(Phosphinoalkyl)silanes. 4.[1] Hydrozirconation as a Non-Photochemical Route to (Phosphinopropyl)silanes: Facile Assembly of the Bis(3-(diphenylphosphino)propyl)silyl (“biPSi”) Ligand Framework. Access to the Related Poly(3-(dimethylsilyl)propyl)phosphines $R_nP(CH_2CH_2CH_2SiMe_2H)_{3-n}$ ($n = 1$, R = Ph; $n = 0$)

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Treatment of $SiEt_3(CH{=}CH_2)$ with $ZrCp_2HCl$ (Schwartz’s reagent) followed by reaction with PPh_2Cl provides a high-yield (75%) route to $Ph_2PCH_2CH_2SiEt_3$, and accordingly hydrozirconation of $CH_2{=}CHCH_2SiHMe_2$ affords the intermediate $ZrCp_2(CH_2CH_2CH_2SiHMe_2)Cl$ (**2**). The latter, which is very sensitive to hydrolysis and reacts with HCl forming $SiHMe_2Pr^n$ and with NBS or I_2 affording $SiHMe_2CH_2CH_2CH_2X$ (X = Br (**3**), I (**4**)), behaves similarly with PPh_2Cl, $PPhCl_2$, or PBr_3 undergoing cleavage to the known $Ph_2PCH_2CH_2CH_2SiMe_2H$ (*i.e.* chelH, **A**) and the novel bis- and tris(silylpropyl)phosphines $PhP(CH_2CH_2CH_2SiMe_2H)_2$ (**5**) and $P(CH_2CH_2CH_2SiMe_2H)_3$ (**6**), respectively, with concomitant formation of $ZrCp_2Cl_2$. Corresponding hydroboration of allylsilanes is facile, but subsequent phosphine halide cleavage yields (phosphinoalkyl)silanes only as constituents of intractable mixtures. Hydrozirconation followed by phosphination with PPh_2Cl also converts $SiHMe(CH_2CH{=}CH_2)_2$ to $SiHMe(CH_2CH_2CH_2PPh_2)_2$ (*i.e.* biPSiH, **B**) together with a propyl analogue $Ph_2PCH_2CH_2CH_2SiMe(Pr^n)H$ (**7**) of **A** (*ca.* 2:1 ratio), as well as $SiH(CH_2CH{=}CH_2)_3$ to a mixture (*ca.* 5:2:1 ratio) of $SiH(CH_2CH_2CH_2PPh_2)_3$ (*i.e.* triPSiH, **C**), a new analogue $SiH(Pr^n)(CH_2CH_2CH_2PPh_2)_2$ (**8**) of **B**, and a further analogue $Ph_2PCH_2CH_2CH_2SiHPr^n{}_2$ (**9**) of **A**. A further analogue $SiH_2(CH_2CH_2CH_2PPh_2)_2$ (**10**) of biPSiH (**B**) is obtained similarly starting from $SiH_2(CH_2CH{=}CH_2)_2$. Steric control of silylalkyl cleavage from **2** is indicated by the fact that, like PPh_2Cl (which forms **B**), two further biPSiH analogues $SiH(Me)[CH_2CH_2CH_2P(n\text{-hex})_2]_2$ (**11**) and $SiH(Me)(CH_2CH_2CH_2PPhBz)_2$ (**12**) were obtained using $P(n\text{-hex})_2Cl$ (*i.e. n*-hex = $CH_3(CH_2)_4CH_2-$) or PPhBzCl (*i.e.* Bz = $-CH_2C_6H_5$), respectively, whereas neither $PPr^i{}_2Cl$ nor $PBu^t{}_2Cl$ led to (phosphinoalkyl)silane formation. The surface-substrate linking reagent $Ph_2PCH_2CH_2CH_2Si(OEt)_3$ (**D**) is formed efficiently by similar means from $Si(OEt)_3(CH_2CH{=}CH_2)$. NMR data (^1H, ^{13}C, ^{29}Si, ^{31}P) for **2**−**12** have been measured and are discussed.

Introduction

The chemistry of (phosphinoalkyl)silyl (“PSi”) complexes, in which a silyl group is *anchored* to a transition-metal center, has been developed using *chelate-assisted* addition reactions of (phosphinoalkyl)silanes.[2] The prototypal P,Si chelate precursor **A** (Chart 1), together with its analogues **B** (“biPSiH”) and **C** (“triPSiH”) that add to form polydentate silyl ligands (as the biPSi or triPSi frameworks), have hitherto been synthesized[3,4] through photochemical P−H bond addition to allyl(methyl)silanes; see eq 1. While this method is very efficient in terms

$$SiHMe_x(CH_2CH{:}CH_2)_{3-x} + (3 - x)PPh_2H = SiHMe_x(CH_2CH_2CH_2PPh_2)_{3-x} \quad (1)$$

