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# Structure of Hydroxo(methyl)bis(η⁵-pentamethylcyclopentadienyl)tantalum(V) Hydroxotris(pentafluorophenyl)borate

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**Abstract.** $[Ta(C_{10}H_{15})_2(OH)(CH_3)][B(OH)(C_6F_5)_3]$, $M_r = 1001.63$, monoclinic, $P2_1/n$, $a = 12.217\,(2)$, $b = 16.848\,(6)$, $c = 18.834\,(3)$ Å, $\beta = 100.37\,(2)°$, $V = 3813.1\,(15)$ Å$^3$, $Z = 4$, $D_x = 1.75$ g cm$^{-3}$, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 29.52$ cm$^{-1}$, $F(000) = 1972$, room temperature, $R = 0.031$ for 3534 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Ta cation has the expected geometry, with Ta—C and Ta—O distances 2.211 (6) and 1.865 (5) Å, respectively. The anion has not been characterized previously; its geometry is irregular with tetrahedral angles at boron ranging from 103.6 (6) to 113.8 (6)°, and systematic angular distortions in the $C_6F_5$ rings.

**Introduction.** Recent interest in the reactive oxo chemistry of organometallic complexes has increased due to the possible roles of these compounds in the activation of hydrocarbons by the 2 + 2 addition of an aliphatic or aryl C—H bond to the metal oxo moiety. Bent metallocene complexes which would model this reaction chemistry, $[(\eta^5\text{-}C_5H_5)_2\text{-}Zr(OH)(C_6F_5)]$ (Chaudhari & Stone, 1966), $[(\eta^5\text{-}C_5Me_5)_2Hf(OH)Ph]$ (van Asselt, Santarsiero & Bercaw, 1986; Vaughn, Rupert & Hillhouse, 1987), $[(\eta^5\text{-}C_5Me_5)_2Zr(OH)Ph]$ (Schrock & Marks, 1988) and $[(\eta^5\text{-}C_5Me_5)_2Zr(OH)\{CPh=CPhNH(N=CPh_2)\}]$

(Vaughn, Hillhouse & Rheingold, 1990), have been synthesized by routes which do not involve 2 + 2 addition chemistry.

We have been investigating the reaction chemistry of the cation $[(\eta^5\text{-}C_5Me_5)_2Ta(CH_3)_2]^+$ with a variety of counterions. Initial attempts to prepare this cation with perfluorotetraphenylborate as the counterion by the metathesis of $[(\eta^5\text{-}C_5Me_5)_2Ta(CH_3)_2]SO_3CF_3$ with $[NaB(C_6F_5)_4]$ resulted in the isolation of a crystal found to be $[(\eta^5\text{-}C_5Me_5)_2Ta(OH)(CH_3)]$-$[B(OH)(C_6F_5)_3]$. The crystal structure of this complex is described herein.

**Experimental.** Material synthesized by RWQ; pale orange crystal, irregular chunk with maximum dimensions 0.26 × 0.35 × 0.48 mm; CAD-4 diffractometer, $\omega$ scans; 25 reflections with $34 < 2\theta < 37°$ used for cell dimensions; absorption correction based on $\psi$ scans of three reflections and their Friedel mates, with relative transmission from 0.857 to 1.081; $(\sin\theta/\lambda)_{max}$ of 0.54 Å$^{-1}$, $h$ from $-13$ to 0, $k$ from $-18$ to 18, $l$ from $-20$ to 20; three standard reflections ($\bar{3}03$, 015, 025) showed no variation greater than predicted by counting statistics; 10 622 reflections measured, 4975 independent; goodness-of-fit for merging was 1.10 ($R_{merge}$ for 3831 reflections with exactly two observations 0.032); all reflections used in solution and refinement of the structure.

