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# Polynuclear Oxo-Bridged Cyclopentadienyl Transition-Metal Complexes. Formation and Structural Characterization of the Titanoxane Tetramer, $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$

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The crystal structure of *cyclo*-tetrakis($\mu$-oxo-chloro(methylcyclopentadienyl)titanium(IV)), $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$, has been determined by X-ray diffraction methods. The compound consists of four $(\eta^5\text{-}C_5H_4CH_3)TiCl$ moieties linked together by four oxo groups to produce a molecular core of $D_{2d}$ symmetry, which contains an eight-membered ring of alternating Ti and O atoms. The tetramer's molecular geometry is constrained by a crystallographic twofold rotation axis which passes through two opposite O atoms. The relatively short Ti–O bonds of 1.8 Å (average) support the presence of partial double-bond character arising from the donation of electron density from filled $p_\pi$ oxygen orbitals to unfilled metal orbitals on the electron-deficient $d^0$ Ti atoms. The $Ti_4$ arrangement possesses a butterfly structure with the dihedral angle between any two $Ti_3$ planes which share a diagonal edge being 154.0°. The methyl substituents of the cyclopentadienyl rings introduce additional inter-ring repulsions, which produce an 8° increase in this dihedral angle and a larger variation in the independent Ti–O–Ti bond angles in comparison to $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$. The tetramer is prepared by the hydrolysis of $(\eta^5\text{-}C_5H_4CH_3)TiCl_3$. The compound crystallizes in a monoclinic space group, $C2/c$, with refined lattice parameters $a = 18.344$ (4) Å, $b = 10.195$ (2) Å, $c = 17.178$ (3) Å, $\beta = 114.68$ (1)°, $V = 2918.7$ (9) Å$^3$, and $Z = 4$. Block-diagonal least-squares refinement of 1700 diffractometry data with $|F_o| > \sigma(|F_o|)$ led to final discrepancy indices of $R(F_o) = 0.036$ and $R_w(F_o) = 0.046$ with $\sigma_1 = 1.66$. A qualitative scheme for the tetramer's formation is discussed.

## Introduction

Metallocene derivatives containing early transition metals such as Ti and Zr have received considerable attention during the past several years because of their ability in some cases to activate several important reactions including the hydrogenation of CO to $CH_4$,[1] reduction of $N_2$ to $N_2H_4$,[2] and the carbonylation of olefins.[3] However, due to their hard-acid behavior, Ti and Zr are susceptible to the formation of strong metal–oxygen bonds. Consequently, the chemistry of this important class of electron deficient complexes is stoichiometric rather than catalytic for the most part. In some instances stable polynuclear oxo-bridged species have been isolated. For example, the aerobic oxidation of $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$[4] and the hydrolysis of $(\eta^5\text{-}C_5H_5)TiCl_3$[5,6] result in the formation of two similar oxo-bridged titanium dimers, $[(\eta^5\text{-}C_5H_5)_2TiCl]_2O$[4] and $[(\eta^5\text{-}C_5H_5)TiCl_2]_2O$,[5,6] respectively. For the latter complex, Giddings suggested its linear Ti–O–Ti bond would be expected to promote chain growth and polymer formation rather than cyclization leading to ring closure. Similar oxo-bridged species of Zr such as $[(\eta^5\text{-}C_5H_5)_2ZrCl]_2O$[7,8] can be prepared by the hydrolysis of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ in the presence of triethylamine. Finally, Caulton and co-workers[1] have identified and structurally characterized from the homogeneous hydrogenation of CO in the presence of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ a chemically inactive titanium hexamer, $(\eta^5\text{-}C_5H_5)_6Ti_6O_8$, consisting of six $(\eta^5\text{-}C_5H_5)Ti$ groups at the corners of an octahedran which is face bridged by the eight oxygen atoms. From these examples, a variety of oxo-bridged species appear possible depending upon the metal and the chemical reactivity and stereochemical constraints imposed by the parent metallocene complex. In particular the removal of one cyclopentadienyl ring should reduce inter-ring repulsions and thereby enhance the formation of polynuclear complexes. As part of a systematic investigation to extend our understanding of the chemical properties and structural characteristics of these oxo-bridged systems, we have isolated a tetrameric titanium derivative, $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$, in which cyclization rather than chain formation has occurred. The outcome of an X-ray diffraction analysis as well as a qualitative description of the bonding and formation of this complex is discussed.

Table I. Space Group and Unit Cell Data for $[(C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$

| | | | |
|---|---|---|---|
| cryst system | monoclinic | $d$(obsd), g/cm$^3$ | 1.62 |
| | | $d$(calcd), g/cm$^3$ | 1.624 |
| $d$, Å | 18.344 (4) | $Z$ | 4 |
| $b$, Å | 10.195 (2) | $\mu$, cm$^{-1}$ | 14.8 |
| $c$, Å | 17.178 (3) | range of transmission coeff | 0.77–0.86 |
| $\beta$, deg | 114.68 (1) | | |
| vol, Å$^3$ | 2918.7 (9) | | |
| fw | 713.90 | space group | $C2/c$ ($C_{2h}^6$, No. 15) |
| | | systematic absences | $\{hkl\}$: $h + k = 2n + 1$<br>$\{h0l\}$: $l = 2n + 1$ |

## Experimental Section

**Reagents.** Bis(methylcyclopentadienyl)titanium dichloride was prepared by published methods.[9] All solvents were dried by using normal techniques and distilled under a $N_2$ or Ar atmosphere. $TiCl_4$ was purchased from Fisher Scientific, Inc. The Schlenk glassware used in the preparation of $(\eta^5\text{-}C_5H_4CH_3)TiCl_3$ was flame dried before use.