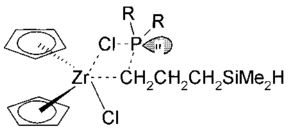
of overall conversion and tolerates some changes in organic functionality at Si or P, long reaction times and awkward scale-up logistics have led us to seek an alternate preparative strategy. Molecules related to **A**−**C** in which the three-carbon unit connection between P and Si is made through a planar benzenoid skeleton (“mcPSi” ligand frameworks;[1] mc = modified chelate) can readily be constructed[1] from benzylic carbanions, but this is an approach that cannot easily be adapted to assemble unsubstituted polymethylene backbones[3,4] (*i.e.* as in **A**−**C**). Framework flexibility has been shown[5] to be an important influence on substrate approach and binding at the reactive metal site in coordinatively unsaturated PSi complexes, so that in spite of the availability of the skeletally more rigid mcPSi analogues[1] the unmodified precursors (**A**−**C**) remain desirable targets. An old report describing[6] alkyl group transfer from B to P led us to investigate hydroboration[7] of appropriate allylsilanes as an intermediate step, but although borylalkylsilane[8] synthesis (*e.g.* of $R_2BCH_2CH_2CH_2SiMe_2H$, R_2 = 9-BBN) proved to be facile, subsequent B−C bond cleavage using PR_2Cl (R = Ph or Pr^i)

Chart 1

$SiHMe_2(CH_2CH_2CH_2PPh_2)$ **A** ('chelH')

$SiHMe(CH_2CH_2CH_2PPh_2)_2$ **B** ('biPSiH')

$SiH(CH_2CH_2CH_2Ph_2)_3$ **C** ('triPSiH')



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gave analogues of **A** only as constituents of intractable mixtures. We have found, however, that alkenyl hydrometalation/alkyl transfer mediated by Zr (rather than B) provides an efficient chemical (*vs* photochemical[3,4]) synthesis of PSi precursors (including **A**−**C**): This is a further adaptation of the "metallacycle transfer" route to main-group heteroles and heterocycles devised by Nugent and co-workers.[9]

Experimental Section

All manipulations were conducted under dry argon gas using standard inert-atmosphere techniques. Solvents were dried over sodium and benzophenone and were redistilled immediately prior to use. Zirconocene chloride hydride (Schwartz's Reagent), allyldimethylsilane, diallylmethylsilane, triallylsilane, triethylvinylsilane, and triethoxylvinylsilane were prepared by established methods. Reactions involving the use of $ZrCp_2HCl$ were shielded from daylight using glassware wrapped in aluminum foil. Chlorodiphenylphosphine, dichlorophenylphosphine, phosphorus trichloride, and phosphorus tribromide were commercial products (Aldrich Co.). Chlorodi-*n*-hexylphosphine was prepared by reaction of *n*-hexylmagnesium chloride with phosphorus trichloride. Chloro(benzyl)phenylphosphine was made similarly using benzylmagnesium chloride and dichlorophenylphosphine. The ^1H, ^{31}P, and ^{13}C NMR spectra were recorded using a Bruker AMX360 FT spectrometer; ^{29}Si NMR spectra were recorded using a Bruker WM250 FT spectrometer. IR spectra were obtained using a Bruker IFS25 FT spectrometer; mass spectroscopic data were measured on a Kratos Concept system using CH_4 chemical ionization. Microanalytical data were supplied by Canadian Microanalytical Ltd., Vancouver, British Columbia, Canada.

Synthesis of Compounds. I. (Silylalkyl)zirconocene Reagents. i. (2-(Triethylsilyl)ethyl)zirconocene Chloride, 1. Triethylvinylsilane (0.95 mL, 5.1 mmol) in benzene (10 mL) was added dropwise to a slurry of zirconocene chloride hydride ("Schwartz's reagent", Cp_2ZrHCl) (1.3 g, 5.1 mmol) in benzene (15 mL). The suspension gradually dissolved to give a yellow solution. The reaction mixture was stirred (5 h, 25 °C) and then volatiles were removed *in vacuo* to leave a very air-sensitive yellow solid residue (2.0 g, 100%). This product was characterized using NMR spectroscopy in dry C_6D_6 (see Table 1).

ii. (3-(Dimethylsilyl)propyl)zirconocene Chloride, 2. In a typical reaction allyldimethylsilane (0.28 mL, 2.0 mmol) in benzene (4 mL) was added to a slurry of Cp_2ZrHCl (0.54 g, 2.1 mmol) in benzene (10 mL). The suspension dissolved slowly to give a yellow solution. After stirring (16 h, 25 °C) with the reaction mixture protected from the light, removal of volatiles left an air-sensitive yellow powder (0.74 g, 100%), which was characterized using NMR spectroscopy (Table 1).

II. (2-(Diphenylphosphino)ethyl)triethylsilane. To a yellow solution in benzene (10 mL) of the (silylalkyl)zirconocene reagent **1** (2.8 mmol scale) was added chlorodiphenylphosphine (0.50 mL, *ca*. 2.8 mmol) in benzene (10 mL). The color faded, and after stirring (18 h, 25 °C), volatiles were removed under vacuum and then the solid residue was extracted with hexanes (15 mL). Evaporation of the solvent left the *product* as a colorless oil (0.69 g, 2.1 mmol, 75%). Anal. Calcd (found): C, 73.12 (73.08); H, 8.90 (8.24).

