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The Structures of Two Permethylzirconocene Ketene Isomers: (O-*l*)- and (O-*c*)-$[\eta^5\text{-}C_5(CH_3)_5]_2Zr[COCHP(CH_3)_3]H$†

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Abstract. (O-*l*)-Hydridobis(η-pentamethylcyclopentadienyl)(trimethylphosphinoketene)zirconium–toluene (2/1), $C_{25}H_{41}OPZr.\frac{1}{2}C_7H_8$, $M_r = 525{\cdot}86$, monoclinic, $P2_1/n$, $a = 15{\cdot}125\,(3)$, $b = 10{\cdot}646\,(4)$, $c = 18{\cdot}306\,(4)$ Å, $\beta = 90{\cdot}168\,(25)°$, $V = 2948\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}19$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}35$ cm^{-1}, $F(000) = 1116$, $T \simeq 290$ K, S (goodness-of-fit) $= 4{\cdot}25$ (1192 reflections), $R = 0{\cdot}109$ (1108 reflections, $I > 0$), $R_{3\sigma} = 0{\cdot}086$ (847 reflections, $I > 3\sigma$). (O-*c*)-Hydridobis(η-pentamethylcyclopentadienyl)(trimethylphosphinoketene)zirconium, $C_{25}H_{41}OPZr$, $M_r = 479{\cdot}79$, monoclinic, $P2_1/c$, $a = 9{\cdot}9362\,(12)$, $b = 10{\cdot}0229\,(12)$, $c = 25{\cdot}937\,(3)$ Å, $\beta = 96{\cdot}262\,(10)°$, $V = 2567{\cdot}5\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}24$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu = 4{\cdot}93$ cm^{-1}, $F(000) = 1016$, $T \simeq 290$ K, $S = 1{\cdot}52$ (4800), $R = 0{\cdot}042$ (4413 reflections, $I > 0$), $R_{3\sigma} = 0{\cdot}028$ (3486 reflections, $I > 3\sigma$). The cyclopentadienyl rings coordinate to Zr to form a binding pocket at the Zr atom called the equatorial wedge. In the O-*l* isomer the O atom is on a lateral coordination site (external in the equatorial wedge) while the O-*c* isomer has the O atom on the central (internal) coordination site in the equatorial wedge.

Introduction. Although the metallated ylide complex $Cp^*_2\overline{Zr(H)CH_2(PMe_2)C}H_2$ ($Me \equiv CH_3$, $Cp^* \equiv C_5Me_5$) is unreactive towards H_2 and ethylene, it does react with CO at 273 K to generate the η^2-acyl-hydride complex (*A*), (O-*l*)-$Cp^*_2Zr(COCHPMe_3)(H)$ (O-$l \equiv$ oxygen lateral; Moore, 1984). If the sample is allowed to warm to room temperature, a second η^2-acyl-hydride complex (*B*), (O-*c*)-$Cp^*_2Zr(COCHPMe_3)(H)$ (O-$c \equiv$ oxygen central), is found to be in equilibrium with (*A*) ($K_{eq} = 1{\cdot}58$, $A \rightleftharpoons B$ 298 K). Notable NMR and IR spectroscopic differences: ^{1}H NMR, $(Zr\text{—}\underline{H})$ (*A*) δ 3·90, (*B*) δ 4·30; ν_{CO}, (*A*) 1427, (*B*) 1417 cm^{-1} (Moore, 1984). We report herein on the structures of (*A*) and (*B*).

