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Article

Phosphato, Chromato, and Perrhenato Complexes of Titanium(IV) and Zirconium(IV) Containing Kläui's Tripodal Ligand

Xiao-Yi Yi, Qian-Feng Zhang, Tony C. H. Lam, Eddie Y. Y. Chan, Ian D. Williams, and Wa-Hung Leung*

Department of Chemistry, The Hong Kong University of Science and Technology,
Clear Water Bay, Kowloon, Hong Kong, P. R. China

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Treatment of titanyl sulfate in dilute sulfuric acid with 1 equiv of NaL_{OEt} ($L_{OEt}^- = [(\eta^5\text{-}C_5H_5)Co\{P(O)(OEt)_2\}_3]^-$) in the presence of Na_3PO_4 and $Na_4P_2O_7$ led to isolation of $[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}PO_4)]$ (**1**) and $[(L_{OEt}Ti)_2(\mu\text{-}O)(\mu\text{-}P_2O_7)]$ (**2**), respectively. The structure of **1** consists of a Ti_3O_3 core capped by a μ_3-phosphato group. In **2**, the $[P_2O_7]^{4-}$ ligands binds to the two Ti's in a μ:η^2,η^2 fashion. Treatment of titanyl sulfate in dilute sulfuric acid with NaL_{OEt} and 1.5 equiv of $Na_2Cr_2O_7$ gave $[(L_{OEt}Ti)_2(\mu\text{-}CrO_4)_3]$ (**3**) that contains two $L_{OEt}Ti^{3+}$ fragments bridged by three μ-CrO_4^{2-}-*O*,*O*′ ligands. Complex **3** can act as a 6-electron oxidant and oxidize benzyl alcohol to give ca. 3 equiv of benzaldehyde. Treatment of $[L_{OEt}Ti(OTf)_3]$ ($OTf^- =$ triflate) with $[n\text{-}Bu_4N][ReO_4]$ afforded $[\{L_{OEt}Ti(ReO_4)_2\}_2(\mu\text{-}O)]$ (**4**). Treatment of $[L_{OEt}MF_3]$ (M = Ti and Zr) with 3 equiv of $[ReO_3(OSiMe_3)]$ afforded $[L_{OEt}Ti(ReO_4)_3]$ (**5**) and $[L_{OEt}Zr(ReO_4)_3(H_2O)]$ (**6**), respectively. Treatment of $[L_{OEt}MF_3]$ with 2 equiv of $[ReO_3(OSiMe_3)]$ afforded $[L_{OEt}Ti(ReO_4)_2F]$ (**7**) and $[\{L_{OEt}Zr(ReO_4)_2\}_2(\mu\text{-}F)_2]$ (**8**), respectively, which reacted with Me_3SiOTf to give $[L_{OEt}M(ReO_4)_2(OTf)]$ (M = Ti (**9**), Zr (**10**)). Hydrolysis of $[L_{OEt}Zr(OTf)_3]$ (**11**) with $Na_2WO_4\cdot xH_2O$ and wet CH_2Cl_2 afforded the hydroxo-bridged complexes $[\{L_{OEt}Zr(H_2O)\}_3(\mu\text{-}OH)_3(\mu_3\text{-}O)][OTf]_4$ (**12**) and $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2][OTf]_4$ (**13**), respectively. The solid-state structures of **1**–**3**, **6**, and **11**–**13** have been established by X-ray crystallography. The $L_{OEt}Ti^{IV}$ complexes can catalyze oxidation of methyl *p*-tolyl sulfide with *tert*-butyl hydroperoxide. The bimetallic Ti/ Re complexes **5** and **9** were found to be more active catalysts for the sulfide oxidation than other Ti(IV) complexes presumably because Re alkylperoxo species are involved as the reactive intermediates.

Introduction

Metal ions in oxygen-rich coordination environments have attracted much attention because of their relevance to metal oxo surfaces in heterogeneous catalysts.[1] In this connection, a lot of efforts have been made to synthesize mononuclear and polynuclear metal complexes containing O-donor ligands as molecular models for metal oxide catalysts. Of importance are oxygen-rich titanium complexes due to the significance of titanium-containing silicates and zeolites in catalytic organic oxidation. Thus, Ti(IV) complexes with polydentate oxygen ligands such as calixarenes,[2–5] trialkoxides,[6] and bis(phenolates)[7] have been synthesized and their catalytic activities have been studied extensively.

We have a long-standing interest in the organometallic chemistry of Kläui's tripodal ligand L_{OEt}^- ($[CpCo\{P(O)(OEt)_2\}_3]^-$, where Cp = η^5-C_5H_5) (Chart 1) that has been

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* To whom correspondence should be addressed. E-mail: chleung@ust.hk.

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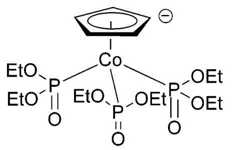
Chart 1



$L_{OEt}^{\ominus}$

recognized as an oxygen analogue of cyclopentadienyl.[8] Although L_{OEt}^- can form stable complexes with a range of metal ions,[8] the coordination chemistry of its group 4 complexes has not been well developed[9,10] presumably due to its strong tendency to form saturated $[(L_{OEt})_2M]^{2+}$ (M = Ti, Zr) complexes. Previously, we have demonstrated that titanyl and zirconyl species in aqueous media could be stabilized by L_{OEt}^-. Depending upon reaction conditions, interactions of titanyl and zirconyl compounds with NaL_{OEt} afforded a variety of oxo- and hydroxo-bridged $L_{OEt}M^{IV}$ clusters including $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{4+}$ and $[(L_{OEt}Ti)_2(\mu\text{-}O)_2(\mu\text{-}SO_4)]$.[11−13]

To prepare new oxygen-rich Ti(IV) cluster compounds, we set out to investigate the self-assembly of L_{OEt}Ti(IV) species with other oxyanions in aqueous media. Of special interest are Ti(IV) phosphato complexes given the various applications of Ti(IV) phosphate solid-state materials.[14] Compared with the phosphonato analogues,[15] molecular Ti(IV) phosphato complexes are relatively less explored.[16,17] Ti(IV) phosphato complexes are generally synthesized from Ti(IV) alkoxides and phosphoric acid or phosphates in nonaqueous media. Previously, we synthesized $[L_{OEt}Zr(\mu_3\text{-}PO_4)]_4$ and $[(L_{OEt}Zr)_3(\mu\text{-}OH)_3(\mu_3\text{-}O)(\mu_3\text{-}PO_4)]^+$ by reactions of $L_{OEt}Zr^{IV}$ complexes with $(4\text{-}NO_2C_6H_4)_2P(O)(OH)$ and Na_3PO_4, respectively,[12] demonstrating the usefulness of aqueous self-assembly in the synthesis of $L_{OEt}Zr^{IV}$ cluster compounds. We here describe the reactions of titanyl sulfate with PO_4^{3-}, $P_2O_7^{4-}$, and $Cr_2O_7^{2-}$ in the presence of L_{OEt}^- in aqueous media and the solid-state structures of the resulting phosphato and chromato cluster compounds. Ti(IV) and Zr(IV) perrhenato complexes have also been synthesized from $[L_{OEt}MF_3]$ and $[ReO_3(OSiMe_3)]$ in CH_2Cl_2. Moreover, the hydrolysis of $[L_{OEt}Zr(OTf)_3]$ (OTf = triflato) and the solid-state structures of the resulting Zr(IV) hydroxo complexes are reported.