Position of Ta atoms found from Patterson map, remaining atoms located by successive structure factor–Fourier calculations; values of $F^2$ (positive and negative) used in least-squares refinement; H-atom positions obtained from difference maps calculated in their expected planes, with atoms placed at idealized positions except on OH groups; isotropic displacement parameters for H atoms assigned as 1.2 times the equivalent isotropic displacement parameter of the bound C atom; H atoms of Cp*2 (Cp* = pentamethylcyclopentadienyl) were disordered in two sets, arbitrarily given populations of 0.5 each; H-atom parameters not refined, but adjusted once near the conclusion of refinement; positional and anisotropic displacement parameters refined in one full matrix for all other atoms, plus a scale factor and a secondary-extinction parameter (524 parameters). Weights taken as $1/\sigma^2(F_o^2)$. Final $R$ (on $F$) for 4601 reflections with $F_o^2 > 0$ was 0.049, for 3534 reflections with $F_o^2 > 3\sigma(F_o^2)$, $R = 0.031$, $wR$ (on $F^2$) = 0.004, final goodness-of-fit for 4975 total reflections was 1.45. Variances $[\sigma^2(I)]$ derived from counting statistics plus an additional term, $(0.014I)^2$; variances of the merged data by propagation of error plus another additional term, $(0.014I)^2$. In final least-squares refinement, ratio of maximum shift to e.s.d. in any parameter was 0.23; final difference map had peaks of 0.65 e Å$^{-3}$ and holes of up to 0.75 e Å$^{-3}$. The secondary-extinction parameter [Larson (1967), equation (3)] refined to $0.016\,(9) \times 10^{-6}$. Atomic scattering factors and anomalous-dispersion corrections $(f')$ were taken from Cromer & Waber (1974) and Cromer (1974). Computer programs used were those of the *CRYM* crystallographic computing system (Duchamp, 1964) and *ORTEP* (Johnson, 1976). Final refined parameters of the atoms are listed in Table 1.†

**Discussion.** The Ta–bis(Cp*) cation in this structure (Fig. 1) resembles closely other such species whose structures we have determined (van Asselt, Trimmer, Henling & Bercaw, 1988; Schaefer, Henling, Quan & Bercaw, 1991). The Ta–Cp* centroid distances (2.151, 2.153 Å) are at the short end of the normal range and the centroid–Ta–centroid angle (137.3°) is essentially the same as the average found for eight other structures (138.0°). (The centroids are the averages of the five ring C-atom coordinates.) The Ta—O(H) distance, 1.864 (5) Å, is comparable to those we have found earlier [average of three,

