

First Example of a Heptacyclic Tetranuclear, Five- and Six-coordinate Titanium Complex, $[\{(\text{PrO})_2\text{Ti}(\mu^3\text{-O})\text{TiCl}(\text{PrO})((\text{OC}_6\text{H}_4)_2\text{PPh})\}_2]$

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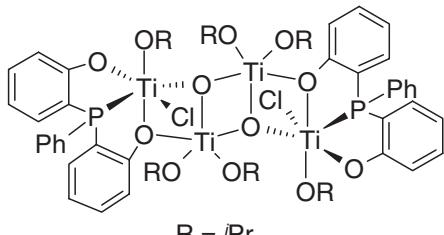
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Novel heptacyclic tetranuclear titanium complex containing penta- and hexacoordinated titanium centers was synthesised by the reaction of bis(*o*-phenol)phenylphosphine with titanium tetrachloride.

The development of new generation titanium complexes containing ansa-metallocenes and ancillary ligands for synthetic applications is emerging as a research area of great importance.¹ However, the cyclopentadienyl groups are known for reducing the electropositive character of titanium complexes thereby diminishing the reactivity. In order to retain electrophilic character and coordinative unsaturation at titanium centers, aryloxides,² or alkoxides³ with bulky substituents are preferred and such complexes can be potential reagents/catalysts in homogeneous catalysis⁴ and also in polymerisation processes.^{5,6} When bulky phenolate ligands are employed instead of metallocenes better results were obtained in polymerisation of olefins. Incorporation of phenolate moieties into tertiary phosphines would result in interesting functionalized phosphines, which can form interesting titanium complexes with rich chemistry and potential catalytic applications. As a part of our interest⁷ and of others⁸ on functionalized phosphines, herein we report a fortuitous tetranuclear titanium complex of bis(*o*-phenol)phenylphosphine, $[\{(\text{PrO})_2\text{Ti}(\mu^3\text{-O})\text{TiCl}(\text{PrO})((\text{OC}_6\text{H}_4)_2\text{PPh})\}_2]$.



R = iPr

The reaction of bis(*o*-phenol)phenylphosphine with TiCl_4 in toluene at -78°C in the presence of *i*PrOH affords a mixture of products as confirmed from the ^{31}P NMR spectroscopic data.⁹ However, the tetranuclear complex, $[\{(\text{PrO})_2\text{Ti}(\mu^3\text{-O})\text{TiCl}(\text{PrO})((\text{OC}_6\text{H}_4)_2\text{PPh})\}_2]$ was isolated from the reaction mixture in low yield by crystallizing it in diethyl ether at room temperature. The ^{31}P NMR spectrum shows a single resonance at -17.9 ppm with a shift of 53 ppm indicating the involvement of phosphorus in the complex formation. The ^1H NMR spectrum of the complex shows only one type of isopropyl groups although, the X-ray structure depicts the presence of both the bridging and the terminal isopropoxy groups. The isopropyl groups exhibit doublets (1.17 ppm) and septets (4.02 ppm) for $-\text{CH}_3$ and $-\text{CH}$ groups, respectively. The mass spectral data support the tetranuclear complex. The structure was established by single crystal X-ray diffraction studies.¹⁰

The perspective view of molecule is shown in Figure 1 with selected bond parameters. The structure reveals the centrosymmetric and dimeric nature of the molecule where the phenolato oxygen and oxo groups bridge the metal centers to result in three four-membered Ti_2O_2 rings. The μ^3 -bridging oxygen present in the compound could be due to the trace amount of atmospheric oxygen present in the system. The interesting feature of these rings is their arrangement in 3-D space, which resembles a flat chair where alternate corners are occupied by titanium and oxygen atoms. The angles $\text{Ti}(1.3)-\text{O}(3.3)-\text{Ti}(2)$ and $\text{O}(3.3)-\text{Ti}(2)-\text{O}(1)$ are $140.89(8)^\circ$ and $150.83(6)^\circ$ indicating that all four-membered rings are bent with respect to each other. The $\text{Ti}-\text{Ti}$ distances of 3.187 and 3.095 Å indicate that there is no true metal-metal bond interaction.¹² The two central titanium atoms are penta-coordinated and the other two metal atoms are hexa-coordinated. The geometry around the $\text{Ti}(2)$ is distorted trigonal bipyramidal where the phenolato oxygen $\text{O}(1)$ and μ^3 -bridged oxo $\text{O}(3)$ occupy the apical positions and the isopropoxy oxygens $\text{O}(5)$, $\text{O}(6)$ and μ^3 -bridged oxo $\text{O}(3)$ are in the equatorial plane. $\text{Ti}(1)$ is in a distorted octahedral geometry where P , phenolato oxygen $\text{O}(1)$ and phenolato oxygen $\text{O}(2)$ are *trans* to μ^3 -bridged oxo $\text{O}(3)$, isopropyl oxygen $\text{O}(4)$, and Cl , respectively. The phenolato groups of bis(*o*-phenol)phenylphosphine are arranged in such a way that the oxygen atoms occupy *cis* positions with $\text{O}(1)-\text{Ti}(1)-\text{O}(2)$ angle of $88.17(6)^\circ$.

