# Structural Isomers of a Terminal Phosphinidene Complex

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The reactions of ArP(Li)($SiMe_3$) (Ar = 2,4,6-$Bu^t_3C_6H_2$) with $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $(\eta^5\text{-}C_5H_4Me)_2WCl_2$ afford $(\eta^5\text{-}C_5H_5)_2Zr(Cl)P(SiMe_3)(Ar)$ and two isomers of composition $(\eta^5\text{-}C_5H_4Me)WH[\eta^5\text{-}C_5H_3Me(PAr)]$, respectively, the structures of which have been determined.

In a series of elegant studies, Mathey *et al.*[1] have demonstrated the viability of transient terminal phosphinidene complexes in the vapour phase. However, to date these interesting species have eluded isolation. Since several multiply-bonded phosphorus compounds have been stabilised kinetically,[2] we were prompted to employ the bulky group strategy in an attempt to produce an isolable terminal phosphinidene complex.

Treatment of $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ with an equimolar quantity of ArP(Li)($SiMe_3$) in $Et_2O$ solution at 0 °C, followed by solvent removal, n-hexane extraction, and crystallisation, resulted in an 85% yield of red $(\eta^5\text{-}C_5H_5)_2Zr(Cl)P(SiMe_3)(Ar)$, (**1**) ($^{31}P$ n.m.r., +156 p.p.m.). The constitution of (**1**) was established by 70 eV electron impact mass spectrometry ($M^+$, $m/z$ 604), and the structure was elucidated by *X*-ray diffraction.† The terminal phosphido unit functions as a three-electron donor as evidenced by the trigonal planar geometry at phosphorus (Figure 1)‡ and the fact that the Zr–P distance [2.541(14) Å] is somewhat shorter than those in other zirconium phosphides {*e.g.* 2.618(3) and 2.613(3) Å in $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}PPh_2)Mo(CO)_4]$}[3]. Unfortunately, it was not possible to generate $(\eta^5\text{-}C_5H_5)_2ZrPAr$ by thermal or photochemical elimination of $Me_3SiCl$ from (**1**).

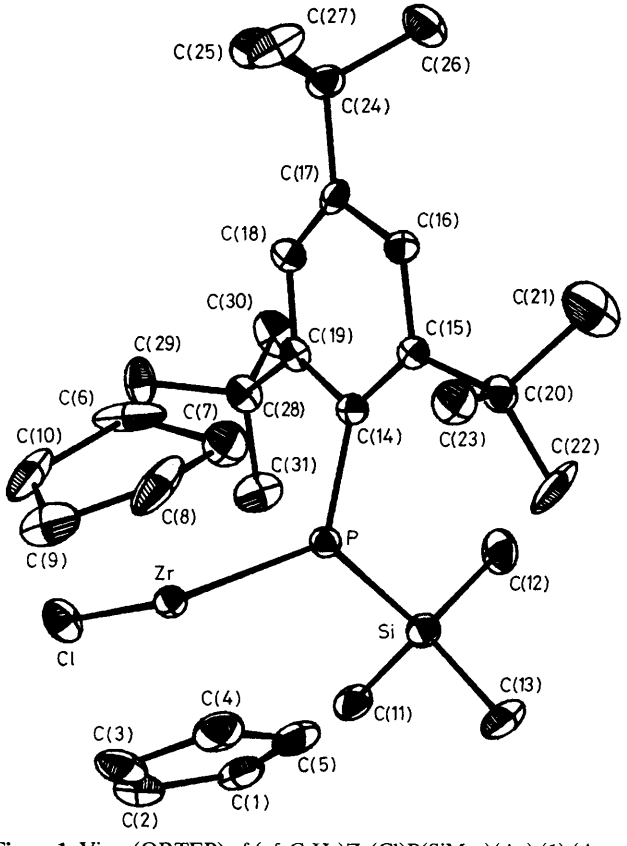



**Figure 1.** View (ORTEP) of $(\eta^5\text{-}C_5H_5)Zr(Cl)P(SiMe_3)(Ar)$ (**1**) (Ar = 2,4,6-$Bu^t_3C_6H_2$) showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: P–Zr 2.541(4), P–Si 2.268(6), P–C(14) 1.858(15); Zr–P–C(14) 120.1(5), Zr–P–Si 127.7(2), Si–P–C(14) 111.7(5).

