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Tetravalent Titanium, Zirconium, and Cerium Oxo and Peroxo Complexes Containing an Imidodiphosphinate Ligand

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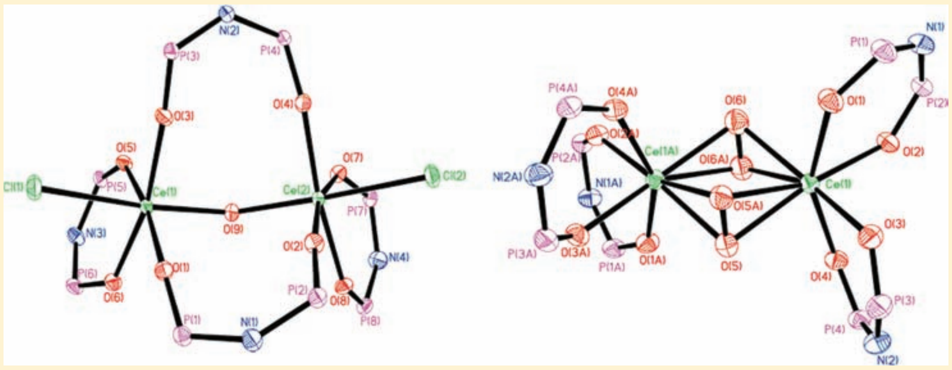
Supporting Information



ABSTRACT: Dinuclear Ti(IV), Zr(IV), and Ce(IV) oxo and peroxo complexes containing the imidodiphosphinate ligand $[N(i\text{-}Pr_2PO)_2]^-$ have been synthesized and structurally characterized. Treatment of $Ti(O\text{-}i\text{-}Pr)_2Cl_2$ with $KN(i\text{-}Pr_2PO)_2$ afforded the Ti(IV) di-μ-oxo complex $[Ti\{N(i\text{-}Pr_2PO)_2\}_2]_2(\mu\text{-}O)_2$ (**1**) that reacted with 35% H_2O_2 to give the peroxo complex $Ti[N(i\text{-}Pr_2PO)_2]_2(\eta^2\text{-}O_2)$ (**2**). Treatment of $HN(i\text{-}Pr_2PO)_2$ with $Zr(O\text{-}t\text{-}Bu)_4$ and $Ce_2(O\text{-}i\text{-}Pr)_8(i\text{-}PrOH)_2$ afforded the di-μ-peroxo-bridged dimers $[M\{N(i\text{-}Pr_2PO)_2\}_2]_2(\mu\text{-}O_2)_2$ [M = Zr (**3**), Ce (**4**)]. **4** was also obtained from the reaction of $Ce[N(i\text{-}Pr_2PO)_2]_3$ with 35% H_2O_2. Treatment of $(Et_4N)_2[CeCl_6]$ with 3 equiv of $KN(i\text{-}Pr_2PO)_2$ afforded $Ce[N(i\text{-}Pr_2PO)_2]_3Cl$ (**5**). Reaction of $(Et_4N)_2[CeCl_6]$ with 2 equiv of $KN(i\text{-}Pr_2PO)_2$ in acetonitrile, followed by treatment with Ag_2O, afforded the μ-oxo-bridged complex $[Ce\{N(i\text{-}Pr_2PO)_2\}Cl]_2[\mu\text{-}N(i\text{-}Pr_2PO)_2]_2(\mu\text{-}O)$ (**6**). **6** undergoes ligand redistribution in CH_2Cl_2 in air to give **5**. The solid-state structures of $[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$ and complexes **1**−**6** have been determined.

■ INTRODUCTION

The Ce^{4+} ion in oxygen-rich coordination spheres are of interest because they are related to the active sites of ceria-containing materials that are widely used in industrial and environmental catalysis, e.g. automotive three-way catalysis and chemical wet oxidation.[1−3] Although the exact mechanism is not well understood, it is believed that the oxygen release/uptake ability and facile +4/+3 redox couple of Ce play important roles in the oxidation capability of the ceria catalysts.[3] However, such reversible oxygen release/uptake chemistry has not been observed in molecular Ce(IV) complexes.

In order to gain insight into the mechanisms of ceria-based catalysis, we sought to synthesize molecular Ce(IV) oxo complexes in oxygen-rich ligand environments and to explore their reactivity. Despite the oxophilicity of cerium, relatively few molecular Ce(IV) oxo[4−6] and peroxo[7] complexes have been isolated to date. Although a theoretical study suggested that the bis(cyclopentadienyl) complexes Cp_2CeX (X = oxo, imido, carbene) containing cerium-ligand multiple bonds are legitimate synthetic targets,[8] Ce(IV) terminal oxo complexes remain elusive. Isolated Ce(IV) oxo complexes are mostly polynuclear μ-oxo complexes supported by O-donor ligands such as alkoxide, carboxylate, and dialkylcarbamate.[4] Recently, Lappert and co-workers reported that interactions of $Ce^{III}(NR_2)_3$ ($R = SiMe_3$) with a stoichiometric amount of oxygen or 2,6-di-*tert*-butylbenzoquinone at low temperature afforded Ce(IV) and Ce(IV)/M(I) (M = Na, K) μ-oxo complexes, possibly via superoxo and peroxo intermediates. The peroxo complex $Ce_2(\mu\text{-}O_2)(NR_2)_6$ has also been isolated at low temperature. These Ce(IV) oxo and peroxo amido complexes are thermally sensitive and decompose readily in solutions at ambient temperature.[6]

Imidodiphosphinates, $[N(R_2PO)_2]^-$ (R = aryl, alkyl; Chart 1), which have been recognized as inorganic analogues of acetylacetonate, can form stable complexes with main group and d- and f-block elements. In particular, the coordination and organometallic chemistry of $[N(Ph_2PO)_2]^-$ (or $tpip^-$) has been studied extensively.[9−17] Metal−tpip complexes have been used as NMR shift agents,[10] luminescent materials,[11−13] and catalysts for organic oxidations.[14,15] By contrast, very few studies have been made on the more soluble isopropyl substituted analogue,

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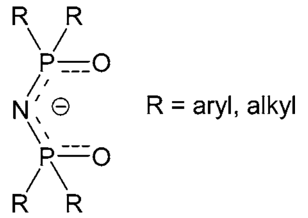
Chart 1