**Analyses.** Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

**Preparation of $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$.** *cyclo*-Tetrakis($\mu$-oxo-chloro(methylcyclopentadienyl)titanium(IV)) was prepared by the hydrolysis of freshly sublimed $(\eta^5\text{-}C_5H_4CH_3)TiCl_3$.[10] A 5.0-g (18-mmol) sample of $(\eta^5\text{-}C_5H_4CH_3)_2TiCl_2$ was added to 150 mL of dry xylene. A 9.5-g (50-mmol) sample of $TiCl_4$ was then added to the mixture, and the reaction was refluxed overnight. The solvent and excess reagents were removed in vacuo to yield 7.0 g of crude product, which was sublimed to produce 4.7 g (20 mmol, 56%) of crystalline $(\eta^5\text{-}C_5H_4CH_3)TiCl_3$. The trichloride is quite susceptible to hydrolysis, and upon addition of 1.5 g (6.4 mmol) of the trichloride to boiling heptane (in air), the solution's color changes from orange to bright yellow. Subsequent workup yielded 1.0 g (1.4 mmol, 88%) of the tetramer. Crystals suitable for the X-ray diffraction and chemical analyses were obtained by recrystallization in boiling heptane. Anal. Calcd for $C_{24}H_{28}Ti_4Cl_4O_4$: C, 40.38; H, 3.95; O, 8.96. Found: C,

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(1) Huffman, J. C.; Stone, J. G.; Krusell, W. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1976**, *98*, 6733.
(2) Manriquez, J. M.; Sanner, R. D.; Marsh, R. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 3042.
(3) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679 and references cited therein.
(4) Giddings, S. A. *Inorg. Chem.* **1964**, *3*, 684.
(5) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 5510.
(6) Thewalt, U.; Schomburg, D. *J. Organomet. Chem.* **1977**, *127*, 169.
(7) Reid, A. F.; Shannon, J. S.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173.
(8) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr., Sect. B* **1974**, *30*, 2267.
(9) Eisch, J. J.; King, R. B. "Organometallic Synthesis"; Academic Press: New York, 1965; Vol. 1, p 75.
(10) See ref 9, p 78.

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Table II. Intensity Statistics for X-ray Diffraction Data of $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$

| | | theoret | |
|---|---|---|---|
| | exptl | centrosym | non-centrosym |
| $E^2$ | 1.000 | 1.000 | 1.000 |
| MOD($E^2 - 1$) | 0.914 | 0.968 | 0.736 |
| MOD($E$) | 0.815 | 0.798 | 0.886 |

40.32; H, 3.63; O, 9.21. $\nu$(Ti–O) infrared spectrum (KBr): 850 (sh), 785 (vs) cm$^{-1}$.

**Data Collection.** A parallelepiped-shaped crystal of dimensions 0.21 mm × 0.13 mm × 0.35 mm was used to collect the X-ray diffraction data. Preliminary oscillation and Weissenberg photographs of the crystal were taken with Cu K$\alpha$ radiation and showed the Laue symmetry to be monoclinic $C_{2h}$-$2/m$. Systematic absences for $\{hkl\}$ of $h + k = 2n + 1$ and $\{h0l\}$ of $l = 2n + 1$ are compatible with two possible space groups $C2/c$ ($C_{2h}{}^6$, No. 15) and $Cc$ ($C_s{}^4$, No. 9).

The crystal, mounted nearly along the $a$ axis, was transferred to a Picker goniostat under computer control by a Krisel Control diffractometer automation system. After optical alignment, the angular coordinates ($\omega$, $\chi$, and $2\theta$) of 20 diffraction peaks within a $2\theta$ range of 25–33° were centered automatically[11] and least squares refined to give the final lattice parameters in Table I and the orientation matrix. The experimental density was measured by flotation in a $CH_2I_2/CCl_4$ solution.

Intensity data ($hkl$, $\bar{h}kl$) were measured with zirconium-filtered Mo K$\alpha$ radiation at a takeoff angle of 2° within a detector range of $5° \leq 2\theta \leq 45°$. The $\theta$–$2\theta$ scan mode was employed to scan each peak with constant precision scans in which the peak and background counting times were apportioned such that the ratio of $\sigma_c(I)/I$ was ca. 0.005. For each peak the scan width was determined from the expression $2.0 + 0.7 \tan \theta$; variable scan rates (1–8°/min) based upon the overall peak intensity were employed. Background counts were obtained at the extremes of each scan with the stationary-crystal, stationary-counter method. A scintillation counter was used with the pulse-height analyzer adjusted to accept 90% of the diffraction peak.

During data collection the intensities of two standard reflections were measured after every 120 min of exposure time. Their combined intensity did not vary by more than 4%. The standard deviation for each of the 2000 measured peaks was calculated from the expression $\sigma^2(I) = \sigma_c{}^2(I) + (0.04I)^2$ where $\sigma_c{}^2(I) = W^2(S/t_s{}^2 + B/t_b{}^2)$ and $I = W(S/t_s - B/t_b)$. In these relationships $S$ represents the total scan count measured in time $t_s$, $B$ the combined background count in time $t_b$, and $W$ the scan width. The intensity data were corrected for background, absorption, and Lorentz-polarization effects. The standard deviation of each structure amplitude, $|F_o| = (I/Lp)^{1/2}$, was calculated from the expression $\sigma(|F_o|) = \sigma(F_o{}^2)/2|F_o|$. Duplicate reflections were averaged to yield 1700 independent reflections with $|F_o| > \sigma(|F_o|)$.

