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Oxidation of Alkylbenzenes with Cerium Complexes Containing a Tripodal Oxygen Ligand

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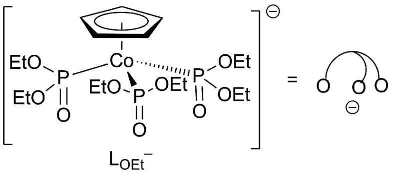
The treatment of $[Ce(L_{OEt})_2(NO_3)_2]$ (L_{OEt}^- = $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$) with $KMnO_4$ in water afforded a diamagnetic purple solid **1**, which is tentatively formulated as a Ce^{IV} permanganate complex, "$[Ce(L_{OEt})_2(MnO_4)_2]$". The Zr^{IV} analogue, $[Zr(L_{OEt})_2(MnO_4)_2]$ (**2**), has been prepared similarly from $[Zr(L_{OEt})_2(NO_3)_2]$ and $KMnO_4$. The recrystallization of **1** from CH_2Cl_2/hexanes at –18 °C led to the isolation of dinuclear $[(CeL_{OEt})_2(\mu\text{-}L_{OEt}')_2][MnO_4]_2$ (**3**), which contains the dianionic tripodal ligand $[L_{OEt}']^{2-}$ ($[(\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_2\{P(O)_2(OEt)\}]^{2-}$). The reactions of **1** with $K[ReO_4]$ and $[NH_4][OsO_3N]$ afforded the heterodimetallic complexes $[Ce(L_{OEt})_2(ReO_4)_2]$ (**4**) and $[Ce(L_{OEt})_2(NOsO_3)_2]$ (**5**), respectively. The crystal structures of **3** and **5** have been determined. Freshly prepared **1** can oxidize alkylbenzenes such as toluene, ethylbenzene, and cumene at room temperature to give the corresponding ketone and/or alcohol products. Ce–L_{OEt} complexes are efficient promoters of the aerobic oxidation of alkylbenzenes by a radical mechanism. For example, cumene in the presence of $[Ce(L_{OEt})_2(H_2O)_2]Cl$ (1 mM) in air at 100 °C for 10 h afforded a ca. 6:1 mixture of 2-phenyl-2-propanol and acetophenone with a total turnover number of 6810.

Introduction

Cerium(IV) compounds in oxygen ligand environments are of interest owing to the widespread applications of cerium(IV) oxides in industrial and environmental catalysis.[1–4] Although the molecular mechanisms of cerium-based heterogeneous catalysis are not well understood, it is believed that the facile Ce^{4+}/Ce^{3+} redox couple, their oxygen storage capacity, and metal–ceria interactions play important roles in their catalytic functions.[4] To gain insight into the mechanisms of ceria-based catalysts, we sought to synthesize heterometallic Ce^{IV}–O–M complexes and to investigate their redox and oxidation chemistry.

The Kläui tripodal ligand $[Co(\eta^5\text{-}C_5H_5)\{P(O)(OEt)_2\}_3]^-$ (denoted as L_{OEt}^- hereafter, Scheme 1) can stabilize metal ions in high oxidation states owing to its π-donating ability.[5] Previously, we found that L_{OEt}^- can stabilize tetravalent metal ions such as Ce^{4+} ions in aqueous solution.[5] Ce^{IV}–L_{OEt} complexes can hydrolyze phosphate diesters and undergo self-assembly with oxyanions to give heterometallic oxo compounds and clusters.[6] The reactions of $[Ce(L_{OEt})_2(NO_3)_2]$ with $Na_2Cr_2O_7$ and $[NH_4]_6[Mo_7O_{24}]$ afforded $[Ce(L_{OEt})_2(\eta^2\text{-}Cr_2O_7)]$ and the Ce^{IV}/Mo^{VI} oxo cluster $[H_4(CeL_{OEt})_6Mo_9O_{38}]$, respectively.[7] $[Ce(L_{OEt})_2(\eta^2\text{-}Cr_2O_7)]$ is a stoichiometric oxidant of alcohols, but it is inactive toward hydrocarbon substrates.[7] As an extension of this study, we sought to synthesize a Ce^{IV}–L_{OEt} permanganate complex, which we expected to be a stronger oxidizing agent than the dichromate analogue.



Scheme 1. Structure of the Kläui tripodal ligand L_{OEt}^-.

High-valent heterometallic Ce/Mn complexes are of special interest because they are potentially relevant to Mn-doped ceria materials, which exhibit high activity in wet chemical oxidation.[8] Recently, Ce^{IV}/Mn^{III} and Ce^{IV}/Mn^{IV} clusters have been synthesized by the self-assembly of Ce^{IV} ions with Mn^{III} salts or permanganate ions, and their magnetic properties and catalytic activities have been investigated.[9] Previously, we synthesized and structurally characterized a heterometallic Ce^{IV} permanganate complex containing an imidodiphosphinate ligand, $[Ce_2\{N(i\text{Pr}_2PO)_2\}_6\text{-}$

