

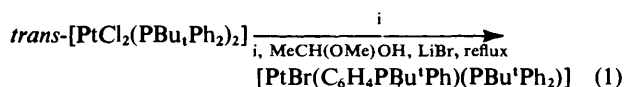
Phosphinoalkylsilanes: Synthesis and Spectroscopic Properties of Phosphino(silyl)methanes, 1-Phosphino-2-silylethanes, and 1-Phosphino-3-silylpropanes

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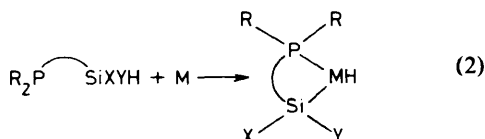
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Synthesis of thirty-three compounds $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{SiXYZ}$ ($n = 1, 2, \text{ or } 3$) and $\text{Me}_2\text{P}(\text{CH}_2)_2\text{SiXYZ}$ in which X, Y, or Z = H, Me, Ph, or Cl has been accomplished by (a) reaction at -78°C in tetrahydrofuran between alkyl(chloro)silanes and $\text{Ph}_2\text{PCH}_2\text{Li}\cdot\text{tmeda}$ for $n = 1$, or (b) u.v. irradiation of chloro(vinyl)silanes or allyl(chloro)silanes with Ph_2PH or Me_2PH for $n = 2$ or 3, with (c) reduction of the chlorosilyl products to Si-H analogues. Characterization of the phosphinoalkylsilane derivatives includes full ^1H , ^{13}C , and ^{31}P n.m.r. data which are discussed in terms of dependence on the number of methylene groups, n , in the backbone and on the substituents, X, Y, Z, at Si, together with comparisons to related compounds.

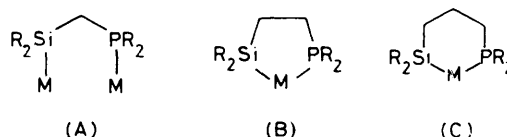
Organophosphorus compounds have been of paramount importance in the evolution of co-ordination chemistry. The soft-base character of the phosphorus centre combined with its ability to behave as an electron acceptor in relation to π back-donation results in formation of a vast range of complexes with the heavier transition elements and in stabilization of metal atoms in low formal oxidation states. Introduction of bifunctionality as in the α,ω -bis(phosphino)alkanes $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$ can thus provide a way of (a) bridging between two metal centres¹ when $n = 1$ [bis(diphenylphosphino)methane, dpm] or (b) chelating at a single metal atom² for $n = 2$ [bis(diphenylphosphino)ethane, diphos] or higher.³ Modification to incorporate two different donor sites, as for example⁴ in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{AsPh}_2$, affords a route to unsymmetrical bridging or chelating units, in which two non-identical ligating atoms are involved in co-ordination. A somewhat similar situation is effected by the so-called 'internal metalation,' 'cyclometallation,' or 'orthometallation' reaction⁵ typified by the example⁶ shown in equation (1): heteroatom coordination at M is accompanied by M-C bond formation, representing a specific type of C-H bond activation which frequently involves transfer of the H to M.



Seeking to establish a related reaction involving the lower members of group 4 (for which hydrometallation at transition-metal centres is not uncommon)⁷ led us to explore chelate-assisted hydrosilylation represented by equation (2) as a means for anchoring a silyl group to a metal site. In so doing we found that synthesis of only very few α -phosphino- ω -silylalkanes,



$\text{R}_2\text{P}(\text{CH}_2)_n\text{SiXYZ}$, had previously been reported and accordingly no systematic description of the properties of these compounds was available. Here we present synthetic details and spectral data for a family of such derivatives (1)–(33), with $n = 1$ [precursors to a structure with a novel bridging arrangement (A)] or $n = 2$ or 3 [precursors to chelate geometries (B) and (C)].



