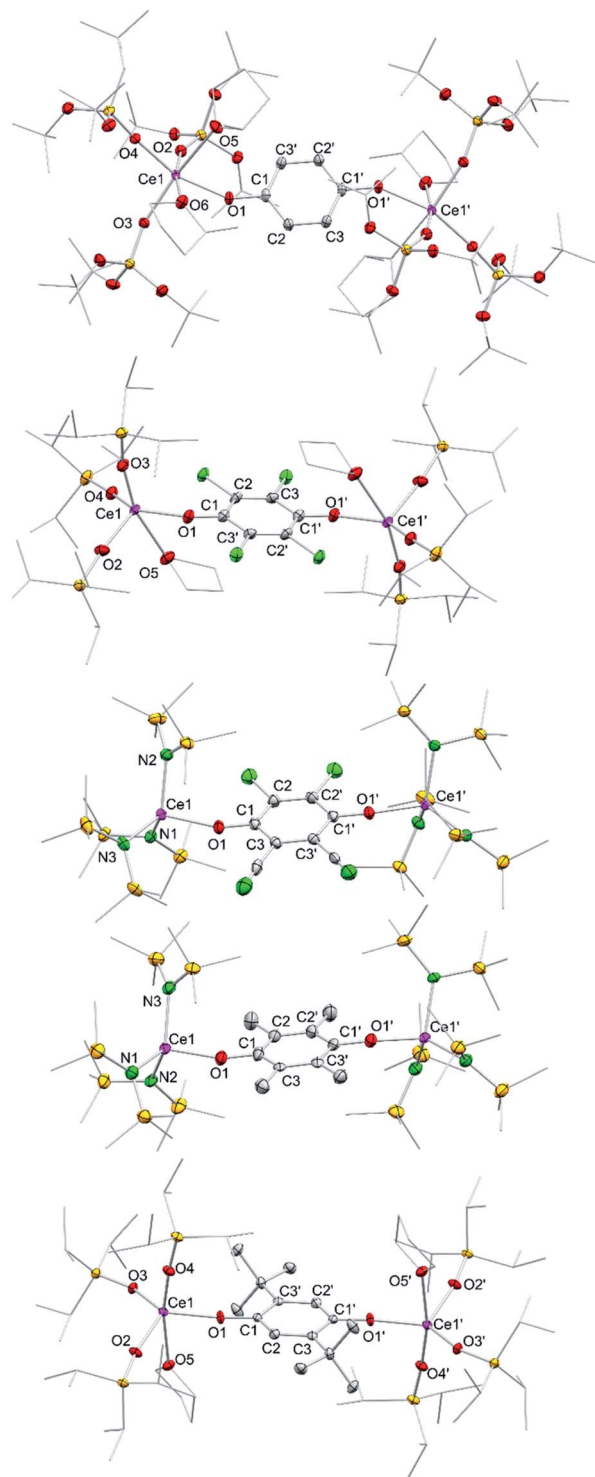


Fig. 2 Crystal structures of  $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_3(\text{Me-thf})_2]_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)$  (**5<sup>hq</sup>**·2MeTHF),  $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf})_2]_2(\mu_2\text{-O}_2\text{C}_6\text{Cl}_4)$  (**6<sup>Cl4hq</sup>**),  $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{Cl}_2\text{CN}_2)$  (**4<sup>ddq</sup>**),  $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)$  (**4<sup>Me4hq</sup>**), and  $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf})_2]_2(\mu_2\text{-O}_2\text{C}_6t\text{Bu}_2\text{H}_2)$  (**6<sup>tBu2hq</sup>**) (from top down). Ellipsoids are shown at the 50% probability level. Hydrogen atoms, disordered ligands and lattice solvents are omitted for clarity. Selected interatomic distances for **5<sup>hq</sup>**, **6<sup>Cl4hq</sup>**, **4<sup>ddq</sup>**, and **4<sup>Me4hq</sup>** are given in Tables 1 and 2. Selected bond lengths for **6<sup>tBu2hq</sup>** [Å]: Ce1–O1 2.109(3), Ce1–O2 2.104(3), Ce1–O3 2.097(3), Ce1–O4 2.107(3), C1–C2 1.391(6), C2–C3 1.391(6), C1–C3' 1.405(6), C1–O1 1.350(5).

**Table 1** Selected analytical data of complexes **4<sup>hq</sup>**, **4<sup>Cl4hq</sup>**, **4<sup>ddhq</sup>**, **4<sup>Me4hq</sup>**, **4<sup>tBu2hq</sup>**, **4<sup>nhq</sup>**. Interatomic distances are given in [Å], angles in [°], chemical shifts in [ppm],  $\mu_{\text{eff}}$  in [BM], UV/Vis absorption band in [nm], and  $E_{\text{pc}}/E_{\text{pa}}$  in [V vs. Fc/Fc<sup>+</sup>]

