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Synthesis, Structure, and Reactivity of Homoleptic Cerium(IV) and Cerium(III) Alkoxides

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The reaction of $Ce(OC^tBu_3)_3$ (**1**) with the following oxidants has been studied: benzoyl peroxide, BzP; di-*tert*-butyl peroxide, DTBP; *tert*-butyl peroxybenzoate, BPB; benzoquinone, Bq; 2,6-di-*tert*-butylbenzoquinone, DBBq. $Ce(OC^tBu_3)_3(OC(O)Ph)$ (**2**) was formed in the reaction of **1** with BzP. **1** and DTBP reacted in 1:1 ratio to generate the unstable Ce(IV) species $Ce(OC^tBu_3)_2(O^tBu)_2$ (**3**). On the other hand, a 1:0.5 ratio of reactants resulted in the formation of the Ce(III) compound $[Ce(OC^tBu_3)_2(O^tBu)]_2$ (**4**). The X-ray crystal structure of **4** ($P2_1/c$; $a = 11.783$ (2) Å, $b = 23.606$ (6) Å, $c = 11.544$ (2) Å, $\beta = 95.19$ (2)°; 3240 independent reflections with $F_o \geq 6\sigma(F_o)$; $R(F) = 3.79\%$, $R_w(F) = 4.08\%$; GOF = 1.126) indicated it to be dimeric with a pseudotetrahedral geometry around each cerium atom. The interconversions between **1**, **3**, and **4** were examined. The reaction of **1** with BPB caused the formation of equal amounts of **2** and **3**. **1** was found to react with Bq to form $(^tBu_3CO)_3CeOC_6H_4OCe(OC^tBu_3)_3$ (**5**). **5** was structurally characterized ($P\bar{1}$; $a = 12.629$ (4) Å, $b = 12.736$ (5) Å, $c = 18.148$ (8) Å, $\alpha = 83.60$ (3)°, $\beta = 76.83$ (3)°, $\gamma = 61.57$ (3)°; 6403 independent reflections with $F_o \geq 5\sigma(F_o)$; $R(F) = 7.70\%$, $R_w(F) = 7.97\%$; GOF = 1.466). The two cerium atoms in the molecule are bridged by a hydroquinonediolate moiety. As expected, the Ce(IV)–O distances were shorter than the Ce(III)–O bond lengths. Finally, the reaction of **1** with DBBq resulted in the formation of the radical $(^tBu_3CO)_3CeOC_6H_2{}^tBu_2O^{\bullet}$ (**6**).

Homoleptic cerium(IV) alkoxides were synthesized first as an extension of a systematic study of the oligomeric nature of homoleptic alkoxides of group 4 metals.[1] In addition, an ebulliometric study of their hydrolysis products, bridged oxo–alkoxide oligomers, produced a model by which the average molecular weight could be calculated for a given degree of hydrolysis.[2] More recently, $Ce(O^iPr)_4$ has been used to prepare the organometallic species $Ce(cyclooctatetraene)_2$,[3,4] $Ce_2(cycloctatetraene)_3$,[3,4] and $(C_5H_5)_3Ce(O^iPr)$.[4,5] However, these represent the only exploitation of a cerium(IV) alkoxide for synthetic purposes, and the structure of the starting material remains unknown. The absence of many structurally characterized homoleptic alkoxides[6] led to the present study. Such species are of considerable interest as precursors to other cerium(IV) compounds, as well as to cerium(IV) oxide.

Tri-*tert*-butyl methoxide (OC^tBu_3) was chosen as the ancillary ligand on the basis of its large size (cone angle of 125°),[7] which should lead to monomeric complexes. This ligand is also readily available in one step from commercial reagents.[8]

All the cerium(IV) compounds described herein were obtained by oxidation of corresponding cerium(III) alkoxides, and NMR spectroscopy was a particularly convenient probe for monitoring the interconversion between cerium(III) and cerium(IV) species. Whereas the Ce^{4+} ion is diamagnetic, Ce^{3+} is paramagnetic and serves as a "shift reagent" for its ligands. Hence, for the same ligand, very different chemical shifts are obtained depending on whether the ligand is attached to a Ce^{4+} or a Ce^{3+} center.

Results and Discussion

$Ce(OC^tBu_3)_3$ (**1**) was synthesized by the reaction of $Ce[N(SiMe_3)_2]_3$ with 3 equiv of $^tBu_3COH$ in pentane.[9] **1** is an O_2- and H_2O-sensitive yellow solid that is readily soluble in nonpolar organic solvents. The NMR spectrum of **1** indicated that it is monomeric in solution, and although its crystal structure has not been determined, it is safe to assume that it is also monomeric in the solid state. We have previously shown that the compound $Ce(2,6\text{-}^tBu_2C_6H_3O)_3$ is monomeric in the solid state,[10] and models indicate that OC^tBu_3 is significantly more bulky than $2,6\text{-}^tBu_2C_6H_3O$.

Reaction with Benzoyl Peroxide. The reaction of **1** with benzoyl peroxide (BzP) was relatively simple. A ^1H NMR titration in C_6D_6 indicated that the reaction was facile at ambient temperature and that the stoichiometry was 2:1 **1**:BzP (eq 1).

$$\underset{\mathbf{1}}{2Ce(OC^tBu_3)_3} + \underset{BzP}{PhC(O)OOC(O)Ph} \xrightarrow[25\ ^\circ C]{C_6D_6} \underset{\mathbf{2}}{2Ce(OC^tBu_3)_3(OC(O)Ph)} \quad (1)$$

The cerium(IV) alkoxide carboxylate, **2**, was more stable in solution than as a solid. For example, while the NMR titration gave a product that was ca. 95% pure (see Table I for NMR data), the workup of a preparative-scale reaction gave an orange oil that was only 60% pure and contained a number of cerium(III) impurities, as indicated by its ^1H NMR spectrum. The decomposition to cerium(III) products was not significantly retarded in the presence of an excess of BzP.

Reaction with Di-*tert*-butyl Peroxide. A 1:1 mixture of **1** and di-*tert*-butyl peroxide (DTBP) in C_6D_6 was allowed to react in an NMR tube. The reaction was quite slow at ambient temperature but reasonably fast at elevated temperatures (80–100 °C), which allowed it to be followed by ^1H and ^{13}C NMR spectroscopy. As the reaction proceeded, the original alkoxide and peroxide resonances disappeared and were replaced by ones consistent with one new O^tBu and two new OC^tBu_3 moieties, all diamagnetic. When the reaction was complete, the volatiles were removed and collected. The nonvolatile portion was comprised one O^tBu and one OC^tBu_3 resonance (in a 1:1 ratio) and was formulated as $Ce(OC^tBu_3)_2(O^tBu)_2$ (**3**) (see Table I for NMR data). The volatile fraction consisted of mostly $^tBu_2CO$ with small amounts of isobutylene, $^tBu_3COH$, and other *tert*-butyl-containing organics. It is apparent, then, that the volatile portion of the original mixture contained a single $^tBu_3CO$ moiety but did not survive the workup. For this reason, and in order to satisfy mass balance, this product was formulated as the peroxide $[^tBu_3COOC^tBu_3]$ (eq 2).

$$\underset{\mathbf{1}}{Ce(OC^tBu_3)_3} + \underset{DTBP}{2\,^tBuOO^tBu} \xrightarrow{C_6H_6} \underset{\mathbf{3}}{Ce(OC^tBu_3)_2(O^tBu)_2} + [^tBu_3COOC^tBu_3] \quad (2)$$

