Synthesis and Characterisation of Zirconium Complexes with the Diphosphinophosphide Ligands $^{-}P(CH_2CH_2PR_2)_2$ (R = Me or Et); Crystal Structure of Bis[bis(2-dimethylphosphinoethyl)phosphido]pentachlorohydridodizirconium(IV)†

Andreas A. Danopoulos, Peter G. Edwards,* Mary Harman, Michael B. Hursthouse and Julian S. Parry
School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff CF1 3TB, UK

A new high-yield selective synthesis of the ditertiary phosphino secondary phosphines $P(CH_2CH_2PR_2)_2H$ (R = Me or Et) has been developed. Following deprotonation, the multidentate anionic phosphides have been applied to the synthesis of new classes of zirconium and hafnium phosphides. New compounds of the form $[ZrCl_2L_2]$, $[Zr_2Cl_6L_2]$, $[Zr_2Cl_5HL_2]$ and $[Zr_2Cl_3L_3]$ [L = $^{-}P(CH_2CH_2PMe_2)_2$] are reported and are characterised by spectroscopic and analytical methods. The crystal structure of the hydrido complex has been determined and shows a binuclear structure containing bridging phosphide and hydride ligands.

Although the importance and potentially interesting chemistry of ligands containing anionic and neutral phosphorus atoms has already been recognised,[1] the synthetic methods for their precursors, *i.e.* polyphosphines containing both secondary and tertiary phosphorus atoms, are limited. The situation is most restricted for alkylated tertiary–secondary–tertiary triphosphines, for which only a few examples have been prepared in rational[2] or serendipitous[3] manners. The benzyl group has been used as a protecting function for amines[4] where cleavage of the nitrogen–benzyl bond may be accomplished by either catalytic hydrogenation[5] or by alkali-metal reduction in liquid ammonia[6] in which sulfides and quaternary ammonium or phosphonium salts behave similarly.[7] The cleavage of benzyl from quaternary phosphonium salts by $LiAlH_4$ has been used in the selective synthesis of heterocyclic diphosphines.[8] The use of the naphthylmethyl group as a protection for phosphorus sulfides has been reported.[9] In this paper we describe a selective, high-yield synthetic route to phosphines of the type $P(CH_2CH_2PR_2)_2H$ (R = Me or Et) by radical coupling of benzyldivinylphosphine with simple secondary phosphines, followed by reductive cleavage of the phosporus–benzyl bond with sodium in liquid ammonia to liberate the required secondary phosphine. We also present results of reactions of the anionic diphosphinophosphides, $^{-}P(CH_2CH_2PR_2)_2$, prepared by action of alkyllithium reagents on the appropriate secondary phosphine, with zirconium halides. Preliminary results of this study have appeared.[10]

Experimental

Procedures.—All manipulations involving phosphines were performed under inert atmospheres or *in vacuo* in Schlenkware. Solvents were dried [diethyl ether, tetrahydrofuran, light petroleum (b.p. 40–60 °C) over sodium or potassium–benzophenone; toluene, C_6D_6 over Na] by reflux under nitrogen and distilled immediately prior to use. The compounds PMe_2H,[11] PEt_2H[12] and $P(CH_2Ph)Cl_2$[13] were prepared by literature procedures. Metal halides were sublimed under vacuum. Other reagents were used as purchased.

Photolyses were by a medium-pressure 125 W mercury-arc lamp in quartz apparatus. Spectrometers used were: NMR, Bruker WM360 operating at 360 (^{1}H), 145 (^{31}P) and 90 MHz (^{13}C), and JEOL FX90Q operating at 89.55 (^{1}H), 36.23 (^{13}P) and 22.49 MHz (^{13}C); IR, Perkin Elmer 783 calibrated with polystyrene and Nicolet 510 FT. Mass spectra were obtained from diethyl ether solutions, using a V.G. Mass Lab 12-253 GC/MS instrument in electron impact (EI) mode (70 eV, *ca.* 1.12×10^{-17} J). The NMR spectra were obtained from solutions in C_6D_6 and referenced internally using residual protic benzene impurity (^{1}H, δ 7.27), externally using 85% H_3PO_4 (^{31}P, δ 0, chemical shifts upfield of the reference are negative in accord with current conventions) or internally to solvent carbons (^{13}C, C_6D_6, δ 128.0; $C_6D_5CD_3$, δ 137.5).

The C, H and N analyses were performed by Mikroanalytisches Labor Pascher (Bonn), Butterworths Laboratories (Middlesex) or CHN Analysis (Leicester).

Preparations.—*Benzyldivinylphosphine* $P(CH_2Ph)(CH{=}CH_2)_2$. A solution of $P(CH_2Ph)Cl_2$ (21.2 g, 0.11 mol) in tetrahydrofuran (thf) (100 cm^3) was added dropwise with stirring to a solution of vinylmagnesium chloride [0.244 mol in thf (500 cm^3, 0.122 mol dm^{-3})] at −60 °C. Towards the end of the addition, magnesium chloride precipitated. The mixture was allowed to warm to ambient temperature, stirred (8 h) and then refluxed (2 h). After cooling and hydrolysing (deoxygenated saturated NH_4Cl solution, 300 cm^3), the organic phase and ether washings (3 × 100 cm^3) were dried ($MgSO_4$). The volatile solvents were distilled at atmospheric pressure and the residue fractionated at reduced pressure. The fraction boiling at 58–60 °C (0.05 mmHg) was collected as a colourless liquid. Yield 14.5 g, 75% based on $P(CH_2Ph)Cl_2$. IR: 3080m, 3030s, aromatic C–H stretch; 2980s, 2950m, 2880m, aliphatic C–H stretch; 1590m, C=C bend; 1440s, C–H bend; 980s, 910s, $CH{=}CH_2$; 745s, aromatic C–H bend; 680s cm^{-1}, aromatic ring deformation.

Benzylbis(2-dimethylphosphinoethyl)phosphine, $P(CH_2Ph)(CH_2CH_2PMe_2)_2$. (*i*) The compound PMe_2H (10 g, 0.16 mol dm^{-3}) was transferred to a stainless-steel autoclave (capacity 1 l) containing $P(CH_2Ph)(CH{=}CH_2)_2$ (12 g, 0.068 mol), aibn [2,2′-azobis(2-methylpropionitrile)] (0.5 g) and light

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: mmHg ≈ 133 Pa.

petroleum (500 cm^3). After sealing the autoclave the mixture was heated (110 to 125 °C) whilst stirring for 48 h. After this period the mixture was cooled (0 °C), transferred to a distillation apparatus and the volatile components distilled at atmospheric pressure. The colourless oily residue was heated (100 °C) under dynamic vacuum (0.05 mmHg) for 3 h since it could not be distilled without decomposition, but was pure enough (> 95% by NMR spectroscopy) for further use. Yield 16.8 g, 82% based on $P(CH_2Ph)(CH{=}CH_2)_2$.

(*ii*) Benzyldivinylphosphine (53.0 g, 0.30 mol) and PMe_2H (75.0 g, 1.2 mol) were transferred to a photolysis vessel and irradiated with stirring at ambient temperature (48 h). The excess of PMe_2H was removed by vacuum transfer to leave a colourless viscous oil in virtually quantitative yield (90.0 g, 0.30 mol) which was pure (> 95%) by $^{31}P-\{^1H\}$ NMR spectroscopy. IR: 3080m, 3040m, aromatic C–H stretch; 2980s, 2890s, aliphatic C–H stretch; 1490s, 1440m, 1410s, C–H bend; 750s, aromatic C–H bend; 690s cm^{-1}, aromatic ring deformation.