III. Silylalkyl Cleavage from 2. Investigation by *in Situ* NMR Spectroscopy. i. By HCl. A stream of dry HCl gas was bubbled (30 s) through a solution of the (silylpropyl)zirconocene intermediate **2**, prepared *in situ* in C_6D_6 as described in **Iii**. The yellow color was discharged with precipitation of a white solid, and $SiHMe_2Pr^n$ and $ZrCp_2Cl_2$ were identified by their ^1H and ^{13}C NMR spectra.

ii. By *N*-Bromosuccinimide (NBS). Formation of (3-Bromopropyl)dimethylsilane, 3. A solution of **2** (7.0 mmol), synthesized as in **Iii** but using tetrahydrofuran (THF, 30 mL) as solvent, was treated with a solution of NBS (1.2 g, 7.0 mmol) dissolved in THF (20 mL). After stirring at 20 °C (48 h), THF was evaporated leaving a brown waxy

Table 1. NMR Data[a] for Compounds **1**−**12**, **A**, and **B**

	^{31}P	^{29}Si	^1H						^{13}C						
compd	$\delta(PR_2)$	$\delta(SiR_3)$	$\delta(X^bCH_2)$	$\delta(XCH_2CH_2)$	$\delta(SiCH_2)$	$\delta(SiH)$	$\delta(SiCH_3)$	$^3J(CHSiH)$	$\delta(XCH_2)$	$^1J(P-C)$	$\delta(XCH_2CH_2)$	$^2J(P-C)$	$\delta(SiCH_2)$	$^3J(P-C)$	$\delta(SiCH_3)$
1[c]			0.94		0.49				46.34				16.04		
2			1.17	1.72	0.70	4.22	0.14	3.7	29.25		59.48		21.59		−3.89
3			3.40	1.88	0.69	3.86	0.09	3.6	36.65		28.30		13.38		−4.58
4			3.10	1.59	0.42	3.94	−0.09	3.6	*d*						
A	−16.5	−13.8	2.04	1.57	0.67	4.03	−0.06	3.5	32.23	13.0	21.50	18.0	16.29	12.1	−4.53
5	−27.1	−13.8	1.71	1.53	0.65	4.07	−0.04, −0.05	3.6	32.34	12.7	21.23	15.9	16.03	10.9	−4.82, −4.85
6	−34.6	−13.7	1.46	1.60	0.70	4.13	0.04	4.5	32.06	14.6	21.71	15.0	16.62	10.5	−4.40
7[e]	−17.1	−11.1	2.05	1.58	0.70	3.98	−0.06	3.7	32.37	12.8	21.61	17.7	14.97	11.9	−6.23
B	−17.0	−11.3	2.04	1.57	0.67	3.96	−0.10	3.9	32.29	12.9	21.56	17.4	14.76	12.1	−6.40
8[f]	−17.1	−8.9	2.03	1.53	0.68	3.89		3.5	32.40	13.1	21.72	17.6	13.43	12.1	
9[g]	−17.1	−8.3	2.08	1.60	0.74	3.94			*d*						
10	−16.9	−30.4	1.99	1.53	0.63	3.75		3.7	31.88	13.3	22.43	18.2	11.09	12.2	
11[h]	−32.8	−10.9	1.49	1.64	0.78	4.11	0.09	3.7	32.16	14.8	21.83	15.3	15.30	10.1	−6.10
12[i]	−19.9	−11.3	1.64	1.39	0.50	3.86	−0.18	3.5	31.24	17.1	21.43	14.8	14.81	16.7	−6.37

[a] C_6D_6 was used as solvent except for compound **3** ($CDCl_3$); ^{31}P chemical shifts vs external 85% H_3PO_4; ^{29}Si chemical shifts vs external tetramethylsilane; coupling constants were measured in Hz. [b] X = Zr in compound **1** and **2**; X = Br in compound **3**; X = I in compound **4**; X = P in compounds **5**−**12**, **A**, and **B**. [c] NMR data for ethyl group: ^1H, $\delta(SiCH_2) = 0.61$ ppm, $\delta(SiCH_2CH_3) = 1.08$ ppm; ^{13}C, $\delta(SiCH_2) = 3.10$ ppm, $\delta(SiCH_2CH_3) = 7.69$ ppm. [d] ^{13}C NMR not measured. [e] NMR data for propyl group: ^1H, $\delta(SiCH_2) = 0.45$ ppm, $\delta(SiCH_2CH_2) = 1.30$ ppm, $\delta(CH_3) = 0.91$ ppm; ^{13}C, $\delta(SiCH_2) = 15.35$ ppm, $\delta(SiCH_2CH_2) = 18.26$ ppm, $\delta(CH_3) = 18.07$ ppm. [f] NMR data for propyl group: ^1H, $\delta(SiCH_2) = 0.42$ ppm, $\delta(SiCH_2CH_2) = 1.26$ ppm, $\delta(CH_3) = 0.89$ ppm; ^{13}C, $\delta(SiCH_2) = 13.82$ ppm, $\delta(SiCH_2CH_2) = 18.39$ ppm, $\delta(CH_3) = 18.11$ ppm. [g] NMR data for propyl group: ^1H, $\delta(SiCH_2) = 0.50$ ppm, $\delta(SiCH_2CH_2) = 1.32$ ppm, $\delta(CH_3) = 0.93$ ppm. [h] NMR data for hexyl group: ^1H, $\delta(PCH_2) = 1.27$ ppm, $\delta(PCH_2CH_2) = 1.39$ ppm, $\delta(PC_2H_4CH_2) = 1.39$ ppm, $\delta(PC_3H_6CH_2) = 1.48$ ppm, $\delta(PC_4H_8CH_2) = 1.22$ ppm, $\delta(PC_5H_{10}CH_2) = 0.89$ ppm; ^{13}C, $\delta(PCH_2) = 31.88$ ppm, $^1J(P-C) = 18.0$ Hz, $\delta(PCH_2CH_2) = 31.61$ ppm, $^2J(P-C) = 10.3$ Hz, $\delta(PC_2H_4CH_2) = 28.18$ ppm, $^3J(P-C) = 13.9$ Hz, $\delta(PC_3H_6CH_2) = 26.55$ ppm, $^4J(P-C) = 13.5$ Hz, $\delta(PC_4H_8CH_2) = 22.96$ ppm, $^5J(P-C) = 8.2$ Hz, $\delta(PC_5H_{10}CH_2) = 14.29$ ppm, $^6J(P-C) = 7.9$ Hz. [i] NMR data for benzyl group: ^1H, $\delta(PCH_2) = 2.91$ ppm, $^2J(PCH_2) = 13.2$ Hz; ^{13}C, $\delta(PCH_2) = 36.91$ ppm, $^1J(P-C) = 4.9$ Hz.