Table 1. *Final heavy-atom parameters* $(\times 10^4)$ *for the title compound*

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Ta | 1416 (.2) | 2186 (.2) | 1866 (.1) | 448 (1) |
| O1 | 561 (4) | 1263 (3) | 1786 (2) | 811 (15) |
| C1 | −44 (5) | 2978 (4) | 1605 (3) | 621 (19) |
| Cp1 | 3025 (6) | 2353 (5) | 1246 (3) | 627 (21) |
| Cp2 | 2512 (6) | 1616 (4) | 1058 (3) | 516 (18) |
| Cp3 | 1471 (7) | 1766 (5) | 623 (4) | 625 (22) |
| Cp4 | 1310 (7) | 2589 (6) | 587 (4) | 721 (25) |
| Cp5 | 2260 (8) | 2944 (4) | 982 (4) | 667 (22) |
| Cp6 | 4247 (7) | 2497 (6) | 1493 (4) | 1067 (31) |
| Cp7 | 3042 (8) | 813 (5) | 1200 (4) | 1009 (28) |
| Cp8 | 683 (7) | 1154 (6) | 252 (4) | 1127 (31) |
| Cp9 | 381 (9) | 3008 (7) | 104 (5) | 1473 (41) |
| Cp10 | 2482 (10) | 3839 (5) | 979 (5) | 1370 (39) |
| Cp11 | 1046 (6) | 2193 (5) | 3100 (3) | 655 (18) |
| Cp12 | 1392 (7) | 2978 (4) | 2978 (3) | 624 (22) |
| Cp13 | 2502 (6) | 2959 (4) | 2880 (3) | 551 (19) |
| Cp14 | 2861 (6) | 2161 (5) | 2951 (3) | 620 (18) |
| Cp15 | 1972 (7) | 1699 (4) | 3099 (4) | 631 (21) |
| Cp16 | −48 (7) | 1938 (5) | 3271 (5) | 1018 (27) |
| Cp17 | 753 (7) | 3728 (5) | 3055 (4) | 941 (27) |
| Cp18 | 3225 (7) | 3682 (5) | 2875 (4) | 822 (24) |
| Cp19 | 4042 (7) | 1862 (5) | 3069 (4) | 930 (27) |
| Cp20 | 2033 (8) | 822 (5) | 3275 (4) | 1100 (32) |
| B | 8085 (7) | 115 (5) | 1816 (5) | 631 (25) |
| O2 | 9307 (4) | 111 (3) | 1827 (3) | 833 (19) |
| C11 | 7668 (5) | 955 (4) | 1407 (4) | 500 (18) |
| C12 | 7366 (6) | 1644 (4) | 1693 (4) | 600 (20) |
| C13 | 7147 (6) | 2349 (4) | 1331 (5) | 685 (25) |
| C14 | 7198 (7) | 2378 (5) | 612 (5) | 783 (26) |
| C15 | 7493 (6) | 1722 (5) | 282 (4) | 690 (23) |
| C16 | 7721 (6) | 1036 (4) | 676 (4) | 626 (21) |
| F12 | 7312 (4) | 1679 (2) | 2406 (2) | 887 (14) |
| F13 | 6883 (4) | 3005 (2) | 1678 (3) | 1034 (17) |
| F14 | 6981 (4) | 3067 (3) | 250 (3) | 1137 (17) |
| F15 | 7578 (5) | 1754 (3) | −414 (2) | 1148 (17) |
| F16 | 8028 (4) | 408 (3) | 305 (2) | 926 (14) |
| C21 | 7512 (6) | −689 (4) | 1387 (4) | 561 (19) |
| C22 | 6535 (6) | −738 (4) | 893 (4) | 617 (21) |
| C23 | 6098 (7) | −1418 (5) | 536 (4) | 686 (23) |
| C24 | 6695 (8) | −2097 (5) | 661 (4) | 709 (22) |
| C25 | 7662 (7) | −2111 (5) | 1153 (4) | 710 (23) |
| C26 | 8031 (6) | −1415 (4) | 1496 (4) | 612 (21) |
| F22 | 5899 (3) | −76 (3) | 730 (2) | 887 (15) |
| F23 | 5152 (4) | −1400 (3) | 73 (2) | 1077 (16) |
| F24 | 6311 (4) | −2778 (3) | 322 (2) | 1085 (15) |
| F25 | 8225 (4) | −2789 (3) | 1281 (3) | 1070 (16) |
| F26 | 8991 (4) | −1474 (2) | 1990 (3) | 885 (15) |
| C31 | 7778 (7) | 50 (4) | 2637 (4) | 672 (23) |
| C32 | 6708 (8) | 120 (4) | 2758 (4) | 722 (25) |
| C33 | 6416 (10) | 37 (5) | 3430 (6) | 949 (34) |
| C34 | 7211 (15) | −123 (7) | 4003 (6) | 1259 (53) |
| C35 | 8265 (13) | −217 (7) | 3938 (8) | 1282 (50) |
| C36 | 8532 (10) | −137 (5) | 3254 (6) | 974 (32) |
| F32 | 5884 (4) | 292 (2) | 2198 (2) | 835 (13) |
| F33 | 5301 (6) | 124 (3) | 3483 (3) | 1362 (21) |
| F34 | 6830 (7) | −218 (3) | 4653 (3) | 1792 (29) |
| F35 | 9019 (7) | −384 (4) | 4512 (3) | 1927 (30) |
| F36 | 9625 (5) | −266 (3) | 3226 (3) | 1377 (22) |

1.889 (31) Å] and the Ta—C distance, 2.211 (6) Å, is slightly shorter than Ta—C distances to benzyl C atoms [2.323 (9) and 2.299 (5) Å]. The C—Ta—O angle of 93.8 (2)° is again as expected from other work. The methyl group is 55° to one side of the centroid–Ta–centroid plane, while the OH group is 39° on the other side. In the Cp* rings, the C—C distances average 1.405 (8) Å, the C—CH$_3$ distances average 1.506 (11) Å and the average deviation of an internal angle from 108° is 0.8°; all these are normal values for Cp* groups.

The O1 (on Ta) to O2 (on B) distance is quite short, 2.483 (7) Å, indicating a strong hydrogen bond between these O(H) groups. O1 has no other

neighbor closer than 3.5 Å, whereas O2 has a close approach to F36 [2.671 (7) compared to 2.75 Å for a van der Waals contact]. Thus we expect O1 to donate a hydrogen bond to O2 and O2 to donate a weak one to F36. The angles involved are satisfactory. Because we did not locate these H atoms in difference maps, we can only surmise about the situation.