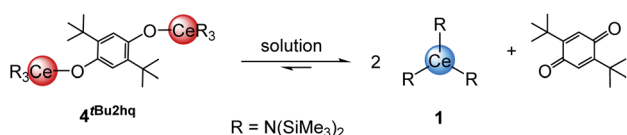
Complex	<b>4<sup>hq24c</sup></b>	<b>4<sup>Cl4hq</sup></b>	<b>4<sup>ddhq</sup></b>	<b>4<sup>Me4hq</sup></b>	<b>4<sup>tBu2hq</sup></b>	<b>4<sup>nhq</sup></b>
Ce1–O1	2.0895(13)	2.149(4)	2.1731(15)	2.082(6)	2.117(2)	—
Ce1–N1	2.2388(14)	2.265(5)	2.2206(18)	2.280(7)	2.235(2)	—
Ce1–N2	2.2398(15)	2.230(5)	2.2112(18)	2.229(7)	2.246(2)	—
Ce1–N3	2.2487(14)	2.244(5)	2.2467(19)	2.238(7)	2.259(2)	—
C–C <sub>arom</sub>	1.387(3)–1.399(2)	1.383(8)–1.392(8)	1.390(4)–1.407(3)	1.390(11)–1.408(12)	1.388(4)–1.405(4)	—
C1–O1	1.356(2)	1.324(7)	1.318(3)	1.366(10)	1.378(3)	—
Ce1–O1–C1	173.13(11)	156.1(4)	161.02(15)	162.4(6)	146.79(18)	—
<sup>1</sup> H NMR <sup>a</sup>	0.43	0.45	0.45	0.43 <sup>d</sup>	0.49	0.44
<sup>13</sup> C{ <sup>1</sup> H} NMR <sup>a</sup>	—	—	5.6	—	—	5.6
<sup>29</sup> Si{ <sup>1</sup> H} NMR <sup>a</sup>	—	–8.1	–7.3	–8.8	—	–8.1
$\mu_{\text{eff}}$	0.67	0.68	0.59	0.89	—	1.19
UV-Vis absorption bands <sup>b</sup>	485	319/518	384/511	362/411/681	—	339/425/474/677
$E_{\text{pc}}$ <sup>c</sup>	–0.699/–0.966	–0.415/–0.624	–0.546	—	—	—
$E_{\text{pa}}$ <sup>c</sup>	–0.558	–0.290	–0.1685	—	—	—
$E_{1/2}$	–0.76	–0.46	–0.36	—	—	—
$\Delta E$	0.408	0.334	0.377	—	—	—

<sup>a</sup> NMR spectra recorded in C<sub>6</sub>D<sub>6</sub>. <sup>b</sup> UV-Vis spectra recorded in toluene. <sup>c</sup> Determined in THF using  $c(\text{analyte}) = 2 \text{ mM}$  and  $c(\text{electrolyte}) = 0.1 \text{ M}$  and a scan rate of  $50 \text{ mV s}^{-1}$ . <sup>d</sup> Determined in toluene-*d*<sub>8</sub> at  $0^\circ \text{C}$ .

### Quinone oxidation of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (**1**)

Treatment of Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (**1**) with each 0.5 equivalents of DDQ, Cl<sub>4</sub>BQ, Me<sub>4</sub>BQ, *t*Bu<sub>2</sub>BQ and NQ, in a mixture of toluene and *n*-hexane, immediately led to a colour change from yellow to dark brown. Upon recrystallisation from toluene/*n*-hexane mixtures it was possible to isolate the hydroquinolato-bridged complexes [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>) (**4<sup>Cl4hq</sup>**), [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>Cl<sub>2</sub>(CN)<sub>2</sub>) (**4<sup>ddhq</sup>**), [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>Me<sub>4</sub>) (**4<sup>Me4hq</sup>**), [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>*t*Bu<sub>2</sub>H<sub>2</sub>) (**4<sup>tBu2hq</sup>**) and [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>10</sub>H<sub>6</sub>) (**4<sup>nhq</sup>**) in very good crystalline yields of 71 to 90% (Scheme 1). The crystal structures of the new complexes **4<sup>xhq</sup>** are isostructural to the previously reported derivative **4<sup>hq24c</sup>** and only differ in the bridging hq linker (Fig. 2). The Ce1–O1 distances of 2.084(6) to 2.173(2) Å (for a full list of interatomic distances see Table 1) are in the same range as found for other hq-bridged cerium complexes (2.086(10)–2.143(5) Å).<sup>20g,24</sup> Likewise, the Ce1–N bond lengths compare well to other Ce<sup>IV</sup> silylamides like [Ce{N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (2.2388(14)–2.2487(14) Å),<sup>24c</sup> Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl (2.217(3) Å),<sup>20a</sup> and Ce[N(SiHMe<sub>2</sub>)<sub>2</sub>]<sub>4</sub> (2.2378(11)–2.2574(11) Å).<sup>20d</sup> Also, the C–C distances of the hq linker converge as the expected aromatic ring is formed and the C–O distances of 1.318(3) to 1.378(3) Å corroborate the formation of C–O single bonds.

The <sup>1</sup>H NMR spectra of compounds **4<sup>xhq</sup>** in C<sub>6</sub>D<sub>6</sub> show singlets for the trimethylsilyl (TMS) groups at 0.43 to 0.45 ppm along with signals for the bridging hydroquinolato moieties.



**Scheme 2** Equilibrium between **4<sup>tBu2hq</sup>** and reformation of reactants in solution and solid state.

Further, the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **4<sup>ddhq</sup>** and **4<sup>nhq</sup>** display a singlet for the TMS groups at 5.6 ppm and signals in the aromatic region for the different hydroquinolates, indicative of a successful reduction of the respective benzoquinone derivatives. The characterisation of **4<sup>tBu2hq</sup>** in solution (C<sub>6</sub>D<sub>6</sub>) was not feasible, due to the prevailing equilibrium shown in Scheme 2, and ready back-formation of **1** and 2,5-di-*tert*-butyl-1,4-benzoquinone.