$\text{Ph}_2\text{PCH}_2\text{SiXYZ}$

- (1) X = Y = Z = Me
- (2) X = Y = Me, Z = Cl
- (3) X = Y = Me, Z = H
- (4) X = Me, Y = Ph, Z = Cl
- (5) X = Me, Y = Ph, Z = H
- (6) X = Y = Ph, Z = Cl
- (7) X = Y = Ph, Z = H
- (8) X = Y = Z = Ph
- (9) X = Ph, Y = Z = Cl
- (10) X = Ph, Y = Z = H

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiXYZ}$

- (11) X = Y = Me, Z = Cl
- (12) X = Y = Me, Z = H
- (13) X = Me, Y = Ph, Z = Cl
- (14) X = Me, Y = Ph, Z = H
- (15) X = Y = Ph, Z = Cl
- (16) X = Y = Ph, Z = H
- (17) X = Me, Y = Z = Cl
- (18) X = Me, Y = Z = H
- (19) X = Ph, Y = Z = Cl
- (20) X = Ph, Y = Z = H
- (21) X = Y = Z = Cl
- (22) X = Y = Z = H

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{SiXYZ}$

- (23) X = Y = Z = Me
- (24) X = Y = Me, Z = Cl
- (25) X = Y = Me, Z = H
- (26) X = Y = Z = Cl
- (27) X = Y = Z = H

$\text{Me}_2\text{PCH}_2\text{CH}_2\text{SiXYZ}$

- (28) X = Y = Me, Z = Cl
- (29) X = Me, Y = Ph, Z = Cl
- (30) X = Me, Y = Z = Cl
- (31) X = Y = Me, Z = H
- (32) X = Me, Y = Ph, Z = H
- (33) X = Me, Y = Z = H

Experimental

General.—All synthetic manipulations were carried out using standard inert atmosphere techniques and all solvents were dried and distilled under dry dinitrogen gas. N.m.r. spectra were obtained with Perkin-Elmer R32 (^1H , 90 MHz), Nicolet TT-14 (^{13}C , 15.1 MHz; ^{31}P , 24.3 MHz), and Bruker WM250 (^1H , 250 MHz; ^{13}C , 93.6 MHz) spectrometers. I.r. spectra were recorded using a Perkin-Elmer 283 spectrophotometer.

The simple silanes, diphenylphosphine, and methyldiphenylphosphine were purchased (Aldrich, Strem Chemicals, or Petrarch) or synthesized by literature procedures and were distilled under dry dinitrogen gas immediately prior to use. The lithium salt $\text{LiCH}_2\text{PPh}_2\cdot\text{tmeda}$ (tmeda = tetramethylethylenediamine) was prepared from methyldiphenylphosphine as recently described by Schore *et al.*⁸ Most of the new compounds deteriorated rapidly in air, the chlorosilyl derivatives being particularly sensitive. Purity of products was established by microanalysis (Canadian Microanalytical

Table 1. Analytical data

Compound	Analysis ^a		Yield (%)	I.r. (cm ⁻¹) ^b	B.p. ^c
	C	H			
(1)	71.22 (70.55)	7.57 (7.77)	62		124—138
(2)	62.06 (61.53)	6.90 (6.20)	76	475	116
(3)	69.77 (69.73)	8.07 (7.41)	80	2 120	105
(4)	68.80 (67.69)	6.04 (5.68)	61	470	175—180
(5)	74.29 (74.94)	6.68 (6.60)	63	2 120	150—155
(6)	71.66 (72.07)	5.86 (5.32)	40	490	200—210
(7)	75.26 (74.50)	6.40 (6.06)	40	2 140	170—175
(8)	80.30 (81.19)	6.25 (5.93)	76		^d
(9)	61.43 (60.80)	5.84 (4.57)	35	460	190
(10)	74.67 (74.47)	6.40 (6.25)	80	2 150	160
(11)	64.47 (62.64)	6.44 (6.53)	71	470	145—150
(12)	70.64 (70.54)	7.19 (7.77)	78	2 105 ^e	130—135
(13)	65.15 (68.39)	6.75 (5.97)	68	490	170
(14)	75.76 (76.17)	7.56 (6.69)	63	2 118 ^f	160
(16)	78.12 (78.79)	6.80 (6.31)	68	2 105 ^g	180 ^h
(17)	55.14 (55.05)	5.51 (5.20)	75	540	178
(18)	70.14 (69.75)	7.05 (7.36)	65	2 135 ⁱ	180
(20)	74.86 (75.00)	6.72 (6.56)	57	2 140	175
(21)	48.40 (48.37)	4.16 (4.03)	67	570	150—160
(22)	67.18 (68.85)	6.64 (6.97)	68	2 160	145
(23)	72.60 (71.95)	8.60 (8.39)	15		190
(24)	68.02 (63.63)	6.16 (6.91)	30	470	180—190
(25)	71.90 (71.28)	8.96 (8.09)	40	2 105	150—160
(26)	50.75 (49.81)	5.41 (4.46)	65	505	165—180
(27)	70.67 (69.73)	8.04 (7.41)	80	2 150	160—170