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Table I. NMR Spectral Data in C_6D_6 (ppm)

compd	^1H data	$^{13}C\{^1H\}$ data
$^tBu_3COH$	1.22 (1 H), 1.09 (27 H)	85.1, 45.0, 33.6
$Ce(OC^tBu_3)_3$ (**1**)	3.9	134.4, 63.0, 37.2
$Ce(OC^tBu_3)_3(OC(O)Ph)$ (**2**)	8.39 (2 H), 7.1–7.0 (3 H), 1.54 (81 H)	182.6, 133.3, 132.4, 130.3, 128.5, 111.2, 47.4, 34.3
$Ce(OC^tBu_3)_2(O^tBu)_2$ (**3**)	1.45 (54 H), 1.38 (18 H)	103.6, 82.4, 46.9, 33.7, 33.5
$[Ce(OC^tBu_3)_2(O^tBu)]_x$ (**4**)	7.0 (54 H), −39.0 (9 H)	
$(^tBu_3CO)_3CeOC_6H_4OCe(OC^tBu_3)_3$ (**5**)	7.19 (4 H), 1.48 (162 H)	165.4, 118.9, 107.7, 47.1, 34.3
$(^tBu_3CO)_3CeOC_6H_2{}^tBu_2O^\bullet$ (**6**)	6.1 (18 H), 1.4 (81 H)	117.8, 48.3, 34.6
$[^tBu_3COOC^tBu_3]$	1.49	105.7, 47.0, 34.4

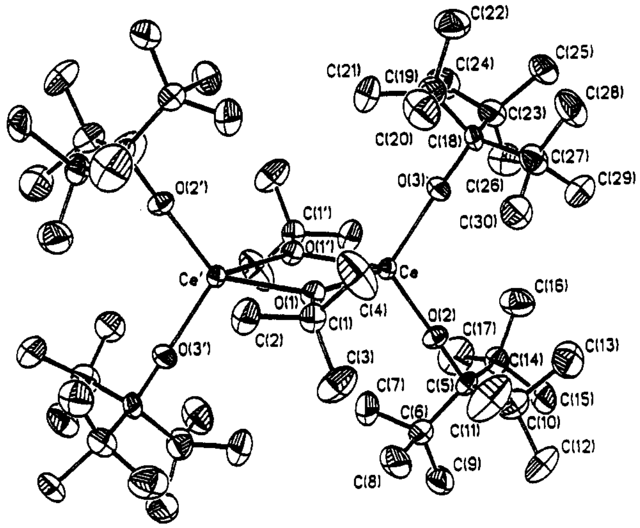

Figure 1. Crystal structure of compound **4**.

An attempt was made to characterize further $Ce(OC^tBu_3)_2(O^tBu)_2$ (**3**) by hydrolyzing a freshly prepared solution of the complex. The $^tBu_3COH$:^tBuOH ratio in the hydrolysate was 1.2:1. However, the high solubility of ^tBuOH in water may have resulted in its incomplete partition into the organic layer.

When the same reaction was followed using a deficiency of DTBP, the same products were initially observed. However, over several hours at ambient temperature, pale yellow crystals coated the inside of the tube. These were barely soluble in C_6D_6 and gave a very broad and unassignable ^1H NMR spectrum and no detectable ^{13}C NMR spectrum. Fortunately, the material grew as large, clean, single crystals suitable for X-ray diffractometry and was characterized by this technique.

Consistent with its broad NMR spectra, the material was a Ce(III) complex, $[Ce(OC^tBu_3)_2(O^tBu)]_2$ (**4**), the structure of which appears in Figure 1. Each cerium adopts a pseudotetrahedral geometry, with the angle to the bridging oxygens (O(1)–Ce–O(1′) = 72.3 (2)°) greatly contracted relative to that for the terminal oxygens (O(2)–Ce–O(3) = 110.9 (2)°). The bridging *tert*-butoxide oxygens and ceriums are constrained to a single plane by a crystallographic inversion center lying at the centroid of these four atoms. This plane forms a dihedral angle of 87.1° with each of the planes formed by a single cerium and its terminal oxygens. The average Ce–O(terminal) and Ce–O(bridging) distances are 2.156 (4) and 2.426 (4) Å, respectively. The average Ce–O–C angle for the terminal alkoxides is 171.6 (6)°. The above values are similar to those observed for the compound $[Ce(OCH^tBu)_3]_2$.[9] The Ce–O(terminal) distances in the compound $Ce(OSiPh_3)_3(THF)_3$ are, however, somewhat longer (average 2.222 (4) Å).[11] The atomic coordinates and selected bond distances and angles for **4** are given in Tables II and III, respectively. Note that **4** is only the second dimeric lanthanide alkoxide that has been characterized by X-ray diffraction.[9] Additionally, structurally characterized dimeric yttrium alkoxides are known.[12]

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for Compound **4**

	x	*y*	*z*	U^a
Ce	1280.4 (3)	47.5 (1)	6203.0 (3)	31.0 (1)
O(1)	774 (4)	65 (2)	4122 (3)	41 (1)
O(2)	1876 (4)	821 (2)	7056 (4)	45 (2)
O(3)	2101 (4)	−682 (2)	7036 (4)	48 (2)
C(1)	1382 (6)	136 (3)	3098 (6)	46 (2)
C(2)	603 (7)	27 (4)	2033 (6)	66 (3)
C(3)	1842 (9)	729 (4)	3074 (8)	88 (4)
C(4)	2360 (8)	−291 (5)	3153 (8)	104 (5)
C(5)	2319 (6)	1341 (3)	7513 (6)	40 (2)
C(6)	1455 (7)	1830 (3)	6997 (8)	66 (3)
C(7)	206 (7)	1655 (4)	6937 (9)	89 (4)
C(8)	1560 (10)	1912 (4)	5652 (7)	104 (5)
C(9)	1578 (8)	2421 (4)	7513 (9)	85 (4)
C(10)	3566 (8)	1405 (4)	7049 (8)	69 (3)
C(11)	3637 (9)	1157 (5)	5823 (9)	115 (6)
C(12)	4127 (8)	1987 (4)	7102 (9)	92 (4)
C(13)	4481 (8)	1007 (4)	7760 (10)	97 (5)
C(14)	2365 (8)	1296 (3)	8904 (7)	58 (3)
C(15)	3116 (8)	1746 (4)	9579 (7)	79 (4)
C(16)	2683 (10)	713 (4)	9371 (8)	93 (5)
C(17)	1151 (9)	1380 (5)	9383 (8)	105 (5)
C(18)	2750 (6)	−1167 (3)	7384 (6)	41 (2)
C(19)	2309 (8)	−1665 (4)	6508 (8)	69 (3)
C(20)	2716 (9)	−1595 (4)	5267 (7)	94 (5)
C(21)	993 (8)	−1649 (4)	6235 (8)	90 (4)
C(22)	2607 (9)	−2275 (3)	6902 (8)	93 (5)
C(23)	2521 (8)	−1305 (4)	8728 (8)	67 (4)
C(24)	1340 (8)	−1578 (4)	8857 (9)	92 (5)
C(25)	3414 (8)	−1706 (4)	9375 (7)	74 (4)
C(26)	2462 (9)	−768 (4)	9450 (7)	83 (4)
C(27)	4064 (7)	−995 (4)	7280 (8)	66 (3)
C(28)	4894 (7)	−1499 (4)	7191 (9)	89 (4)
C(29)	4609 (8)	−616 (4)	8268 (8)	85 (4)
C(30)	4166 (7)	−605 (7)	6186 (7)	75 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for Compound **4**