While the <sup>1</sup>H NMR spectrum of **4<sup>tBu2hq</sup>** primarily shows signals for the starting materials and only minor product signals, its DRIFT spectrum indicated the absence of any strong C=O absorption band, and therefore the stability of **4<sup>tBu2hq</sup>** in the solid state (see Fig. S10 and S45 in ESI†). In contrast, complexes **4<sup>hq</sup>**, **4<sup>Cl4hq</sup>** and **4<sup>ddhq</sup>** derived from the stronger oxidizing quinones are very stable in the solid state and in solution. This fits again well with the already pronounced instability of **4<sup>Me4hq</sup>** and **4<sup>nhq</sup>** which slowly decompose in *n*-hexane and toluene at ambient temperature and rapidly undergo decomposition in THF. Tracking of the progress of the decomposition by <sup>1</sup>H NMR spectroscopy revealed the formation of **1** and other paramagnetic Ce<sup>III</sup> species which, however, could not be identified. The progressing decomposition can also be seen in the ligand-to-metal charge transfers observed in the UV-Vis spectra (Fig. S68, ESI†). As the spectra of **4<sup>hq</sup>**, **4<sup>Cl4hq</sup>** and **4<sup>ddhq</sup>** show mainly one strong absorption band at around 500 nm ( $\epsilon > 5060 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), the spectra of **4<sup>Me4hq</sup>** and **4<sup>nhq</sup>** show several absorption bands with significantly lower intensities ( $\epsilon < 4400 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) indicative of Ce<sup>III</sup> species and therefore redox decomposition of the compounds.

All attempts to isolate putative **4<sup>ahq</sup>**, derived from the weakest oxidising quinone under study, namely 9,10-anthraquinone ( $E^0 = 89 \text{ mV}$ ;  $2e^-/2H^+$ , vs. NHE),<sup>5</sup> were unsuccessful with the reaction mixtures showing no colour change immediately after addition of the anthraquinone. However, a colour change from





**Table 2** Selected analytical data of complexes **5<sup>hq</sup>**, **5<sup>Cl4hq</sup>**, **5<sup>ddq</sup>**, **6<sup>hq</sup>**, **6<sup>Cl4hq</sup>**, **6<sup>ddq</sup>**. Interatomic distances are given in [Å], angles in [°], chemical shifts in [ppm],  $\mu_{\text{eff}}$  in [BM], UV/Vis absorption band in [nm], and  $E_{\text{pc}}/E_{\text{pa}}$  in [V vs. Fc/Fc<sup>+</sup>]

Complex	<b>5<sup>hq</sup></b>	<b>5<sup>Cl4hq</sup></b>	<b>5<sup>ddq</sup></b>	<b>6<sup>hq</sup></b>	<b>6<sup>Cl4hq</sup></b>	<b>6<sup>ddq</sup></b>
Ce1–O1	2.1244(10)	2.184(3)	—	—	2.207(2)	2.2325(16)
Ce1–O2	2.1534(10)	2.091(3)	—	—	2.095(2)	2.0841(16)
Ce1–O3	2.1334(11)	2.094(3)	—	—	2.066(2)	2.0710(17)
Ce1–O4	2.1396(11)	2.104(3)	—	—	2.080(2)	2.091(2)
C–C <sub>arom</sub>	1.390(2)–1.395(2)	1.373(8)–1.406(5)	—	—	1.380(4)–1.407(4)	1.379(5)–1.415(3)
C1–O1	1.3540(17)	1.326(4)	—	—	1.322(3)	1.316(3)
Ce1–O1–C1	151.76(10)	140.0(2)	—	—	138.54(18)	144.85(14)
<sup>1</sup> H NMR <sup>a</sup>	1.36	1.36	1.36	—	1.12/1.05	1.12/1.05
<sup>13</sup> C{ <sup>1</sup> H} NMR <sup>a</sup>	72.5/32.6	72.8/32.4	73.0/32.5	—	18.0/14.0	19.1/15.1
<sup>29</sup> Si{ <sup>1</sup> H} NMR <sup>a</sup>	–103.2	–104.6	–105.3	7.0	9.6	10.7
$\mu_{\text{eff}}$	0.82	0.54	0.60	0.68	0.50	0.66
UV-Vis absorption band <sup>b</sup>	369/622	493	384/450	526 <sup>c</sup>	511	381/470
$E_{\text{pc}}$ <sup>d</sup>	–1.7855	–1.414	–1.353	–1.116/–1.816	–1.580	–1.149/–1.484
$E_{\text{pa}}$ <sup>d</sup>	–0.3625	–0.521	0.130	–1.273/–0.817	–0.729	–0.751
$\Delta E$	1.416	0.893	1.483	0.999	0.851	0.733

<sup>a</sup> NMR spectra recorded in THF-*d*<sub>8</sub>. <sup>b</sup> Spectra recorded in toluene. <sup>c</sup> Spectra recorded in THF. <sup>d</sup> Determined in THF using  $c(\text{analyte}) = 2 \text{ mM}$  and  $c(\text{electrolyte}) = 0.1 \text{ M}$  and a scan rate of  $50 \text{ mV s}^{-1}$ .

yellow to green occurred after two days and the respective <sup>1</sup>H NMR spectrum showed multiple paramagnetic signals.