^a Calc. values in parentheses. ^b Characteristic $\nu(\text{SiX})$, X = Cl or H, as appropriate. ^c Approximate boiling point or range ($^{\circ}\text{C}/10^{-2}$ mmHg). ^d Isolated as an oily, low-melting solid. ^e $\nu(\text{SiD})$ at $1\ 532\ \text{cm}^{-1}$ in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiMe}_2\text{D}$. ^f $\nu(\text{SiD})$ at $1\ 540\ \text{cm}^{-1}$ in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiMePhD}$. ^g $\nu(\text{SiD})$ at $1\ 530\ \text{cm}^{-1}$ in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiPh}_2\text{D}$. ^h Solidified to crystalline material, m.p. $83\ ^{\circ}\text{C}$. ⁱ $\nu(\text{SiD})$ at $1\ 548\ \text{cm}^{-1}$ in $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiMe}_2\text{D}_2$.

Services Ltd., Vancouver) and by the spectroscopic data. Analytical data are listed in Table 1.

Synthetic Procedures.—The following are typical of the preparative reactions. (i) *2-Chlorodimethylsilyl-1-diphenylphosphinoethane* (11). Diphenylphosphine (1.96 g, 1.05 mmol) and chlorodimethylvinylsilane (2.17 g, 1.66 mmol) were loaded into a quartz reaction tube fitted with a greaseless high-vacuum stopcock, which was then evacuated, placed

approximately 5 cm from a medium-pressure mercury lamp and irradiated (5 h). The viscous oily liquid phase was separated from a small quantity of solid material by dissolution in dry benzene (20 cm³). This solution was transferred to a Schlenk tube from which all volatile material was removed by pumping at $20\ ^{\circ}\text{C}/10^{-2}$ mmHg; the remaining fraction was evaporated ($145\text{--}150\ ^{\circ}\text{C}$, 10^{-2} mmHg) onto a water-cooled finger to give the colourless liquid *product* (11) (2.30 g, 7.51 mmol, 71%).

(ii) *2-Dimethylsilyl-1-diphenylphosphinoethane* (12) To a solution of compound (11) (2.25 g, 7.34 mmol) in dry Et₂O (20 cm³) in a Schlenk tube was added LiAlH₄ (excess) and the reaction mixture was stirred at $20\ ^{\circ}\text{C}$. After 2 h, all volatiles were removed under reduced pressure and the fraction evaporating at $130\text{--}135\ ^{\circ}\text{C}/10^{-2}$ mmHg was collected yielding the colourless liquid *product* (12) (1.66 g, 6.09 mmol, 83%).