Experimental Section

General Considerations. Unless otherwise stated, all manipulations were carried out under nitrogen using standard Schlenk techniques. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 282.5, and 121.5 MHz for ^1H, ^{19}F, and ^{31}P, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H), $CF_3C_6H_5$ (^{19}F), and 85% H_3PO_4 (^{31}P). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Surrey, U.K. The ligand NaL_{OEt},[18] $[L_{OEt}MF_3]$,[11] and $[L_{OEt}M(OTf)_3]$[13] (M = Ti, Zr) were prepared as described elsewhere. A stock solution of titanyl sulfate in sulfuric acid ([Ti] = 0.13 M) was prepared by diluting 1 mL of commercial titanyl sulfate solution (15% in dilute sulfuric acid, Aldrich) with 9 mL of water.

$[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}PO_4)]$ (1). To the stock solution of titanyl sulfate (1 mL, 0.0921 mmol Ti) in water (7 mL) was added NaL_{OEt} (46 mg, 0.082 mmol) in water (3 mL); the mixture was stirred at room temperature in air for 10 min, and then Na_3PO_4 (67 mg, 0.41 mmol) in water (1 mL) was added. The resulting solution was stirred overnight and extracted with CH_2Cl_2. The extract was dried over anhydrous Na_2SO_4 and evaporated to dryness. Recrystallization from acetone/hexane afforded yellow crystals that were suitable for X-ray analysis (yield: 43 mg, 28%). ^1H NMR ($CDCl_3$): δ 1.26 (overlapping t, 54H, CH_3), 4.00−4.26 (m, 36H, CH_2), 5.00 (s, 15H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 116.9 (pseudo d, L_{OEt}), 124.0 (pseudo t, L_{OEt}), 5.36 (s, PO_4). Anal. Calcd for $C_{51}H_{105}Co_3O_{34}P_{10}Ti_3\cdot 4CH_2Cl_2\cdot 4H_2O$: C, 28.7; H, 5.3. Found: C, 28.6; H, 5.4.

$[(L_{OEt}Ti)_2(\mu\text{-}O)_2(\mu\text{-}P_2O_7)]$ (2). This compound was prepared similarly as for **1** from 1 mL of the titanyl sulfate stock solution, NaL_{OEt} (47 mg, 0.084 mmol), and $Na_4P_2O_7\cdot 10H_2O$ (110 mg, 0.25 mmol). Recrystallization from acetone/hexane afforded yellow crystals that were suitable for X-ray analysis (yield: 34 mg, 30%). ^1H NMR (acetone-d_6): δ 1.45 (overlapping t, 36H, CH_3), 4.30−4.48 (m, 24H, CH_2), 5.37 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 119.6 (m, L_{OEt}), 124.9 (m, L_{OEt}), 131.9 (m, L_{OEt}), −9.6 (s, P_2O_7). Anal. Calcd for $C_{34}H_{70}Co_2O_{26}P_8Ti_2\cdot CH_2Cl_2$: C, 28.8; H, 5.0. Found: C, 28.6; H, 4.9.

$[(L_{OEt}Ti)_2(\mu\text{-}CrO_4)_3]$ (3). To 1.1 mL of the titanyl sulfate stock solution (0.1 mmol Ti) in water (7 mL) was added NaL_{OEt} (52 mg, 0.093 mmol) in water (3 mL), and the mixture was stirred at room temperature for 10 min. A solution of $Na_2Cr_2O_7\cdot 2H_2O$ (139 mg, 0.465 mmol) in water (10 mL) was added. The yellow precipitate was collected, washed with water, and air-dried. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals that were suitable for X-ray analysis (yield: 79 mg, 56%). ^1H NMR (acetone-d_6): δ 1.44 (t, J = 7.2 Hz, 36H, CH_3), 4.26−4.31 (m, 24H, CH_2), 5.36 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 123.9 (s). Anal. Calcd

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for $C_{34}H_{70}Co_2Cr_3O_{30}P_6Ti_2\cdot 3CH_2Cl_2$: C, 25.2; H, 4.4. Found: C, 24.9; H, 4.4.

Oxidation of Benzyl Alcohol by 3. A mixture of **3** (50 mg, 0.034 mmol) and benzyl alcohol (50 μL, 0.48 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature under nitrogen for 30 min. The benzaldehyde produced was determined (ca. 3 equiv with respect to **3**) by GLC analysis (HP1 column) using iodobenzene as internal standard. A similar amount of benzaldehyde was obtained when the oxidation was carried out in air or in the presence of terminal oxidants such as iodosobenzene.

$[\{L_{OEt}Ti(ReO_4)_2\}_2(\mu\text{-}O)]$ (4). A mixture of $[n\text{-}Bu_4N][ReO_4]$ (66 mg, 0.134 mmol) and $[L_{OEt}Ti(OTf)_3]$ (46 mg, 0.045 mmol) in CH_2Cl_2 (5 mL) was stirred under nitrogen at room temperature for overnight. The volatiles were pumped off, and the yellow residue was washed with Et_2O and extracted into toluene/CH_2Cl_2 (1:1). Recrystallization from THF/Et_2O afforded yellow blocks. Yield: 22 mg (44%). ^1H NMR ($CDCl_3$): δ 1.03 (t, J = 7.0 Hz, 36H, CH_3), 4.05−4.40 (m, 24H, CH_2), 5.15 (s, 10H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 129.0 (m). Anal. Calcd for $C_{34}H_{70}Co_2O_{27}P_6Re_2Ti_2\cdot 1.6[n\text{-}Bu_4N][ReO_4]$: C, 29.0; H, 5.2; N, 0.9. Found: C, 29.0; H, 5.2; N, 0.9.

$[L_{OEt}Ti(ReO_4)_3]$ (5). To $[ReO_3(OSiMe_3)]$ (110 mg, 0.34 mmol) in CH_2Cl_2 (1 mL) was added $[L_{OEt}TiF_3]$ (54 mg, 0.085 mmol) in CH_2Cl_2 (3 mL). After the solution was stirred at room temperature for 2 h, the color changed from yellow to yellow-orange. The volatiles were removed under reduced pressure, and the resultant yellow-orange residue was washed with Et_2O and extracted into CH_2Cl_2. Recrystallization from CH_2Cl_2/hexane afforded orange needles. Yield: 98 mg (86%). ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.0 Hz, 18H, CH_3,), 4.26 (m, 12H, CH_2), 5.27 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 130.5 (s). Anal. Calcd for $C_{17}H_{35}CoO_{21}P_3TiRe_3$: C, 15.3; H, 2.7 Found: C, 15.0; H, 2.6.

$[L_{OEt}Zr(ReO_4)_3(H_2O)]$ (6). This compound was prepared similarly as for **5** using $[L_{OEt}ZrF_3]$ in place of $[L_{OEt}TiF_3]$. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded yellow blocks that were suitable for X-ray analysis. Yield: 59%. ^1H NMR ($CDCl_3$): δ 1.38 (t, J = 7.0 Hz, 18H, CH_3), 4.22 (m, 12H, CH_2), 5.23 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 124.0 (s). Anal. Calcd for $C_{17}H_{37}CoO_{22}P_3Re_3Zr$: C, 14.8; H, 2.6. Found: C, 15.0, H, 2.7.

$[L_{OEt}Ti(ReO_4)_2F]$ (7). To $[L_{OEt}TiF_3]$ (145 mg, 0.23 mmol) in CH_2Cl_2 (4 mL) was added $[ReO_3(OSiMe_3)]$ (152 mg, 0.47 mmol) in CH_2Cl_2 (4 mL), and the mixture was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the residue was washed with Et_2O and dried in vacuo. Yield: 205 mg (83%). ^1H NMR ($CDCl_3$): δ 1.39 (t, J = 6.9 Hz, 18H, CH_3,) 4.26 (b, 12H, OCH_2), 5.22 (s, 5H, Cp). ^{19}F NMR ($CDCl_3$): δ 273.4. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 123.8 (m), 130.7 (m). Anal. Calcd for $C_{17}H_{35}CoFO_{17}P_3Re_2Ti$: C, 18.5; H, 3.2. Found: C, 18.4; H, 3.1.

