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Preliminary communication

A new class of silicon-phosphorus heterocycles: 4-silaphosphorinanes

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Abstract

Radical reactions of Me_3SiPH_2 with $Me_2Si(CH{=}CH_2)_2$ or $Si(CH{=}CH_2)_4$ yield the 4-silaphosphorinanes $Me_2Si(CH_2CH_2)_2PSiMe_3$, $(CH_2{=}CH)_2Si(CH_2CH_2)_2PSiMe_3$, or $[Me_3SiP(CH_2CH_2)_2]_2Si$; methanolysis of these produces quantitatively the secondary phosphorinanes $Me_2Si(CH_2CH_2)_2PH$, $(CH_2{=}CH)_2Si(CH_2CH_2)_2PH$, or $[HP(CH_2CH_2)_2]_2Si$. $Me_2Si(CH_2CH_2)_2PSiMe_3$ with O_2/H_2O yields the phosphinic acid $Me_2Si(CH_2CH_2)_2P(O)OH$. All compounds are characterized by spectral data; an X-ray crystal analysis confirms the structure of $Me_2Si(CH_2CH_2)_2P(O)OH$.

Phosphorus or silicon-substituted cyclohexanes are currently of considerable interest; phosphacyclohexanes (phosphorinanes) for their anticarcinostatic [1] and ring isomeric properties [2–4] and silacyclohexanes as new silicon-substituted drug molecules (silapharmaca) [5]. These observations raise questions of what properties could arise in saturated six-membered rings which contain both silicon and phosphorus in the ring system. We now report the synthesis of a new class of such compounds, the transannularly substituted 4-silaphosphorinanes, from the radical addition of Me_3SiPH_2 to vinylsilanes.

Reactions of Me_3SiPH_2 with the vinyl silanes $Me_2Si(CH{=}CH_2)_2$ or $Si(CH{=}CH_2)_4$ in benzene at 85 °C initiated by AIBN (AIBN = 2,2′-azobis(isobutyronitrile)) [6 *], occur cleanly to yield (90% conversion, 90% yield) the new 4-silaphosphorinanes

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* Reference numbers with asterisks indicate notes in the list of references.

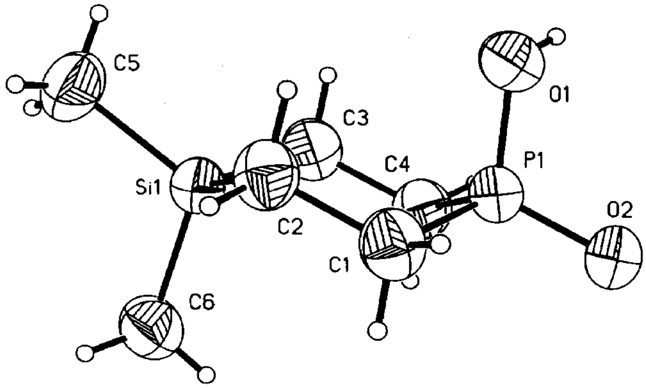
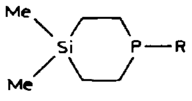


Fig. 1. Structure and atom numbering system of $Me_2Si(CH_2CH_2)_2P(O)OH$ (7). Thermal ellipsoids are at the 50% level. Selected bond distances (Å) and angles (deg): P–O(1), 1.560(2); P–O(2), 1.495 (2); P–C(1), 1.785(3); P–C(4), 1.795(2); C(1)–C(2), 1.534(4); C(3)–C(4), 1.537(4); C(2)–Si, 1.869(2); C(3)–Si, 1.872(3); Si–C(5), 1.867(4); Si–C(6), 1.854(2); O(1)–P–O(2), 113.2(1); P–C(1)–C(2), 113.3(2); P–C(4)–C(3), 114.1(1); C(1)–P–C(4), 107.0(1); C(2)–Si–C(3), 105.7(1); Si–C(3)–C(4), 113.6(1); Si–C(2)–C(1), 113.6(1); C(5)–Si–C(6), 111.0(2).



