

Note

Titanium(IV) terminal hydroxo complexes containing chelating bis(phosphine oxide) ligands

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Abstract

Treatment of $[L_{OEt}Ti(OTf)_3]$ ($L_{OEt}^- = [CpCo\{P(O)(OEt)_2\}_3]^-$, $OTf^- =$ triflate) with *S*-binapO₂ (binap = 2,2'-bis(diphenylphosphinoyl)-1,1'-binaphthyl) afforded the terminal hydroxo complex $[L_{OEt}Ti(S\text{-binapO}_2)(OH)](OTf)_2$ (**1**). Treatment of $[L_{OEt}Ti(OTf)_3]$ with K(tpip) (tpip⁻ = $[N(Ph_2PO)_2]^-$) afforded $[L_{OEt}Ti(tpip)(OTf)](OTf)$ (**2**) that reacted with CsOH to give $[L_{OEt}Ti(tpip)(OH)](OTf)$ (**3**). The structures of **1** and **2** have been determined.

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1. Introduction

Metal complexes in oxygen-rich coordination environments are of interest due to their relevance to oxide-based heterogeneous catalysts and supports. We have a long-standing interest in group 4 compounds containing Kläui's tripodal ligand $[CpCo\{P(O)(OEt)_2\}_3]^-$ [**1**] (designated as L_{OEt}^- , Scheme 1), which may serve as models of metal oxo surfaces and metal ions in aqueous media. Previously, we have synthesized $L_{OEt}Ti(IV)$ compounds containing oxygen-donor ligands such as catecholate [**2**], sulfate [**3**], phosphate, and chromate [**4**]. As our continuing effort to explore the catalytic chemistry of Ti complexes in oxygen-rich ligand environments, we sought to synthesize $L_{OEt}Ti(IV)$ complexes with chelating phosphine oxide ligands. Of particular interest is the chiral phosphine oxide binapO₂ (binapO₂ = 2,2'-bis(diphenylphosphinoyl)-1,1'-binaphthyl) that are expected to have high affinity for hard metal ions. While binap [**5**] and its monoxide binapO [**6**] are versatile ligands for metal-catalyzed asymmetric organic reactions, the coordination chemistry of binapO₂ has not

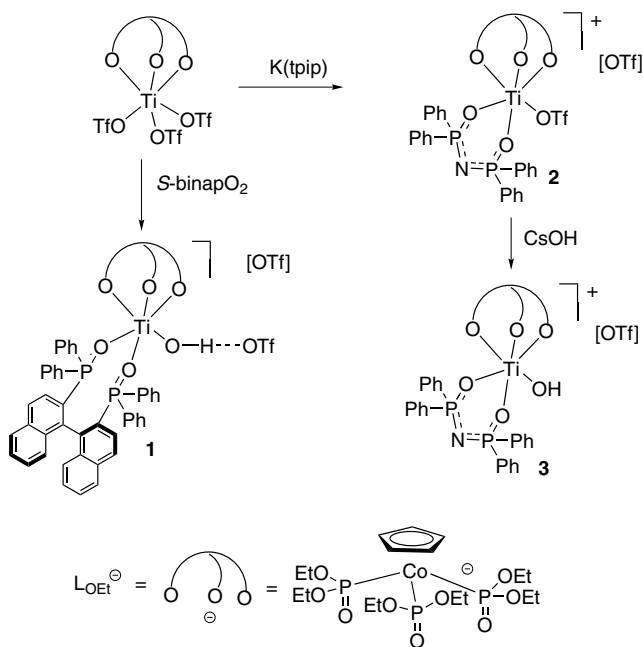
been well explored. Metal-free asymmetric organocatalysis based on binapO₂ has been reported recently [**7**]. In this paper, we describe the synthesis and crystal structure of a $L_{OEt}Ti(IV)$ terminal hydroxo complex containing optically active *S*-binapO₂. In addition, the synthesis of $L_{OEt}Ti(IV)$ complexes with tetraphenylimidodiphosphinate (tpip⁻) will be reported.