	(a) Bond Distances (Å)		
Ce–O(1)	2.422 (4)	C(18)–C(19)	1.606 (11)
Ce–O(2)	2.162 (4)	C(18)–C(23)	1.632 (12)
Ce–O(3)	2.157 (4)	C(18)–C(27)	1.615 (11)
Ce–Ce′	3.918 (1)	C(1)–C(2)	1.489 (10)
Ce–O(1′)	2.430 (4)	C(1)–C(3)	1.504 (12)
O(1)–C(1)	1.446 (8)	C(1)–C(4)	1.528 (13)
O(2)–C(5)	1.416 (8)	C(5)–C(6)	1.616 (11)
O(3)–C(18)	1.415 (8)	C(5)–C(10)	1.617 (12)
		C(5)–C(14)	1.605 (10)
	(b) Bond Angles (deg)		
O(1)–Ce–O(2)	118.6 (2)	O(3)–C(18)–C(19)	106.2 (5)
O(1)–Ce–O(3)	121.1 (2)	O(3)–C(18)–C(23)	107.4 (6)
O(2)–Ce–O(3)	110.9 (2)	O(3)–C(18)–C(27)	105.8 (6)
O(1)–Ce–Ce′	36.2 (1)	C(1)–O(1)–Ce′	116.5 (3)
O(2)–Ce–Ce′	124.7 (1)	Ce–O(2)–C(5)	174.3 (4)
O(3)–Ce–Ce′	123.8 (1)	Ce–O(3)–C(18)	168.8 (5)
O(1)–Ce–O(1′)	72.3 (2)	O(1)–C(1)–C(2)	109.9 (6)
O(2)–Ce–O(1′)	116.1 (2)	O(1)–C(1)–C(3)	109.2 (6)
O(3)–Ce–O(1′)	112.4 (2)	O(1)–C(1)–C(4)	108.5 (6)
Ce′–Ce–O(1′)	36.1 (1)	O(2)–C(5)–C(6)	106.5 (5)
Ce–O(1)–C(1)	135.8 (4)	O(2)–C(5)–C(10)	105.8 (6)
Ce–O(1)–Ce′	107.7 (2)	O(2)–C(5)–C(14)	107.1 (5)

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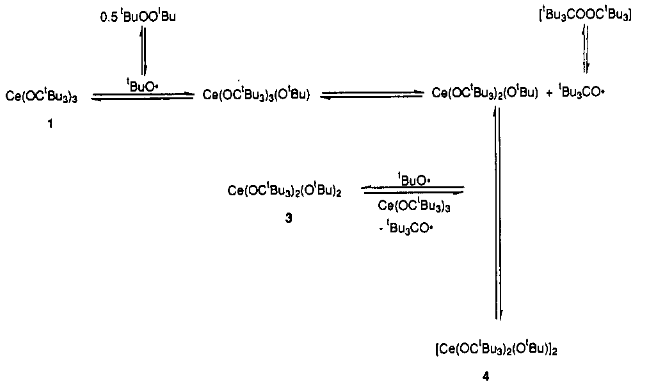
Scheme I



All attempts to isolate **3** in pure form were frustrated by its instability, problems separating it from [^{t}Bu$_3$COOC^{t}Bu$_3$], its apparent existence as an oil at ambient temperature, and its infinite solubility in pentane and other noncoordinating solvents. The presence of trace amounts of HN(SiMe$_3$)$_2$ in **1** may also contribute to the problem of isolating pure **3**. **3** was prepared and stored in impure form as a very thick, sticky, orange-brown oil. Decomposition occurred over a period of several weeks at ambient temperature. The diamagnetic impurities were chiefly ^{t}Bu$_3$COH and ^{t}Bu$_2$CO, as shown by NMR spectroscopy. There were several broad resonances between 12.0 and 3.0 ppm, none very large relative to the **3** and [^{t}Bu$_3$COOC^{t}Bu$_3$] peaks.

The cerium(III) dimer, **4**, was prepared from **1** and 0.5 equiv of DTBP. The pale yellow microcrystalline solid exhibited similar slight solubility in C$_6$D$_6$ and gave a pattern of humps in the ^{1}H NMR spectrum identical with that of the material obtained from the NMR tube experiments. In addition, it gave acceptable microanalytical data for carbon and hydrogen.

Isolations of **3** and **4** allowed the interconversion of these complexes to be studied. Thus, when a mixture of the former compound and **1** was allowed to react at ambient temperature in C$_6$D$_6$, fine, pale yellow crystals formed. In addition, the same pattern of the broad humps was observed in the ^{1}H NMR spectrum as in the NMR-scale reaction, from which single crystals of **4** were isolated.

On the other hand, when **4** was heated with 1 molar equiv of DTBP, **3** was produced, but no [^{t}Bu$_3$COOC^{t}Bu$_3$] was observed. In fact, this was the cleanest route to **3** and represented the best, if not the simplest, synthetic method available.

The results presented thus far are summarized in Scheme I. The first step in the reaction between **1** and DTBP is almost certainly an attack of the *tert*-butoxyl radical (formed by homolysis of the peroxide) on the alkoxide to give Ce(OC^{t}Bu$_3$)$_3$(O^{t}Bu). Indeed, this is the reaction (eq 3) which was expected at the outset of the work and is analogous to that observed when benzoyl peroxide was used (eq 1).

$$\underset{\mathbf{1}}{\mathrm{Ce(OC^tBu_3)_3}} + 0.5\underset{\mathrm{DTBP}}{^t\mathrm{BuOO}^t\mathrm{Bu}} \rightarrow \mathrm{Ce(OC^tBu_3)_3(O^tBu)} \quad (3)$$

A further reason that the attack of the *tert*-butoxyl radical on Ce(OC^{t}Bu$_3$)$_3$ is a plausible first step stems from the observation that the reaction was very slow at ambient temperature but proceeded at a convenient rate at 80–100 °C. Many radical-initiated reactions utilize alkoxyl or carboxyl radicals which are derived from the corresponding peroxides by thermolysis in this temperature range.[13]

The fate of the Ce(OC^{t}Bu$_3$)$_3$(O^{t}Bu) intermediate is unclear, but two paths to the observed products suggest themselves, both of which lead to the trivalent mixed alkoxide [Ce(OC^{t}Bu$_3$)$_2$(O^{t}Bu)]$_x$ (x = 1, 2). The indicated reductive homolysis pathway is just the formal reverse of the oxidative combination that formed Ce(OC^{t}Bu$_3$)$_3$(O^{t}Bu) in the first place; that is, a ^{t}Bu$_3$CO moiety is lost as the ^{t}Bu$_3$CO$^•$ radical with formal one-electron reduction of the metal. This overall net substitution is almost certainly driven by steric factors. The greater stability of Ce(OC^{t}Bu$_3$)$_2$(O^{t}Bu) over Ce(OC^{t}Bu$_3$)$_3$ stems from the ability of the former to dimerize, thereby increasing the coordination number of cerium from 3 to 4. It is well-known that lanthanides react in ways which maximize their coordination number.[14]

The other plausible route from Ce(OC^{t}Bu$_3$)$_3$(O^{t}Bu) to the Ce(III) system involves a bimolecular reductive elimination. This would lead to the formation of [^{t}Bu$_3$COOC^{t}Bu$_3$] without involving a free ^{t}Bu$_3$CO$^•$ radical. However, this would require a dimeric intermediate (or transition state) with presumably unrealistic steric congestion.

One question which arises involves the monomer/dimer nature of Ce(OC^{t}Bu$_3$)$_2$(O^{t}Bu). It is clear from the crystal structure that the complex exists as a dimer in the solid state. Its very low solubility in C$_6$D$_6$ and very broad NMR spectra are reminiscent of [Ce(OCH^{t}Bu$_2$)$_3$]$_2$ and may be general properties of polynuclear complexes of this type. However, the position of the monomer/dimer equilibrium in solution is not clear. Either species (or both) may react with the *tert*-butoxyl radical to form the cerium(IV) mixed alkoxide **3** (eq 4).

$$\underset{\mathbf{4}}{[\mathrm{Ce(OC^tBu_3)_2(O^tBu)}]_x} + {}^t\mathrm{Bu_3O^\bullet} \rightarrow \underset{\mathbf{3}}{\mathrm{Ce(OC^tBu_3)_2(O^tBu)_2}} \quad (4)$$

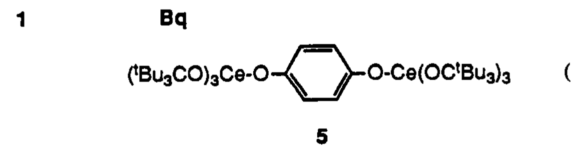
Reaction with *tert*-Butyl Peroxybenzoate. The reaction of **1** with the unsymmetrical peroxide *tert*-butyl peroxybenzoate (BPB) in C$_6$H$_6$ led to the formation of products observed with *both* benzoyl peroxide and di-*tert*-butyl peroxide (eq 5). Titration of

$$\underset{\mathbf{1}}{6\mathrm{Ce(OC^tBu_3)_3}} + \underset{\mathrm{BPB}}{4^t\mathrm{BuOOC(O)Ph}} \xrightarrow[25\ ^\circ\mathrm{C}]{\mathrm{C_6H_6}} \underset{\mathbf{2}}{4\mathrm{Ce(OC^tBu_3)_3(OC(O)Ph)}} + \underset{\mathbf{3}}{2\mathrm{Ce(OC^tBu_3)_2(O^tBu)_2}} + [^t\mathrm{Bu_3COOC^tBu_3}] \quad (5)$$

1 with BPB led to the immediate formation of the three products in what appeared, by inspection, to be the appropriate amounts (overlapping signals prevented a quantitative analysis of the reaction mixture). The formation of these products was further confirmed by ^{13}C NMR spectroscopy (Table I).

