

layers. The P_3O_9 ring anion has a twofold symmetry through the P(2) atom and the O(L11) bonding oxygen atom. This kind of internal symmetry has up to now never been observed for this type of anion. The K atom located halfway between P_3O_9 layers (Fig. 1) has an eightfold coordination made by six external O atoms of the ring anion and two bonding O atoms of this ring. The participation of bonding O atoms of a phosphoric ring to a metal coordination is rather rare in condensed phosphate chemistry.

Table 2 reports the main interatomic distances and bond angles in the various entities of the arrangement and gives the numerical data corresponding to the three-dimensional network of hydrogen bonds connect-

ing the NH_3 radicals to the external oxygen atoms of the P_3O_9 ring anions.

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Structure of a Permethyl Zirconocene Ylide Complex:



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Abstract. (Dimethylphosphinodimethylidene-*C,C'*-hydridobis(pentamethylcyclopentadienyl)zirconium, $C_{24}H_{41}PZr$, $M_r = 451.78$, monoclinic, $P2_1/c$, $a = 13.7765$ (14), $b = 10.9262$ (12), $c = 15.9459$ (19) Å, $\beta = 93.358$ (9)°, $V = 2396.1$ (8) Å³, $Z = 4$, $D_x = 1.25$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 5.2$ cm⁻¹, $T \approx 290$ K, $F(000) = 960$; S (goodness-of-fit) = 2.20 (5540 reflections), $R = 0.077$ (4990 reflections, $I > 0$), $R = 0.052$ (3456 reflections, $I > 3\sigma$). Important structural features: Zr–C(1), 2.486 (5), Zr–C(2), 2.467 (6), Zr–H, 1.88 (4) Å, C(1)–Zr–C(2), 65.9 (2)°.

Introduction. Phosphorus ylides are used commonly as methylene transfer reagents in organic synthesis. Recently, phosphoranes have found application as reagents in the synthesis of organometallic compounds. Permethylzirconocene dihydride, $Cp_2^*ZrH_2$ (Me \equiv CH₃, $Cp^* \equiv$ C₅Me₅; Wolczanski, Threlkel & Bercau, 1979), reacts with a threefold excess of CH₂PMe₃ at room temperature to generate two permethylzirconocene complexes: $Cp_2^*Zr(H)Me$, 71%,

and $Cp_2^*Zr(H)CH_2PMe_2CH_2$, 29%; the latter can also be cleanly generated by the reaction of two equivalents of CH₂PMe₃ with $Cp_2^*Zr(H)Cl$ (Hillhouse & Bercau, 1984) at room temperature for 12 h (Moore, 1984). We report herein on the structure of $Cp_2^*Zr(H)CH_2PMe_2CH_2$.

Experimental. Orange crystals from toluene, air-sensitive, sealed in glass capillary under N₂. Crystal size 0.20 × 0.30 × 0.40 mm. Space group $P2_1/c$ by oscillation and Weissenberg photographs (systematic absences: $h0l$ for l odd, $0k0$ for k odd). Diffractometry: Syntex $P2_1$, graphite monochromator, Mo $K\alpha$ radiation. Lattice constants by least-squares refinement of 15 average 2θ values (four settings for each reflection: $\pm\theta$, $\pm\omega$, φ , χ and $\pm\theta$, $\pm\omega$, $\varphi+\pi$, $-\chi$; $25 \leq 2\theta \leq 40^\circ$). Intensity measurements: 12020 reflections ($+h\pm k\pm l$), $2\theta \leq 55^\circ$, θ – 2θ scans at 2.02° min⁻¹ with 2θ width of 2.0° plus angular dispersion; scan-time-to-background-time ratio $r = t_s/t_b = 2.0$; stationary-counter-stationary-crystal background counts fore and aft. Four check reflections every 96 reflections; no decomposition. No absorption correction, averaging over $2/m$ symmetry, preliminary scaling by Wilson (1942) plot. Structure derivation: Patterson and electron density maps. Refinement: full-matrix least squares on F^2 , all reflections, weights w , $w^{-1} = [s + r^2b + (0.02s)^2]k^4 / (Lp)^2$ (s = scan counts, b = total background counts,

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k = scale factor), anisotropic Gaussian amplitudes for Zr, P, C(1), C(2), C(M1) and C(M2), isotropic otherwise, atomic form factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for Zr and P.

The coordinates of H atoms were determined from difference Fourier maps, and only five H atoms were refined. CRYRM program library (Duchamp, 1964); final S (goodness-of-fit) = 2.20 (5540 total averaged reflections, 234 parameters), R = 0.077 (4990 reflections, $I > 0$), R = 0.052 (3456 reflections, $I > 3\sigma$), maximum peak 0.7 e Å⁻³ in final ΔF map, mean and maximum ratio of shift/e.s.d. in final cycle: 0.05 and 0.10. The coordinates and U 's are given in Table 1.

