oxidizing power of Hg(III) relative to other M(III) complexes.[36] The weak d-d transition is obscured either by these charge-transfer bands or, more likely, by the intense charge-transfer bands of $[Hg([14]aneN_4)]^{2+}$ in the uv region.

Conclusions

Visible spectroscopy, cyclic voltammetry, and ESR each lead to the same value of the half-life of the initial product of electrochemical oxidation of $[Hg^{II}([14]aneN_4)]^{2+}$. The spectral properties of this product are consistent with the formation of mercury(III). This is the first example of the removal of a d electron from a group 2b element in a condensed phase. While a tetranitrogen macrocyclic complex of mercury(III) is unstable under the conditions employed in this investigation, attempts to stabilize mercury(III) in complexes such as $KHgF_4$ or K_3HgF_6 appear feasible.

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Synthesis and Structure of the Hydroxyl Derivative of "Titanocene"

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Abstract: The crystal and molecular structures of μ-(η^5:η^5-fulvalene)-di-μ-hydroxyl-bis(cyclopentadienyltitanium), the hydroxyl derivative of "titanocene", were determined from x-ray counter data. The molecular structure is a $(C_5H_5)Ti(OH)(C_5H_4-)$ dimer; the titanium atoms are bridged by two OH ligands and the fulvalene ligand, which is η^5-bonded to both titanium atoms. Each dimeric molecule crystallizes with one molecule of tetrahydrofuran which hydrogen bonds to one of the bridging OH's. Two types of Ti-OH-Ti geometries result with Ti-O of 2.10 (2) Å and Ti-O-Ti of 98.8 (5)° for the oxygen involved in hydrogen bonding and Ti-O of 2.05 (1) Å and Ti-O-Ti of 102.7 (6)° for the other OH bridge. The Ti···Ti separation is 3.195 Å. The fulvalene ligand is folded with 15.1° between C_5 rings which are separated by 1.43 (3) Å. The angle subtended at Ti by the centroids of the two η^5-C_5 rings is 133.5 (1)°. Crystals are orthorhombic, space group $Pna2_1$, with a = 10.143 (6), b = 23.571 (14), and c = 9.009 (8) Å with four dimers and four solvent molecules per cell (ρ(calcd) = 1.42 g cm^{-3}). The refinement gave a conventional R value of 0.110 for 1122 reflections with $F_o > 2\sigma(F_o)$.

We report here the isolation and crystal structure of the hydroxyl derivative of "titanocene", μ-(η^5:η^5-fulvalene)-di-μ-hydroxyl-bis(cyclopentadienyltitanium), $[(C_5H_5)(C_5H_4)TiOH]_2$. The crystal structure of this compound allows us to define in detail the geometry of a structure believed to be closely related to titanocene. In addition, study of this molecule provides information on a product of partial hydrolysis of a titanium(III) compound. Direct structural information on the course of hydrolysis of low-valent titanium compounds is extremely rare.

Much of the recent interest in the nature of titanocene was stimulated by the work of Brintzinger and Bercaw[1] who formulated the stable green form of the molecule as a dimeric titanium hydride $[(C_5H_5)(C_5H_4)TiH]_2$. Since then there has been some controversy about its structure, especially concerning the character of the C_5H_4 ligands.[2] Titanocene is frequently formed as the stable end product of reduction of biscyclopentadienyltitanium(IV) complexes. Conversion of the reduced intermediate to titanocene is accompanied by loss of activity of the complexes as olefin hydrogenation catalysts,[3] and loss of reactivity with dinitrogen.[4] Determination of the structure of titanocene is important in understanding the chemistry of the reduced species and the mechanism of their deactivation. Additionally, this structure is of interest as it relates to the structures of similar compositions, such as $[(C_5H_5)(C_5H_4)MH]$ (M = Nb,[5] Ta,[5] $TiAlEt_2$[6]). Crystals of titanocene are unsuitable for x-ray study. Our approach to the structure has been to study the crystal structures and chemistry of compounds derived from titanocene. In a previous communication[7] the isolation, structure, and chemistry of $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ led us to the conclusion that the best description of titanocene is that of a fulvalene and hydride bridged dimer, although the aluminum derivative lacked the full symmetry expected for titanocene. Very recently Davison and Wreford[8] found that the ^{13}C NMR spectrum of titanocene is consistent with the presence of the fulvalene ligand in a molecule of C_{2v} symmetry. Hydroxytitanocene, with a nearly symmetrical bridging OH system, is the best model for titanocene yet determined. The structure confirms the previously postulated fulvalene bridge. The location of the hydroxyl groups allows refinement of the probable positions of the hydride ligands in $[(C_5H_5)(C_5H_4)TiH]_2$.

Experimental Section

Titanocene, $[(C_5H_5)(C_5H_4)TiH]_2$, was made by hydrogenation[9] of $(C_5H_5)_2TiMe_2$. Reaction of 0.415 g (1.17 mmol of dimer) in tetrahydrofuran (THF) solution with 0.1 g (5.6 mmol) of water produced 2.05 mmol of hydrogen (0.88 mol of H_2/Ti). On a synthesis scale, a solution of 0.38 ml (21 mmol) of water in 50 ml of THF was added dropwise at room temperature to a stirred mixture of 3.7 g (10 mmol) of titanocene in 50 ml of THF. Gas evolution commenced as the addition was begun. After partial evaporation of the solvent, the mixture was heated to the boiling point and chilled to −15° to produce 2.9 g of a deep reddish purple crystalline product. Crystals for the x-ray study were not dried. The sample for analysis was heated at 70° under vacuum for 5 h to remove THF. Anal. Calcd for $C_{20}H_{20}Ti_2O_2$: C, 61.9; H, 5.2. Found: C, 61.2; H, 5.3. The mass spectrum contained no parent ion. The highest mass peak found was 371.0339, corresponding to $C_{20}H_{19}OTi_2$ (calcd 371.0395). The infrared spectrum between 4000 and 600 cm^{-1} (Nujol mull) contains absorptions at 3623 (s, OH), 3103 (w, ring CH), 1442 (m), 1376 (m), 1401 (m), 1263 (w), 1123 (m), 1062 (m), 1050 (m), 1016 (m), 1007 (m), 925 (w), 895 (w), 792 (s), and 634 (m) cm^{-1}. This spectrum is much like that of titanocene,[1] except for the presence of the OH band, and the absence of the bridging hydride band at 1223 cm^{-1}.