The above work demonstrates that peroxides can be useful reagents for synthesizing Ce(IV) complexes. They presumably act by initial homolysis to form the alkoxyl (or carboxyl) radical which accepts an electron to become an alkoxide (or carboxylate) ligand. The complication seen for DTBP stems from the creation of an environment which is too sterically encumbered to be stable under the reaction conditions. However, in the absence of this condition, the method should be quite general for the oxidation of Ce(III) complexes of nonoxidizable ligands to the tetravalent state.

Reaction with Benzoquinone. The titration of **1** with benzoquinone (Bq) was the cleanest and most easily characterized oxidation of any in this study. The stoichiometry and NMR spectra (Table I) were consistent with formation of a binuclear complex bridged by a hydroquinonediolate (eq 6). The resultant complex, **5**, was somewhat less soluble than the starting alkoxide and precipitated from solution as single, well-formed, medium-



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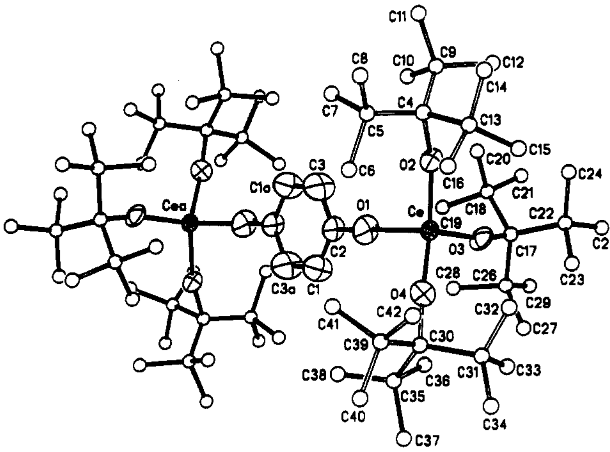

Figure 2. Crystal structure of compound **5**. The *t*-Bu groups are drawn with isotropic carbon atoms for clarity.

brown plates suitable for X-ray diffraction. The crystals, once isolated, gave back purple solutions in C_6D_6 that yielded the same NMR data as seen in the titration.

$(^t\mathrm{Bu}_3\mathrm{CO})_3\mathrm{CeOC}_6\mathrm{H}_4\mathrm{OCe}(\mathrm{OC}^t\mathrm{Bu}_3)_3$ (**5**) lies on the inversion center with a molecule of benzene (not shown) in the lattice (Figure 2). The Ce–O–C angles of the terminal alkoxide groups in this compound are in the same range as those in the other alkoxides studied. The cerium atoms adopt a pseudotetrahedral geometry with the O–Ce–O angles ranging from 102.4 to 115.3 (3)°. Predictably, the angles involving a terminal alkoxide oxygen and the hydroquinone diolate oxygen (103–104°) were smaller than those between only the terminal alkoxide oxygens (114–116°) due to the greater steric demand of a $^t\mathrm{Bu}_3\mathrm{CO}$– group versus $-\mathrm{OC}_6\mathrm{H}_4\mathrm{OCe}(\mathrm{OC}^t\mathrm{Bu}_3)_3$. The Ce–O bond distances (2.093 (10) Å average for the terminal alkoxides and 2.086 (10) Å for the phenolate) are at the high end of the range observed with other neutral cerium(IV) alkoxides[6] (2.025 (5)–2.115 (10) Å) and presumably reflect the large steric size of the $\mathrm{OC}^t\mathrm{Bu}_3$ ligand. Not unexpectedly, a longer Ce–O(terminal) distance of 2.141 (4) Å was observed for the anionic Ce(IV) complex $\mathrm{Ce(OCMe_3)_2(\mu\text{-}OCMe_3)_2(\mu_3\text{-}OCMe_3)_2Na_2(DME)_2}$.[6b] However, these comparisons should be treated with caution because of differences in coordination number of the Ce(IV) ion. Perhaps, a more meaningful comparison is between compounds **4** and **5**, both of which are 4-coordinate with terminal $\mathrm{OC}^t\mathrm{Bu}_3$ ligands. The 0.063 Å difference in Ce–O(terminal) bond lengths is significantly shorter than predicted. According to Shannon,[15] the differences in ionic radii between Ce(III) and Ce(IV) are 0.14 and 0.173 Å for coordination numbers 6 and 8, respectively. While the corresponding difference for the 4-coordinate ion has not been established, the above trend would appear to indicate a value that is significantly higher than that derived experimentally from compounds **4** and **5**. One possible explanation for this discrepancy is that the steric bulk of the $\mathrm{OC}^t\mathrm{Bu}_3$ ligand prevents its close approach to the smaller Ce(IV) center. Our earlier observations[9] that (a) $\mathrm{Ce(OC^tBu_3)_3}$ is monomeric, (b) it thermally decomposes by expelling a $^t\mathrm{Bu}^\bullet$ radical, and (c) the resultant complex $[\mathrm{Ce(OCH^tBu_2)_3}]_2$ is dimeric, where the Ce(III) center is now 4-coordinate, are consistent with this explanation. If the Ce(IV)–$\mathrm{OC}^t\mathrm{Bu}_3$ bond is indeed weaker due to steric reasons, that would explain the relative instability of Ce(IV) complexes incorporating this ligand. As illustrated in Scheme I and our studies, the Ce(IV)–$\mathrm{OC}^t\mathrm{Bu}_3$ bond is particularly susceptible to homolysis and, for example, is weaker than the Ce(IV)–$\mathrm{O}^t\mathrm{Bu}$ bond in this regard. The atomic coordinates and selected bond distances and angles for **5** are given in Tables IV and V, respectively.

The facility of the reaction with benzoquinone was demonstrated graphically when, during a preparative-scale reaction, the yellow solids started to react with one another before the benzene was added. The reaction described in the Experimental Section gave an 80% yield of brown-black microcrystalline **5** which was 99% pure by ^{1}H NMR spectroscopy. **5**, in the solid state, was found to decompose slowly over a period of several weeks to various paramagnetic species, again demonstrating the relative instability of the tetravalent state.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($\text{Å}^2 \times 10^3$) for Compound **5**