Discussion. The molecular structure is depicted in Fig. 1† with selected bond lengths and angles. The structure can be described as a distorted trigonal bipyramid with H and C(1) axial and R_1 , R_2 (ring centroids) and C(2) equatorial. A better description recognizes a pocket for the ylide created by the steric bulk of the Cp* groups, and the pocket is referred to as the equatorial wedge, with the Cp* rings axial. H and C(1) reside in lateral sites, and C(2) sites in the central site of the wedge. The Cp* ligands are disordered and attempts to model this disorder resulted in a 60:40 ratio of electron density for rings A and B ; A is tilted from B by about 3° in each case. No unusual non-bonding contacts between the H atoms of the pentamethylcyclopentadienyl ligands and atoms of the metallacycle ring are observed. The atom numbering is indicated in Fig. 2.

The atoms of the metallacycle ring are very nearly coplanar, with the P atom displaced from the plane by 0.05 Å. The Zr—C [2.486 (5), 2.467 (6) Å] and P—C [1.735 (5), 1.713 (6) Å] bond lengths, and the C—Zr—C, 65.9 (2)°, and C—P—C, 102 (3)°, angles are similar to that of Zr₂[(CH₂)₂PMe₂]₄(μ -CPMe₃)₂ (Rice, Ansell, Modrick & Zentz, 1983). In contrast, the Zr—C bond lengths are unusually long when compared with those observed for typical zirconocene-alkyl complexes, e.g. Cp₂Zr(CH₂SiMe₃)₂ (2.28 Å) or Cp₂Zr(CH₂CMe₃)₂ (2.29 Å; Jeffrey, Lappert, Luong-Thi, Webb, Atwood & Hunter, 1981), or zirconocene-acyl complexes, e.g. Cp₂Zr(COCH₃)CH₃ (2.34 Å; Fachinetti, Floriani, Marchetti & Merlino, 1976). However, the sterically encumbered molecule Cp₂Zr(CHPh)₂ displays an average Zr—C bond length of 2.51 Å (Atwood, Barker, Holton, Hunter, Lappert & Pearce, 1977), suggesting perhaps, that the long Zr—C bond lengths are characteristic of steric crowding in the

Table 1. Atom coordinates ($\times 10^4$) and B 's or U_{eq} 's ($\text{Å}^2 \times 10^4$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Zr	x	y	z	U_{eq} * or B
P	2444.8 (3)	196.4 (3)	2506.4 (3)	388 (1)*
C(1)	1515.4 (10)	922.9 (11)	722.3 (7)	613 (4)*
C(2)	2550 (4)	1516 (5)	1245 (3)	607 (19)*
C(M1)	1106 (4)	-106 (6)	1431 (3)	555 (21)*
C(M2)	636 (5)	2059 (6)	395 (5)	1114 (32)*
C(11A)	1732 (5)	243 (7)	-263 (4)	1512 (33)*
C(11B)	2019 (6)	785 (6)	4022 (4)	3.23 (11)
C(12A)	1205 (5)	1156 (6)	3501 (4)	3.09 (11)
C(13A)	1510 (5)	2125 (7)	3004 (4)	3.36 (11)
C(14A)	2511 (7)	2348 (6)	3197 (5)	3.85 (13)
C(15A)	2825 (5)	1539 (8)	3845 (5)	3.61 (13)
C(21A)	1951 (6)	-127 (8)	4732 (5)	6.65 (19)
C(22A)	172 (6)	734 (7)	3544 (5)	6.18 (18)
C(23A)	843 (7)	2968 (8)	2476 (6)	6.73 (20)
C(24A)	3141 (7)	3392 (8)	2919 (6)	6.75 (20)
C(25A)	3740 (7)	1664 (8)	4418 (6)	7.29 (22)
C(11B)	1554 (9)	651 (10)	3784 (7)	3.96 (19)
C(12B)	1184 (9)	1502 (11)	3187 (7)	4.07 (19)
C(13B)	1925 (10)	2328 (9)	2991 (7)	3.56 (18)
C(14B)	2754 (7)	2019 (10)	3479 (7)	3.18 (17)
C(15B)	2541 (9)	994 (10)	3990 (6)	3.21 (17)
C(21B)	1015 (12)	-293 (14)	4268 (10)	9.17 (40)
C(22B)	104 (12)	1508 (14)	2921 (10)	8.68 (39)
C(23B)	1723 (11)	3478 (12)	2517 (9)	7.79 (34)
C(24B)	3694 (13)	2704 (14)	3553 (10)	8.96 (40)
C(25B)	3129 (11)	585 (12)	4778 (9)	7.60 (34)
C(31A)	3843 (6)	-1094 (7)	3125 (4)	3.43 (11)
C(32A)	4228 (5)	-352 (7)	2477 (5)	4.00 (12)
C(33A)	3807 (6)	-801 (7)	1697 (5)	4.15 (13)
C(34A)	3134 (6)	-1749 (7)	1873 (5)	3.96 (13)
C(35A)	3165 (5)	-1911 (6)	2760 (5)	3.77 (12)
C(41A)	4311 (7)	-1203 (8)	4002 (6)	6.94 (21)
C(42A)	5004 (7)	559 (8)	2572 (6)	7.23 (21)
C(43A)	4159 (7)	-521 (8)	844 (6)	7.12 (21)
C(44A)	2592 (7)	-2620 (8)	1278 (6)	6.64 (20)
C(45A)	2690 (7)	-2927 (7)	3244 (6)	6.48 (19)
C(31B)	4187 (7)	-682 (9)	2914 (7)	3.25 (16)
C(32B)	4198 (8)	-365 (10)	2051 (7)	3.69 (17)
C(33B)	3574 (8)	-1214 (9)	1623 (7)	3.27 (17)
C(34B)	3160 (8)	-1976 (9)	2200 (7)	3.54 (18)
C(35B)	3538 (8)	-1634 (10)	3002 (7)	3.50 (17)
C(41B)	4954 (12)	-255 (14)	3578 (10)	8.99 (39)
C(42B)	4897 (11)	535 (13)	1758 (10)	8.23 (37)
C(43B)	3559 (11)	-1358 (13)	682 (9)	7.88 (35)
C(44B)	2552 (11)	-3048 (13)	1958 (10)	7.70 (34)
C(45B)	3364 (12)	-2362 (13)	3765 (10)	8.20 (37)
H	1564 (29)	-1052 (33)	2759 (23)	6.25 (99)