$[\{L_{OEt}Zr(ReO_4)_2\}_2(\mu\text{-}F)_2]$ (8). This compound was prepared similarly as for **7** using $[L_{OEt}ZrF_3]$ in place of $[L_{OEt}TiF_3]$. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded yellow crystals. Yield: 79%. ^1H NMR ($CDCl_3$): δ 1.37 (t, J = 6.9 Hz, 18H, CH_3), 4.25 (m, 12H, OCH_2), 5.20 (s, 5H, Cp). ^{19}F NMR ($CDCl_3$): δ 9.2. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 124.7 (s). Anal. Calcd for $C_{34}H_{70}Co_2F_2O_{34}P_6Re_4Zr_2$: C, 17.9; H, 3.2. Found: C, 17.8; H, 3.2.

$[L_{OEt}Ti(ReO_4)_2(OTf)]$ (M = Ti (9), Zr (10)). To a solution of **7** (143 mg, 0.13 mmol) in CH_2Cl_2 (3 mL) was added Me_3SiOTf (36 μL, 0.20 mmol). After the solution was stirred at room temperature for 1 h, the volatiles were removed under reduced pressure, and the orange residue was washed with Et_2O. Recrystallization from CH_2Cl_2/E_2O/hexane afforded orange needles. Yield: 135 mg (77%). ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.0 Hz, 18H, CH_3,), 4.28 (m, 12H, CH_2), 5.27, (s, 5H, Cp). ^{19}F NMR ($CDCl_3$): δ −77.6. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 130.5 (s). Anal. Calcd for $C_{18}H_{35}CoF_3O_{20}P_3Re_2STi\cdot 3CH_2Cl_2$: C, 17.0; H, 2.8. Found: C, 16.7; H, 2.8. The Zr analogue **10** was prepared similarly from **8** and Me_3SiOTf. Yield: 80%. ^1H NMR ($CDCl_3$): δ 1.39 (t, J = 6.9 Hz, 18H, CH_3), 4.24 (m, 12H, CH_2), 5.25 (s, 5H, Cp). ^{19}F NMR ($CDCl_3$): δ −77.7. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 126.4 (m). Anal. Calcd for $C_{18}H_{35}CoF_3O_{20}P_3Re_2SZr$: C, 16.9; H, 2.7. Found: C, 16.5; H, 2.9.

$[\{L_{OEt}Zr(H_2O)(\mu\text{-}OH)\}_3(\mu_3\text{-}O)][OTf]_4$ (12). To a solution of $[L_{OEt}Zr(OTf)_3]$ (**11**) (116 mg, 0.11 mmol) in THF (6 mL) was added $Na_2WO_4\cdot xH_2O$ (48 mg), and the mixture was stirred under nitrogen at room temperature overnight. The volatiles were removed under reduced pressure, and the residue was washed with hexane and Et_2O. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded yellow block crystals that were suitable for X-ray analysis. Yield: 56 mg (55%). ^1H NMR ($CDCl_3$): δ 1.31 (t, J = 6.9 Hz, 54H, CH_3), 4.00−4.19 (m, 36H, CH_2), 5.17 (s, 15H, Cp), 7.96 (s, 3H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 121.8 (s). Anal. Calcd for $C_{54}H_{114}Co_3F_{12}O_{46}P_9S_4Zr_3\cdot CH_2Cl_2\cdot 6H_2O$: C, 24.1; H, 4.6. Found: C, 23.9, H, 4.5.

$[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2][OTf]_4$ (13). A solution of **11** (65 mg, 0.061 mmol) in CH_2Cl_2 (3 mL) was left to stand in air overnight. The solvent was removed by a rotavapor and the residue washed with Et_2O. Recrystallization from CH_2Cl_2/Et_2O/hexane afforded yellow crystals that were suitable for X-ray diffraction study. Yield: 32 mg (54%). ^1H NMR ($CDCl_3$): δ 1.32 (t, 36H, CH_3), 4.20 (m, 24H, CH_2), 4.81 (br s, 8H, H_2O), 5.18, (s, 10H, Cp), 9.00 (s, 2H, OH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 122.6 (s). Anal. Calcd for $C_{38}H_{88}Co_2F_{12}O_{40}P_6S_4Zr_2$: C, 22.5; H, 4.4. Found: C, 22.6, H, 4.4.

Catalytic Oxidation of Methyl *p*-Tolyl Sulfide. Typically, a mixture of methyl *p*-tolyl sulfide (40 μL, 0.3 mmol), *tert*-butyl hydroperoxide (0.36 mmol, 70 μL of 5.5M solution in decane, Aldrich), and the Ti catalyst (0.015 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 1.5 h. The organic products formed were determined by GLC analysis (HP1 column) and quantified by an internal standard method (iodobenzene).

X-ray Crystallography. A summary of crystallographic data and experimental details for complexes **1**−**3**, **6**, and **11**−**13** are compiled in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The collected frames were processed with the software SAINT.[19] Structures were solved by the direct methods and refined by full-matrix least squares on F^2 using the SHELXTL software package.[20] The atomic positions of non-hydrogen atoms were refined with anisotropic parameters. In **3**, the C5 atom in the cyclopentadienyl ring and the C33 and C34 atoms in an ethoxy group were found to be disordered and were refined isotropically without hydrogen atoms. In **11**, the phosphorus atoms and some ethoxy groups in one L_{OEt}^- ligand were found to be disordered, and the two sites were refined with occupancies 0.70 and 0.30.

Results and Discussion

Ti(IV) Phosphato Complexes. The syntheses of Ti(IV) phosphato and chromato complexes in aqueous media are summarized in Scheme 1. Treatment of titanyl sulfate in dilute sulfuric acid with 1 equiv of NaL_{OEt} followed by addition of Na_3PO_4 led to precipitation of a yellow solid.

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(19) *BrukerSMART and SAINT+*, version 6.02a; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998.

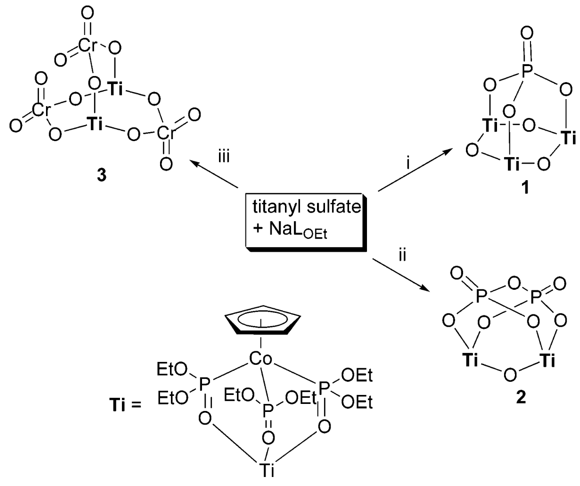
(20) Sheldrick, G. M. *SHELXTL-Plus V5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, WI, 1997.