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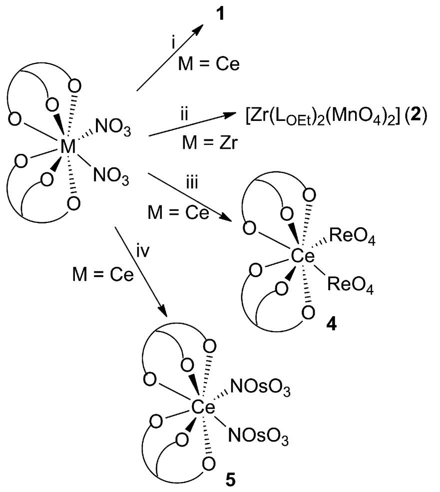
$(MnO_4)_2]$, which shows a weak Ce···O=Mn interaction in the solid state.[10] $[Ce_2\{N(iPr_2PO)_2\}_6(MnO_4)_2]$ can oxidize ethylbenzene to acetophenone at room temperature more efficiently than free permanganate; this suggests that the permanganate moieties are activated by the electrophilic Ce^{IV} center.[10]

We herein describe the synthesis of a reactive Ce^{IV} permanganate complex by the reaction of $[Ce(L_{OEt})_2(NO_3)_2]$ with $KMnO_4$ in water. This Ce^{IV} permanganate complex, tentatively formulated as "$[Ce(L_{OEt})_2(MnO_4)_2]$", can oxidize alkylbenzenes at room temperature. We also found that Ce^{III}–L_{OEt} and Ce^{IV}–L_{OEt} complexes can function as efficient promoters for the aerobic oxidation of alkylbenzenes, presumably by a radical mechanism.

Results and Discussion

Reactions of $[M(L_{OEt})_2(NO_3)_2]$ (M = Ce, Zr) with $KMnO_4$

The syntheses of heterometallic Ce^{IV} complexes are summarized in Scheme 2. The treatment of $[Ce(L_{OEt})_2(NO_3)_2]$ with $KMnO_4$ in water resulted in the precipitation of a reactive purple solid, **1**, which decomposes readily in solution (vide infra). The IR spectrum of **1** showed the Mn–O band at $\tilde{\nu} \approx 900\ cm^{-1}$. No N–O bands were found; thus, both nitrate ligands in $[Ce(L_{OEt})_2(NO_3)_2]$ have been replaced by permanganate ions. The ^1H NMR spectrum of a freshly prepared, dried sample of **1** in $CDCl_3$ displayed well-resolved signals for the L_{OEt}^- ligands and is, therefore, indicative of diamagnetic behavior. When the purple $CDCl_3$ solution of **1** was left to stand at room temperature, it turned brown gradually, and ill-resolved broad ^1H NMR signals were observed. The resulting $^{31}P\{^1H\}$ NMR spectrum showed a broad singlet at $\delta = 165$ ppm, which is characteristic of Ce^{III}–L_{OEt} complexes {e.g., $\delta = 164$ ppm for $[Ce(L_{OEt})_2(H_2O)_2]Cl$}.



Scheme 2. Synthesis of heterometallic Ce^{IV} and Zr^{IV} complexes. Reagents: (i) $KMnO_4$, water, 0 °C; (ii) $KMnO_4$, water, room temp.; (iii) $KReO_4$, water, room temp.; (iv) $[NH_4][OsO_3N]$, water, room temp.

A Zr^{IV} permanganate complex has been synthesized to model the reactive Ce^{IV} analogue **1**. The treatment of $[Zr(L_{OEt})_2(NO_3)_2]$ with $KMnO_4$ yielded a purple complex, which has been characterized as $[Zr(L_{OEt})_2(MnO_4)_2]$ (**2**). The NMR and IR spectra of **2** are very similar to those of **1**. Owing to their similar spectroscopic data, we believe that **1** has a similar composition to that of **2**, that is, "$[Ce(L_{OEt})_2(MnO_4)_2]$". However, unlike **1**, **2** is stable in solution and cannot oxidize alkylbenzenes. This is probably because the permanganate ions in **1** are coordinated and, therefore, "activated" by the Ce^{IV} ions (vide infra), whereas those in **2** are non-coordinating. Six-coordinate $[Zr(L_{OEt})_2]^{2+}$ complexes such as $[Zr(L_{OEt})_2](OTs)_2$[11] (OTs^- = tosylate) have been reported previously.

Compound **1** decomposes gradually to an unidentified brown species in CH_2Cl_2 solution at room temperature. It is unstable even in the solid state and turned brown slowly at –18 °C under nitrogen. Therefore, in subsequent studies, **1** was freshly prepared from $[Ce(L_{OEt})_2(NO_3)_2]$ and $KMnO_4$ and used immediately. The UV/Vis spectrum of **1** in CH_2Cl_2 showed the characteristic permanganate-based ligand-to-metal charge transfer (LMCT) band centered at $\lambda \approx 526$ nm. The intensity of the LMCT band gradually decreased as the solution changed from purple to brown. Recently, Lau and co-workers reported that Lewis acids such as BF_3 and $[Sc(OTf)_3]$ (OTf^- = triflate) induce the intramolecular O–O coupling of $[MnO_4]^-$ to give O_2.[12] We believe that a similar pathway is involved in the decomposition of **1** in CH_2Cl_2 and that the permanganate moieties in **1** are activated through coordination to the Lewis acidic Ce^{IV} center.