$[(C_5H_5)(C_5H_4)TiOH]_2$ is stable for long periods as a solid at room temperature under an inert atmosphere. The compound in aqueous THF is noticeably degraded within a day; in air it is rapidly oxidized.

X-Ray Data, Structure Solution, and Refinement. Crystals of $[(C_5H_5)TiOH]_2(C_{10}H_8)\cdot C_4H_8O$ are orthorhombic with cell dimensions of $a = 10.143$ (6), $b = 23.571$ (14), and $c = 9.009$ (8) Å. These parameters were refined from the angular positions of seven reflections carefully centered on the diffractometer. There is one tetrahydrofuran molecule of solvation per titanium dimer. The systematic absences as observed on precession and Weissenberg photographs are $0kl$ ($k + l = 2n + 1$) and $h0l$ ($h = 2n + 1$) consistent with the space groups $Pna2_1$ and $Pnam$ (nonstandard setting).[10] The calculated density for four formula units per cell is 1.42 g cm^{-3}. We had trouble measuring the density, but estimate it to be slightly less than 1.50 g cm^{-3}. Crystals were enclosed in capillaries for the x-ray studies.

A prismatic crystal of dimensions 0.32 × 0.32 × 0.17 mm was mounted on a Picker four-circle automatic diffractometer with the c axis along the diffractometer ϕ axis. Data (1516 reflections) were measured out to 45° 2θ using the θ–2θ scan technique and Zr-filtered Mo radiation (λ 0.7107 Å). Data were scanned at 1° per min. starting 0.75° before the $K\alpha_1$ peak and ending 0.75° after $K\alpha_2$ peak. Backgrounds of 15 s were measured at the beginning and end.

The data were corrected for Lorentz, polarization, and absorption effects.[11] The linear absorption coefficient for Mo Kα radiation is 7.93 cm^{-1}. The crystal was defined by six plane faces for the absorption correction. The minimum and maximum calculated transmission factors were 0.61 and 0.77, respectively. Structure factor errors were estimated as previously described.[12] The data with $F_o < 2\sigma(F_o)$ were given zero weight in the refinement which minimized the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$.

A serious decomposition problem was encountered during the data collection. The intensity drop-off was gradual, the total decline being 17% in F. The decomposition profile was monitored in two ways. Standard reflections measured periodically provided one measure of decomposition. Another measure was obtained by remeasuring some 50 strong reflections at the end of the data collection. These were selected to span the entire data set; differences observed between the intensities at the end of the run and the prior measurement are a measure of decomposition. An average decomposition profile was derived and the data were corrected accordingly.

The structure solution was initiated in the centric space group, but no satisfactory model could be obtained; the acentric space group $Pna2_1$ was then used for all further work. There is no space group imposed molecular point symmetry in $Pna2_1$. The structure model was built up by Patterson superposition techniques[13] at first and then by least-squares and Fourier techniques. The R value $(\sum ||F_o| - |F_c|| / \sum |F_o|)$ was 0.20 with the nonhydrogen atoms in the model with isotropic temperature factors (solvent excluded here). Electron density difference maps were examined for possible solvent molecules. One molecule of THF was found; the peaks were broad, suggestive of some static positional disordering. The R value was 0.136 when the THF was added to the model with all atoms still having isotropic temperature factors. All atoms were then refined with anisotropic temperature factors giving an R of 0.116 and R_w, $[\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, of 0.095. An electron density difference map was examined for the hydrogen atoms. There was evidence for all hydrogen atoms in the molecule itself (0.1–0.3 e $Å^{-3}$); however, they were placed in calculated positions (C–H = 1.0 Å, $B = 5.0$ $Å^2$) and not refined. Solvent hydrogen atoms were not included. Several further cycles of refinement with anisotropic factors were done varying the scale factor and the positional and thermal parameters in the following two groups: (a) the titanium atoms, the carbon atoms for both C_5H_5 rings, and the THF heavy atoms; (b) the titanium atoms, hydroxyl oxygen atoms, and the carbon atoms of the $C_{10}H_8$ ligand. The final R values for 1122 reflections with $F_o > 2\sigma(F_o)$ were 0.110 for R and 0.088 for R_w.

Additional refinements were done in an attempt to establish the absolute configuration of the molecule with respect to the polar c cell axis. These refinements were done with the molecule inverted with respect to the c axis. We could not establish the absolute conformation with any certainty since both refinements and their resulting structural parameters were nearly identical; the model we report here is the one with the lowest R and R_w values. The largest variation in bond distance between the two refinements was 0.02 Å; the average deviation over all the bond distances was 0.009 (Å). We tried remounting the crystal and measuring differences in Friedel pairs, but the crystal had completely decomposed by this time.