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(8) Few such compounds appear to have been reported. See: Soderquist, J. A.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 3571. Soderquist, J. A.; Colberg, J. C.; Del Valle, L. *J. Am. Chem. Soc.* **1989**, *111*, 4873.

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residue that was extracted with *n*-pentane (20 mL). Removal of the latter left a yellow liquid mixture, a portion of which was shown by ^{1}H NMR (see Table 1) to contain (3-bromopropyl)dimethylsilane. Distillation *in vacuo* led to recovery of a pure sample of this product, as a colorless liquid (0.11 g, 0.61 mmol, 8.5%) condensing at −78 °C.

iii. By Diiodine. Formation of (3-Iodopropyl)dimethylsilane, 4. A reaction similar to that described in **IIIii** afforded a yellow, waxy residue that was subsequently extracted with hexanes. Evaporation of the solvent left yellow, liquid material shown (^{1}H NMR) to contain the iodo analogue **4** of compound **3**.

IV. (Phosphinoalkyl)silanes. i. (3-(Diphenylphosphino)propyl)dimethylsilane, A ("chelH"). On addition of PPh_2Cl (0.38 mL, 2.1 mmol) to a solution in benzene of **2** (2.1 mmol), the yellow color of the latter was discharged during stirring (20 h, 25 °C) as a white solid slowly precipitated. Removal of volatiles left a sticky residue that was extracted with hexanes (15 mL) to give a clear solution; reduction in volume to 3 mL was followed by further stirring (10 h), during which time more of the white material deposited. Removal of the supernatant using a syringe followed by solvent evaporation *in vacuo* left a colorless oil identified by NMR (Table 1) as[3] pure $PPh_2CH_2CH_2CH_2SiMe_2H$, **A** (0.45 g, 1.6 mmol, 79%). The white solid was identified (NMR) as $ZrCp_2Cl_2$.

ii. Bis(3-(dimethylsilyl)propyl)phenylphosphine, 5. In a reaction similar to that described in **IVi** after $PPhCl_2$ (0.80 mL, 5.9 mmol) in benzene (15 mL) was added to a yellow solution of **2** (12 mmol) also in benzene (60 mL), the mixture was stirred (18h, 25 °C) and then volatiles were removed under vacuum (25 °C/10^{-2} mmHg). The residue was extracted with hexanes (30 mL); removal of the latter left an oil which was distilled at reduced pressure (110 °C/10^{-2} mmHg) to afford the pure product as a moderately air-sensitive, colorless liquid (0.58 g, 1.7 mmol, 29%). Anal. Calcd (found): C, 61.88 (62.51); H, 10.06 (9.78).

iii. Tris(3-(dimethylsilyl)propyl)phosphine, 6. In a further similar reaction, PBr_3 (0.25 mL, 2.6 mmol) in benzene (5 mL) was added to a solution in the same solvent (50 mL) of **2** (8.0 mmol). After the mixture was stirred at gentle reflux (18 h, 75 °C), volatiles were removed and then the residue was extracted with hexanes (20 mL). Evaporation of the latter left an oil which was distilled at reduced pressure (75 °C/10^{-2} mmHg) to afford the pure product as an air-sensitive yellow liquid (0.13 g, 0.39 mmol, 15%). Anal. Calcd (found): C, 53.82 (53.29); H, 11.74 (11.28).

iv. Bis(3-(diphenylphosphino)propyl)methylsilane, B ("biPSiH") and (3-(Diphenylphosphino)propyl)propylmethylsilane, 7. Using procedures that paralleled those described in **Iii**, diallylmethylsilane (1.2 mL, 7.6 mmol) in benzene (20 mL) was added to $ZrCp_2HCl$ (4.0 g, 16 mmol) in the same solvent (30 mL). The mixture was stirred in the dark (16 h, 25 °C), and then PPh_2Cl (2.71 mL, 15 mmol) in benzene (20 mL) was added. After further stirring, removal of volatiles, and extraction with, and then evaporation of, hexanes (20 mL), as described in **IVi**, a colorless oil remained, from which the product **7** (0.50 g, 1.6 mmol), which is an analogue of **A**, was distilled at reduced pressure (120 °C/10^{-2} mmHg); this left behind a viscous oily residue which was identified (NMR) as[4] $SiHMe(CH_2CH_2CH_2PPh_2)_2$, **B** (1.9 g, 3.8 mmol, 51%).