The recrystallization of **1** from a saturated CH_2Cl_2/hexanes solution at –18 °C afforded dark brown crystals in 25% yield (with respect to Ce). The crystals were identified as the dinuclear Ce^{IV} complex $[\{(L_{OEt})Ce\}_2(\mu\text{-}L_{OEt}')_2][MnO_4]_2$ (**3**; $[L_{OEt}']^{2-} = [CoCp\{P(O)(OEt)_2\}\{P(O)_2(OEt)\}]^{2-}$, Cp = cyclopentadienyl), which contains two dealkylated tripodal ligands ($[L_{OEt}']^{2-}$) and two $[MnO_4]^-$ anions (Scheme 3). The other two MnO_4^- ligands derived from **1** may decompose by a Ce-induced intramolecular O–O coupling.[12] The $^{31}P\{^1H\}$ NMR spectrum of **3** showed two resonances at $\delta = 118.7$ and 88.0 ppm, which are attributed to the L_{OEt}^- and $L_{OEt}'^{2-}$ ligands, respectively. Also, two singlets were found at $\delta = 5.09$ and 5.11 ppm for the cyclopentadienyl protons of the two tripodal ligands.

The dealkylation of L_{OEt}^- to give the dianionic $L_{OEt}'^{2-}$ ligand by a metal-assisted Arbuzov reaction and the elimination of alkyl chloride has been reported. For example, the treatment of NaL_{OEt} with $YbCl_3$ and $ZrCl_4$ afforded $[L_{OEt}Y]_2(\mu\text{-}L_{OEt}')_2$ and $[Zr(L_{OEt}')_2]_2$, respectively.[13] However, in the absence of nucleophilic chloride ligands, we believe that the formation of **3** possibly involves the Ce^{IV}-mediated hydrolysis of the P–OEt group in L_{OEt}^- (to give a P–OH intermediate and EtOH) instead of the Arbuzov-type reaction. It should be noted that Ce^{IV} compounds are very active catalysts for the hydrolysis of phosphate diesters and DNA.[14]

The structure of the complex cation in **3** is shown in Figure 1, and selected bond lengths and bond angles are listed in Table 1. The structure consists of two symmetry-related eight-coordinate $[Ce(L_{OEt})(L_{OEt}')(H_2O)]^+$ units that are

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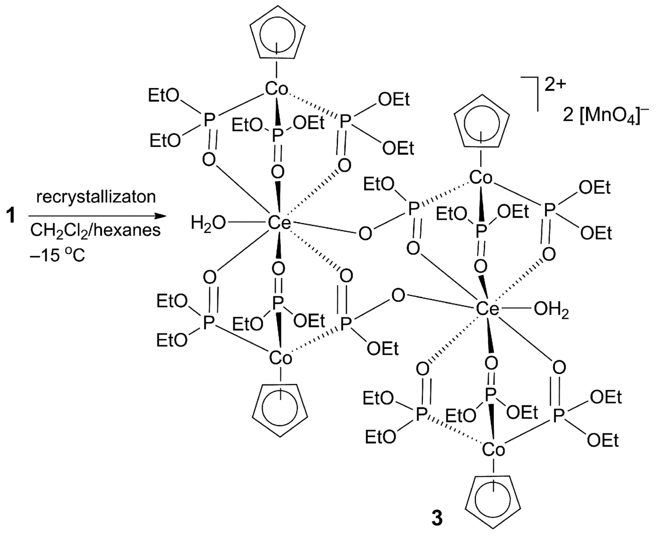

Scheme 3. Formation of **3** from **1**.

linked together through a P=O group of $[L_{OEt}']^{2-}$. A center of inversion is located at the center of the complex cation. The Ce–OP(OEt)$_2$ distances for $[L_{OEt}']^{2-}$ [average 2.344 Å] are similar to those for L_{OEt}^- [average 2.340 Å][6] The PO$_2$(OEt) group in $[L_{OEt}']^{2-}$ binds to the two Ce centers symmetrically with Ce–O distances of 2.265(4) and 2.234(4) Å. The Ce–OH$_2$ bond [2.488(4) Å] is shorter than that in the Ce^{IV} oxo–aqua complex $[Ce(L_{OEt})_2(O)(H_2O)]\cdot Me_2CONH_2$ [2.572(3) Å].[15]

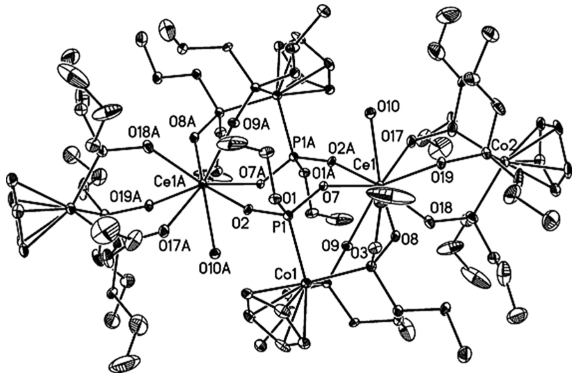

Figure 1. Molecular structure of the complex cation in **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Symmetry transformations used to generate equivalent atoms: A = –*x* + 1, –*y* + 1, –*z* + 1.