Table 1. Crystallgraphic Data and Experimental Details for $[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}PO_4)]\cdot 8H_2O$ (**1**·8H$_2$O), $[(L_{OEt}Ti)_2(\mu\text{-}O)(\mu\text{-}P_2O_7)]\cdot 5H_2O$ (**2**·5H$_2$O), $[(L_{OEt}Ti)_3(\mu\text{-}CrO_4)_3]$ (**3**), $[L_{OEt}Zr(ReO_4)_3(H_2O)]\cdot THF$ (**6**·THF), $[L_{OEt}Zr(OTf)_3]$ (**11**), $[\{L_{OEt}Zr(H_2O)\}_3(\mu\text{-}OH)_3(\mu_3\text{-}O)][OTf]_4$ (**12**), and $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2][OTf]_4$ (**13**)

param	**1**·8H$_2$O	**2**·5H$_2$O	**3**	**6**·THF	**11**	**12**	**13**
formula	$C_{51}H_{121}Co_3O_{42}P_{10}Ti_3$	$C_{34}H_{80}Co_2O_{31}P_8Ti_2$	$C_{34}H_{70}Co_2Cr_3O_{30}P_6Ti_2$	$C_{21}H_{45}CoO_{23}P_3Re_3Zr$	$C_{20}H_{35}CoF_9O_{18}P_3S_3Zr$	$C_{55}H_{114}Co_3F_{12}O_{46}P_9S_4Zr_3$	$C_{38}H_{84}Co_2F_{12}O_{38}P_6S_4Zr_2$
fw	2144.76	1446.40	1514.38	1467.23	1073.72	2596.88	1991.41
a, Å	21.2171(6)	17.615(4)	18.4085(9)	18.456(2)	11.932(1)	16.164(1)	12.794(2)
b, Å	21.2171(6)	18.853(4)	18.6209(9)	26.907(3)	17.462(2)	20.997(2)	14.583(2)
c, Å	21.2171(6)	19.594(4)	16.9501(9)	15.971(2)	19.380(2)	30.440(2)	22.458(3)
α, deg	90	90	90	90	90	90	90
β, deg	90	114.652(5)	90	93.818(2)	95.349(2)	90	98.823(2)
γ, deg	90	90	90	90	90	90	90
V, Å^3	9551.2(5)	5914(2)	5810.2(5)	7913.9(17)	4020.6(6)	10331.3(13)	4140.4(9)
Z	12	4	4	8	4	4	2
cryst system	cubic	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	$P2_13$	$C2/c$	$Pca2_1$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/n$
ρ_{calc}, g cm^{-3}	1.119	1.624	1.731	2.460	1.774	1.670	1.597
T, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
μ, mm^{-1}	0.752	1.114	1.607	10.010	1.774	1.087	0.961
F(000)	3360	3000	3096	5520	2160	5280	2024
no. of reflcns	58 658	13 764	33 804	39 333	23 690	61 351	21 587
no. of indep reflcns	7774	4864	11 491	13 695	6259	18 052	5188
R$_{int}$	0.0481	0.0981	0.0462	0.0983	0.0568	0.0423	0.0487
R1, wR2 ($I > 2.0\sigma(I)$)	0.0454, 0.1218	0.0613, 0.1173	0.0390, 0.0843	0.0498, 0.0881	0.0467, 0.1061	0.0539, 0.1358	0.0479, 0.1124
R1, wR2 (all data)	0.0503, 0.1265	0.1165, 0.1373	0.0497, 0.0889	0.1028, 0.0985	0.0890, 0.1289	0.0729, 0.1457	0.0829, 0.1227
goodness of fit^a	1.092	1.003	1.015	1.025	1.018	1.055	1.010

[a] $\text{GoF} = [(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

Scheme 1. Preparations of $L_{OEt}Ti^{IV}$ Phosphato and Chromato Complexes in Aqueous Media[a]



[a] Reagents: (i) Na_3PO_4; (ii) $Na_4P_2O_7$; (iii) $K_2Cr_2O_7$.

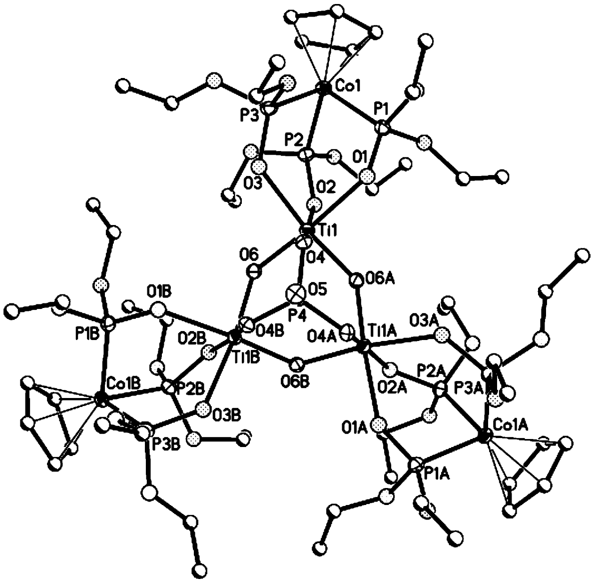


Figure 1. Molecular structure of $[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}PO_4)]$ (**1**). Selected bond lengths (Å) and angles (deg): Ti(1)−O(L_{OEt}) 2.043(2)−2.117(2), Ti(1)−O(4) 1.913(2), Ti(1)−O(6) 1.798(3), Ti(1)−O(6A) 1.860(3), P(4)−O(5) 1.509(4), P(4)−O(4) 1.561(2); Ti(1)−O(6)−Ti(1A) 132.7(1), P(4)−O(4)−Ti(1) 127.0(2), O(6)−Ti(1)−O(4) 94.54(1), O(6)−Ti(1)−O(6A) 94.9(2).

Upon recrystallization from CH_2Cl_2/hexane, yellow single crystals characterized as the trinuclear phosphato compound $[(L_{OEt}Ti)_3(\mu_3\text{-}PO_4)(\mu\text{-}O)_3]$ (**1**) were isolated. It may be noted that reaction of zirconyl nitrate with NaL$_{OEt}$ in dilute nitric acid afforded trinuclear $[(L_{OEt}Zr)_3(\mu\text{-}OH)_3(\mu_3\text{-}PO_4)(\mu_3\text{-}O)]$-$[NO_3]$ that contains a $Zr_3(OH)_3$ core capped by a μ_3-PO_4^{3-} and a μ_3-O^{2-} ligand whereas $[(L_{OEt}Zr)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_2]^{4+}$ reacted with $(4\text{-}NO_2C_6H_4O)_2P(O)(H)$ to give the cubane cluster $[L_{OEt}Zr(\mu_3\text{-}PO_4)]_4$.[12] The $^{31}P\{^1H\}$ NMR spectrum of **1** displays a weak signal at δ 4.06 ppm assignable to the PO_4^{3-} ligand along with broad signals at δ 116.9 and 124.0 ppm due to the L_{OEt}^- ligands. The solid-state structure of **1** (Figure 1) consists of a Ti_3O_3 core that has been found in $[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}SO_4)]^+$.[13] The Ti_3O_3 core is roughly planar with the average Ti−O−Ti angle of 132.7°. The Ti−O−Ti bridges are slightly unsymmetrical with the

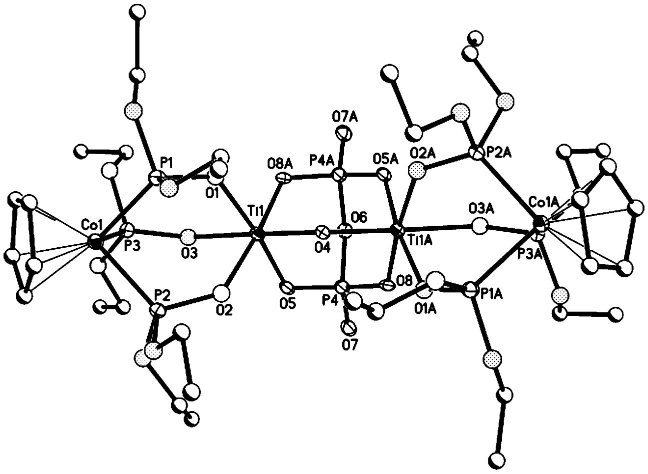


Figure 2. Molecular structure of $[(L_{OEt}Ti)_2(\mu\text{-}O)(\mu\text{-}P_2O_7)]$ (**2**). Selected bond lengths (Å) and angles (deg): Ti(1)−O(L_{OEt}) 1.980(4)−2.042(4), Ti−O(4) 1.824(2), Ti(1)−O(P) 1.927(4)−1.934(4), P(5)−O(6) 1.615(3), P(5)−O(7) 1.471(5), P−O(Ti) 1.539(4)−1.548(4); Ti(1)−O(4)−Ti(1A) 136.6(3), P(5)−O(6)−P(5A) 122.6(4), O(5)−Ti−O(8A) 89.5(2), O−P(5)−O′.