v. Tris(3-(diphenylphosphino)propyl)silane, C ("triPSiH"), (3-(Diphenylphosphino)propyl)dipropylsilane, 8, and Bis(3-(diphenylphosphino)propyl)propylsilane, 9. Triallylsilane (0.50 mL, 2.63 mmol) in benzene (5 mL) was added to $ZrCp_2HCl$ (2.24 g, 8.7 mmol) in benzene (20 mL). After stirring (18 h, 25 °C), PPh_2Cl (1.56 mL, 8.7 mmol) in benzene (15 mL) was added; subsequent treatment as in **IViv** left a viscous, oily mixture. The analogue **9** (0.20 g, 0.58 mmol) of **A** was distilled out under vacuum (170 °C/10^{-2} mmHg), leaving a very viscous residue shown by NMR spectroscopy to be a mixture of[4] $SiH(CH_2CH_2CH_2PPh_2)_3$, **C**, and the analogue **8** of **B** (∼2:1, 1.0 g).

vi. Bis(3-(diphenylphosphino)propyl)silane, 10. Diallylsilane (0.45 mL, 3.0 mmol) in benzene (10 mL) was added to $ZrCp_2HCl$ (1.6 g, 6.3 mmol) in benzene (20 mL). After stirring (16 h, 25 °C), PPh_2Cl (1.1 mL, 6.3 mmol) in benzene (10 mL) was added, and then the mixture was treated as in **IViv** above, affording a colorless oil. Removal from the latter of all material volatile at 120 °C/10^{-2} mmHg left the pure product as an oily residue (0.86 g, 1.8 mmol, 59%). Anal. Calcd (found): C, 74.35 (73.38); H, 7.07 (7.26).

vii. Bis(3-(di-*n*-hexylphosphino)propyl)methylsilane, 11. Hydrozirconation of $SiHMe(CH_2CH{=}CH_2)_2$ (0.33 mL, 2.0 mmol) in benzene (total 15 mL) as described in **IViv** followed by addition of chlorodi-*n*-hexylphosphine (1.0 mL, 4.0 mmol) in benzene (10 mL) and then further treatment as described in **IVvi** above afforded the pure product as an air-sensitive oil (0.49 g, 0.92 mmol, 46%). Anal. Calcd (found): C, 70.13 (69.81); H, 12.91 (11.98).

viii. Bis(3-(benzylphenylphosphino)propyl)methylsilane, 12. In a manner similar to that described in **IVvi** above, the bis-hydrozirconated intermediate (2.7 mmol) in benzene (25 mL) was treated with benzyl(chloro)phenylphosphine (1.3 g, 5.6 mmol) in benzene (10 mL) after which the reaction mixture was allowed to react and then worked up similarly, yielding the pure product as a viscous colorless oil (0.80 g, 1.5 mmol, 56%). Anal. Calcd (found): C, 75.25 (74.69); H, 7.66 (7.45).

V. (3-(Diphenylphosphino)propyl)triethoxysilane, D. Allyltriethoxysilane (0.50 mL, 2.2 mmol) in benzene (10 mL) was added to $ZrCp_2HCl$ (0.60 g, 2.3 mmol) also in benzene (10 mL), and then the mixture was stirred at ambient conditions overnight in the dark. Chlorodiphenylphosphine (0.4 mL, 2.2 mmol) in benzene (10 mL) was added. After the mixture was stirred for 1 day (25 °C), volatiles were removed under vacuum and the sticky residue was extracted with hexanes (15 mL). Evaporation of the solvent left the colorless oily product (0.62 g, 1.6 mmol, 73%). Anal. Calcd (found): C, 64.58 (64.09); H, 8.00 (7.29).

Results

Hydroboration of alkenylsilanes, an operation that has hitherto only been cursorily investigated,[8] proved to be straightforward (eq 2) using Brown's reagent,[7] 9-BBN, *i.e.* bis(9-borabicyclo-

$$SiHMe_x(CH_2CH{:}CH_2)_{3-x} + (3-x)BR_2H = SiHMe_x(CH_2CH_2CH_2BR_2)_{3-x} \quad (2)$$

[3.3.1]nonane) or alternatively dichloroborane (Me_2S adduct). Although the borylalkylsilanes so derived [from methyl(vinyl)-, methyl(allyl)-, or trialkenylsilanes, *etc.*] react violently with moisture (some burning spontaneously in air with a characteristic lime-green flame), they are completely stable *in vacuo* or under argon and were fully characterized by elemental analysis as well as by using multinuclear NMR spectroscopy. We found, however, that subsequent B−C cleavage reactions with organophosphine halides (including PPh_2Cl, $PPhCl_2$, $PPr^i{}_2Cl$, and PCl_3), which were investigated *in situ* by using NMR spectroscopy, were very slow (days) and formed intractable product mixtures. Consequently, while signals attributable to target (phosphinoalkyl)silanes (*i.e.* like **A**−**C**) were clearly discernible, boron-mediated synthesis was abandoned as a useful route to pure compounds.

