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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 $[\text{Ce}\{\text{OSi}(\text{Pr}_3)_3\}_2]_2$ 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 (Cl_4BQ) 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 (tBu_2BQ) 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 (Me_4BQ) 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, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{29}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.^{1,2} Of particular note is their importance in biological electron-transfer processes (photosynthesis, respiration)³ and in industrial catalysis (anthraquinone process for hydrogen peroxide production).⁴ Quinones can engage in one or two electron redox processes involving the formation of either semiquinolates or hydroquinolates.⁵ 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.^{5,6} As a consequence, tetrachloro-1,4-benzoquinone (chloranil, Cl_4BQ) and even more so 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) emerged as efficient oxidants in organic synthesis.⁷ DDQ has been further successfully applied in photoredox catalysis.⁸ Moreover, anionic η^4 -1,4-benzoquinone manganese tricarbonyl features a quinoid π -complex, broadly used for the fabrication of supramolecular metal-organometallic coordination networks.⁹ Relatedly, deprotonated variants of 2,5-dihydroxy-1,4-benzoquinone (DHBQ) were shown to act

as rigid ditopic linkers,¹⁰ 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.¹¹ DHBQ was also probed as a bridging redox-active ligand in bimetallic $[\text{LnCl}_2(\text{thf})_3]_2(\mu\text{-bobq})$ ($\text{Ln} = \text{Y}, \text{Dy}$; $\text{bobq} = 2,5\text{-bisoxide-1,4-benzoquinolate}$) to build single-molecule magnets.¹² 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 FeCl_3 .¹³ Semiquinolato-bridged scandium(III) species were reported to promote self-organised electron transfer from d-transition metals (Ir, Fe) to 1,4-quinones.^{14,15}

Targeted metal-redox chemistry with quinones has been a recurring issue for the rare-earth-metal couples $\text{Ln}(\text{II})/\text{Ln}(\text{III})$ ¹⁶ and $\text{Ce}(\text{III})/\text{Ce}(\text{IV})$.¹⁷ Especially in the case of molecular cerium chemistry,¹⁷ 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 synthesis¹⁸ to photoredox catalysis.¹⁹ On the other hand, redox protocols are known to provide efficient access to metalorganic Ce^{IV} complexes. Typically, such $\text{Ce}^{\text{III}} \rightarrow \text{Ce}^{\text{IV}}$ transformations are promoted by halogenating oxidants (e.g. C_2Cl_6 , Ph_3CCl , PhICl_2 , TeCl_4 , FcPF_6 , FcBF_4 , Ph_3CBF_4 , Ph_3CPF_6 , I_2),²⁰ silver salts (AgX , $\text{X} = \text{F}, \text{I}, \text{BF}_4, \text{OTf}$)²¹ or dioxygen.^{20b,22}

Archetypical 1,4-benzoquinone (BQ) has been established as a versatile oxidant for the synthesis of homoleptic ceric complexes 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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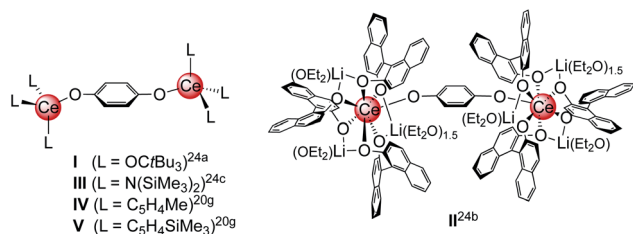


Chart 1 Structurally characterised dicerium(IV) hydroquinolate complexes (I–V),^{20g,24} obtained *via* oxidation of cerous precursor with BQ.

monoanionic ligand, M = alkali metal and do = donor solvent; separation of an alkali-metal hydro-/semiquinolate).²³ In the presence of sterically demanding ligands L, BQ was also shown to form hydroquinolato (hq)–bridged ceric complexes of the general composition $[L_3Ce-OC_6H_4O-CeL_3]$.^{20g,24} This very $Ce^{III} \rightarrow Ce^{IV}$ transformation was pioneered by Sen *et al.* in 1992, resulting in the isolation of $[(tBu_3CO)_3Ce(OC_6H_4O)Ce(OCtBu_3)_3]$ (Chart 1, I).^{24a} In the same paper, the oxidation of $Ce(OCtBu_3)_3$ with 2,6-di-*tert*-butyl-1,4-benzoquinone to the terminal Ce^{IV} -semiquinolate radical $(tBu_3CO)_3Ce(O_2C_6H_2tBu_2)$ was described as evidenced by ¹H NMR and EPR spectroscopic measurements.^{24a} More recently, Schelter *et al.* reported on hq-bridged complex II resulting from the oxidation of cerous $Ce(BINolate)_3(thf)Li_3(thf)_4$ with 0.5 equivalents of BQ.^{24b} Similarly, our group synthesized $[Ce\{N(SiMe_3)_2\}_2]_2(\mu_2-O_2C_6H_4)$ ^{24c} (III) and $(CeCp^R)_2(\mu_2-O_2C_6H_4)$ ($Cp^R = C_5H_4Me$ (IV) and $C_5H_4(SiMe_3)$ (V)).^{20g} In contrast, the reaction of BQ with $[Ce(Me_2pz)_3]_x$ featuring the sterically less demanding and increasingly nucleophilic 3,5-dimethylpyrazolato ligand (Me_2pz) led in fact to a transient Ce^{IV} hydroquinolate species (as indicated by the characteristic colour change), which, however, at ambient temperature was converted into the isolable trimetallic Ce^{III}