Ti(1)−O(6) and Ti(1)−O(6A) distances of 1.798(3) and 1.860(3) Å, respectively, which are comparable to those in $[(L_{OEt}Ti)_3(\mu\text{-}O)_3(\mu_3\text{-}SO_4)]^+$.[13] The Ti−O($L_{OEt}$) distances 2.043(2)−2.117(2) Å are typical for Ti(IV)−L_{OEt} complexes.[13] The average Ti−O(PO_4) distance of 1.913 Å are shorter than those found in $[(Cp^*Ti)_2(P_4O_{10})]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (1.963(3)−1.995(2) Å).[16f] The terminal P═O bond (1.509(4) Å) is apparently shorter than the P−O(Ti) bonds (1.561(2) Å).

Similarly, dinuclear $[(L_{OEt}Ti)_2(\mu\text{-}P_2O_7)(\mu\text{-}O)]$ (**2**) was prepared from titanyl sulfate, NaL_{OEt}, and $Na_4P_2O_7$ in sulfuric acid. The $^{31}P\{^1H\}$ NMR spectrum of **2** displays a singlet at δ −9.6 ppm due to the $[P_2O_7]^{4-}$ ligand along with the L_{OEt}^- resonances at δ 119.6, 124.9, and 131.9 ppm. The solid-state structure of **2** is shown in Figure 2. The bridged tetradentate pyrophosphato group binds to the two Ti atoms in a μ:η^2,η^2 fashion. The Ti−O(oxo) distance (1.824(2) Å) and Ti−O−Ti angle (136.6(3)°) are similar to those in $[(L_{OEt}Ti)_2(\mu\text{-}O)(\mu\text{-}SO_4)_2]$.[13] The terminal P═O bonds (1.471(5) Å) are shorter than the P−O(P) and P−O(Ti) bonds (1.544(4) and 1.615(3) Å, respectively). The average Ti−O(P_2O_7) distance of 1.927(4) Å is similar to that in **1**. Treatment of titanyl sulfate with NaL_{OEt} in the presence of $Na_5P_3O_{10}$ failed to give any isolable products.

Ti(IV) Chromato Complex. Encouraged by the successes in the syntheses of Ti(IV) phosphato complexes, we studied the reaction of $L_{OEt}Ti^{IV}$ species with other oxyanions. Treatment of titanyl sulfate in dilute sulfuric acid with NaL_{OEt} followed by addition of $K_2Cr_2O_7$ led to precipitation of the Ti(IV)/Cr(VI) complex $[(L_{OEt}Ti)_2(\mu\text{-}CrO_4)_3]$ (**3**). Despite the acidic reaction condition (pH < 3), which should favor the formation of dichromate complexes, **3** was isolated exclusively. It may noted that a related Ti(IV) chromato complex $[\{Cp^*{}_3Ti_3Cl_2(\mu\text{-}CrO_4)\}(\mu\text{-}O)_3]$ containing a Ti_3O_3 core has been prepared previously from $[(Cp^*TiCl)_3(\mu\text{-}O)_3]$ and Ag_2CrO_4.[21] The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a single resonance at δ 123.9 ppm for the L_{OEt}^- ligands. The optical spectrum of **3** in CH_2Cl_2 shows a shoulder at ca. 335 nm, which was assigned as the ligand-to-metal charge transfer (LMCT) [pπ(O)−dπ(Cr)] transition. By comparison, the LMCT band for uncomplexed $[CrO_4]^{2-}$ was observed at 363 nm. The IR Cr═O stretching mode could not be assigned due to overlap with intense P═O bands of the L_{OEt}^- ligands.

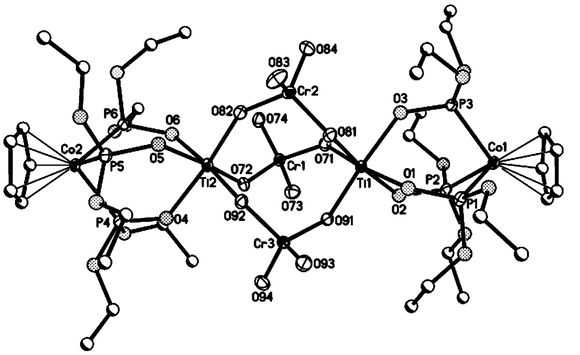


Figure 3. Molecular structure of $[(L_{OEt}Ti)_2(\mu\text{-}CrO_4)_3]$ (**3**). Selected bond lengths (Å) and angles (deg): Ti(1)−O(L_{OEt}) 1.995(3)−2.032(3), Ti−O(Cr) 1.850(3)−1.921(3), Cr−O_t 1.585(3)−1.597(3), Cr−O(Ti) 1.700(3)−1.740(3); O−Cr−O 107.4(2)−111.7(1), Ti−O−Cr 131.6(2)−141.4(2).

Complex **3** is capable of oxidizing alcohols but inactive toward hydrocarbons. For example, treatment of benzyl alcohol with **3** afforded ca. 3 equiv of benzaldehyde. The green, paramagnetic inorganic product, possibly a Ti(IV)/Cr(IV) or Ti(IV)/Cr(III) species, has not been characterized yet. Similar amounts of benzaldehyde was obtained when the oxidation of benzyl alcohol was carried out in air or in the presence of terminal oxidant such iodosobenzene, indicating that **3** can only act as a stoichiometric 6-electron oxidant for alcohols.

The solid-state structure of **3** (Figure 3) consists of two L_{OEt}Ti(IV) fragments bridged by three μ-CrO_4^{2-}-*O,O′* ligands. A similar $M_2(CrO_4)_3$ core has been found for a related Fe(III)/Cr(VI) complex $[(LFe)_2(\mu\text{-}CrO_4)_3]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclonane).[22] The Ti−O(CrO_4) distances are in the range 1.850(3)−1.921(3) Å. The geometry around Cr is approximately tetrahedral with the O−Cr−O′ angle in the range of 107.4(2)−111.7(1)°. The Cr−O(Ti) (1.700(3)−1.740(3) Å) and the terminal Cr═O distances (1.585(3)−1.597(3) Å) are similar to those in $[(LFe)_2(\mu\text{-}CrO_4)_3]$.