† *Crystal data* for (**1**): $C_{31}H_{48}ClPSiZr$, $M$ = 606,46, triclinic, space group $P\bar{1}$ (No. 2), $a$ = 10.614(3), $b$ = 14.525(3), $c$ = 10.844(4) Å, $\alpha$ = 103.00(2), $\beta$ = 98.84(3), $\gamma$ = 84.59(2)°, $U$ = 1606.5 Å$^3$, $Z$ = 2, $D_c$ = 1.254 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 5.2 cm$^{-1}$. (**2**): $C_{30}H_{43}PW$, $M$ = 618.50, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 15.462(2), $b$ = 11.173(3), $c$ = 16.150(3) Å, $\beta$ = 94.63(1)°, $U$ = 2780.9 Å$^3$, $Z$ = 4, $D_c$ = 1.477 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 43.1 cm$^{-1}$. (**3**): $C_{30}H_{43}PW$, $M$ = 618.50, triclinic, $P\bar{1}$ (No. 2), $a$ = 9.811(3), $b$ = 10.499(3), $c$ = 13.898(2) Å, $\alpha$ = 107.87(2), $\beta$ = 92.77(2), $\gamma$ = 99.79(2)°, $U$ = 1334.9 Å$^3$, $Z$ = 2, $D_c$ = 1.539 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 44.9 cm$^{-1}$. Totals of 5352, 4888, and 4712 unique reflections were measured using the $\theta$–2$\theta$ scan mode over the ranges 3.0 ≤ 2$\theta$ ≤ 48.0°, 3.0 ≤ 2$\theta$ ≤ 50.0°, and 3.0 ≤ 2$\theta$ ≤ 50.0° for (**1**), (**2**), and (**3**), respectively, on an Enraf-Nonius CAD-4 diffractometer. The data were corrected for Lorentz, polarisation, and decay effects. Empirical absorption corrections were applied in all three cases. The structures were solved (direct methods) and refined (difference Fourier, full-matrix least-squares) using 2993, 2630, and 3516 reflections [$I > 3.0\ \sigma(I)$] for (**1**), (**2**), and (**3**), respectively. The final unweighted residuals were $R$ = 0.0962 for (**1**), 0.0492 for (**2**), and 0.0472 for (**3**). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ A very similar compound, $(\eta^5\text{-}C_5H_5)_2Zr(Cl)P(SiMe_3)_2$, has been prepared by M. F. Lappert and E. Hey. We thank Professor Lappert for kindly providing this information prior to publication.

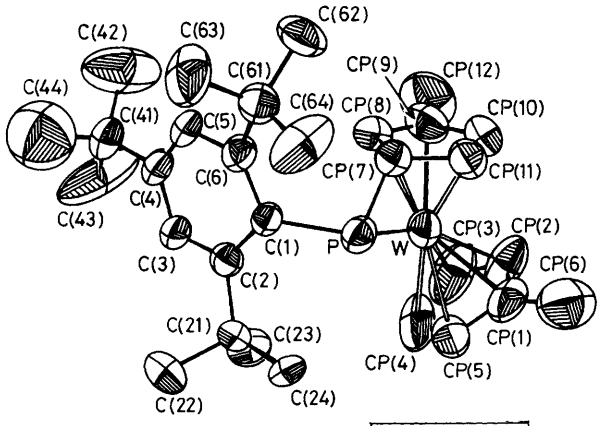
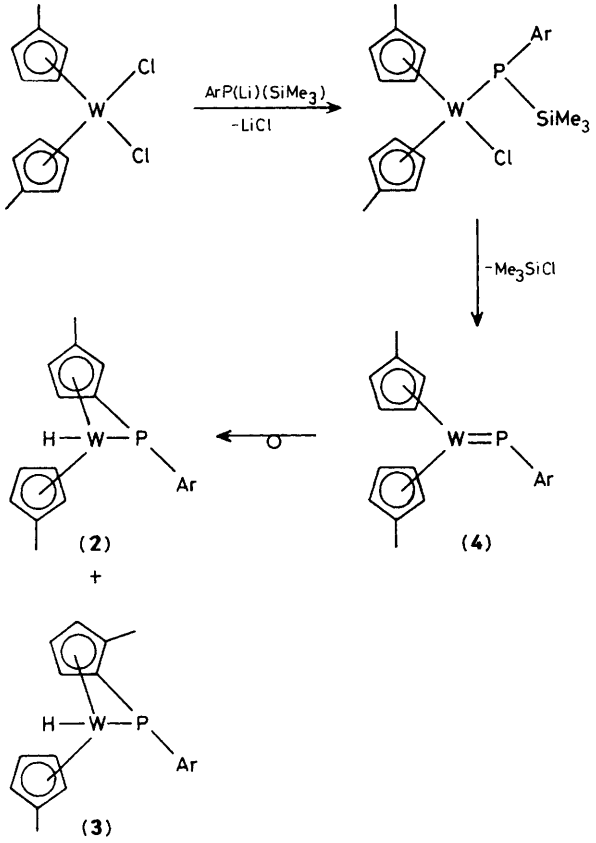