Experimental. (O-*l*): Blue-white crystals from toluene, air-sensitive, sealed in glass capillary under N_2, 0·25 × 0·30 × 0·60 mm. Space group $P2_1/n$ by oscillation and Weissenberg photographs (systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd). Diffractometry: Syntex $P2_1$,

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graphite monochromator. Lattice constants by least-squares refinement of fifteen average 2θ values (two settings for each reflection: $\pm\theta$, $\pm\omega$, φ, χ; $20 < 2\theta < 25°$). Intensity measurements: 2838 reflections ($+h$, $\pm k$, $\pm l$; $h_{\max}=11$, $k_{\max}=7$, $l_{\max}=13$), $2\theta \leq 20°$, θ–2θ scans at 5·86° min^{-1} with 2θ width of 2·4° plus angular dispersion, ~40 h exposure time; scan-time-to-background-time ratio r = 1·0; stationary-counter–stationary-crystal background counts fore and aft. Three check reflections, every 97 reflections, −5% overall decomposition. (Substantial decomposition and poor diffraction for next shell of data limited useful data to $2\theta < 20°$.) No absorption correction, averaging over $2/m$ symmetry, preliminary scaling on F_o by Wilson (1942) plot. Structure derivation: Patterson and electron density maps. Refinement: full-matrix least squares on F^2, all reflections, weights w, $w^{-1} = [s + r^2b + (0{\cdot}02s)^2]k^4/(\mathrm{Lp})^2$ (s = scan counts, b = total background counts, k = scale factor), mixed isotropic and anisotropic Gaussian amplitudes, atomic form factors from *International Tables for X-ray Crystallography* (1974), including f' and f'' for Zr. Toluene disorder over center of symmetry, coordinates from ΔF map; no H-atom coordinates included. *CRYRM* program library (Duchamp, 1964); final S(goodness-of-fit) = 4·52 (1192 total, averaged reflections, 203 parameters), R=0·109 (1108 reflections, $I>0$), $R_{3\sigma}$=0·086 (847 reflections, $I > 3\sigma$), maximum peak 1 e Å^{-3} in final ΔF map, mean and maximum ratio of shift/e.s.d. in final cycle: 0·05 and 0·10. Owing to the poor precision of the derived results, the coordinates and U's have been deposited.*

(O-c): Colorless crystals from toluene, air-sensitive, sealed in glass capillary under N_2, 0·3 × 0·3 × 0·3 mm. Space group $P2_1/c$ by oscillation and Weissenberg photographs (systematic absences: $h0l$ for l odd, $0k0$ for k odd). Diffractometry as above. Lattice constants: 15 average 2θ values (two settings: $\pm\theta$, $\pm\omega$, φ, χ; $25 \leq 2\theta \leq 40°$). Intensity measurements: 10 174 reflections ($+h$,$\pm k$,$\pm l$; $h_{\max} = 12$, $k_{\max} = 7$, $l_{\max} = 13$), $2\theta \leq 51°$, θ–2θ scans at 2° min^{-1} with 2θ width of 1·9° plus angular dispersion; r = 1. Three check reflections, every 97 reflections – no decomposition. No absorption correction, averaging over $2/m$ symmetry, scaling on F_o by Wilson (1942) plot; 35 reflections with unusual backgrounds deleted. Structure derivation and refinement as above; all non-H atoms anisotropic, all H atoms refined. S = 1·52 (4800 reflections, 417 parameters), R=0·042 (4413 reflections, $I>0$), $R_{3\sigma}$=0·028 (3486 reflections, $I > 3\sigma$), maximum peak 0·40 e Å^{-3}, in final ΔF map, mean and maximum ratio of shift/e.s.d. in the final cycle: 0·05 and 0·10. The coordinates and U's are given in Table 1. The C=C(H)P(CH$_3$)$_3$ group can be modelled as a rigid-body unit and corrected bond lengths and angles are reported here (*THMB*-3; Trueblood, 1978).

Table 1. *Atom coordinates for* (B)