There are four types of $\text{Ti}-\text{O}$ bonds present in complex, arising from isopropoxy group, phenolato group (monodentate and bridging), and μ^3 -bridged oxo oxygen. The relatively short $\text{Ti}-\text{O}$ (isopropoxy) bond distances ($1.761(2)$ – $1.780(2)$ Å) and the widening of $(^i\text{Pr})\text{C}-\text{O}-\text{Ti}$ angles ($142.4(2)$ – $148.0(2)^\circ$) are

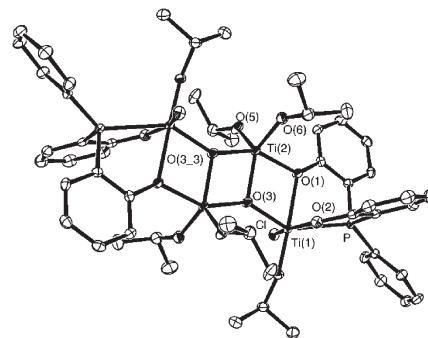


Figure 1. Molecular structure of $[\{(\text{PrO})_2\text{Ti}(\mu^3\text{-O})\text{TiCl}(\text{PrO})((\text{OC}_6\text{H}_4)_2\text{PPh})\}_2]$. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): $\text{Ti}(1)-\text{Cl} = 2.353(1)$; $\text{Ti}(1)-\text{P} = 2.563(1)$; $\text{Ti}(1)-\text{O}(1) = 2.180(1)$; $\text{Ti}(1)-\text{O}(2) = 1.908(2)$; $\text{Ti}(1)-\text{O}(3) = 1.910(1)$; $\text{Ti}(1)-\text{O}(4) = 1.761(2)$; $\text{Ti}(2)-\text{O}(1) = 2.020(1)$; $\text{Ti}(2)-\text{O}(5) = 1.761(2)$; $\text{Ti}(2)-\text{O}(6) = 1.780(2)$; $\text{Ti}(2)-\text{O}(3.3) = 1.957(2)$.

consistent with π donation to the metal center. The sequence of bond order for the oxygen donors towards the titanium center is: $i\text{PrO}^- >$ monodentate phenolate $\approx \mu^3\text{-oxo} >$ bridged phenolate. This order shows that the complex obeys the simple rule "the strong ligand *trans* to weak ligand" formulated for six coordinated titanium complexes.¹³ Thus the weaker phenolate oxygen donors are *trans* to strong chloro and alkoxide ligands.

In summary, we have synthesised a novel heptacyclic tetra-nuclear titanium complex containing four different types of oxygen bindings with formal titanium–phosphorus bonds. The preferential binding of soft π -phosphorus atoms to oxophilic titanium centers is due to the diphenolate substituents on phosphorus centers, which bring the Ti and P atoms in close proximity to establish Ti–P bonds. Presently, we are making efforts to cleave the Ti–P bonds in the presence of platinum metals to make heteronuclear complexes for their possible utility in both homogeneous and heterogeneous catalysis. The cleaving of Ti–P bond also induces coordinative unsaturation at titanium centers.

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- 9 **Preparation of $\{(\text{iPrO})_2\text{Ti}(\mu^3\text{-O})\text{TiCl}(\text{iPrO})((\text{OC}_6\text{H}_4)_2\text{PPh})\}_2$.** To a solution of bis(*o*-phenol)phenylphosphine (0.20 g, 0.60 mmol) in toluene (10 mL), was added dropwise a solution of TiCl_4 (0.60 mmol) also in toluene (5 mL) at -78°C during which time the solution turned yellow. After the completion of addition, the yellow reaction mixture was warmed to room temperature and allowed to stir for 6 h. The reaction mixture was cooled to 0°C and isopropanol (15 mL) was added and stirring was continued for further 2 h. The solvent was evaporated under reduced pressure and the residue obtained was extracted with diethyl ether (3×10 mL) and the solution was stored at room temperature to give yellow crystalline product. The ^{31}P NMR spectra of the insoluble portion indicated the presence of more than one product. Further attempts to isolate the products from the residue have been unsuccessful. Yield: 50% (0.22 g, 0.15 mmol). mp: $> 250^\circ\text{C}$. ^1H NMR (CDCl_3): δ 1.17 (d, CH , $^3J_{\text{HH}} = 6.23$ Hz, 6H), 4.02 (septet, CH_3 , $^3J_{\text{HH}} = 6.23$ Hz, 3H), 7.07–7.51 (br m, *phenyl*, 26H). $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): δ –17.9 (s). MS (FAB, m/z) 1233 (M^+).
- 10 **X-ray structure determination details:** A single crystal of titanium complex ($\text{C}_{54}\text{H}_{68}\text{Cl}_2\text{O}_{12}\text{P}_2\text{Ti}_4$) was mounted in a CryoloopTM with a drop of Paratone oil and placed in the cold nitrogen stream of the KryoflexTM attachment of a Bruker APEX CCD diffractometer. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at $\varphi = 0, 120$ and 240° using the SMART software package [Bruker-AXS SMART Version 5.625: Madison, WI (2000)]. The raw data were reduced to F^2 values using the SAINT+ software [Bruker-AXS SAINT+ Version 6.35A: Madison, WI (2002)] and multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection [(SADABS) G. M. Sheldrick, SADABS Version 2.05: University of Göttingen, Germany (2002)]. The structure was solved by direct methods and refined by full-matrix least squares procedures using the SHELXTL program package [Bruker-AXS SHELXTL Version 6.1: Madison, WI (2000); G. M. Sheldrick, SHELXS97 and SHELXL97: University of Göttingen, Germany (1997)]. Crystallographic data:¹¹ Monoclinic; $P2_1/n$ (No.14); $a = 13.303(1)$ Å; $b = 15.332(2)$ Å; $c = 14.676$ (1) Å; $\beta = 98.043(2)^\circ$; $V = 2964.0(5)$ Å³; $Z = 2$; $D_{\text{calcd}} = 1.382$ g cm^{–3}; Crystal Size (mm): 0.20 × 0.22 × 0.25; $R = 0.0443$; $wR = 0.0983$.
- 11 Crystallographic data reported in this paper are deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 215605. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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