$[N(i\text{-}Pr_2PO)_2]^-$.[16] Previously, we reported the synthesis of *cis*-Ti(tpip)$_2$Cl$_2$ and [V(O)(μ-tpip)(μ-O)]$_3$ and their use in catalytic oxidation of organic sulfides with *tert*-butyl hydroperoxide.[15] As an extension of this study, we sought to synthesize tetravalent M(IV) (M = Ti, Zr, Ce) complexes with $[N(i\text{-}Pr_2PO)_2]^-$ and to investigate their oxidation chemistry. We found that the treatment of HN(i-Pr$_2$PO)$_2$ with Zr(O-t-Bu)$_4$ and Ce$_2$(i-OPr)$_8$(i-PrOH)$_2$ led to formation of the μ-peroxo complexes $[M\{N(i\text{-}Pr_2PO)_2\}_2]_2(\mu\text{-}O_2)_2$ (M = Zr, Ce), whereas the μ-oxo complexes $[Ti\{N(i\text{-}Pr_2PO)_2\}_2]_2(\mu\text{-}O)_2$ and $[Ce\{N(i\text{-}Pr_2PO)_2\}Cl]_2[\mu\text{-}N(i\text{-}Pr_2PO)_2]_2(\mu\text{-}O)$ were obtained from the reactions of KN(i-Pr$_2$PO)$_2$ with Ti(O-i-Pr)$_2$Cl$_2$ and (Et$_4$N)$_2$[CeCl$_6$]/Ag$_2$O, respectively. The solid-state structures of these dinuclear peroxo and oxo complexes will be reported.

■ 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 and 161.9 MHz for ^{1}H and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (^{31}P). Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, UK.

HN(i-Pr$_2$PO)$_2$,[16] Zr(O-t-Bu)$_4$,[17] (Et$_4$N)$_2$[CeCl$_6$],[18] and Ce$_2$(O-i-Pr)$_8$(i-PrOH)$_2$[19] were prepared according to literature methods. Ce[N(i-Pr$_2$PO)$_2$]$_3$ was prepared by reaction of Ce(NO$_3$)$_3$ with KN(i-Pr$_2$PO)$_2$ in water according to a modified literature method[13] and characterized by elemental analyses.

Syntheses. *KN(i-Pr$_2$PO)$_2$.* To a solution of K(O-t-Bu) (400 mg, 3.56 mmol) in methanol (20 mL) was added HN(i-Pr$_2$PO)$_2$ (1.0 g, 3.56 mmol). The mixture was stirred at room temperature for 2 h and evaporated to dryness in vacuo. The residue was washed with Et$_2$O/hexane (1:4, v/v) and redissolved in tetrahydrofuran (THF). Slow evaporation in air afforded colorless crystals that were suitable for X-ray diffraction. Yield: 795 mg (70%). ^{1}H NMR (D$_2$O): δ 1.07 (m, 24H, *Me*$_2$CH), 1.9 (m, 4H, Me$_2$C*H*). ^{31}P {^{1}H} NMR (D$_2$O): δ 47.0 (s).

[Ti{N(i-Pr$_2$PO)$_2$}$_2$]$_2$(μ-O)$_2$ (**1**). To a solution of Ti(O-i-Pr)$_2$Cl$_2$ (47 mg, 0.19 mmol) in THF (10 mL) was added 2 equiv of KN(i-Pr$_2$PO)$_2$ (122 mg, 0.38 mmol), and the mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was extracted with hexane (10 mL). Concentration to ca. 2 mL and cooling at −18 °C of the filtrate afforded colorless crystals that were suitable for X-ray diffraction. Yield: 65 mg (55%). ^{1}H NMR (C$_6$D$_6$): δ 1.12 (m, 48H, *Me*$_2$CH), 1.26 (d, 24H, J = 7.2 Hz, *Me*$_2$CH), 1.42 (d, 24H, J = 7.2 Hz, *Me*$_2$CH), 1.82 (m, 8H, Me$_2$C*H*), 2.21 (sept, 8H, J = 7.2 Hz, Me$_2$C*H*). ^{31}P {^{1}H} NMR (C$_6$D$_6$): δ 54.1 (s). Anal. Calcd for C$_{48}$H$_{112}$N$_4$O$_{10}$P$_8$Ti$_2$: C, 46.16; H, 9.04; N, 4.49. Found: C, 45.86; H, 9.37; N, 4.45.

Ti[N(i-Pr$_2$PO)$_2$]$_2$(η^2-O$_2$) (**2**). To a solution of **1** (137 mg, 0.11 mmol) in hexane (10 mL) was added H$_2$O$_2$ (35% in water) (200 μL, 2.4 mmol), and the mixture was stirred at room temperature for 2 h and evaporated to dryness. The residue was extracted with hexane (5 mL). Concentration the filtrate to ca. 2 mL and cooling at −18 °C afforded orange crystals that were suitable for X-ray diffraction. Yield: 84 mg (60%). ^{1}H NMR (C$_6$D$_6$): δ 1.12−1.22 (m, 36H, *Me*$_2$CH), 1.27 (d, 12H, J = 7.2 Hz, *Me*$_2$CH), 1.76−1.86 (m, 4H, Me$_2$C*H*), 2.09 (sept, 4H, J = 7.2 Hz, Me$_2$C*H*). ^{31}P {^{1}H} NMR (C$_6$D$_6$): δ 55.3 (s). IR (KBr, cm^{-1}): 874 [ν(O$_2$)]. Anal. Calcd for C$_{24}$H$_{56}$N$_2$O$_6$P$_4$Ti: C, 45.01; H, 8.81; N, 4.37. Found: C, 45.11; H, 8.67; N, 4.31.

