

Heterometallic Cerium(IV) Perrhenate, Permanganate, and Molybdate Complexes Supported by the Imidodiphosphinate Ligand $[N(i\text{-Pr}_2\text{PO})_2]^-$

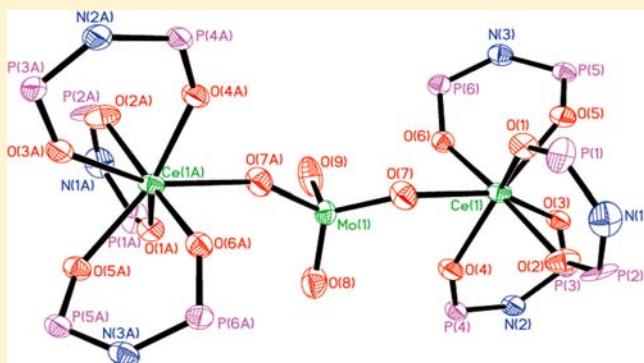
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Supporting Information

ABSTRACT: Heterometallic cerium(IV) perrhenate, permanganate, and molybdate complexes containing the imidodiphosphinate ligand $[N(i\text{-Pr}_2\text{PO})_2]^-$ have been synthesized, and their reactivity was investigated. Treatment of $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_3\text{Cl}$ (**1**) with AgMO_4 ($M = \text{Re}, \text{Mn}$) afforded $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_3(\text{ReO}_4)$ (**2**) or $\text{Ce}_2[N(i\text{-Pr}_2\text{PO})_2]_6(\text{MnO}_4)_2$ (**3**). In the solid state, **3** is composed of a $[\text{Ce}_2\{N(i\text{-Pr}_2\text{PO})_2\}_6(\text{MnO}_4)]^+$ moiety featuring a weak Ce–OMn interaction [Ce–OMn distance = 2.528(8) Å] and a noncoordinating MnO_4^- counteranion. While **3** is stable in the solid state and acetonitrile solution, it decomposes readily in other organic solvents, such as CH_2Cl_2 . **3** can oxidize ethylbenzene to acetophenone at room temperature. Treatment of **1** with AgBF_4 , followed by reaction with $[n\text{-Bu}_4\text{N}]_2[\text{MoO}_4]$, afforded $[\text{Ce}\{N(i\text{-Pr}_2\text{PO})_2\}_3]_2(\mu\text{-MoO}_4)$ (**4**). Reaction of *trans*- $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_2(\text{NO}_3)_2$ (**5**), which was prepared from $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ and $\text{K}[N(i\text{-Pr}_2\text{PO})_2]$, with 2 equiv of $[n\text{-Bu}_4\text{N}][\text{Cp}^*\text{MoO}_3]$ yielded *trans*- $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_2(\text{Cp}^*\text{MoO}_3)_2$ (**6**). **4** can catalyze the oxidation of methyl phenyl sulfide with *tert*-butyl hydroperoxide with high selectivity. The crystal structures of complexes **3**–**6** have been determined.



INTRODUCTION

Despite the widespread use of Ce(IV)-containing compounds and materials in organic synthesis¹ and bioinorganic² and environmental catalysis,^{3,4} the coordination and organometallic chemistry of tetravalent cerium has not been well-explored due, in part, to the high oxidizing power of Ce(IV). The functions of Ce(IV) reagents and catalysts are critically dependent on the facile Ce(IV)/III redox couple and high Lewis acidity of the Ce(IV) center. Also, the metal–ceria interaction is believed to play a role in catalytic performances of ceria-supported catalysts.³ Nevertheless, not many studies have been devoted to investigate the influence of the electrophilic, oxidizing Ce(IV) center on the reactivity of molecular heterometallic Ce(IV) complexes.^{5,6}

Relatively few heterobimetallic Ce(IV)-O-M complexes and clusters have been reported in the literature.^{7–12} Examples include those supported by alkoxide⁷ and carboxylate⁸ coligands and Ce(IV)-containing polyoxometalates.⁹ We are particularly interested in heterometallic Ce/Mn complexes because Mn-doped ceria materials have been shown to exhibit high catalytic activity in wet chemical oxidation.³ Recently, a series of Ce(IV)/Mn(III,IV) clusters have been synthesized by reactions of cerium ammonium nitrate with KMnO_4 in the

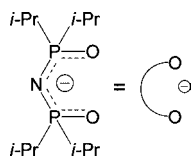
presence of carboxylic acids and their magnetic and catalytic properties of these Ce/Mn complexes have been studied.⁸ In one report, it was found that the high oxidation state of the Ce and Mn ions (+4) in a CeMn_6 cluster is essential for its catalytic activity in aerobic oxidation of alcohols with TEMPO.⁵ Whereas coordination polymers containing the permanganate ion are well-documented,¹³ to our knowledge, molecular Ce(IV)/Mn(VII) complexes have not been isolated to date.

In this work, we synthesized and structurally characterized heterometallic Ce(IV)-O-M complexes supported by a bidentate imidodiphosphinate ligand,¹⁴ $[N(i\text{-Pr}_2\text{PO})_2]^-$ (Chart 1), which can be considered as an inorganic analogue of acetylacetonate.

In contrast with the well-known $[N(\text{Ph}_2\text{PO})_2]^-$ ligand, the coordination chemistry of the more soluble isopropyl analogue $[N(i\text{-Pr}_2\text{PO})_2]^-$ is not well-developed.¹⁴ In a previous paper, we reported the synthesis of tetravalent Ce- $[N(i\text{-Pr}_2\text{PO})_2]$ oxo and peroxo complexes, demonstrating that the imidodiphosphinate can serve as a good spectator ligand for the oxidizing Ce(IV) ion.¹⁵ Herein, we describe the synthesis, structures, and

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Chart 1. Structure of $[N(i\text{-Pr}_2\text{PO})_2]^-$ 

reactivity of Ce(IV)- $[N(i\text{-Pr}_2\text{PO})_2]$ perrhenate, permanganate, and molybdate complexes featuring Ce(IV)-O-M (M = Re, Mn, Mo) linkages and their activity in oxidations of ethylbenzene and organic sulfides.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified by standard procedures, distilled, and degassed prior to use. NMR spectra were recorded on a Bruker ARX 400 spectrometer operating at 400, 161.9, and 376.4 MHz for ^1H , ^{31}P , and ^{19}F , respectively. Chemical shifts (δ , ppm) were reported with reference to SiMe_4 (^1H), H_3PO_4 (^{31}P), and $\text{CF}_3\text{C}_6\text{H}_6$ (^{19}F). Infrared (IR) and UV–visible spectra were recorded on Perkin-Elmer 16 PC FT-IR and Hewlett-Packard 8452A UV–visible spectrophotometers, respectively. Elemental analyses were performed by Medac Ltd., Surrey, U.K.