2. Experimental

2.1. General

All manipulations were carried out under nitrogen by standard Schlenk techniques. Solvents were purified, distilled, and degassed prior to use. NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300, 282.5, and 121.5 MHz for ¹H, ¹⁹F, and ³¹P, respectively. Chemical shifts (δ, ppm) were reported with reference to SiMe₄ (¹H), CF₃C₆H₅ (¹⁹F), and 85% H₃PO₄ (³¹P). Elemental analyses were performed by Medac Ltd., Surrey, UK. (*S*)-(-)-2,2'-bis(diphenylphosphinoyl)-1,1'-binaphthyl (*S*-binapO₂) was prepared by oxidation (*S*)-(-)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (Aldrich Ltd.) with 30% H₂O₂ and recrystallized from CH₂Cl₂-

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Et₂O. The ligand K(tpip) (tpip = [N(Ph₂PO)₂]⁻) [8] and [L_{OEt}Ti(OTf)₃] (OTf = triflate) [3] were synthesized as described elsewhere.

2.2. [L_{OEt}Ti{(S)-binapO₂}(OH)][OTf]₂ (1)

To a solution of [L_{OEt}Ti(OTf)₃] (170 mg, 0.17 mmol) in CH₂Cl₂ (8 cm³) was added *S*-binapO₂ (110 mg, 0.17 mmol) in CH₂Cl₂ (10 cm³) at 0 °C, and the reaction mixture was stirred at room temperature overnight. The solvent was pumped off and the residue was washed with hexane and Et₂O. Recrystallization from THF–hexane afforded yellow crystals which were suitable to X-ray diffraction analysis. Yield: 248 mg (94%). Anal. Calc. for C₆₃H₆₈O₁₈S₂P₅F₆TiCo · 1/2Et₂O: C, 49.1; H, 4.6. Found: C, 49.4; H, 4.6%. ¹H NMR (CDCl₃): δ 0.78 (t, *J* = 7.1 Hz, 3H, CH₃), 1.15–1.38 (overlapping t, 15H, CH₃), 3.44–3.62 (m, 2H, CH₂), 3.92–4.19 (m, 7H, CH₂), 4.25–4.41 (m, 3H, CH₂), 5.17 (s, 5H, Cp), 6.46 (d, *J* = 4.4 Hz, 2H), 6.67–7.15 (m, 10H), 7.34–8.13 (m, 20H). ³¹P {¹H} NMR (CDCl₃): δ 44.3 (s, binapO₂), 116.4 (pseudo t, *J* = 145 Hz, L_{OEt}), 127.6 (pseudo d, *J* = 74 Hz, L_{OEt}). ¹⁹F {¹H} NMR (CDCl₃): δ -78.6 (s). MS (FAB): *m/z* 1254 (M⁺-OTf).

2.3. [L_{OEt}Ti(tpip)(OTf)][OTf] (2)

To a solution of [L_{OEt}Ti(OTf)₃] (194 mg, 0.19 mmol) in THF (8 cm³) was added K(tpip) (88 mg, 0.19 mmol) in THF (30 ml), and the mixture was stirred overnight. The solvent was pumped off and the residue washed with hexane and Et₂O. Recrystallization from CH₂Cl₂–Et₂O–hexane afforded yellow crystals which were suitable to X-ray diffraction analysis. Yield: 238 mg (97%). Anal. Calc. for C₄₃H₅₅O₁₇S₂P₅F₆NTiCo · 1/4Et₂O: C, 40.1; H, 4.4; N,

1.1. Found: C, 40.4, H, 4.4, N, 1.1%. ¹H NMR (CDCl₃): δ = 0.89 (t, *J* = 6.9 Hz, 6H, CH₃), 1.32–1.40 (overlapping t, 12H, CH₃), 3.21–3.29 (m, 2H, CH₂), 3.45–4.53 (m, 2H, CH₂), 4.12–4.23 (m, 4H, CH₂), 4.29–4.41 (m, 4H, CH₂), 5.33 (s, 5H, Cp), 7.28–7.36 (m, 5H), 7.40–7.47 (m, 2H), 7.49–7.57 (m, 4H), 7.59–7.69 (m, 5H), 7.83–7.90 (m, 4H). ³¹P {¹H} NMR (CDCl₃): δ 34.5 (s, tpip), 130.9 (s, L_{OEt}). ¹⁹F {¹H} NMR (CDCl₃): δ -78.2 (s), -78.6 (s).