[Zr{N(i-Pr$_2$PO)$_2$}$_2$]$_2$(μ-O$_2$)$_2$ (**3**). To a solution of Zr(O-t-Bu)$_4$ (192 mg, 0.5 mmol) in THF (10 mL) was added 2 equiv of HN(i-Pr$_2$PO)$_2$ (281 mg, 1 mmol), and the mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue was extracted with hexane (15 mL). Concentration to about 5 mL and cooling at −18 °C afforded colorless crystals that were suitable for X-ray diffraction. Yield: 184 mg (54%). ^{1}H NMR (C$_6$D$_6$): δ 1.18−1.55 (m, 96H, *Me*$_2$CH), 1.86−2.07 (m, 12H, *Me*$_2$CH), 2.56 (sept, 4H, J = 7.2 Hz, Me$_2$C*H*). ^{31}P {^{1}H} NMR (C$_6$D$_6$): δ 51.0 (d, J = 18.4 Hz), 50.5 (d, J = 18.4 Hz), 50.2 (d, J = 18.4 Hz), 50.0 (d, J = 18.4 Hz). IR (KBr, cm^{-1}): 1023 (s) [ν(O$_2$)]. Anal. calcd for C$_{48}$H$_{112}$N$_4$O$_{12}$P$_8$Zr$_2$ 0.5Et$_2$O: C, 42.75; H, 8.40; N, 3.99. Found: C, 43.01; H, 8.99; N, 4.32.

[Ce{N(i-Pr$_2$PO)$_2$}$_2$]$_2$(μ-O$_2$)$_2$ (**4**). *Method A.* A solution of HN(i-Pr$_2$PO)$_2$ (240 mg, 0.8 mmol) in THF (10 mL) was added to a solution of Ce$_2$(O-i-Pr)$_8$(i-PrOH)$_2$ (175.5 mg, 0.2 mmol) in THF (10 mL) dropwise. The reaction mixture was stirred at room temperature overnight. The solvent was pumped off, and the residue was extracted with Et$_2$O (15 mL). Recrystallization from a saturated solution of Et$_2$O/MeCN (1:2, v/v) at −18 °C afforded red crystals that were suitable for X-ray diffraction. 150 mg (51%). ^{1}H NMR (C$_6$D$_6$): δ 1.24−1.34 (m, 72H, *Me*$_2$CH), 1.43 (d, 24H, J = 7.2 Hz, *Me*$_2$CH), 1.93 (sept, 8H, J = 7.2 Hz, Me$_2$C*H*), 2.14 (sept, 8H, J = 7.2 Hz, Me$_2$C*H*). ^{31}P {^{1}H} NMR (C$_6$D$_6$): δ 47.9 (s). IR (KBr, cm^{-1}): 1020 [ν(O$_2$)]. Anal. calcd for C$_{48}$H$_{112}$Ce$_2$N$_4$O$_{12}$P$_8$: C, 39.34; H, 7.70; N, 3.82. Found: C, 39.68; H, 7.97; N, 3.88.

Method B. To a solution of Ce[N(i-Pr$_2$PO)$_2$]$_3$ (98.1 mg, 0.1 mmol) in acetone (10 mL) was added H$_2$O$_2$ (35 wt % in water, 68.7 μL, 0.8 mmol). The reaction mixture was stirred at room temperature overnight to give a red solid. Recrystallization from a saturated solution of Et$_2$O/MeCN (1:2, v/v) at −18 °C afforded red crystals of **4** in 70%.

Ce[N(i-Pr$_2$PO)$_2$]$_3$Cl (**5**). To a solution of (Et$_4$N)$_2$[CeCl$_6$] (80 mg, 0.13 mmol) in MeCN (25 mL) were added 3 equiv of KN(i-Pr$_2$PO)$_2$ (124.5 mg, 0.39 mmol), and the mixture was stirred at room temperature overnight. The solvent was removed in vacuo and the residue was extracted with Et$_2$O (10 mL). Evaporation of the solvent afforded a yellow solid, which was recrystallized from Et$_2$O/MeCN (1:6, v/v) at −18 °C to give yellow crystals. Yield: 105 mg (80%). ^{1}H NMR (CDCl$_3$): δ 1.18 (m, 72H, *Me*$_2$CH), 1.95 (sept, J = 7.2 Hz, 12H, Me$_2$C*H*). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 55.7 (s). Anal. Calcd for C$_{36}$H$_{84}$CeClN$_3$O$_6$P$_6$: C, 42.54; H, 8.33; N, 4.13. Found: C, 42.64, N, 8.79; N, 4.15.

[Ce{N(i-Pr$_2$PO)$_2$}Cl]$_2$[μ-N(i-Pr$_2$PO)$_2$]$_2$(μ-O) (**6**). To a solution of (Et$_4$N)$_2$[CeCl$_6$] (423 mg, 0.69 mmol) in MeCN (35 mL) was added 2 equiv of KN(i-Pr$_2$PO)$_2$ (440 mg, 1.38 mmol), and the mixture was stirred at room temperature for 2 h. Et$_2$O (20 mL) was added and the white precipitate was removed. To the yellow filtrate was added a suspension of Ag$_2$O (80 mg, 0.345 mmol) in MeCN (10 mL). The mixture was stirred at room temperature for 1.5 h and filtered. The filtrate was concentrated to ca. to 10 mL under vacuum to give a yellow solid. Recrystallization from CH$_2$Cl$_2$/MeCN (1:4, v/v) at −18 °C afforded yellow crystals. Yield: 231 mg (45%). ^{1}H NMR (CDCl$_3$): δ 1.13−1.45 (m, 96H, *Me*$_2$CH), 2.06 (sept, 12H, J = 7.2 Hz, Me$_2$C*H*), 2.22 (sept, 4H, J = 7.2 Hz, Me$_2$C*H*). ^{31}P {^{1}H} NMR (CDCl$_3$): δ 50.25 (br s) and 49.43 (br s). IR (KBr, cm^{-1}): 998 [ν(Ce$_2$O)]. Anal. calcd for C$_{48}$H$_{112}$Ce$_2$Cl$_2$N$_4$O$_9$P$_8$: C, 38.74; H, 7.58; N, 3.76. Found: C, 38.91; H, 7.92; N, 3.78.