Hydrozirconation as a parallel approach was examined in a preliminary experiment by addition of triethylvinylsilane to a slurry in dry benzene of zirconocene chloride hydride. NMR spectroscopy suggested that the yellow, very air-sensitive powder recovered from the clear yellow solution so formed was a (triethylsilylethyl)zirconocene derivative **1**, eq 3; further

$$ZrCp_2HCl + SiEt_3(CH{:}CH_2) = ZrCp_2(CH_2CH_2SiEt_3)Cl \quad (3)$$

reaction with PPh_2Cl (1 mol equiv) led to detection (NMR: see Table 1) of $ZrCp_2Cl_2$ and to isolation in high yield (>75%) of colorless, liquid ((diphenylphosphino)ethyl)(triethyl)silane (eq 4), *i.e.* to successful formation of the desired Si−polymethylene−P connectivity. To test the regioselectivity as well as the

$$ZrCp_2(CH_2CH_2SiEt_3)Cl + PPh_2Cl = PPh_2CH_2CH_2SiEt_3 + ZrCp_2Cl_2 \quad (4)$$

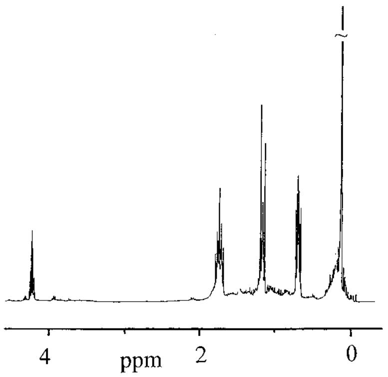
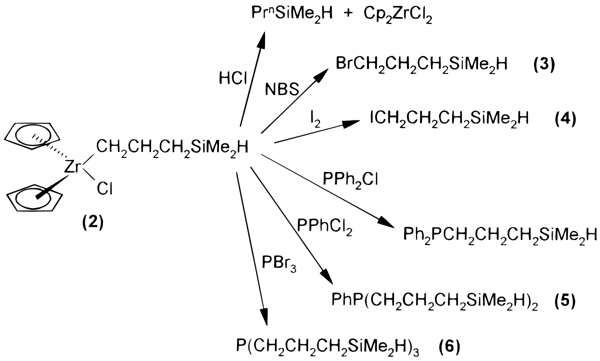


Figure 1. ^{1}H NMR spectrum (360 MHz; 0−5 ppm region) of $ZrCp_2(CH_2CH_2CH_2SiMe_2H)Cl$, **2**.

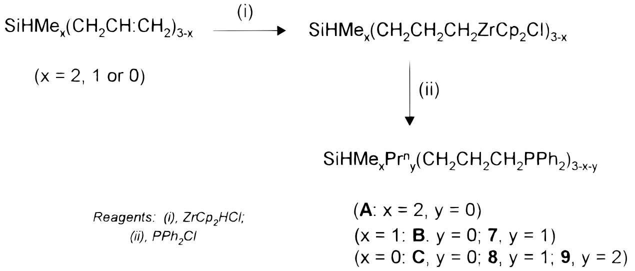
Scheme 1



generality of this chemistry, hydrozirconation using $ZrCp_2HCl$ (Schwartz's reagent) of allyl(dimethyl)silane ($CH_2{=}CHCH_2SiHMe_2$, *i.e.* already incorporating the Si−H functionality required for oxidative complexation at a low-valent transition-metal center[2]) was subsequently investigated. This affords exclusively the (dimethylsilyl)propyl analogue **2** of **1** (see eq 3), immediately distinguishable from its (2-(methylsilyl)ethyl)-zirconium regioisomer in the ^{1}H NMR spectrum (Table 1). In the 0−5 ppm range, which is shown in Figure 1, the Si*Me* signal is split into a doublet by coupling (^3J = 3.7 Hz) to Si*H*, the latter appearing as a septet at δ 4.22, accompanied by three well-separated methylene resonances. Direct comparison of the appearance of this region with that illustrated[3] elsewhere for $Ph_2P(CH_2)_3SiMe_2H$ (*i.e.* chelH, **A**; Table 1) highlights an upfield shift (δ 1.17) for the CH_2 protons α to the electropositive Zr center, to a position between the methylene hydrogens α and β to Si (δ 0.70, 1.72, respectively). The identity of **2** was further confirmed by its characteristic reactivity:[10] With traces of moisture, progressive replacement of the C_5H_5 NMR signal of **2** (δ 5.80) by a new Cp peak at δ 6.05 occurred, together with accumulation of a prominent triplet at δ 0.96 attributable to the CH_3 resonance of $SiHMe_2Pr^n$. Similarly, when dry HCl was bubbled into a solution of **2** in C_6D_6, the yellow color was discharged with precipitation of white $ZrCp_2Cl_2$ (observed at δ 5.88) and the pattern of multiplets due to $SiHMe_2Pr^n$ was again evident. Oxidative cleavage by addition to solutions of **2** of either *N*-bromosuccinimide (NBS) or diiodine (1 mol equiv) afforded products identified by ^{1}H NMR as (3-halogenopropyl)-(dimethyl)silanes, **3** or **4**, respectively; see Scheme 1.