Atomic scattering factors for the neutral atoms were used.[14] The real and imaginary parts of the anomalous scattering of titanium were included in the calculations.[15]

The final positional and thermal parameters for the nonhydrogen atoms are given in Table I. The positions of the hydrogen atoms are listed in Table II. A list of observed and calculated structure factors is available.[16]

Results and Discussion

Reaction of titanocene with water occurs according to the equation

$$[(C_5H_5)(C_5H_4)TiH]_2 + 2H_2O \rightarrow [(C_5H_5)(C_5H_4)TiOH]_2 + 2H_2$$

The crystal structure of the hydrolysis products is made up of the packing of discrete molecules of $[(C_5H_5)Ti(OH)]_2C_{10}H_8$, each hydrogen bonded to one THF of solvation. The hydrogen

Table I. Final Parameters for the Nonhydrogen Atoms in $[(C_5H_5)Ti(OH)]_2C_{10}H_8$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0.4874 (3)	0.3562 (1)	0.25	65 (3)	18 (1)	119 (5)	−1 (2)	−23 (5)	−2 (2)
Ti(2)	0.2649 (3)	0.4513 (1)	0.2827 (6)	73 (4)	18 (1)	110 (5)	1 (2)	−11 (5)	−4 (2)
O(1)	0.2945 (10)	0.3637 (5)	0.3271 (14)	45 (11)	22 (3)	174 (27)	−2 (5)	−29 (14)	−13 (8)
O(2)	0.4185 (12)	0.4275 (5)	0.1483 (16)	101 (15)	17 (3)	112 (23)	2 (6)	32 (17)	−6 (8)
C(1)	0.6453 (20)	0.4203 (10)	0.3429 (21)	98 (23)	23 (6)	89 (31)	−31 (10)	12 (24)	−14 (11)
C(2)	0.7144 (24)	0.3684 (10)	0.3462 (27)	183 (32)	17 (6)	210 (46)	−4 (12)	−103 (31)	−18 (14)
C(3)	0.6318 (23)	0.3326 (10)	0.4478 (29)	105 (28)	22 (7)	189 (43)	11 (12)	−39 (30)	−6 (16)
C(4)	0.5364 (22)	0.3663 (11)	0.5130 (25)	147 (34)	21 (7)	163 (39)	−15 (13)	−97 (31)	21 (15)
C(5)	0.5387 (16)	0.4210 (10)	0.4429 (23)	31 (19)	27 (6)	92 (33)	−2 (10)	−37 (21)	−26 (12)
C(6)	0.4406 (23)	0.4635 (11)	0.4560 (27)	81 (28)	32 (7)	148 (40)	−14 (12)	13 (29)	−10 (15)
C(7)	0.4318 (20)	0.5171 (10)	0.3693 (23)	104 (25)	20 (6)	118 (34)	−2 (10)	29 (25)	−15 (12)
C(8)	0.3086 (26)	0.5389 (10)	0.4058 (27)	183 (36)	18 (6)	140 (35)	0 (13)	−81 (32)	−20 (13)
C(9)	0.2356 (20)	0.5096 (12)	0.5068 (29)	124 (27)	28 (7)	190 (44)	−19 (13)	52 (34)	−25 (16)
C(10)	0.3154 (21)	0.4612 (12)	0.5337 (22)	119 (27)	41 (9)	106 (35)	−8 (13)	9 (26)	−60 (16)
C(11)	0.4981 (26)	0.3252 (10)	−0.0078 (22)	203 (34)	24 (6)	70 (29)	−10 (14)	−33 (32)	−9 (12)
C(12)	0.3762 (22)	0.3013 (9)	0.0609 (24)	198 (32)	9 (5)	97 (36)	−33 (11)	8 (32)	9 (12)
C(13)	0.4294 (22)	0.2624 (10)	0.1745 (26)	178 (35)	17 (6)	112 (42)	−27 (12)	35 (32)	−7 (14)
C(14)	0.5653 (21)	0.2619 (10)	0.1718 (28)	87 (29)	16 (6)	194 (97)	10 (11)	36 (30)	−7 (14)
C(15)	0.6018 (19)	0.2996 (11)	0.0667 (30)	83 (25)	25 (7)	196 (49)	−15 (11)	23 (31)	−33 (16)
C(21)	0.1526 (21)	0.4481 (14)	0.0445 (26)	117 (29)	40 (9)	117 (38)	−26 (14)	−39 (30)	−6 (18)
C(22)	0.1450 (19)	0.5046 (12)	0.0998 (32)	54 (22)	27 (7)	258 (51)	−9 (11)	−51 (30)	26 (17)
C(23)	0.0635 (19)	0.4968 (10)	0.2301 (31)	50 (20)	28 (6)	244 (59)	22 (10)	−16 (33)	28 (17)
C(24)	0.0347 (16)	0.4425 (10)	0.2584 (33)	42 (19)	29 (7)	249 (46)	−29 (9)	−1 (34)	24 (21)
C(25)	0.0873 (20)	0.4114 (10)	0.1369 (30)	85 (25)	25 (6)	171 (41)	33 (11)	−80 (28)	−36 (15)
O(3)	0.6439 (18)	0.1888 (8)	0.5768 (21)	197 (27)	50 (7)	201 (35)	−18 (11)	72 (27)	3 (13)
C(31)	0.5156 (24)	0.1770 (14)	0.5438 (44)	81 (28)	50 (10)	410 (89)	−8 (14)	−20 (44)	−16 (27)
C(32)	0.4475 (45)	0.1818 (21)	0.6851 (48)	464 (91)	91 (17)	168 (62)	−3 (33)	6 (72)	49 (31)
C(33)	0.5430 (34)	0.1784 (21)	0.8078 (41)	225 (48)	115 (22)	213 (66)	−55 (30)	124 (53)	38 (29)
C(34)	0.6550 (49)	0.1939 (17)	0.7398 (34)	559 (89)	67 (13)	93 (53)	7 (27)	−169 (59)	16 (23)

[a] The standard deviations here and in the other tables are given in parentheses. The anisotropic temperature factors (×10^4) are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Positional Parameters for the Hydrogen Atoms[a]

Atom	x	y	z
H(1)	0.6705	0.4533	0.2740
H(2)	0.7944	0.3560	0.2922
H(3)	0.6484	0.2904	0.4690
H(4)	0.4731	0.3523	0.5951
H(7)	0.5002	0.5334	0.2982
H(8)	0.2734	0.5764	0.3541
H(9)	0.1454	0.5218	0.5498
H(10)	0.2847	0.4271	0.5978
H(11)	0.4991	0.3533	−0.0970
H(12)	0.2796	0.3075	0.0356
H(13)	0.3738	0.2365	0.2410
H(14)	0.6288	0.2387	0.2367
H(15)	0.6986	0.3116	0.0425
H(21)	0.2000	0.4319	−0.0494
H(22)	0.1855	0.5407	0.0489
H(23)	0.0365	0.5288	0.3022
H(24)	−0.0199	0.4275	0.3456
H(25)	0.0731	0.3678	0.1299
H(O1)	0.2339	0.3342	0.3718
H(O2)	0.4527	0.4479	0.0553

[a] All hydrogen atoms had isotropic temperature factors of 5.0 Å^2.