	x	y	z
Zr	0·21779 (2)	0·23647 (2)	0·12409 (1)
P	−0·12805 (8)	0·54373 (7)	0·17243 (3)
C1	0·0616 (3)	0·3899 (2)	0·1328 (1)
C2	−0·0320 (3)	0·4904 (3)	0·1246 (1)
O	0·0815 (2)	0·3239 (2)	0·1763 (1)
C3	−0·2230 (3)	0·4163 (3)	0·1993 (2)
C4	−0·2457 (5)	0·6666 (4)	0·1457 (2)
C5	−0·0304 (4)	0·6160 (4)	0·2268 (1)
C11	0·0139 (3)	0·0961 (3)	0·0916 (1)
C12	0·0418 (3)	0·1747 (3)	0·0492 (1)
C13	0·1657 (3)	0·1318 (3)	0·0342 (1)
C14	0·2153 (3)	0·0274 (3)	0·0675 (1)
C15	0·1202 (3)	0·0050 (2)	0·1029 (1)
C21	0·4728 (2)	0·2401 (3)	0·1485 (1)
C22	0·4543 (3)	0·2942 (3)	0·0978 (1)
C23	0·3833 (3)	0·4158 (3)	0·1005 (1)
C24	0·3644 (3)	0·4394 (3)	0·1530 (1)
C25	0·4173 (3)	0·3303 (3)	0·1822 (1)
C31	−0·1121 (3)	0·1044 (3)	0·1192 (2)
C32	−0·0518 (4)	0·2722 (4)	0·0188 (1)
C33	0·2178 (4)	0·1724 (4)	−0·0162 (1)
C34	0·3355 (3)	−0·0626 (3)	0·0619 (2)
C35	0·1235 (4)	−0·1074 (3)	0·1411 (2)
C41	0·5496 (3)	0·1164 (3)	0·1655 (1)
C42	0·5238 (3)	0·2464 (4)	0·0524 (1)
C43	0·3491 (4)	0·5121 (4)	0·0563 (2)
C44	0·3093 (3)	0·5647 (3)	0·1747 (2)
C45	0·4232 (3)	0·3161 (4)	0·2403 (1)
H	0·2437 (21)	0·1218 (21)	0·1820 (9)

Discussion. The Cp* rings bind in the traditional pentahapto fashion with average Zr—C bond lengths of 2·56 Å. The steric bulk of the Cp* rings creates a binding pocket at the zirconium center for additional ligation; the pocket is denoted as the equatorial wedge. The Cp* methyl groups are not coplanar with the rings, but are bent back away from Zr, on average by 0·16 Å.

Although the hydride atom was not located in (A), the disposition of the O atom and the Zr—C1—C2—P unit from the R_1—Zr—R_2 plane ($R \equiv$ Cp*-ring centroid) indicates a lateral (external in the equatorial wedge) coordination site for the O atom (Fig. 1). The PMe$_3$ group is Z relative to the OZrCp$_2^*$ moiety, and the Zr, O, C1, C2 and P atoms are all coplanar. The crystal structure of (A) is rather imprecise, and it is therefore difficult to make valid comparisons with other η^2-acyl complexes. However, it is important to note that the structure of Cp$_2^*$Th(COCHCMe$_3$)Cl (Fagan, Manriquez, Marks, Day, Vollmer & Day, 1980) is the only other structurally characterized example of an (O-l) acyl complex.

In contrast to the structure of (A), the η^2-acyl O atom of (B) occupies the central (internal) coordination site in

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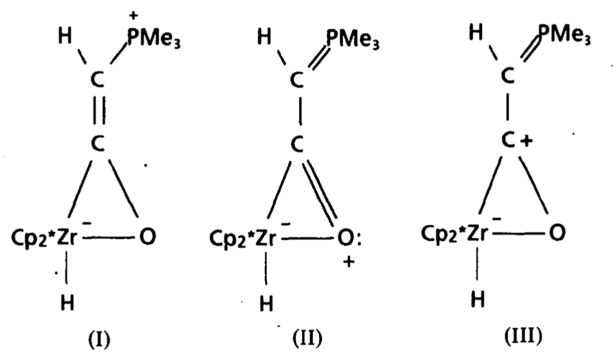
* All fractional atom coordinates and U's for (A), fractional atom coordinates for H atoms, anisotropic Gaussian amplitudes for non-H atoms, complete listing of bond lengths and angles, least-squares-plane information, and a listing of structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51509 (42 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the equatorial wedge. Similar to (*A*), the PMe_3 group is *Z* relative to the $OZrCp_2^*$ fragment about the olefinic bond, and the H, Zr, O, C1, C2 and P atoms (Fig. 2) are all approximately coplanar.