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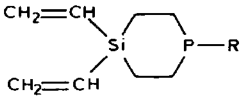

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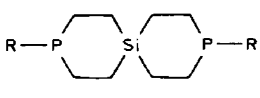

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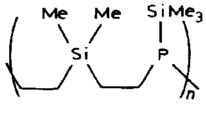
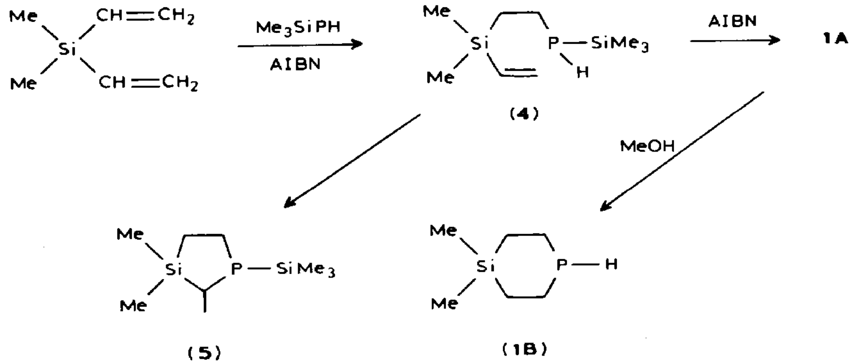


(6)

(1A-3A , R = $SiMe_3$; 1B-3B , R = H)

1A–3A [7*]. Methanolysis of **1A–3A** yields $MeOSiMe_3$ and the new secondary phosphine 4-silaphosphorinanes **1B–3B** [8*,9*], quantitatively. Reaction mixtures were separated and new compounds were purified by high-vacuum column distillation. Reactions occur, illustrated by the $Me_3SiPH_2/Me_2Si(CH{=}CH_2)_2$ system, as shown in Scheme 1.



Scheme 1

Me_3SiPH_2 and the vinyl silanes react in 1/1 (mol/mol) reactant ratios yielding **1A** and **2A** as major products; **3A** is obtained using a 2/1 (mol/mol) $Me_3SiPH_2/(CH_2{=}CH)_4Si$ ratio. ^{31}P NMR spectral analysis of reaction mixtures during reaction or in systems containing excess Me_3SiPH_2 ($> 2/1$) showed evidence for acyclic intermediates, e.g. **4** in the $Me_3SiPH_2/Me_2Si(CH{=}CH_2)_2$ reaction. Reactions are highly regioselective for six membered ring formation. In none of the reactions studied was greater than 10% of material tentatively characterized as the five-membered ring Markovnikov addition product (5) observed. Only small quantities of oligomer or polymer (6) were observed as reaction residues upon removal of volatile reaction materials and solvent from reaction vessels. At higher Me_3SiPH_2/vinyl silane reactant ratios (> 2/1) larger amounts of oligomer/polymer were seen.

The silaphosphorinanes **1–3** were characterized [7*–9*] by spectral (^{31}P, ^{13}C, and ^{1}H NMR, IR, and MS) data. All exhibit parent (M^+) mass spectral ions. **1A–3A** each display $^{31}P(^{1}H)$ NMR spectral resonances in the chemical shift region (ca. −95) consistent with those expected for silyl-substituted tertiary phosphines [4,10]. Each half of the ^{1}H NMR P–H resonances of **1B–3B** is a triplet of triplets, arising from a relatively large (ca. 10 Hz) and a considerably smaller (ca. 2 Hz) coupling constant. Based on Karplus plot correlations of coupling constants with geometry in rigid systems [4,11], it is expected that an axially located P–H group will have a $^{3}J_{ae}$ coupling constant larger than the $^{3}J_{aa}$ value. In the equatorial conformer both $^{3}J_{ae}$ and $^{3}J_{aa}$ would be of about the same magnitude. Although the P–H units appear to be axial, as has been observed previously in the parent phosphorinane [12], the bulky Me_3SiP unit in **1A–3A** could be equatorial. The ^{1}H NMR spectrum of **1B** has been examined over the temperature range +100 °C to −100 °C. The spectrum is temperature independent, except that at low temperatures slight resolution loss in the spectrum occurs. Even at −100 °C the large $^{3}J_{ae}$ coupling constant is maintained, indicating that a significant contribution of an equatorial conformation does not occur. Compounds **3A** and **3B** are present as a single enantiomeric pair; no evidence exists for diastereomers as would be the case if two conformational forms were present.

Characterization of the 4-silaphosphorinane ring system of **1–3** is further verified by derivatization of **1A**. Oxidation of **1A** with O_2/H_2O yields the phosphinic acid $Me_2Si(CH_2CH_2)_2P(O)OH$ (7) quantitatively [13*]. It is important to note that in one case the **1A**-O_2/H_2O reaction mixture exploded violently; thus the reaction should be conducted with great care. Sublimation of **7** yields pure crystalline product which was characterized by spectral and X-ray analysis [14*]. Crystals of **7** contain four molecules per unit cell. The molecules have approximate C_s molecular symmetry. **7** is a symmetrical six-membered ring, in a chair conformation, with the P=O bond unit in an equatorial position. Ring silicon–carbon (mean, 1.87 Å) and phosphorus–carbon (mean, 1.79 Å) bond distances are typical [4,15,16]. Bond angles are also as expected. Angles around silicon and phosphorus are close to tetrahedral. The ring is distorted slightly from that of cyclohexane; dihedral angles between the C(1),C(2),C(3),C(4) plane and the P,C(1),C(2) and Si,C(3),C(4) planes are 50.9 deg and 44.8 deg, respectively.

