Inorg. Chem. **1994,** *33,* 4813–4814

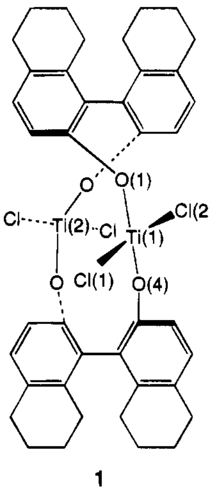
A Torsionally Constrained Diolate Ligand: Novel Complexes of Octahydrobinaphthol with Titanium(IV)

Nancy W. Eilerts,[†] Joseph A. Heppert,[*,†] Michelle L. Kennedy,[‡] and Fusao Takusagawa[†]

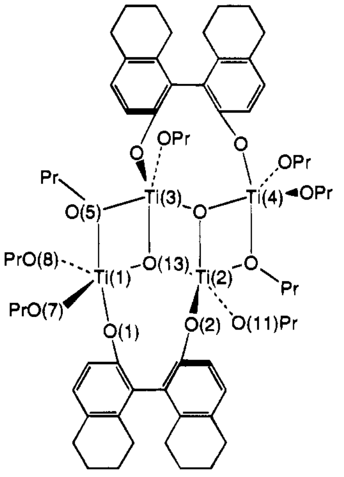
Departments of Chemistry, University of Kansas, Lawrence, Kansas 66045, and Hastings College, Hastings, Nebraska 68901

Received February 15, 1994

Strategies for the synthesis of architecturally defined transition metal complexes often rely on imposing structural constraints through variations in ligand topology. A classical example of this is seen in a comparison of DPPM, in which the methylene linker enforces a bridging bonding mode, with DPPE, in which a more flexible ethylene linker allows the ligand to achieve a classical chelating mode.[1] Diolate ligands, such as binaphtholates and tartrate esters, which are employed as asymmetric auxiliaries, exhibit a diverse and frequently unpredictable range of bonding modes.[2,3] This can further complicate the task of structurally characterizing catalytically significant coordination complexes containing these ligands. To probe the structure and reactivity of titanium (IV) binaphtholate complexes, we undertook reactions involving 5,5′,6,6′,7,7′,8,8′-octahydrobinaphthol ($HYDBINOH_2$) with titanium (IV) alkoxides and chlorides.[4] Structural studies on products obtained with this ligand show two new unusual classes of titanium complexes: a 14-membered dititanamacrocycle, and a tetratitanium di-μ_3-oxo cluster. These structures reveal that the significant torsional restriction of the HYDBINO ligand, like the methylene linker of the DPPM ligand, forces it to adopt exclusively a bridging binding mode.