The hydroxotris(pentafluorophenyl)borate anion shows marked departures in structure from what we had anticipated. We find no references in the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) to this species and only one to a hydroxo(triphenyl)borate (von Dueten, von Schlabrendorff & Klar, 1980), but that is not an isolated ion, so even the B—O distances are not comparable. We find B—O to be 1.490 (10) Å, shorter than the 1.540 (7) Å reported by von Deuten *et al.* Such a difference is to be expected; the B—O bond will be longer if the O atom is bonded to another group – in the example of von Deuten *et al.*, an N atom in an ethylnitrosolato group. The B—C distances in their triphenylborate ion average 1.628 (13) Å, shorter by 0.029 Å than the 1.657 (9) Å we found. Our C—C and C—F distances in the pentafluorophenyl rings are normal [1.370 (17) and 1.353 (22) Å] but the rings show systematic angular distortions related to their substitution, particularly for the C—C—C angle adjacent to BOH at 112.1 (7)° (Domenicano, Vaciago & Coulson, 1975). As explained by Domenicano *et al.*, an electron-donating substituent on a benzene ring leads to a smaller endocyclic angle at the C atom bonded to the substituent and for electron-withdrawing substituents the reverse is true.
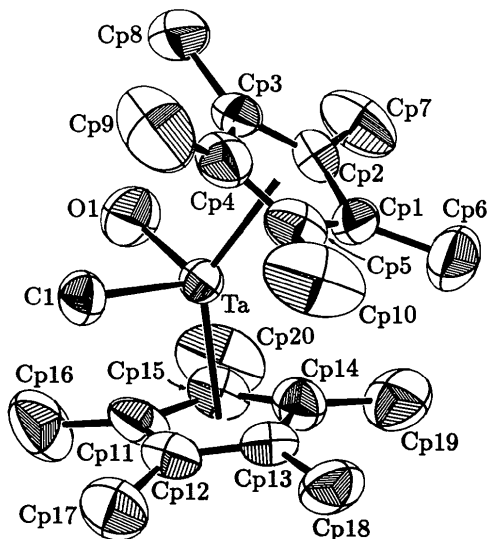
Table 2. *Selected distances* (Å) *and angles* (°) *for the title compound*

| Ta—C1 | 2.211 (6) | B—O2 | 1.490 (10) |
| Ta—O1 | 1.865 (5) | B—C11 | 1.648 (11) |
| Ta–Cp*1 | 2.151 (1)† | B—C21 | 1.665 (11) |
| Ta–Cp*2 | 2.153 (1) | B—C31 | 1.658 (11) |
| | | | |
| O1—Ta—C1 | 93.8 (2) | C11—B—O2 | 103.6 (6) |
| Cp*1–Ta–Cp*2 | 137.3 | C21—B—O2 | 109.6 (6) |
| Cp*1–Ta—O1 | 106.3 (1) | C31—B—O2 | 112.5 (6) |
| Cp*1–Ta—C1 | 101.9 (2) | C21—B—C11 | 113.8 (6) |
| Cp*2–Ta—O1 | 106.6 (1) | C31—B—C11 | 112.9 (6) |
| Cp*2–Ta—C1 | 102.3 (2) | C31—B—C21 | 104.7 (6) |

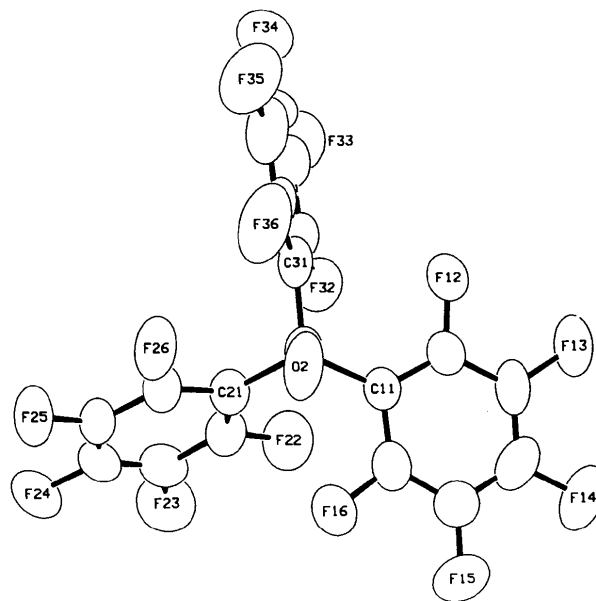† Cp*1 and Cp*2 are the centroids of the five C atoms of the Cp* rings.