(iii) *Chlorodimethylsilyl(diphenylphosphino)methane* (2). Dichlorodimethylsilane (80 cm³) in tetrahydrofuran (THF) (150 cm³) was cooled to $-78\ ^{\circ}\text{C}$ and treated dropwise (2 h) with a solution of Ph₂PCH₂Li-tmeda (10.0 g, 31 mmol) in THF (30 cm³). The mixture was warmed to ambient temperature and all volatile material was removed under reduced pressure after which the residue was extracted with hexane ($3 \times 40\ \text{cm}^3$ then $3 \times 20\ \text{cm}^3$). The extracts were combined, the solvent removed under reduced pressure, and the product evaporated ($125\text{--}130\ ^{\circ}\text{C}$) to give, on a water-cooled probe, the colourless liquid *product* (2) (6.4 g, 22 mmol, 71%).

(iv) *Dimethylsilyl(diphenylphosphino)methane* (3).—Compound (2) (3.4 g, 12 mmol) was added dropwise to a suspension of LiAlH₄ (0.40 g, 10 mmol) in Et₂O (20 cm³). The mixture was stirred at $20\ ^{\circ}\text{C}$ (1 h), then all volatiles were removed under reduced pressure and the residue was extracted with hexane ($6 \times 15\ \text{cm}^3$). The extracts were combined and the hexane removed, and the colourless, liquid *product* (3) (2.5 g, 10 mmol, 83%) was collected after evaporation at $115\text{--}120\ ^{\circ}\text{C}$ by condensing it on a water-cooled finger.

(v) *3-Chlorodimethylsilyl-1-diphenylphosphinopropane* (24). Diphenylphosphine (2.20 g, 12.0 mmol) and allyldimethylchlorosilane (2.20 g, 16.0 mmol) were allowed to react in an evacuated quartz tube (8 h) under irradiation from a medium-pressure mercury lamp (*ca.* 5 cm distant). The product mixture was taken up in dry benzene (20 cm³), transferred to a Schlenk tube, and the benzene and excess of silane were removed under reduced pressure. Material evaporating from the residue at $180\text{--}190\ ^{\circ}\text{C}/10^{-2}$ mmHg was identified as the oily liquid *product* (24) (2.08 g, 6.48 mmol, 41%).

(vi) *3-Dimethylsilyl-1-diphenylphosphinopropane* (25). Compound (24) (1.00 g, 3.12 mmol), dry Et₂O (20 cm³), and LiAlH₄ (excess) were stirred together at $20\ ^{\circ}\text{C}$ (1 h) in a Schlenk tube. After the solid had settled, the supernatant layer was recovered by syringe; volatiles were removed under reduced pressure and the colourless liquid *product* (25) (0.81 g, 2.82 mmol, 90%) evaporated ($150\text{--}160\ ^{\circ}\text{C}/10^{-2}$ mmHg) and collected as before.

(vii) *2-[²H₆]Dimethylsilyl-1-diphenylphosphinoethane[²H₆]* (12). Repetition of reaction (ii) using LiAlD₄ gave the *product* (84%) with $>95\%$ incorporation (i.r.) of ²H.

(viii) *1-Diphenylphosphino-2-phenylsilylethane* (20). Irradiation (4 h) of a mixture of Ph₂PH (1.09 g, 5.86 mmol) and H₂Si(CH₂:CH₂)Ph (0.79 g, 5.90 mmol) yielded after work-up as in (i)—(vi) the *product* (1.18 g, 3.69 mmol, 63%).

Results and Discussion

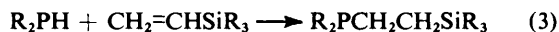
The synthesis of tris(trimethylsilylmethyl)phosphine by Grignard alkylation of PCl₃ was reported in 1958 by Seyferth,⁹ but the addition of P-H bonds across an unsaturated group

Table 2. N.m.r. spectral data ^a for the diphenylphosphinomethylsilanes (1)–(10)