### Quinone oxidation of siloxides [Ce{OSi(O<sup>*t*</sup>Bu)<sub>3</sub>}]<sub>2</sub> (**2**) and [Ce{OSi<sup>*i*</sup>Pr<sub>3</sub>}]<sub>2</sub> (**3**)

Reacting cerous siloxides **2** and **3** with the selected quinones in THF immediately gave a colour change of the reaction mixtures (from colourless to: dark purple (BQ), dark red (Cl<sub>4</sub>BQ), dark yellow/orange (DDQ), pale purple (*t*Bu<sub>2</sub>BQ), pale blue (Me<sub>4</sub>BQ), pale green (NQ)). The ceric compounds [CeL<sub>3</sub>(thf)]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (**5<sup>hq</sup>**, **6<sup>hq</sup>**), [CeL<sub>3</sub>(thf)]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>Cl<sub>4</sub>) (**5<sup>Cl4hq</sup>**, **6<sup>Cl4hq</sup>**), [CeL<sub>3</sub>(thf)]<sub>2</sub>(μ<sub>2</sub>-O<sub>2</sub>C<sub>6</sub>Cl<sub>2</sub>(CN)<sub>2</sub>) (**5<sup>ddq</sup>**, **6<sup>ddq</sup>**), with L = OSi(O<sup>*t*</sup>Bu)<sub>3</sub> or OSi<sup>*i*</sup>Pr<sub>3</sub> derived from quinones with a relatively strong oxidising effect were successfully isolated from these reactions (Scheme 1).

However, the weakly oxidizing quinones Me<sub>4</sub>BQ and NQ did not lead to tetravalent cerium species, as indicated by the detection of only paramagnetic signals in the <sup>1</sup>H NMR spectra (for an example of such a <sup>1</sup>H NMR spectrum, see Fig. S34 in the ESI;† formation of semiquinolates, *vide infra*). The accessible complexes **5** and **6** were obtained in moderate to good crystalline yields of 42 to 71% upon recrystallisation from THF or THF/Et<sub>2</sub>O mixtures. Crystals suitable for XRD analysis were obtained for complexes **5<sup>hq</sup>**, **5<sup>Cl4hq</sup>**, **6<sup>Cl4hq</sup>**, **6<sup>ddq</sup>** and **6<sup>tBu2hq</sup>**, revealing the same structural motif as complexes **4**, that is two CeL<sub>3</sub> moieties connected *via* a hydroquinolato linker (Fig. 2).

Strikingly, the <sup>1</sup>H NMR spectrum of **6<sup>tBu2hq</sup>** indicated the existence of an equilibrium similar to that of ceric **4<sup>tBu2hq</sup>** (*cf.* Scheme 2). However, along with the reactants **3** and *t*Bu<sub>2</sub>BQ additional signals assignable to distinct dia- and paramagnetic decomposition products were detected. Further, the crystal structures of complexes **5** and **6** show that the cerium atoms are additionally coordinated by THF donor molecules. The Ce1–O<sub>siloxide</sub> distances of 2.066(2) to 2.1534(10) (see Table 2 for a complete list of interatomic distances) compare well to other ceric siloxides like Ce{OSi(O<sup>*t*</sup>Bu)<sub>3</sub>}<sub>4</sub> (2.089(2)–2.157(2) Å<sup>26</sup> and

2.084–2.160 Å<sup>21d</sup>) or Ce{OSiPh<sub>3</sub>}<sub>4</sub>(dme) (2.098(1)–2.133(1) Å).<sup>29</sup> Also, as seen for the silylamides **4**, the Ce1–O<sub>hq</sub> distances of 2.1244(10) to 2.2325(16), as well as the C–C and C–O distances underline the formation of an aromatic hq linker.<sup>20g,24</sup> <sup>1</sup>H NMR spectroscopic measurements also validate the formation of Ce<sup>IV</sup> species, showing a sharp singlet for the *tert*-butyl groups and a doublet plus a septet for the iso-propyl groups depending on the siloxy co-ligand.

### Electrochemical investigation of complexes **4<sup>xhq</sup>**, **5<sup>xhq</sup>** and **6<sup>xhq</sup>**

Cyclic voltammetry (CV) measurements of complexes **4<sup>xhq</sup>**, **5<sup>xhq</sup>** and **6<sup>xhq</sup>** have been conducted at ambient temperature in 0.2 mM solutions in THF and 0.1 M [nPr<sub>4</sub>N][B(C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>-3,5)<sub>4</sub>] as a support electrolyte, and referenced vs. Fc/Fc<sup>+</sup>. Due to the low stability of compounds **4<sup>Me4hq</sup>**, **4<sup>tBu2hq</sup>** and **4<sup>nhq</sup>** in polar solvents CV measurements of these complexes were not feasible. Most of the CV measurements revealed successive quasireversible (**4**) or irreversible (**5/6**) Ce<sup>IV</sup> → Ce<sup>III</sup> reduction steps, but badly resolved (for  $E_{\text{pc}}$  values see Tables 1 and 2). The detection of two closely adjacent redox events ( $E_{\text{pc}}$  values) in some cyclic voltammograms may correspond to a successive reduction/oxidation of the cerium centres. Similar features were also described for the hq-bridged Ce(IV)–BINOLate complex **II**.<sup>24b</sup> All complexes under study display redox processes with a large separation of  $E_{\text{pc}}$  and  $E_{\text{pa}}$  ( $\Delta E \approx 0.6 \text{ V}$  for **4**; 1.5 V for **5** and 1.0 V for **6**).