	x	*y*	*z*	U^a
Ce	2425.7 (6)	4818.0 (7)	2507.9 (4)	41.8 (3)
O(1)	1560 (10)	4641 (11)	3605 (5)	92 (6)
O(2)	4000 (7)	4851 (8)	2651 (5)	62 (4)
O(3)	1103 (9)	6453 (8)	2154 (5)	77 (5)
O(4)	2738 (8)	3330 (8)	1933 (5)	68 (5)
C(1)	−140 (19)	4515 (19)	4414 (9)	117 (14)
C(2)	780 (13)	4806 (15)	4297 (7)	73 (8)
C(3)	927 (17)	5292 (21)	4876 (10)	126 (14)
C(4)	5221 (16)	4595 (17)	2807 (10)	99 (11)
C(5)	5611 (11)	3521 (14)	3349 (6)	140 (14)
C(6)	5236 (18)	2586 (15)	3168 (10)	189 (21)
C(7)	5014 (12)	3920 (17)	4196 (7)	179 (21)
C(8)	7050 (10)	2890 (23)	3270 (11)	298 (27)
C(9)	5050 (8)	5785 (11)	3141 (5)	141 (16)
C(10)	3896 (11)	6230 (15)	3800 (7)	168 (17)
C(11)	6191 (13)	5555 (18)	3471 (10)	183 (23)
C(12)	4846 (13)	6788 (17)	2529 (8)	278 (42)
C(13)	6034 (11)	4244 (16)	1876 (10)	164 (19)
C(14)	7235 (10)	4365 (12)	1800 (11)	269 (32)
C(15)	5244 (13)	5139 (24)	1321 (11)	220 (33)
C(16)	6395 (21)	2943 (19)	1658 (15)	226 (28)
C(17)	308 (18)	7615 (13)	2030 (11)	101 (10)
C(18)	21 (18)	8379 (8)	2832 (11)	187 (22)
C(19)	−757 (34)	8046 (21)	3521 (15)	335 (50)
C(20)	1336 (19)	7935 (16)	2978 (17)	324 (34)
C(21)	−615 (11)	9757 (7)	2712 (10)	189 (20)
C(22)	988 (10)	8024 (10)	1248 (9)	300 (33)
C(23)	1378 (15)	6994 (10)	701 (11)	360 (47)
C(24)	2142 (13)	8089 (14)	1359 (17)	904 (83)
C(25)	74 (17)	9236 (10)	953 (16)	787 (68)
C(26)	−1043 (15)	7629 (14)	1969 (7)	217 (20)
C(27)	−834 (25)	6869 (21)	1285 (6)	327 (39)
C(28)	−1283 (20)	6986 (11)	2722 (5)	295 (37)
C(29)	−2174 (23)	8879 (13)	1934 (12)	298 (29)
C(30)	2671 (13)	2434 (12)	1536 (8)	65 (7)
C(31)	2937 (19)	2850 (16)	627 (9)	227 (33)
C(32)	3958 (28)	3257 (26)	442 (12)	214 (32)
C(33)	1683 (24)	3961 (17)	542 (15)	419 (48)
C(34)	3260 (18)	1881 (16)	33 (11)	145 (15)
C(35)	1254 (12)	2507 (7)	1930 (5)	362 (32)
C(36)	352 (20)	3873 (10)	1935 (10)	276 (28)
C(37)	928 (21)	1873 (17)	1389 (7)	175 (20)
C(38)	1067 (26)	1995 (12)	2750 (5)	365 (39)
C(39)	3822 (18)	1130 (13)	1705 (11)	144 (16)
C(40)	3653 (19)	60 (15)	1515 (11)	135 (14)
C(41)	3926 (33)	1029 (21)	2556 (12)	314 (37)
C(42)	5048 (22)	1046 (26)	1199 (17)	338 (40)
Cs(1)	1189 (28)	9462 (68)	4973 (30)	235 (37)
Cs(2)	639 (48)	10557 (56)	4631 (22)	242 (36)
Cs(3)	−513 (56)	11077 (41)	4746 (20)	194 (27)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Distances and Angles for Compound **5**

(a) Bond Distances (Å)			
Ce–O(1)	2.086 (10)	O(1)–C(2)	1.375 (15)
Ce–O(2)	2.084 (11)	C(2)–C(1)	1.35 (4)
Ce–O(3)	2.102 (8)	C(2)–C(3)	1.37 (3)
Ce–O(4)	2.092 (11)	C(3)–C(1a)	1.40 (2)

(b) Bond Angles (deg)			
O(1)–Ce–O(2)	104.1 (4)	Ce–O(2)–C(4)	167.5 (10)
O(1)–Ce–O(3)	102.4 (4)	Ce–O(4)–C(30)	167.6 (8)
O(1)–Ce–O(4)	104.5 (5)	O(1)–C(2)–C(6)	121 (2)
O(2)–Ce–O(3)	114.2 (4)	O(1)–C(2)–C(3)	120 (2)
O(2)–Ce–O(4)	115.3 (3)	C(1)–C(2)–C(3)	119 (2)
O(3)–Ce–O(4)	114.3 (4)	C(2)–C(1)–C(3a)	120 (2)
Ce–O(1)–C(2)	165.9 (9)	C(2)–C(3)–C(1a)	121 (2)
Ce–O(3)–C(17)	168.0 (13)		

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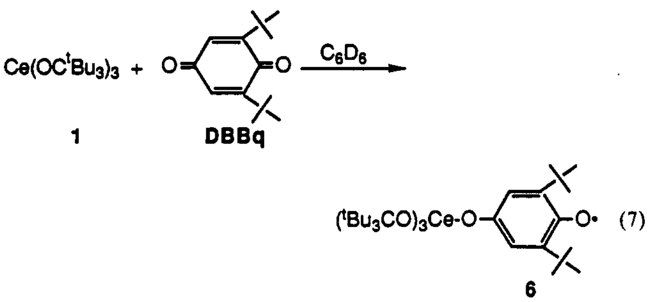
(15) Shannon, D. *Acta Crystallogr.* **1976**, *A32*, 751.

Reaction with 2,6-Di-*tert*-butylbenzoquinone. In an attempt to perform only half of the two-electron quinone oxidation of $Ce(OC^tBu_3)_3$, 2,6-di-*tert*-butylbenzoquinone (DBBq) was used. It was reasoned that the *tert*-butyl groups would block the space around the 1-oxygen, preventing approach of a second $Ce(OC^tBu_3)_3$ molecule. This was indeed the case. The ^1H NMR titration was consistent with immediate formation of a paramagnetic species in which the lone electron was localized on the incoming oxidant, forming a hemiquinone complex (eq 7). The absence of a proton signal for the 3,5-protons, the extremely broad resonance for the ring tert-butyl groups, and "normal" chemical shift of the $^tBu_3CO$ ligands indicated that the unpaired electron was delocalized about the ring but not on the cerium. This is consistent with ESR results obtained for the product of DBBq and the paramagnetic $Co(CN)_5^{3-}$.[16]



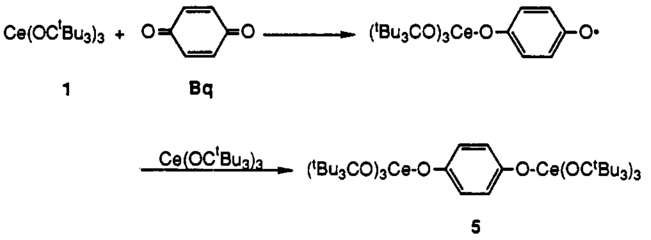
1 DBBq

6 (7)

This cerium(IV) product, **6**, however, was markedly less stable in solution than $(^tBu_3CO)_3CeOC_6H_4OCe(OC^tBu_3)_3$ (**5**), showing signs of decomposition after several hours at ambient temperature in C_6D_6. Of the byproducts observed as this decomposition progressed, the two identified were $^tBu_2CO$ and isobutylene. This suggests that a $^tBu_3CO$ radical was being released which decomposed to the ketone and the *tert*-butyl radical.

The hemiquinone complex, **6**, was generated in an ESR cavity, and a spectrum was observed. A single sharp line was seen at $g = 1.9993$ on top of a very broad and ill-defined signal. The signal for free hemiquinone is a triplet with coupling to the 3,5-protons and a coupling constant of 2.14 G. Evidently, complexation to cerium restricts the delocalization of the spin around the ring.[16a] The oxidative complexation of DBBq to other radicals (metal-, metalloid-, or non-metal-centered) has been reported.[16,17]

The oxidation of two molecules of $Ce(OC^tBu_3)_3$ by quinones almost certainly takes place in two steps. The initial one-electron oxidation forms a hemiquinone complex, and this combines with a second alkoxide molecule to form the final product (eq 8).