Compound	³¹ P	¹ H					¹³ C		
	δ(³¹ P)	δ[C(1)H ₂]	δ(SiCH ₃)	δ(SiH)	³ J(CH ₂ SiH)	³ J(CH ₃ SiH)	δ[C(1)]	¹ J[PC(1)]	δ(SiCH ₃)
(1)	-163	1.45	0.05				14.6	29	-0.3
(2)	-165	1.84	0.35				17.8	26	2.7
(3)	-162	1.22	-0.03	4.12	3.3	3.7	12.5	30	-3.2
(4)	-165	2.00	0.54				17.1	30	1.1
(5)	-162	1.75	0.38	4.20	3.6	4.5	11.8	29	-4.7
(6)	-166	2.37					15.7	32	
(7)	-162	1.90		4.30			9.4	n.o.	
(8)	-164	2.27					11.9	33	
(9)	-167	2.36					20.4	33	
(10)	-160	1.65		4.25	4.5		8.2	29	

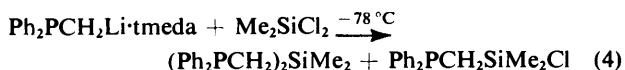
^a ³¹P N.m.r. chemical shifts are relative to external trimethyl phosphite. ¹H N.m.r. chemical shifts are relative to tetramethylsilane [δ(CH₂Cl₂) 5.3]. ¹³C N.m.r. are recorded in CDCl₃ throughout, high frequency relative to δ 77.2 p.p.m. for CDCl₃ (central component of triplet). All coupling constants are in Hz. Resonances due to phenyl substituents were observed in the range 7.0–7.5 (¹H) or 125–140 p.p.m. (¹³C) showing a multiplet structure which was not analysed in detail.

attached to silicon as a potentially more versatile route to phosphinoalkylsilanes does not appear to have been explored before 1969, when Grobe and Möller effected the reaction



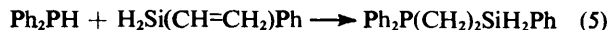
shown in equation (3) for R = Me and two other vinylsilanes.¹⁰ Subsequently, using photochemical conditions proven earlier to be successful in the anti-Markovnikov radical addition of secondary phosphines across an olefinic double bond,¹¹ the same authors prepared¹² a small range of 1-phosphino-2-silylethanes functionalised by Cl or F at the Si atom; analogous P–H addition to octenylsilanes has also been achieved.¹³ Unidentate complexation (through P) to transition-metal centres has been reported^{13–15} for several of the compounds produced in this way; however, chelation leading to the geometry represented by structure (B) had received scant attention¹⁵ prior to our initial communication.¹⁶

A different approach is required to assemble the corresponding phosphino(silyl)methanes; a suitable route has been described very recently^{8,17} (equation 4) which uses the tetramethylethylenediamine complex of (diphenylphosphino)methyl-lithium [Ph₂PCH₂Li·tmeda], first reported in 1967 by Peterson.¹⁸ Thus, reactions (3) and (4), combined with



reduction of chlorosilyl compounds to the Si–H analogues using LiAlH₄ (or LiAlD₄) works very well as a general synthetic pathway to phosphinoalkylsilanes, Ph₂P(CH₂)_nSiXYZ, where n = 1, 2, or 3 [compounds (1)–(10), (11)–(22), and (23)–(27), respectively]. The products are thermally very stable, distilling under reduced pressure at temperatures in the 115–190 °C range, but are air-sensitive and must be handled using rigorous inert-atmosphere techniques to avoid decomposition. A small number of dimethylphosphinoethane derivatives (28)–(33) were also isolated and were found to be extremely reactive in the presence of traces of oxygen or moisture. Although route (3) has been previously reported^{10,19} to necessitate the use of an initiator (either base or peroxide) and extended reaction times (>24 h), we found neither to be required and our syntheses involving vinylsilanes were complete within 5 h while with allylsilanes reaction was only a little slower. Products with n = 2 or 3 incorporating Si–H bonds were routinely prepared by P–H addition to the appropriate alkenyl(chloro)silane followed by LiAlH₄ reduction. However, it is noteworthy that under the photolytic

conditions employed, Si–H addition²⁰ must compete ineffectively with P–H addition because when we used vinyl-silicon hydrides we were able to isolate only products corresponding to the latter reaction, *e.g.* equation (5).