Representatively, the cyclic voltammograms of the DDQ-functionalized Ce<sup>III</sup>/Ce<sup>IV</sup> redox couples are depicted in Fig. 3 (top graphic). The silylamide complexes **4** gave reduction potentials similar to those reported for halogenido-functionalised ceric complexes Ce[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>X ( $E_{1/2} = -0.56$  (X = F),  $-0.30$  (X = Cl),  $-0.31$  (X = Br)) with  $E_{1/2}$  values of  $-0.46 \text{ V}$  for **4<sup>Cl4hq</sup>** and  $-0.36 \text{ V}$  for **4<sup>ddhq</sup>**.<sup>30</sup> Only **4<sup>hq</sup>** with  $E_{1/2} = -0.76 \text{ V}$  gave a significantly higher stabilisation by 0.20 V. The extra-large separation of the reduction/oxidation events



observed for the siloxide complexes **5** and **6** had been noticed previously for rare-earth-metal siloxides and was assigned to oxidation-state-dependent ligand reorganisation processes.<sup>31</sup>

Stabilisation of the tetravalent oxidation state of cerium in complexes **4**, **5**, and **6** increases in the order of  $\text{N}(\text{SiMe}_3)_2 < \text{OSi}(\text{OtBu}_3)_3 < \text{OSi}^i\text{Pr}_3$  as co-ligand (Fig. 3/bottom) which is in accordance with previous findings.<sup>20f,26,30,31c</sup> Surprisingly, the stabilisation of  $\text{Ce}^{\text{IV}}$  proceeds in reverse order of the oxidation potential of the 1,4-quinones under study giving the most stable complexes for the hydroquinolato-bridged complexes and the least stable compounds for its 2,3-dichloro-5,6-dicyano-hydroquinolato congeners. A reason for this trend could be the increasingly electron-deficient nature of the aromatic hydroquinolato linkers due to the large  $-I$  effect of the substituents. The  $\text{Ce}^{\text{IV}}$  oxidation state can be stabilised by increasing donor strength of the ligands.<sup>32</sup> Based on this, it seems surprising that isolable complexes **4<sup>Me4hq</sup>** and **4<sup>hq</sup>**, derived from weakly oxidizing quinones, are not stable in solution at ambient temperature. This might be a result of another reaction pathway preferred after formation of the hydroquinolato-bridged  $\text{Ce}^{\text{IV}}$  complexes (like following up redox processes and the formation of  $\text{Ce}^{\text{III}}$  semiquinolates, *cf. vide infra*).

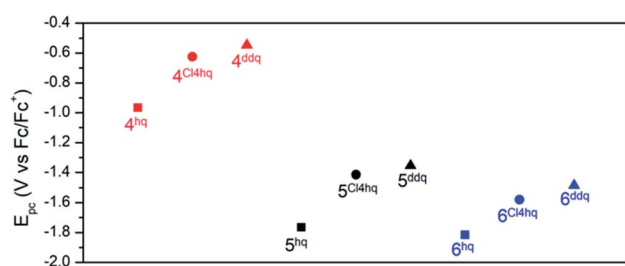
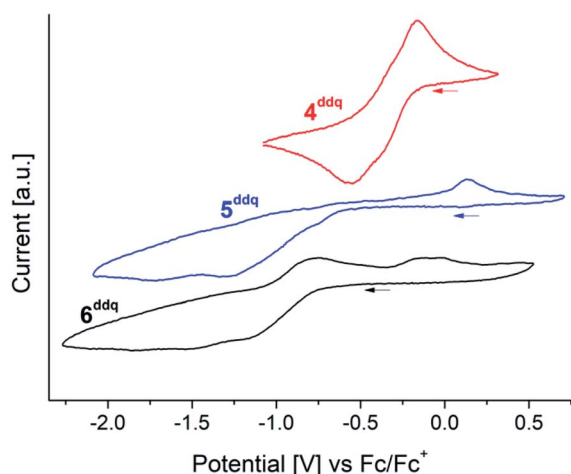
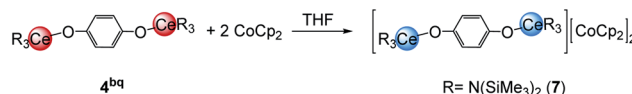


Fig. 3 Top: Stacked cyclic voltammograms of complexes **4<sup>ddq</sup>** (red), **5<sup>ddq</sup>** (blue), **6<sup>ddq</sup>** (black) in THF ( $\nu = 50 \text{ mV s}^{-1}$ ;  $c(\text{analyte}) = 2 \text{ mM}$ ;  $c([\text{InPr}_4\text{N}][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5)_4]) = 0.1 \text{ M}$ ). Bottom: comparison of the second reduction potentials of complexes **4** (red), **5** (black), and **6** (blue) in THF vs.  $\text{Fc}/\text{Fc}^+$ . Squares: complexes with bridging 1,4-hydroquinolates; circles: complexes with bridging tetrachloro-1,4-hydroquinolates; triangles: complexes with bridging 2,3-dichloro-5,6-dicyano-1,4-hydroquinolates.



Scheme 3 Reduction of **4<sup>hq</sup>** with two equivalents of  $\text{CoCp}_2$ .

### Reduction of silylamide **4<sup>hq</sup>** with cobaltocene

Having investigated the electrochemical reduction of compounds **4**, **5** and **6**, the chemical reduction with cobaltocene ( $\text{CoCp}_2$ ) ( $-1.31 \text{ V vs. Fc}/\text{Fc}^+$  in DME)<sup>2a</sup> was attempted, as it has already been shown to engage in such reductions.<sup>31a,33</sup> Accordingly, treatment of a solution of **4<sup>hq</sup>** in THF with two equivalents of  $\text{CoCp}_2$  resulted in a colour change from dark brown to pale yellow (Scheme 3). The  $^1\text{H}$  NMR spectrum of the reaction mixture showed complete consumption of  $\text{CoCp}_2$  and only broadened signals indicating the formation of a paramagnetic  $\text{Ce}^{\text{III}}$  species. Crystallisation from a concentrated THF- $d_8$  solution at  $-40^\circ\text{C}$  gave light brown crystals of the composition  $[(\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3)_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)][\text{CoCp}_2]_2$  (**7**) (Fig. 4).