Ti(IV) and Zr(IV) Perrhenato Complexes. Attempts to synthesize Ti(IV) perrhenato complexes by reacting titanyl sulfate with NaL_{OEt} in dilute H_2SO_4 in the presence of $K[ReO_4]$ were unsuccessful. Treatment of $[L_{OEt}Ti(OTf)_3]$[13] with 3 equiv of $[n\text{-}Bu_4N][ReO_4]$ afforded the oxo-bridged dimer $[\{L_{OEt}Ti(ReO_4)_2\}_2(\mu\text{-}O)]$ (**4**). A recrystallized sample of **4** was found to be contaminated with some unreacted $[n\text{-}Bu_4N][ReO_4]$, which has yet to be separated. It seems likely that moisture-sensitive $[L_{OEt}Ti(OTf)_3]$ hydrolyzed by the moisture of the solvent/reagent rapidly before it reacted with $[ReO_4]^-$. Previously, we have synthesized $[L_{OEt}Zr(OTf)_3]$ by the reaction of $[L_{OEt}ZrF_3]$ with Me_3SiOTf.[13] The driving force for this reaction is the formation of strong Si−F

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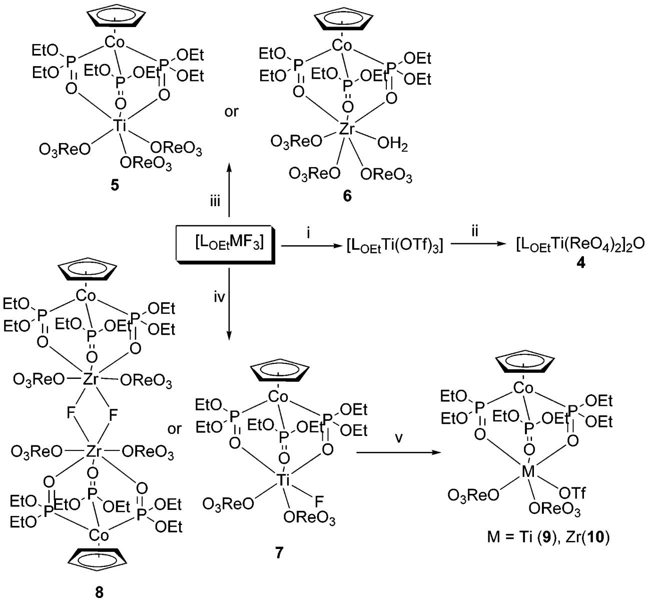
(21) Abarca, A.; Martín, A.; Mena, M.; Raithby, P. R. *Inorg. Chem.* **1995**, *34*, 5437.

(22) Chaudhuri, P.; Winter, M.; Wieghardt, K.; Gehring, S.; Haase, W.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1988**, *27*, 1564.

Scheme 2. Preparations of Ti(IV) and Zr(IV) Perrhenato Complexes[a]



[a] Reagents: (i) 3 equiv of Me_3SiOTf; (ii) $[n\text{-}Bu_4N][ReO_4]$; (iii) 3 equiv of $[ReO_3(OSiMe_3)]$; (iv) 2 equiv of $[ReO_3(OSiMe_3)]$; (v) Me_3SiOTf.

and Zr−O bonds. Thus, to synthesize Ti and Zr perrhenato complexes, we attempted the reaction between $[L_{OEt}MF_3]$ and $[ReO_3(OSiMe_3)]$ (Scheme 2). Treatment of $[L_{OEt}MF_3]$ with 3 equiv of $[ReO_3(OSiMe_3)]$ afforded the tris(perrhenato) complexes $[L_{OEt}Ti(ReO_4)_3]$ (**5**) and $[L_{OEt}Zr(ReO_4)_3(H_2O)]$ (**7**) in good yield. The presence of the aqua ligand in **7** has been confirmed by an X-ray diffraction study (see later section). Similarly, the bis(perrhenato) complexes $[L_{OEt}Ti(ReO_4)_2F]$ (**7**) and $[L_{OEt}Zr(ReO_4)_2]_2(\mu\text{-}F)_2$ (**8**) were prepared from $[L_{OEt}MF_3]$ and 2 equiv of $[ReO_3(OSiMe_3)]$. The presence of fluoride ligand in **7** and **8** has been confirmed by ^{19}F NMR spectroscopy (δ_F 273.3 and 9.2 ppm, respectively). The dinuclear structure of **8** has been established by a preliminary X-ray diffraction study.[23] Once again, in contrast to the Ti analogue, 7-coordination was found for the Zr complex **8**. Treatment of **7** and **8** with Me_3SiOTf afforded the perrhenato triflato complexes $[L_{OEt}M(ReO_4)_2(OTf)]$ (M = Ti (**9**), Zr(**10**)). The ^{19}F NMR spectra of **9** and **10** show the absence of fluoride signals and the appearance of the triflate resonance at ca. δ −77.7 ppm, indicating that the fluoride ligands in the two complexes have been replaced by triflate.

The solid-state structure of **6** has been established by X-ray crystallography. The unit cell of **6** consists of two independent molecules, the structure of one of which is shown in Figure 4. Although heterometallic perrhenato complexes are well documented,[24] to our knowledge, **6** is the first example of Zr(IV) perrhenato complex. The $Zr-O(L_{OEt})$ (2.090(9)−2.161(8) Å) and $Zr-OH_2$ (2.196(8) and 2.197(8) Å) distances are comparable to those in $[\{L_{OEt}Zr(SO_4)(H_2O)\}_2(\mu\text{-}SO_4)]$.[12] The $Zr-OReO_3$ distances are in the range 2.088(8)−2.179(8) Å. The Re−O(Zr) distances of 1.746(9)−1.809(8) Å are apparently longer than the terminal Re−O distances (1.663(9)−1.73(1) Å). The geometry around Re is roughly tetrahedral (O−Re−O′ angles of 106.4(4)−112.9(4)°). The Zr−O−Re angles are in the range 137.2(4)−164.9(5)°.

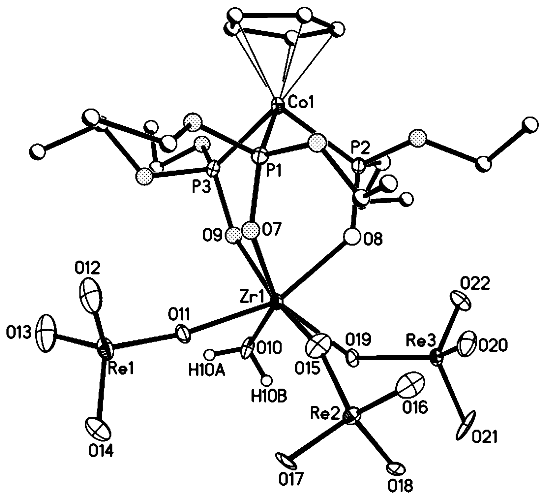
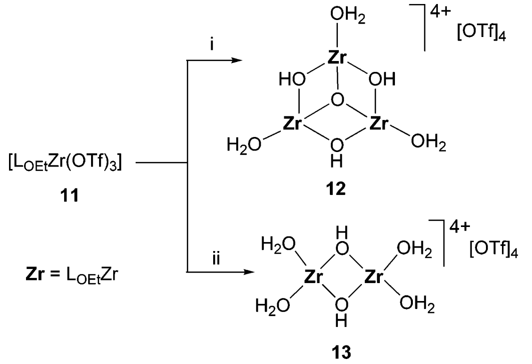


Figure 4. Molecular structure of $[L_{OEt}Zr(ReO_4)_3(H_2O)]$ (**6**). Selected bond lengths (Å) and angles (deg): $Zr-O(L_{OEt})$ 2.090(9)−2.161(8), Zr−O(Re) 2.088(8)−2.179(8), $Zr-OH_2$ 2.196(8) and 2.197(8), Re−O(Zr) 1.746(9)−1.809(8), $Re-O_t$ 1.663(9)−1.73(1); O−Re−O′ 106.4(4)−112.9(4), Ti−O−Re 137.2(4)−164.9(5).