Bis(2-*dimethylphosphinoethyl*)*phosphine* $P(CH_2CH_2PMe_2)_2H$. The compound $P(CH_2Ph)(CH_2CH_2PMe_2)_2$ (90.0 g, 0.30 mol) in diethyl ether (200 cm^3) was added with stirring to a solution of Na (36.0 g, 1.6 mol) in ammonia (1.4 l) held at −50 °C, during 15 min. The blue solution became deep green. It was stirred (at −40 °C) for 2 h after which the ammonia was allowed to evaporate. The resultant yellow slurry was hydrolysed with deoxygenated water (300 cm^3) with cooling (5 °C) and ether (800 cm^3) was added. The organic phase and ether washings (2 × 300 cm^3) were dried ($MgSO_4$) and the volatile materials distilled at atmospheric pressure. The residue was fractionated at reduced pressure. The fraction boiling at 68–72 °C (0.05 mmHg) was collected as a colourless viscous liquid. Yield 56.1 g, 0.267 mol, 89% based on $P(CH_2Ph)(CH_2CH_2PMe_2)_2$. Mass spectrum: found M^+ m/z 210(2), $M^+ - Me$ 195(18), $M^+ - PMe_2$ 149(15) and $M^+ - PMe_2CH_2CH_2$ 121(100%); $C_8H_{21}P_3$ (M^+) requires m/z 210.2. IR: 2970s, 2930s, C–H stretch; 2268s, P–H stretch; 1415s, 1430s cm^{-1}, C–H bend.

Benzylbis(2-*diethylphosphinoethyl*)*phosphine* $P(CH_2Ph)(CH_2CH_2PEt_2)_2$. To a solution of $P(CH_2Ph)(CH{=}CH_2)_2$ (9.92 g, 0.056 mol) and PEt_2H (15 g, 0.17 mol) in light petroleum (400 cm^3) was added aibn (0.5 g) and the mixture was photolysed with stirring at ambient temperature for 15 h. After this period further portions of PEt_2H (9.3 g, 0.034 mol) and aibn (0.2 g) were added and the photolysis continued for 6 h. At this time there was no unreacted vinylphosphine (NMR spectroscopy). The volatile materials were distilled at atmospheric pressure leaving an off-white viscous oily residue which was heated (100 °C) under dynamic vacuum (0.05 mmHg) for 3 h. The oil could not be distilled without decomposition but was pure enough for use (> 95% by NMR spectroscopy). Yield 12.9 g, 65% based on $P(CH_2Ph)(CH{=}CH_2)_2$. IR: 3080m, 3060m, aromatic C–H stretch; 2960s, 2920s, 2880s, aliphatic C–H stretch; 1445s, 1380s, aliphatic C–H bend; 770m, aromatic C–H bend; 700m cm^{-1}, aromatic ring deformation.

Bis(2-*diethylphosphinoethyl*)*phosphine* $P(CH_2CH_2PEt_2)_2H$. Debenzylation of $P(CH_2Ph)(CH_2CH_2PEt_2)_2$ (21 g) was effected in a manner directly analogous to the preparation of $P(CH_2CH_2PMe_2)H$ above, except that with Na (5.5 g) it provided $P(CH_2CH_2PEt_2)_2H$ (6.85 g, 44%) as a colourless viscous liquid which distilled at 110–114 °C (0.002 mmHg). Mass spectrum: found M^+ m/z 266(5), $M^+ - Et$ 237(37), $M^+ - PEt_2$ 177(20) and $M^+ - Et_2PCH_2CH_2$ 149(100%); $C_{12}H_{29}P_3$ (M^+) requires m/z 266.3. IR: 2985s, 2920s, 2840s, C–H stretch; 2260m, P–H stretch; 1450s, 1415s, 1370s cm^{-1}, C–H bend.

Bis(2-*dialkylphosphinoethyl*)*phosphidolithium* $LiP(CH_2CH_2PR_2)_2$ (R = Me *or* Et). Deprotonation of $P(CH_2CH_2PR_2)H$ (R = Me or Et) was readily effected in light petroleum by dropwise addition of a stoichiometric quantity of $LiBu^n$ in hexane with cooling (−20 °C). After warming to room temperature, stirring (2 h) and recooling, the lithium phosphide was reclaimed as a pyrophoric white powder by filtration. The methyl derivative, $LiP(CH_2CH_2PMe_2)_2$, was used as a standard solution in toluene–thf (5:1 v/v) whereas the ethyl derivative, $LiP(CH_2CH_2PEt_2)_2$, could be used in toluene due to enhanced solubility.

Bis[*bis*(2-*dimethylphosphinoethyl*)*phosphido*]*hexachlorodizirconium*(IV) $[Zr_2Cl_4(\mu\text{-}Cl)_2\{P(CH_2CH_2PMe_2)_2\}_2]$ **1**. Zirconium chloride (0.33 g, 1.41 mmol), was suspended in Et_2O (20 cm^3), cooled (−80 °C) and stirred and $LiP(CH_2CH_2PMe_2)_2$ solution (0.31 g, 1.41 mmol) in toluene–thf (5:1, 7 cm^3) added *via* canula. The suspension immediately became red. It was allowed to warm to room temperature and stirred (12 h) by which time a lemon-yellow solution and pale precipitate had developed. The solvents were removed *in vacuo*, and the residue was washed with light petroleum (2 × 20 cm^3), extracted into toluene (80 + 40 cm^3) and filtered. The filtrate was concentrated to 20 cm^3 and cooled (−50 °C, 7 d), affording complex **1** as bright yellow prisms (0.27 g, 0.33 mmol, 23%) (Found: C, 23.9; H, 5.2. $C_8H_{20}Cl_3P_3Zr$ requires C, 23.6; H, 4.9%). IR: 1420m, 1295m, 1270s, 1250m, 1200w, 1170w, 1150w, 1125w, 1095s, 1020m, 975w, 950s, 920s, 890m, 850m, 800m, 710s, 665m, 645m, 635m, 450w, 350m, 330s, 300m, 260m, 255w, 240m, 220m and 210m cm^{-1}. The compound does not melt up to 300 °C.

Bis[*bis*(2-*diethylphosphinoethyl*)*phosphido*]*hexachlorodizirconium*(IV) $[Zr_2Cl_4(\mu\text{-}Cl)_2\{P(CH_2CH_2PEt_2)_2\}_2]$ **2**. The preparation was similar to that above except for the addition of a light petroleum solution of $LiP(CH_2CH_2PEt_2)_2$ (7.5 cm^3, 0.286 mol dm^{-3}, 2.14 mmol) to $ZrCl_4$ (0.50 g, 2.14 mmol) in diethyl ether (80 cm^3) at −90 °C. Colour changes and work-up were as for complex **1**. The product was recrystallised from toluene–light petroleum (10 cm^3 : 50 cm^3) at −20 °C. Yield 0.61 g, 33%. The compound does not melt up to 300 °C.

Bis[*bis*(2-*dimethylphosphinoethyl*)*phosphido*]*dichlorozirconium*(IV) $[ZrCl_2\{P(CH_2CH_2PMe_2)_2\}_2]$ **3**. Zirconium chloride (1.2 g, 5.14 mmol) was suspended in Et_2O (80 cm^3) and cooled (−80 °C). The compound $LiP(CH_2CH_2PMe_2)_2$ (2.23 g, 0.01 mol) in toluene–thf (5:1, 40 cm^3) was added *via* canula with stirring. The suspension immediately turned red. It was allowed to warm slowly to room temperature and stirred (12 h) by which time the solution had turned deep red-brown. The solvents were removed *in vacuo* and the residue was extracted into light petroleum (120 + 60 + 60 cm^3) and filtered. The filtrate was concentrated to 40 cm^3 and cooled (−20 °C, 4 d) affording complex **3**, as delicate pale red-brown needles (0.45 g, 0.78 mmol, 15%) (Found: C, 33.1; H, 7.1; Cl, 11.6. $C_{16}H_{40}Cl_2P_6Zr$ requires C, 33.1; H, 6.9; Cl, 12.2%). IR: 1290m, 1270w, 1255w, 1200w, 1170m, 1150w, 1120w, 1070m, 1040w, 970m, 940s, 915m, 885w, 800m, 680w, 640m, 455m, 430w, 300w and 270m cm^{-1}. M.p. 160–164 °C.

Bis[*bis*(2-*diethylphosphinoethyl*)*phosphido*]*dichlorozirconium*(IV) $[ZrCl_2\{P(CH_2CH_2PEt_2)_2\}_2]$ **4**. A method directly analogous to that above was used. The product was isolated from light petroleum as a viscous red oil in 25% yield based on $ZrCl_4$. Attempts to crystallise it failed (Found: C, 42.2; H, 8.2. $C_{24}H_{56}Cl_2P_6Zr$ requires C, 41.6; H, 8.1%). IR (neat thin film): 2955s, 2920s, 2905s, 2850s, 1455s, 1405s (br), 1365m, 1255m, 1240m (br), 1205w, 1170m (br), 1100m (br), 1020m (br), 980w, 935m, 900m, 850s (br), 785m, 770m, 750w, 650m, 460m, 430w, 305w and 260w cm^{-1}.