**Figure 2.** View (ORTEP) of $(\eta^5\text{-}C_5H_4Me)\overline{WH[\eta^5\text{-}C_5H_3Me(PAr)]}$ (**2**), (Ar = 2,4,6-$Bu^t_3C_6H_2$) showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: P–C(1) 1.877(12), P–CP(7) 1.780(15), P–W 2.583(4), W–CP(7) 2.196(11); W–P–CP(7) 56.9(4), P–CP(7)–W 80.3(5), P–W–CP(7) 42.8(4), C(1)–P–W 112.7(4).




**Scheme 1.** Ar = 2,4,6-$Bu^t_3C_6H_2$.

We attribute this to the halogenophilicity of Zr and possibly to the reluctance of an RP moiety to serve as a four-electron donor. We therefore turned our attention to more electron-rich organometallic fragments. Treatment of $(\eta^5{=}C_5H_4Me)_2WCl_2$ with ArP(Li)($SiMe_3$), as described above for (**1**), resulted in a 62% yield of (**2**), a material of composition $C_{30}H_{43}PW$ [high resolution mass spectrum, calcd. ($^{182}W$ isotope) 616.2584; found, 616.2572]. A second material of the same composition, (**3**), was isolated in 15% yield after subjecting the mother liquor to column chromatography (silica gel/n-hexane) followed by recrystallisation from n-hexane. Both compounds exhibit a peak at δ −12.31 in the $^1H$ n.m.r.§ and absorption between 2335 and 2360 $cm^{-1}$ in the i.r. spectra, thus indicating the presence of a W–H bond. The observation that the $^{31}P$ n.m.r. chemical shifts of (**2**) (+83 p.p.m.) and (**3**) (+90 p.p.m.) are close implies similar structures for these compounds. Moreover, these chemical shifts and the $^{31}P$–$^{183}W$ coupling constants (~11 Hz) are not indicative of phosphorus–tungsten multiple bonding.[4] An *X*-ray crystal determination† revealed that (**2**) and (**3**) are, in fact, structural isomers of the terminal phosphinidene complex, $(\eta^5\text{-}C_5H_4Me)_2W{=}PAr$, (**4**).¶ The phosphorus–cyclopentadienyl ring attachments are indicated by the P–C(7) distance of 1.780(15) Å in (**2**) (Figure 2) and the P–C(8) distance of 1.805(9) Å in (**3**). Both compounds exhibit highly pyramidal phosphorus geometries, the sums of angles at this centre being 269.1 and 265.9° in (**2**) and (**3**), respectively. The phosphorus–tungsten bond lengths of 2.583(4) Å in (**2**) and 2.582(2) Å in (**3**) are consistent with a bond order of unity. The isolation of (**1**) suggests that the reaction of $(\eta^5\text{-}C_5H_4Me)_2WCl_2$ with ArP(Li)($SiMe_3$) proceeds *via* $(\eta^5\text{-}C_5H_4Me)_2W(Cl)P(SiMe_3)(Ar)$, which loses $Me_3SiCl$ to afford (**4**) (Scheme 1). In turn, the conversion of (**4**) into a mixture of (**2**) and (**3**) can be considered to result from insertion of the two-co-ordinate phosphorus atom of (**4**) into the appropriate $C_5H_4Me$ ring C–H bond, followed by a 1,2 migration of H from phosphorus to tungsten. Labelling studies will, however, be necessary to establish that, in fact, the tungsten hydride originates from one of the $MeC_5H_4$ rings.

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§ The $^1H$ n.m.r. spectra for (**2**) and (**3**) are virtually indistinguishable: ($C_6D_6$, 300 MHz, ambient temperature) δ 1.28 (9H, s, *para*-$Bu^t$), 1.58 (9H, br. s, *ortho*-$Bu^t$), 1.73 [3H, dd, two $^4J_{HH}$ 6 and 8 Hz, CP(12)Me], 1.87 [12H, br. s, *ortho*-$Bu^t$ plus CP(6)Me], 3.3—4.7 (7H, br. m, CPH), 7.23 (2H, d, $^4J_{PH}$ 20 Hz, ArH), −12.31 (1H, br. s, WH).

¶ The interesting compound, $[Os(P{=}C[O]CF_3)(CO)_2(PPh_3)_2]$, is also a structural isomer of a terminal phosphinidene complex. In this case, the increase of co-ordination occurred *via* interaction of the acyl oxygen with osmium. See D. S. Bohle, C. E. F. Rickard, and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1985, 1594.