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Synthesis, Structure, and Alcoholysis of η^5-1,3-Bis(trimethylsilyl)cyclopentadienyltitanium *cis*-1,3,5-Cyclohexanetrialkoxide, an Adamantane-Framework Complex of a Polydentate Alkoxide Ligand

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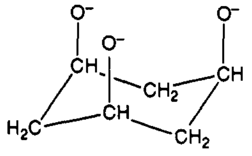
Organotransition metal alkoxide complexes are a subject of continuing interest with respect to structure and reactivity.[1] Transition metal complexes of tridentate and higher-dentate alkoxide ligands have received less attention, with present studies limited to those of aryloxides such as calixarenes,[2] and of the aminoalkoxide-based atranes.[3] Polydentate alkoxide ligands may be effective ancillary ligands for the early transition metals because of their high negative charge, which stabilizes high-oxidation-state, electropositive metal ions. Rigidity and chelating properties of the ligand may also prevent intramolecular C–H bond metallation.[4] We report a cyclopentadienyltitanium complex of *cis*-1,3,5-cyclohexanetrialkoxide (**1**), its structure, and the kinetic stability of **1** in this complex to exchange with monodentate alcohols. To our knowledge, this is the first organometal complex and the first structurally characterized metal complex of the *cis*-1,3,5-cyclohexanetrialkoxide ligand, although some main-group element complexes are known.[5]



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Reaction, under a nitrogen atmosphere, of η^5-[1,3-$(Me_3Si)_2$-C_5H_3]$TiCl_3$[6] with a tetrahydrofuran solution of 1 molar equiv of *cis*-1,3,5-cyclohexanetriol[7] and 3 molar equiv of triethylamine, followed by filtration to remove $Et_3N{\cdot}HCl$, evaporation of solvent under reduced pressure, and crystallization from hexanes affords pale-yellow crystalline **2** in 31% yield.[8]

$$\eta^5\text{-}[1,3\text{-}(Me_3Si)_2C_5H_3]TiCl_3 + (HO)_3C_6H_9 + 3Et_3N \rightarrow \underset{\mathbf{2}}{\eta^5\text{-}[1,3\text{-}(Me_3Si)_2C_5H_3]Ti(O_3C_6H_9)} + 3Et_3N{\cdot}HCl \quad (1)$$

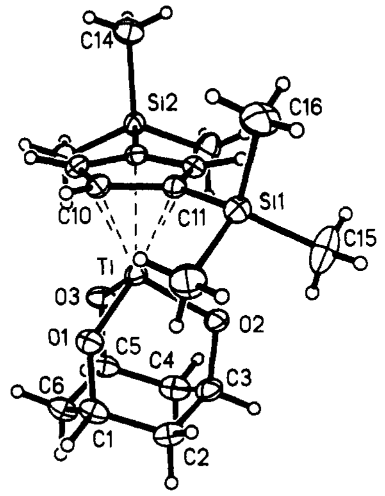

Figure 1. Molecular structure of η^5-[1,3-$(Me_3Si)_2C_5H_3$]$Ti(O_3C_6H_9)$ (**2**), with thermal ellipsoids drawn at the 50% probability level.

Compound **2** is stable to dry air in the solid state for three days and to dry air in hexane solution for 30 s. It may be refluxed in toluene under a nitrogen atmosphere for 2 weeks without noticeable decomposition.

The carbon-13 NMR spectrum of **2** measured from room temperature to −90 °C contains two signals for coordinated trialkoxide, one at δ 74.1, assigned to O*C*H groups, and one at δ 36.1, assigned to *C*H_2 groups. Thus, free rotation of the $(Me_3Si)_2C_5H_3$ ring persists to −90 °C, consistent with the "tied-back" geometry of the trialkoxide, which has a low steric impact on titanium.