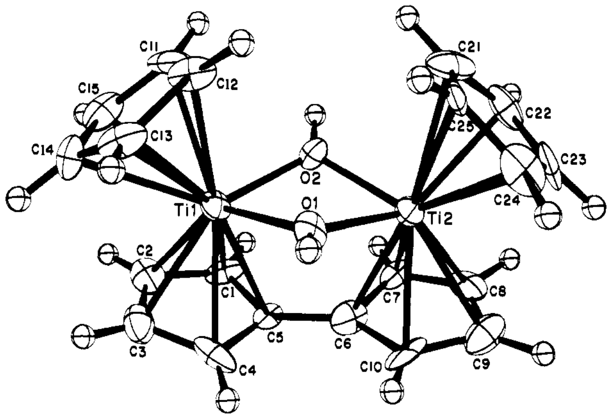


Figure 1. The molecular structure of $[(C_5H_5)Ti(OH)]_2C_{10}H_8$.

bond is between the donor oxygen of one of the bridging hydroxyl groups and the acceptor oxygen of the THF. The molecular configuration illustrating the atom labeling used here is shown in Figure 1; the thermal elipsoids are plotted at the 30% probability level. The molecule has two η^5-C_5H_5 ligands, a bridging η^5:η^5-fulvalene ($C_{10}H_8$) ligand, and two bridging hydroxyl ligands. Thus the molecule is μ-(η^5:η^5-fulvalene)-di-μ-hydroxyl-bis(cyclopentadienyltitanium). The donor oxygen for the hydrogen bond is O(1). The molecule has approximate C_{2v} (*mm*2) point symmetry, but the symmetry breaks down when the C_5H_5 ring conformations are examined in detail. This is evident in Figure 2 which shows side and top views of the molecule. Figure 2b illustrates the obviously different steric requirements of the two C_5H_5 ligands and the fused C_5H_4 ligands; the OH bridging geometry is bent away from the fulvalene ligand toward the C_5H_5 ligands.

The bond distances are listed in Table III and interatomic angles in Table IV. All four cyclopentadienyl-titanium interactions are essentially equivalent with respect to all structural parameters. The average Ti-C distance is 2.40 (1) Å and the average Ti-C_5 ring plane distance is 2.080 Å (2.069-2.102 Å range). The average C_5H_5(centroid)-Ti-C_5H_4(centroid) angle is 133.5 (1)°. These data are similar to values observed for other bis(cyclopentadienyl)titanium complexes as, for example, in $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)(C_{10}H_8)$ and

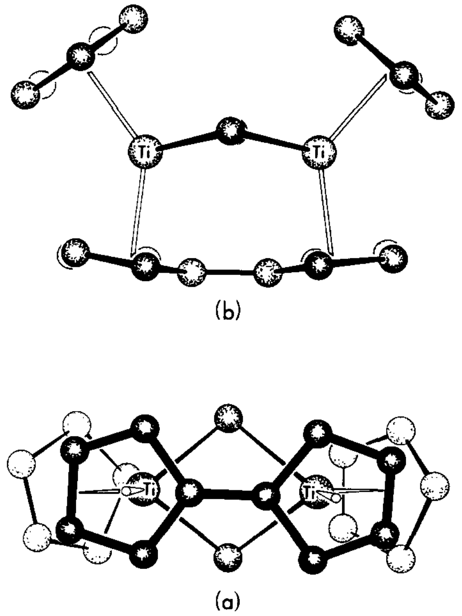


Figure 2. Top (b) and side (a) views of the $[(C_5H_5)Ti(OH)]_2C_{10}H_8$ molecule.

$[(C_5H_4)TiHAlEt_2]_2(C_{10}H_8)$,[7] $[(C_5H_5)Ti(C_5H_4)HAlEt_2]_2$,[17,18] $(C_5H_5)_3Ti$,[19] $(C_5H_5)_2TiBH_4$,[20] $(C_5H_5)_2TiC_6H_4COO$,[21] $(C_5H_5)_4Ti$,[22] $(C_5H_5)_2TiS_5$,[23] $[(CH_2)_3(C_5H_4)_2]TiCl_2$,[24] $(C_5H_5)_2Ti(SMe)_2Mo(CO)_4$,[25] $(C_5H_5)_2Ti(C_6H_5)_2$,[26] and $(C_5H_5)_2Ti(C_3H_3Me_2)$.[27] Generally angles between 117 and 146° have been observed between C_5 rings in bis(cyclopentadienyl)-metal complexes.[28] In this structure the C_5 rings on Ti(1) have an eclipsed conformation while those on Ti(2) are staggered; both conformations are observed generally.

