(Phosphinoalkyl)silanes. 2. Synthesis and Spectroscopic Properties of the Poly(phosphinoalkyl)silanes $SiHR[(CH_2)_nPR'_2]_2$ (R = Me or Ph; *n* = 2 or 3; R' = Ph or Cyclohexyl) and $SiH[(CH_2)_nPR'_2]_3$ (R = Me or Ph; *n* = 2, R' = Ph or Cyclohexyl; *n* = 3, R' = Ph)

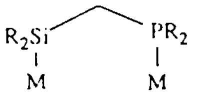
Frederick L. Joslin and Stephen R. Stobart*

Department of Chemistry, University of Victoria, British
Columbia, Canada V8W 2Y2

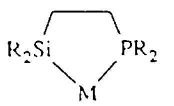
Received October 6, 1992

Introduction

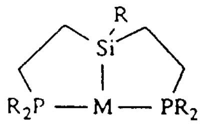
An earlier paper[1] reported the synthesis of an extensive family of modified silanes in which a phosphorus atom is linked to silicon by a polymethylene chain, including the compounds $Ph_2P(CH_2)_nSiHXY$ (*n* = 1, 2, or 3; X or Y = Me or Ph), which also contain a Si–H bond. Interaction of the latter with coordinatively unsaturated, low-valent transition-metal centers ("oxidative addition") accompanied by coordination through phosphorus has given rise to new classes of complex in which bonds between silicon and a platinum-group metal are stabilized in bridged[2] (A) or chelate[3] (B) geometries (leading inter alia to novel homogeneous hydroformylation catalysts[4] and models[5] for metal–support interactions in silica-derived systems for heterogeneous catalysis). A related strategy can be envisioned for assembly of multidentate or "cage" environments such as C or D, in which the silyl function is "anchored" at the transition-metal center in a more extended framework. Steric constraints so imposed on a metal coordination sphere may limit substrate entry to sites which experience the strongly labilizing trans effect of the silyl group, with potential implications in catalysis.



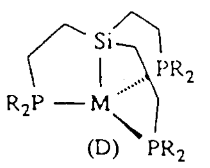
(A)



(B)



(C)



(D)

We describe here the isolation of $SiH(CH_2CH_2PPh_2)_3$, "triPSiH", and some of its relatives. That such poly(phosphinoalkyl)silanes are suitable as precursors to poly(phosphinoalkyl)silyl ligand cages has been established:[4] from "triPSiH", a reactive rhodium(I) silyl is generated which may be trapped as its crystallographically characterized[6] carbonyl adduct [Rh(triPSi)CO]. Tridentate complexation by alkyltris(phosphinoalkyl)silanes related to triPSiH has also recently been described,[7] i.e. through binding of all three P atoms (but *not* of Si).

Experimental Section

Synthetic manipulations and spectroscopic measurements were carried out as reported previously.[1] Vinyl and allyl magnesium bromides (1.0 M solution in THF or Et_2O respectively), dichloromethylsilane, dichlorophenylsilane, trichlorosilane, diphenylphosphine, dicyclohexylphosphine, and tricyclohexylphosphine were obtained from commercial sources (Aldrich; Petrarch). Grignard reactions were used to produce the required poly(alkenyl)silanes as colorless liquids, (>50% yields, purified by vacuum distillation or fractional condensation) which were identified by IR and ^1H and ^{13}C NMR spectroscopy. Microanalytical data were supplied by Canadian Microanalytical Services, Vancouver, Canada, or Atlantic Microlab. Inc., Atlanta, GA.

Synthesis of Compounds. (i) Bis(diphenylphosphinoethyl)methylsilane (1). A mixture of divinylmethylsilane (ca. 11 mmol in THF/Et_2O solution) and diphenylphosphine (6.0 mL, 6.42 g, 34 mmol) was irradiated (60 h) in a Pyrex tube clamped ca. 25 cm from a medium-pressure mercury lamp (450 W). Removal of volatile material in vacuo yielded the viscous colorless liquid product (3.0 g; ca. 60%). Anal. Calcd (found): C, 74.0 (73.8); H, 6.9 (6.9). The corresponding *phenylsilane* $SiH(Ph)(CH_2CH_2PPh_2)_2$ (**2**) was obtained similarly in 98% yield. Anal. Calcd (found): C, 76.6 (76.1); H, 6.4 (6.4).