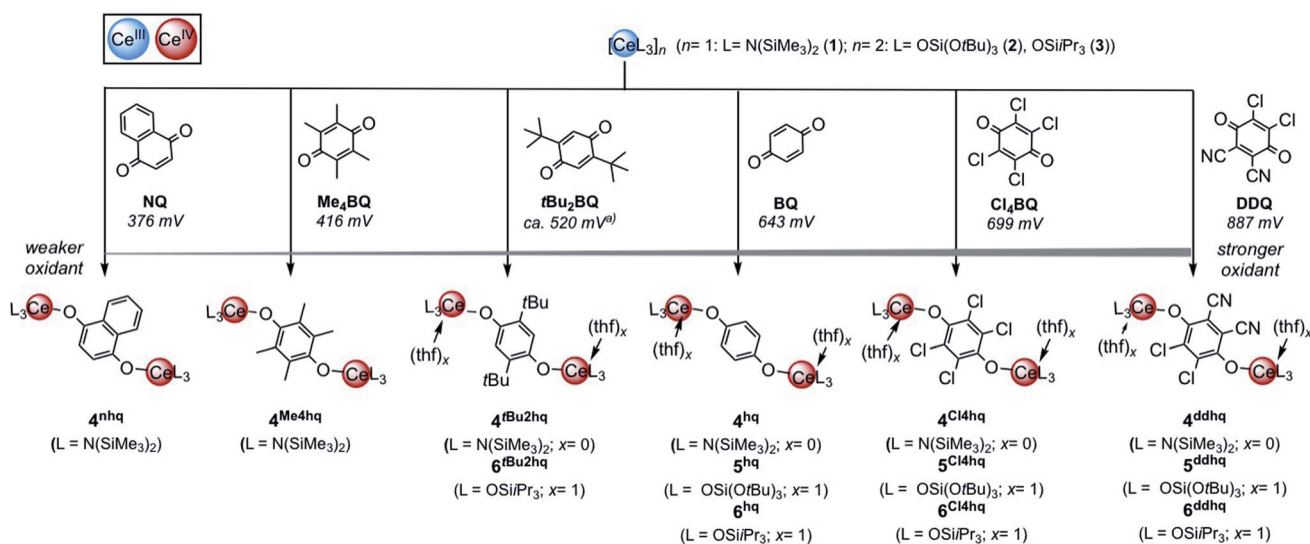
complex $Ce_3(pchd)_2(Me_2pz)_5(thf)_2$ ($pchd = 1,4$ -bis(3,5-dimethylpyrazol-1-yl)cyclohex-2,5-diene-1,4-diolato).^{23c} Apparently, the new pchd ligand formed *via* 1,4-nucleophilic attack at bq by two adjacent Me_2pz ligands. This nucleophilic reaction pathway could be prevented by using bulky *t*Bu groups on the pz ligand, but homoleptic $Ce(tBu_2pz)_4$ was formed as the main ceric product *via* irreversible ligand rearrangement.^{23c}

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^{III} precursor. The present study uncovers some unexpected correlation between Ce^{IV} -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_4BQ), 1,4-benzoquinone (BQ), tetramethyl-1,4-benzoquinone (Me_4BQ), 2,5-di-*tert*-butyl-1,4-benzoquinone (tBu_2BQ), 1,4-naphthoquinone (NQ), and 9,10-anthraquinone (AQ). All are commercially available and were selected according to their reduction potentials spanning a E^0 range of 89 to 887 mV ($2e^-/2H^+$, vs. NHE, *cf.*, Scheme 1).^{5,25} 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 $Ce[N(SiMe_3)_2]_3$ (1) appeared to be an ideal benchmark system.^{24c} 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 $2e^-/2H^+$ reductions potentials are given in mV versus NHE according to ref. 5. (a) Calculated value.