2.4. [L_{OEt}Ti(tpip)(OH)][OTf]₂ (3)

A mixture solution of **2** (100 mg, 0.077 mmol) and CsOH (13 mg, 0.086 mmol) in THF (5 cm³) was stirred at room temperature overnight. The solvent was pumped off and the yellow solid washed with hexane and Et₂O. Recrystallization from CH₂Cl₂–Et₂O–hexane afforded yellow needles. Yield: 75 mg (83%). Anal. Calc. for C₄₂H₅₆O₁₅S-P₅F₃NTiCo: C, 43.3; H, 4.8; N, 1.2. Found: C, 43.2; H, 5.1; N, 1.0%. ¹H NMR (CDCl₃): δ 0.72 (t, *J* = 7.1 Hz, 6H, CH₃), 1.26 (t, *J* = 7.1 Hz, 6H, CH₃), 1.39 (t, *J* = 7.1 Hz, 6H, CH₃), 3.10–3.13 (m, 2H, CH₂), 3.23–3.28 (m, 2H, CH₂), 4.01–4.10 (m, 2H, CH₂), 4.11–4.15 (m, 2H), 4.33–4.37 (m, 4H), 5.04 (s, 5H, Cp), 7.18–7.26 (m, 6H), 7.42–7.49 (m, 6H), 7.58–7.66 (m, 4H), 7.88–7.95 (m, 4H). ³¹P {¹H} NMR (CDCl₃): δ 29.5 (s, tpip), 114.7 (pseudo t, *J* = 115 Hz, L_{OEt}), 125.1 (pseudo d, *J* = 72 Hz, L_{OEt}). ¹⁹F {¹H} NMR (CDCl₃): δ -78.6 (s). MS (FAB): *m/z* 1015 (M⁺-OTf).

2.5. X-ray crystallography

Crystallographic data and experimental details for **1** and **2** are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å). The collected frames were processed with the software SAINT. Structures were solved by the direct methods and refined by full-matrix least-squares on *F*² using the SHELXTL software package [9]. In **3**, the Cp ring of the L_{OEt}⁻ ligand was found to be rotationally disordered. The disordered ethoxy carbon atom C(16) and the triflate fluorine atoms F(12), F(13), F(21), and F(22) were split into two sites with occupancy of 0.5 each whereas the occupancies for the two sites for the disordered triflate oxygen atoms O(22) and O(23) are 0.55 and 0.45, respectively. Selected bond lengths and angles for complexes **1** and **2** are listed in Tables 2 and 3, respectively.

3. Results and discussion

3.1. Ti(IV) hydroxo complex with *S*-binapO₂

Treatment of [L_{OEt}Ti(OTf)₃] with *S*-binapO₂ in CH₂Cl₂ afforded the Ti(IV) terminal hydroxo complex [L_{OEt}Ti(*S*-binapO₂)(OH)](OTf)₂ (**1**) (Scheme 1). The hydroxo group in **1** was apparently derived from the moisture in *S*-binapO₂ that was prepared by oxidation of *S*-binap with

Table 1
Crystallographic data and experimental details for **1** and **2**

Compound	1	2
Empirical formula	C ₆₃ H ₆₈ O ₁₈ S ₂ P ₅ F ₆ TiCo	C ₄₃ H ₅₅ F ₆ NO ₁₇ P ₅ S ₂ TiCo
Formula weight	1552.97	1297.68
Crystal system	Monoclinic	Monoclinic
<i>a</i> (Å)	11.200(1)	17.304(14)
<i>b</i> (Å)	12.474(1)	16.667(13)
<i>c</i> (Å)	24.017(2)	20.295(17)
α (°)	90	90
β (°)	93.538(1)	90.065(16)
γ (°)	90	90
<i>V</i> (Å ³)	3348.8(5)	5853(8)
Space group	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	2	4
<i>D</i> _{calc} (g cm ⁻³)	1.540	1.473
Temperature (K)	100(2)	250(2)
<i>F</i> (000)	1600	2664
μ (Mo K α) (mm ⁻¹)	0.636	0.710
Total reflections	17900	40610
Independent reflections	10010	10183
<i>R</i> _{int}	0.0302	0.0274
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0386, 0.0870	0.0594, 0.1645
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0491, 0.0908	0.0776, 0.1784
Goodness-of-fit	1.003	1.009
Flack parameter	-0.009(13)	

Table 2
Selected bond lengths and angles for **1**

Bond length (Å)			
Ti(2)–O(7)	2.071(3)	Ti(2)–O(10)	1.758(3)
Ti(2)–O(8)	1.952(2)	Ti(2)–O(11)	1.956(2)
Ti(2)–O(9)	1.964(3)	Ti(2)–O(12)	1.969(3)
Bond angle (°)			
O(10)–Ti(2)–O(8)	92.7(1)	O(11)–Ti(2)–O(12)	87.0(1)
O(10)–Ti(2)–O(11)	94.9(1)	O(9)–Ti(2)–O(12)	171.1(1)
O(8)–Ti(2)–O(11)	172.0(1)	O(10)–Ti(2)–O(7)	176.5(1)
O(10)–Ti(2)–O(9)	93.0(1)	O(8)–Ti(2)–O(7)	86.0(1)
O(8)–Ti(2)–O(9)	89.8(1)	O(11)–Ti(2)–O(7)	86.7(1)
O(11)–Ti(2)–O(9)	92.6(1)	O(9)–Ti(2)–O(7)	83.9(1)
O(10)–Ti(2)–O(12)	96.0(1)	O(12)–Ti(2)–O(7)	87.2(1)
O(8)–Ti(2)–O(12)	89.5(1)		