The ligand $K[N(i\text{-Pr}_2\text{PO})_2]^{15}$ was prepared according to a literature method. The compounds $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_3\text{Cl}$ (**1**),¹⁵ AgReO_4 ,¹⁶ AgMnO_4 ,¹⁷ $(n\text{-Bu}_4\text{N})_2[\text{MoO}_4]^{18}$ and $(n\text{-Bu}_4\text{N})[\text{Cp}^*\text{MoO}_3]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)¹⁹ were synthesized as described elsewhere. All other reagents were purchased from commercial sources and used as received.

Synthesis of $\text{Ce}[N(i\text{-Pr}_2\text{PO})_2]_3(\text{ReO}_4)$ (2**).** To a solution of AgReO_4 (35.8 mg, 0.1 mmol) in MeCN (10 mL) was added a solution of **1** (101.6 mg, 0.1 mmol) in MeCN (10 mL), and the mixture

solution was stirred at room temperature for 1 h. The AgCl formed was filtered off, and the solvent was removed under reduced pressure. Recrystallization from Et_2O afforded a yellow crystalline solid. Yield: 69 mg (56%). ^1H NMR (C_6D_6): δ 1.19 (m, 36H, $(\text{CH}_3)_2\text{CH}$), 1.28 (m, 36H, $(\text{CH}_3)_2\text{CH}$), 2.04 (sept, 12H, $J = 7.2$ Hz, $(\text{CH}_3)_2\text{CH}$). ^{31}P $\{^1\text{H}\}$ NMR (C_6D_6): δ 52.38 (s). Anal. Calcd for $\text{C}_{36}\text{H}_{84}\text{CeN}_3\text{O}_{10}\text{P}_6\text{Re}$: C, 35.12; H, 6.88; N, 3.41. Found: C, 35.05; H, 6.99; N, 3.60.

Synthesis of $\text{Ce}_2[N(i\text{-Pr}_2\text{PO})_2]_6(\text{MnO}_4)_2$ (3**).** To a solution of AgMnO_4 (0.154 mmol) in MeCN (10 mL) was added a solution of **1** (157 mg, 0.154 mmol) in MeCN (10 mL), and the mixture was stirred at room temperature for 0.5 h and filtered. The filtrate was concentrated to ca. 5 mL under vacuum and cooled to -18 °C to give purple crystals that were suitable for X-ray diffraction. Yield: 85 mg (50%). ^1H NMR (CD_3CN): δ 1.20 (m, 144H, $(\text{CH}_3)_2\text{CH}$), 2.01 (sept, 24H, $J = 7.2$ Hz, $(\text{CH}_3)_2\text{CH}$). ^{31}P $\{^1\text{H}\}$ NMR (CD_3CN): δ 56.4 (s). Anal. Calcd for $\text{C}_{72}\text{H}_{168}\text{Ce}_2\text{Mn}_2\text{N}_6\text{O}_{20}\text{P}_{12}$: C, 39.31; H, 7.70; N, 3.82. Found: C, 38.73; H, 8.23; N, 3.80.

Kinetic Study of Decomposition of **3 in CH_2Cl_2 .** The kinetics of decomposition of **3** in CH_2Cl_2 at room temperature was studied by monitoring the absorbance of the LMCT band of the MnO_4^- moiety at 526 nm. The first-order rate constant, k_{obs} , was determined according to the equation, $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{\text{obs}}t)$, where A_0 and A_∞ are the initial and final absorbance, respectively. Rate constants for decomposition of **3** in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ solutions were determined similarly.

Stoichiometric Oxidation of Ethylbenzene with **3.** A solution of **3** (36 mg, 0.0163 mmol) in ethylbenzene/MeCN (1:5, 4 mL) or neat ethylbenzene (4 mL) was stirred at room temperature under nitrogen for 2 h. The organic products were analyzed by GLC using PhBr as the internal standard.

Iodometric Titration. The Mn oxidation state of the inorganic product for the oxidation of ethylbenzene by **3** was determined by an iodometric method.²⁰ At the end of reaction, a 1.0 mL aliquot of the solution was transferred to a 10 mL volumetric flask containing 0.019 g of $n\text{-Pr}_4\text{NI}$. Glacial acetic acid (1 mL) was added, followed by CH_2Cl_2 ,

Table 1. Crystallographic Data and Experimental Details for Heterometallic Ce-O-M Complexes 3–6