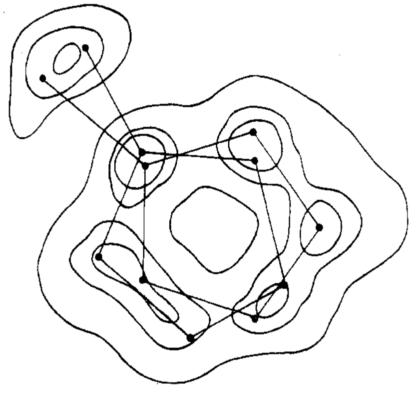

Figure 1. Difference Fourier contour map calculated through the disordered methylcyclopentadienyl ring in $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$. The approximate orientations of the rings are projected on the map. The contour lines are drawn at 0.7, 0.4, and 0.1 of the maximum density.

**Structural Analysis and Refinement.** The structural analysis was initiated by assuming the titanium compound was dimeric with eight molecules per unit cell. Attempts to determine the heavy-atom positions from a Patterson synthesis were unsuccessful. However, the initial coordinates of the two Ti atoms, two Cl atoms, and two of the three independent O atoms were interpolated from an $E$ map generated by the direct-methods program MULTAN78.[12] The corresponding intensity statistics given in Table II substantiate that the centrosymmetric $C2/c$ space group is preferred. The $E$ map further revealed that the titanium complex is actually a tetramer rather than a dimer since it lies on a crystallographic twofold rotation axis which passes through two opposite bridging O atoms, O(1) and O(3). Subsequent Fourier analyses provided the approximate locations of the remaining nonhydrogen atoms. During the course of the structure refinement, it became apparent that one of the methylcyclopentadienyl rings is disordered or exhibits excessive thermal motion. This problem was reflected by the wider variation of the calculated C–C separations and the large thermal parameters for the corresponding C atoms near the end of the refinement. For investigation of this problem, a difference Fourier map was calculated (without any contribution from the second methylcyclopentadienyl ring) through the plane of the ring (see Figure 1). The difference map reveals that the second methylcyclopentadienyl ring is disordered between two orientations. Approximate carbon positions (as depicted by the darkened circles) were determined and fit to an idealized methylcyclopentadienyl ring structure by MIRAGE.[13] The half-weighted C positions with isotropic temperature factors were refined; their subsequent values were again fit to an idealized ring structure with MIRAGE. This procedure was repeated several times until the idealized carbon positions used in the refinement remained fairly constant. With the carbon positions held fixed, anisotropic temperature parameters were introduced into the refinement. An attempt to vary all of the parameters simultaneously (with damping factors set at 0.5) unfortunately led to nonpositive definite thermal parameters for several ring atoms. Because of the small separation between some of the disordered carbon positions (i.e., C(6)···C(6′) is ca. 0.4 Å), the corresponding correlation coefficients for some of their parameters were rather large (above 0.80). This situation led to a shallow, poorly defined convergence minimum for the full-matrix refinement. Subsequently, block-diagonal least-squares methods were introduced to reduce this problem and obtain reasonable values for the anisotropic thermal parameters. The structural parameters for the independent atoms of the $[TiCl(\mu\text{-}O)]_4$ core, the one ordered methylcyclopentadienyl ring, and one orientation of the disordered ring were varied in one block and the remaining orientation of the disordered ring was varied in the other. Several cycles of block-diagonal least-squares refinement[14] including fixed contributions from the hydrogen atoms[15] led to the final discrepancy values[16–20] of $R(F_o) = 0.036$ and $R_w(F_o) = 0.046$ with $\sigma_1 = 1.66$ for 1700 reflections with $|F_o| > \sigma(|F_o|)$. A difference Fourier analysis revealed no residuals

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(11) The automatic peak centering algorithm is similar to that described by Busing: Busing, W. R. "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 319. The $\omega$, $\chi$, and $2\theta$ angles are optimized with respect to the K$\alpha_1$ peak ($\lambda$ = 0.709 26 Å).

(12) Declerq, J. P.; Germain, D.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1973**, *29*, 231.

(13) Calabrese, J. C., Ph.D. Dissertation, University of Wisconsin, Madison, WI, 1971, Appendix II.

(14) Calabrese, J. C. "A Crystallographic Variable Matrix Least-Squares Refinement Program"; University of Wisconsin: Madison, WI, 1972.

(15) Idealized hydrogen positions located ca. 0.95 Å from the disordered ring carbon atoms were calculated from MIRAGE.[13] Approximate hydrogen positions for the ordered methylcyclopentadienyl ring were interpolated from a difference Fourier map. An isotropic temperature factor of $B_{iso}$ = 8.0 Å$^2$ was assigned to all hydrogen atoms included in the structural model.

(16) The least-squares refinement[17] of the X-ray diffraction data was based upon the minimization of $\sum w_i||F_o| - |F_c||$, where the individual weights, $w_i$, equal $1/\sigma^2(|F_o|)$. The discrepancy indices were calculated from the expressions $R(F_o) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F_o) = [\sum w_i||F_o| - |F_c||^2/\sum w_i F_o{}^2]^{1/2}$. The final goodness-of-fit parameter is $\sigma_1 = [\sum w_i|F_o{}^2 - F_c{}^2|/(n - p)]^{1/2}$ where $n$ is the number of observations and $p$ is the number of parameters (viz., 218) varied. Final data to parameter ratio for 1700 data with $|F_o| > \sigma(|F_o|)$ is 7.8:1.