The new compounds were characterized initially by their i.r. spectra and subsequently by microanalysis and by ¹H, ¹³C, and ³¹P n.m.r. spectroscopy. I.r. maxima, consistently found near 2 920w, 2 900m, 1 140m, 1 070m, and 690s cm⁻¹ and remaining invariant on alteration of substituents X, Y, Z at Si, are considered to arise mainly from vibrations of the skeletal methylene groups, while bands at 3 080m, 3 060m, 1 585w, 1 480m, and 1 435s are recognizable as PPh₂ modes. The chlorosilanes showed an absorption at 490 cm⁻¹ due to ν(SiCl), splitting into two components when more than one Cl atom was present. The spectra of compounds incorporating SiH bonds contained very strong contours near 2 105 and 885 cm⁻¹ (SiH stretching and bending modes) which were shifted to *ca.* 1 550 and 625 cm⁻¹ in the deuterio-analogues.

N.m.r. Spectra.—The data for the methanes, ethanes, propanes, and dimethylphosphino-derivatives are summarized in Tables 2–5 respectively. As well as confirming the identity of each compound, several interesting relationships become apparent when the parameters are compared. For the methanes (1)–(10), assignment of signals at δ 1.22–2.37 p.p.m. to the methylene protons is unequivocal, but for the remaining compounds resonances due to chemically different methylene groups overlap one another and cannot be distinguished at 90 MHz. Individual proton environments are resolved at 250 MHz, however, as is illustrated in Figures 1 and 2 for Ph₂P-(CH₂)_nSiClMe₂, n = 2 or 3 [(11) and (24)]. Shifts appearing to low field near δ 2.0 are attributed to protons attached to C-1 (*i.e.* that adjacent to P) while methylene protons adjacent to Si resonate nearer to tetramethylsilane as expected and on the basis of earlier assignments.¹³ The multiplicity observed in this region for compound (17) (Figure 1) may be accounted for²¹ in terms of an AA'XX' pattern perturbed by coupling to P which is stronger to the more distant methylene protons, *i.e.* ³J(P–H) > ²J(P–H). Similarly the splitting of the three envelopes for compound (24) is qualitatively consistent with ³J(P–H) > ²J(P–H) or ⁴J(P–H). Interpretation of the ¹³C chemical shifts parallels that for the proton data, as suggested in Tables 2–5, and leads to the conclusion that carbon-phosphorus coupling persists to methylene C-3 and indeed that the magnitude of ⁿJ(P–C) is comparable for n = 1, 2, or 3.

Table 3. N.m.r. spectral data ^a for the diphenylphosphinoethylsilanes (11)–(22)

Compound	³¹ P δ(³¹ P)	¹ H				¹³ C				
		δ[C(1)H ₂]	δ[C(2)H ₂]	δ(SiH)	³ J(CH ₂ SiH)	δ[C(1)]	δ[C(2)]	¹ J[PC(1)]	² J[PC(2)]	δ(SiCH ₃)
(11)	-150	2.1	0.8	0.36	3.7	20.7	14.7	15	13	1.6
(12)	-151	2.0	0.6	0.05	3.87	22.3	9.9	15	10	-4.5
(13)	-150	2.1	1.2	0.69	3.7	20.5	13.6	14	10	0.5
(14)	-151	2.2	1.0	0.43	4.0	22.3	9.3	15	12	-5.5
(15)	-150	2.4	1.5		4.0	20.0	12.1	12	13	
(16)	-150	2.1	1.4		4.1	22.3	8.1	15	12	
(17)	-151	2.3	1.2	0.74	3.7	20.4	17.6	18	12	5.2
(18)	-151	2.1	0.8	0.09	3.7	23.3	6.6	14	12	-8.3
(19)	-151	2.1	1.2		3.5	20.2	18.0	18	13	
(20) ^b	-151	2.1	1.0	4.32	3.5	22.1	6.2	14	13	
(21)	-151	2.2	1.4		3.57	20.1	20.0	20	14	
(22)	-152	2.1	0.8			24.7	2.4	15	15	