Bis[*bis*(2-*dimethylphosphinoethyl*)*phosphido*]*pentachlorohydridodizirconium*(IV) $[Zr_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)\{P(CH_2CH_2PMe_2)_2\}_2]$ **5**. Zirconium chloride (0.72 g, 3.09 mmol) was suspended in Et_2O (50 cm^3) and cooled (−80 °C). The compound $LiP(CH_2CH_2PMe_2)_2$ (1.33 g, 6.16 mmol) in toluene–thf (5:1, 36 cm^3) was added with stirring. The mixture was allowed to warm to room temperature and stirred (12 h). The solvent was removed and the residue extracted into light petroleum (100 + 40 cm^3) and filtered. Trimethylaluminium (0.22 g, 3.09 mmol) in light petroleum (20 cm^3) was added with stirring. A pale brown precipitate developed and the intensity of the solution colour decreased. The mixture was stirred (12 h) and then filtered. The residue was washed with light petroleum (2 × 20 cm^3), extracted with toluene (60 cm^3) and stirred (8 h). The solvent was removed and the red gum extracted into Et_2O (60 cm^3) and filtered. The red filtrate was concentrated (20 cm^3) and allowed to stand (7 d); red prisms of complex **5** were deposited in low yield (Found: C, 24.9; H, 5.5. $C_{16}H_{41}Cl_5P_6Zr_2$ requires C, 24.6; H, 5.3%). IR: (before dissolution in toluene) 1301m, 1278m, 1266m, 1164s, 1135w, 1094m, 1072m, 1021m, 941s, 916s, 894m, 849w, 818m, 804m, 770w, 684s, 668s, 617m, 519m, 458w and 420m; (after dissolution) 1299m, 1260s, 1167m, 1093s (br), 1020s (br), 942m, 917m, 893w, 868w, 800s, 701m, 614w, 575w, 516w and 467m cm^{-1}. M.p., ill defined, approximately 180 °C.

Tris[bis(2-dimethylphosphinoethyl)phosphido]trichlorodizirconium(III) $[Zr_2Cl_2(\mu\text{-}Cl)\{P(CH_2CH_2PMe_2)_2\}_3]$ **6**. Zirconium chloride (0.256 g, 1.098 mmol) was suspended in diethyl ether (20 cm^3) with stirring and cooled (−80 °C). Three mole equivalents of $LiP(CH_2CH_2PMe_2)_2$ (0.711 g, 3.293 mmol) in cold thf (10 cm^3, −40 °C) were added *via* canula. A deep red colour developed immediately. The suspension was allowed to warm slowly to room temperature and stirred (12 h), by which time the colour was deep brown. The solvents were removed *in vacuo* and the black residue was extracted into light petroleum (100 + 20 cm^3), filtered and concentrated to 20 cm^3. The clear brown solution was left to stand at room temperature (2 d) affording large brown-black blocks of complex **6** (0.04 g). Concentrating the mother-liquor further afforded a second crop (0.06 g). Total yield (recrystallised material) 0.1 g, 0.11 mmol, 10% based on $ZrCl_4$ (Found: C, 32.3; H, 6.8. $C_{24}H_{60}Cl_3P_9Zr_2$ requires C, 31.4; H, 6.5%). IR: 1385m, 1265w, 1145m, 1110w, 1070m, 960m, 930s, 910s, 880w, 835w, 800m, 770m, 635m, 450m, 420w, 330w, 315w, 295w, 260m and 230m cm^{-1}. M.p. 128–130 °C.

Crystallography.—X-Ray measurements were made on a crystal of complex **5** of approximate dimensions 0.20 × 0.25 × 0.35 mm sealed under nitrogen in a thin-walled glass capilliary. Following preliminary X-ray photography, unit-cell dimensions and intensity data were recorded at room temperature (288 K) to $\theta_{max} = 25°$ $(+h, +k, +l)$ using standard procedures and a CAD4 diffractometer operating in the ω–2θ scan mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The intensity data were corrected for absorption using ψ-scan profiles. The structure was solved *via* the heavy-atom method and refined by full-matrix least squares using SHELX 76.[14] Non-hydrogen atoms were refined with anisotropic thermal parameters, and whilst 'organic' hydrogens were included in idealised positions a peak located on a difference map in a reasonable position for the bridging hydride could be refined isotropically as such. All calculations were performed on a T800 transputer hosted by a 286AT PC computer.

Crystal data. $C_{16}H_{41}Cl_5P_6Zr_2$, M_r = 779.05, tetragonal, space group $P4_12_12$, $a = b$ = 10.230(2), c = 31.36(1) Å, U = 3283.9 Å^3, Z = 4, D_c = 1.58 g cm^{-3}, μ(Mo-Kα) = 13.32 cm^{-1}, $F(000)$ = 1568.

Data collection and refinement. 3303 Reflections were measured giving 2878 unique (R_{int} = 0.045) and 2205 observed $[F_o > 3\sigma(F_o)]$. 133 Parameters, $w = [\sigma(F_o) + 0.0017F_o^2]^{-1}$, R = 0.0495, R' = 0.0695. Final atomic coordinates are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

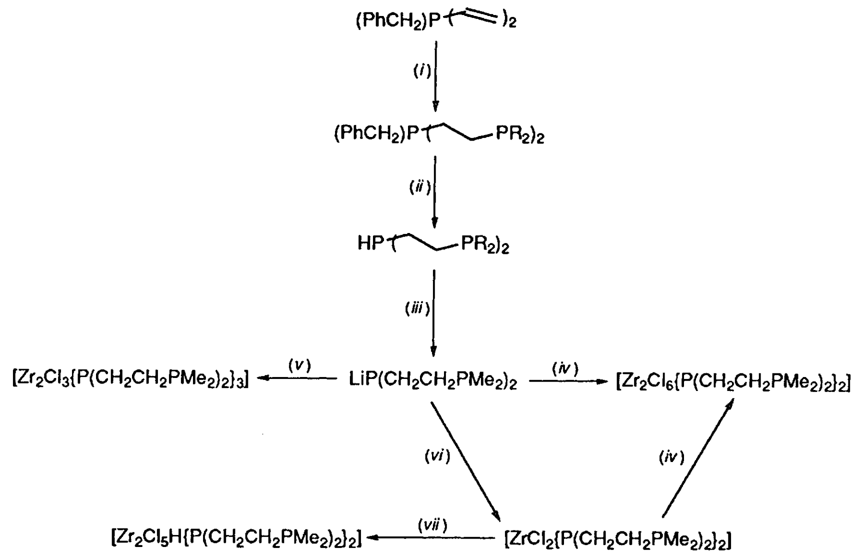
The $^{31}P\text{-}\{^1H\}$, ^{31}P and ^1H NMR data are collected in Table 1. Chemical transformations are represented in Scheme 1.