Fig. 2. An *ORTEP* drawing of the tris(pentafluorophenyl)borate anion with the atom-numbering system indicated (F12 bonded to C12, *etc.*). The view is perpendicular to the plane of C11, C21 and C31 and the ellipsoids are shown at the 50% probability level.

In this anion we have two types of substituents, F atoms and a BOH group. The F atoms all tend to increase the angle at their C atom and since there are five the remaining endocyclic angle is reduced, generally by 3–4° (Domenicano *et al.*, 1975). The BOH group is an electron-releasing group and its tendency will be to reduce the endocyclic angle at the C atom to which it is bonded. Thus the two effects reinforce each other and the result is an average angle of 112.1 (7)° in the three phenyl rings, close to the smallest observed in the phenyl rings of tetraphenylborate ions. The Cambridge Structural Database (Allen *et al.*, 1983) contains 301 examples of such ions, with the smallest endocyclic angle at the C atom bonded to the B atom being 111.2° and 35 (of 1204 angles) being smaller than 113°. The adjacent angles in all three rings expand to an average value of 125.2 (9)° to maintain the planarity of the group



Fig. 1. An *ORTEP* drawing of the cation showing the atom-numbering system with thermal ellipsoids at the 50% probability level.

(the sums of the interior angles are 719.9, 720.0 and 719.9°). The B atom is in the plane of the phenyl ring as shown by the sum of the angles at the C atom bonded to it (359.6, 359.9 and 359.7°). The three pentafluorophenyl groups, instead of being propeller blades about the B—O axis, are each oriented differently. The plane of the first is almost perpendicular to that axis, the plane of the second is at an angle of about 20° and the plane of the third is nearly parallel to it (Fig. 2). The B···o-F distances range from 2.88 to 3.07 Å, all greater than van der Waals contacts, but the O2···F26 and O2···F36 distances are short, 2.723 (6) and 2.671 (7) Å, respectively, compared to 2.75 Å for a van der Waals contact.

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# Bis[di(imidazol-2-yl)phosphinato-$N^3$,$N^{3'}$]platinum(II) Tetrahydrate

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**Abstract.** [Pt{(C$_3$H$_3$N$_2$)$_2$O$_2$P}$_2$].4H$_2$O, $M_r = 661.4$, triclinic, $P\bar{1}$, $a = 7.473$ (1), $b = 7.779$ (2), $c = 9.787$ (2) Å, $\alpha = 109.46(3)$, $\beta = 98.56$ (3), $\gamma = 98.29$ (3)°, $V = 518.9$ (3) Å$^3$, $Z = 1$, $D_m = 2.11$ (1), $D_x = 2.116$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71073 Å, $\mu = 7.038$ mm$^{-1}$, $F(000) = 320$, $T = 293$ (1) K, $R = 0.0268$, $wR = 0.0324$ for 4521 unique reflections and 136 parameters. The ligand molecule is chelated through the N(3) atoms of the imidazole rings to the Pt atom, which lies on an inversion centre. Bond lengths and angles are normal.

**Introduction.** We have previously prepared di(imidazol-2-yl)phosphinic acid (Howard-Lock, Lock, Penny & Turner, 1989) and characterized some of its iron, copper and zinc complexes (Seidel, 1990). Ball, Brown & Cocho (1984) have prepared the zinc complex of a related C(4),C(5)-substituted acid and characterized the compound by X-ray crystallography. In all these complexes the metal is bound to the N(3) atom of one of the rings and to one of the O atoms of the phosphinate group. This is hardly surprising, since the acid exists in the zwitterion form. Both N atoms in the second imidazole ring are protonated, and thus unavailable for coordination. It was of interest, therefore, to prepare a platinum(II) complex of this acid in which one might obtain an N$_2$O$_2$ coordination arrangement. We were unsuccessful, however, and the title compound was obtained instead. The compound was prepared by the direct reaction of aqueous solutions of phosphinic acid (0.2 g in 10 mL) and potassium tetrachlo-

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