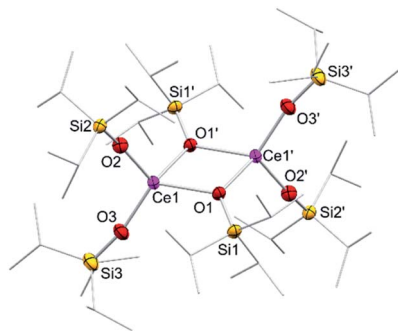


Fig. 1 Crystal structure of $[\text{Ce}(\text{OSi}^i\text{Pr}_3)_3]_2$ (**3**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ce1–O1 2.3951(12), Ce1–O2 2.1659(14), Ce1–O3 2.1671(14); Ce1–O2–Si2 163.03(9), 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 Me_2pz and ligand redistribution (formation of $\text{Ce}(t\text{Bu}_2\text{pz})_4$).^{23c} 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 $\text{Ce}_3(\text{bpad})(\text{pasq})(\text{Me}_2\text{pz})_6(\text{thf})$ ($\text{bpad} = 1,4$ -bis(3,5-dimethylpyrazol-1-yl)anthra-1,4-diolato; $\text{pasq} = 1$ -(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 Ce^{III} halides was discarded mainly for solubility issues.

In addition to silylamide **1**, the siloxide derivatives $[\text{Ce}\{\text{OSi}(\text{O}t\text{Bu})_3\}_2]_2$ (**2**)^{21d,26} 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.²⁶ The crystal structure of the new complex **3** revealed a dimeric arrangement with two μ_2 -bridging and four terminal siloxy groups (Fig. 1), similar to that found for tris(*tert*-butoxy)siloxo congener **2** or $[\text{Ce}(\text{OSiPh}_3)_3]_2$ ²⁷ or $[\text{Ce}(\text{OCH}t\text{Bu}_2)_3]_2$.²⁸ The Ce–O_{terminal} (2.1659(14) and 2.1671(14) Å) and the Ce–O _{μ_2} distances (2.3951(12) and 2.4030(12) Å) of **3** are slightly shorter than those in **2** (Ce–O_{terminal} 2.202(3), 2.186(3) Å; Ce–O _{μ_2} 2.532(2) Å) and $[\text{Ce}(\text{OSiPh}_3)_3]_2$ (Ce–O_{terminal} 2.141(7), 2.185(6) Å; Ce–O _{μ_2} 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_{terminal} 2.142(2), 2.152(3) Å; Ce–O _{μ_2} 2.363(3) Å).²⁸ The ¹H NMR spectrum of **3** in C_6D_6 shows two singlets at –28.82 and –17.23 ppm for the μ_2 -OSi^{*i*}Pr₃ 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 THF-*d*₈, only two signals for the OSi^{*i*}Pr₃ groups appeared, in accordance with the formation of a monomeric adduct $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf}-d_8)_x]$.