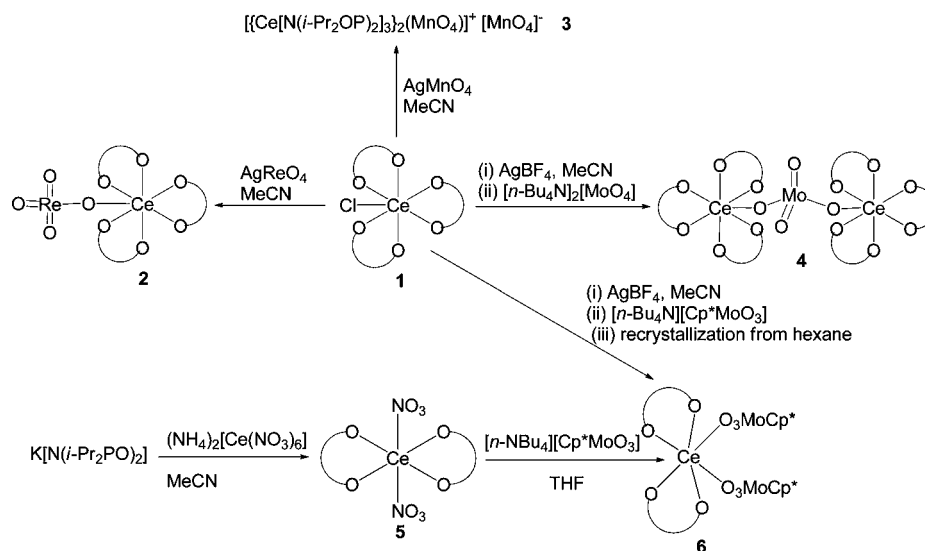
compound	3	4	5	6
formula	$\text{C}_{72}\text{H}_{168}\text{Ce}_2$ $\text{Mn}_2\text{N}_6\text{O}_{20}\text{P}_{12}$	$\text{C}_{72}\text{H}_{168}\text{Ce}_2$ $\text{MoN}_6\text{O}_{16}\text{P}_{12}$	$\text{C}_{24}\text{H}_{56}\text{Ce}$ $\text{N}_4\text{O}_{10}\text{P}_4$	$\text{C}_{44}\text{H}_{87.33}\text{Ce}$ $\text{Mo}_2\text{N}_2\text{O}_{10.67}\text{P}_4$
fw	2199.88	2121.94	824.73	1271.04
T, K	173(2)	173(2)	173(2)	172.9(3)
wavelength, Å	0.71073	0.71073	1.54178	0.71073
cryst syst	hexagonal	triclinic	monoclinic	monoclinic
space group	$P\bar{3}_1c$	$P\bar{1}$	$P2_1$	$C2/c$
a, Å	12.5734(2)	12.6951(11)	9.6503(2)	18.7983(4)
b, Å	12.5734(2)	13.0938(12)	14.9612(2)	14.1982(4)
c, Å	38.3973(10)	17.7937(16)	13.6574(2)	21.6789(4)
α , deg		78.786(2)		
β , deg	120	79.1360(10)	108.785(2)	95.839(2)
γ , deg		62.8470(10)		
V, Å ³	5256.98(18)	2564.7(4)	1866.82(5)	5756.1(2)
Z	2	1	2	4
ρ_{calc} , Mg/m ³	1.390	1.374	1.467	1.467
μ , mm ⁻¹	1.326	1.236	11.479	1.368
F(000)	2296	1108	852	2611
no. of reflns	32 867	8632	6880	33 384
no. of indep reflns	3815	12671	4853	5638
R_{int}	0.0344	0.0240	0.0507	0.0371
GOF ^a	1.008	1.034	1.017	1.021
$R1^b$	0.0324	0.0752	0.0508	0.0250
$wR_2^c(I > 2\sigma)$	0.0982	0.2056	0.1196	0.0794
R1	0.0355	0.0985	0.0534	0.0261
wR_2 (all data)	0.1009	0.2348	0.1206	0.0803

$$^a\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}. \quad ^bR_1 = (\sum(|F_o| - |F_c|) / \sum|F_o|). \quad ^c wR_2 = [\sum w^2(|F_o| - |F_c|)^2 / \sum w^2|F_o|^2]^{1/2}.$$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3–6

	3 (M = Mn)	4 (M = Mo)	5	6 (M = Mo)
Ce-O(P)	2.2258(17)–2.631(16)	2.267(6)–2.320(6)	2.232(5)–2.238(5)	2.2568(16)–2.2775(17)
Ce-O(M)	2.528(8)	2.236(6)		2.1640(17)
M-O _t	1.571(5)–1.576(8)	1.677(17)–1.697(7)		1.7154(19)–1.7204(19)
M-O(Ce)	1.643(8)–1.736(7)	1.872(6)		1.8606(17)
P-O	1.5438(18)–1.5493(17)	1.522(6)–1.535(8)	1.538(6)–1.549(6)	1.5407(17)–1.5479(17)
P-N	1.584(2)–1.588(2)	1.538(11)–1.585(7)	1.558(7)–1.605(7)	1.589(2)–1.592(2)
Ce-O-M	180	141.8(4)–150.5(4)		168.74(10)
P-N-P	128.04(13)	125.7(5)–126.9(6)	131.1(4)–131.3(5)	128.91(14)

Scheme 1. Synthesis of Heterometallic Cerium(IV) Complexes



to bring the total volume to 10 mL, and the mixture was stirred thoroughly. An aliquot of the solution was promptly transferred to a cuvette, and the UV/vis spectrum was recorded. The concentration of I_3^- formed was calculated assuming that $\epsilon_{365}(I_3^-) = 26\,200\text{ M}^{-1}\text{ cm}^{-1}$.²¹ The result of iodometric titration indicated that the inorganic product is about four oxidizing levels below the monomeric unit of 3. Therefore, the Ce and Mn oxidation states of the inorganic product are tentatively assigned as +3 and +4 (vide infra), respectively.

Reaction of 1 with $AgBF_4$. A mixture of 1 (10.4 mg, 0.01 mmol) and $AgBF_4$ (2 mg, 0.01 mmol) in CD_3CN (0.5 mL) was stirred at room temperature for 10 min and filtered. 1H NMR (CD_3CN): δ 1.20 (m, 72H, $(CH_3)_2CH$), 2.01 (sept, 12H, $J = 7.2$ Hz, $(CH_3)_2CH$). ^{31}P { 1H } NMR (CD_3CN): δ 56.4 (s). ^{19}F { 1H } NMR (CD_3CN): δ -151.9 (s).

Synthesis of $[Ce\{N(i-Pr_2PO)_2\}_3]_2(\mu-MoO_4)$ (4). To a solution of $[Ce\{N(i-Pr_2PO)_2\}_3][BF_4]$ prepared from 1 (203 mg, 0.2 mmol) and $AgBF_4$ (39 mg, 0.2 mmol) in MeCN (5 mL) as described above was added a solution of $[n-Bu_4N]_2[MoO_4]$ (64 mg, 0.1 mmol) in MeCN (5 mL), and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was extracted with hexane. Concentration and cooling at -10 °C afforded yellow crystals. Yield: 62 mg (53%). 1H NMR ($CDCl_3$): δ 1.15–1.33 (m, 72H, $(CH_3)_2CH$), 1.94–2.02 (m, 12H, $(CH_3)_2CH$). ^{31}P { 1H } NMR ($CDCl_3$): δ 53.1 (s). We were not able to obtain satisfactory analytical data. However, this compound has been well-characterized by a spectroscopic method and X-ray diffraction.