(17) The scattering factors utilized in all calculations were those of Cromer and Mann[18] for the nonhydrogen atoms and those of Stewart et al.[19] for the hydrogen atoms with corrections included for anomalous dispersion.[20]

(18) Cromer, D. T.; Mann, J. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(19) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(20) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

Table III. Positional and Thermal Parameters for $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$[a,b]

| atom | $x$ | $y$ | $z$ | $10^5\beta_{11}$ | $10^5\beta_{22}$ | $10^5\beta_{33}$ | $10^5\beta_{12}$ | $10^5\beta_{13}$ | $10^5\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ti(1) | 0.39933 (3) | 0.07531 (6) | 0.67327 (4) | 227 (2) | 659 (7) | 266 (2) | 61 (3) | 95 (2) | 13 (3) |
| Ti(2) | 0.41521 (3) | −0.27103 (6) | 0.65072 (4) | 226 (2) | 653 (6) | 202 (2) | 8 (3) | 55 (2) | 28 (3) |
| Cl(1) | 0.39615 (7) | 0.16521 (13) | 0.55082 (7) | 687 (5) | 1487 (15) | 452 (4) | 250 (7) | 307 (3) | 353 (7) |
| Cl(2) | 0.31147 (6) | −0.35029 (13) | 0.67547 (8) | 305 (3) | 1524 (15) | 759 (6) | −172 (6) | 208 (3) | 121 (8) |
| O(1) | $^1/_2$ | 0.1086 (4) | $^3/_4$ | 235 (11) | 1103 (45) | 424 (15) | 0 | 90 (10) | 0 |
| O(2) | 0.3998 (1) | −0.0976 (2) | 0.6518 (2) | 405 (9) | 724 (28) | 436 (10) | 78 (14) | 195 (7) | −9 (14) |
| O(3) | $^1/_2$ | −0.3059 (4) | $^3/_4$ | 243 (11) | 989 (41) | 232 (12) | 0 | 63 (9) | 0 |
| MeC(1) | 0.3630 (3) | −0.0411 (6) | 0.8346 (3) | 664 (18) | 1812 (73) | 597 (19) | 292 (31) | 383 (13) | 237 (33) |
| C(1) | 0.3349 (2) | 0.0576 (4) | 0.7645 (2) | 316 (11) | 1160 (49) | 418 (14) | 73 (20) | 228 (9) | 20 (23) |
| C(2) | 0.2760 (2) | 0.0380 (5) | 0.6818 (3) | 255 (12) | 1383 (54) | 465 (16) | −39 (22) | 168 (10) | −149 (26) |
| C(3) | 0.2676 (2) | 0.1530 (5) | 0.6368 (3) | 307 (14) | 1723 (63) | 507 (19) | 306 (25) | 119 (13) | 124 (31) |
| C(4) | 0.3202 (2) | 0.2451 (4) | 0.6912 (3) | 530 (15) | 921 (49) | 794 (21) | 256 (22) | 410 (12) | 76 (27) |
| C(5) | 0.3610 (2) | 0.1859 (4) | 0.7699 (3) | 421 (14) | 1109 (49) | 529 (16) | −51 (22) | 266 (11) | −326 (24) |
| MeC(2) | 0.5234 (6) | −0.5405 (9) | 0.6393 (7) | 689 (45) | 1175 (104) | 589 (49) | 534 (52) | 87 (39) | −19 (63) |
| C(6) | 0.4672 (5) | −0.4339 (8) | 0.5873 (5) | 546 (33) | 1119 (99) | 323 (27) | −3 (48) | 210 (22) | −261 (45) |
| C(7) | 0.5021 (5) | −0.3115 (10) | 0.5811 (5) | 476 (29) | 1541 (119) | 424 (30) | 29 (54) | 279 (21) | −153 (54) |
| C(8) | 0.4409 (5) | −0.2321 (10) | 0.5293 (5) | 709 (35) | 1707 (132) | 420 (30) | 271 (58) | 387 (22) | 36 (55) |
| C(9) | 0.3672 (5) | −0.2995 (9) | 0.5032 (5) | 438 (32) | 1406 (107) | 179 (25) | 18 (52) | 65 (22) | 35 (47) |
| C(10) | 0.3860 (6) | −0.4260 (8) | 0.5416 (6) | 577 (42) | 832 (89) | 375 (35) | −153 (51) | −11 (32) | −404 (45) |
| MeC(2′) | 0.5541 (7) | −0.4730 (15) | 0.6254 (8) | 661 (48) | 4289 (227) | 651 (58) | 997 (79) | 3 (43) | −581 (96) |
| C(6′) | 0.4765 (4) | −0.4057 (7) | 0.5802 (5) | 334 (24) | 840 (83) | 367 (28) | 118 (38) | 174 (19) | −37 (42) |
| C(7′) | 0.4638 (5) | −0.2813 (10) | 0.5470 (5) | 456 (27) | 2258 (137) | 454 (28) | −400 (54) | 328 (19) | −605 (54) |
| C(8′) | 0.3858 (5) | −0.2474 (8) | 0.5039 (5) | 620 (36) | 920 (91) | 265 (27) | 21 (49) | 180 (23) | 232 (42) |
| C(9′) | 0.3413 (5) | −0.3576 (9) | 0.5135 (5) | 344 (28) | 1316 (101) | 237 (27) | 23 (47) | 45 (21) | −262 (46) |
| C(10′) | 0.3996 (5) | −0.4563 (9) | 0.5609 (5) | 594 (33) | 893 (97) | 502 (33) | −40 (49) | 308 (24) | −144 (49) |

[a] The estimated standard deviations in parentheses for this and all subsequent tables refer to the least significant figures. [b] The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

greater than 0.5 e/Å$^3$. No correction for secondary extinction effects was necessary.