X-ray Crystallography. Crystallographic data and experimental details for $[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$ and complexes **1**−**6** are listed in Table 1. Intensity data were collected on a Bruker APEX CCD diffractometer and Oxford Xcalibur PD X-ray diffractometer. The collected frames were processed with the software SAINT.[20] Structures were solved by the direct methods and refined by full-matrix

Table 1. Crystallographic Data and Experimental Details for $[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$ and 1–6

compounds	$[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$	**1**	**2**	**3**·0.5Et$_2$O	**4**	**5**	**6**
formula	$C_{24}H_{72}K_2N_2O_{12}P_4$	$C_{51}H_{119}N_4O_{10}P_8Ti_2$	$C_{24}H_{56}N_2O_6P_4Ti$	$C_{50}H_{117}N_4O_{12.5}P_8Zr_2$	$C_{48}H_{112}Ce_2N_4O_{12}P_8$	$C_{36}H_{84}CeClN_3O_6P_6$	$C_{48}H_{112}Ce_2Cl_2N_4O_9P_8$
f_w	782.92	1292.06	640.49	1404.68	1465.42	1016.45	1488.32
T, K	173.15	173(2)	298(2)	100(2)	100.0	173.0	173.15
wavelength, Å	1.54178	1.54178	0.71073	0.71073	0.71073	1.54178	1.54178
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/n$	$P2/c$	$P2_1/c$	$P2_1/c$
a, Å	8.6985(5)	13.5594(5)	14.918(4)	13.6095(14)	15.197(8)	13.0200(1)	15.13180(10)
b, Å	9.8922(7)	23.8906(6)	15.585(4)	24.495(3)	13.107(7)	13.0871(1)	13.78290(10)
c, Å	13.7471(9)	21.9309(6)	15.326(4)	21.535(2)	18.862(10)	30.0224(3)	34.7835(3)
α, deg	75.538(6)	90	90	90	90	90	90
β, deg	78.294(5)	92.523(3)	101.077(3)	91.149(2)	112.255(6)	92.661(1)	96.2230(10)
γ, deg	69.645(6)	90	90	90	90	90	90
V, Å^3	1065.09(12)	7097.5(4)	3497.0(14)	7177.3(13)	3477(3)	5110.1(8)	7211.70(9)
Z	1	4	4	4	2	4	4
ρ_{calc}, Mg/m^3	1.221	1.209	1.217	1.300	1.400	1.321	1.371
μ, mm^{-1}	3.804	4.015	0.463	0.521	1.528	9.460	12.354
$F(000)$	424	2788	1376	2980	1520	2136	3080
no. of refln	5617	25534	8406	50506	25716	19287	48144
no. of indep refln	3726	12651	2994	14018	7513	9187	12956
R_{int}	0.0242	0.0477	0.0222	0.0589	0.0589	0.0488	0.0745
GoF^a	1.041	1.013	1.044	1.015	1.034	1.038	1.022
$R_1{}^b$, $wR_2{}^c$ ($I > 2\sigma$)	0.0532, 0.1393	0.0452, 0.1059	0.0443, 0.1171	0.0498, 0.1132	0.0441, 0.1146	0.0380, 0.0976	0.0330, 0.0826
R_1, wR_2 (all data)	0.0552, 0.1419	0.0570, 0.1087	0.0546, 0.1237	0.0867, 0.1143	0.0535, 0.1192	0.0428, 0.1011	0.0364, 0.0836

[a] $\mathrm{GoF} = [\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$. [b] $R_1 = (\sum(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $wR_2 = [\sum w^2(|F_o| - |F_c|)^2/\Sigma w^2|F_o|^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1−6

	1	2	3	4	5	6
bond lengths						
M−O(P)	1.9883(16)-2.0794(17)	1.9703(19)-2.016(2)	2.131(2)-2.161(3)	2.287(3)-2.299(3)	2.251(2)-2.317(2)	2.228(2)-2.285(2)
M−O(oxo)	1.8343(18)-1.8626(17)					2.075(2)-2.099(2)
M−O(peroxo)		1.830(2)	2.145(3)-2.177(3)	2.276(3)-2.293(3)		
O−O(peroxo)		1.475(5)	1.394(4)-1.401(4)	1.412(6)-1.430(6)		
M−Cl					2.6852(9)	2.6683(8), 2.6813(8)
M−M	2.7795(6)		3.1045(5)	3.3993(19)		3.9996(2)
P−O	1.5192(18)-1.5344(17)	1.525(2)-1.527(2)	1.522(3)-1.537(3)	1.511(3)-1.521(3)	1.521(3)-1.538(3)	1.527(2)-1.545(2)
P−N	1.585(2)-1.597(2)	1.588(2)	1.580(3)-1.601(3)	1.560(3)-1.574(3)	1.581(3)-1.591(3)	1.578(3)-1.592(3)
bond angles						
P−N−P	123.54(14)−124.21(16)	124.00(14)	125.3(2)−126.1(2)	128.5(2)−129.5(2)	125.6(2)−127.1(2)	129.67(18)−137.10(19)
$M-O_{oxo}-M$	97.48(8)−97.50(8)					146.75(11)

least-squares on F^2 using the SHELXTL software package.[21] Atomic positions of non-hydrogen atoms were refined with anisotropic parameters. Some isopropyl groups of the $[N(i\text{-}Pr_2PO)_2]^-$ ligands in complexes **1**−**6** were found to be disordered. Selected bond distances and angles for complexes **1**−**6** are listed in Table 2.

■ RESULTS AND DISCUSSION

Ligand Synthesis. Similar to K(tpip),[22] the potassium salt $KN(i\text{-}Pr_2PO)_2$ was synthesized by deprotonation of $HN(i\text{-}Pr_2PO)_2$ with K(O-*t*-Bu) in methanol. $KN(i\text{-}Pr_2PO)_2$ is soluble in both water and organic solvents such as THF. The $^{31}P\ \{^1H\}$ NMR spectrum of $KN(i\text{-}Pr_2PO)_2$ in D_2O displayed a singlet at δ 47.0 ppm, which is more upfield than that for $HN(i\text{-}Pr_2PO)_2$ (δ 55.5 ppm).[16] Recrystallization from THF in air afforded off-white crystals characterized as the polymer $[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$. Figure 1 shows the solid-state structure of the repeating unit of the polymer, which consists of two symmetry-related $[K\{N(i\text{-}Pr_2PO)_2\}(H_2O)_2]$ fragments and four cocrystallized water molecules (not shown). An inversion center was found at the center of the unit. The K atoms in the polymer chain are linked together by bridging aqua groups. The K−O distances of the bridging aqua groups are not symmetrical [shorter: 2.6524(17), 2.6529(17) Å; longer: 3.161(2), 3.164(2) Å, respectively]. The imidodiphosphinate ligand binds to K in a bidentate mode with K−O distances of 2.7378(14) and 2.7380(14) Å.