Complex **7** shows the same structural motif as **4<sup>hq</sup>** but is flanked by two cobaltocenium cations. Compared to **4<sup>hq</sup>**, the Ce-N and Ce1-O1 distances are elongated by approximately  $0.19 \text{ \AA}$  as expected for the larger  $\text{Ce}^{\text{III}}$  ion size.<sup>34</sup> On the contrary, the bonding parameters within the bridging hydroquinolato linker did not change, further corroborating a cerium-borne redox chemistry. Reacting **4<sup>hq</sup>** with one equivalent of  $\text{CoCp}_2$  did not lead to a mixed  $\text{Ce}^{\text{III/IV}}$  complex but gave a mixture of **7** and 50% of unreacted starting material.

The reactions of  $\text{CoCp}_2$  with other complexes **4** to **6** in THF- $d_8$  showed immediate decolourisation of the solution while the  $^1\text{H}$  NMR spectra of the reaction mixtures displayed only paramagnetic signals (for an example, see Fig. S33 in the ESI†). However, the isolation of additional reduced species similar to **7** was not successful.

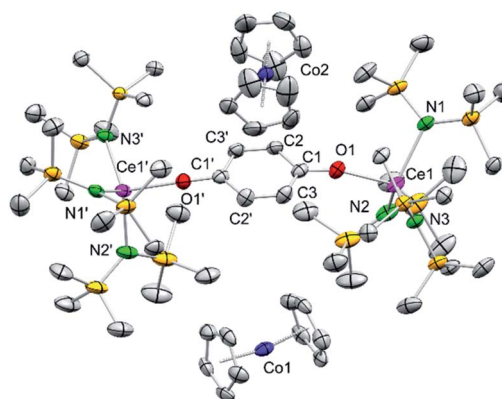
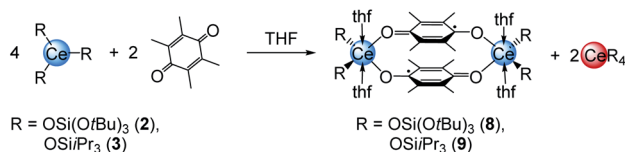


Fig. 4 Crystal structure of  $[(\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3)_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)][\text{CoCp}_2]_2$  (**7**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms, disordering of the cyclopentadienyl ligands and lattice THF are omitted for clarity. Selected interatomic distances [ $\text{\AA}$ ]: Ce1-N1  $2.420(2)$ , Ce1-N2  $2.402(2)$ , Ce1-N3  $2.418(2)$ , Ce1-O1  $2.202(2)$ , C1-O1  $1.344(4)$ , C1-C2  $1.391(4)$ , C1-C3  $1.392(4)$ , C2-C3'  $1.392(4)$ .



Scheme 4 Formation of cerous semiquinolates **8** and **9** from the reaction of **2** or **3** with  $\text{Me}_4\text{BQ}$ .

### Cerium semiquinolates

A closer look at the reactions of cerous siloxides **2** and **3** with the weakly oxidising quinone  $\text{Me}_4\text{BQ}$  (which did not produce any tetravalent cerium species; *vide supra*) revealed another important detail of the cerium–quinone redox system. Treatment of **2** or **3** with 0.5 equivalents of  $\text{Me}_4\text{BQ}$  led to a colour change from colourless to light blue. Upon recrystallisation from THF dark blue crystals suitable for X-ray diffraction could be grown and were identified as cerous semiquinolates  $[\text{Ce}_2(\text{thf})_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$  (with  $\text{L} = \text{OSi}(\text{OtBu})_3$  (**8**) or  $\text{OSi}^i\text{Pr}_3$  (**9**)) (Scheme 4).

Examining the reaction mixtures by  $^1\text{H}$  NMR spectroscopy in  $\text{THF-}d_8$  showed, besides paramagnetic signals for **8** and **9**, a sharp singlet at 1.39 ppm (for **8**) or a doublet plus a septet at 1.13 and 1.04 ppm (for **9**), indicating the formation of homoleptic  $\text{Ce}[\text{OSi}(\text{OtBu})_3]_4$  or  $[\text{Ce}(\text{OSi}^i\text{Pr}_3)_4]$ , respectively, as a result of the one-electron reduction of  $\text{Me}_4\text{BQ}$  followed by ligand redistribution. Crucially, such a reaction pathway seems unfeasible for complexes **4**, since putative homoleptic “ $\text{Ce}[\text{N}(\text{SiMe}_2)_2]_4$ ” is unknown.<sup>20a</sup> Emergent kinetic constraints in the case of ceric complexes **4** were also suggested by the redox behaviour of  $[\text{Ce}\{\text{N}(\text{SiHMe}_2)_2\}_3]_2$  derived from a less bulky silylamido ligand. Accordingly, the cerous bis(dimethylsilyl)amide complex was treated with one equivalent of both BQ and  $\text{Me}_4\text{BQ}$  in  $\text{THF-}d_8$  and  $\text{C}_6\text{D}_6$  (see Fig. S38–S41, ESI†). The  $^1\text{H}$  NMR spectra of these reactions suggest the formation of a tetravalent species of the composition “ $[\text{Ce}\{\text{N}(\text{SiHMe}_2)_2\}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)$ ”. However, the ceric products appear to be unstable in solution at ambient temperature. In  $\text{C}_6\text{D}_6$ , the formation of  $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_4$  was observed in the reaction with BQ as well as other insoluble products. In  $\text{THF-}d_8$ , the resulting product seemed more stable but after 24 h in solution also traces of decomposition products were found. The  $\text{Me}_4\text{BQ}$  reaction in  $\text{C}_6\text{D}_6$  also indicated successful oxidation, however, after 24 h the  $^1\text{H}$  NMR spectrum revealed signals for trivalent decomposition products as well as traces of  $\text{Ce}[\text{N}(\text{SiHMe}_2)_2]_4$ . In  $\text{THF-}d_8$ , the putatively formed hydroquinolate complex was even less stable, showing signals for trivalent by-products directly after addition of  $\text{Me}_4\text{BQ}$ . In addition, the stability of **4**<sup>bq</sup> was investigated in  $\text{THF-}d_8$  showing small amounts of decomposition products like  $\text{Ce}[\text{N}(\text{SiMe}_2)_2]_3$  after 24 h (Fig. S42, ESI†).