There are two types of Ti-O distances to the hydroxyl ligands, 2.10 (2) to O(1) and 2.05 (1) Å to O(2). The differences from the mean of 2.07 (2) Å are only marginally significant but probably real, compensating for O(1)'s involvement in the hydrogen bond to the THF. There are no OH bridged titanium structures for comparison, but these data are similar to the values observed for OR bridged Ti complexes, i.e., 2.036 Å in $[Ti(OC_6H_5)_4HOC_6H_5]_2$,[29] 1.97-2.06 Å in $[(CH_3)_2TiO_2C_6H_{12}]_2$,[30] 1.96-2.07 Å in $[Ti(OCH_3)_4]_4$,[31] 1.96 Å in $TiCl_2(OC_2H_5)_2$,[32] 1.910 and 2.122 Å in $TiCl_2(OC_6H_5)_2$,[33] and 2.03 Å in $Ti_4(OC_2H_5)_{16}$.[34] For comparison, observed data for μ-oxo complexes are 1.776-1.779 Å in $[(C_5H_5)TiClO]_4$,[35] 1.79 and 1.81 Å in $[TiCl(C_5H_7O_2)_2]_2O{\cdot}CHCl_3$,[36] and 1.78 Å in $[TiCl_2(C_5H_5)]_2O$;[37] the angles subtended at the O atom in these complexes exceed 160°. A di-μ-oxo-dititanium bridging system was observed in $[TiO(C_5H_7O_2)_2]_2$ characterized by 1.831 (3) Å for Ti-O, 96.6 (2)° forTi-O-Ti, and 83.4 (2)° for O-Ti-O.[38]

The cyclopentadienyl C-C distances vary from 1.34 (3) to 1.50 (3) Å with an average of 1.42 (1) Å, while the C-C-C angles vary from 101.3 (21) to 117.3 (22)° with an average of 107.9 (10)°. We consider these distances and angles equivalent within the experimental errors which are relatively large, probably because of the crystal decomposition and the partial disordering of the THF molecule. We note that C-C distances within the fulvalene ligand are equivalent even in structures where there is higher precision as in $[(C_5H_5)Ti]_2(H)(H_2AlEt_2)C_{10}H_8$,[7] $[(C_5H_4)TiHAlEt_2]_2C_{10}H_8$,[7] and $(C_{10}H_8)_2Fe_2$.[39]

The data for the least-squares planes through the cyclopentadienyl rings are given in Table V. There is, incidentally, a difference of 3.1° in the angle between C_5 rings on Ti(1) depending on whether centroids (Table IV) or plane normals (Table V) are used. All individual rings are planar within experimental error. The whole fulvalene ligand is not planar (max deviation 0.18 Å, plane 3). The data in Table VI show the M···M separation, dihedral angle, and C-C separation between C_5 rings for the fulvalene ligand in similar complexes. The $(C_{10}H_8)_2Fe_2$ was included because it represents the equilibrium distance between nonbonded metal atoms joined only by fulvalene ligands. The other complexes all have additional bonding between the metal atoms. The dihedral angle correlates directly with the M···M separation and is primarily a folding to accommodate Ti···Ti separations shorter than the optimum for a perfectly planar fulvalene.

The data on M···M separations illustrate another feature, namely the problem in determining whether or not there are M-M bonds in these multibridged systems. In fact, we are still hesitant to make a definitive statement on the question of a Ti-Ti bond here. The Ti···Ti separation is a poor criterion for assessing metal-metal bonding since it is certainly influenced by the bridging fulvalene and hydroxyl groups. Diamagnetism may be achieved by either a direct Ti-Ti bond or a superexchange through the bridging OH ligands. The same considerations apply to titanocene. In fact we find $[(C_5H_5)Ti$-

Table III. Interatomic Distances in $[(C_5H_5)Ti(OH)]_2C_{10}H_8$[a]

	Bonding Distances (Å)		
Ti(1)-O(1)	2.08 (1)	O(3)-C(31)	1.36 (3)
Ti(2)-O(1)	2.12 (1)	O(3)-C(34)	1.48 (4)
	2.10 (2)	C(31)-C(32)	1.45 (6)
		C(32)-C(33)	1.47 (6)
Ti(1)-O(2)	2.04 (1)	C(33)-C(34)	1.34 (6)
Ti(2)-O(2)	2.05 (1)		
	2.05 (1)	Ti(1)-C(1)	2.36 (2)
		Ti(1)-C(2)	2.48 (2)
C(1)-C(2)	1.41 (3)	Ti(1)-C(3)	2.37 (2)
C(2)-C(3)	1.50 (3)	Ti(1)-C(4)	2.43 (2)
C(3)-C(4)	1.38 (3)	Ti(1)-C(5)	2.37 (2)
C(4)-C(5)	1.44 (3)	Ti(1)-C(11)	2.44 (2)
C(5)-C(1)	1.41 (3)	Ti(1)-C(12)	2.42 (2)
C(6)-C(7)	1.49 (3)	Ti(1)-C(13)	2.39 (2)
C(7)-C(8)	1.39 (3)	Ti(1)-C(14)	2.46 (2)
C(8)-C(9)	1.36 (4)	Ti(1)-C(15)	2.42 (3)
C(9)-C(10)	1.42 (4)	Ti(2)-C(6)	2.39 (2)
C(10)-C(6)	1.45 (3)	Ti(2)-C(7)	2.42 (2)
C(11)-C(12)	1.49 (3)	Ti(2)-C(8)	2.39 (2)
C(12)-C(13)	1.48 (3)	Ti(2)-C(9)	2.46 (3)
C(13)-C(14)	1.48 (3)	Ti(2)-C(10)	2.33 (2)
C(14)-C(15)	1.35 (4)	Ti(2)-C(21)	2.43 (2)
C(15)-C(11)	1.39 (3)	Ti(2)-C(22)	2.40 (3)
C(21)-C(22)	1.42 (4)	Ti(2)-C(23)	2.35 (2)
C(22)-C(23)	1.45 (4)	Ti(2)-C(24)	2.35 (2)
C(23)-C(24)	1.34 (3)	Ti(2)-C(25)	2.42 (2)
C(24)-C(25)	1.42 (4)		2.40 (1)
C(25)-C(21)	1.37 (4)		
	1.42 (1)		
C(5)-C(6)	1.43 (3)		
	Nonbonding Contacts (Å)		
Ti(1)···Ti(2)	3.195 (4)	C(9)···C(23)	3.06 (4)
Ti(1)···C(6)	3.17 (3)	C(8)···H(23)	2.92
Ti(2)···C(5)	3.21 (2)	C(9)···H(23)	2.77
O(1)···O(2)	2.54 (2)	H(2)···H(15)	2.66
O(1)···C(12)	2.93 (2)	H(3)···H(14)	2.43
O(1)···C(25)	2.93 (3)	H(8)···H(23)	2.69
O(2)···C(12)	3.11 (3)	H(9)···H(23)	2.49
O(2)···C(21)	2.89 (3)	H(12)···H(21)	3.14
C(2)···C(15)	3.20 (4)	H(12)···H(25)	2.67
C(3)···C(14)	3.07 (4)	H(1)···H(7)	2.57
C(8)···C(23)	3.11 (3)	H (4)···H(10)	2.60