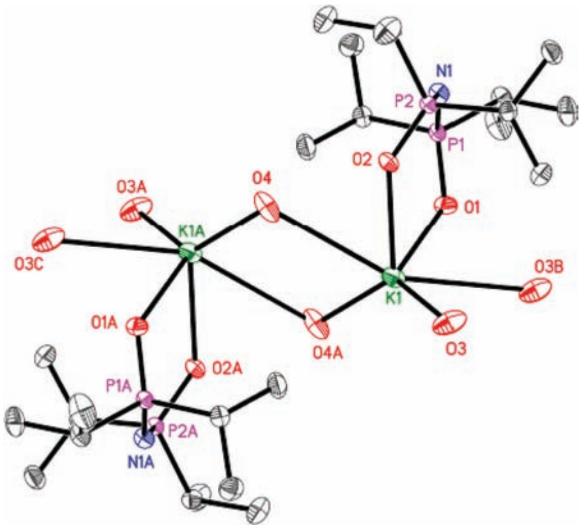
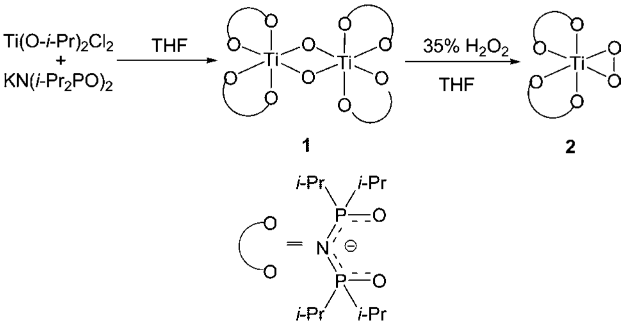


Figure 1. Structure of the repeating unit in $[K_2\{N(i\text{-}Pr_2PO)_2\}_2(H_2O)_8]_n$. The four cocrystallized water molecules and hydrogen atoms of the ligands are omitted. Selected bond distances (Å) and angles (deg): K(1)−O(1) 2.7378(14), K(1)−O(2) 2.7380(14), K(1)−O(3) 2.6524(17) Å, K(1)−O(4) 3.161(2), K(1)−O(4)A 2.6529(17), K(1)−O(3)B 3.164(2), P(1)−O(1) 1.5222(14), P(2)−O(2) 1.5211(13), P(1)−N(1) 1.5838(16), P(2)−N(1) 1.5904(15); P(1)−N(1)−P(2) 139.91(11). Symmetry code: A = −*x*, −*y* + 2, −*z* + 1; B = −*x* + 1, −*y* + 1, −*z* + 1.

Ti(IV) Oxo and Peroxo Complexes. The syntheses of $Ti\text{-}[N(i\text{-}Pr_2PO)_2]$ complexes are summarized in Scheme 1.

Scheme 1. Synthesis of Ti(IV) Oxo and Peroxo Complexes



Treatment of $Ti(O\text{-}i\text{-}Pr)_4$ with $HN(i\text{-}Pr_2PO)_2$ in THF gave a pale yellow oil that did not crystallize. On the other hand, the reaction of $Ti(O\text{-}i\text{-}Pr)_2Cl_2$ with $KN(i\text{-}Pr_2PO)_2$ in THF led to isolation of a white solid characterized as the Ti(IV) di-*μ*-oxo complex $[Ti\{N(i\text{-}Pr_2PO)_2\}_2]_2(\mu\text{-}O)_2$ (**1**). It seems likely that the formation of **1** involves the hydrolysis of a $Ti[N(i\text{-}Pr_2PO)_2]_2$ alkoxide/chloride intermediate with the water ligands/cocrystallized water molecules in the ligand. It may be noted that the dialkoxide species *cis*-$Ti(tpip)_2(O\text{-}i\text{-}Pr)_2$ has been isolated from the reaction of $Ti(O\text{-}i\text{-}Pr)_2Cl_2$ with K(tpip).[15] **1** is air stable in both the solid state and solutions. The $^{31}P\ \{^1H\}$ NMR spectrum of **1** showed a single resonance for the imidodiphosphinate ligand at δ 54.2 ppm. The structure of **1** is shown in Figure 2. Ti(IV) oxo complexes containing the $Ti_2(\mu\text{-}O)_2$ core are well documented.[23] The geometry around each Ti center is pseudo-octahedral. The Ti−O(*μ*-oxo) distances [1.8343(18)−1.8628(17) Å] and Ti−O−Ti angles [97.48(8)° and 97.50(8)°] are similar to those in $[L_{OEt}Ti]_2(\mu\text{-}O)_2(\mu\text{-}SO_4)$ $[L_{OEt}^- = CpCo\{P(O)(OEt)_2\}_3]^-]$.[24] The O−O

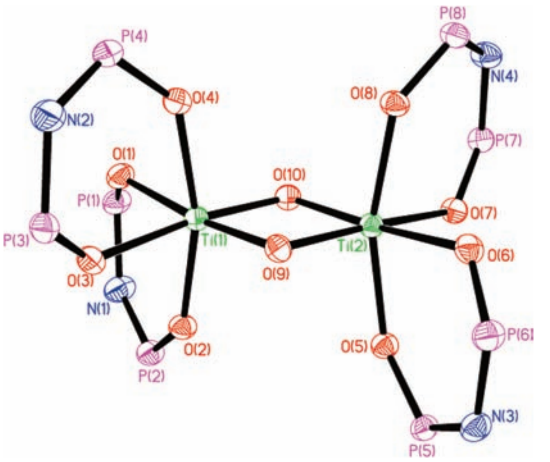


Figure 2. Molecular structure of **1**. The isopropyl groups of the imidodiphosphinate ligands are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level.

separation of 2.438 Å is considerably longer than that of peroxide, consistent with the formulation of **1** as a di-μ-oxo complex. The Ti−O(P) distances in **1** [1.9883(16)−2.0794(17) Å] are longer than those in *cis*-Ti(tpip)$_2$Cl$_2$ [1.923(2)−1.958(2) Å].[15]