Preparation of $P(CH_2Ph)(CH_2CH_2PR_2)_2$.—Two methods for the preparation of these compounds were investigated. That with R = Me may be prepared in high yield (typically around 80%) by the thermolytic aibn-catalysed radical coupling of $P(CH_2Ph)(CH{=}CH_2)_2$ with PMe_2H. The reaction is conveniently carried out on a small scale (typically 8–16 g product) in a

Table 1 Phosphorus-31 and ^1H NMR data for phosphorus compounds and complexes[a]

	$\delta(^{31}P)$, J/Hz		
Compound	Internal phosphorus	Terminal phosphorus	$\delta(^1H)$,[b] J/Hz
$P(CH_2Ph)(CH{=}CH_2)_2$	−20 (s)		2.84 (2 H, $C\mathit{H}_2Ph$), 5.66 [4 H, m, $(C\mathit{H}_2{=}CH)P$], 7.22 (5 H, $CH_2C_6\mathit{H}_5$)
$P(CH_2Ph)(CH_2CH_2PMe_2)_2$	−17.5 (t)	−49 [d, ^3J(P–P) = 22]	0.86 [12 H, d, PCH_3, ^2J(P–H) 2.6], 1.26–1.52 (8 H, m, $PC\mathit{H}_2C\mathit{H}_2P$), 2.68 (2 H, $C\mathit{H}_2C_6H_5$), 7.16 (5 H, $CH_2C_6\mathit{H}_5$)
$P(CH_2CH_2PMe_2)_2H$	−58.6 (t)	−49.6 [d, ^3J(P–P) = 19.6, ^1J(P–H) = 192]	0.85 (12 H, d, $PC\mathit{H}_3$, ^2J(P–H) 2.8], 1.32–1.72 (8 H, m, $PC\mathit{H}_2C\mathit{H}_2P$), 3.53 [1 H, d of qnt, PH, ^1J(P–H) 192.5, ^3J(H–H) 6.7]
$P(CH_2Ph)(CH_2CH_2PEt_2)_2$	−17.1 (t)	−20.1 [d, ^3J(P–P) = 20.3]	1.10 (12 H, d of t, $PCH_2C\mathit{H}_3$), 1.40 (12 H, q, $PC\mathit{H}_2CH_3$), 1.60–1.80 (8 H, m, $PC\mathit{H}_2C\mathit{H}_2P$), 2.95 (2 H, $C\mathit{H}_2C_6H_5$), 7.20 (5 H, $CH_2C_6\mathit{H}_5$)
$P(CH_2CH_2PEt_2)_2H$	−58.2 (t)	−21.1 [d, ^3J(P–P) = 18.2, ^1J(P–H) = 193]	1.10 [12 H, d of t, $PCH_2C\mathit{H}_3$, ^3J(P–H) 6.1], 1.40 [12 H, q, $PC\mathit{H}_2CH_3$, ^3J(H–H) 7.9], 1.50–1.80 (8 H, m, $PC\mathit{H}_2C\mathit{H}_2P$), 3.38 [1 H, d of qnt, ^1J(P–H) 193, ^3J(H–H) 6.8]
1 $[Zr_2Cl_4(\mu\text{-}Cl)_2\{P(CH_2CH_2PMe)_2\}_2]$	−58.0 (q)	−4.0 [t, ^3J(P–P) = 13.0]	
2 $[Zr_2Cl_4(\mu\text{-}Cl)_2\{P(CH_2CH_2PEt_2)_2\}_2]$	−55.1 (q)	13.8 [t, ^3J(P–P) = 12.2	
3 $[ZrCl_2\{P(CH_2CH_2PMe_2)_2\}_2]$	133 (m), 128 (m), 76 (s)	16 (m), 13 (m), 2 (m), −52 (d of d)	
5 $[Zr_2Cl_4(\mu\text{-}Cl)(\mu\text{-}H)\{P(CH_2CH_2\text{-}PMe_2)_2\}_2]$	74.0 (m)	1.09 (m), 4.18 (m)	
6 $[Zr_2Cl_2(\mu\text{-}Cl)\{P(CH_2CH_2PMe_2)_2\}_3]$	139.8 (m), 130.4 (m), 126.6 (m)	15.0 (m), 10.1 (m), 8.4 (m), 0.0 (m), −58.1 (m)	

[a] See Experimental section for details of data acquisition. [b] See text for discussion of ^1H NMR data for compounds **1**–**6**.



Scheme 1 (*i*) 2 PR_2H (R = Me or Et); (*ii*) Na; (*iii*) LiBu; (*iv*) $ZrCl_4$; (*v*) $\frac{1}{3}ZrCl_4$; (*vi*) $\frac{1}{2}ZrCl_4$; (*vii*) $MBPh_4$ (M = Na or Ag)

pressure vessel and is not accompanied by significant polymerisation if performed in an inert solvent such as light petroleum under suitably dilute conditions (1 l solvent). However, attempts to scale up this route resulted in the generation of significant quantities of intractable polymeric material and corresponding lowering of yield. Vinyl polymerisation can be suppressed by using an excess of PMe_2H but becomes wasteful in secondary phosphine unless it is reclaimed (*e.g.* by fractional distillation or as the hydrochloride). The coupling also appears dependent on the concentration of the reagents, high dilution favouring high yield, thus this route is limited by the volume of standard pressure vessels available. Attempted coupling of $P(CH_2Ph)H_2$ with $P(S)(CH{=}CH_2)Me_2$ catalysed by $KOBu^t$ in thf, conditions similar to those reported by King and Cloyd,[3] resulted in a product $P(CH_2Ph)[CH_2CH_2P(S)Me_2]_2$ (with the expected ^1H NMR spectrum) which was contaminated with polymeric materials and was desulfurised ($LiAlH_4$ in boiling dioxane or $SiMe_3Cl$–$LiAlH_4$–thf[15]) only in low yields. The reduced product could not be readily purified.

In contrast, in the coupling of $P(CH_2Ph)(CH{=}CH_2)_2$ with PEt_2H in refluxing cyclohexane catalysed by aibn or at 110–120 °C in an autoclave, the products include monocoupled $P(CH_2Ph)(CH{=}CH_2)(CH_2CH_2PEt_2)$ (by ^1H NMR spectroscopy) as well as polymeric materials. However if the coupling is carried out at ambient temperatures using aibn under UV photolysis according to Dahlenburg and co-workers,[16] the reaction proceeds smoothly and selectively enough that the resulting $P(CH_2Ph)(CH_2CH_2PEt_2)_2$ can be used directly in the next step. This latter method was also applied to the large-scale synthesis of $P(CH_2Ph)(CH_2CH_2PMe_2)_2$ by the coupling of $P(CH_2Ph)(CH{=}CH_2)_2$ in neat PMe_2H under ultraviolet irradiation; aibn is not required. If the reaction is performed with a 100% excess of secondary phosphine and in the absence of other solvents, the yield is virtually quantitative and PMe_2H can be recovered for reuse by simple vacuum-transfer techniques. Below an 80% excess, polymerisation of $P(CH_2Ph)(CH{=}CH_2)_2$ competes increasingly.

Debenzylation of Compounds $P(CH_2Ph)(CH_2CH_2PR_2)_2$.—Debenzylation may be readily accomplished in liquid ammonia with an excess of Na. The reaction usually occurs in high yield and the work-up is straightforward. Similar attempts to introduce the secondary phosphorus function by cleavage of the phosphorus–phenyl bond in $PPh(CH_2CH_2PMe_2)_2$ failed. The success of debenzylation is presumably due to the relative stability of the benzyl radical anion formed by P–C (benzyl) cleavage. Also unsuccessful were attempts to use Et_2N as a protecting function. Although compounds of the type $P(CH{=}CH_2)_2(NEt_2)$ are readily prepared,[17] the radical-catalysed coupling with secondary phosphines produced pyrophoric involatile oily and presumably polymeric residues in our hands, and is reported[18] to be low yield. Proton NMR spectroscopy of these residues indicated the presence of PR_2 functions but absence of Et_2N groups. This is in accord with the radical catalysed coupling of (dialkylamino)vinylphosphines with phenylphosphine reported by Issleib and Becker.[17]

Spectroscopic Studies.—The identity of the phosphines described above is adequately defined by NMR, IR and mass spectroscopies. Phosphorus-31 NMR spectroscopy is especially informative since chemical shifts between secondary and tertiary phosphines are normally widely separated, P–H coupling constants to directly bound hydrogens in secondary phosphines [^1J(P–H)] are typically more than one order of magnitude greater than those involving any other hydrogen atoms in the molecule, benzyl or vinyl functions introduce a significant downfield shift to ^{31}P resonances in comparison to the methyl phosphorus groups in the compounds $P(CH_2Ph)(CH_2CH_2PMe_2)_2$ and $P(CH_2CH_2PMe_2)_2H$ and lastly, comparative data are readily available in the literature.[19] In addition, IR spectroscopy is also useful in detecting P–H bonds since the P–H stretch in secondary phosphines is readily observable, typically between 2200 and 2300 cm^{-1}. The benzyl and vinyl derivatives also have characteristic absorbances of course. In the discussion below, A is assigned to the terminal tertiary phosphorus atom (P_a).