Scheme 3. Hydrolysis of $[L_{OEt}Zr(OTf)_3]$[a]



[a] Reagents: (i) $Na_2WO_4 \cdot xH_2O$; (ii) wet CH_2Cl_2 in air.

Hydrolysis of $[L_{OEt}Zr(OTf)_3]$. Reactions of titanyl sulfate or zirconyl nitrate with NaL_{OEt} in the presence of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ gave yellow solutions. Extraction of the aqueous reaction mixtures into CH_2Cl_2 followed by precipitation with hexanes afforded yellow solids that were found to contain mixtures of $L_{OEt}M(IV)$ species. Treatment of **5** with $[n\text{-}NBu_4]_2[MoO_4]$ afforded a yellow oily material which did not crystallize. Interestingly, reaction of $[L_{OEt}Zr(OTf)_3]$ (**11**) with $Na_2WO_4 \cdot xH_2O$ in THF led to hydrolysis of the complex and isolation of the trinuclear Zr(IV) oxo hydroxo cluster $[\{L_{OEt}Zr(H_2O)\}_3(\mu\text{-}OH)_3(\mu_3\text{-}O)][OTf]_4$ (**12**) in 55% yield (Scheme 3). Although the resonance for the aqua ligands was not observed in the ^1H NMR spectrum, the hydroxo protons in **12** appear as a sharp singlet at δ 7.96 ppm. The outcome of hydrolysis of **11** was found to be dependent upon the source of moisture and experimental conditions. Exposure of a dichloromethane solution of **11** in air resulted in isolation of the dinuclear complex $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2][OTf]_4$ (**13**) in 54% yield. The OH reso-

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(23) A preliminary study showed that **8** is a dinuclear complex containing two bridged fluoride ligands. However, high *R* values were found due to poor quality of the crystal. Crystal data for **8**: monoclinic, $P2_1/c$; $a = 19.33(1)$, $b = 18.03(1)$, $c = 18.92(1)$ Å; $\beta = 93.28(1)°$; $V = 6581(8)$ Å^3; $Z = 4$; refinement converged to R1 = 0.1125 and wR2 = 0.3177 for 8631 reflections with $I > 2.0\sigma(I)$.

(24) Chakravorti, M. C. *Coord. Chem. Rev.* **1990**, *106*, 205.

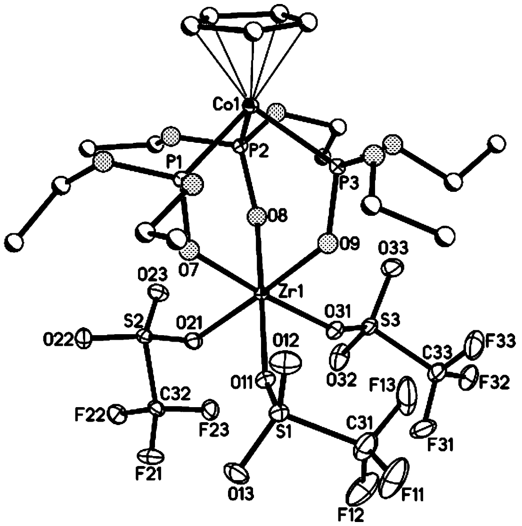

Figure 5. Molecular structure of $[L_{OEt}Zr(OTf)_3]$ (**11**). Selected bond lengths (Å): Zr−O(L_{OEt}) 2.031(3)−2.033(3), Zr−OTf 2.101(3)−2.114(3).

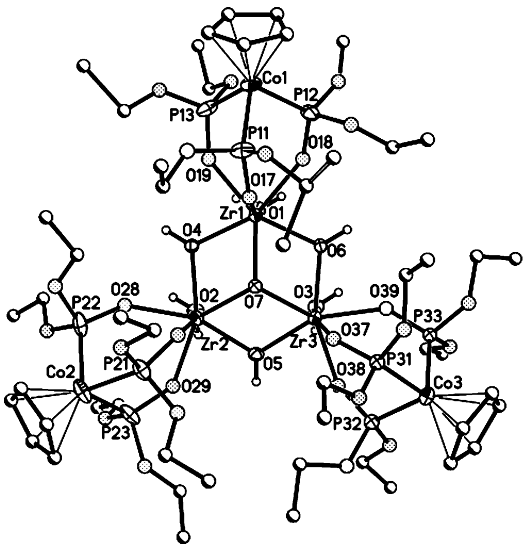

Figure 6. Molecular structure of the tetractaion $[\{L_{OEt}Zr(H_2O)\}_3(\mu_3\text{-}O)(\mu\text{-}OH)_3]^{4+}$ in **12**. Selected bond lengths (Å) and angles (deg): Zr−O(L_{OEt}) 2.035−2.163, Zr−O(7) 2.081(4)−2.111(4), Zr−OH 2.124(4)−2.138(4), Zr−OH_2 2.200(4)−2.215(4); Zr−O−Zr′ 109.5(2)−111.7(2), Zr−OH−Zr′ 108.7(2)−109.5(2).

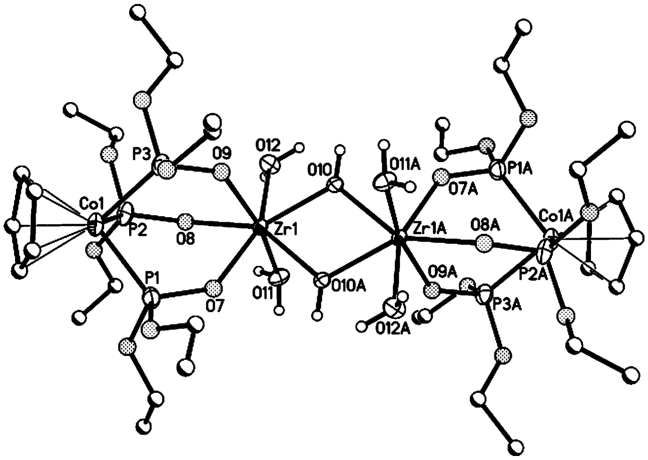

Figure 7. Molecular structure of the tetracation $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2]^{4+}$ in **13**. Selected bond lengths (Å) and angles (deg): Zr−O(L_{OEt}) 2.060(3)−2.136(3), Zr−OH 2.121(2) and 2.136(2), Zr−OH_2 2.161(2) and 2.225(2); Zr−OH−Zr 113.6(1).

nance for **13** was observed at δ 9.00 ppm that is more downfield than that in **12**. While both **12** and **13** are stable in CH_2Cl_2 solutions, they hydrolyze readily in acetone/H_2O to give tetranuclear $[(L_{OEt}Zr)_4(\mu\text{-}OH)_4(\mu_3\text{-}O)_2(H_2O)_2]^{4+}$, which appears to be the most stable form of $L_{OEt}Zr^{IV}$ species in weakly acidic solutions, according to $^{31}P\{^1H\}$ NMR spectroscopy. It may be noted that $[L_{OEt}Zr(NO_3)_3]$ also hydrolyzes in water to give $[\{L_{OEt}Zr\}_4(\mu\text{-}OH)_4(\mu_3\text{-}O)_2(H_2O)_2]^{4+}$.[12]