Treatment of **1** with 35% H_2O_2 led to formation of a red species characterized as the peroxo complex Ti[N(*i*-Pr$_2$PO)$_2$]$_2$(η^2-O$_2$) (**2**). The UV−visible spectrum of **2** in CH_2Cl_2 displayed an band centered at 375 nm, tentatively assigned as the ligand-to-metal [p_π(peroxo) → d_π(Ti)] charge transfer (LMCT) transition. Similar LMCT bands have been found for reported Ti(IV) peroxo complexes.[25,26] The IR spectrum of **2** displayed the ν(O−O) band at 874 cm^{-1}, which is similar to that in $(NH_4)_4[Ti_2(O_2)_2(C_6H_4O_7)_2]\cdot 2H_2O$ (876 cm^{-1}).[25] **2** is air stable in both the solid state and solution. The structure of **2** featuring a side-on peroxide ligand is shown in Figure 3. An inversion center was found at the center of the molecule. The geometry around Ti is distorted octahedral due to the small O−Ti−O angle for the peroxo group. The O−O [1.475(5) Å] and Ti−O [1.830(2) Å] distances for the peroxo ligand in **2** compare well with those of reported Ti(IV) peroxo complexes.[27] The Ti−O(P) distances [1.9703(19) and 2.016(2) Å] are similar to those in **1** [1.9883(16)−2.0794(17) Å].

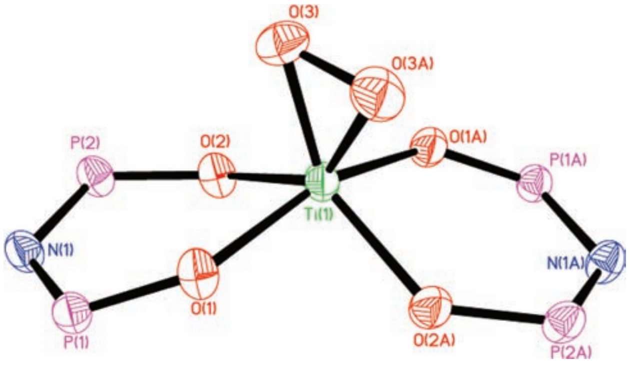
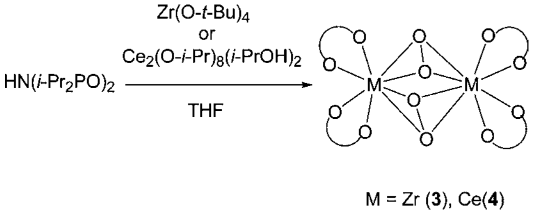


Figure 3. Molecular structure of **2**. The isopropyl groups of the imidodiphosphinate ligands are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level. Symmetry code: A = $-x + 1, y, -z + 1/2$.

Zr(IV) Peroxo Complex. Treatment of Zr(O-*t*-Bu)$_4$ with 2 equiv of HN(*i*-Pr$_2$PO)$_2$ in THF led to formation of the di-μ-peroxo complex [Zr{N(*i*-Pr$_2$PO)$_2$}$_2$]$_2$(μ-η^2:η^2-O$_2$)$_2$ (**3**; Scheme 2). The exact mechanism for the formation of the peroxo ligands in **3** is not clear. It may be noted that a dinuclear Hf(IV) peroxo porphyrin complex containing a $Hf_2(O_2)_2$ core has been isolated from the reaction $HfCl_4$ with porphyrin and sodium acetate.[28] Also, the Zr(IV) polyoxometalates [$Zr_2(O_2)_2$(α-$XW_{11}O_{39})_2$]$^{12-}$ (X = Si, Ge) have been synthesized by the reaction of $ZrCl_4$ with K_8[α-$XW_{11}O_{39}$], followed by treatment with H_2O_2.[29] The ^{31}P {^{1}H} NMR spectrum of **3** displayed four doublets at δ 51.0, 50.5, 50.2, and 50.0 ppm. The IR spectrum showed a band at 1023 cm^{-1}, which is tentatively assigned as ν(O−O) [cf. 1016 cm^{-1} for (NN)$_2$Zr(η^2-O$_2$)$_2$ where NN = glyoxal-bis(2,6-diisopropylphenyl)diimine[30]]. The solid-state structure of **3** is shown in Figure 4. The geometry around each Zr atom can be described as pseudo-dodecahedral. The Zr−O distances for the peroxo and [N(*i*-Pr$_2$PO)$_2$]$^-$ ligands are 2.145(3)−2.177(3) and 2.131(2)−2.161(3) Å, respectively. The O−O distances of the peroxo ligands in **3** [1.394(4) and 1.401(4) Å] are shorter than those in [Zr_2O_2(α-$XW_{11}O_{39})_2$]$^{12-}$ [X = Si (1.491(11) Å), Ge (1.529(13) Å)].[29]

Scheme 2. Synthesis of Zr(IV) and Ce(IV) Peroxo Complexes



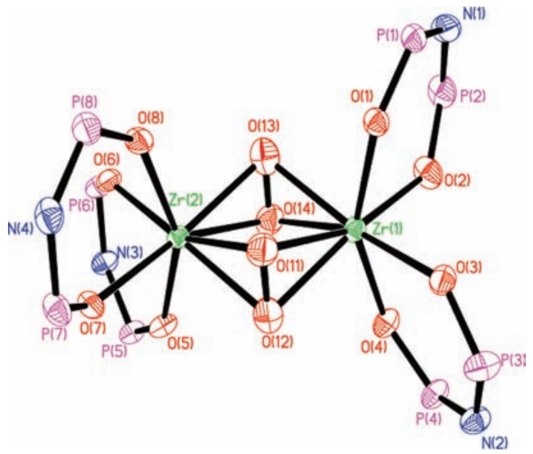


Figure 4. Molecular structure of **3**. The isopropyl groups of the imidodiphosphinate ligands are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level.