^a ³¹P N.m.r. chemical shifts are in p.p.m. relative to external trimethyl phosphite. ¹H N.m.r. shifts are relative to tetramethylsilane (δ 0.0). ¹³C N.m.r. are recorded in CDCl₃ throughout, high frequency relative to δ 77.2 p.p.m. for CDCl₃ (central component of triplet). All coupling constants are in Hz. Resonances due to phenyl substituents were observed in the range 7.0–7.5 (¹H) or 125–140 p.p.m. (¹³C) showing a multiplet structure which was not analysed in detail. ^b ³J(CH₂SiH) 3.5 Hz, ⁴J(PSiH) 1.2 Hz.

Table 4. N.m.r. spectra data ^a for the diphenylphosphinopropylsilanes (23)–(27)

Compound	³¹ P δ(³¹ P)	¹ H				¹³ C					
		δ[C(1)H ₂]	δ[C(2)H ₂]	δ[C(3)H ₂]	δ(SiH)	δ[C(1)]	δ[C(2)]	δ[C(3)]	¹ J[PC(1)]	² J[PC(2)]	δ(SiCH ₃)
(23)	-152	2.00	1.38	0.60	0.05	32.3	20.8	18.9	10	16	-1.4
(24)	-157	2.20	1.60	1.05	0.42	32.6	20.5	20.5	11	18	7.8
(25) ^b	-157	2.22	1.74	0.89	0.12	32.3	21.5	16.3	13	19	-4.3
(26)	-158	2.22	1.74	1.57	4.18	29.9	19.0	25.5	9	18	13
(27) ^c	-158	2.15	1.55	0.87	3.41	32.8	20.4	15.9	n.o. ^d	n.o. ^d	n.o.

^a ³¹P N.m.r. chemical shifts are relative to external trimethyl phosphite. ¹H N.m.r. chemical shifts are relative to tetramethylsilane [δ(CH₂Cl₂) 5.3]. ¹³C N.m.r. are recorded in CDCl₃ throughout, high frequency relative to δ 77.2 p.p.m. for CDCl₃ (central component of triplet). All coupling constants are in Hz. Resonances due to phenyl substituents were observed in the range 7.0–7.5 (¹H) or 125–140 p.p.m. (¹³C) showing multiplet structure which was not analysed in detail. ^b ³J(CH₂SiH) 3.3 Hz, ^c ²J(-CH₂SiH) 11 Hz. ^d Not observed.

Table 5. N.m.r. spectra data ^a for the dimethylphosphinoethylenes (28)—(33)

Compound	³¹ P			¹³ C						¹ H							
	δ(³¹ P)	¹ J[PC(1)]	² J[PC(2)]	δ[C(1)]	δ[C(2)]	¹ J[PC(1)]	² J[PC(2)]	δ(SiCH ₃)	δ(PCH ₃)	¹ J(PCH ₃)	δ[C(1)H ₂]	δ[C(2)H ₂]	δ(SiCH ₃)	δ(PCH ₃)	δ(SiH)	³ J(CH ₃ SiH)	³ J(HCP)
(28)	-186	11.2	8.2	24.4	14.4	11.2	8.2	1.6	13.6	12.6	1.3	0.8	0.31	0.89	3.86	3.4	2.1
(29)	-185	11.6	9.4	24.3	13.5	11.6	9.4	0.3	13.6	13.8	1.4	0.8	0.69	1.00	4.31	n.o. ^b	n.o. ^b
(30)	-185	11.6	10.4	23.4	17.2	11.6	10.4	5.3	13.5	12.5	1.4	0.9	0.75	0.98	3.71	4.2	2.1
(31)	-186	9.8	7.5	26.0	9.4	9.8	7.5	-4.4	13.7	13.2	1.4	0.7	0.00	0.91	3.86	3.4	n.o.
(32)	-186	11.4	8.9	25.8	8.8	11.4	8.9	-5.6	13.3	13.3	1.5	0.6	0.29	0.90	4.31	3.5	1.8
(33)	-186	11.6	9.5	26.9	6.0	11.6	9.5	-8.3	13.7	13.8	1.4	0.6	0.16	0.98	3.71	4.2	2.0