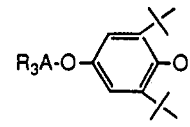


1 Bq

5

(8)

Precedent for the first step comes not only from the reaction of $Ce(OC^tBu_3)_3$ with DBBq but also from numerous other reactions using this quinone. Thus, "radical adducts" are formed when $R_3A^\bullet$ ($R = CH_3, C_2H_5$; $A = C, Si, Ge, Sn, Pb$) is generated in the presence of DBBq and have the structure shown, as determined by ESR analysis.[17a,b]



Similar adducts of $Ph_2P^\bullet$, $PhS^\bullet$, and a wide range of silyl radicals were also reported. Further evidence comes from the reactions of $Co(CN)_5^{3-}$ and $CpMo(CO)_3$ with quinones.[16,17c,d] As mentioned earlier, DBBq gives the hemiquinone complex with concomitant oxidation of the cobalt to the 3+ state.[16] However, even Bq gives $(NC)_5CoOC_6H_4O^\bullet$ (characterized by ESR spectroscopy) under some conditions, and when $(NC)_5CoOC_6H_4OCo(CN)_5$ was observed, it was apparently formed in two steps.[16] A similar reaction occurs when $CpMo(CO)_3$ is generated photochemically from the dimer in the presence of a wide range of quinones.[17d]

The second step of this proposed scheme is a radical combination reminiscent of the mechanism discussed for the DTBP oxidation of $Ce(OC^tBu_3)_3$. The spin density in the hemiquinone complexes is primarily on the uncoordinated oxygen rather than delocalized evenly about the ring,[16,17b,d] so this acts like an aryloxyl radical and oxidatively adds to $Ce(OC^tBu_3)_3$.

Conclusion

We have demonstrated the use of several classes of oxidants in the direct oxidation of homoleptic Ce(III) alkoxides to the corresponding Ce(IV) compounds. Additionally, the crystal structures of related Ce(III) and Ce(IV) alkoxides have been determined. From a synthetic standpoint, the high tendency of the tri-*tert*-butyl methoxide group to dissociate off Ce(IV) as a radical greatly limits its utility as a ligand. As discussed above, to a large extent, the weakness of the $Ce(IV)-OC^tBu_3$ bond is due to greater steric congestion present around the smaller Ce(IV) ion. On the other hand, $Ce(O^iPr)_4$, containing the less sterically demanding isopropoxide group, is stable. Unfortunately, the use of smaller ligands also results in the formation of oligomeric species incorporating bridging alkoxide groups.[18]

Experimental Section

General Considerations. Unless otherwise noted, all manipulations were performed with rigorous exclusion of oxygen and water under an atmosphere of dinitrogen or argon. To this end was used either a Schlenk line (mechanical pump for vacuum, 10^{-1}–10^{-2} Torr; prepurified N_2 or Ar used as received), a high-vacuum line (diffusion pump for vacuum, 10^{-5} Torr; Ar further purified by passage first through MnO supported on Vermiculite and then through molecular sieves), or a Vacuum Atmospheres drybox (N_2 purified with copper chromite and molecular sieves).

Nuclear magnetic resonance spectra were recorded on either a Varian EM360 (^1H; CW; 60 MHz), a Bruker WM-200 (^1H, ^{13}C; FT; 200 MHz for proton), or a Bruker AM-300 spectrometer (^1H, ^{13}C; FT; 300 MHz for proton). Chemical shifts are reported in parts per million relative to tetramethylsilane and were standardized against the chemical shift of the proton impurity or the carbon shift of the solvent (C_6D_5H, 7.15 ppm; C_6D_6, 128.0 ppm; $C_6D_5CD_2H$, 2.09 ppm; $C_6D_5CD_3$, 20.4 ppm). Infrared spectra were recorded on a Perkin-Elmer 281B spectrometer. Gas chromatographic analyses were carried out on a Varian Model 3700 using a 10-ft column of SP2100 on 80/100 Supelcoport (Supelco), nitrogen as the carrier gas, a flame ionization detector (hydrogen/air), and various conditions to meet experimental needs. GC/MS analysis was carried out on a Finnigan 9500 gas chromatograph coupled to a Finnigan 3200 mass spectrometer with a Finnigan 6000 spectral data system. Electron ionization spectra were run at 70 eV, and chemical ionization spectra utilized methane as the reagent gas. Microanalyses of air-stable samples were performed by Galbraith Laboratories Inc., and those of air-sensitive samples, by Dornis und Kolbe Mikroanalytisches Laboratorium under argon using V_2O_5 as a combustion aid.

Materials. Hydrocarbon and ethereal solvents were predried with molecular sieves and then distilled under dinitrogen from solutions of potassium or sodium benzophenone ketyl. In the case of alkanes, tetraethylene glycol dimethyl ether was added to dissolve the drying agent.

Cerium chloride (anhydrous, Aldrich or Alfa) was either used as received or dried by refluxing with $SOCl_2$ for 48 h. $SOCl_2$ was removed, and the solid was dried under vacuum for 24 h at 110 °C. The lithium and sodium salts of bis(trimethylsilyl)amide (Aldrich) were used as received. $Ce[N(SiMe_3)_2]_3$ was prepared in poor to moderate yields using

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[16] (a) Vlcek, A.; Klima, J.; Vlcek, A. A. *Inorg. Chim. Acta* **1981**, *58*, 75. (b) Vlcek, A.; Klima, J.; Vlcek, A. A. *Inorg. Chim. Acta* **1983**, *69*, 191. (c) Vlcek, A. A.; Hanzlik, J. *Inorg. Chem.* **1967**, *6*, 2053.

[17] (a) Chen, K. S.; Foster, T.; Wan, J. K. S. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1288. (b) Alberti, A.; Hudson, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1908. (c) Nishinaga, A.; Tomita, H.; Matsuura, M. *Tetrahedron Lett.* **1989**, *21*, 4853. (d) Hanaya, M.; Iwaizumi, M. *Organometallics* **1989**, *8*, 672.

[18] Reference 14a, p 70.

the method of Bradley from $CeCl_3$ and $Li[N(SiMe_3)_2]$ in THF.[19] $^tBu_3COH$ was synthesized from ^tBuLi and either diethyl carbonate or ethyl pivalate according to the procedure given by Syper.[8]

Di-*tert*-butyl peroxide was dried by stirring over 4-Å molecular sieves, degassed, and vacuum-transferred into a tube equipped with a Teflon valve for storage. Benzoyl peroxide was dried at ambient temperature for several hours under vacuum (10^{-5} Torr) and then taken into the glovebox. *tert*-Butyl peroxybenzoate was dried by stirring over molecular sieves for ca. 30 min. The sieves were separated from the mixture by filtration, and the peroxide was recrystallized by partial freezing twice. This material was then poured into a tube equipped with a Teflon joint, degassed, and stored. (Note that all manipulations were carried out in grease-free apparatus. Teflon tape was used to separate ground-glass joints.) Quinones were purified by vacuum sublimation, collected in the glovebox, and stored in screw-capped vials in the freezer.

Synthesis of $Ce(OC^tBu_3)_3$ (1). In the glovebox, a 100-mL Solv-seal flask was charged with $Ce[N(SiMe_3)_2]_3$ (3.96 g, 6.37 mmol) and a stir bar. Another flask was charged with $^tBu_3COH$ (3.85 g, 19.2 mmol, 3.01 equiv) and a stir bar; and a small amount of pentane was added to wash the sticky alcohol off the funnel into the flask. The flasks were connected to a frit apparatus; the assembly was brought out and attached to a vacuum line, care being taken that the reagents would not mix.

The frit was slowly evacuated, resulting in evaporation of the pentane. When the frit was fully evacuated, ca. 40 mL of pentane was condensed into the $Ce[N(SiMe_3)_2]_3$ flask. The assembly was left under static vacuum, the pentane warmed to ambient temperature, and the $Ce[N(SiMe_3)_2]_3$ allowed to dissolve. The $^tBu_3COH$ was added to the $Ce[N(SiMe_3)_2]_3$ by condensing pentane on the top of the frit and allowing it to dissolve the $^tBu_3COH$ and bring it through the frit into the flask containing the $Ce[N(SiMe_3)_2]_3$. As the addition proceeded, the solution turned orange and a dull yellow solid deposited. The reaction was allowed to stir for 1 h at ambient temperature and for an additional 1 h at 0 °C. The solid was filtered off, washed with one 5-mL portion of cold pentane, and dried in vacuo for ca. 3 h.