[a] The errors of the mean values were calculated according to $[\sum(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and $\bar{d}$ are the distance and mean distance, respectively.

Table IV. Interatomic Angles in $[(C_5H_5)Ti(OH)]_2C_{10}H_8$[a]

Ti(1)-O(1)-Ti(2)	98.8 (5)	O(1)-Ti(1)-O(2)	76.0 (5)
Ti(1)-O(2)-Ti(2)	102.7 (6)	O(1)-Ti(2)-O(2)	74.8 (5)
O(1)-Ti(1)-CNT1	108.0 (7)	C(1)-C(2)-C(3)	103.0 (19)
O(1)-Ti(1)-CNT3	108.5 (7)	C(2)-C(3)-C(4)	109.0 (21)
O(2)-Ti(1)-CNT1	107.5 (7)	C(3)-C(4)-C(5)	108.5 (21)
O(2)-Ti(1)-CNT3	108.7 (7)	C(4)-C(5)-C(1)	106.5 (19)
O(1)-Ti(2)-CNT2	108.7 (7)	C(5)-C(1)-C(2)	112.1 (19)
O(1)-Ti(2)-CNT4	108.9 (8)	C(6)-C(7)-C(8)	104.1 (19)
O(2)-Ti(2)-CNT2	106.5 (7)	C(7)-C(8)-C(9)	117.3 (22)
O(2)-Ti(2)-CNT4	108.9 (8)	C(8)-C(9)-C(10)	102.2 (21)
	108.2 (3)	C(9)-C(10)-C(6)	112.7 (22)
		C(10)-C(6)-C(7)	103.5 (20)
CNT1-Ti(1)-CNT3	133.4 (9)	C(11)-C(12)-C(13)	102.6 (18)
CNT2-Ti(2)-CNT4	133.6 (10)	C(12)-C(13)-C(14)	111.0 (19)
	133.5 (1)	C(13)-C(14)-C(15)	106.4 (20)
		C(14)-C(15)-C(11)	114.7 (21)
C(1)-Ti(1)-C(2)	33.8 (8)	C(15)-C(11)-C(12)	105.3 (19)
C(2)-Ti(1)-C(3)	36.0 (8)	C(21)-C(22)-C(23)	101.3 (21)
C(3)-Ti(1)-C(4)	33.4 (8)	C(22)-C(23)-C(24)	113.6 (23)
C(4)-Ti(1)-C(5)	34.8 (8)	C(23)-C(24)-C(25)	105.4 (22)
C(5)-Ti(1)-C(1)	34.7 (7)	C(24)-C(25)-C(21)	108.8 (23)
C(6)-Ti(2)-C(7)	36.0 (8)	C(25)-C(21)-C(22)	110.6 (23)
C(7)-Ti(2)-C(8)	33.6 (8)		107.9 (10)
C(8)-Ti(2)-C(9)	32.6 (8)		
C(9)-Ti(2)-C(10)	34.4 (8)	C(1)-C(5)-C(6)	126.9 (21)
C(10)-Ti(2)-C(6)	35.8 (8)	C(4)-C(5)-C(6)	125.9 (19)
C(11)-Ti(1)-C(12)	35.8 (8)	C(7)-C(6)-C(5)	126.7 (21)
C(12)-Ti(1)-C(13)	35.8 (8)	C(10)-C(6)-C(5)	128.9 (22)
C(13)-Ti(1)-C(14)	33.0 (7)		127.1 (6)
C(14)-Ti(1)-C(15)	32.1 (8)		
C(15)-Ti(1)-C(11)	33.2 (8)	C(31)-O(3)-C(34)	107.9 (27)
C(21)-Ti(2)-C(22)	34.3 (10)	O(3)-C(31)-C(32)	104.2 (30)
C(22)-Ti(2)-C(23)	35.4 (8)	O(3)-C(34)-C(33)	111.5 (34)
C(23)-Ti(2)-C(24)	33.0 (8)	C(31)-C(32)-C(33)	109.9 (34)
C(24)-Ti(2)-C(25)	34.6 (9)	C(32)-C(33)-C(34)	101.5 (34)
C(25)-Ti(2)-C(21)	32.8 (9)		
	34.3 (3)		

[a] Footnote to Table III applies here also. CNT stands for the ring centroid: CNT1 for C(1)-C(5), CNT2 for C(6)-C(10), CNT3 for C(11)-C(15), and CNT4 for C(21)-C(25).