The structure of (*B*) is very similar to that reported for the Zr–ketene $Cp_2^*Zr(COCH_2)$–pyridine (Moore, Straus, Armantrout, Santarsiero, Grubbs & Bercaw, 1983), Zr–acetyl $Cp_2Zr(COCH_3)(CH_3)$ (hereafter FFMM; Fachinetti, Floriani, Marchetti & Merlino, 1976) or the trinuclear Zr_2,Al–ketene complexes $[Cp_2Zr(OCCHR)]_2(\mu\text{-}AlR'_2)(\mu\text{-}X)$ (Waymouth, Santarsiero, Coots, Bronikowski & Grubbs, 1986). In each case, the O atom is at a central coordination site and the C atom is at a lateral coordination site in the equatorial wedge. The electronic structure of (*B*) is best represented as a composite of three canonical forms.



The metrical details of the ketene complexes, *cf.* $[Cp_2Zr(OCCHC_2H_5)]_2(\mu\text{-}AlMe_2)(\mu\text{-}Me)$ (Waymouth, Santarsiero & Grubbs, 1984), with roughly equal Zr—O and Zr—C bond lengths of 2·18 Å, and C—O and C=C bond lengths of 1·40 and 1·32 Å, respectively, suggest that (I) is the dominant contributor. In contrast, the acetyl complex FFMM, with bond lengths Zr—O 2·29, Zr—C 2·20, C=O 1·21 and C—C 1·49 Å, suggest that (II) is the dominant form. For (*B*), both (I) and (II) are dominant resonance forms, and the contribution of (III) leads to somewhat lengthened Zr—C and C—C bond lengths, and a shortened P—C2 bond length of 1·73 Å.

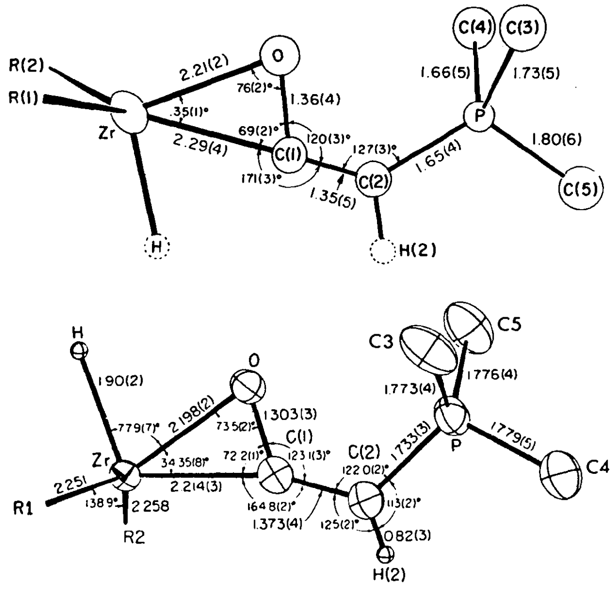


Fig. 1. Skeletal views of (*A*) and (*B*) with bond lengths (Å) and angles.

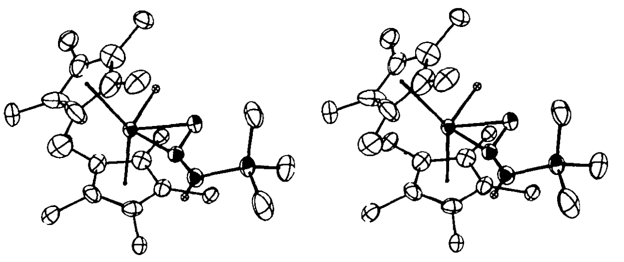


Fig. 2. Stereoview of (*B*) isomer.

The Zr–H bond length of 1·89 (2) Å is reasonable [*cf.* 1·88 (4) Å, $Cp_2^*Zr(H)CH_2PMe_2CH_2$ (Moore & Santarsiero, 1988); 1·93 (4) Å, $Cp_2W{=}C(H)OZr(H)Cp_2^*$ (Wolczanski, Threlkel & Santarsiero, 1983)].

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