Synthesis of $trans-Ce\{N(i-Pr_2PO)_2\}_2(NO_3)_2$ (5). To a solution of $(NH_4)_2Ce(NO_3)_6$ (110 mg, 0.2 mmol) in MeCN (10 mL) was added $K\{N(i-Pr_2PO)_2\}$ (128 mg, 0.4 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was pumped off, and the residue was extracted with Et_2O . Slow evaporation of the solvent afforded orange crystals. Yield: 90 mg (55%). 1H NMR ($CDCl_3$): δ 1.16 (m, 48H, $(CH_3)_2CH$), 1.94 (sept, 8H, $J = 7.2$ Hz, $(CH_3)_2CH$).

^{31}P { 1H } NMR ($CDCl_3$): δ 54.4 (s). IR (KBr, cm^{-1}): 1384 (s) [$\nu(NO_3)$]. Anal. Calcd for $C_{24}H_{36}CeN_4O_{10}P_4$: C, 34.95; H, 6.84; N, 6.79. Found: C, 35.09; H, 6.96; N, 6.65.

Synthesis of $Ce\{N(i-Pr_2PO)_2\}_2(Cp^*MoO_3)_2$ (6). To a solution of $[n-Bu_4N][Cp^*MoO_3]$ (103 mg, 0.197 mmol) in THF (5 mL) was added a solution of 5 (81.4 mg, 0.0985 mmol) in THF (5 mL) at -78 °C, and the mixture was warmed to room temperature and stirred for 1 h. The solvent was pumped off, and the residue was extracted with Et_2O (10 mL). Recrystallization from MeCN at -18 °C afforded red crystals. Yield: 78 mg (63%). 1H NMR ($CDCl_3$): δ 1.20 (m, 48H, $(CH_3)_2CH$), 1.98 (m, 8H, $(CH_3)_2CH$), 2.07 (s, 30H, C_5Me_5). ^{31}P { 1H } NMR ($CDCl_3$): δ 51.4 (s). Anal. Calcd For $C_{44}H_{86}CeMo_2N_2O_{10}P_4$: C, 41.97; H, 6.88; N, 2.22. Found: C, 41.83; H, 6.62; N, 2.26.

Catalytic Oxidation of Organic Sulfides. Typically, a mixture of methyl *p*-tolyl sulfide (10 μ L, 0.0743 mmol), *tert*-butyl hydroperoxide (0.11 mmol, 18.5 μ L of 6.0 M solution in decane), and catalyst (0.003 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 h. The organic products were analyzed by GLC using iodobenzene as the internal standard.

X-ray Crystallography. Crystallographic data, experimental details, and selected bond lengths and angles for complexes 3–6 are listed in Tables 1 and 2, respectively. Intensity data were collected on a Bruker Smart CCD diffractometer and an Oxford Xcalibur PD X-ray diffractometer. The collected frames were processed with the software SAINT.²² Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.²³ Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. The MnO_4^- moiety in the complex cation of 3 is 50:50 disordered, and the two disordered parts are related by a 2-fold axis. In complex 4, the Mo(1), O(8), and O(9) atoms are disordered over two symmetry-equivalent positions with 50% occupancy.

RESULTS AND DISCUSSION

Perrhenate Complex. The syntheses of heterometallic Ce(IV) complexes are summarized in Scheme 1. Treatment of **1** with AgReO₄ in acetonitrile afforded the Ce(IV)/Re(VII) complex Ce[N(*i*-Pr₂PO)₂]₃(ReO₄) (**2**). Complex **2** is air-stable in both the solid state and solution. The ³¹P {¹H} NMR spectrum of **2** in C₆D₆ displayed a singlet at δ 52.3 ppm, which is more downfield than that of **1** (δ 49.5 ppm).¹⁵ We were not able to assign the Re=O stretch for **2** due to overlap with intense ν(P–O) bands of the ligand in the IR spectrum. A preliminary X-ray diffraction study²⁴ (Figure 1) revealed that **2** is a 7-coordinated compound containing an η¹-ReO₄[−] ligand. Unfortunately, the crystal structure has not been refined satisfactorily due to disorder problems.

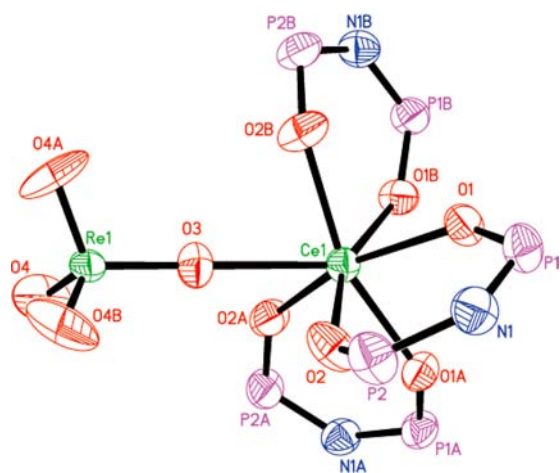


Figure 1. Molecular structure of **2**. Isopropyl groups of the ligands are omitted for clarity. Symmetry code: A = $-y + 1, x - y + 1, z$; B = $-x + y, -x + 1, z$.

Permanganate Complex. Similarly, treatment of **1** with AgMnO₄ in acetonitrile afforded a purple solid (**3**) analyzed as “Ce[N(*i*-Pr₂PO)₂]₃(MnO₄)”. While complex **3** is stable in acetonitrile, it decomposes readily in other organic solvents, such as CH₂Cl₂ (vide infra). Recrystallization of **3** from acetonitrile at -18 °C afforded purple crystals identified as [Ce₂{N(*i*-Pr₂PO)₂]₆(MnO₄)⁺(MnO₄[−]) by X-ray diffraction. Figure 2 shows the structure of the complex cation in **3**. The permanganate moiety in the complex cation is 50:50 disordered, and the two disordered parts are related by a 2-fold axis. A weak interaction was found between the disordered permanganate and the two Ce(IV) centers [Ce(1)–O(3) and Ce(1A)–O(3A) distances of 2.528(8) Å, cf. 2.236(6) Å for the molybdate analogue **4** (vide infra)]. The geometry around Ce in **3** can be described as monocoordinated octahedral with Ce–O(P) distances of 2.2258(17)–2.2631(16) Å that are comparable to those in Ce[N(*i*-Pr₂PO)₂]₃Cl.¹⁵ Although permanganate-based coordination polymers, such as [AgMnO₄]_n,²⁵ have been isolated, to our knowledge, **3** is the first structurally characterized molecular heterometallic permanganate complex showing a Ce–O(Mn) interaction.