^a ³¹P N.m.r. chemical shifts are relative to external trimethyl phosphite. ¹H N.m.r. chemical shifts are relative to tetramethylsilane [δ(CH₂Cl₂) 5.3]. ¹³C N.m.r. are recorded in CDCl₃ throughout, high frequency relative to δ 77.2 p.p.m. for CDCl₃ (central component of triplet). All coupling constants are in Hz. In appropriate spectra resonances due to phenyl substituents were observed in the range 7.0—7.5 (¹H) or 125—140 p.p.m. (¹³C), showing multiplet structure which was not analysed in detail. ^b Not observed.

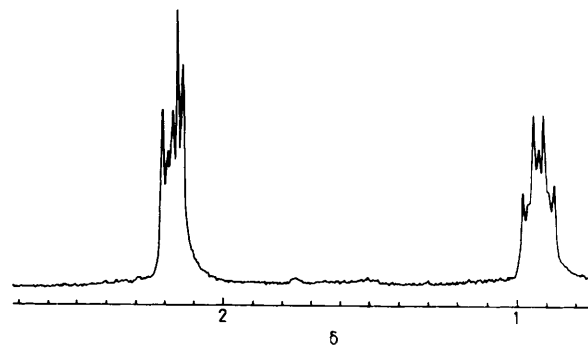


Figure 1. ¹H N.m.r. spectrum (250 MHz) of compound (11) in the region δ 0.7—2.5. Use of C₆D₆ as solvent and lock-frequency results in a shift to low field of resonance positions compared with those listed in Table 3

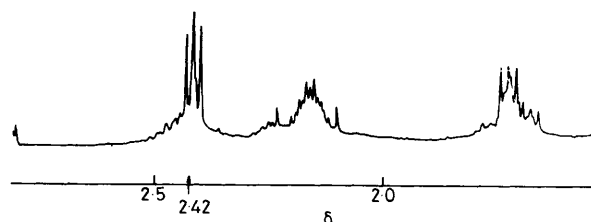


Figure 2. ¹H N.m.r. spectrum of compound (24), in C₆D₆ solution

The chemical shift of the methylene protons α to Si changes in a consistent pattern, depending on X,Y,Z substitution at Si and moving progressively downfield in the sense Cl < Ph < H < Me. A similar substituent effect on the position of δ(SiH) (found characteristically ²² in the range δ 4.89—3.41) is evident in the ¹H spectra of the fifteen compounds containing Si—H bonds and further analysis leads to additivity constants, A_H for the effect of substituent *i* on δ(SiCH₃): A_H = 0.10, A_{Ph} = 0.35, and A_{Cl} = 0.42 p.p.m., comparing favourably with corresponding values of 0.06, 0.24, and 0.38 reported earlier ²³ for simple methylsilane derivatives. Related trends are exaggerated but in the same direction in ¹³C spectra: for example δ(C-2) shifts by 17.6 p.p.m. between compounds (21) and (22), and δ(C-3) by 9.6 p.p.m. between compounds (26) and (27).

The ³¹P n.m.r. data are less informative, showing little variation apart from that of ca. 30 p.p.m. on substituting Ph at P by Me in compounds (28)—(33), although for the methanes [e.g. (9) and (10)] more electronegative substituents at Si do generate more negative chemical shifts. The most distant coupling to ³¹P was that with the SiH proton (⁴J 1.2 Hz) in compound (20).

Acknowledgements

We thank the N.S.E.R.C., Canada and the University of Victoria for financial support.

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Received 9th August 1982; Paper 2/1379