For the compounds $P(CH_2Ph)(CH_2CH_2PR_2)_2$ (R = Me or Et) the ^{31}P-{^1H} NMR spectra display simple A_2M patterns with the benzylic phosphorus (P_m) at lower field ($\delta_M = -17.5$ and -17.1 respectively). The spectra of the debenzylated products $P(CH_2CH_2PR_2)H$ are also simple A_2M patterns which demonstrate the upfield shift of the secondary phosphine ($\delta_M = -58.6$ and -58.2 respectively). The ^{31}P NMR spectra allow unequivocal assignments of the secondary phosphines [^1J(P–H) = 192 for R = Me and 193 Hz for R = Et]. In the ^1H NMR spectra of the secondary phosphines $P(CH_2CH_2PR_2)_2H$ the phosphorus-bound hydrogen atom gives rise to a resonance in the expected region (*ca.* δ 3.3–3.5) and is readily assigned on the basis of ^1J(P–H) as well as intensity. The spectra are otherwise complex but unremarkable and are consistent with the formulations.

In addition, for the compounds $P(CH_2CH_2PR_2)_2H$, mass spectroscopy supports the NMR characterisations. In each case a weak molecular ion is observed. The major fragmentation pathway appears to be by cleavage of a P–C bond of the internal phosphorus atom giving rise to base peaks at m/z 121 and 149 for R = Me and Et respectively. Other fragmentations involve loss of alkyl groups from the terminal phosphorus atoms as well as loss of R_2P groups. Similar fragmentation patterns have been reported for closely related compounds.[15]

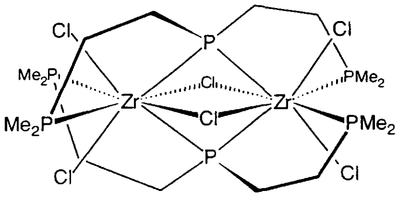
Zirconium Compounds.—The equimolar reaction of $LiP(CH_2CH_2PMe_2)_2$ with $ZrCl_4$ in diethyl ether at −80 °C generates an intense red solution in the presence of unreacted $ZrCl_4$. On warming the red colour dissipates and dissolution of $ZrCl_4$ is complete after *ca.* 8 h leaving a suspension of LiCl. The isolated compound is insoluble in aliphatic hydrocarbons but can be crystallised from toluene as moderately air-sensitive yellow needles for which microanalysis indicates an empirical formula $ZrCl_3\{P(CH_2CH_2PMe_2)_2\}$ **1**. The ^1H NMR spectrum reveals diastereotopic methyl protons which are coupled to each other and to phosphorus as two virtual triplets, and the $^{31}P\text{-}\{^1H\}$ NMR spectrum gives a quintet at δ −58 (δ_M) for co-ordinated phosphide coupled to four-co-ordinated phosphines (δ_A). The latter are resolved as a triplet at δ −4 coupled to the phosphides and the spin system approximates to A_4M_2 [^3J(P–P) = 13 Hz] indicating that the structure contains equivalent phosphides and equivalent phosphines at room temperature on the NMR time-scale.

The results can be interpreted if complex **1** has a dimeric structure supported by bridging phosphides and chlorides where the phosphido and phosphine sites are rendered equivalent by a centre of inversion but which lacks planar symmetry (hence diastereotopic methyl groups). We propose a structure of the form indicated where chirality (of the molecule) arises by virtue of the phosphide ligands wrapping themselves helically around the metal–metal axis to form a 'corkscrew'-like molecule. This bridging arrangement has been observed before in the only reported complex of this phosphide.[10] This structure is also reasonable in view of the propensity for zirconium to form eight-co-ordinate adducts with chelating phosphines.[20] Although dialkyl- (and diaryl-)phosphides have long been known to bridge in bis(cyclopentadienyl)zirconium(III) compounds,[21] there are no other suitable compounds with which to compare **1**.

Thus complex **1** differs from the empirically analogous amide $[Zr\{N(SiMe_2CH_2PMe_2)_2\}Cl_3]$[22] which is monomeric with a distorted-octahedral geometry. No doubt the differences arise from the ability of R_2P^- to bridge *versus* the bulky dimethylsilyl groups of the disilylamide which may sterically encumber such dimerisations. As in the amide complex, the chloride ligands can be metathesised with LiR (R = Me or Me_3SiCH_2) to yield yellow-brown hydrocarbon solutions from which pure materials could not be isolated.

$[ZrCl_2\{P(CH_2CH_2PMe_2)_2\}_2]$ **3**. From the synthesis of complex **1** it was evident that there were two stages to the reaction: an initial red stage at low temperature which decays to give rise to the final yellow product once all the $ZrCl_4$ had been consumed. Since the reaction appeared heterogeneous, it was assumed that the initial temporary excess of ligand (as zirconium chloride reacted) was related to the transient deep red colour.

Addition of 2 mol equivalents of $LiP(CH_2CH_2PMe_2)_2$ at −80 °C in Et_2O again generates the deep red colour but on warming and after extended periods this colour persists. From these solutions a dark red material can be isolated and crystallised from aliphatic hydrocarbons in low yield as exceedingly air-sensitive red-brown needles. If the reaction is performed in thf no product is isolated. The difference in physical properties from those of complex **1** suggests a greater ligand-to-metal ratio. Microanalysis confirms a formulation $[ZrCl_2\{P(CH_2CH_2PMe_2)_2\}_2]$. The ^1H NMR spectrum consists of a complex series of multiplets, characteristic of ^nJ(P–H) ($n > 1$) coupled systems, centred at δ +2, but otherwise uninterpretable. The $^{31}P\text{-}\{^1H\}$ NMR spectrum is more revealing. Multiplets assigned to terminal phosphide are centred at δ +133 and +128. In addition there is a small singlet at δ +76 followed by a series of three multiplets between δ +17 and 0 ascribed to co-ordinated phosphine and a doublet at δ −52 assigned to pendant phosphine.



1

The stereochemistry of the analogous bis(amidophosphine) complex $[Zr\{N(SiMe_2CH_2PMe_2)_2\}_2Cl_2]$ has been determined by a combination of NMR spectroscopy and single-crystal X-ray diffraction studies.[23] The compounds are similar in that apparently they both have pendant phosphine donors, two in the case of the amide. The $^{31}P\text{-}\{^1H\}$ NMR spectrum for $[ZrCl_2\{P(CH_2CH_2PMe_2)_2\}_2]$ does not integrate for two pendant donors and is invariant in the range −80 to +40 °C, the resonances from the pendant phosphines remaining sharp throughout. Since seven-co-ordination normally leads to stereochemical non-rigidity (*via* facile interconversions),[24] it is not likely that there is one pendant phosphine in a seven-co-ordinate complex as fluxionality and associated temperature-dependant NMR behaviour would be predicted. It is possible that the complex is six-co-ordinate and stereochemically rigid, with each ligand behaving in a bidentate fashion generating two pendant donors; the existence of isomers could then explain the complexity of the ^{31}P NMR spectrum. A third alternative is that complex **3** is dimeric for which many isomers could be envisaged since both halide and phosphide are potential bridging ligands and the latter could be monodentate, bidentate chelating or bridging or tridentate bridging. If zirconium is eight-co-ordinate, the phosphide ligands would either all have to be bidentate or there would be a mixture of different bonding modes. We favour this last alternative since a similar and varied arrangement of phosphide ligands is precedented in the only reported structurally characterised zirconium complex of this phosphide[10] and which appears stereochemically rigid in virtue of its temperature-invariant ^{31}P NMR spectrum (−80 to +90 °C). Again, the presence of isomers would explain both multiple phosphido and tertiary phosphine resonances observed in the NMR spectra. A structure of this form is supported by the ^{31}P NMR spectrum which is consistent with the presence of bridging and terminal phosphido functions. Unfortunately, reliable cryoscopic molecular weight data were not obtained and crystals of **3** were unsuitable for X-ray diffraction studies (as they were also for the ethyl analogue **4**). Attempted substitutions of halide in **3** and **4** with alkyl Grignard reagents resulted in unreacted starting complex; the analogous zirconium amide is similarly inert.