Table 1. Selected bond lengths [Å] and angles [°] for **3**.

Ce(1)–O(2)A	2.234(4)	Ce(1)–O(7)	2.265(4)
Ce(1)–O(8)	2.347(4)	Ce(1)–O(9)	2.340(4)
Ce(1)–O(10)	2.488(4)	P(1)–O(2)	1.521(4)
P(1)–O(7)	1.522(4)	P(1)–O(1)	1.620(5)
P(1)–O(2)–Ce(1)A	162.7(3)	P(1)–O(7)–Ce(1)	141.6(2)
P(2)–O(8)–Ce(1)	138.0(3)	P(3)–O(9)–Ce(1)	137.0(2)

Heterometallic Ce^{IV}/Re^{VII} and Ce^{IV}/Os^{VIII} Complexes

To gain insight into the identity of **1**, Ce^{IV} complexes containing more-stable third-row d^0 metal–oxo anions were synthesized. The treatment of $[Ce(L_{OEt})_2(NO_3)_2]$ with KReO$_4$ in water afforded $[Ce(L_{OEt})_2(ReO_4)_2]$ (**4**). The $^{31}P\{^1H\}$ NMR spectrum of **4** in CDCl$_3$ displayed a singlet at δ = 119.9 ppm. The IR spectrum of **4** showed a ν(Re–O) band at $\tilde{\nu}$ = 869 cm^{-1}, which is lower than that of uncoordinated $[ReO_4]^-$ (912 cm^{-1}). Unfortunately, we have not been able to crystallize **4** for structure determination. It seems likely that **4** is an eight-coordinate Ce^{IV} complex containing two η^1-ReO$_4^-$ ligands.

Similarly, the treatment of $[Ce(L_{OEt})_2(NO_3)_2]$ with 2 equiv. of $[NH_4][OsO_3N]$ in water led to the precipitation of an orange solid. Recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded orange crystals that were identified as $[Ce(L_{OEt})_2(NOsO_3)_2]$ (**5**) by X-ray diffraction. The IR spectrum of **5** showed sharp peaks at $\tilde{\nu}$ = 887 and 902 cm^{-1}, assignable to ν(Os–O). By comparison, the Os–O stretches for $[NH_4][OsO_3N]$ are found at $\tilde{\nu}$ = 871 and 891 cm^{-1} and that of $[Au(PPh_3)(NOsO_3)]$ occurs at $\tilde{\nu}$ = 894 cm^{-1}.[16] The ν(Os–N) band for **5** has not been determined owing to the overlap with the P=O bands of the L_{OEt}^- ligand. The molecular structure of **5** is shown in Figure 2. Owing to the disorder of the nitridoosmate(VIII) ligands, the bond lengths of the complex have not been analyzed. Nevertheless, the identity of **5** with two N-bound nitridoosmate(VIII) ligands has been confirmed by the X-ray diffraction study. To the best of our knowledge, **5** is the first example of a heterometallic Ce^{IV}/Os^{VIII} complex.

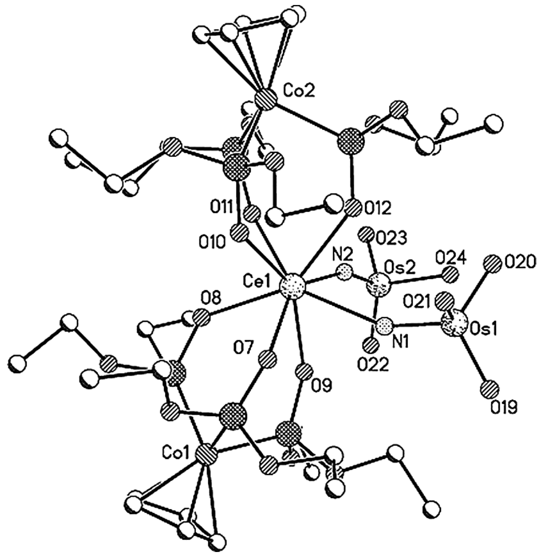

Figure 2. Molecular structure of **5**. Hydrogen atoms are omitted for clarity.

Stoichiometric Oxidation of Alkylbenzenes by 1

Similar to previously reported Lewis acid/KMnO$_4$ systems,[17] **1** is a stoichiometric oxidant for alkylbenzenes. As **1** is unstable in most organic solvents, the oxidation of neat alkylbenzenes with **1** was studied (Table 2). Although **1** is only slightly soluble in ethylbenzene, stirring a suspension of **1** in ethylbenzene at room temperature for 2 min resulted

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in a homogeneous purple solution that gradually turned brown in 30 min. Gas–liquid chromatography (GLC) analysis revealed that acetophenone was formed as the sole organic product; no 1-phenylethanol or benzoic acid was detected. The reaction was complete in ca. 2 h. Iodometric titration indicated that the inorganic product is approximately seven oxidizing levels below the starting material **1**, which suggests that the inorganic product is possibly a Ce^{III}/Mn^{IV} complex. As **1** is a seven-electron oxidant and the conversion of ethylbenzene to acetophenone is a four-electron process, the yield of acetophenone was calculated to be 85%. No significant difference in the yield was found when the oxidation was performed in air. Under the same conditions, ethylbenzene was oxidized by $[n\mathrm{Bu_4N}][\mathrm{MnO_4}]$ or $[\mathrm{Ce(L_{OEt})_2(NO_3)_2}]$ to give acetophenone in less than 5% yield. Thus, it appears that the permanganate moieties in **1** are activated by the Lewis acidic Ce^{IV} center (possibly through coordination of the Mn=O group to the Ce center).