Following a procedure similar to that of eq 4, addition of PPh_2Cl to a yellow solution in benzene of the silylpropyl **2** led again to discharge of the color, to formation of $ZrCp_2Cl_2$, and to the isolation in high yield (~80%) of the known[3] (phosphinoalkyl)silane $Ph_2PCH_2CH_2CH_2SiMe_2H$ (*i.e.* **A**), Scheme 1. Under the same conditions, reaction of **2** with either $PPhCl_2$ or PBr_3 afforded (Scheme 1) the corresponding bis- or tris(silylpropyl)phosphines $PhP(CH_2CH_2CH_2SiMe_2H)_2$ (**5**) and $P(CH_2CH_2CH_2SiMe_2H)_3$ (**6**) as colorless or yellow oily liquids that were purified by using short-path distillation at reduced pressure. These new polysilyls showed strong IR absorption near 2100 cm^{-1} (ν_{Si-H}) and were further characterized by the NMR data of Table 1: In the ^{1}H NMR, the methylene hydrogens α and β to Si are essentially invariant and the γ protons (*i.e.* α to P) shift progressively to higher field as Ph at P is replaced by $-CH_2CH_2CH_2SiMe_2H$, while the distinctive multiplet family due to this latter group make up the entire spectrum for **6**, which is a homoleptic trialkylphosphine. As has been observed before for related compounds including[3,4] **A**, in the ^{13}C NMR coupling to ^{31}P persists for all successive carbons of the polymethylene chain; by contrast the ^{29}Si resonances are observed as sharp singlets, although for $Ph_2PCH_2CH_2SiEt_3$ (*i.e.* with Si and P separated by only two methylene units) $^3J_{SiP}$ = 20 Hz (Table 1).

Scheme 2



Access using parallel operations to the poly(phosphinoalkyl)-silanes biPSiH, **B**, or triPSiH, **C**, requires that hydrozirconation occurs across each terminal alkenyl group in a diallyl- or triallylsilane. After a solution in benzene of $SiH(Me)(CH_2CH{=}CH_2)_2$ was added to $ZrCp_2HCl$ (2 mol equiv), ^{1}H NMR showed that all allyl groups had reacted, clearly establishing that multiple hydrozirconation of the precursor silane is possible. New signals at δ 0.15, 0.30 (doublets) and 4.17, 4.34 (multiplets) are attributable to the $SiCH_3$ and Si*H* hydrogens, respectively, of mono- and biszirconated intermediates related to **2**. A characteristic triplet (δ 1.03) due to Pr^n attached to Si in the monosubstituted species confirms that it originates from partial hydrolysis, and although its formation could be suppressed, it was never eliminated under the experimental conditions employed. Thus in a typical further reaction with PPh_2Cl an oily mixture (*ca.* 2:1) of the known[4] biPSiH (**B**) and a propyl analogue $Ph_2PCH_2CH_2CH_2SiMe(Pr^n)H$ (**7**) of **A** was formed; these two compounds proved to be separable by distillation, giving pure **B** in ~50% yield. Both the latter and **7** (δ 0.91, triplet; Pr^n group) are cleavage products of a bis-zirconated intermediate related to **2**, and accordingly a similar sequence, see Scheme 2, converted $SiH(CH_2CH{=}CH_2)_3$ to a mixture (*ca.* 5:2:1 ratio) of the known[4] triPSiH, a new biPSiH analogue $SiH(Pr^n)(CH_2CH_2CH_2PPh_2)_2$ (**8**), and a further analogue $Ph_2PCH_2CH_2CH_2SiHPr^n{}_2$ (**9**) of **A**. These three products, of which only **9** could be obtained pure by distillation *in vacuo*, were shown by using *in situ* ^{1}H NMR to be formed from tris-, bis-, and monozirconated intermediates characterized by Si*H* resonances at δ 4.44, 4.31, and 4.18 (apparent sextets), respectively. A further analogue $SiH_2(CH_2CH_2CH_2PPh_2)_2$ (**10**) of biPSiH (**B**) was also prepared similarly, starting from diallylsilane[11] $SiH_2(CH_2CH{=}CH_2)_2$. NMR data for **8**−**10** are included in Table 1.

The zirconium-mediated chemistry of Schemes 1 and 2 suggests that choice of R in the reagent PR_2Cl may offer a

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straightforward method for varying substituent groups at P in PSi ligand precursors. The commercially available alkylphosphine chlorides PR_2Cl ($R = Pr^i$ or Bu^t) behaved differently from one another, but in reactions monitored by using NMR neither yielded a (phosphinoalkyl)silane. Thus with $R = Pr^i$, precursor **2** (Scheme 1) was consumed to afford a new $-SiHMe_2$ derivative that did not however contain P, together with a product tentatively identified as $P_2Pr^i_4$, while with $R = Bu^t$ only slow hydrolysis of **2** was observed with no evidence for formation of $ZrCp_2Cl_2$. There was also no reaction of PBu^t_2Cl with a solution containing hydrozirconated $SiH(Me)(CH_2CH{=}CH_2)_2$, but by contrast treatment of the latter with $P(n\text{-hex})_2Cl$, *i.e.* $n\text{-hex} = CH_3(CH_2)_4CH_2-$, did behave according to Scheme 2. This facilitated isolation in good yield of a further new biPSiH analogue $SiH(Me)[CH_2CH_2CH_2P(n\text{-hex})_2]_2$ (**11**), and another congener $SiH(Me)(CH_2CH_2CH_2PPhBz)_2$ (**12**) was similarly recovered (~60%) by using PPhBzCl (*i.e.* $Bz = -CH_2C_6H_5$). NMR data for **11** and **12** are listed in Table 1. The diastereoisomeric character of **12** (*rac vs meso*) could not be detected by NMR (^{31}P, ^{29}Si).