The UV/vis spectrum of **3** in acetonitrile displayed the permanganate-based ligand-to-metal charge transfer (LMCT) band centered at 526 nm (Figure 3) that is very similar to that of [n-Bu₄N][MnO₄]. Both the ¹H and the ³¹P {¹H} NMR spectra of **3** in CD₃CN are almost identical with those for [Ce{N(*i*-Pr₂PO)₂]₃][BF₄] (vide infra). Thus, it is reasonable to

assume that **3** completely ionizes to the ion pair [Ce{N(*i*-Pr₂PO)₂]₃]⁺BF₄[−] in acetonitrile solution. On the other hand, complex **3** decomposes readily in less polar solvents, such as CH₂Cl₂, as evidenced by UV/vis and NMR spectroscopy. Purple solutions of **3** in CH₂Cl₂ gradually turned brown and the permanganate LMCT band vanished completely in ca. 2 h at room temperature. The ³¹P {¹H} NMR spectrum of the resulting brown solution showed a broad resonance at δ 59.6 ppm, which is close to that for Ce[N(*i*-Pr₂PO)₂]₃ (cf. δ 60 ppm).¹⁵ After the brown solution was left to stand in air overnight, a dark precipitate (presumably MnO₂) and a pale yellow solution, from which Ce[N(*i*-Pr₂PO)₂]₃ could be isolated, were formed. Under the same conditions, no significant UV/vis and NMR spectral change was found for [n-Bu₄N][MnO₄] in CH₂Cl₂. The kinetics of the degradation of **3** in CH₂Cl₂ has been studied by monitoring the absorbance of the LMCT band at 526 nm (Figure 3). At 25 °C, the decay of **3** in CH₂Cl₂ followed first-order kinetics with a rate constant (*k*_{obs}) of $(6.0 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$. The decomposition of **3** in CH₂Cl₂ was found to be decelerated by addition of acetonitrile. Thus, the *k*_{obs} for decomposition of **3** in 1:4 and 1:1 (v/v) CH₂Cl₂/MeCN mixtures were determined to be $(3.8 \pm 0.1) \times 10^{-4}$ and $(2.5 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$, respectively. At a lower concentration of acetonitrile (CH₂Cl₂/MeCN volume ratio > 1), the decomposition of **3** did not follow simple first-order kinetics and appeared to consist of more than one step. Additional study is required to determine the rate constants of this complex, multistep kinetics. The ease of decomposition of **3** in CH₂Cl₂ can be attributed to coordination and activation of the MnO₄[−] moiety by the electrophilic Ce(IV) center. Lewis acid induced decomposition of MnO₄[−] is well-documented. Recently, Lau and co-workers reported that, upon coordination of Lewis acids, such as BF₃, to the Mn=O group, MnO₄[−] undergoes intramolecular O–O coupling to generate O₂ and MnO₂.²⁶ We believe that a similar pathway is responsible for the decomposition of **3** in CH₂Cl₂.

Oxidation of Ethylbenzene by **3.** **3** can oxidize ethylbenzene in acetonitrile, but rather slowly. The oxidation of ethylbenzene by **3** in acetonitrile (ethylbenzene/MeCN, 1:5 v/v) at room temperature afforded acetophenone in 15% yield (with respect to the monomeric unit of **3**, vide infra) in 2 h. The yield increased to ca. 38% in 5 h, and no further increase was found in a longer time. When CH₂Cl₂ was used as the solvent (ethylbenzene/CH₂Cl₂, 1:5 v/v), acetophenone was obtained in 10% yield in 2 h. The yield remained the same in 10 h, suggesting that the complex had decomposed. On the other hand, acetophenone was formed almost quantitatively (vide infra) in 2 h from the reaction of **3** with neat ethylbenzene. Under the same conditions, very little acetophenone/benzoic acid was detected for the reaction of [n-Bu₄N][MnO₄] with neat ethylbenzene in 2 h. The oxidation of neat ethylbenzene with **3** gave a brown solution that possibly contained a Ce(III) species (³¹P resonance at δ 59.6 ppm). Iodometric titration indicated that the inorganic product is about four oxidizing levels below the monomeric unit of the Ce(IV)/Mn(VII) starting material **3**. After the brown solution was left to stand in air overnight, a brown precipitate (presumably MnO₂) along with a pale yellow solution, from which crystals of Ce[N(*i*-Pr₂PO)₂]₃ could be isolated, was formed. Therefore, it is reasonable to assume that the Ce and Mn oxidation states of the inorganic product are +3 and +4, respectively, as represented by the following stoichiometric equation (eq 1).