The yellow powder was collected in the glovebox. The yield was 79%. Anal. Calcd for $Ce(OC_{13}H_{27})_3$: C, 63.46; H, 11.06; N, 0.00. Found: C, 61.24; H, 10.27; N, 0.67. Note that this poor analysis is consistent with the presence of residual $N(SiMe_3)_2$ groups bound to cerium or entrained as $HN(SiMe_3)_2$. ^1H NMR spectra of various batches suggested the latter.

Reaction of 1 with Benzoyl Peroxide (BzP). In the glovebox, an NMR tube was charged with **1** (27 mg, 36.6 μmol) and C_6D_6. A vial was charged with BzP (45 mg, 185.7 μmol) and C_6D_6 to make 0.90 mL of solution. Both were capped with septa and brought out of the box.

An initial ^1H NMR spectrum of **1** was recorded; this solution was then titrated with BzP. Addition of the peroxide caused a slight darkening of the yellow color. The reaction appeared to be instantaneous, and the titration was halted after 0.45 equiv had been added.

As the titration progressed, the resonance due to **1** diminished, and peaks consistent with $Ce(OC^tBu_3)_3(OC(O)Ph)$ (**2**) appeared (Table I). A ^{13}C NMR spectrum was also consistent with this oxidized product. However, a ^1H NMR spectrum recorded after the carbon data had been collected revealed reductive decomposition. A number of paramagnetically broadened and shifted peaks indicated the presence of various Ce(III) species. Also present was a trace of isobutylene.

In the glovebox, a two-necked, 100-mL Solv-seal flask was charged with **1** (450 mg, 0.610 mmol). A 30-mL flask was charged with BzP (78 mg, 0.32 mmol). The latter was attached to one neck of the former, and care was taken not to mix the solids. The second neck of the 100-mL flask was attached to a frit assembly, and the whole apparatus was brought out of the box and attached to a vacuum line.

Under static vacuum, 30 mL of pentane was condensed onto **1**. The mixture was allowed to warm to ambient temperature, resulting in an orange solution with some yellow, undissolved **1**. The BzP was added all at once; this mixture was stirred for 5 min, over which time **1** dissolved. After another 5 min, the BzP had dissolved as well. The solution was filtered, and the solvent was removed in vacuo, leaving an orange oil.

It became evident that as the material was manipulated (as pentane was added or removed to wash the sides of the flask), the material was slowly decomposing. Finally, the oil was dried in vacuo for 3 h.

^1H NMR spectroscopy indicated that the oil was mainly **2**, as expected from the NMR titration, contaminated with $^tBu_3COH$ and several Ce(III) species.

Reaction of 1 with Di-*tert*-butyl Peroxide (DTBP). In the glovebox, an NMR tube was charged with **1** (65 mg, 88.1 μmol) and C_6D_6. A separate vial was charged with DTBP. Both were capped with septa and removed from the box. One equivalent (16.2 μL) of the peroxide was removed from the vial and injected into the NMR tube using a dinitrogen-flushed syringe. A ^1H NMR spectrum was recorded, followed by the recording of a ^{13}C NMR spectrum and finally another ^1H NMR spectrum. The second ^1H NMR spectrum was recorded to monitor changes in the reaction that may have taken place during the collection of the ^{13}C NMR data. (The spectra revealed that very little reaction had taken place during this time.)

The NMR tube was heated in a 75 °C oil bath for 8 min. The same progression of ^1H and ^{13}C NMR spectra were recorded, indicating that a reaction had taken place but that it was not complete.

The NMR tube was heated again, this time to 100 °C for 5 min. NMR analysis showed that the starting materials had been consumed and that products consistent with diamagnetic species had formed. See Table I for NMR data.

In another experiment, 1 equiv of DTBP was added to **1** in C_6D_6 and the reaction followed by ^1H and ^{13}C NMR spectroscopy. When the reaction reached completion, the NMR tube was returned to the glovebox and attached to a bushing adapter which allowed connection to a vacuum line. The assembly was removed from the box and attached to a vacuum line, and the solvent and volatiles were removed to a U-trap (cooled to −196 °C) in vacuo. After 2 h, an orange gel remained. This residue was redissolved in C_6D_6; the volatiles were allowed to thaw, and both fractions were reanalyzed by ^1H and ^{13}C NMR spectroscopy.

The results of these two experiments were consistent with the formation of two diamagnetic products from the reaction of 1 equiv of DTBP with **1**. The volatile product contained a single $^tBu_3CO$ moiety but did not survive the evacuation and recondensation process. Instead, di-*tert*-butyl ketone was observed, along with $^tBu_3COH$, isobutylene, and other organics which contained *tert*-butyl groups. This product was never isolated, but the NMR data (Table I), stoichiometry, mass balance, and decomposition products were consistent with the peroxide, $[^tBu_3COOC^tBu_3]$.

In the glovebox, an NMR tube was charged with 58 mg of **1** (78.6 μmol) and C_6D_6. A separate vial was charged with DTBP. Both were capped with septa and removed from the box. DTBP (40.7 μL, 0.52 equiv) was transferred from the vial to the NMR tube via a nitrogen-flushed syringe. The reaction was then followed by ^1H and ^{13}C NMR spectroscopy in a manner similar to that described above.

In addition to the diamagnetic products seen in the experiments with 1 equiv of DTBP, paramagnetic products were also present. After approximately 4 h, a thick layer of small pale yellow crystals was observed. These were isolated in the glovebox by decanting the solution, and then more C_6D_6 was added. The crystals were barely soluble. ^1H and ^{13}C NMR spectra was recorded for this new pale yellow solution.

In an experiment similar to the preceding one, the crystals formed in the reaction were of sufficient size and quality for X-ray structural analysis. The crystals were isolated by decantation in the glovebox, washed quickly with pentane, allowed to dry, and mounted in 0.5-mm capillary tubes. The material was shown to be $[Ce(OC^tBu_3)_2(O^tBu)]_2$ (**4**) by X-ray crystallography.

Synthesis of $Ce(OC^tBu_3)_2(O^tBu)_2$ (3). In a preparative experiment, a 30-mL Solv-seal flask was charged with 1.03 g of **1** (1.40 mmol). The flask was attached to a frit assembly, which was then removed from the glovebox. On the vacuum line, ca. 20 mL of benzene was condensed into the reaction flask at 0 °C. The mixture was stirred and allowed to warm to ambient temperature. When **1** had dissolved, 265 μL (1.03 equiv) of DTBP was added by syringe against a rapid flush of argon. The reaction was heated with an oil bath to 95 °C for 15 min, during which time the color changed from yellow to a dark orange-brown. The reaction mixture was filtered (no significant amount of solid was noted), the benzene was removed, and the residue was dried in vacuo for 6 h. The ^1H NMR spectrum showed the solid to be a 1:1 mixture of **3** and $[^tBu_3COOC^tBu_3]$.

Synthesis of $[Ce(OC^tBu_3)_2(O^tBu)]_2$ (4). In the glovebox a 100-mL Solv-seal flask was charged with 0.52 g of **1** (0.70 mmol). The flask was attached to a frit assembly, and the whole apparatus was removed from the box and attached to a vacuum line. The frit was evacuated, and ca. 15 mL of benzene was condensed onto **1** at 0 °C. The mixture was allowed to warm to ambient temperature, and when **1** had dissolved, the solution was filtered. The frit was back-filled with argon, and under flush 65 μL (0.50 equiv) of DTBP was added. The reaction mixture was heated to 100 °C for 8 minutes and then allowed to stand. Over 3 days, a fine pale yellow powder precipitated from the orange solution. This solid was filtered off and dried in vacuo for 3 h. The frit was taken into the box, and the solid was collected, weighed, and stored (yield 0.163 g, 38% based on **1**). Anal. Calcd: C, 58.88; H, 10.38. Found: C, 58.10; H, 10.41.

Reactions of 3 and 4. In the glovebox, an NMR tube was charged with 8 mg (ca. 6.5 μmol) of **4** and C_6D_6. A vial was charged with DTBP. Both were capped with septa and removed from the box.