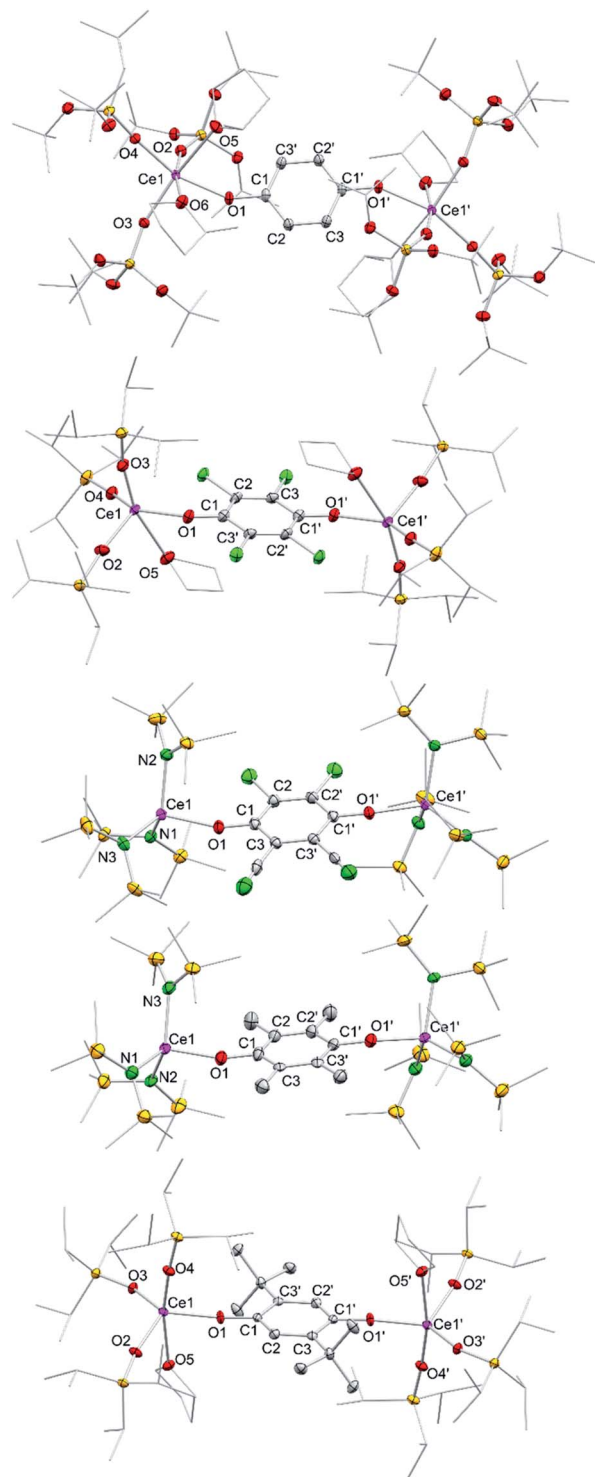


Fig. 2 Crystal structures of $[\text{Ce}\{\text{OSi}(\text{O}t\text{Bu})_3\}_3(\text{Me}-\text{thf})_{212}(\mu_2-\text{O}_2\text{C}_6\text{H}_4)]_2$ ($5^{\text{ha}} \cdot 2\text{MeTHF}$), $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf})_2(\mu_2-\text{O}_2\text{C}_6\text{Cl}_4)]_2$ (6^{Cl4ha}), $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]_2(\mu_2-\text{O}_2\text{C}_6\text{Cl}_2\text{CN}_2)$ (4^{ddq}), $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]_2(\mu_2-\text{O}_2\text{C}_6\text{Me}_4)$ (4^{Me4ha}), and $[\text{Ce}\{\text{OSi}^i\text{Pr}_3\}_3(\text{thf})_2(\mu_2-\text{O}_2\text{C}_6t\text{Bu}_2\text{H}_2)]_2$ (6^{tBu2ha}) (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 6^{tBu2ha} [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^{hq} , $4^{\text{Cl}4\text{hq}}$, 4^{ddhq} , $4^{\text{Me}4\text{hq}}$, $4^{\text{tBu}2\text{hq}}$, 4^{nhq} . Interatomic distances are given in [Å], angles in [°], chemical shifts in [ppm], μ_{eff} in [BM], UV/Vis absorption band in [nm], and $E_{\text{pc}}/E_{\text{pa}}$ in [V vs. Fc/Fc⁺]

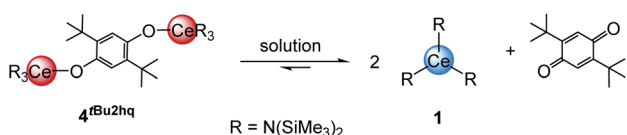
Complex	$4^{\text{hq}24\text{c}}$	$4^{\text{Cl}4\text{hq}}$	4^{ddhq}	$4^{\text{Me}4\text{hq}}$	$4^{\text{tBu}2\text{hq}}$	4^{nhq}
Ce1–O1	2.0895(13)	2.149(4)	2.1731(15)	2.082(6)	2.117(2)	—
Ce1–N1	2.2388(14)	2.265(5)	2.2206(18)	2.280(7)	2.235(2)	—
Ce1–N2	2.2398(15)	2.230(5)	2.2112(18)	2.229(7)	2.246(2)	—
Ce1–N3	2.2487(14)	2.244(5)	2.2467(19)	2.238(7)	2.259(2)	—
C–C _{arom}	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)	—
¹ H NMR ^a	0.43	0.45	0.45	0.43 ^d	0.49	0.44
¹³ C{ ¹ H} NMR ^a	—	—	5.6	—	—	5.6
²⁹ Si{ ¹ H} NMR ^a	—	–8.1	–7.3	–8.8	—	–8.1
μ_{eff}	0.67	0.68	0.59	0.89	—	1.19
UV-Vis absorption bands ^b	485	319/518	384/511	362/411/681	—	339/425/474/677
E_{pc}^c	–0.699/–0.966	–0.415/–0.624	–0.546	—	—	—
E_{pa}^c	–0.558	–0.290	–0.1685	—	—	—
$E_{1/2}$	–0.76	–0.46	–0.36	—	—	—
ΔE	0.408	0.334	0.377	—	—	—

^a NMR spectra recorded in C₆D₆. ^b UV-Vis spectra recorded in toluene. ^c Determined in THF using $c(\text{analyte}) = 2 \text{ mM}$ and $c(\text{electrolyte}) = 0.1 \text{ M}$ and a scan rate of 50 mV s^{-1} . ^d Determined in toluene-*d*₈ at 0 °C.