1



2

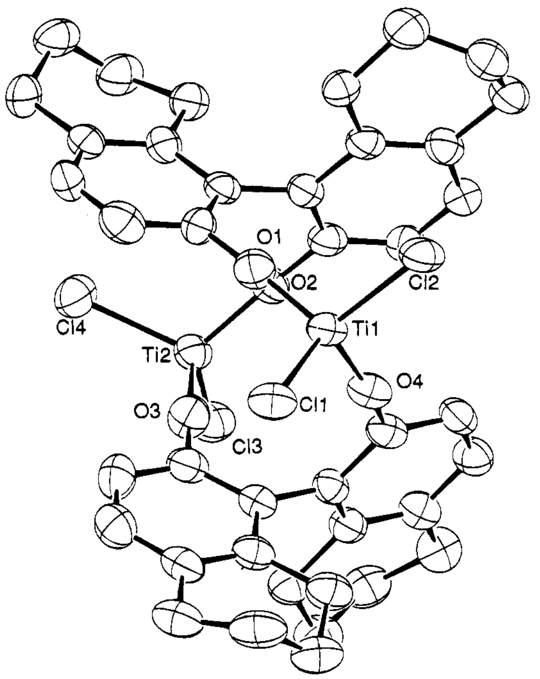


Figure 1. ORTEP representation of the 14-membered macrocycle **1**. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): Ti(1)–O(1) 1.750(5), Ti(1)–O(4) 1.727(5), Ti(2)–O(2) 1.750(5), Ti(2)–O(3), 1.740(5); O(1)–Ti(1)–O(4) 110.7(2), O(2)–Ti(2)–O(3) 112.5(2), Ti(1)–O(1)–C(2) 160.6(5), Ti(2)–O(3)–C(22) 164.0(5), Ti(2)–O(2)–C(12) 172.5(5), Ti(1)–O(4)–C(32) 177.5(5); C(2)–C(1)–C(11)–C(20) −79.2(9), C(22)–C(21)–C(31)–C(40) −83.8(9).

Reactions between the bis(trimethylsilyl) ether of hydrogenated binaphthol, ($HYDBINO(TMS)_2$) and 1 equiv of $TiCl_4$ in toluene solution at −78 °C generate a complex of empirical formula [Ti(HYDBINO)Cl_2] (**1**). The ^{1}H and ^{13}C NMR spectra of **1** reveal only one set of tetrahydronaphtholate resonances over the temperature range of −60 to +30 °C, and are identical regardless of whether optically pure or racemic ligand is employed in the synthesis. A solution molecular weight study revealed that **1** exists as a dimer in solution, and an X-ray crystallographic study confirmed this as the solid-state structure.[5] The core of **1** consists of a 14-membered dimetallamacrocycle with bridging HYDBINO ligands of like chirality, as illustrated in Figure 1. As with other titanium binaphtholate complexes characterized in our laboratory, the homochiral complex is the exclusive product, with no evidence of other diastereoisomers in the NMR spectra of crude reaction mixtures.[2] In comparison, the solid-state structure of (dimethyltartrato)zirconocene dimer forms an open 10-membered dimetallacycle with optically pure ligand, but exhibits a four-membered Zr_2O_2 core with unidentate bridging tartrates of unlike chirality when synthesized with racemic ligand.[3a] Four-coordinate titanium complexes such as **1** are usually formed only when bulky aryloxide ligands prevent the formation of dative bridges.[6] In **1**, the 93° dihedral angle imposed by the three-dimensionality of the hydrogenated rings

---

[†] University of Kansas.

[‡] Hastings College.

(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1988; p 900.

(2) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112.

(3) (a) Erker, G.; Dehnicke, S.; Rump, M.; Krüger, C.; Werner, S.; Nolte, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1349. (b) Pedersen, S. F.; Dewan, J. D.; Eckman, R. R.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 1279.

(4) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930.

(5) X-ray structure analysis of **1** ($Ti_2Cl_4O_4C_{40}H_{40}Cl_{1.5}C_{3.80}$): orange crystals, crystal dimensions 0.500 × 0.300 × 0.300 mm; $M_r = 921.19$; space group *C*2/*c* (No. 15), $a = 22.602(3)$ Å, $b = 21.933(3)$ Å, $c = 13.401(3)$ Å, $\beta = 116.33(8)°$, $V = 8175(9)$ Å^3, $Z = 8$, $\varrho_{calcd} = 1.497$ g cm^{-3}, μ(Cu Kα) = 70.88 cm^{-1}; 5539 symmetry-independent reflections ($2\theta_{max} = 112.6°$), of which 4776 reflections with $I > 0.01\sigma(I)$ were used for the structure solution (direct methods) and refinement (500 variable parameters); non-hydrogen atoms were refined anisotropically.