Table 2. Stoichiometric oxidation of alkylbenzenes by freshly prepared **1**.[a]

Alkylbenzene	Products (yield, %)[b]
Toluene	benzaldehyde (31)
Ethylbenzene	acetophenone (85)
Cumene	2-phenyl-2-propanol (35), benzaldehyde (36)
Diphenylmethane	benzophenone (75)

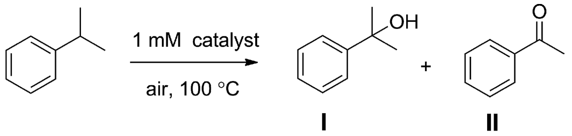
[a] Experimental conditions: freshly prepared **1** (0.011 M), neat alkylbenzene, 23 °C, 2 h, under nitrogen. [b] Yields were determined by GLC with the assumption that **1** is a seven-electron oxidant (vide infra).

Similarly, stirring a suspension of **1** in toluene resulted in a brown solution in ca. 3 h. GLC analysis showed that benzaldehyde was formed in 31% yield; no benzoic acid was detected. The yield of toluene oxidation is lower than that for ethylbenzene apparently because of the stronger benzylic C–H bonds [the bond dissociation energies (BDEs) for toluene and ethylbenzene are 90 and 85 kcal/mol, respectively].[18] Unlike those of ethylbenzene and toluene, the oxidation of cumene by **1** afforded 2-phenyl-2-propanol (in 35% yield, assuming two-electron oxidation) along with benzaldehyde (36%). The oxidation of diphenylmethane gave benzophenone in 75% yield.

Ce-Promoted Aerobic Oxidation of Alkylbenzenes

Although **1** cannot catalyze the oxidation of alkylbenzenes with molecular oxygen at room temperature, it was found to be an efficient initiator for the autoxidation of alkylbenzenes at higher temperatures. For example, cumene in the presence of 1 mM of **1** at 100 °C afforded a mixture of 2-phenyl-2-propanol and acetophenone with a conversion of 52% and a total turnover number (TON) of 3250 (Table 3).

Table 3. Ce-promoted aerobic oxidation of cumene.[a]



Catalyst	Conv. [%]	Yield [%][b] I	Yield [%][b] II	Total TON
1	52	10	35	3250
$[\mathrm{Ce(L_{OEt})_2(NO_3)_2}]$	81	12	69	5800
$[\mathrm{Ce(L_{OEt})(NO_3)_3}]$	77	10	53	4480
$[n\mathrm{Bu_4N}][\mathrm{MnO_4}]$	trace	trace	trace	–
$[\mathrm{Ce(L_{OEt})_2(NO_3)}]$	76	43	33	5420
$[\mathrm{Ce(L_{OEt})_2(H_2O)_2}]\mathrm{Cl}$	95	82	13	6810

[a] Experimental conditions: cumene (2.25 mL), Ce complex (1 mM), air, 100 °C, 10 h. [b] Product yields were determined by NMR spectroscopy after reduction with PPh_3. Small amounts of α-methylstyrene were also detected.

To find out whether the Ce or Mn center is responsible for the catalytic activity of **1**, the aerobic oxidation of cumene with various Ce–L_{OEt} complexes and $[n\mathrm{Bu_4N}][\mathrm{MnO_4}]$ was examined (Table 4). $[n\mathrm{Bu_4N}][\mathrm{MnO_4}]$ is not capable of catalyzing the aerobic oxidation of cumene; only trace amounts of products were detected, presumably as a result of the stoichiometric oxidation of cumene with permanganate. On the other hand, Ce–L_{OEt} complexes are active promoters of cumene oxidation. For example, heating cumene with catalytic $[\mathrm{Ce(L_{OEt})_2(NO_3)_2}]$ at 100 °C afforded a ca. 1:6 mixture of 2-phenyl-2-propanol and acetophenone with 81% conversion and a total TON of 5800. Similar conversions and TONs were found for $[\mathrm{Ce^{IV}(L_{OEt})(NO_3)_3}]$ and $[\mathrm{Ce^{III}(L_{OEt})_2(NO_3)}]$. Of all the Ce complexes studied, the Ce^{III} complex $[\mathrm{Ce(L_{OEt})_2(H_2O)_2}]\mathrm{Cl}$ (conversion = 95%, total TON = 6810) is the most-active catalyst. This result indicates that the Ce center instead of the Mn center is responsible for the catalytic activity of **1** in the aerobic oxidation.