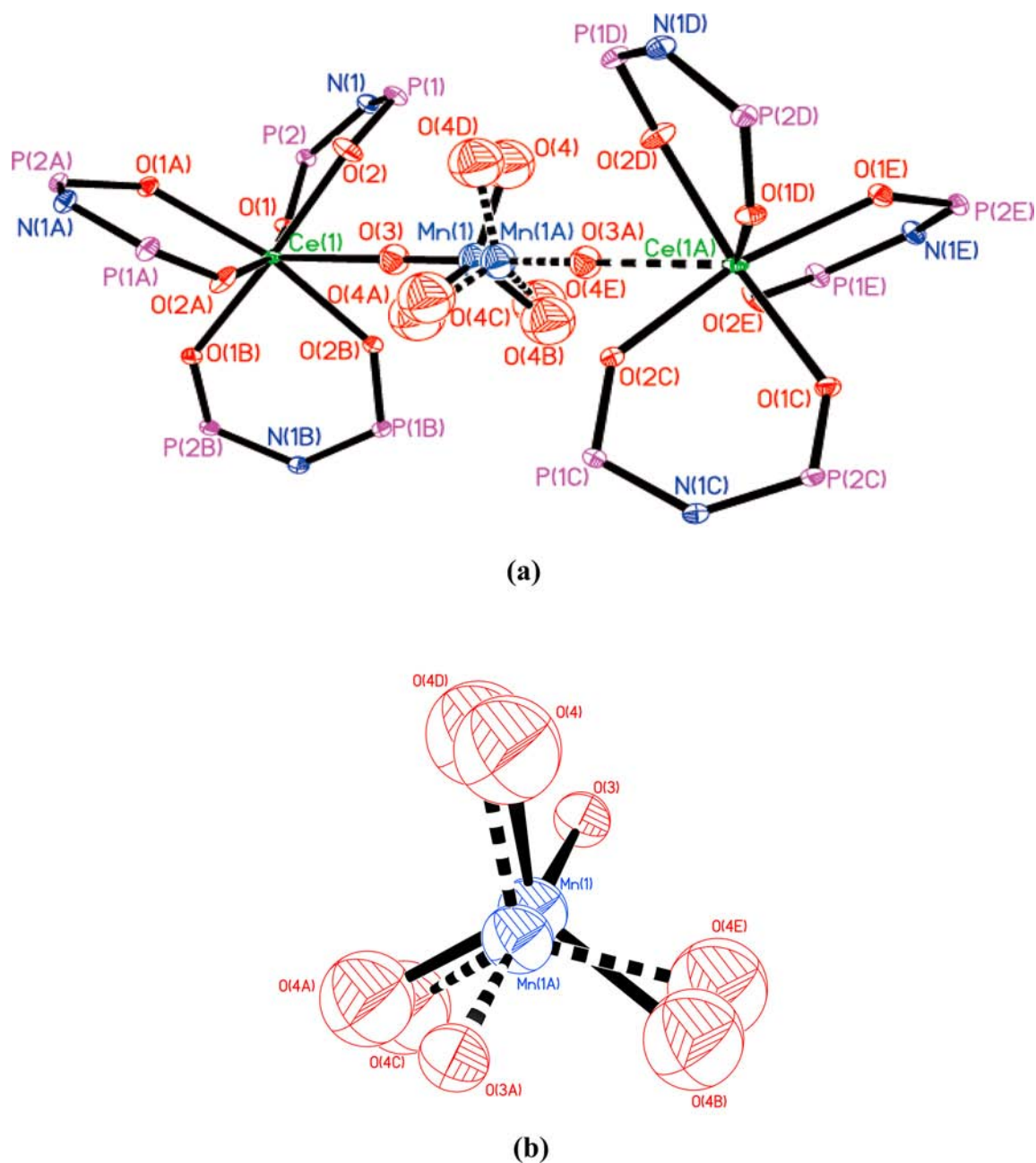
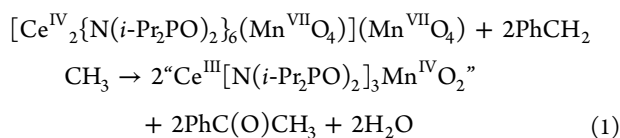


Figure 2. (a) Molecular structure the complex cation in 3. (b) A view of the disordered permanganate moiety. Isopropyl groups of the ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level. Symmetry code: A = $-y + 1, x - y, z$; B = $-x + y + 1, -x + 1, z$; C = $-y + 1, -x + 1, -z + 3/2$; D = $-x + y + 1, y, -z + 3/2$; E = $x, x - y, -z + 3/2$.



Assuming that the oxidation of ethylbenzene to acetophenone is a 4-electron process and dimeric 3 is an overall 8-electron oxidant, the yield of acetophenone²⁷ was determined to be ca. 100% based on complex 3. The oxidation of other alkylbenzenes, such as cumene, has not been examined due to the poor solubility of 3 in these alkylbenzenes. Lau and co-workers reported that Lewis acids, such as BF_3 , and metal triflates accelerate the KMnO_4 oxidation of hydrocarbons through the coordination of the $\text{Mn}=\text{O}$ group to the Lewis

acid.²⁸ We believe that a similar mechanism was involved in the oxidation of ethylbenzene by 3. Attempts to use 3 as a catalyst for the oxidation of ethylbenzene with terminal oxidants, such as *tert*-butyl hydroperoxide or PhIO , failed, possibly because the reoxidation of the $\text{Ce}(\text{III})\text{-Mn}(\text{IV})$ species to 3 is difficult.

Molybdate Complexes. No reaction was found between 1 and Ag_2MoO_4 , presumably due to poor solubility of Ag_2MoO_4 in acetonitrile. Thus, an alternative route to $\text{Ce}(\text{IV})\text{-molybdate}$ starting from $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3]^+$ and $[\text{MoO}_4]^{2-}$ was attempted. Treatment of 1 with AgBF_4 in MeCN resulted in immediate formation of AgCl . The resulting cationic $\text{Ce}(\text{IV})$ complex, possibly $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$, has been characterized by NMR spectroscopy. However, “ $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$ ” is not very stable in solution. Recrystallization of