0020-1669/94/1333-4813$04.50/0

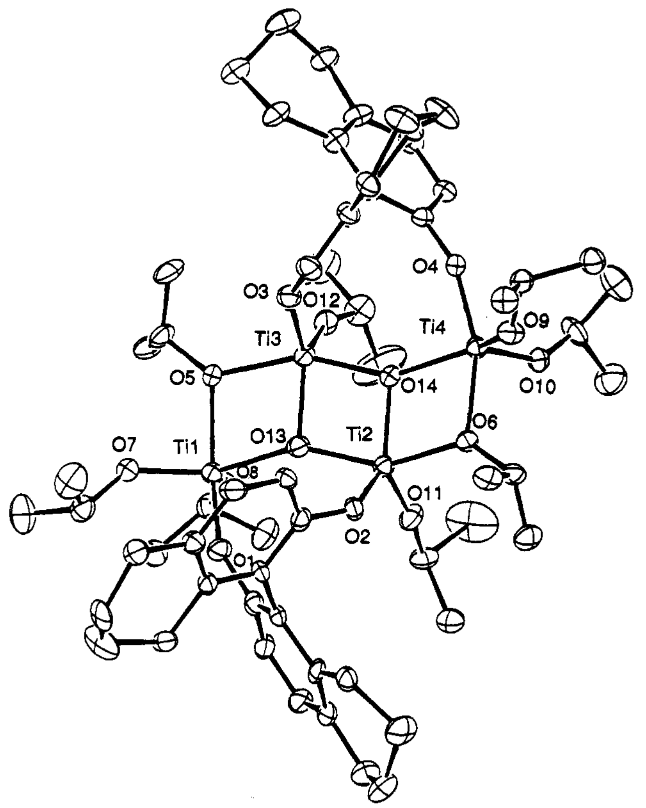


Figure 2. ORTEP representation of the titanium oxo cluster **2**. Selected bond lengths (Å), bond angles (deg), and torsion angles (deg): Ti(1)–O(1) 1.827(7), Ti(1)–O(5) 2.046(7), Ti(1)–O(7) 1.757(9), Ti(1)–O(13) 1.987(8), Ti(2)–O(11) 1.739(9); Ti(1)–O(13)–Ti(2) 149.2(4), Ti(1)–O(13)–Ti(3) 107.0(3), Ti(1)–O(1)–C(2) 157.0(7); C(2)–C(1)–C(11)–C(12) −80(1), C(22)–C(21)–C(31)–C(32) −88(1).

prevents the ligand from adopting a chelating structure. The Ti–O bond lengths are extremely short at an average of 1.742 Å, and the Ti–O–C angle is nearly linear at 168°, indicating an unusually large degree of π-bonding character for a phenoxide ligand.[6]

When a partially hydrated HYDBINOH$_2$ is reacted with Ti(O-*i*-Pr)$_4$, a new class of titanium oxo alkoxide complex is generated. X-ray quality crystals of [Ti$_4$(HYDBINO)$_2$(O-*i*-Pr)$_8$O$_2$] (**2**) were produced from a hexane solution.[7] As illustrated in Figure 2, the complex consists of a Ti$_4$(μ_3-O)$_2$ core having virtual C_2-symmetry, in which both oxo ligands adopt a μ_3 environment. The HYDBINO ligands bridge between adjacent titanium atoms on opposite sides of the tetranuclear core, and exhibit binaphthyl dihedral angles of 80 and 88°. The HYDBINO ligands apparently occupy sufficient space around the periphery of the complex to prevent its aggregation into a higher nuclearity cluster. In contrast to a pair of recently published titanium oxo alkoxide clusters,[8] **2** contains a relatively planar Ti$_4$O$_2$ core, with a Ti$_1$–Ti2–Ti$_3$–Ti$_4$ dihedral angle of 178°. This core structure is reminiscent of that observed in [Cp*MeTaN]$_3$, which contains a planar six-membered cyclic Ta$_3$N$_3$ core,[9] and [(*t*-BuCH$_2$)$_2$TaN]$_5$, which contains a core of five tantalum atoms, three μ_3-N, and two μ_2-N ligands.[10] The Ta–μ_3-N–Ta angles in this core average 95°, resulting in a ladderlike structure. In **2**, the Ti–μ_3-O-Ti angles average 102°, approximating a zigzag arrangement. Each titanium center adopts a distorted square pyramidal geometry, with Ti–O bond distances increasing in the following order: terminal alkoxide < phenoxide < oxo < bridging isopropoxide. It is noteworthy that Ti–O$_{\mathrm{Ph}}$ distances in this molecule average 1.81 Å, more consistent with typical non-π-bonded Ti–O$_{\mathrm{Ar}}$ distances.