Quinone oxidation of Ce[N(SiMe₃)₂]₃ (1)

Treatment of Ce[N(SiMe₃)₂]₃ (1) with each 0.5 equivalents of DDQ, Cl₄BQ, Me₄BQ, *t*Bu₂BQ 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(SiMe₃)₂]₃]₂(μ₂-O₂C₆Cl₄) ($4^{\text{Cl}4\text{hq}}$), [Ce{N(SiMe₃)₂]₃]₂(μ₂-O₂C₆Cl₂(CN)₂) (4^{ddhq}), [Ce{N(SiMe₃)₂]₃]₂(μ₂-O₂C₆Me₄) ($4^{\text{Me}4\text{hq}}$), [Ce{N(SiMe₃)₂]₃]₂(μ₂-O₂C₆*t*Bu₂H₂) ($4^{\text{tBu}2\text{hq}}$) and [Ce{N(SiMe₃)₂]₃]₂(μ₂-O₂C₁₀H₆) (4^{nhq}) in very good crystalline yields of 71 to 90% (Scheme 1). The crystal structures of the new complexes 4^{xhq} are isostructural to the previously reported derivative $4^{\text{hq}24\text{c}}$ 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).^{20g,24} Likewise, the Ce1–N bond lengths compare well to other Ce^{IV} silylamides like [Ce{N(SiMe₃)₂]₃]₂(μ₂-O₂C₆H₄) (2.2388(14)–2.2487(14) Å),^{24c} Ce[N(SiMe₃)₂]₃Cl (2.217(3) Å),^{20a} and Ce[N(SiHMe₂)₂]₄ (2.2378(11)–2.2574(11) Å).^{20d} 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 ¹H NMR spectra of compounds 4^{xhq} in C₆D₆ 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 $4^{\text{tBu}2\text{hq}}$ and reformation of reactants in solution and solid state.

Further, the ¹³C{¹H} NMR spectra of 4^{ddhq} and 4^{nhq} 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 $4^{\text{tBu}2\text{hq}}$ in solution (C₆D₆) 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 ¹H NMR spectrum of $4^{\text{tBu}2\text{hq}}$ 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 $4^{\text{tBu}2\text{hq}}$ in the solid state (see Fig. S10 and S45 in ESI[†]). In contrast, complexes 4^{hq} , $4^{\text{Cl}4\text{hq}}$ and 4^{ddhq} 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 $4^{\text{Me}4\text{hq}}$ and 4^{nhq} 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 ¹H NMR spectroscopy revealed the formation of **1** and other paramagnetic Ce^{III} 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^{hq} , $4^{\text{Cl}4\text{hq}}$ and 4^{ddhq} show mainly one strong absorption band at around 500 nm ($\epsilon > 5060 \text{ L mol}^{-1} \text{ cm}^{-1}$), the spectra of $4^{\text{Me}4\text{hq}}$ and 4^{nhq} show several absorption bands with significantly lower intensities ($\epsilon < 4400 \text{ L mol}^{-1} \text{ cm}^{-1}$) indicative of Ce^{III} species and therefore redox decomposition of the compounds.

All attempts to isolate putative 4^{ahq} , derived from the weakest oxidising quinone under study, namely 9,10-anthraquinone ($E^0 = 89 \text{ mV}$; $2e^-/2H^+$, vs. NHE),⁵ 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^{hq}**, **5^{Cl⁴hq}**, **5^{ddq}**, **6^{hq}**, **6^{Cl⁴hq}**, **6^{ddq}**. Interatomic distances are given in [Å], angles in [°], chemical shifts in [ppm], μ_{eff} in [BM], UV/Vis absorption band in [nm], and $E_{\text{pc}}/E_{\text{pa}}$ in [V vs. Fc/Fc⁺]

Complex	5^{hq}	5^{Cl⁴hq}	5^{ddq}	6^{hq}	6^{Cl⁴hq}	6^{ddq}
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 _{arom}	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)
¹ H NMR ^a	1.36	1.36	1.36	—	1.12/1.05	1.12/1.05
¹³ C{ ¹ H} NMR ^a	72.5/32.6	72.8/32.4	73.0/32.5	—	18.0/14.0	19.1/15.1
²⁹ Si{ ¹ H} NMR ^a	–103.2	–104.6	–105.3	7.0	9.6	10.7
μ_{eff}	0.82	0.54	0.60	0.68	0.50	0.66
UV-Vis absorption band ^b	369/622	493	384/450	526 ^c	511	381/470
E_{pc} ^d	–1.7855	–1.414	–1.353	–1.116/–1.816	–1.580	–1.149/–1.484
E_{pa} ^d	–0.3625	–0.521	0.130	–1.273/–0.817	–0.729	–0.751
ΔE	1.416	0.893	1.483	0.999	0.851	0.733