The X-ray structure of **2**[9] (Figure 1) shows that the cyclopentadienyltitanium unit is bound via titanium to the trialkoxide. This gives a TiO_3C_6 adamantane-like framework with a slight distortion of the ligand. The average C–C–C–C torsion angle within the cyclohexane ring is 54.5(2)° as compared with the value in cyclohexane of 55.9(4)° (gas-phase electron diffraction).[10]

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(8) Anal. Calcd for $C_{17}H_{30}O_3Si_2Ti$: C, 52.83; H, 7.82. Found: C, 52.84; H, 7.90. IR (Nujol, 400–4000 cm^{-1}): 410 (m), 438 (s), 458 (w), 473 (m), 596 (s), 623 (s), 631 (s), 643 (s), 693 (w), 758 (s), 768 (s), 838 (s), 883 (s), 893 (w, sh), 913 (m), 923 (s), 928 (w, sh), 1003 (m), 1010 (m), 1053 (m), 1098 (s), 1163 (w, br), 1218 (s), 1253 (s), 1290 (w), 1297 (w), 1323 (w), 1338 (w), 1400 (w), 3118 (w) cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 7.05 (t, 1 H, Si–C–C*H*–C–Si); 6.93 (d, 2 H, Si–C–C*H*–C*H*–C–Si); 4.57 (3H, m, OC*H* of $O_3C_6H_9$); 1.29-1.40 (6H, m, C*H*$_2$ of $O_3C_6H_9$); 0.39 (18H, s, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 131.2, 127.1, 124.1 (s, *C*$_5H_3(SiMe_3)_2$); 74.1 (s, O*C*H); 36.1 (s, *C*H_2); −0.2 (s, Si*Me*$_3$); MS (EI, 70 eV): 386 amu (M^+).

(9) Crystal data for **2**: $C_{17}H_{30}O_3Si_2Ti$, $M = 386.5$, monoclinic, space group $P2_1/n$, $a = 6.444(2)$ Å, $b = 28.216(7)$ Å, $c = 11.162(3)$ Å, $\beta = 97.06(2)°$, $V = 2014.2(9)$ Å^3; $Z = 4$; $D_c = 1.27$ g/cm^3; $\mu(\text{Mo } K\alpha)_{calc} = 0.55$ mm^{-1}. A pale-yellow needle of **2** of dimensions 0.18 × 0.24 × 0.52 mm was coated with hydrocarbon oil and attached to a glass fiber with silicone grease. It was mounted on the goniometer of a Siemens R3m/V diffractometer and cooled to 130 K using a locally-modified Enraf-Nonius low-temperature apparatus. A total of 5145 data having $2\theta(\text{Mo } K\alpha) < 55°$ were collected using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.710\,73$ Å) and 1.00° wide ω scans and averaged to 4639 ($R_{int} = 0.014$) independent reflections. The data were corrected empirically for absorption effects. Structure solution was by SHELXTL PLUS (Siemens) direct methods. Full-matrix least-squares refinement of structural parameters (hydrogens as riding atoms) gave $R = 0.0358$ and $R_w = 0.0487$ for 3734 observed reflections with $F > 4\sigma(F)$.

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Table I. Selected Bond Lengths (Å) and Angles (deg) for η^5-[1,3-$(Me_3Si)_2C_5H_3$]Ti$(O_3C_6H_9)$

Ti–O(1)	1.832(2)	Ti–O(2)	1.824(2)
Ti–O(3)	1.833(2)	Ti–C(7)	2.378(2)
Ti–C(8)	2.404(2)	Ti–C(9)	2.385(2)
Ti–C(10)	2.387(2)	Ti–C(11)	2.397(2)
O(1)–C(1)	1.442(3)	O(2)–C(3)	1.450(3)
O(3)–C(5)	1.443(3)	C(7)–C(8)	1.421(3)
C(7)–C(11)	1.416(3)	C(8)–C(9)	1.422(3)
C(9)–C(10)	1.404(3)	C(10)–C(11)	1.427(3)
O(1)–Ti–O(2)	97.1(1)	O(1)–Ti–O(3)	97.0(1)
O(2)–Ti–O(3)	97.6(1)	Ti–O(1)–C(1)	114.9(1)
Ti–O(2)–C(3)	115.1(1)	Ti–O(3)–C(5)	115.0(1)

The difference in torsion angles indicates that the cyclohexane ring is slightly flattened (as opposed to puckered) relative to cyclohexane in the gas phase. This distortion occurs due to a spreading-out of the oxygens, necessary to coordinate titanium.[11] Bond distances and angles, given in Table I, are otherwise as expected. For example, the Ti–O bond distances, which average 1.830(2) Å, and Ti–C bond distances, which average 2.390(2) Å, are similar to values previously observed for organotitanium complexes of mono- and polydentate alkoxides.[2a,3a,b,12]