$[Zr_2Cl_5H\{P(CH_2CH_2PMe_2)_2\}_2]$ **5**. Addition of $MBPh_4$ (M = Na or Ag) to complex **3** in thf produces red solutions and a precipitate in the latter case, presumably AgCl, from which clear deep red prisms of **5** may be isolated in low yield. This complex is insoluble in light petroleum but soluble in toluene and Et_2O, from which it can be crystallised; the solubility properties are very similar to those of the dimer **1**. It was characterised by NMR spectroscopy, analysis and X-ray crystallography. The ^1H NMR spectrum is complicated (Fig. 1). As well as resonances attributable to ligand 'backbone' protons, four equally intense doublets are observed in the phosphine alkyl region which are indicative of two sets of diastereotopic phosphorus methyl groups [δ 1.59, 1.52, 1.39, 1.33; ^2J(P–H) = 7.9 Hz]. A weak resonance of at least 13 lines (separation of outer lines = 246 Hz) centred at δ −0.118 is assigned to the hydrido proton. In the ^{31}P-{^{1}H} NMR spectrum [Fig. 1(*b*)] three resonances are observed in equal intensities; a multiplet centred at δ +74 attributed to bridging phosphide and a pair of multiplets at δ +4.81 and +1.09 indicating an AA′BB′MM′ spin system (where δ_M is due to the phosphido-phosphorus atoms). This is consistent with the molecule having two phosphide ligands with two sets of pairwise inequivalent tertiary phosphines and explains the presence of two sets of methyl resonances in the ^{1}H NMR spectrum. The ^{31}P NMR spectrum can be adequately simulated on this spin model.* The formation of **5** must occur *via* a complex rearrangement, however no other Zr-containing materials could be identified in the reaction mixture; the ligand oxidation product $(Me_2PCH_2CH_2)_2P{-}P(CH_2CH_2PMe_2)_2$,† was observed by ^{31}P NMR spectroscopy in the supernatant solution remaining after crystallisation of **5**, indicating some reduction at Zr. Attempts to increase the yield by synthesising **5** directly from **3** using NaH or LiAlH$_4$ led to recovery of starting materials only.

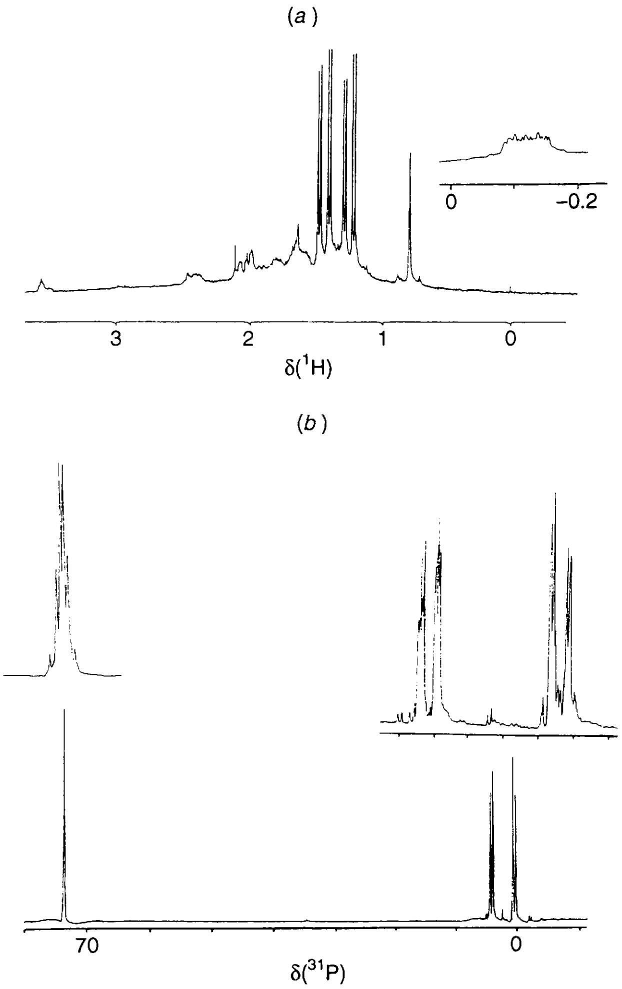


Fig. 1 The NMR spectra of compound **5**: (*a*) 360 MHz ^{1}H NMR spectrum, obtained in C_6D_6; the inset is the resonance assigned to μ-H centred at δ −0.118; (*b*) 145 MHz ^{31}P NMR spectrum, obtained in C_6D_6; the insets are expanded views of the resonances at δ 74.0, 4.81 and 1.09 respectively

A single-crystal X-ray diffraction study of complex **5** was performed. The structure shows an unusual dimer supported by bridging hydride, phosphide and chloride ligands (Fig. 2). Bond lengths and angles are given in Table 3. Complexes containing both hydride and dialkylphosphide are rare for early transition metals.[25] The structure has a central core of M_2P_2 and M_2HCl frameworks virtually orthogonal to each other. The methylene backbone and tertiary phosphines of the phosphide ligand, span the dimer in an S shape which, with the terminal chlorides, make the co-ordination number around each zirconium centre up to eight. Since the bridging atoms are all coplanar and define a distorted square and are approximately staggered with respect to the terminal donor atoms, distortion from any idealised structure is significant as the terminal donors are not coplanar and are approximately pairwise distinguishable in bond lengths. The co-ordination geometry around the zirconium atoms may then be described as square antiprismatic with a distortion tending towards D_{2d} dodecahedral.

The Zr–H distance of 2.051 Å is virtually identical to that observed [2.05(2) Å] for the bridging hydride in $[\{Zr(\eta^5\text{-}C_5H_4Me)_2H(\mu\text{-}H)\}_2]$.[26] The only other comparable Group 4 metal complex containing both bridging phosphides and hydrides, $[\{Hf(\eta^5\text{-}C_5Me_5)(\mu\text{-}H)_2(\mu\text{-}PBu^t{}_2)\}_2]$,[25f] has *r*(Hf–μ-H) = 2.12(13) Å. Although the only structurally characterised zirconium(IV) complexes with bridging phosphides with which to compare **5** are heterobimetallic, the Zr–μ-P distances in **5** [2.722(5) Å] are somewhat longer than previously

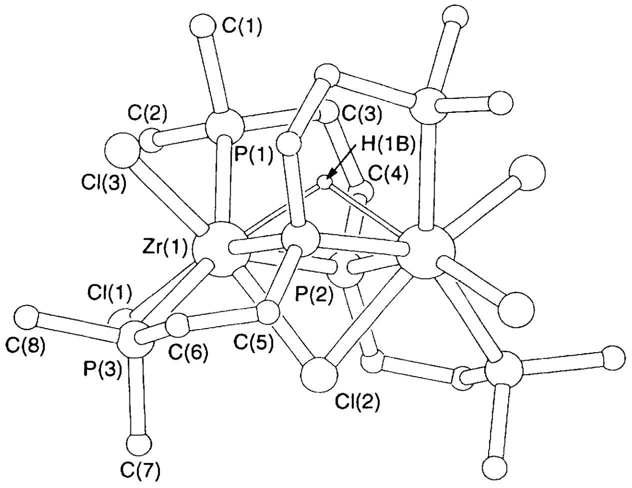


Fig. 2 The molecular structure of complex **5**

Table 2 Fractional atomic coordinates for compound **5**

Atom	*x*	*y*	*z*
Zr(1)	1.148 16(7)	0.985 49(7)	0.462 12(2)
Cl(1)	1.219 7(3)	0.754 5(2)	0.453 17(9)
Cl(2)	0.920 7(2)	0.920 7(2)	0.5
Cl(3)	1.256 5(3)	1.085 0(3)	0.399 76(8)
P(1)	1.393 4(2)	1.053 7(3)	0.491 42(9)
P(2)	1.165 2(2)	0.960 0(2)	0.548 35(7)
P(3)	0.985 1(3)	0.903 8(3)	0.396 20(8)
C(1)	1.477 6(13)	1.194 2(14)	0.466 8(4)
C(2)	1.512 8(12)	0.922 1(15)	0.487 4(5)
C(3)	1.393 7(11)	1.107 6(13)	0.547 2(4)
C(4)	1.317 9(12)	1.009 1(13)	0.574 5(4)
C(5)	1.108 1(13)	0.822 9(11)	0.581 4(4)
C(6)	0.863 6(14)	1.032 0(17)	0.381 8(5)
C(7)	0.883 7(28)	0.765 7(25)	0.406 6(8)
C(8)	1.061 0(18)	0.868 1(22)	0.344 9(4)
H(1B)	1.147(5)	1.147(5)	0.5

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* Simulation using the Bruker ‘Panic’ software assuming $\delta_A = 1.09$, $\delta_B = 4.81$, $\delta_M = 73.80$ and negative ^{2}J coupling constants: $J(A{-}B) = 61$, $J(A{-}A') = J(A{-}B') = J(B{-}B') = J(A{-}M') = 0$, $J(A{-}M) = J(B{-}M') = 13$, $J(B{-}M) = 7$, $J(M{-}M') = 10.5$ Hz.