To develop a more quantitative comparison between the conformational flexibility of this ligand and binaphthol, calculations using the Sybyl 6.0 Molecular Graphics program were undertaken to determine the effect of the dihedral angle on ligand energy. The free ligands were modeled as dimethyl ethers to eliminate any tendency for hydrogen bonding interactions to distort the dihedral angle. The results of these calculations reveal that the total energy curve of the BINO(Me)$_2$ is shallow and relatively invariant over the range of 60 to 120°. In contrast, the curve for the HYDBINO(Me)$_2$ is much more torsionally restricted. Its minimum energy value, like that for BINO(Me)$_2$, is centered at 90°, but angular deviations beyond ±10° of this value cause precipitious increases in energy. These calculations parallel the range of dihedral angles found for 3,3′-R$_2$BINO ligands in a variety of binding modes. The O···O distances spanned by the two extreme dihedral angles were calculated at 2.78 Å for a 60° dihedral and 3.69 Å for a 90° dihedral angle. Clearly the prefered HYDBINO dihedral angle of 90° enforces an O···O distance incompatible with a chelating binding mode to titanium and more readily adopts a bridging configuration.

Initial experiments with **1** suggest that it acts as a Lewis acid catalyst for a variety of organic transformations. Research is currently underway to determine its utility as an enantioselective catalyst.

Acknowledgment. This research was funded by the National Science Foundation and the University of Kansas EPSCoR program. M.L.K. acknowledges the NSF REU program for financial support. We thank Mr. W. L. Kueper III and Dr. R. G. Carlson for their assistance in the hydrogenation reactions, and Dr. D. G. Vander Velde and Dr. M. D. Morton for helpful discussions.

Supplementary Material Available: Experimental procedures for the synthesis of **1** and **2**, additional ORTEP views of **1**, and tables giving crystal data, experimental details, positional and thermal parameters, and bond distances and angles for **1** and **2** (29 pages). Ordering information is given on any current masthead page.

---

(6) Latesky, S. L.; Keddington, J.; McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 995.

(7) X-ray structure analysis of **2** (Ti$_4$O$_{14}$C$_{64}$H$_{96}$): yellow crystals, crystal dimensions 0.300 × 0.300 × 0.200 mm; M_r = 1281.05; space group $P2_1$ (No. 4), a = 12.776(2) Å, b = 18.254(3) Å, c = 15.252(2) Å, β = 109.16(2)°, V = 3360 (2)° Å^3, Z = 2, ϱ_{calcd} = 1.266 g cm^{-3}, μ(Cu Kα) = 44.01 cm^{-1}; 4608 symmetry-independent reflections ($2\theta_{\max}$ = 112.7°), of which 4189 reflections with $I > 0.01\sigma(I)$ were used for the structure solution (direct methods) and refinement (738 variable parameters); non-hydrogen atoms were refined anisotropically.

(8) Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Park, C. W.; Rosenberg, F. S. *J. Am. Chem. Soc.* **1991**, *113*, 8190.

(9) Banaszak Holl, M. M.; Kersting, M.; Pendley, B. D.; Wolczanski, P. T. *Inorg. Chem.* **1990**, *29*, 1518.

(10) Banaszak Holl, M. M.; Wolczanski, P. T.; Van Duyne, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 7989.

(11) Klebe, J. F.; Finkbeiner, H.; White, D. M. *J. Am. Chem. Soc.* **1966**, *88*, 3390.

(12) Boyle, T. J.; Eilerts, N. W.; Heppert, J. A.; Takusagawa, F. *Organometallics* **1994**, *13*, 2218.