Regrettably, purification of complexes **8** and **9** was impeded by co-crystallisation with the ceric by-products  $\text{CeL}_4$ . The crystal structures of **8** and **9** revealed two six-coordinate cerium atoms surrounded by two siloxy ligands, two THF donor molecules and two bridging tetramethyl semiquinolato moieties (Fig. 5). The  $\text{Ce1-O}_{\text{silanolato}}$  distances are elongated by about 0.1 Å compared to the respective tetravalent compounds **5** and **6** and in

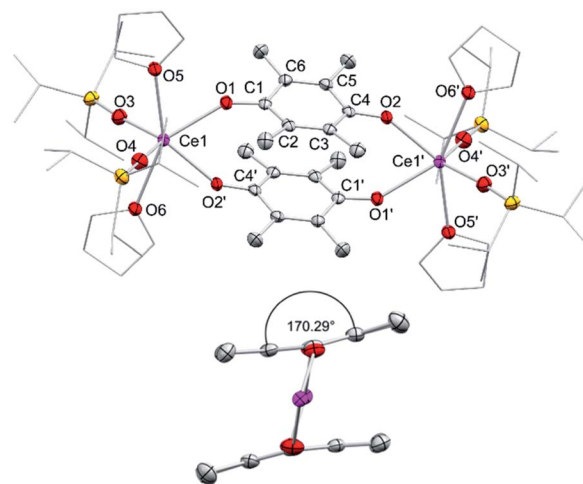


Fig. 5 Top: Crystal structure of  $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_2(\text{thf})_2](\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2$  (**9**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]:  $\text{Ce1-O1}$  2.446(7),  $\text{Ce1-O2}$  2.422(7),  $\text{Ce1-O3}$  2.219(9),  $\text{Ce1-O4}$  2.237(6),  $\text{Ce1-O5}$  2.648(7),  $\text{Ce1-O6}$  2.644 (7),  $\text{C1-O5}$  1.306(5),  $\text{C4-O6}$  1.307(5),  $\text{C1-C2}$  1.458(6),  $\text{C2-C3}$  1.401(6),  $\text{C3-C4}$  1.449(8),  $\text{C4-C5}$  1.463(6),  $\text{C5-C6}$  1.388(6),  $\text{C1-C6}$  1.463(8). Bottom: side view of  $[(\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_2(\text{thf})_2)(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$  (**9**).

accordance with other  $\text{Ce}^{\text{III}}$  siloxides like **3**,  $\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_3(\text{thf})_3$  (2.243(2)–2.249(2) Å),  $[\text{Ce}\{\text{OSi}(\text{OtBu})_3\}_3]_2$  ( $\text{Ce-O}_{\text{term}}$  2.186(3)–2.202(3) Å),<sup>26</sup>  $\text{Ce}\{\text{OSiPh}_3\}_3(\text{thf})_3$  ( $\text{Ce-O}_{\text{avg}}$  2.222(4) Å)<sup>35</sup> and  $[\text{Ce}\{\text{OSiPh}_3\}_3]_2$  ( $\text{Ce-O}_{\text{term}}$  2.141(7)–2.184(6) Å).<sup>27</sup> As expected for semiquinolato ligands the six-membered rings display two shortened C–C and four elongated C–C bonds. Additionally, the six-membered rings are slightly bent in comparison to the flat aromatic hydroquinolato linkers in complexes **4**, **5** and **6** resulting in an angle of 170.34° for **8** and 170.29° for **9**, respectively (see Fig. 5, bottom). Notwithstanding, the bridging radicals engage in significant  $\pi$ -stacking as indicated by close semiquinolato–semiquinolato distances of 3.112 Å for **8** and 3.156 Å for **9**. Overall, complexes **8** and **9** display the same arrangement of the semiquinolato radical bridges as observed in complexes  $[\text{LnCl}_2(\text{THF})_3(\mu\text{-Me}_4\text{sq})_2]$  ( $\text{Ln} = \text{Y, Gd}$ ) ( $\text{Ct}\cdots\text{Ct}$  3.097 Å; Ct = centroid of benzene rings).<sup>13</sup>