Table 3
Selected bond lengths and angles for **2**

Bond length (Å)			
Ti(1)–O(7)	1.922(3)	Ti(1)–O(11)	1.935(3)
Ti(1)–O(8)	1.936(3)	Ti(1)–O(12)	1.912(3)
Ti(1)–O(9)	1.939(3)	Ti(1)–O(13)	2.068(3)
P(11)–O(11)	1.553(2)	P(12)–O(12)	1.562(3)
P(11)–N(1)	1.584(3)	P(12)–N(1)	1.590(3)
Bond angle (°)			
O(7)–Ti(1)–O(8)	89.4(1)	O(11)–Ti(1)–O(9)	178.2(1)
O(7)–Ti(1)–O(9)	88.3(1)	O(11)–Ti(1)–O(13)	89.4(1)
O(7)–Ti(1)–O(11)	90.0(1)	O(12)–Ti(1)–O(7)	178.6(1)
O(7)–Ti(1)–O(13)	89.7(1)	O(12)–Ti(1)–O(8)	92.0(1)
O(8)–Ti(1)–O(9)	88.1(1)	O(12)–Ti(1)–O(9)	91.8(1)
O(8)–Ti(1)–O(13)	177.8(1)	O(12)–Ti(1)–O(11)	89.9(1)
O(9)–Ti(1)–O(13)	89.9(1)	O(12)–Ti(1)–O(13)	88.9(1)
O(11)–Ti(1)–O(8)	92.7(1)		

30% H₂O₂. Complex **1** is air stable in both the solid state and solution. The OH resonance was not observed in the ¹H NMR spectrum, possibly due to the hydrogen bonding between the OH group and the triflate anion. The ³¹P {¹H} NMR spectrum of **1** shows a singlet at δ 44.3 ppm due to the binapO₂ ligand, which is more downfield than that for free binapO₂ (δ 29.52 ppm), along with the L_{OEt}⁻ resonances at δ 116.4 and 127.2 ppm. The ¹⁹F {¹H} NMR spectrum displays a singlet at δ -78.6 ppm, suggesting that both triflate groups are essentially non-coordinating in solution, although the solid-state structure indicates that one triflate is hydrogen-bonded to the OH ligand (vide infra).

Fig. 1 shows the structure of the cation [L_{OEt}Ti(S-binapO₂)(OH)]⁺ along with the hydrogen-bonded triflate; selected bond lengths and angles are listed in Table 2. It should be noted that terminal hydroxo complexes of Ti(IV) are rather rare. Examples of structurally characterized Ti(IV) terminal hydroxo complexes include those supported by cyclopentadienyl [10–12] and a tripodal amino-triphenoxide ligand [13]. The geometry around Ti is pseudo octahedral. The average Ti–O(L_{OEt}) distance of 1.996 Å is typical for L_{OEt}Ti(IV) complexes [2,3]. The Ti–O(binapO₂) distances (1.956(2) and 1.969(3) Å) are similar to that in [TiCl₂(NH)(OPPh₃)₂] (2.023(8) and 2.009(7) Å) [14]. The angle between the two naphthyl rings in the binapO₂ ligand (77.1(4)°) is smaller than that in free binapO₂ (94.17(3)°) [14] as a result of the metal chelation. One triflate is hydrogen-bonded to the OH ligand with the O(10)···O(1S) separation of ca. 2.624(4) Å. The Ti–OH distance of 1.758(3) Å is short compared with that in [LTi(OH)] (LH₃ = tris(2-hydroxy-3,5-di-*tert*-butylbenzyl)-amine) (1.810(2) Å) [13], but is significantly longer than typical terminal Ti=O bonds (e.g., 1.619 Å in oxotitanyl (IV) porphyrin compounds [15]). Thus, **1** is best described as a Ti(IV) hydroxo complex with a hydrogen-bonded triflate rather than an oxo complex hydrogen-bonded with