The Me_3Si substituted 4-silaphosphorinanes are uniquely obtained using the Me_3SiPH_2 reagent with vinylsilanes. Analogous reactions between PH_3 and the vinylsilanes give more complex, possibly polymeric, products [17]. **1A–3A** may prove to be interesting synthons for further silaphosphorinane derivative development because of the generally high reactivity of the Si–P bonds. Extension of the chemistry herein to derivatives containing reactive functionality on the ring silicon atom can be expected. Such studies are in progress and will be reported later.

Acknowledgement

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References and Notes

1 D.L. Hill, A Review of Cyclophosphamides, C.C. Thomas, Springville, IL, 1975.

2 R.R. Holmes, R.O. Day, W.N. Setzer, A. E. Sopchik, and W.G. Bentrude, J. Am. Chem. Soc., 106 (1984) 2353.

3 (a) W.N. Setzer, A.E. Sopchik, and W.G. Bentrude, J. Am. Chem. Soc., 107 (1985) 2083, and ref. contained therein.

4 D.E.C. Corbridge, The Structural Chemistry of Phosphorus, Elsevier Publishing Company, Amsterdam, 1974.

5 W.S. Sheldrick, H. Linoh, R. Tacke, G. Lambrecht, U. Moser, and E. Mutschler, J. Chem. Soc. Dalt. Trans., (1985) 1743.

6 All operations were carried out in vacuum line and Schlenk apparatus. ^{1}H, ^{31}P, and ^{13}C NMR spectra were obtained at 90.0, 40.5, and 22.5 MHz, respectively. Chemical shifts were measured relative to internal Me_4Si and external H_3PO_4. Shifts downfield from the standards are given + values.

7 Characterization data. **1A**: Anal. Found: C, 49.26; H, 10.48; P, 13.90. $C_9H_{23}PSi_2$ calcd.: C, 49.49; H, 10.61; P, 14.18%. $^{31}P(^{1}H)$ NMR (C_6D_6), δ −95.0 (s); ^{1}H NMR (C_6D_6), δ −0.04 (s, a 3, $SiCH_3$) and 0.00 (s, a 3, $SiCH_3$), 0.11 [d, ^{3}J(PH) 3.4 Hz, a 9, $PSi(CH_3)_3$], 0.85 (m, a 4, CH_2), 1.65 (m, a 4, CH_2); $^{13}C(^{1}H)$ NMR (C_6D_6), δ 16.4 (d, J(PC) 15.2 Hz, a 2, CH_2), 14.6 (d, J(PC) 11.3 Hz, a 2, CH_2), −2.3 [d, J(PC) 10.7 Hz, a 3, $Si(CH_3)_3$], −1.7 (s, a 1, $SiCH_3$), −4.1 (s, a 1, $SiCH_3$); IR (KBr), ν, 400 (Si–P) cm^{-1}; MS, M^+, 218 ($^{12}C_9H_{23}P^{28}Si_2{}^+$). **2A**:Anal. Found: C, 54.23; H, 9.53; P, 12.85. $C_{11}H_{23}PSi_2$ calcd.: C, 54.49; H, 9.56; P, 12.78%. $^{31}P(^{1}H)$ NMR (C_6D_6), δ −95.3 (s); ^{1}H NMR (C_6D_6), δ 0.06 [d, J(PH) 3.9 Hz, a 9, $PSi(CH_3)_3$], 1.35 (m, a 8, CH_2, 5.85 (m, a 6, $Si(CHCH_2)_2$]; $^{13}C(^{1}H)$ (C_6D_6) NMR, δ 137.0 (s, a 1, $SiCHCH_2$), 135.8 (s, a 1, $SiCHCH_2$), 134.8 (s, a 1, $SiCHCH_2$), 134.2 (s, a 1, $SiCHCH_2$), 16.7 (d, J(PC) 14.6 Hz, a 2, CH_2), 12.3 (d, J(PC) 11.0 Hz, a 2, CH_2), −1.7 [d, J(PC) 9.7 Hz, a 3, $Si(CH_3)_3$]; IR (KBr), ν, 467 (Si–P) cm^{-1}; MS, M^+, 242 ($^{12}C_{11}H_{23}P^{28}Si_2{}^+$). **3A**: Anal. Found: C, 48.47; H, 9.47; P, 17.63. $C_{14}H_{34}P_2Si_3$ calcd.: C, 48.23; H, 9.83; P, 17.77%. $^{31}P(^{1}H)$ NMR (C_6D_6), δ −94.3 (s); ^{1}H NMR (C_6D_6), δ 0.06 [d, J(PH) 3.9 Hz, a 9, $Si(CH_3)_3$], 0.9 (m, a 4, CH_2), 1.6 (complex, a 4, CH_2); $^{13}C(^{1}H)$ NMR (C_6D_6), δ 16.6 (d, J(PC) 14.7 Hz:, a 2, PCH_2), 13.7 (d, J(PC) 11.1 Hz, a 1, $SiCH_2$), 10.6 (d, J(PC) 12.2 Hz, a 1, $SiCH_2$), −1.8 [d, J(PC) 9.8 Hz, a 3, $Si(CH_3)_3$]; MS, M^+ at 348 ($^{12}C_{14}H_{34}P^{28}Si_3{}^+$).