Mass spectrometry was used for further characterization of the new PSi precursors **5**−**12**. Using CH_4 chemical ionization, parent ions were prominent in all cases; fragmentation was much simpler than that observed[1] for mcPSi analogues and was dominated by loss of organic groups from Si or P, so that for the tris(silylpropyl)phosphine **6** the only abundant ions were those corresponding to loss of one or two “arms” from P. In further synthetic experiments unrelated to those described above it was also shown that neither $SiMe_3Cl$ nor $SiHMe_2Cl$ led to cleavage of **2** analogous to that effected by the phosphorus halides (Scheme 1) and that hydrozirconation followed by phosphination using PPh_2Cl provides an efficient way of converting $Si(OEt)_3(CH_2CH{=}CH_2)$ to a known target[12] for use as a surface-substrate linking reagent, the triethoxysilyl derivative $Ph_2PCH_2CH_2CH_2Si(OEt)_3$ (**D**).

Discussion

It is apparent that hydrozirconation using $ZrCp_2HCl$ opens up a new route to 1-phosphino, 3-silylpolymethylene connectivity by cleavage using halogenophosphines of 3-(silylalkyl)zirconium complexes (including **2**, Scheme 1) that are formed as intermediates from poly- as well as monoalkenylsilanes. This acts as a convenient and versatile chemical synthesis of (phosphinoalkyl)silanes that are required[5] as precursors to transition metal PSi complexes. Thus in the silane $SiHR^1_x[(CH_2)_nPR^2_2]_{3-x}$, with R^1 and n determined by appropriate choice of alkenylsilane precursor (with silaalkyl attachment at Zr expected to be independent of n), it has been shown here that x can be varied at the intermediate stage, by using poly(hydrozirconation), Scheme 2, and that R^2 can be introduced as alkyl (*n*-hex) instead of aryl (Ph). In the latter context, it is clear that halogenophosphine cleavage of the (silylalkyl)zirconium intermediate is controlled by steric rather than electronic influences, as has been suggested previously.[9] This is expected for group-transfer by σ-bond metathesis at the Zr center, **E**, constrained by the zirconocene “bite”, *i.e. via* the transition state proposed by Nugent *et al.*[9] The shutdown of alkyl transfer from Zr to P (accompanied by formation of $ZrCp_2Cl_2$) is observed to occur between PPhBzCl and PPr^i_2Cl (with PBu^t_2Cl totally unreactive), *i.e.* follows expectations based on phosphine group “cone-angle”[13] considerations; this suggests in particular that $-PMe_2$ groups could be introduced in this way although this has not been investigated. Residual zirconium-containing material can in principle be recycled to $ZrCp_2HCl$ although this was also not attempted.

A cationic (silylalkyl)zirconocene complex related to **2**, $ZrCp_2(CH_2CH_2SiMe_3)(THF)^+$ (BPh_4^- salt), has been structurally characterized previously by Jordan *et al.*[14] The hydrolysis and oxidative dealkylation reactions of Scheme 1 are typical of alkylzirconocene derivatives,[10] but despite the synthetic versatility of such chemistry zirconium-mediated group transfer onto phosphorus (*i.e.* related to that of the silylpropyl of **2**; see eq 4) has only recently been reported.[9] Fryzuk *et al.*[15,16] and Majoral *et al.*[17] have shown respectively that dienyl or alkylphosphine fragments can be attached at P in this way, providing novel routes to dienylphosphines or biphosphines. Chlorosilanes do not[9,15] however induce similar group transfer at Zr (*i.e.* onto Si) and, accordingly, do not cause dealkylation of **2**.

The poly(silapropyl)phosphines $PhP(CH_2CH_2CH_2SiMe_2H)_2$ (**5**) and $P(CH_2CH_2CH_2SiMe_2H)_3$ (**6**) belong to a new subgroup of PSi precursors that are expected to induce chelate-assisted multiple[18] Si−H bond addition at transition-metal centers: This chemistry is under investigation. Successive substitution of aryl by alkyl at P along the family of **A**, **5**, and **6** results in monotonic changes in ^{31}P and PCH_2 NMR shifts as is expected (Table 1). Two methyl resonances are observed in both ^1H and ^{13}C NMR spectra for **5**, a reflection[4] of its low molecular symmetry (C_s) *vs* that of the trisubstituted compound **6** (the idealized geometry of which belongs to the point group C_{3v}).

The methodology described above also offers a more direct route to the linking reagent[12] **D** than the earlier synthesis[19] using $Si(OEt)_3CH_2CH_2CH_2Cl$, a precursor that in any case might most easily be made *via* the chemistry of Scheme 1.

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(11) The precursor was synthesized by a modified procedure: To trimethoxysilane (13.9 g, 0.11 mol) in diethyl ether (100 mL) was added dropwise allylmagnesium chloride (0.22 mol) also in ether (230 mL), leading to immediate formation of a white precipitate. The mixture was stirred (12 h) and then filtered through a glass frit; evaporation of ether left clear, liquid diallylmethoxysilane which was purified by fractional condensation at −78 °C. Yield: 12.3 g, 0.086 mol, 79%. This product (5.0 g, 0.035 mol) was taken up in ether (50 mL) and cooled to −78 °C, and then a solution of lithium aluminum hydride (0.83 g, 0.022 mol) in ether (80 mL) was added dropwise and the mixture was allowed to warm to ambient and stirred (6 h). Removal of ether followed by distillation at reduced pressure afforded a first fraction of pure (^1H NMR) diallylsilane (1.5 g, 0.013 mol, 38%) condensed at −78 °C.

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