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

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

Quinone oxidation of siloxides [Ce{OSi(O*t*Bu)₃}]₂ (**2**) and [Ce{OSi^{Pr}}]₃ (**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 (Cl₄BQ), dark yellow/orange (DDQ), pale purple (*t*Bu₂BQ), pale blue (Me₄BQ), pale green (NQ)). The ceric compounds [CeL₃(thf)]₂(μ₂-O₂C₆H₄) (**5^{hq}**, **6^{hq}**), [CeL₃(thf)]₂(μ₂-O₂C₆Cl₄) (**5^{Cl⁴hq}**, **6^{Cl⁴hq}**), [CeL₃(thf)]₂(μ₂-O₂C₆Cl₂(CN)₂) (**5^{ddq}**, **6^{ddq}**), with L = OSi(O*t*Bu)₃ or OSi^{Pr}₃ derived from quinones with a relatively strong oxidising effect were successfully isolated from these reactions (Scheme 1).

However, the weakly oxidizing quinones Me₄BQ and NQ did not lead to tetravalent cerium species, as indicated by the detection of only paramagnetic signals in the ¹H NMR spectra (for an example of such a ¹H 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/Et₂O mixtures. Crystals suitable for XRD analysis were obtained for complexes **5^{hq}**, **5^{Cl⁴hq}**, **6^{Cl⁴hq}**, **6^{ddq}** and **6^{tBu₂hq}**, revealing the same structural motif as complexes **4**, that is two CeL₃ moieties connected *via* a hydroquinolato linker (Fig. 2).

Strikingly, the ¹H NMR spectrum of **6^{tBu₂hq}** indicated the existence of an equilibrium similar to that of ceric **4^{tBu₂hq}** (*cf.* Scheme 2). However, along with the reactants **3** and *t*Bu₂BQ 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_{siloxide} 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*t*Bu)₃}]₄ (2.089(2)–2.157(2) Å²⁶ and

2.084–2.160 Å^{21d}) or Ce{OSiPh₃}]₄(dme) (2.098(1)–2.133(1) Å).²⁹ Also, as seen for the silylamides **4**, the Ce1–O_{hq} 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.^{20g,24} ¹H NMR spectroscopic measurements also validate the formation of Ce^{IV} 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^{xhq}**, **5^{xhq}** and **6^{xhq}**

Cyclic voltammetry (CV) measurements of complexes **4^{xhq}**, **5^{xhq}** and **6^{xhq}** have been conducted at ambient temperature in 0.2 mM solutions in THF and 0.1 M [nPr₄N][B(C₆H₃(CF₃)₂-3,5)₄] as a support electrolyte, and referenced vs. Fc/Fc⁺. Due to the low stability of compounds **4^{Me⁴hq}**, **4^{tBu₂hq}** and **4^{hq}** 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^{IV} → Ce^{III} reduction steps, but badly resolved (for E_{pc} values see Tables 1 and 2). The detection of two closely adjacent redox events (E_{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**.^{24b} All complexes under study display redox processes with a large separation of E_{pc} and E_{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^{III}/Ce^{IV} 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(SiMe₃)₂]₃X ($E_{1/2} = -0.56$ (X = F), -0.30 (X = Cl), -0.31 (X = Br)) with $E_{1/2}$ values of -0.46 V for **4^{Cl⁴hq}** and -0.36 V for **4^{ddq}**.³⁰ Only **4^{hq}** 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.³¹

Stabilisation of the tetravalent oxidation state of cerium in complexes **4**, **5**, and **6** increases in the order of $N(\text{SiMe}_3)_2 < \text{OSi}(\text{OtBu}_3)_3 < \text{OSi}^i\text{Pr}_3$ as co-ligand (Fig. 3/bottom) which is in accordance with previous findings.^{20f,26,30,31c} Surprisingly, the stabilisation of Ce^{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 Ce^{IV} oxidation state can be stabilised by increasing donor strength of the ligands.³² Based on this, it seems surprising that isolable complexes **4^{Me4hq}** and **4^{nhq}**, 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 Ce^{IV} complexes (like following up redox processes and the formation of Ce^{III} semiquinolates, *cf. vide infra*).