The tetramer's positional and thermal parameters from the final least-squares cycle are provided in Table III. Interatomic distances and bond angles with estimated standard deviations calculated from the variance–covariance matrix are given in Table IV. Structure factor tables and least-squares planes[21] of interest are available in the supplementary material.

## Results and Discussion

**General Description of the Crystal and Molecular Structure.** The molecular configuration of $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$, as illustrated in Figure 2, consists of four $(\eta^5\text{-}C_5H_4CH_3)TiCl$ molecular units linked by four oxo bridges to produce an eight-membered central ring of alternating Ti and O atoms. This type of cyclo structure was first reported by Skapski and Troughton[22] for $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$, which is prepared similarly by the hydrolysis of $(\eta^5\text{-}C_5H_5)TiCl_3$ in methanol. Floriani and co-workers[23] have recently characterized $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}O)]_3$, which represents the first example of a $M_3O_3$ six-membered ring system. The tetramer's geometry is constrained by a crystallographic twofold rotation axis which passes through O(1) and O(3) and thereby reduces the number of molecules in the orthorhombic unit cell to four. The arrangement of the four molecules in the centrosymmetric crystal lattice is depicted stereographically in Figure 3. The crystallographic asymmetric unit consists of two Ti atoms, two Cl atoms, three O atoms, and two methylcyclopentadienyl rings (one of which is disordered).

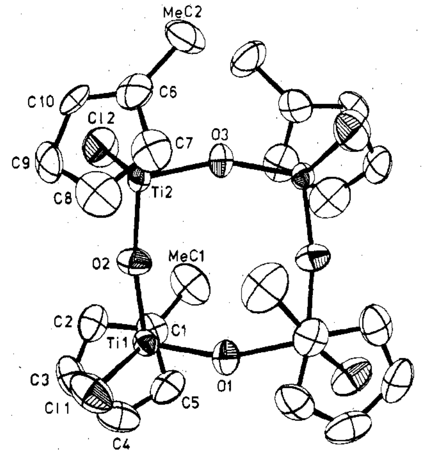

**Figure 2.** Molecular configuration of $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$ with atom labeling. The tetramer lies on a crystallographic twofold rotation axis which passes through O(1) and O(3). Only one orientation for the disordered methylcyclopentadienyl ring is shown for purposes of clarity. The thermal ellipsoids for this and all subsequent drawings were scaled to enclose 50% probability.

The pseudotetrahedral arrangement about each d$^0$ Ti(IV) atom is comprised of a methylcyclopentadienyl ring, a chloride ligand, and two oxo bridges. Due to the relatively close Ti···Ti separations across the ring diagonals of ca. 5.0 Å, the methyl groups of the planar methylcyclopentadienyl rings are directed away from one another to reduce steric interactions. As shown in Figure 4, the $[TiCl(\mu\text{-}O)]_4$ core possesses $D_{2d}$ symmetry with the corresponding independent Ti–O and Ti–Cl bond distances and O–Ti–O and O–Ti–Cl bond angles being essentially equivalent. The three independent Ti–O–Ti bridging angles deviate substantially from linearity with the angles between the symmetry-related Ti atoms of 157.2 (2) and 158.2 (2)° being more than 10° smaller than the Ti(1)–O–Ti(2) angle of 169.1 (2)°. Since the electronic structure about each metal atom is essentially the same, these differences are probably due to steric effects inherent to this tetrameric structure.

The eight-membered $[Ti(\mu\text{-}O)]_4$ ring is not strictly planar. The configuration of the four Ti atoms somewhat resembles a pair of butterfly wings with the dihedral angle between the Ti(1), Ti(2), and Ti(2*) and Ti(1), Ti(1*), and Ti(2*) planes

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(21) The computer programs which were used to perform the necessary calculations for the X-ray diffraction analysis with the accession names in the "World List of Crystallographic Computer Programs" are as follows: data reduction and absorption correction, DATALIB; data averaging and sorting, DATASORT; Fourier summation, CNTFOR, modification of FORDAP; direct methods analysis, MULTAN (1978 version); error analysis of distances and angles, OR FFE3; and structure plotting, ORTEP II. Least-squares planes were calculated with the program PLNJO based upon the method of Blow: Blow, D. *Acta Crystallogr.* **1960**, *13*, 168.