Table 4. Aerobic oxidation of alkylbenzenes with $[\mathrm{(L_{OEt})_2Ce(H_2O)_2}]\mathrm{Cl}$.[a]

Alkylbenzene	Products (yield, %)	Total TON
Toluene[b]	benzyl alcohol (0.5) benzaldehyde (0.6)	81
Ethylbenzene[b]	1-phenylethanol (12) acetophenone (13)	1910
Cumene[c]	2-phenyl-2-propanol (82) acetophenone (13)	6810

[a] Conditions: alkylbenzene (2.25 mL), [Ce] = 1 mM, air, 10 h, 100 °C. [b] Product yields were determined by GLC after reduction with PPh_3. [c] Product yields were determined by ^1H NMR spectroscopy after reduction with PPh_3.

As $[\mathrm{Ce(L_{OEt})_2(H_2O)_2}]\mathrm{Cl}$ appears to be an efficient initiator for cumene autoxidation, the aerobic oxidation of other alkylbenzenes with this Ce^{III} complex was studied (Table 4). Heating ethylbenzene at 100 °C in the presence of 1 mM of $[\mathrm{Ce(L_{OEt})_2(H_2O)_2}]\mathrm{Cl}$ afforded a ca. 1:1 mixture of 1-phenylethanol and acetophenone with a total TON of 1910. A smaller TON (81) was found for toluene because of its stronger benzyl C–H bonds.[17]

The metal-catalyzed oxidation of benzylic C–H bonds with molecular oxygen has been studied extensively. Generally, free radical mechanisms involving peroxy radicals and hydroperoxide intermediates have been proposed.[19]

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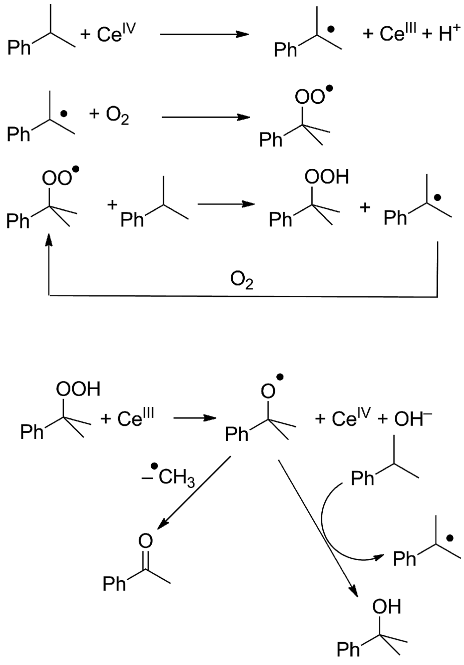
We believe that similar pathways are involved in the Ce-promoted aerobic oxidation of alkylbenzenes such as cumene (Scheme 4). The oxidation of cumene by a Ce^{IV} species followed by reaction with oxygen gives a peroxy radical. Subsequent hydrogen atom abstraction from cumene yields cumene hydroperoxide. The reduction of the hydroperoxide with a Ce^{III} species gives an oxy radical, which is finally converted to 2-phenyl-2-propanol or acetophenone.[20] Consistent with this radical mechanism, the Ce-based aerobic oxidation of cumene was completely quenched by radical traps such as 2,6-di-*tert*-butyl-4-methylphenol and (2,2,6,6-tetramethylpiperidin-1-yl)oxy. The high catalytic activity of the Ce–L_{OEt} complexes in the aerobic oxidation can be attributed to their facile Ce^{IV}/Ce^{III} redox couples (e.g., the Ce^{IV}/Ce^{III} redox couple for $[Ce(L_{OEt})_2(NO_3)_2]$ in acetonitrile occurs at ca. 0 V vs. $Cp_2Fe^{+/0}$,[21]). It may be noted that cerium(IV) ammonium nitrate has also been used as a catalyst for the oxidation of alkylbenzenes with bromate salts.[22]



Scheme 4. Proposed mechanism for the Ce-promoted aerobic oxidation of cumene.

Conclusions

We have synthesized heterodimetallic Ce^{IV}/Mn^{VII}, Ce^{IV}/Re^{VII}, and Ce^{IV}/Os^{VIII} complexes by the reactions of $[Ce(L_{OEt})_2(NO_3)_2]$ with the corresponding anionic metal–oxo complexes in water. The structure of the Ce^{IV}/Os^{VIII} complex $[Ce(L_{OEt})_2(NOsO_3)_2]$ featuring two η^1-$[OsO_3N]^-$ ligands has been established by X-ray crystallography. Upon recrystallization from CH_2Cl_2/hexanes, the Ce^{IV} permanganate complex, possibly "$[Ce(L_{OEt})_2(MnO_4)_2]$", was converted to dinuclear $[(L_{OEt}Ce)_2(\mu\text{-}L_{OEt}')_2][MnO_4]_2$, which contains two bridged dealkylated tripodal ligands. "$[Ce(L_{OEt})_2(MnO_4)_2]$" can oxidize alkylbenzenes more efficiently than free $[MnO_4]^-$ ions; this suggests that the permanganate ions are activated by the Ce^{IV} center (possibly through coordination to the Ce atom). Ce–L_{OEt} complexes, notably the Ce^{III} complex $[Ce(L_{OEt})_2(H_2O)_2]Cl$, can promote the aerobic oxidation of alkylbenzenes such as ethylbenzene and cumene, presumably by a free radical pathway.