(ii) Tris(diphenylphosphinoethyl)silane (3), "triPSiH". In a typical synthesis a solution of trivinylsilane (ca. 0.4 g) in ether/THF (4 mL) was added to diphenylphosphine (2.0 mL, 2.14 g, 11 mmol) in a Pyrex reactor held at 25 cm from the UV source. Irradiation (70 h) of this mixture was followed by recovery of the *product* as a sticky white solid. Anal. Calcd (found): C, 75.4 (74.9); H, 6.6 (6.5).

(iii) ((Diphenylphosphino)ethyl)phenylvinylsilane (1-(diphenylphosphino)-3-phenyl-3-silapent-4-ene) and ((Dicyclohexylphosphino)ethyl)((diphenylphosphino)ethyl)phenylsilane (4). Phenyldivinylsilane (1.79 g, 11.2 mmol), Et_2O (20 mL), and diphenylphosphine (1.96 mL, 2.10 g, 11.2 mmol) were loaded into a Pyrex reactor and the resulting mixture was irradiated (50 h). Vacuum distillation (10^{-2} mmHg) yielded unreacted silane (80 °C) and then the colorless liquid *product* (1.04 g, 28%) at ca. 200 °C. A sample of this material (1.0 g, 3.0 mmol) was subsequently irradiated (200 h) with Et_2O (2 mL) and dicyclohexylphosphine (0.6 g, 3.2 mmol). Removal of the solvent and unreacted starting materials left the clear colorless *product* (1.45 g, 94%). Anal. Calcd (found): C, 73.4 (73.7); H, 8.2 (8.5). The analogues bis((dicyclohexylphosphino)ethyl)methylsilane (**5**), bis((dicyclohexylphosphino)ethyl)phenylsilane (**6**), and tris((dicyclohexylphosphino)ethyl)silane (**7**), of **1–3**, were prepared similarly from $PHCy_2$, so that after irradiation (100 h) ca. 25 cm from the light source of a mixture of phenyldivinylsilane (1.5 mL, 1.34 g, 8.4 mmol), Et_2O (2 mL), and dicyclohexylphosphine (4.0 mL, 3.62 g, 18.2 mmol), removal of solvent and excess phosphine afforded the very viscous liquid **6** (4.34 g, 93%).

(iv) Bis(diphenylphosphinopropyl)(methyl)silane (8). Irradiation (150 h) of a mixture of diallylmethylsilane (1.6 mL, 1.21 g, 9.6 mmol) and diphenylphosphine (3.58 g, 9.6 mmol) contained in an air-cooled Pyrex reactor mounted 6 cm from the UV lamp followed by removal of volatile material yielded the colorless liquid *product* (4.65 g, 97%). Anal. Calcd (found): C, 74.7 (74.8); H, 7.1 (7.1). Bis((diphenylphosphino)propyl)(phenyl)silane (**9**), tris((diphenylphosphino)propyl)silane (**10**), and the dicyclohexylphosphino analogues **11** and **12** of **8** and **9** were prepared in a similar fashion. **(v) Bis((diphenylphosphino)butyl)methylsilane (13).** After reaction (114 h) as described in part iv above, $PHPh_2$ with $SiH(CH_2CH_2CH{=}CH_2)_2Me$ gave the *product* in 88% yield. Anal. Calcd (found): C, 74.4 (74.9); H, 7.4 (7.6).

Results and Discussion

Construction of triPSiH [i.e. $HSi(CH_2CH_2PPh_2)_3$] and related poly(phosphinoalkyl)silanes by P–H bond addition[1] depends on access to appropriate poly(alkenyl)silanes $SiHR_2R'$ or $SiHR_3$(R = $CH{=}CH_2$ or $CH_2CH{=}CH_2$). These latter compounds have

---

[1] Holmes-Smith, R. D.; Osei, R. D.; Stobart, S. R. *J. Chem. Soc., Perkin Trans. I* **1983**, 861.