Table V. Least-Squares Planes for $[(C_5H_5)Ti(OH)]_2C_{10}H_8$

Planes and Atom Deviations (Å)[a]

1. $0.6045X + 0.3096Y + 0.7340Z - 9.314 = 0$
   C(1) − 0.02, C(2)0.04, C(3) − 0.05, C(4)0.04, C(5) − 0.01, Ti(1) − 2.073
2. $0.4205X + 0.4954Y + 0.7601Z - 10.404 = 0$
   C(6)0.01, C(7)0.00, C(8) − 0.02, C(9)0.02, C(10) − 0.02, Ti(2) − 2.069
3. $0.5093X + 0.4118Y + 0.7557Z - 9.720 = 0$
   C(1)0.03, C(2) − 0.10, C(3) − 0.18, C(4)0.10, C(5)0.16, Ti(1) − 2.044; C(7)0.04, C(8) − 0.13, C(9) − 0.11, C(10)0.02, C(6)0.16, Ti(2) − 2.046
4. $0.0029X + 0.7384Y + 0.6744Z - 5.630 = 0$
   C(11)0.00, C(12)0.00, C(13)0.01, C(14) − 0.01, C(15)0.01, Ti(1)2.102
5. $0.8392X - 0.1291Y + 0.5283Z - 0.154 = 0$
   C(21) − 0.01, C(22)0.02, C(23) − 0.03, C(24)0.03, C(25) − 0.01, Ti(2)2.074

Dihedral Angles (deg)[b]

Ti(1)O(1)Ti(2) Ti(1)O(2)Ti(2)	147.0	C(6)-C(10) C(21)-C(25)	133.7
C(1)-C(5) C(6)-C(10)	15.1	C(11)-C(15) C(21)-C(25)	105.3
C(1)-C(5) C(11)-C(15)	136.5		

[a] The titanium atoms were not used in the planes calculation. [b] The angles are between the actual planes as opposed to the plane normals.

$(OH)]_2C_{10}H_8$ is weakly paramagnetic (0.84 μ_B, Evans method). This weak paramagnetism, coupled with the somewhat atypical ^{1}H NMR spectra of these two complexes, makes the metal-metal bonding a question still speculative as far as we are concerned. We feel a more detailed study of the magnetic behavior of these complexes would be helpful.

The large thermal motion of the carbon atoms in the THF prevents a good conformational determination. There may be some static disordering involving this molecule; THF is known to have a very low barrier to pseudo-rotation,[40] quite aside from the fact that its position in this cell may be poorly determined. The observed conformation, as well as the magnitudes of the thermal ellipsoids, is shown in Figure 3. The C(33)-C(34) distance of 1.34 (6) Å is surely forshortened by thermal effects; these atoms are the most anisotropic with the largest amplitudes of vibration (maximum root-mean-square amplitude of 0.588 Å for C(33) and 0.560 Å for C(34)). Similar large thermal parameters with large anisotropy were observed in $[C_{16}H_{14}N_2O_2Cl_2Ti]\cdot C_4H_8O$.[41] The twisted configuration is frozen out in the fully substituted complex 3,3,4,4-tetrahy-

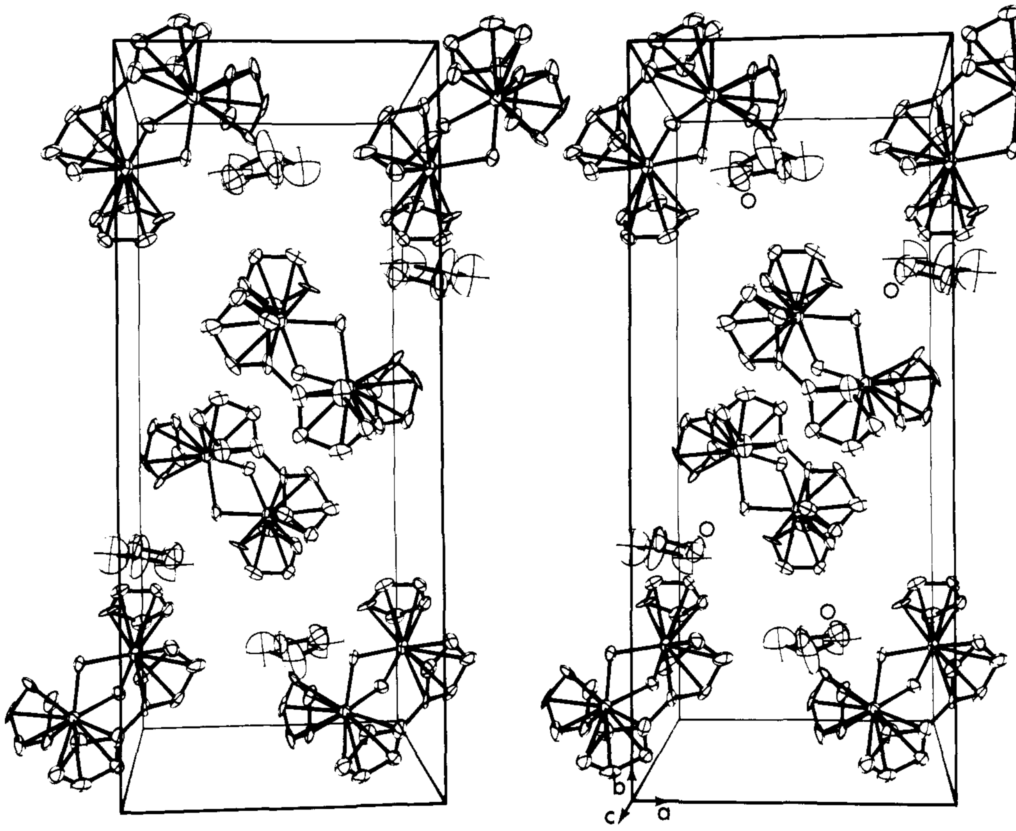


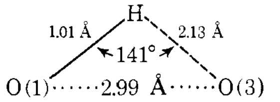
Figure 3. Crystal packing in $[(C_5H_5)Ti(OH)]_2C_{10}H_8{\cdot}C_4H_8O$.