Ce(IV) Peroxo and Oxo Complexes. The successes in isolation of Ti(IV) and Zr(IV) peroxo complexes prompted us to synthesize analogous Ce(IV) peroxo complexes using Ce(IV) alkoxide precursors. Similar to the Zr(IV) analogue, the treatment of Ce$_2$(O-*i*-Pr)$_8$(*i*-PrOH)$_2$ with HN(*i*-Pr$_2$PO)$_2$ in THF afforded the di-μ-peroxo complex [Ce{N(*i*-Pr$_2$PO)$_2$}$_2$]$_2$(μ-η^2:η^2-O$_2$)$_2$ (**4**). Alternatively, complex **4** could be obtained by the oxidation of Ce[N(*i*-Pr$_2$PO)$_2$]$_3$ with H_2O_2. Thus, the treatment of Ce[N(*i*-Pr$_2$PO)$_2$]$_3$ with 35% H_2O_2 led to formation of **4** in 70% yield along with HN(*i*-Pr$_2$PO)$_2$ that was characterized by NMR spectroscopy. Ce(IV) peroxo complexes are usually prepared by reaction of Ce(III) salts with hydrogen peroxide in alkaline solutions.[7] To our knowledge, this is the first report of formation of a Ce(IV) peroxide from a Ce(IV) alkoxide. It may also be noted that visible irradiation and thermal treatment of $Ce_2(O\text{-}i\text{-}Pr)_8(i\text{-}PrOH)_2$ yielded the μ_4-oxo complexes $Ce_4(O)(O\text{-}i\text{-}Pr)_{13}(i\text{-}PrOH)$[4a] and $Ce_4(O)(O\text{-}i\text{-}Pr)_{14}$,[4c] respectively. **4** is air stable in both solid state and solutions. In order to study the oxo transfer ability of **4**, the reactions between **4** and tertiary phosphines were performed. However, no reactions were found when **4** was reacted with tertiary phosphines such as PPh_3 at room temperature. The UV−visible spectrum of **4** in CH_2Cl_2 displayed a shoulder at 406 nm tentatively assigned as an LMCT [p_π(peroxo) → d_π(Ce)] transition. The IR spectrum displayed the ν(O−O) band at 1020 cm^{-1}, which is similar to that for **3**. Unlike **3**, the $^{31}P\{^1H\}$ NMR spectrum of **4** displayed a single peak at δ 47.9 ppm, indicative of a symmetrical coordination environment around Ce. The structure of complex **4** containing a $Ce_2(O_2)_2$ core, which is commonly found in reported Ce(IV) peroxo complexes,[7] is shown in Figure 5. The molecule possesses a 2-fold rotational axis that passes through the midpoints of the two peroxo O−O bonds. The O−O distances of the peroxo ligands in **4** [1.412(6) and 1.430(6) Å] are longer than that in $[Ce\{N(SiMe_3)_2\}_3](\mu\text{-}O_2)_2$ [1.328(6) Å] but shorter than those in reported $Ce_2(O_2)_2$ complexes [1.44−1.488(4) Å]. The Ce−O(peroxo) and Ce−O(P) distances in **4** [2.276(3)−2.293(3) and 2.287(3)−2.299(3) Å, respectively] are longer than those in the Zr(IV) analogue **3**.

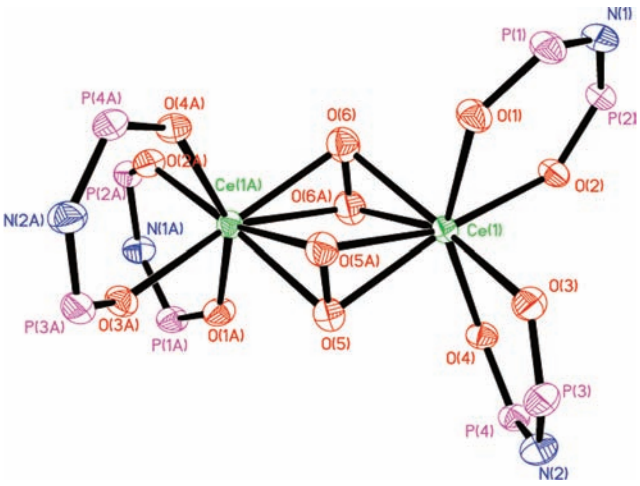
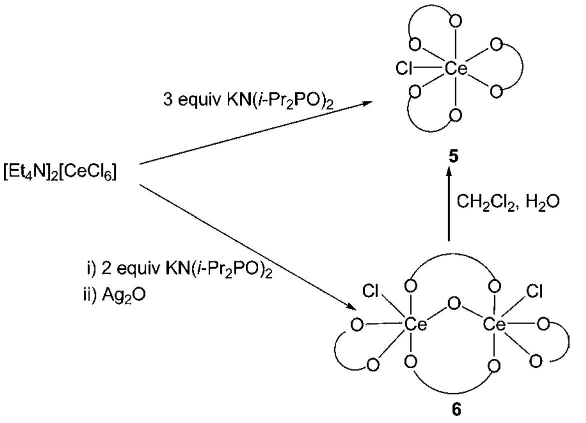


Figure 5. Molecular structure of **4**. The isopropyl groups of the imidodiphosphinate ligands are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level. Symmetry code: A = −*x*, −*y*, 1/2 − *z*.

Treatment of $(Et_4N)_2[CeCl_6]$ with 3 equiv of $KN(i\text{-}Pr_2PO)_2$ in acetonitrile afforded $Ce[N(i\text{-}Pr_2PO)_2]_3Cl$ (**5**, Scheme 3). On the other hand, treatment of $(Et_4N)_2[CeCl_6]$ with 2 equiv of $KN(i\text{-}Pr_2PO)_2$ in MeCN gave an air-sensitive diamagnetic yellow species, possibly the dichloride compound $Ce[N(i\text{-}Pr_2PO)_2]_2Cl_2$, along with a small amount of **5**. Upon recrystallization from MeCN at −18 °C, this air-sensitive yellow species slowly hydrolyzed to the μ-oxo complex $[Ce\{N(i\text{-}Pr_2PO)_2\}Cl]_2[\mu\text{-}N(i\text{-}Pr_2PO)_2]$ (μ-O) (**6**) in low yield (ca. 10%). **6** could be obtained in higher yield (45%) by treatment of the reaction mixture of $(Et_4N)_2[CeCl_6]$ and $KN(i\text{-}Pr_2PO)_2$ with 0.5 equiv of Ag_2O. The ^{31}P $\{^1H\}$ NMR spectrum of **6** in $CDCl_3$ at room temperature showed two broad peaks δ 50.25 and 49.43 ppm, which are tentatively assigned to the chelating and bridging $[N(i\text{-}Pr_2PO)_2]^-$ ligands, respectively. In order to explore the oxo transfer activity of the Ce(IV) oxo complex, reactions of **6** with phosphines were studied. However, no reactions were found when **6** was reacted with tertiary phosphines such as PPh_3 at room temperature. While **6** is stable in solution under nitrogen, it undergoes ligand redistribution in air readily to afford **5**. The remaining Ce-containing product, presumably a polynuclear Ce(IV) oxide, has not been characterized.