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**Table IV.** Interatomic Distances (Å) and Bond Angles (Deg) for $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$

| | | | |
|---|---|---|---|
| **A. Bond Distances** | | | |
| Within the $[TiCl(\mu\text{-}O)]_4$ Core | | | |
| Ti(1)–O(1) | 1.797 (1) | Ti(2)–O(3) | 1.800 (1) |
| Ti(1)–O(2) | 1.801 (3) | Ti(2)–O(2) | 1.792 (3) |
| Ti(1)–Cl(1) | 2.273 (2) | Ti(2)–Cl(2) | 2.265 (2) |
| Ti(1)–C(1) | 2.330 (5) | Ti(2)–C(6) | 2.392 (9) |
| Ti(1)–C(2) | 2.358 (4) | Ti(2)–C(7) | 2.395 (11) |
| Ti(1)–C(3) | 2.366 (4) | Ti(2)–C(8) | 2.357 (10) |
| Ti(1)–C(4) | 2.361 (5) | Ti(2)–C(9) | 2.328 (8) |
| Ti(1)–C(5) | 2.344 (5) | Ti(2)–C(10) | 2.336 (9) |
| Ti(1)–Cp1(c)[a] | 2.039 (6) | Ti(2)–C(6′)[b] | 2.398 (9) |
| Ti(2)–Cp2(c) | 2.040 (10) | Ti(2)–C(7′) | 2.303 (10) |
| Ti(2)–Cp2(c)′ | 2.034 (10) | Ti(2)–C(8′) | 2.361 (8) |
| | | Ti(2)–C(9′) | 2.346 (7) |
| | | Ti(2)–C(10′) | 2.380 (9) |
| Within the Methylcyclopentadienyl Rings | | | |
| MeC(1)–C(1) | 1.488 (7) | C(3)–C(4) | 1.390 (6) |
| C(1)–C(2) | 1.393 (5) | C(4)–C(5) | 1.381 (6) |
| C(2)–C(3) | 1.377 (7) | C(5)–C(1) | 1.383 (6) |
| MeC(2)–C(6) | 1.507 (12) | C(8)–C(9) | 1.413 (13) |
| C(6)–C(7) | 1.427 (13) | C(9)–C(10) | 1.424 (12) |
| C(7)–C(8) | 1.369 (12) | C(10)–C(6) | 1.365 (12) |
| MeC(2′)–C(6) | 1.475 (14) | C(8′)–C(9′) | 1.439 (13) |
| C(6′)–C(7′) | 1.371 (12) | C(9′)–C(10′) | 1.447 (11) |
| C(7′)–C(8′) | 1.352 (11) | C(10′)–C(6′) | 1.405 (12) |
| **B. Bond Angles** | | | |
| Within the $[TiCl(\mu\text{-}O)]_4$ Core | | | |
| O(1)–Ti(1)–O(2) | 104.1 (1) | O(3)–Ti(2)–O(2) | 105.2 (1) |
| O(1)–Ti(1)–Cl(1) | 102.9 (1) | O(3)–Ti(2)–Cl(2) | 102.3 (1) |
| O(2)–Ti(1)–Cl(1) | 101.9 (1) | O(2)–Ti(2)–Cl(2) | 101.6 (1) |
| Cp1(c)–Ti(1)–O(1) | 114.7 (1) | Cp2(c)–Ti(2)–O(3) | 111.3 (2) |
| Cp1(c)–Ti(1)–O(2) | 115.5 (2) | Cp2(c)–Ti(2)–O(2) | 115.7 (3) |
| Cp1(c)–Ti(2)–Cl(1) | 116.0 (1) | Cp2(c)–Ti(2)–Cl(2) | 118.9 (3) |
| Ti(1)–O(1)–Ti(1*)[c] | 158.2 (2) | Cp2(c)′–Ti(2)–O(3) | 118.2 (2) |
| Ti(1)–O(2)–Ti(2) | 169.1 (1) | Cp2(c)′–Ti(2)–O(2) | 117.2 (3) |
| Ti(2)–O(3)–Ti(2*) | 157.2 (2) | Cp2(c)′–Ti(2)–Cl(2) | 110.1 (3) |
| Within the Methylcyclopentadienyl Rings | | | |
| MeC(1)–C(1)–C(2) | 126.0 (4) | C(2)–C(3)–C(4) | 108.3 (4) |
| MeC(1)–C(1)–C(5) | 126.3 (3) | C(3)–C(4)–C(5) | 107.7 (4) |
| C(5)–C(1)–C(2) | 107.7 (4) | C(4)–C(5)–C(1) | 108.4 (3) |
| C(1)–C(2)–C(3) | 107.9 (4) | | |
| MeC(2)–C(6)–C(7) | 117.3 (7) | C(7)–C(8)–C(9) | 109.6 (9) |
| MeC(2)–C(6)–C(10) | 134.0 (8) | C(8)–C(9)–C(10) | 106.2 (7) |
| C(10)–C(6)–C(7) | 108.7 (7) | C(9)–C(10)–C(6) | 108.3 (8) |
| C(6)–C(7)–C(8) | 107.1 (8) | | |
| MeC(2′)–C(6′)–C(7′) | 127.4 (9) | C(7′)–C(8′)–C(9′) | 105.0 (7) |
| MeC(2′)–C(6′)–C(10′) | 127.4 (9) | C(8′)–C(9′)–C(10′) | 106.6 (7) |
| C(10′)–C(6′)–C(7′) | 105.2 (7) | C(9′)–C(10′)–C(6′) | 108.1 (8) |
| C(6′)–C(7′)–C(8′) | 114.9 (8) | | |
| **C. Interatomic Separations within the $[TiCl(\mu\text{-}O)]_4$ Core** | | | |
| Ti(1)···Ti(2) | 3.577 (1) | O(1)···O(2) | 2.837 (4) |
| Ti(1)···Ti(1*) | 3.530 (1) | O(1)···O(3) | 4.226 (5) |
| Ti(2)···Ti(2*) | 3.529 (1) | O(2)···O(2*) | 3.811 (5) |
| Ti(1)···Ti(2*) | 4.959 (1) | O(2)···O(3) | 2.854 (4) |

[a] Cp(c) designates the centroid of the cyclopentadienyl ring. [b] The other atoms of the disordered methylcyclopentadienyl ring are indicated by primes. [c] The position of the symmetry-related (starred) atom is determined by a substitution of the position of the corresponding (nonstarred) atom into the relationship $1 - x$, $y$, $1.5 - z$.

being 154.0°. The dihedral angles between two Cl–Ti–O planes, which have an O atom in common, are substantially greater than 90° (viz., ca. 125°).