To investigate the electronic behaviour of the bridging semiquinolates, X-band EPR spectra of compounds **8** and **9** were recorded from a crystal powder sample at 123 K (Fig. 6). For both complexes cw-EPR spectra are composed of two distinct sets of resonances, one that results from the transition within the Kramers doublet corresponding to  $m_j = \pm 1/2$  and one at half-field,  $H \approx 160$  mT. The transition for the  $m_j = \pm 1/2$  state associates with an axial  $g$  tensor with principal components  $g_{\parallel} = 2.094$  and  $g_{\perp} = 2.032$  for **8** and  $g_{\parallel} = 2.088$  and  $g_{\perp} = 2.032$  for **9**, respectively. The transition locating at half-field gives rise to a very broad dispersion line with  $g_{\parallel} \approx 4.359$  for **8** and  $g_{\parallel} \approx 4.351$  for **9**, respectively. Notably, an identical line pattern derives from a frozen 2-Me-THF solution at 77 K; cf. Fig. S67, ESI† for pertinent details. The cw-EPR spectra corroborate the presence of  $\text{Ce}^{3+}$ , and agree with early work on mononuclear complexes of  $\text{Ce}^{3+}$ .<sup>36</sup> This indicates a radical-



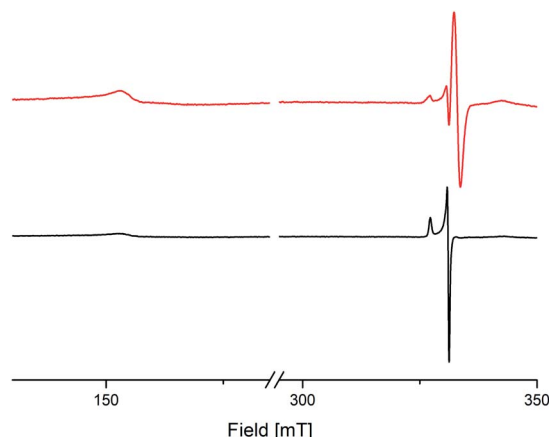


Fig. 6 X-Band cw-EPR spectra of crystalline  $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\text{thf})_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$  (**8**) (black trace) and  $[\text{Ce}(\text{OSiPr}_3)_2(\text{thf})_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$  (**9**) (red trace).

radical  $\pi$ -bonding, as it was recently shown for yttrium and gadolinium semiquinolates  $[\text{LnCl}_2(\text{thf})_2]_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2$  ( $\text{Ln} = \text{Y}$  or  $\text{Gd}$ ).<sup>13</sup> Additionally and also similar to the yttrium semiquinolate, complex **9** shows a signal with a  $g$  value of 1.999, which most likely results from a non-coupled radical impurity.

Note that the reactions of cerium siloxides **2** and **3** with 1,4-naphthoquinone resulted also in the formation of homoleptic ceric siloxides as well as paramagnetic by-products (*cf.* Fig. S36, ESI†) indicating a similar reactivity as observed for  $\text{Me}_4\text{BQ}$ . Unfortunately, any putative semiquinolate complexes could not be isolated.

## Conclusions

Cerium(III) silylamides and siloxides are suitable reagents for assessing the oxidising power/reducibility of differently substituted 1,4-quinones in non-aqueous solutions. The cerium–quinone redox matching is revealed by the ease of formation of  $\text{Ce}^{\text{IV}}$  hydroquinolates  $[\text{CeL}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)$ , in the case of the parent 1,4-benzoquinone (BQ) or when  $\text{R}$  represents electron-withdrawing groups (Cl, CN). Depending on their reduction potential, alkyl-substituted BQs engage in redox equilibria, with the  $\text{Ce}^{\text{IV}}$  hydroquinolate species being preferentially stable in the solid state, but also afford semiquinolates *via* redox ligand redistribution. The structurally characterized siloxide semiquinolate complexes  $[(\text{CeL}_2(\text{thf})_2)(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)]_2$  ( $\text{L} = \text{OSi}(\text{OtBu})_3$ ,  $\text{OSi}^i\text{Pr}_3$ ) exhibit a molecular arrangement, recently detected for  $[\text{LnCl}_2(\text{THF})_3(\mu\text{-Me}_4\text{sq})_2]_2$  ( $\text{Ln} = \text{Y}$ ,  $\text{Gd}$ ).<sup>13</sup> The stabilisation of the tetravalent oxidation state in hydroquinolato-bridged complexes  $[\text{Ce}^{\text{IV}}\text{L}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)$  was examined by electrochemical measurements, as well as NMR and UV/Vis spectroscopies. In accordance with previous findings,<sup>16,18–20</sup> the stability of the ceric complexes increases in the order of  $\text{N}(\text{SiMe}_3)_2 < \text{OSi}(\text{OtBu})_3 < \text{OSi}^i\text{Pr}_3$  as supporting ligand, but surprisingly drops in reverse order of the oxidation potential of the 1,4-quinones, being the least stable for the 2,3-dichloro-5,6-dicyano-hydroquinolato congener. The preferred formation of hydroquinolato-bridged silylamides  $[\text{Ce}$

$\{\text{N}(\text{SiMe}_3)_2\}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)$  seems kinetically favoured. Finally, the electrochemical reduction of the hydroquinolato-bridged ceric complexes  $[\text{Ce}^{\text{IV}}\text{L}_3]_2(\mu_2\text{-O}_2\text{C}_6\text{R}_4)$  can be mimicked by chemical reduction with cobaltocene, as shown for the isolation and structural characterisation of cerous  $[(\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3)_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)][\text{CoCp}_2]_2$ . The cerium–quinone redox matching and tuning might be used as a role-model in tetravalent praseodymium and terbium chemistry.

## Conflicts of interest

There are no conflicts to declare.

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