[2] Auburn, M. J.; Cameron, T. S.; Holmes-Smith, R. D.; Kumari, A.; Stobart, S. R.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1523.

[3] Holmes-Smith, R. D.; Stobart, S. R.; Vefghi, R.; Zaworotko, M. J.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Dalton Trans.* **1987**, 969. Auburn, M. J.; Stobart, S. R. *Inorg. Chem.* **1985**, *24*, 318. Cameron, T. S.; Jochem, K.; Holmes-Smith, R. D.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1981**, 937.

[4] Stobart, S. R.; Grundy, S. L.; Joslin, F. L. U.S. Patent 4,950,798, 1990.

[5] Bruce, G. C.; Stobart, S. R. *Inorg. Chem.* **1988**, *27*, 3879.

[6] Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504.

[7] Boncella, J. M.; Green, M. L. H. *J. Organomet. Chem.* **1987**, *325*, 217; Gardner, T. F.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1987**, 1758.

0020-1669/93/1332-2221$04.00/0

Table I. NMR Data[a] for Poly(phosphinoalkyl)silanes

(a) Phosphinoethylsilanes

		^1H						^{13}C			
compd	^{31}P $\delta(PR_2)$	$\delta(PCH_2)$	$\delta(SiCH_2)$	$\delta(SiH)$	$\delta(SiCH_3)$	$^3J(CH_2SiH)$	δPCH_2	$^1J(P–C)$	$\delta(SiCH_2)$	$^2J(P–C)$
1	−150.8	2.1	0.8	4.0	0.2	nr	22.2	14.7	8.1	11.1
2	−150.3	2.0	1.0	4.4		3.6	22.1	14.4	7.4	12.0
3	−150.8	2.0	0.8	4.0		3.6	22.3	14.5	6.4	11.8
4[b]	−150.5	2.1	1.0	4.3		nr	22.3	14.4	7.5	11.1
4[c]	−137.1	nr	nr			nr	15.2	16.6	9.9	11.2
5	−138.9	nr	0.7	3.8	0.1	3.6	15.3	8.4	10.6	14.8
6	−137.1	nr	1.0	4.3		3.6	15.2	20.2	9.8	14.7
7	−139.0	nr	nr	4.2		3.6	16.4	22.0	9.9	15.8

(b) Phosphinopropylsilanes

		^1H						^{13}C						
compd	^{31}P δ-(PR_2)	δ-(PCH_2)	δ-(PCH_2CH_2)	δ-$(SiCH_2)$	δ-(SiH)	δ-$(SiCH_3)$	^3J-(CH_3SiH)	δ-(PCH_2)	^1J-$(P–C)$	δ-(PCH_2CH_2)	^2J-$(P–C)$	δ-$(SiCH_2)$	^3J-$(P–C)$	δ-$(SiCH_3)$
8	−157.7	2.1	1.5	0.7	3.8	0.0	3.7	31.7	12.0	21.1	17.9	14.5	11.9	−6.4
9	−151.0	2.1	1.6	1.0	4.3			31.6	12.0	21.1	17.1	13.7	12.3	
10	−157.9	2.0	1.4	0.6	3.6			31.9	12.3	21.2	17.7	13.0	12.2	
11	−146.6	nr	nr	nr	4.2	0.1	3.6	25.3	17.6	23.7	20.9	15.1	11.0	−6.2
12	−146.5	nr	nr	nr	4.2			25.0	16.9	23.5	21.0	14.1	11.2	

(c) ^{13}C Data for Poly((dicyclohexylphosphino)alkyl)silanes[d]