Scheme 3. Synthesis and Reactivity of the Ce(IV) Oxo Complex 6



The solid-state structure of **5** is shown in Figure 6. The geometry around Ce can be described as distorted monocapped octahedral. The Ce−O and Ce−Cl distances are 2.251(2)−2.317(2) and 2.6852(9) Å, respectively. The Ce−Cl distance in **5** is slightly longer than those in Cp_3CeCl [2.6666(7) Å][31] and $Ce[N(SiMe_3)_2]_3Cl$ [2.597(2) Å].[32] Figure 7 shows the molecular structure of **6**. Although polynuclear Ce(IV) complexes containing capping oxo ligands are well documented, dinuclear Ce(IV) μ-oxo complexes are rather uncommon.[8] The Ce−O(oxo) distances in **6** (av. 2.097 Å) are similar to those in $[Ce\{N(SiMe_3)_2\}_2]_2(\mu\text{-}O)_2$ (av. 2.095 Å)[6] but significantly shorter than that in the Ce(III) μ-oxo complex $[Cp^*{}_2Ce(THF)]_2(\mu\text{-}O)$ (Cp^* = $\eta^5\text{-}C_5Me_5$) [2.603(5) and

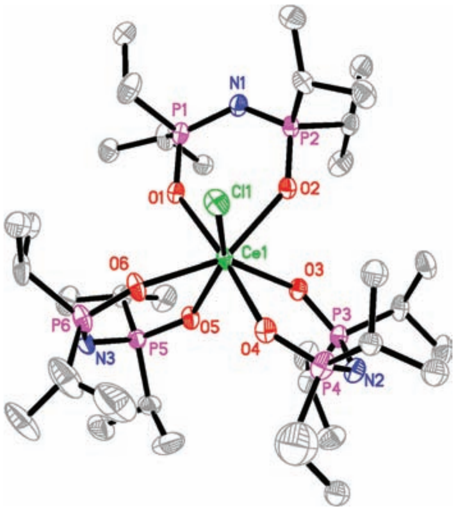


Figure 6. Molecular structure of **5**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level.

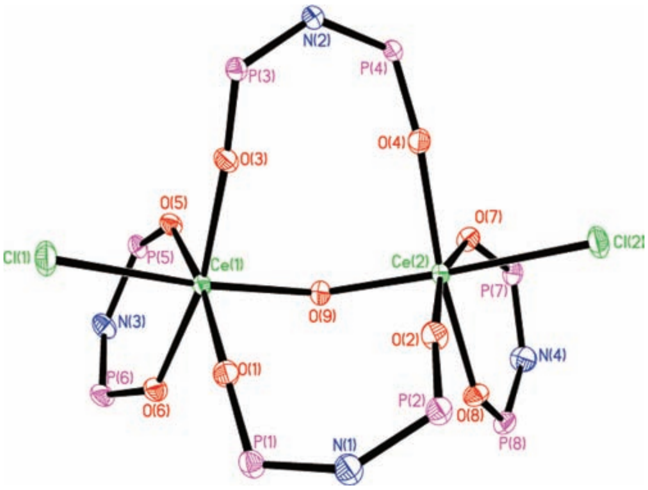


Figure 7. Molecular structure of **6**. The isopropyl groups of the imidodiphosphinate ligands are omitted for clarity. Thermal ellipsoids are drawn at a 30% probability level.

2.605(5) Å].[5] The Ce−O−Ce unit in **6** is bent with an angle of 146.75(11)°. The Ce−O distances for the bridging [N(i-Pr$_2$PO)$_2$]$^-$ ligands [2.228(2)−2.260(2) Å] are similar to those in chelating ones [2.274(2)−2.285(2) Å]. The Ce−Cl distances [2.6683(8) and 2.6813(8) Å] are similar to that in **5**.

■ CONCLUSIONS

We have synthesized and structurally characterized Ti(IV), Zr(IV), and Ce(IV) oxo and peroxo complexes containing the imidodiphosphinate ligand [N(i-Pr$_2$PO)$_2$]$^-$. The Ti(IV) peroxo complex Ti[N(i-Pr$_2$PO)$_2$]$_2$(η^2-O$_2$) was obtained from the reaction of [Ti{N(i-Pr$_2$PO)$_2$}$_2$]$_2$(μ-O)$_2$ with H$_2$O$_2$. Treatment of Zr(IV) and Ce(IV) alkoxides with HN(i-Pr$_2$PO)$_2$ afforded the di-μ-peroxo complexes [M{N(i-Pr$_2$PO)$_2$}$_2$]$_2$(μ-O$_2$)$_2$ (M = Zr, Ce). The Ce(IV) peroxo complex can also be prepared by the oxidation of Ce[N(i-Pr$_2$PO)$_2$]$_3$ with H$_2$O$_2$. The dinuclear Ce(IV) μ-oxo complex [Ce{N(i-Pr$_2$PO)$_2$}Cl]$_2$[μ-N-(i-Pr$_2$PO)$_2$]$_2$(μ-O) was obtained from the reaction of (Et$_4$N)$_2$-[CeCl$_6$] with KN(i-Pr$_2$PO)$_2$, followed by treatment with Ag$_2$O. While this Ce(IV) μ-oxo complex is stable under nitrogen, it undergoes ligand redistribution in solution readily to give Ce[N(i-Pr$_2$PO)$_2$]$_3$Cl when exposed to air. Efforts are being made to prepare other Ce(IV) oxo and peroxo complexes using these synthetic methods and to explore their reaction chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for [K$_2${N(i-Pr$_2$PO)$_2$}$_2$(H$_2$O)$_8$]$_n$ and complexes **1**−**6**. 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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