**Comparison with Other Oxo-Bridged Titanium Compounds.** Structural studies have been performed on several dimeric oxo-bridged cyclopentadienyl titanium compounds[6,24,25] as well as polynuclear species such as $(\eta^5\text{-}C_5H_5)_6Ti_6(\mu_3\text{-}O)_8$[1] and $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$.[22] The available structural data for these oxo-bridged compounds are summarized in Table V. The observed Ti–O bond distances in these compounds (except for the hexamer in which the O atoms behave as triply rather than doubly bridging atoms) are substantially shorter than a typical single Ti–O bond distance of ca. 2.0 Å. This reduction in the Ti–O bond distance strongly supports the presence of partial double-bond character arising from the donation of electron density from filled oxygen $p_\pi$ orbitals to unfilled d orbitals on the electron deficient $d^0$ metals. A similar result has been observed for $[Ti(acac)_2Cl]_2O$[26] in which the Ti–O bond distances for the bridging O atom of 1.79 (2) and 1.81 (2) Å are significantly shorter than the Ti–O distances for the σ-bonded acac ligands which vary between 1.91 and 2.07 Å.

The bonding in $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$ can be better understood by the consideration of a qualitative bonding representation which has been proposed for $[(\eta^5\text{-}C_5H_5)_2ML]_2O$ dimers [M = Ti, Zr].[27,28] In these dimers one unfilled hybridized d orbital is available on each metal atom to accept electron density from the oxygen lone pairs. Consequently, each oxo bridge requires a pair of unfilled metal orbitals. The orthogonality of the oxygen $p_\pi$ orbitals prevents the $(ML)_2O$ core from being planar. For the tetramer the replacement of a cyclopentadienyl ring by an oxo bridge increases the number of available unfilled metal orbitals. Of the nine hybrid orbitals on each Ti atom, six are involved in bonding with the methylcyclopentadienyl ring (three) and the chloride and bridging oxo groups (three). Thus, three metal orbitals remain per Ti atom to accept electron density. Of the tetramer's twelve available metal orbitals, four probably accept from O $p_\pi$ orbitals directed within the $Ti_4O_4$ ring while at least four of the remaining eight metal orbitals interact with O $p_\pi$ orbitals directed approximately normal to the ring.

The availability of structural data for $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$ provides an opportunity to examine the effect that the additional inter-ring repulsion introduced by the methyl substituents has upon the tetramer's geometry. Although the tetramer's basic configuration remains intact, the average dihedral angle between the corresponding $Ti_3$ planes (which intersect along the diagonals of the $Ti_4$ unit) of 146.0° in $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$ is 8° smaller than that of 154.0° in the methylcyclopentadienyl analogue. The inter-ring repulsions introduced by the methyl substituents apparently cause the wings of the $Ti_4$ butterfly arrangement to open wider, which subsequently produces a greater variation of the Ti–O–Ti bond angles in the $[Ti(\mu\text{-}O)]_4$ ring.

**Tetramer Formation.** The formation of these tetrameric species from the parent titanium trichloride compound can be explained qualitatively by the reaction scheme illustrated in Figure 5. The initial hydrolysis of two monomer units leads to formation of the intermediate dimer, $[(C_5H_5)TiCl_2]_2O$, which has been isolated and structurally characterized.[5] This dimer exhibits a linear Ti–O–Ti bond and its geometry is imposed crystallographically by a center of symmetry. A view down the Ti–O–Ti line shows the dimer's staggered ligand disposition with dihedral angles between the O–Ti–X planes, where X is Cl or a ring centroid, of ca. 60°. This staggered arrangement has been similarly observed for other oxo-bridged dimers, such as $[(\eta^5\text{-}C_5H_5)_2Zr(SC_6H_5)]_2O$,[27] in which the dihedral angle between the two S–Zr–O planes is 61.7°. As the dimer concentration increases, two dimers combine via hydrolysis. As the dimers approach one another from either one of two equivalent directions during tetramer formation,