The degree of kinetic lability of **1** is important to our thesis that it may be an effective ancillary ligand, and this is tested by a series of ^{1}H NMR spectroscopically monitored alcohol exchange reactions, wherein alkoxide complexes are reacted with alcohols. Reactions of **2** with 3 molar equiv of methanol or ethanol in benzene give no exchange after 3 h at room temperature. However, exchange with 3 molar equiv of phenol in benzene occurs immediately, precipitating *cis*-1,3,5-cyclohexanetriol, and when solid **2** is dissolved in ethanol, complete exchange is apparent within 15 min. As a basis for comparison, η^5-[1,3-$(Me_3Si)_2C_5H_3$]Ti$(OCy)_3$ (Cy = cyclohexyl)[13] reacts immediately with three molar equivalents of ethanol in benzene (eq 2).

$$\eta^5\text{-}[1,3\text{-}(Me_3Si)_2C_5H_3]Ti(OCy)_3 + 3EtOH \rightarrow \eta^5\text{-}[1,3\text{-}(Me_3Si)_2C_5H_3]Ti(OCy)_{3-x}(OEt)_x + xCyOH + (3-x)EtOH \quad (2)$$

$$x = 0\text{–}3$$

This confirms that the *cis*-1,3,5-cyclohexanetrialkoxide ligand has a greater kinetic inertness to exchange than the monodentate cyclohexyloxide. The rapid displacement of *cis*-1,3,5-cyclohexanetrialkoxide by excess ethanol or 3 molar equiv of phenol occurs for kinetic reasons. A large amount of ethanol will increase the rate of exchange if concentration of ethanol is a term in the rate law. Rapid exchange by 3 equiv of phenol, but not by 3 equiv of methanol or ethanol, may be explained by the greater acidity of phenol compared to methanol or ethanol (aqueous-phase pK_a (PhOH) ≈ 10 vs pK_a (MeOH) ≈ 16). If protonation of oxygens of **1** is necessary to an exchange mechanism, the rapid phenol reaction is consistent with phenol's greater acidity and therefore with a greater degree of protonation of trialkoxide oxygens and faster exchange.

Acknowledgment. Support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We thank Professor Gary Weisman for a gift of *cis*-1,3,5-cyclohexanetriol.

Supplementary Material Available: Tables giving a structure determination summary, positional parameters, anisotropic thermal parameters, bond lengths, bond angles, and hydrogen atom parameters for **2** (8 pages). Ordering information is given on any current masthead page.

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(11) A Cr^{III} complex of an aqueous chelating agent, 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, $(H_2N)_3C_6H_6(OH)_3$, has the CrO_3C_6 adamantane-framework structure: Schmalle, H. W.; Hegetschweiler, K.; Ghisletta, M. *Acta Crystallogr.* **1991**, *C47*, 2047. This chelating inositol in the structurally-characterized hydrate, $[Cr^{III}(C_6H_{14}N_3O_3)(C_6H_{15}N_3O_3)][Cr^{III}(C_6H_{15}N_3O_3)_2][SO_4]_4\cdot30H_2O$, is reported to show no distortion within the accuracy of the structure determination. The ligand conformation may be influenced by extensive hydrogen bonding from nitrogen and oxygen groups of the ligand to sulfate and water groups, however.

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(13) Prepared similarly to **2** (eq 1). Anal. Calcd for $C_{29}H_{54}O_3Si_2Ti$: C, 62.78; H, 9.81. Found: C, 62.89; H, 9.68. IR (Nujol, 400–4000 cm^{-1}): 465 (w), 505 (w), 540 (w), 625 (m), 690 (s), 750 (m), 785 (w), 835 (s, br), 880 (w), 920 (m), 980 (m), 1005 (w), 1015 (w), 1080 (s, br), 1110 (w, sh), 1245 (s), 1320 (w), 1340 (w) cm^{-1}. ^{1}H NMR (C_6D_6, 25 °C): δ 6.94 (t, 1 H, Si–C–C*H*–C–Si); 6.66 (d, 2 H, Si–C–C*H*–C*H*–C–Si); 4.36 (m, 3*H*, OC*H*), 2.04, 1.71, 1.43, 1.28, 1.15 (5 multiplets, 30H total, CH_2 of cyclohexyl), 0.42 (s, 18 H, Si*Me*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 129.3, 126.6, 122.0 ($C_5H_3(SiMe_3)_2$), 84.4 (O*C*H), 36.9, 26.2, 24.9 (3 × CH_2 of cyclohexyl), 0.3 (Si*Me*$_3$). MS (EI, 70 eV): 554 amu (M^+).