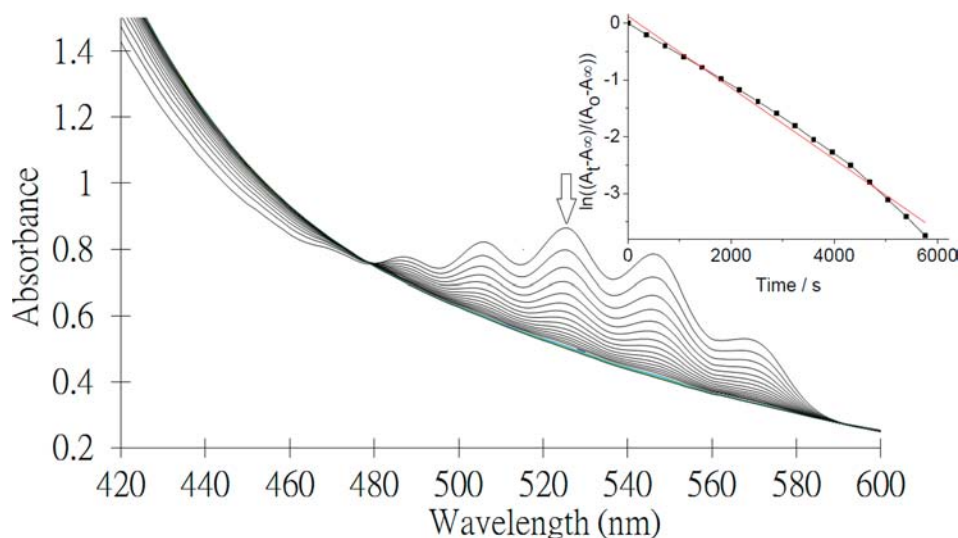


Figure 3. UV/vis spectral change for the decomposition of **2** in CH_2Cl_2 (1 mM) at 298 K (time interval = 6 min). Inset: Plot of $\log(A_t - A_\infty)/(A_0 - A_\infty)$ versus time for the LMCT band ($\lambda = 526$ nm).

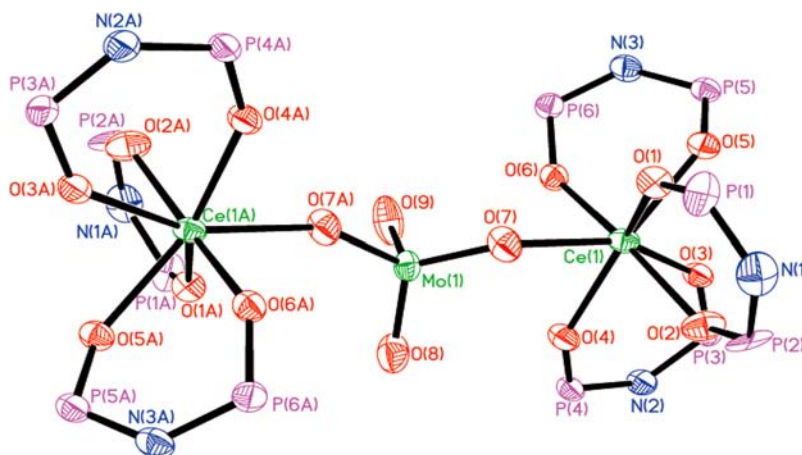


Figure 4. Molecular structure of **4**. Isopropyl groups of the ligands are omitted for clarity. The Mo(1), O(8), and O(9) atoms are disordered over two symmetry-equivalent positions with 50% occupancy. Only one of the disordered parts containing Mo(1), O(8), and O(9) is shown here. The ellipsoids are drawn at 30% probability level. Symmetry code: A = $-x + 2, -y + 2, -z + 1$.

$[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$ from CH_2Cl_2 /hexane resulted in the Ce(IV/III) reduction and formation of $\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3$. Therefore, $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$ was prepared in situ from **1** and AgBF_4 in acetonitrile and used for the subsequent reactions. Treatment of as-prepared $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$ with 0.5 equiv of $[\text{n-Bu}_4\text{N}]_2(\text{MoO}_4)$ afforded the trinuclear complex $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3]_2(\mu\text{-MoO}_4)$ (**4**). The ^{31}P $\{^1\text{H}\}$ NMR spectrum in CDCl_3 displayed a singlet at δ 53.1 ppm. The solid-state structure of **4** (Figure 4) consists of two symmetry-related $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3]^+$ fragments linked by a $\mu_2\text{-O, O' - MoO}_4^{2-}$ anion. An inversion center was found at the center of the molecule. The Mo, O8, and O9 atoms of the molybdate are 50:50 disordered. The Ce–O(P) distances in **4** [2.267(6)–2.320(6) Å] are similar to those in **3**. The Ce–O(Mo) distances [2.236(6) Å] are quite short and comparable to those in $\text{H}_4(\text{CeL}_{\text{OEt}})_6\text{MoO}_3$, where $\text{L}_{\text{OEt}}^- = [\text{Cp}^*\text{Mo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]^-$ [2.217(7)–2.407(8) Å],¹⁰ and the Ce–O–Mo angle is 141.8(4) and 150.5(4)°. The bridging Mo–O(Ce) bond [1.872(6) Å] is obviously longer than the terminal Mo–O bonds [1.677(17)–1.697(7) Å].

Treatment of in situ prepared $[\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3][\text{BF}_4]$ with $[\text{n-Bu}_4\text{N}][\text{Cp}^*\text{MoO}_3]$ in acetonitrile afforded a new species, which is tentatively formulated as a monomolybdate complex, $\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_3(\text{Cp}^*\text{MoO}_3)$, on the basis of ^1H NMR data (ratio of the integration of the Cp^* to $[\text{N}(i\text{-Pr}_2\text{PO})_2]^-$ signals $\sim 1:3$). This monomolybdate species is not stable in solution, as evidenced by NMR spectroscopy, and gradually rearranged to give the bis-molybdate complex $\text{Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_2(\text{Cp}^*\text{MoO}_3)_2$ (**6**), which has been characterized by X-ray diffraction. Alternatively, **6** could be synthesized in higher yield by reaction of a Ce(IV) bis(chelate) starting material and $[\text{n-Bu}_4\text{N}][\text{Cp}^*\text{MoO}_3]$. The dinitrate complex $\text{trans-Ce}\{\text{N}(i\text{-Pr}_2\text{PO})_2\}_2(\text{NO}_3)_2$ (**5**) has been prepared from $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ and 2 equiv of $\text{K}[\text{N}(i\text{-Pr}_2\text{PO})_2]$. X-ray crystallography confirmed that the two nitrates in **5** are mutually trans and bind to the Ce(IV) center in an η^2 -fashion (Figure 5). The Ce–O(nitrate) distances in **6** [2.458(6)–2.516(7) Å] are similar to those in $(\text{L}_{\text{OEt}})_2\text{Ce}(\text{NO}_3)_2$.²⁹ Treatment of **5** with 2 equiv of $[\text{n-Bu}_4\text{N}][\text{Cp}^*\text{MoO}_3]$ afforded **6**. ^1H NMR spectroscopy confirmed that the ratio of the Cp^* and imidodiphosphinate ligands in **6** is 1:1. The ^{31}P $\{^1\text{H}\}$ NMR