coordination (equatorial) wedge of the Zr center. The P—C(1) and P—C(2) bond lengths are somewhat shorter than expected for a single P—C bond (1.84 Å; Dunitz, 1979), implying electron delocalization throughout the CH₂—P—CH₂ frame. (The P—CH₃ bond lengths appear to be short owing to the high librational motion of the methyl groups on P, and are hence unreliable.) The Zr—H bond length of 1.88 (4) Å is reasonable for a terminal hydride of an early transition metal, e.g. 1.78 Å [(C₅H₄CH₃)₂ZrH(μ -H)] (Jones & Peterson, 1981) or 1.90 Å [Cp₂W=CHO—Zr(H)Cp₂*] (Wolczanski, Threlkel & Santarsiero, 1983).

The metallated ylide complex is one of the few structurally characterized Cp₂ZrL₃-type compounds. Similar compounds whose structures have been established by X-ray diffraction are Cp₂Zr(COMe)Me (Fachinetti, Floriani, Marchetti & Merlino, 1976), Cp₂Zr(Cl)SNMe₂S (Silver, Eisenstein & Fay, 1983), and Cp₂Zr(OCCH₂)(pyridine) (Moore, Straus, Armantrout, Santarsiero, Grubbs & Bercaw, 1983). In

† Lists of structure factors, anisotropic Gaussian amplitudes, H-atom parameters, a complete list of bond lengths and angles, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51145 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

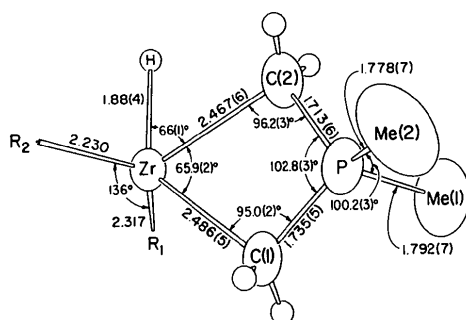


Fig. 1. The metallacycle with bond lengths (Å) and angles.

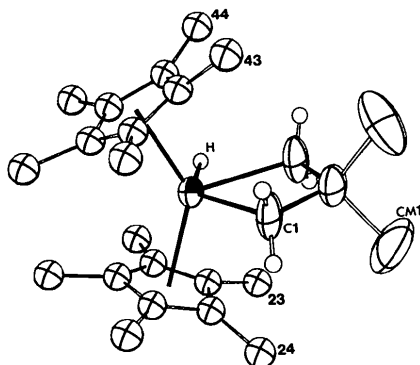


Fig. 2. General view of the title complex, with atom numbering indicated.

each case the internal L (lateral)–Zr– L (central) angles are approximately 65° , whereas the L –Zr– L angle in Cp_2ZrL_2 -type compounds is approximately 95° ; this suggests that there is some compression of the ligands in the equatorial wedge.

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Structure of the Extraction Complex Bis[(dicyclohexano-18-crown-6)oxonium]* Hexanitratothorate(IV) Isomer A

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Abstract. $[(H_3O)(C_{20}H_{36}O_6)]_2[Th(NO_3)_6]$, $M_r = 1483.22$, m.p. = 432 K, triclinic, $P\bar{1}$, $a = 10.713$ (1),

* Dicyclohexano-18-crown-6 = 2,5,8,15,18,21-hexaoxatricyclo-[20.4.0.0^{9,14}]hexacosane.

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