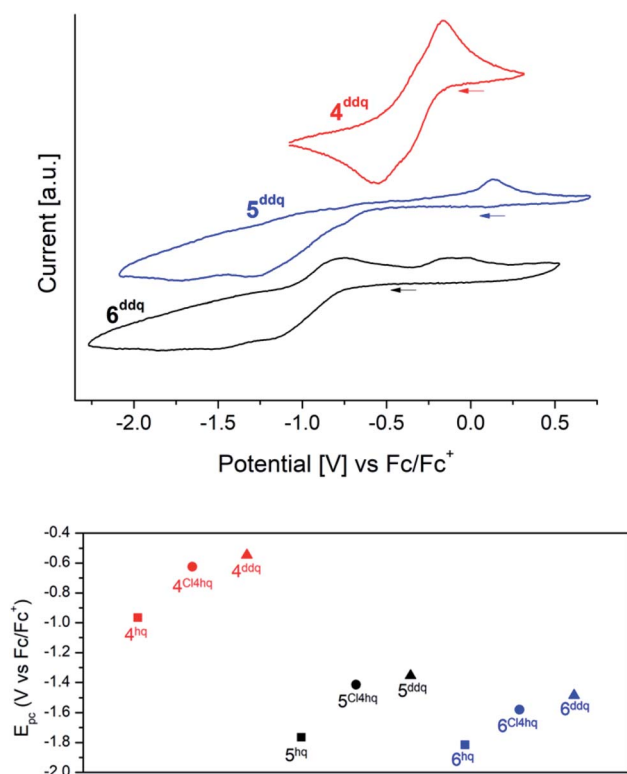
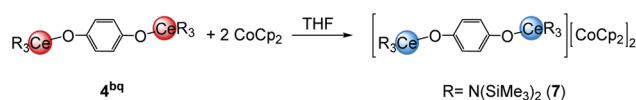


Fig. 3 Top: Stacked cyclic voltammograms of complexes **4^{ddq}** (red), **5^{ddq}** (blue), **6^{ddq}** (black) in THF ($\nu = 50 \text{ mV s}^{-1}$; $c(\text{analyte}) = 2 \text{ mM}$; $c([\text{InPr}_4\text{N}][\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2-3,5)_4]) = 0.1 \text{ M}$). Bottom: comparison of the second reduction potentials of complexes **4** (red), **5** (black), and **6** (blue) in THF vs. Fc/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^{bq}** with two equivalents of CoCp_2 .

Reduction of silylamide **4^{hq}** with cobaltocene

Having investigated the electrochemical reduction of compounds **4**, **5** and **6**, the chemical reduction with cobaltocene (CoCp_2) ($-1.31 \text{ V vs. Fc}/\text{Fc}^+$ in DME)^{2a} was attempted, as it has already been shown to engage in such reductions.^{31a,33} Accordingly, treatment of a solution of **4^{hq}** in THF with two equivalents of CoCp_2 resulted in a colour change from dark brown to pale yellow (Scheme 3). The ^1H NMR spectrum of the reaction mixture showed complete consumption of CoCp_2 and only broadened signals indicating the formation of a paramagnetic Ce^{III} species. Crystallisation from a concentrated THF- d_8 solution at -40°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^{hq}** but is flanked by two cobaltocenium cations. Compared to **4^{hq}**, the Ce–N and Ce1–O1 distances are elongated by approximately 0.19 \AA as expected for the larger Ce^{III} ion size.³⁴ On the contrary, the bonding parameters within the bridging hydroquinolato linker did not change, further corroborating a cerium-borne redox chemistry. Reacting **4^{hq}** with one equivalent of CoCp_2 did not lead to a mixed $\text{Ce}^{\text{III/IV}}$ complex but gave a mixture of 50% of **7** and 50% of unreacted starting material.

The reactions of CoCp_2 with other complexes **4** to **6** in THF- d_8 showed immediate decolourisation of the solution while the ^1H 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.

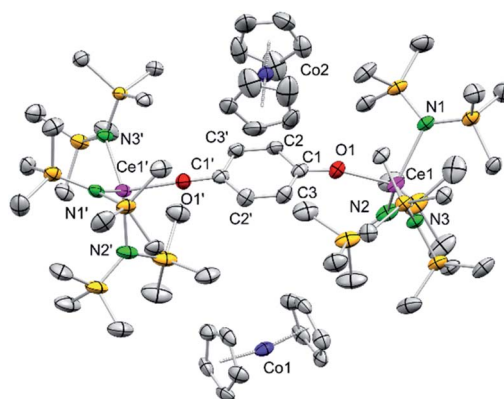
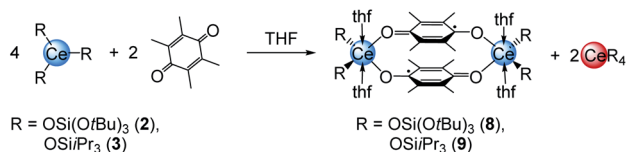


Fig. 4 Crystal structure of $[(\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3)_2(\mu_2\text{-O}_2\text{C}_6\text{H}_4)][\text{CoCp}_2]_2$ (**7**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms, disordering of the cyclopentadienyl ligands and lattice THF are omitted for clarity. Selected interatomic distances [\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 Me_4BQ .

