Structural Isomers of a Terminal Phosphinidene Complex

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The reactions of ArP(Li)(SiMe$_3$) (Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$) with (η^5-C$_5$H$_5$)$_2$ZrCl$_2$ and (η^5-C$_5$H$_4$Me)$_2$WCl$_2$ afford (η^5-C$_5$H$_5$)$_2$Zr(Cl)P(SiMe$_3$)(Ar) and two isomers of composition (η^5-C$_5$H$_4$Me)WH[η^5-C$_5$H$_3$Me(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 (η^5-C$_5$H$_5$)$_2$ZrCl$_2$ with an equimolar quantity of ArP(Li)(SiMe$_3$) in Et$_2$O solution at 0 °C, followed by solvent removal, n-hexane extraction, and crystallisation, resulted in an 85% yield of red (η^5-C$_5$H$_5$)$_2$-Zr(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 [(η^5-C$_5$H$_5$)$_2$Zr(μ-PPh$_2$)Mo(CO)$_4$]}[3]. Unfortunately, it was not possible to generate (η^5-C$_5$H$_5$)$_2$ZrPAr by thermal or photochemical elimination of Me$_3$SiCl from (**1**).

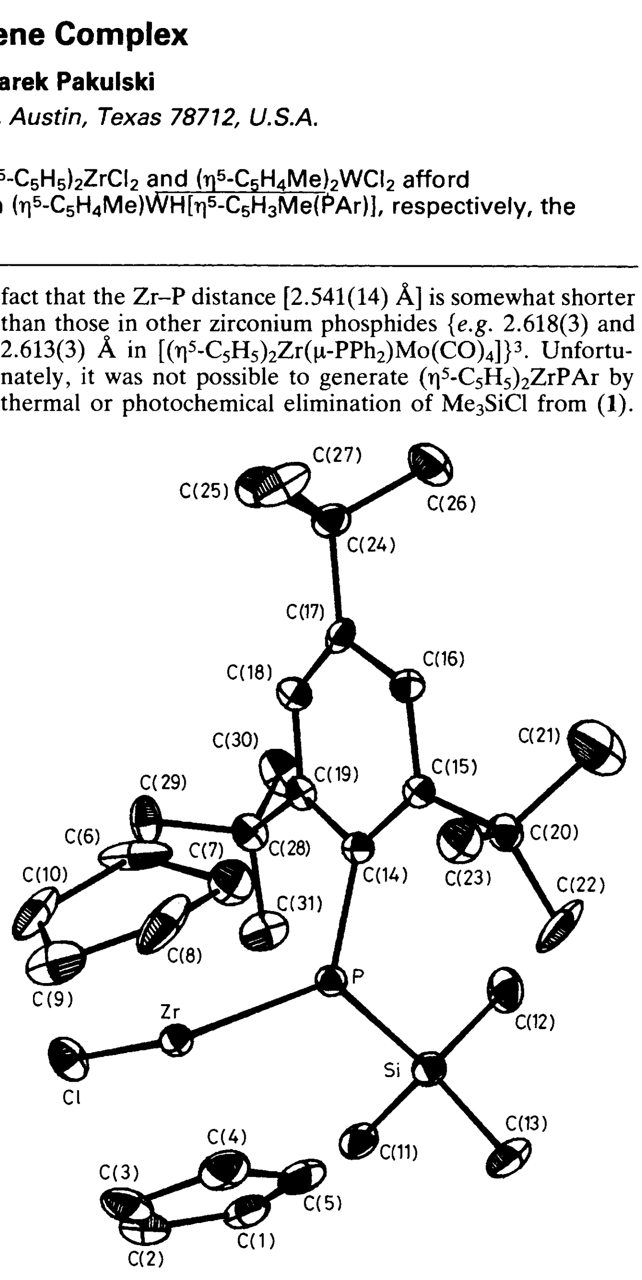

Figure 1. View (ORTEP) of (η^5-C$_5$H$_5$)Zr(Cl)P(SiMe$_3$)(Ar) (**1**) (Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$) showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: P–Zr 2.541(4), P–Si 2.268(6), P–C(14) 1.858(15); Zr–P–C(14) 120.1(5), Zr–P–Si 127.7(2), Si–P–C(14) 111.7(5).