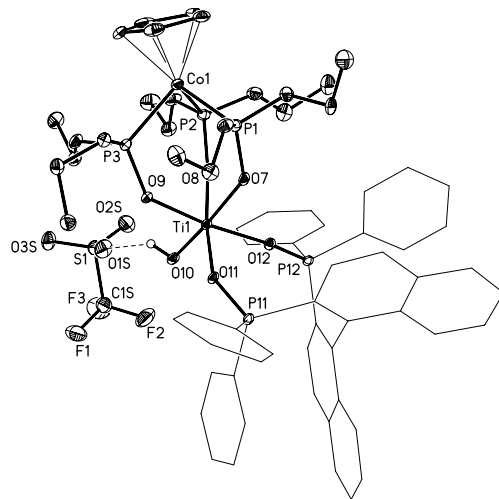


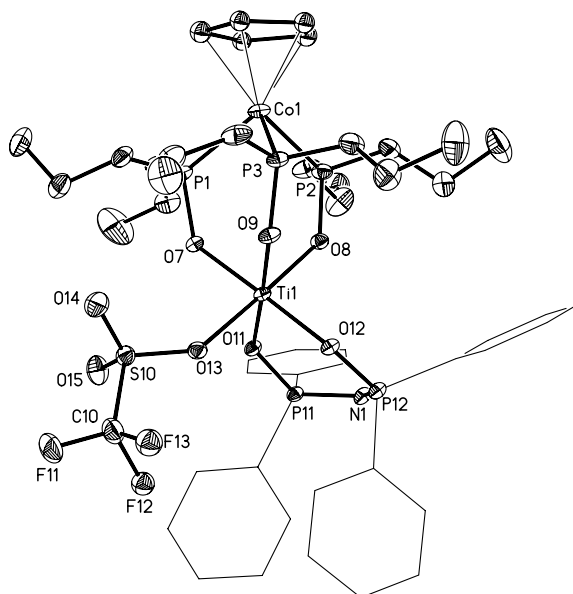
Fig. 1. Perspective view of the dication [L_{OEt}Ti(S-binapO₂)(OH)]²⁺ in **1** showing the hydrogen-bonding between the hydroxo ligand and triflate anion.

HOTf. **1** does not dimerize in solution presumably because of steric effects and/or the 2+ overall charge of the complex.

3.2. Ti(IV) complexes with tpip

Treatment of $[\text{L}_{\text{OEt}}\text{Ti}(\text{OTf})_3]$ with oxides of other diphosphines including dppe and dpmm afforded oily materials that did not crystallize. Thus, we attempted to synthesize mono-cationic $\text{L}_{\text{OEt}}\text{Ti}(\text{IV})$ complexes containing anionic tetraphenylimidodiphosphinate (tpip) ligand, which should crystallize more easily in non-polar solvents. Treatment of $[\text{L}_{\text{OEt}}\text{Ti}(\text{OTf})_3]$ with $\text{K}(\text{tpip})$ led to the formation of the bis-triflate compound $[\text{L}_{\text{OEt}}\text{Ti}(\text{tpip})(\text{OTf})][\text{OTf}]$ (**2**). Compound **2** is remarkably air stable and did not hydrolyze/dimerize even when it was recrystallized in air. Treatment of **2** with CsOH in THF afforded the Ti(IV) hydroxo complex $[\text{L}_{\text{OEt}}\text{Ti}(\text{tpip})(\text{OH})][\text{OTf}]$ (**3**). A preliminary X-ray diffraction study showed that in addition to L_{OEt} and tpip there is an oxygen ligand, either a hydroxo or oxo group, coordinated to Ti(IV) [16]. The formulation of this ligand as hydroxo is consistent with the charge balance. Similar to **1**, the OH resonance for **3** was not observed in the ^1H NMR spectrum, presumably due to the hydrogen bond with the triflate group. The ^{31}P resonant signals for the tpip ligand in **2** and **3** were observed at δ 34.5 and 29.5 ppm, respectively, which are more downfield than that for $\text{K}(\text{tpip})$ (δ 17.62 ppm). The ^{19}F NMR spectrum of **2** shows two singlets at δ -78.2 and -78.6 , which are assigned to the coordinated triflate and the triflate counteranion, respectively, whereas a singlet at δ -78.6 ppm was found for **3**.

Fig. 2 shows the structure of the cation $[\text{L}_{\text{OEt}}\text{Ti}(\text{tpip})(\text{OTf})]^+$ in **2**; selected bond lengths and angles are listed in Table 3. The Ti–O(L_{OEt}) distances (average 1.932 Å)



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