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Table V. X-ray Structural Data for Oxo-Bridged Cyclopentadienyltitanium Compounds

| ref | compd | Ti-O, Å | O-Ti-X, deg | Ti-O-Ti, deg | dihedral angle(s),[a] deg |
|---|---|---|---|---|---|
| 6 | $[(\eta^5\text{-}C_5H_5)TiCl_2]_2O$ | 1.777 (1) | 102.3<br>103.1 | 180 | |
| 24 | $\{[(\eta^5\text{-}C_5H_5)_2Ti(H_2O)]_2O\}(ClO_4)_2 \cdot 2H_2O$ | 1.829 (2) | 94.3 (3) | 175.8 (5) | 74.1 |
| 1 | $(\eta^5\text{-}C_5H_5)_6Ti_6O_8$ | 1.973 av | | | |
| 25 | $[(\eta^5\text{-}C_5H_5)_2Ti(HC{=}C(CF_3)_2)]_2O$ | 1.856 (6) | 94.9 (2) | 171.0 (2) | |
| 22 | $[(\eta^5\text{-}C_5H_5)TiCl(\mu\text{-}O)]_4$ | 1.788 av | X = O 103.6 av<br>X = Cl 102.3 av | 159.7 (4)<br>164.8 (5) | 125–140 |
| this work | $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$ | 1.797 (1)<br>1.802 (2)<br>1.801 (1) | X = O 104.8 av<br>X = Cl 102.2 av | 158.2 (2)<br>169.1 (1)<br>157.2 (2) | 120–125 |

[a] The dihedral angle between two O-Ti-X planes with the bridging O atom in common.

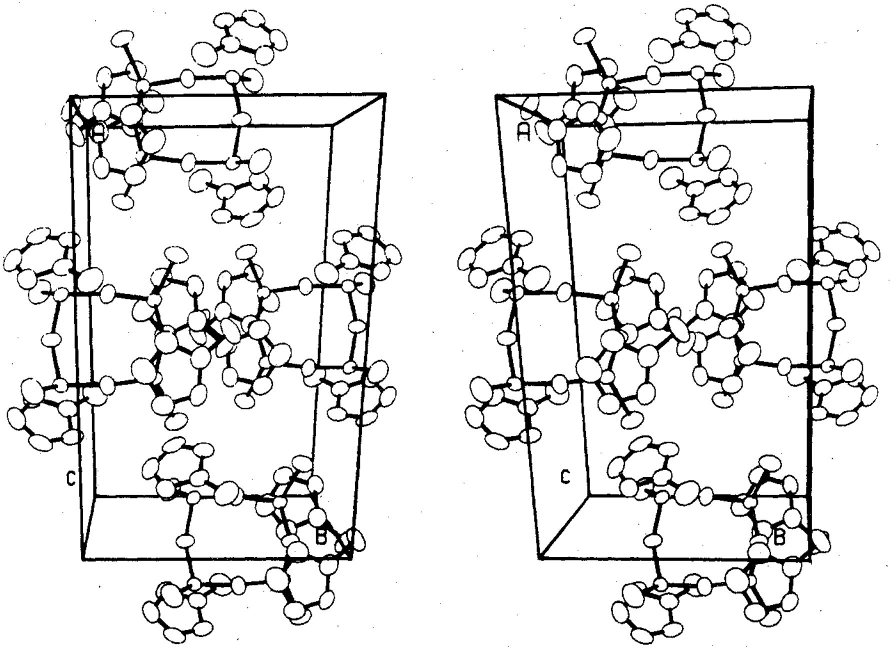

Figure 3. Stereoscopic drawing of the molecular arrangement of four tetramers in the C-centered monoclinic crystal lattice.

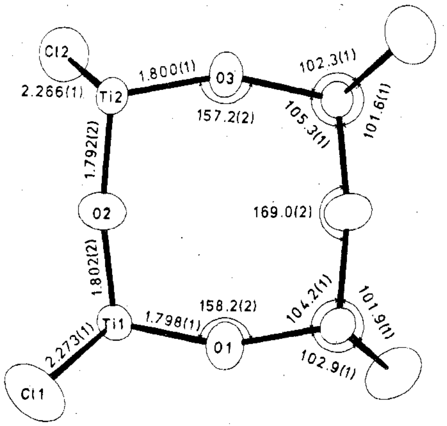

Figure 4. The $[TiCl(\mu\text{-}O)]_4$ core of $D_{2d}$ symmetry with experimentally determined independent bond distances and bond angles.

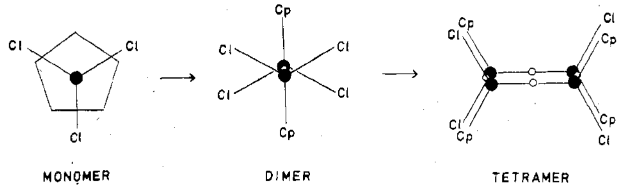

Figure 5. Reaction scheme depicting tetramer formation from the hydrolysis of $(C_5H_5)TiCl_3$.

the $(C_5H_5)TiCl_2$ groups (as shown in Figure 5) rotate about the oxo bridge toward a nearly eclipsed orientation. This rearrangement accounts for the doubling of the O–Ti–X dihedral angles and for the alternating ligand disposition about the tetramer's $[Ti(\mu\text{-}O)]_4$ ring. Therefore, upon the basis of available structural data, this scheme suggests that tetramer formation occurs by a pairwise combination of dimeric units rather than via a trinuclear intermediate, which would require a substantial reduction of the Ti–O–Ti bond angles. Further studies are in progress to examine the chemical and redox properties of these unusual cyclic tetranuclear titanium species.

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**Registry No.** $(\eta^5\text{-}C_5H_4CH_3)_2TiCl_2$, 1282-40-2; $(\eta^5\text{-}C_5H_4CH_3)TiCl_3$, 1282-31-1; $[(\eta^5\text{-}C_5H_4CH_3)TiCl(\mu\text{-}O)]_4$, 72030-10-5.

**Supplementary Material Available:** Tables of positional and thermal parameters, least-squares planes, and structural factor amplitudes (9 pages). Ordering information is given on any current masthead page.