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† *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, α = 103.00(2), β = 98.84(3), γ = 84.59(2)°, U = 1606.5 Å^3, Z = 2, D_c = 1.254 g cm^{-3}, μ(Mo-K_α) = 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, β = 94.63(1)°, U = 2780.9 Å^3, Z = 4, D_c = 1.477 g cm^{-3}, μ(Mo-K_α) = 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, α = 107.87(2), β = 92.77(2), γ = 99.79(2)°, U = 1334.9 Å^3, Z = 2, D_c = 1.539 g cm^{-3}, μ(Mo-K_α) = 44.9 cm^{-1}. Totals of 5352, 4888, and 4712 unique reflections were measured using the θ–2θ scan mode over the ranges $3.0 \leqslant 2\theta \leqslant 48.0°$, $3.0 \leqslant 2\theta \leqslant 50.0°$, and $3.0 \leqslant 2\theta \leqslant 50.0°$ 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, (η^5-C$_5$H$_5$)$_2$Zr(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.

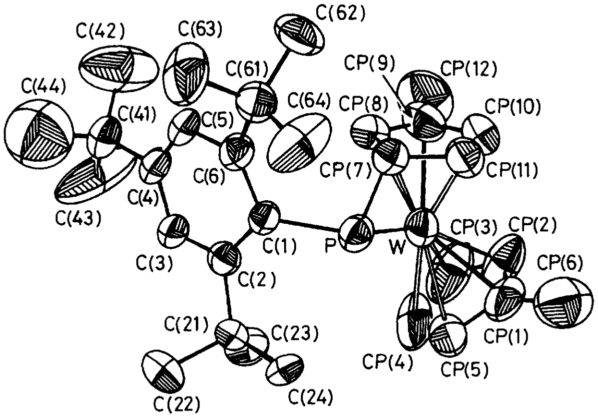
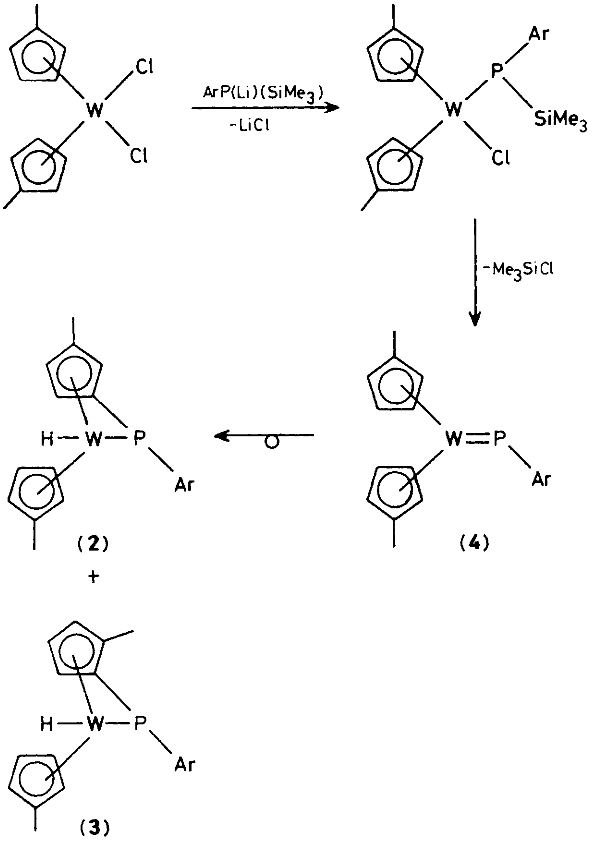


Figure 2. View (ORTEP) of (η^5-C_5H_4Me)$\overline{WH[\eta^5\text{-}C_5H_3Me(P}$$Ar)]$ (**2**), ($Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$) showing the atom numbering scheme. Important bond lengths (Å) and angles (°) are as follows: P–C(1) 1.877(12), P–CP(7) 1.780(15), P–W 2.583(4), W–CP(7) 2.196(11); W–P–CP(7) 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. $Ar = 2,4,6\text{-}Bu^t{}_3C_6H_2$.

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 (η^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, (η^5-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 (η^5-C_5H_4Me)$_2WCl_2$ with $ArP(Li)(SiMe_3)$ proceeds *via* (η^5-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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References

1 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484; A. Marinetti and F. Mathey, *Organometallics*, 1982, **1**, 1488; 1984, **3**, 456; 1984, **3**, 1492; J. Savara and F. Mathey, *ibid.*, 1986, **5**, 1159.

2 For reviews, see, *e.g.*, R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731; A. H. Cowley and N. C. Norman, *Prog. Inorg. Chem.*, 1986, **34**, 1.

3 M. G. B. Drew, S. R. Wade, M. G. H. Wallbridge, and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1986, 713.

4 E. Bross, K. Jörg, K. Fiederling, A. Göttlein, W. Malisch, and R. Boese, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 738.

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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.