Experimental Section

General: NMR spectra were recorded with a Bruker ARX 300 spectrometer operating at 300 and 121.5 MHz for ^1H and ^{31}P NMR spectroscopy, respectively. Chemical shifts (δ, ppm) are reported with reference to $SiMe_4$ (^1H) and H_3PO_4 (^{31}P). Infrared spectra were recorded with a Perkin–Elmer 16 PC FTIR spectrophotometer.

Gas chromatography was performed with a Hewlett Packard 5860 chromatograph equipped with a flame ionization detector (FID). Elemental analyses were performed by Medac Ltd., Surrey, United Kingdom. Toluene, ethylbenzene, and cumene were washed with concentrated H_2SO_4, distilled water, and then 5% aqueous $NaHCO_3$. They were then dried with Na_2SO_4, distilled from CaH_2 under argon, and degassed by three freeze–pump–thaw cycles before use. The complexes $[Ce(L_{OEt})_2(NO_3)_2]$,[6] $[Zr(L_{OEt})_2(NO_3)_2]$,[23] $(NH_4)[OsO_3N]$,[24] and $[Ce(L_{OEt})_2(NO_3)]$[25] were synthesized according to literature methods. $[Ce(L_{OEt})_2(H_2O)_2]Cl$ and $[Ce(L_{OEt})_2(NO_3)]$ were obtained by the reactions of NaL_{OEt} with $CeCl_3$ and $Ce(NO_3)_3$, respectively, in water.[26]

$[Ce(L_{OEt})_2(MnO_4)_2]$ (1): To a solution of $KMnO_4$ (26 mg, 0.16 mmol) in water (1 mL) in an ice bath was added $[(L_{OEt})_2Ce(NO_3)_2]$ (60 mg, 0.045 mmol) in water (10 mL), and the mixture was stirred at 0 °C for 1 min. The purple precipitate **1** was collected, washed with cold water (0.5 mL × 3), and dried with a stream of nitrogen, yield 40 mg (61% relative to Ce). ^1H NMR ($CDCl_3$): δ = 1.25 (t, 36 H, CH_3), 4.08 (m, 24 H, CH_2), 5.12 (s, 10 H, Cp) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 120.5 (s) ppm. UV/Vis (CH_2Cl_2): λ = 526 nm. IR (KBr): $\tilde{\nu}$ = 900 [ν(Mn–O)] cm^{-1}. Satisfactory analytical data could not be obtained owing to the instability of the compound in the solid state.

$[Zr(L_{OEt})_2(MnO_4)_2]$ (2): To a solution of $KMnO_4$ (32 mg, 0.2 mmol) in water (4 mL) was added $[Zr(L_{OEt})_2(NO_3)_2]$ (64 mg, 0.05 mmol) in water (15 mL), and the mixture was stirred at room temperature for 20 min. The purple precipitate was collected, washed with cold water (0.5 mL × 3), and dried in air. Recrystallization from CH_2Cl_2/Et_2O afforded a purple crystalline solid, yield 50 mg (71%). ^1H NMR ($CDCl_3$): δ = 1.26 (t, 36 H, CH_3), 4.07 (m, 24 H, CH_2), 5.13 (s, 10 H, Cp) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 117.6 (s) ppm. IR (KBr): $\tilde{\nu}$ = 900 [ν(Mn–O)] cm^{-1}. $C_{34}H_{70}Co_2Mn_2O_{26}P_6Zr$ (1399.71): calcd. C 29.18, H 5.04; found C 29.09, H 5.09.

$[(L_{OEt}Ce)_2(\mu\text{-}L_{OEt}')_2][MnO_4]_2$ (3): A freshly prepared sample of **1** (65 mg) was dissolved in a minimum amount of CH_2Cl_2 (ca. 1 mL), and Et_2O/hexane (1 mL, 1:1) was added carefully. The mixture was concentrated to ca. 1 mL and cooled to –18 °C overnight to afford dark brown needles that were suitable for X-ray analysis, yield 15 mg (25%). ^1H NMR ($CDCl_3$): δ = 1.18–1.30 (m, 66 H, CH_3), 4.10 (m, 44 H, CH_2), 5.09 (s, 10 H, Cp), 5.11 (s, 10 H, Cp) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 88.0 (s), 118.7 (s) ppm. IR (KBr): $\tilde{\nu}$ = 906 [ν(Mn–O)] cm^{-1}. $C_{64}H_{130}Ce_2Co_4Mn_2O_{44}P_{12}$ (2601.21): calcd. C 29.55, H 5.04; found C 29.20, H 4.95.