Table VI. M···M Separation, Dihedral Angle, and C-C Separation between C_5 Rings for Fulvalene Ligand

Complex	M···M separation (Å)	Dihedral angle (deg)	C-C separation (Å)
$[(C_5H_4)TiHAlEt_2]_2C_{10}H_8$	2.910	25.8	1.46
$[(C_5H_5)Ti(OH)]_2C_{10}H_8$	3.195	15.1	1.42
$[(C_5H_5)Ti]_2(H)(H_2AlEt_2)C_{10}H_8$	3.374	12.5	1.45
$(C_{10}H_8)_2Fe_2$[39]	3.984	2.6	1.48

drofurantetrol, $C_4H_4(OH)_4O$, where a twist of 44° was observed.[42] The large thermal motions preclude our determining whether the THF position is 100% occupied; we have assumed here that it is. Also, if there is additional THF in the cell it has to be in very small concentrations or very randomly distributed. We note that the densities suggest there could be more solvent in the cell, but the complex reacted so quickly with our liquid mixtures in the flotation method that we cannot estimate the errors associated with the observed density.

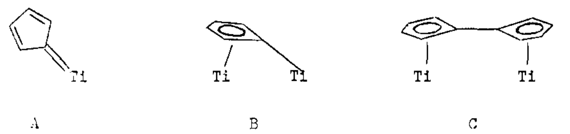
The hydrogen bonding is characterized by

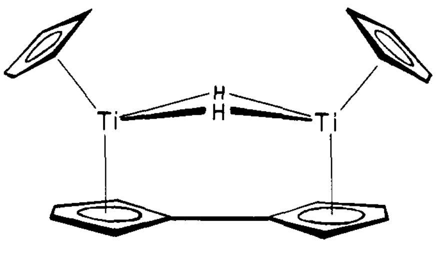


These data fall on the high side for observed hydrogen bonding situations between oxygen donors and acceptors.[43]

The packing is shown in Figure 3. The shortest intermolecular interaction involves H(O2) and the back side of the adjacent fulvalene ligand (2.21 Å to C(7), 2.41 Å to H(7), and 2.52 Å to C(6)). The shortest remaining contacts are 2.37 Å for H···H and 2.69 Å for C···H.

The following models summarize the (C_5H_4) bonding modes considered previously for titanocene. The molecular structure of the hydrolysis product (Figures 2 and 3) shows that C is the correct form for these complexes. The titanocene structure is the same with hydrogens substituted for hydroxyls. This is one of the structures originally postulated by Brintzinger and Bercaw[1] and confirms our structural proposals based on the structures of aluminotitanium hydrides derived from titanocene. It is also consistent with the ^{13}C NMR results of Davison and Wreford.[8]





Supplementary Material Available: A listing of structure factor amplitudes (3 pages). Ordering information is given on any current masthead page.

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Substituent Exchange and Carbon–Oxygen Bond Cleavage with Aryloxycyclophosphazenes[1,2]

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Abstract: Aryloxycyclotriphosphazenes, $[NP(OAr)_2]_3$, such as **I**–**IV**, undergo substituent exchange reactions with organic nucleophiles. This constitutes a route for the preparation of mixed substituent organophosphazenes, some of which are inaccessible by other methods. The ease of displacement of OAr in $[NP(OAr)_2]_3$ by $CF_3CH_2O^-$ decreased with OAr in the order, $OC_6H_4NO_2$-*o* or -*p* > OC_6H_5Cl-*p* ≫ OC_6H_5. When OAr was $OC_6H_4NO_2$-*o* or -*p*, ligand exchange was either accompanied by or replaced by nucleophilic attack at the α-carbon of the aromatic residue. This effect was significant when the attacking nucleophile was $C_6H_5O^-$ or $C_6H_5S^-$, and it predominated when the nucleophile was $C_6H_5NH^-$ or an uncharged primary or secondary amine. The mechanisms of these reactions are discussed.

The majority of known organocyclo- or organopolyphosphazenes has been prepared by the nucleophilic replacement of halogen in halophosphazenes by alkoxide, aryloxide, or amine reagents,[3] by reactions such as:

$$(NPCl_2)_n \xrightarrow[\text{or } RNH_2]{RO^-} [NP(OR)_2]_n \text{ or } [NP(NHR)_2]_n$$

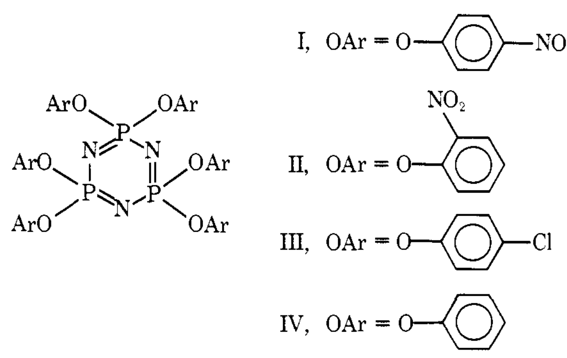
$$(\text{where } n = 3, 4, \text{or} \sim 15\ 000)$$

However, evidence exists from organophosph*ate* chemistry that the replacement of one organic ligand at phosphorus by another can be a facile process.[4] Furthermore, preliminary evidence had been obtained that organic ligand exchange reactions could also occur with cyclophosphazenes.[5] Hence, the prospect existed that the known range of organophosphazene trimers and tetramers might be expanded by the use of organic ligand exchange processes, such as:

$$[NP(OR)_2]_3 + xR'O^- \rightarrow N_3P_3(OR)_{6-x}(OR')_x + xRO^-$$

This work was undertaken with the recognition that ligand exchange data obtained for cyclic trimeric phosphazene systems could ultimately prove valuable for the synthesis of mixed substituent organophosphazene high polymers.[6]

Four aryloxycyclophosphazenes were employed in this investigation. These are depicted as structures I–IV. The solvents employed varied from dimethylformamide (DMF) or hexamethylphosphoramide (HMPA) to dioxane or tetrahydrofuran (THF). A number of attacking nucleophiles were used, including sodium trifluoroethoxide, sodium phenoxide, sodium thiophenoxide, sodium anilide, and various amines.



Two different reaction pathways were identified. The first involved simple replacement of one substituent group at