Cerium semiquinolates

A closer look at the reactions of cerous siloxides **2** and **3** with the weakly oxidising quinone Me_4BQ (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 Me_4BQ 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 $[\text{CeL}_2(\text{thf})_2]_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2$ (with $\text{L} = \text{OSi}(\text{OtBu})_3$ (**8**) or OSiPr_3 (**9**)) (Scheme 4).

Examining the reaction mixtures by ^1H 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 $[\text{Ce}(\text{OSiPr}_3)_4]$, respectively, as a result of the one-electron reduction of Me_4BQ 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.^{20a} 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 Me_4BQ in $\text{THF-}d_8$ and C_6D_6 (see Fig. S38–S41, ESI†). The ^1H 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 C_6D_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 Me_4BQ reaction in C_6D_6 also indicated successful oxidation, however, after 24 h the ^1H 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 hydroquinolato complex was even less stable, showing signals for trivalent by-products directly after addition of Me_4BQ . In addition, the stability of **4**^{bq} 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 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

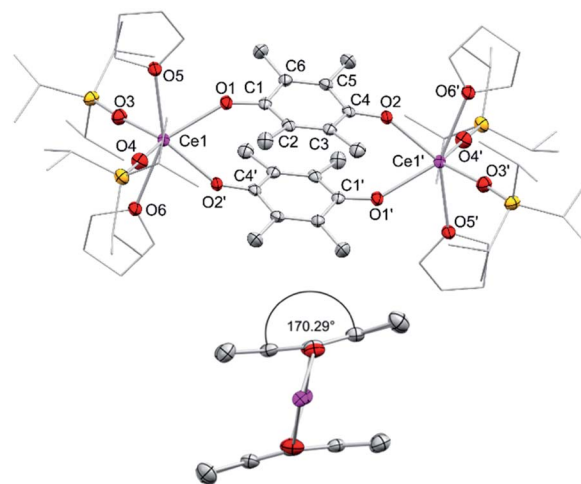


Fig. 5 Top: Crystal structure of $[\text{Ce}\{\text{OSiPr}_3\}_2(\text{thf})_2]_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2$ (**9**). Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances [Å]: Ce1–O1 2.446(7), Ce1–O2 2.422(7), Ce1–O3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

accordance with other Ce^{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),²⁶ $\text{Ce}\{\text{OSiPh}_3\}_3(\text{thf})_3$ (Ce-O_{avg} 2.222(4) Å)³⁵ and $[\text{Ce}\{\text{OSiPh}_3\}_3]_2$ ($\text{Ce-O}_{\text{term}}$ 2.141(7)–2.184(6) Å).²⁷ 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 π -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).¹³

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 Ce^{3+} , and agree with early work on mononuclear complexes of Ce^{3+} .³⁶ This indicates a radical-

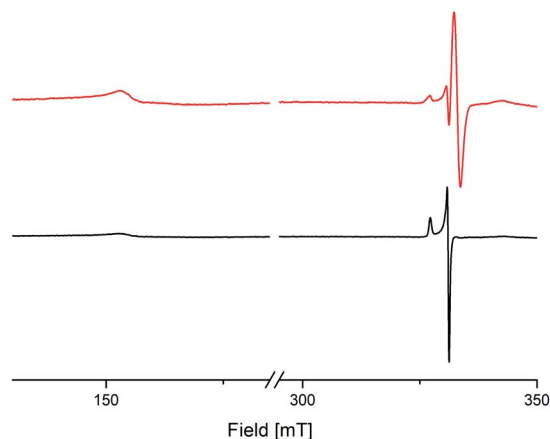


Fig. 6 X-Band cw-EPR spectra of crystalline $[\text{Ce}(\text{OSi}(\text{OtBu})_3)_2(\text{thf})_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$ (**8**) (black trace) and $[\text{Ce}(\text{OSi}(\text{Pr})_3)_2(\text{thf})_2(\mu_2\text{-O}_2\text{C}_6\text{Me}_4)_2]$ (**9**) (red trace).

radical π -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 Gd).¹³ 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 Me_4BQ . 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 Ce^{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 R represents electron-withdrawing groups (Cl, CN). Depending on their reduction potential, alkyl-substituted BQs engage in redox equilibria, with the Ce^{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 $[\text{LnCl}_2(\text{THF})_3(\mu\text{-Me}_4\text{sq})_2]_2$ ($\text{Ln} = \text{Y}, \text{Gd}$).¹³ 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,^{16,18–20} 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.

Acknowledgements

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