	C_α	C_β	C_γ	C_δ
4	33.4[e]	30.4 (11.6); 29.3[e]	27.4;[e] 27.3[e]	26.5[e]
5	33.4 (12.8)	30.4 (13.7); 29.3[e]	27.4;[e] 27.4[e]	26.5[e]
6	33.4 (13.8)	30.4 (13.2); 29.2 (7.6)	27.4;[e] 27.3[e]	26.5[e]
7	32.1 (16.5)	31.0 (14.5); 29.8 (9.1)	27.7 (3.2); 27.7[e]	27.0[e]
11	33.5 (13.2)	30.5 (14.7); 29.0 (8.1)	27.5 (6.3); 27.3[e]	26.6[e]
12	33.2 (12.5)	30.3 (14.2); 28.9 (7.5)	27.3 (7.1); 27.2[e]	26.4[e]

[a] ^{31}P chemical shifts vs trimethylphosphite, 0.0 ppm; ^1H, δ vs TMS; coupling constants are measured in Hz; nr = not resolved. [b] $CH_2CH_2PPh_2$ group. [c] $CH_2CH_2PCy_2$ group. [d] Chemical shifts vs TMS for α, β, γ, and δ carbon atoms of cyclohexyl ring system; coupling constants $^nJ(P–C)$/Hz are given in parentheses. [e] Coupling not resolved.

received only sketchy previous attention.[8] Satisfactory yields are obtainable by alkenylation of readily available chlorosilanes ($SiH_2R'Cl$ or $SiHCl_3$), however, by the action of the Grignard reagents RMgBr, after which the products may be recovered as colorless liquids by distillation under reduced pressure. Complete alkenyl substitution of Cl at Si was observed in all cases and was effected leaving intact the Si–H functionality, evidence for which continued to be obvious in IR and NMR spectra (intense bond-stretching absorption near 2120 cm^{-1}; characteristic ^1H resonance near δ 4 ppm).

Attachment of a PR_2 fragment to terminal alkenyl carbon atoms in the silane precursors was accomplished photochemically through anti-Markovnikov P–H bond addition as described[1,9] earlier. NMR spectroscopy showed that while exposure to UV light (Pyrex reactor) generated mixtures of mono- and polyphosphinated products, continued irradiation led to slow but ultimately complete conversion to the required perphosphinated derivatives: these proved to be very viscous, air-sensitive but thermally stable liquids, which are accordingly awkward to handle but can be purified for subsequent use as ligand precursors[6] simply by complete removal of all more volatile material. No photodegradation of the products was encountered even when very long reaction times were used for optimization of the yields. Interception and isolation in low yield of the monophosphinated species $SiH(Ph)(CH{=}CH_2)(CH_2CH_2PPh_2)$ was also accomplished, establishing a stepwise sequence of addition of $PHPh_2$ to $SiH(Ph)(CH{=}CH_2)_2$ and providing a route by further reaction with $PHCy_2$ (Cy = cyclohexyl) to a chiral, mixed bis(phosphinoethyl) analogue $SiH(Ph)(CH_2CH_2PPh_2)(CH_2CH_2PCy_2)$ (**4**). A single compound in which Si is connected to P through four methylene groups, methylbis((diphenylphosphino)butyl)silane (**13**), was also prepared from a dibutenylsilane precursor.

The photochemical addition of PHR_2 was estimated to be slower by about an order of magnitude for allyl- vs vinylsilanes and for R = Cy vs Ph. These differences are accounted for by the radical character of the reaction: thus hyperconjugative effects[10] will favor nucleophilic $R_2P^\bullet$ attack β (vinyl) rather than γ (allyl) to Si, while the allyl-derived radical (β to Si) so produced will be stabilized by inductive release and hyperconjugation by ca.[11] 10 kJ mol^{-1} vs the α-analogue, i.e. be less reactive than the latter in relation to chain propagation. Both $R_2P^\bullet$ radicals are expected to be nucleophilic, that with R = Cy more so than for Ph; however lack of resonance stabilization, more demanding steric requirements, or simply less efficient photolysis may lead to slower reaction where R = Cy.