† δ − 34.8 [qnt, $(Me_2PCH_2CH_2)_2\mathit{P}{-}\mathit{P}(CH_2CH_2PMe_2)_2$] and −50.4 [t, $(Me_2\mathit{P}CH_2CH_2)_2P{-}P(CH_2CH_2\mathit{P}Me_2)_2$]; full details to be published elsewhere.

Table 3 Bond lengths (Å) and angles (°) for compound **5**

Cl(1)–Zr(1)	2.491(5)	Cl(2)–Zr(1)	2.696(6)
Cl(3)–Zr(1)	2.468(5)	P(1)–Zr(1)	2.761(6)
P(2)–Zr(1)	2.722(5)	P(3)–Zr(1)	2.785(6)
Zr(1) ··· Zr(1a)	3.345(5)	C(1)–P(1)	1.847(15)
C(2)–P(1)	1.822(14)	C(3)–P(1)	1.835(14)
C(4)–P(2)	1.834(14)	C(5)–P(2)	1.840(13)
C(6)–P(3)	1.864(17)	C(7)–P(3)	1.783(24)
C(8)–P(3)	1.824(17)	C(4)–C(3)	1.534(18)

Cl(2)–Zr(1)–Cl(1)	94.0(2)	Cl(3)–Zr(1)–Cl(1)	99.8(2)
Cl(3)–Zr(1)–Cl(2)	147.0(1)	P(1)–Zr(1)–Cl(1)	90.6(2)
P(1)–Zr(1)–Cl(2)	134.4(1)	P(1)–Zr(1)–Cl(3)	75.6(2)
P(2)–Zr(1)–Cl(1)	90.1(2)	P(2)–Zr(1)–Cl(2)	66.0(2)
P(2)–Zr(1)–Cl(3)	143.0(1)	P(2)–Zr(1)–P(1)	68.6(2)
P(3)–Zr(1)–Cl(1)	78.9(2)	P(3)–Zr(1)–Cl(2)	74.7(2)
P(3)–Zr(1)–Cl(3)	78.7(2)	P(3)–Zr(1)–P(1)	150.1(1)
P(3)–Zr(1)–P(2)	138.3(1)	Zr(1)–Cl(2)–Zr(1a)	76.6(2)
C(1)–P(1)–Zr(1)	118.8(5)	C(2)–P(1)–Zr(1)	113.5(6)
C(2)–P(1)–C(1)	103.6(8)	C(3)–P(1)–Zr(1)	113.3(5)
C(3)–P(1)–C(1)	99.4(7)	C(3)–P(1)–C(2)	106.7(8)
C(4)–P(2)–Zr(1)	118.2(5)	C(5)–P(2)–Zr(1)	127.7(5)
C(5)–P(2)–C(4)	103.1(6)	C(6)–P(3)–Zr(1)	111.6(6)
C(7)–P(3)–Zr(1)	116.8(8)	C(7)–P(3)–C(6)	102.4(12)
C(8)–P(3)–Zr(1)	117.4(7)	C(8)–P(3)–C(6)	102.2(10)
C(8)–P(3)–C(7)	104.5(13)	C(4)–C(3)–P(1)	109.5(10)
C(3)–C(4)–P(2)	111.1(9)		

Symmetry operation relating designated atoms to reference atoms at x, y, z: (a) y, x, $1.0 - z$.

observed[27] and **5** more favourably compares with the pseudo-eight-co-ordinate quadruply bridged $[\{Hf(\eta^5\text{-}C_5Me_5)(\mu\text{-}H)_2(\mu\text{-}PBu^t{}_2)\}_2]$ where $r(\text{Hf–}\mu\text{-P}) = 2.806(2)$ Å. The relatively long Zr–μ-P distances in **5** are likely a consequence of steric influences from the number of bridging ligands and constraints imposed by the nature of the simultaneously bridging and chelating phosphide ligands. The terminal zirconium to tertiary phosphorus lengths [2.761(6) and 2.785(6) Å] are also similar to previously reported examples ranging from 2.77 to 2.86 Å.[28]

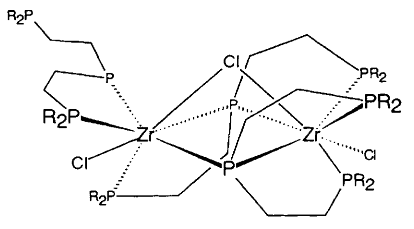
The structure is consistent with the solution NMR properties. In the $^{31}P\text{-}\{^1H\}$ NMR spectrum the phosphides are related by the two-fold axis that runs through the plane of the bridging hydride and chloride and the lack of a centre of inversion renders the co-ordinated tertiary phosphines pairwise inequivalent. In the ^1H NMR spectrum the four doublets assigned to PMe groups indicate diastereotopic methyl functions again pairwise chemically inequivalent as would be expected from the structure. Thus, the solid-state and solution structures of complex **5** are of the same type; the latter is similar to that of **1**. In **1**, however, bridging hydride is replaced by bridging halide thereby generating a centre of inversion and equivalent tertiary phosphines.

Co-ordination of the pendant phosphine donors in complex **3** would be expected to result from addition of a Lewis acid. Thus addition of 1 mole equivalent of $ZrCl_4$ to red **3** generates the yellow bimetallic **1**. This type of reaction has implications for the syntheses of heterobimetallic compounds where it can be envisaged that $ZrCl_4$ may be substituted by a variety of metal halides. However, addition of AlX_3 where X = Cl or Br in toluene, Me or Me_3SiCH_2 in light petroleum to **3** results, ultimately, in the isolation of deep red clear prisms of **5** (identified by ^1H and ^{31}P NMR spectroscopy). It is interesting also that in the reaction of **3** with $ZrCl_4$ variable but minor quantities of **5** also accompany the formation of **1**. In the case of the alkylaluminiums, where both precursors are soluble, the addition can be performed in light petroleum at room temperature and is accompanied by the production of a pale red-brown microcrystalline precipitate in reasonable yield (*e.g.* 54% with $AlMe_3$) concomitant with a loss of solution colour intensity. Subsequent recrystallisation of this precipitate from toluene or Et_2O yields **5** in poor yield.

The synthesis of complex **5** can be compared to that of $[TaH(PPh_2)_2(dmpe)_2]$[25b] (dmpe = $Me_2PCH_2CH_2PMe_2$) where addition of $KPPh_2{\cdot}2C_4H_8O_2$ to $[TaCl_2(dmpe)_2]$ at 0 °C in thf generates the product *via* fast proton abstraction from the solvent (no ESR signal associated with a intermediate was observed during the course of the reaction). The driving force of the reaction was rationalised in terms of a 17-electron species gaining a closed-shell configuration by hydride abstraction and from the viewpoint that replacement of halide by stronger-field ligands leads to species resembling organic radicals which rapidly disproportionate or abstract hydride from solvent. In our example, it is likey that transient co-ordinative unsaturation in the intermediate generated by removal of halide causes hydride abstraction from the solvent. Indeed if the reaction of **3** with AlX_3 or with $MBPh_4$ (M = Na or Ag) is performed in or worked up in $C_6D_5CD_3$, a material with identical physical properties to **5** may be isolated but which shows the absence of a zirconium hydride resonance in the ^1H NMR spectrum and bands assignable to ν(Zr–H) or ν(Zr–D) could not be identified in the IR spectrum (the latter may be obscured by ligand absorptions). Thus it appears that the formation of **5** *via* halide abstraction is a general feature of the reactivity of **3** with a variety of Lewis acids or $MBPh_4$ and that the source of the hydride is the solvent.