Complexes **11**−**13** have been characterized by X-ray diffraction studies. The molecular structure of **11** is shown in Figure 5. The geometry around Zr is pseudooctahedral. The Zr−O(L_{OEt}) distances in **11** of 2.031(3)−2.033(3) Å are similar to those in $[\{L_{OEt}Zr(H_2O)(SO_4)\}_2(\mu\text{-}SO_4)]$ (2.076(7)−2.146(7) Å).[13] The Zr−OTf distances (2.101(3)−2.114(3) Å) are comparable to those in $[Cp^*{}_2Zr(OTf)_2]$ (2.146(2) and 2.153(2) Å).[25] The structure of the tetracation $[\{L_{OEt}Zr(H_2O)\}_3(\mu\text{-}OH)_3(\mu_3\text{-}O)]^{4+}$ in **12** containing a $Zr_3(OH)_3$ core capped by a μ_3-oxo group is shown in Figure 6. A similar $Zr_3(O)(OH)_3$ core has been found in the cyclopentadienyl analogue $[(CpZr)_3(\mu_3\text{-}O)(\mu\text{-}OCOPh)_3(OH)_3][PhCO_2]$.[26] The Zr−O and Zr−OH distances in **12** (2.093 and 2.131 Å, respectively) are comparable to those in $[(CpZr)_3(\mu_3\text{-}O)(\mu\text{-}OCOPh)_3(OH)_3][PhCO_2]$ (2.059(4)−2.079(4) and 2.130(5)−2.144(3), respectively).[26] The Zr−OH_2 distances (2.200(4)−2.215(4)Å) are similar to that in **6**. The Zr−O−Zr angles at the central oxygen (109.5(2)−111.7(2)°) are close to the tetrahedral angle.

The molecular structure of the tetracation $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-}OH)_2]^{4+}$ in **13** is shown in Figure 7. It may note that a related cyclopentadienyl compound $[\{CpZr(H_2O)_3\}_6(\mu\text{-}OH)_2][OTf]_4$ has been prepared from $[Cp_2ZrCl_2]$ with Ag(OTf) followed by addition of water.[27] The Zr−OH (2.121(2) and 2.136(2) Å) and Zr−OH_2 (2.161(2) and 2.225(2) Å) distances and the Zr−OH−Zr angle (113.6(1)°) in **12** are similar to those in $[\{CpZr(H_2O)_3\}_2(\mu\text{-}OH)_2][OTf]_4$ (2.160(2) and 2.075(3), 2.164(3) and 2.168(2) Å, and 110.8(1)°, respectively).[27]

Catalytic Oxidation of Methyl *p*-Tolyl Sulfide. The use of oxide-based materials for catalytic oxidation of organic substrates has received considerable attention recently.[28] In this connection, we have examined the catalytic activity of the L_{OEt}Ti(IV) and -Zr(IV) complexes in organic oxidations. Unfortunately, neither the Ti(IV) nor Zr(IV) complexes are active catalysts for oxidation of olefins. They are, however, capable of catalyzing oxidation of sulfides with *t*-BuOOH. The results of catalytic oxidation of methyl *p*-tolyl sulfide with *t*-BuOOH are summarized in Table 2. Similar to other

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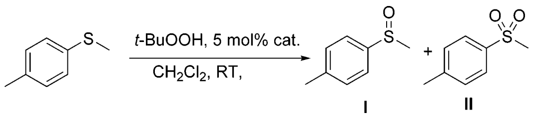
Table 2. Catalytic Oxidation of Methyl *p*-Tolyl Sulfide with *t*-BuOOH[a]



catal	time/h	% yield I	% yield II
$[L_{OEt}Ti(OTf)_3]$[b]	24	43	3
$[(L_{OEt}Ti)_2(\mu\text{-O})(\mu\text{-SO}_4)_2]$[b]	24	67	4
$[(L_{OEt}Ti)_2(\mu\text{-CrO}_4)_3)]$ (**3**)	5	41	3
$[L_{OEt}Ti(ReO_4)_3]$ (**5**)	0.25	88	5
$[L_{OEt}Ti(ReO_4)_2(OTf)]$ (**9**)	0.5	84	5
$[L_{OEt}Zr(ReO_4)_3(H_2O)]$ (**6**)	0.5	56	29
$[L_{OEt}Zr(ReO_4)_2(OTf)]$ (**10**)	1.5	50	34
[*n*-$Bu_4N][ReO_4]$	3	2	trace

[a] Conditions: methyl *p*-tolyl sulfide (0.3 mmol); *t*-BuOOH (0.36 mmol); catalyst (0.015 mmol); CH_2Cl_2 (2 mL). [b] 10 mol % (0.03 mmol) catalyst was used.

Ti-based catalysts,[6c] $L_{OEt}Ti(IV)$ complexes can catalyze oxidation of methyl *p*-tolyl sulfide with *t*-BuOOH to give the sulfoxide **I** selectively. Only small amounts of sulfone **II** were detected. The perrhenato complexes **5** and **9** were found to be considerably more active catalysts than other $L_{OEt}Ti(IV)$ complexes, suggesting that different and more reactive intermediates, presumably Re alkylperoxo species,[29] are involved in the Ti/Re catalyst system. An attempt to isolate this Re alkylperoxo species by treatment of **5** with a stoichiometric amount of *t*-BuOOH failed. [*n*-$NBu_4][ReO_4]$ is not an active catalyst for the sulfide oxidation. It seems likely that, in the bimetallic Ti/Re catalysts, the Ti(IV) center acts as a Lewis acid activating the Re *tert*-butylperoxo moiety that undergoes oxo transfer to the sulfide.[29a] Similarly, the Zr(IV) perrhenato complexes **6** and **10** can catalyze the sulfide oxidation. However, for the Zr/Re system, significant amounts of sulfone **II** were produced. Thus, it appears that for the M/Re bimetallic catalysts the $L_{OEt}M(IV)$ moiety has an influence on the reactivity/selectivity of the Re alkyperoxo active intermediates.

Conclusions

In summary, we have studied the reactions of titanyl sulfate with PO_4^{3-}, $P_2O_7^{4-}$, and $Cr_2O_7^{2-}$ in the presence of L_{OEt}^- in aqueous media. The reactions with PO_4^{3-} and $P_2O_7^{4-}$ gave the corresponding oxo-bridged phosphato complexes whereas that with $Cr_2O_7^{2-}$ afforded a dinuclear complex containing a $Ti_2(CrO_4)$ core. The perrhenato complexes $[L_{OEt}Ti(ReO_4)_3]$ and $[L_{OEt}Zr(ReO_4)_3(H_2O)]$ have been synthesized from $[L_{OEt}MF_3]$ and $[ReO_3(OSiMe_3)]$ in CH_2Cl_2. The outcome of hydrolysis of $[L_{OEt}Zr(OTf)_3]$ was found to be dependent upon experimental conditions. Hydrolysis of $[L_{OEt}Zr(OTf)_3]$ with $Na_2WO_4{\cdot}xH_2O$ gave trinuclear $[\{L_{OEt}Zr(H_2O)\}_3(\mu_3\text{-O})(\mu\text{-OH})_3]^{4+}$, whereas recrystallization of $[L_{OEt}Zr(OTf)_3]$ from CH_2Cl_2 in air led to isolation of dinuclear $[\{L_{OEt}Zr(H_2O)_2\}_2(\mu\text{-OH})_2]^{4+}$. $L_{OEt}Ti(IV)$ complexes are capable of catalyzing oxidation of methyl *p*-tolyl sulfide with *tert*-butyl hydroperoxide. The bimetallic Ti/Re complexes were found to be more active catalysts than other $L_{OEt}Ti(IV)$ complexes presumably because Re alkylperoxo, instead of Ti alkylperoxo, intermediates are involved in the catalytic cycle.

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Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for complexes **1**−**3**, **6**, and **11**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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