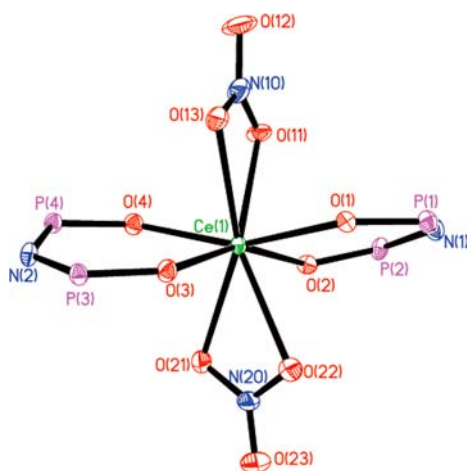


Figure 5. Molecular structure of **5**. Isopropyl groups of the ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level.

spectrum showed a singlet at δ 51.4 ppm. The molecular structure of **6** is shown in Figure 6. Unlike **3** and **4**, the

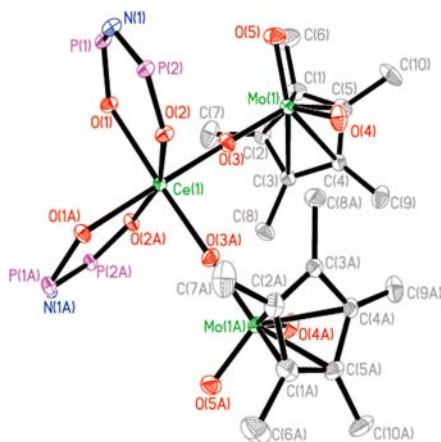


Figure 6. Molecular structure of **6**. Isopropyl groups of the ligands are omitted for clarity. The ellipsoids are drawn at 30% probability level. Symmetry code: A = $-x, y, 1/2 - z$.

geometry around the Ce atom in **6** is pseudo-octahedral. The Ce–O–Mo angles [$168.74(10)^\circ$] are larger than those in **4**, and the Ce–O(Mo) bond distance [$2.1640(17)$ Å] is shorter than that in **4** [$2.236(6)$ Å], suggesting that the Ce–O=Mo interactions in **6** are quite strong and this probably explains why monomolybdate species rearranged to **6** in solution easily. The bridging Mo–O(Ce) bond [$1.8606(17)$ Å] is longer than the terminal ones [$1.7154(19)$ – $1.7204(19)$ Å], which are longer than those in $[\text{Cp}^*\text{MoO}_3]^-$ [$1.742(4)$ – $1.765(4)$ Å].^{19b}

A preliminary study showed that the Ce(IV) molybdate complex **4** is a catalyst for oxidation of organic sulfides (Table 3). For example, the oxidation of phenyl methyl sulfide with *tert*-butyl hydroperoxide (TBHP) in the presence of 4 mol % of **4** afforded a mixture of sulfoxide (**I**) and sulfone (**II**) in 99% yield and a selectivity of 24:1. The sulfoxide was formed selectively, indicating that an electrophilic alkylperoxo/peroxo active species is responsible for the oxo transfer.³⁰ Similar yield and selectivity were found for *p*-tolyl methyl sulfide. Under the same conditions, $[\text{n-Bu}_4\text{N}][\text{MoO}_4]$ can also catalyze the oxidation of the sulfides, but with lower selectivity (I:II ratio of 4.3 and 3, respectively). Unlike other Mo cyclopentadienyl

Table 3. Catalytic Oxidation of Organic Sulfides with *tert*-Butyl Hydroperoxide (TBHP)^a

catalyst	R	% yield	I:II
4	H	99	24:1
4	Me	99	24:1
6	H	0	
Ce[N(<i>i</i> -Pr ₂ O) ₂] ₃ Cl	Me	0	
$[\text{n-Bu}_4\text{N}][\text{MoO}_4]$	H	75	4.3:1
$[\text{n-Bu}_4\text{N}][\text{MoO}_4]$	Me	84	3:1

^aExperimental conditions: Sulfide (0.0743 mmol), TBHP (0.1114 mmol), catalyst (0.003 mmol, 4 mol %), stirred in CH₂Cl₂ at RT for 2 h. Yields based on sulfide determined by GLC.

complexes,³¹ **6** cannot catalyze the sulfoxidation. Ce(IV)-L_{OEt} complexes, such as Ce[N(*i*-Pr₂PO)₃]Cl, are not active catalysts, suggesting that the Mo rather than Ce is the catalytic site for the Ce–Mo-catalyzed oxidation. Recent studies suggest that the mechanism of the Mo-catalyzed sulfoxidation with TBHP involves the formation of a Mo alkylperoxo/peroxo intermediate and the nucleophilic attack of a peroxo oxygen atom by the sulfide substrate.³² We believe that a similar pathway is involved in **4**-catalyzed sulfoxidation. The Ce/Mo complex **4** is a more selective catalyst than $[\text{n-Bu}_4\text{N}][\text{MoO}_4]$, suggesting that the $[\text{Ce}\{\text{N}(\text{i-Pr}_2\text{PO})_2\}_3]^+$ fragments in **4** have an influence on the selectivity and reactivity of the Mo alkylperoxo/peroxo intermediates. Currently, an effort is being made to isolate and characterize the Ce–Mo alkylperoxo/peroxo species and to explore their reactivity.

CONCLUSIONS

We have synthesized and structurally characterized heterometallic Ce(IV) permanganate and molybdate complexes supported by the imidodiphosphinate ligand $[\text{N}(\text{i-Pr}_2\text{PO})_2]^-$ featuring Ce(IV)–O–M linkages. The Ce(IV) permanganate complex **3** decomposes readily in CH₂Cl₂ and can oxidize neat ethylbenzene efficiently at room temperature. These results are suggestive of activation of permanganate by the electrophilic Ce(IV) center. The Ce(IV) molybdate complex **4** is a more selective sulfoxidation catalyst than free $[\text{MoO}_4]^-$, indicating that the selectivity and reactivity of the Mo-bound alkylperoxo active species can be influenced by the $[\text{Ce}\{\text{N}(\text{i-Pr}_2\text{PO})_2\}_3]^+$ fragments.

ASSOCIATED CONTENT

Supporting Information

CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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