$[Zr_2Cl_3\{P(CH_2CH_2PMe_2)_2\}_3]$ **6**. Reduction of metal halides by metathesis with alkali-metal phosphides is well known. The addition of $LiPR_2$ to $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti or Zr; R = Me, Et or Ph) at room temperature generates the dimer $[\{M^{III}(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PR_2)\}_2]$[21b] where for M = Zr and R = Me the oxidation product $Me_2P\text{–}PMe_2$ was observed.[21c] The supernatant liquor following crystallisation of complex **3** was shown to contain the oxidation product $(Me_2PCH_2CH_2)_2P\text{–}P(CH_2CH_2PMe_2)_2$ and was ESR active indicating the presence of d^1 Zr^{III}, although no Zr–P superhyperfine coupling was observed and no other zirconium-containing compounds could be isolated from these solutions. Reduction could be optimised by addition of 3 mol equivalents of $LiP(CH_2CH_2PMe_2)_2$ to $ZrCl_4$ in Et_2O which generates intense red-brown solutions that ultimately afford crystalline **6** in 10% yield and which may be recrystallised from light petroleum as large almost black blocks. It is, however, diamagnetic in the solid state and analyses as $[Zr_2Cl_3\{P(CH_2CH_2PMe_2)_2\}_3]$. Both the $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra are complex. The former indicates the presence of co-ordinated [δ 15.0(m), 10.1(m), 8.4(m), 0.0(m)] and unco-ordinated tertiary phosphine [δ −51.8(m)] assigned on the basis of chemical shift, as well as three distinct phosphide functions [δ 139.8(m), 130.4(m), 126.6(m)]. In addition there are small unassignable peaks which may be due to other species in solution. The chemical shifts of the peaks assigned to phosphido-phosphorus centres are similar to those reported for bridging phosphides, whereas terminal π-bonded dialkylphosphides have been reported to resonate at lower fields[29] [*e.g.* δ 260.1 in a $Hf^{IV}(PEt_2)$ complex], however chemical shifts may be significantly influenced by pyramidal-planar phosphide interconversions[30] and commonly appear in a similar region to those of bridging phosphides.

In a preliminary report[10] we have described the crystal structure of complex **6**; the unique co-ordination environment for Zr is shown. The molecule is binuclear with a Zr ··· Zr distance of 3.361(2) Å and each zirconium centre supporting a terminal chloride is bridged by two phosphides and one chloride. The bridging atoms are quite unsymmetrically disposed around the Zr–Zr axis: the two bridging phosphides and the two zirconium centres are approximately coplanar, this plane being orthogonal to the Zr(1)–Zr(2)–Cl(12) plane. Each bridging phosphide is different however, with one spanning the Zr–Zr axis and each of its terminal tertiary phosphines co-ordinated to different zirconium centres, whilst the other has its tertiary phosphines co-ordinated to only Zr(2). The co-



6 R = Me

ordination sphere of Zr(1) is made up by the third phosphide [P(5)]. This ligand is chelating with a pendant tertiary phosphine [P(6a/b)]. The phosphide P(5) is π-bonded to Zr(1); in one conformation it is quite planar [Σ bond angles = 359.9(23)°] and in the other it is tending toward planar [Σ bond angles = 352.5(24)°]. The zirconium to terminal phosphide distance is within the range observed for other planar, terminal phosphides for which π bonding is proposed (*e.g.* 2.488 Å in $[Hf(\eta^5\text{-}C_5H_5)_2(PEt_2)_2]$, 2.533, 2.475 and 2.504 Å in $[Li{\cdot}dme][Hf\{P(C_6H_{11})_2\}_5]$, dme = 1,2-dimethoxy ethane).[30] The Zr–μ-P distances [2.673(3), 2.665(3) and 2.672(3) Å] are shorter than those observed in **5** but are very similar to those reported for other zirconium(III) binuclear complexes {*e.g.* in $[Zr_2(\eta^5\text{-}C_5H_5)_4(\mu\text{-}PMe_2)_2]$ *r*(Zr–μ-P) = 2.672(5) Å and in $[Zr_2(\eta^5\text{-}C_5H_5)_4(\mu\text{-}Cl)(\mu\text{-}PMe_2)]$, *r*(Zr–μ-P) = 2.648(2) and 2.661(2) Å}.[31] With one exception [P(4), *r*(Zr–P) = 2.703(3) Å] the zirconium to terminal tertiary phosphine distances [2.778(3), 2.782(3), 2.744(3) and 2.748(3) Å] are similar to those in **5**. The Zr–P(4) distance is significantly shortened relative to similar zirconium(IV) dmpe complexes, maybe as a result of the close approach of the π-bonded phosphido-phosphorus end of the chelate causing P(4) to be forced into a closer contact with Zr than would otherwise be observed.

A number of features of the structure are surprising. The co-ordination behaviour of the phosphide ligands is difficult to rationalise, however this compound demonstrates the versatility of the potentially tridentate ligand system since it can clearly co-ordinate Zr in a number of manners including both bridging and terminal environments. Therefore it presumably is able to satisfy co-ordination constraints dictated by the metal, a feature that may be of considerable value in stabilising unusual new classes of complexes.

The compound is diamagnetic in the solid state but contains zirconium(III) centres, hence unpaired electrons must be interacting although the Zr ··· Zr distance is long for a bonding interaction and is greater than that in **5** which cannot have a metal–metal bond. In the diamagnetic zirconium(III) dimer $[Zr_2(\eta^5\text{-}C_5H_5)_4(\mu\text{-}PMe_2)_2]$ metal–metal bonding is said to be absent on structural grounds [*r*(Zr ··· Zr) = 3.653 Å]; spin pairing is presumed to occur *via* the phosphide bridges. An alternative theory of 'superlong' metal–metal bonding has been proposed to explain both the diamagnetism of some zirconium(III) dimers (*e.g.* $[\{Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}I)\}_2]$)[32] with long Zr ··· Zr distances said to be due to ligand–ligand repulsion across the Zr ··· Zr bond. For the model systems $[\{Zr(\eta^5\text{-}C_5H_5)_2(\mu\text{-}PH_2)\}_2]$ and $[Zr_2(\mu\text{-}Cl)_2Cl_2(PH_3)_2]$, diamagnetism is said to arise from a direct M–M interaction at distances greater than 3.5 Å. A more recent theoretical study on the hypothetical $[\{Zr(\eta^5\text{-}C_5H_5)_2\}_2(\mu\text{-}PH_2)_2]$ and $[Zr_2(\mu\text{-}Cl)_2Cl_2(PH_3)_2]$[33] indicates the $Zr^{III} \cdots Zr^{III}$ distance to be dependent on a compromise between metal–metal bonding and steric constraints arising from the need to accommodate bridging ligands of varying bulk and steric interactions between the terminal ligands across the Zr–Zr axis. In this study the nature of any metal–metal interaction (at least in the former example) remains unclear as does the possibility of spin interaction *via* the bridging ligands. Several previous studies on zirconium(III) dimeric complexes have shown that *r*(Zr ··· Zr) is very dependent on the size of the bridging ligand. In $[\{Zr(\eta^5\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-}Te)_2]$, *r*(Zr ··· Zr) = 4.067 Å, whereas in the monooxo analogue $[\{Zr(\eta^5\text{-}C_5H_4Bu^t)_2\}_2(\mu\text{-}Te)(\mu\text{-}O)]$, *r*(Zr ··· Zr) = 3.390 Å.[34] Also, in the complexes $[\{Zr(\mu\text{-}X)X_2(PMe_2Ph)_2\}_2]$, *r*(Zr ··· Zr) = 3.439 Å when X = I and 3.127 Å when X = Cl.[35] In **5** and **6**, ligand interactions across the Zr–Zr unit are similar and since these ligands can clearly support a shorter Zr ··· Zr contact than that observed in **6** the metal–metal distance may be more greatly influenced by the nature of the phosphido linkages rather than the desire to optimise M–M bonding. It is possible that diamagnetism is maintained by spin interaction *via* the bridging phosphido atoms.

Acknowledgements

We thank the SERC for a fellowship (to A. A. D.) and a studentship (to J. S. P.) and access to the Mass Spectrometry Service (University College Swansea).

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Received 18*th November* 1993; *Paper* 3/06889G