Spectroscopic data for the new compounds **1**–**13** which are useful diagnostically include (a) prominent IR absorptions near 2100 cm^{-1} characteristic of Si–H stretching vibrations and (b) well-separated ^{13}C NMR signals showing coupling to ^{31}P due to each of 2, 3, or 4 carbon atoms in the polymethylene chain. The NMR parameters are collected in Table I. For each of the dicyclohexylphosphino species, six signals attributable to Cy carbons were observed in ^{13}C NMR spectra. This superficially puzzling result is an effect of low molecular symmetry: planar reflection (unique σ in point group C_s) relates the two Cy groups, but not the pairs of carbon atoms in either Cy ring. To test this interpretation the ^{13}C NMR spectra of the phosphines $PHCy_2$ and PCy_3 (which do not appear to have been reported previously) were measured: the first (C_s symmetry) also shows six resonances (δ 33.5 ppm, J = 4 Hz; δ 32.7 ppm, J = 19 Hz; δ 30.2 ppm, J

---

[8] Rosenberg, S. D.; Walburn, J. J.; Stankovick, T. D.; Baint, A. E.; Ranscher, H. E. *J. Org. Chem.* **1957**, *22*, 1200. Jenkins, J. W.; Lavery, N. L.; Guenther, P. R.; Post, H. W. *J. Org. Chem.* **1948**, *13*, 862. Glocking, F.; Lyle, M. A.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1974**, 2537.

[9] Brezezinska, Z. C.; Cullen, W. R. *Inorg. Chem.* **1979**, *18*, 3132.

[10] Jarvie, A. W. P. *Organomet. Chem. Rev. A.* **1970**, *6*, 153.

[11] Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

= 10 Hz; δ 27.5 ppm; δ 27.4 ppm, J = 16 Hz; δ 26.7 ppm) but the 3-fold symmetry of PCy_3 reduces this to four (δ 32.3, J = 18 Hz; δ 31.7 ppm, J = 13 Hz; δ 28.1 ppm, J = 9 Hz; δ 27.0 ppm), from which it may also be concluded that rotation of Cy about the P–C bond is rapid at ambient temperature.

The ability of the triPSi unit (derived from compound **3**) to coordinate at a rhodium center,[7] together with the accumulating literature on hypervalent silicon,[12] led us to look for evidence for intramolecular P–Si interactions. It has recently been concluded,[13] on the basis of ^{29}Si NMR spectroscopy and structural characterization of the germanium analogue, that in the tris((dimethylbenzyl)amino)silane $SiH(C_6H_4CH_2NMe_2)_3$ the three NMe_2 groups interact with the central silicon atom. If a parallel situation exists in the fluid state for the tris(phosphinopropyl)silane $SiH(CH_2CH_2CH_2PPh_2)_3$ (**10**), we can find no evidence for it. Thus no anisochronicity among Ph substituents or between backbone CH_2 hydrogens (which would be imposed by a propelloid geometry) could be detected in NMR spectra of compounds **4** or **10**. It should be noted that NMR data for $EH(C_6H_4CH_2NMe_2)_3$(E = Si or Ge) list[13] C–H_2 and NMe_2 resonances as singlets, suggesting that propelloid (C_3) geometries derived from E–N connectivity are not stable in solution; the average Ge–N distance of 3.05 Å in the solid-state structure of the germane is in any case much longer even than that of Hg–N in[14] the related mercury(II) derivative $Hg(C_6H_4CH_2NMe_2)_2$, so that the former approach may simply be a consequence of packing behavior in the crystal. The ^{29}Si chemical shifts for compounds **4** and **10**, observed respectively at -2.0 ppm, ^3J(Si–P) = 20.9 Hz, and ^1J(Si–H) = 180.8 Hz and -9.0 ppm, and ^1J(Si–H) = 174.3 Hz, are unsurprising.

Acknowledgment. We thank the NSERC, Canada, and the University of Victoria for financial support.

---

[12] Katz, H. E. *J. Am. Chem. Soc.* **1986**, *108*, 7640. Hajadasz, D.; Squires, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 3139; Deiters, J. A.; Homes, R. R.; Holmes, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 7672. Corriu, R. J. P.; Guerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265.

[13] Brellere, C.; Carre, F.; Corriu, R. J. P.; Royo, G. *Organometallics* **1988**, *7*, 1006.

[14] Atwood, J. L.; Berry, D. E.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1983**, *22*, 3480.