$[Ce(L_{OEt})_2(ReO_4)_2]$ (4): To a solution of $KReO_4$ (34 mg, 0.12 mmol) in water (2 mL) was added $[(L_{OEt})_2Ce(NO_3)_2]$ (40 mg,

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0.030 mmol) in water (10 mL), and the mixture was stirred at room temperature for 10 min. The orange solid was collected, redissolved in CH_2Cl_2/Et_2O, and dried with anhydrous Na_2SO_4. Slow evaporation of the solvent in air afforded an orange microcrystalline solid, yield 37 mg (72 %). ^1H NMR ($CDCl_3$): δ = 1.29 (t, 36 H, CH_3), 4.12 (m, 24 H, OCH_2), 5.08 (s, 10 H, Cp) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 119.9 (s) ppm. IR (KBr): $\tilde{\nu}$ = 869 [ν(Re–O)] cm^{-1}. $C_{34}H_{70}CeCo_2O_{26}P_6Re_2 \cdot Et_2O$ (1785.26): calcd. C 25.57, H 4.52; found C 25.27, H, 4.35.

$[Ce(L_{OEt})_2(NOsO_3)_2]$ (5): This complex was synthesized similarly to **5** by using $[NH_4][OsO_3N]$ in place of $KReO_4$. Recrystallization from CH_2Cl_2/Et_2O/hexanes afforded orange crystals that were suitable for X-ray analysis, yield 38.5 mg, (75 %). ^1H NMR ($CDCl_3$): δ = 1.29 (t, 36 H, CH_3), 4.12 (m, 24 H, OCH_2), 5.07 (s, 10 H, Cp) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 121.3 (s) ppm. IR (KBr): $\tilde{\nu}$ = 819, 887 [ν(Os–O)], 902 [ν(Os–N)] cm^{-1}. $C_{34}H_{70}O_{24}CeCo_2N_2Os_2P_6 \cdot Et_2O$ (1789.32): calcd. C 25.51, H 4.51, N 1.57; found C 25.43, H 4.38, N 1.54.

Stoichiometric Oxidation of Alkylbenzenes with 1: Typically, to alkylbenzene (2.25 mL) was added freshly prepared **1** (35 mg, 0.024 mmol), and the mixture was stirred at room temperature under nitrogen in the dark for 2 h, during which the solution changed from purple to brown. The yields of the organic product(s) were determined by GLC analysis with bromobenzene as an internal standard.

Iodometric Titration:[27,28] The Mn oxidation state of the inorganic product for the oxidation of alkylbenzenes by **1** was determined by an iodometric method. At the end of reaction, an aliquot (1.0 mL) of the solution was transferred to a volumetric flask containing nPr_4NI (0.019 g). Glacial acetic acid (1 mL) and CH_2Cl_2 were added to bring the total volume to 10 mL. An aliquot of the resulting solution was transferred to a cuvette, and the UV/Vis spectrum was recorded. The concentration of I_3^- ions formed was calculated with the assumption that $\varepsilon_{365}(I_3^-)$ = 26200 $\text{M}^{-1}\,cm^{-1}$. The result of the iodometric titration indicated that the inorganic product is approximately seven oxidizing levels below **1**. Therefore, the Ce and Mn oxidation states of the inorganic product were tentatively assigned as +3 and +4, respectively.

Ce-Catalyzed Aerobic Oxidation of Alkylbenzenes: A mixture of Ce complex (1 mM) in neat alkylbenzene (2.25 mL) was heated at 100 °C in air for 20 h. The yields of the oxidation products were determined by GLC or ^1H NMR spectroscopy[20] (for cumene) analysis after reduction with PPh_3.

X-ray Crystallography: The crystal data and experimental details for **3** and **5** are summarized in Table 5. Preliminary examinations and intensity data collection were performed with a Bruker SMART-APEX 1000 area-detector (for **3**) and a Bruker SMART 1000 diffractometer (for **5**) by using graphite-monochromated Mo-K_α radiation (λ = 0.70173 Å). The collected frames were processed with the software SAINT. The data was corrected for absorption by using the program SADABS.[29] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 by using the SHELXTL software package.[30] Unless stated otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Carbon-bonded hydrogen atoms were included at calculated positions and refined in a riding mode by using the SHELXL97 default parameters.

CCDC-997440 (for **3**) and -1012145 (for **5**) contain the supplementary crystallography data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystallographic data and experimental details for **3** and **5**.

	3	**5**
Formula	$C_{66.60}H_{146}$-$Ce_2Cl_{0.40}Co_4Mn_2O_{46}P_{12}$	$C_{34}H_{70}$-$CeCo_2N_2O_{24}Os_2P_6$
Fw	2694.69	1727.21
a [Å]	13.0067(15)	12.0154(4)
b [Å]	22.051(3)	12.0154(4)
c [Å]	18.548(2)	71.386(5)
α [°]	90	90
β [°]	97.042(2)	90
γ [°]	90	120
V [$Å^3$]	5279.7(11)	8925.2(8)
Z	2	6
Crystal system	monoclinic	hexagonal
Space group	$P2_1/n$	$P6_5$
$\rho_{calcd.}$ [$g\,cm^{-3}$]	1.695	1.928
T [K]	173(2)	293(2)
μ [mm^{-1}]	1.963	5.784
$F(000)$	2749	5076
Reflections	27443	52568
Independent refl.	9110	13972
R_{int}	0.0961	0.0557
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0495, 0.0859	0.0801, 0.1887
$R1$, $wR2$ (all data)	0.1296, 0.0958	0.14, 0.2176
GoF	0.961	1.044

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