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[19] (a) Bradley, D. C.; Ghorta, J. S.; Hart, F. A. *J. Chem. Soc., Chem. Commun.* **1972**, 349. (b) Bradley, D. C.; Ghorta, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.* **1973**, 1021.

Table VI. Crystallographic Data for Compounds **4** and **5**

	4	**5**
	(a) Crystal Parameters	
cryst system	monoclinic	triclinic
space group:	$P2_1/c$	$P\bar{1}$
a, Å	11.783 (2)	12.629 (4)
b, Å	23.606 (6)	12.736 (5)
c, Å	11.544 (2)	18.148 (8)
α, deg		83.60 (3)
β, deg	95.19 (2)	76.83 (3)
γ, deg		61.57 (3)
V, Å^3	3198 (1)	2499 (1)
Z	2	1
cryst dimens, mm	0.25 × 0.25 × 0.40	0.14 × 0.31 × 0.36
D(calcd), g cm^{-3}	1.270	1.105
μ(Mo Kα), cm^{-1}	14.59	9.5
temp, K	296	296
T_{max}/T_{min}	1.098	1.12
	(b) Data Collection	
scan technique	ω	ω
scan limits, deg	$4 < 2\theta < 48$	$4 < 2\theta < 50$
data collected	$\pm h,+k,+l$	$\pm h,\pm k,+l$
no. of reflcns collected	5447	9093
no. of indep reflcns	5017	8790
no. of indep reflcns obsd	3240 $[F_o \geq 6\sigma(F_o)]$	6403 $[F_o \geq 5\sigma(F_o)]$
	(c) Refinement	
$R(F)$, %	3.79	7.70
$R_w(F)$, %	4.08	7.97
Δ/σ (max)	0.008	0.09
$\Delta(\rho)$, e Å^{-3}	0.822	1.6
N_o/N_v	10.55	14.4
GOF	1.126	1.466

A ^{1}H NMR spectrum was recorded, and then 1.2 μL of DTBP (6.5 μmol) was added and the tube was heated to 95 °C for 13 min, over which time the solids dissolved. No precipitate was noted upon cooling to ambient temperature. ^{1}H and ^{13}C NMR spectra were recorded. Two of the very broad peaks in the original ^{1}H NMR spectrum had diminished greatly in intensity relative to the others, and peaks for **3** appeared. (No peaks corresponding to [^{t}Bu$_3$COOC^{t}Bu$_3$] were observed.) The two peaks that diminished (7.0 and −39.0 ppm in a 6:1 ratio) were consistent with **4** and were tentatively assigned as such.

In the glovebox, an NMR tube was charged with roughly equal amounts of **1** and **3**. These were dissolved in C_6D_6, and the tube was capped and removed from the box. ^{1}H NMR spectra were recorded after 1 h and after 11 h of reaction. Peaks for the starting materials were present along with new peaks due to new cerium(III) species. In addition, a fine yellow microcrystalline precipitate was observed and appeared to increase in the amount with time. Examination of this precipitate under a microscope showed it to be similar in color and crystal shape to **4**. Also, the broad peaks in the NMR spectra were identical to those observed when authentic **4** was slurried in C_6D_6.

Reaction of 1 with *tert*-Butyl Peroxybenzoate (BPB). In a manner similar to that described for BzP, **1** was titrated with BPB. Addition of the peroxide resulted in an instantaneous color change from yellow to orange-yellow. The reaction was followed until 0.5 equiv had been added. The mixture was then analyzed by ^{13}C NMR spectroscopy and shown to consist of **2**, **3**, and [^{t}Bu$_3$COOC^{t}Bu$_3$], along with ^{t}Bu$_3$COH, unreacted **1**, and a trace of isobutylene.

Reaction of 1 with 1,4-Benzoquinone (Bq). In a manner similar to that described for previous experiments, 28 mg of **1** (37.9 μmol) was titrated with a 0.196 M solution of Bq in C_6D_6. As the quinone was added, an instantaneous deep purple color formed, and the NMR resonance of **1** diminished. In its place appeared two singlets in a 1:41 ratio (see Table I for NMR data), consistent with the formation of (^{t}Bu$_3$CO)$_3$CeOC$_6$H$_4$OCe(OC^{t}Bu$_3$)$_3$. When the tube was removed from the NMR probe, very thin brown plates were observed on the inside wall.

A small-scale synthesis was performed by charging a tube with 35 mg of **1** (47 μmol) and benzene. When the complex dissolved, 120 μL of a 0.196 M solution (23.5 μmol) of Bq was added. After 30 min, crystals had formed and stuck to the wall of the tube. The tube was inverted and allowed to stand as such in the glovebox overnight to drain the crystals. The cap was removed and the crystals were mounted into 0.5-mm capillaries. One of them was analyzed by X-ray diffractometry. The analysis confirmed the bridged phenylenediolate structure assumed from the NMR data. In addition, some of the remainder of the crystal crop was analyzed by ^{1}H and ^{13}C NMR spectroscopy; these data matched those from the titration experiment.

In a preparative-scale reaction, **1** (450 mg, 0.610 mmol) and Bq (30 mg, 0.278 mmol) were combined in a 30-mL Solv-seal flask. The solids (both yellow) started reacting on contact, as indicated by the purple color that formed at the interface. Benzene (ca. 15 mL) was added, and the flask was swirled. The flask was attached to a frit apparatus which was removed from the box. The assembly was attached to a high-vacuum line, and the reaction mixture (dark purple, homogeneous at that point) was stirred for an additional 20 min. The solvent was removed in vacuo. The product was slurried with pentane (ca. 3 mL) at 0 °C and then collected by filtration and dried in vacuo. The purple-black solid was collected in the glovebox (yield 360 mg, 80% based on benzoquinone).

Reaction of 1 with 2,6-Di-*tert*-butylbenzoquinone (DBBq). **1** was titrated with DBBq in an NMR tube. The first addition resulted in the yellow solution turning deep emerald green, and the color darkened as more quinone was added. The resonance due to **1** diminished, and a new, broad one appeared at 1.4 ppm. In addition, a very broad hump ($w_{1/2}$ = ca. 700 Hz) was observed at 6.1 ppm. The reaction stoichiometry was clearly 1:1 quinone:cerium. After 0.9 equiv had been added, a ^{13}C NMR spectrum was recorded. Three new resonances were observed (Table I), attributable to the carbons in a new ^{t}Bu$_3$CO moiety. A ^{1}H NMR spectrum run after the carbon had collected (ca. 3 h) showed evidence for the onset of decomposition. In addition, the solution had changed to a deep bluish green from emerald green.

In an attempt at characterization by ESR spectroscopy, 0.93 mL of a 4.29 mM solution of **1** in toluene was prepared and placed in an ESR probe. No signal was observed. DBBq (100 μL of a 38.4 mM toluene solution; 0.95 equiv) was added, affecting the previously observed color change to emerald green. The resulting ESR signal was very strong and very broad. The sample was diluted with toluene until a reasonably sharp signal was obtained. The signal is best described as a sharp singlet superimposed on a broad hump. No change in concentration improved this line shape.

Crystal Structure Determinations. The crystal data and parameters used in data collection and structure refinement for compounds **4** and **5** are given in Table VI. No correction for absorption was required.

The Ce atom was located by heavy-atom methods. The remaining non-hydrogen atoms were located through subsequent difference Fourier synthesis and least-squares analyses. All non-hydrogen atoms were refined anisotropically. For **5**, the *tert*-butyl groups were fixed to rigid tetrahedral geometry [d(C–C) = 1.56 Å]. Hydrogen atoms were incorporated as idealized, isotropic contributions [d(C–H) = 0.960 Å, U = 1.2U of the attached C atom].

All computations used P3 and SHELXTL (G. Sheldrick; version 5.1) software from Nicolet XRD, Madison, WI.

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Supplementary Material Available: Tables of anisotropic thermal parameters and H atom coordinates for **4** and **5** (6 pages); tables of observed and calculated structure factors for **4** and **5** (25 pages). Ordering information is given on any current masthead page.