8 **1B**: ^{31}P NMR (C_6D_6), δ −52.8 (d, J(PH) 192 Hz); ^{1}H NMR (C_6D_6), δ −0.08 (s, a 3, $SiCH_3$), and −0.04 (s, a 3, $SiCH_3$), 0.40–2.20 (complex m, a 9, CH_2 + 0.5 PH), 4.22 (t of t, J(HH) 9.9 Hz, J(HH) 1.8 Hz, 0.5 PH); $^{13}C(^{1}H)$ NMR (C_6D_6), δ −4.00 (s, a 1, $SiCH_3$), −1.8 (s, a 1, $SiCH_3$), 16.5 (s, a 2, $SiCH_2$), +17.0 (d, J(PC) 12.2 Hz, a 2, PCH_2); IR (KBr), ν, 2260 (P–H) cm^{-1}; MS, M^+, 146 ($^{12}C_6H_{15}P^{28}Si^+$). **2B**: ^{31}P NMR (C_6D_6), δ −53.6 (d, J(PH) 192 Hz); ^{1}H NMR (C_6D_6), δ 0.9 (m, a 4, CH_2), 1.1 (m, a 4, CH_2), 4.2 (t of t, J(HH) 10.4 Hz, J(HH) 1.9 Hz, a 1/2, 0.5 PH, upfield 1/2 obscured by the ring CH_2 resonances), 5.9 [complex, a 6, $Si(CHCH_2)_2$]; $^{13}C(^{1}H)$ NMR (C_6D_6), δ 140.3 (s, a 1), 136.6 (s, a 1), 134.9 (s, a 1), 134.2 (s, a 1), 13.7 (s, a 2, CH_2), 16.7 (d, J(PC) 12.2 Hz, a 2, CH_2); MS, M^+, 170 ($^{12}C_8H_{15}{}^{28}SiP^+$). **3B**: ^{31}P NMR (C_6D_6), δ −53.0 (d, J(PH) 192 Hz); ^{1}H NMR (C_6D_6), 0.5–2.0 (m, a 8, CH_2), 4.2 (t of t, J_{aa} 10.2 Hz, J_{ae} 2.2 Hz, a 1/2, 0.5 PH, upfield 1/2 obscured by CH_2 resonances). $^{13}C(^{1}H)$ NMR (C_6D_6), δ 12.2 (s, a 2, CH_2), 14.6 (s, a 2, CH_2), 16.6 (b, J(PC) 12.2 Hz, a 4, CH_2); MS, M^+, 204 ($^{12}C_8H_{18}P_2{}^{28}Si^+$).

9 Owing to their oxidative instability, elemental analyses of **1B**–**3B** were not obtained.

10 (a) D.M. Schubert, A.D. Norman, Inorg. Chem., 23 (1984) 4130; (b) K. Issleib, U. Kuhne, and F. Krech, Phosphorus and Sulfur, 21 (1985) 367.

11 (a) W. Kung, R.E. Marsh, and M. Kainosho, J. Am. Chem. Soc., 99 (1977) 5471; (b) J.B. Lambert, R.G. Keske, and D.K. Weary, J. Am. Chem. Soc., 89 (1967) 5921.

12 (a) K. Issleib, K. Standtke, Chem. Ber., 96 (1963) 279; (b) K. Issleib, G. Doll, ibid., 96 (1963) 1544; (c) J.B. Lambert, W.L. Oliver, Tetrahedron, 27 (1971) 4245.

13 **7**: $^{31}P(^{1}H)$ NMR (C_6D_6), δ 49.5 (s); ^{1}H NMR (C_6D_6), δ −0.2 (s, a 6, $SiCH_3$), 0.90 (m, a 4, ring CH_2), 1.9 (m, a 4, ring CH_2); IR (KBr), ν, 2300 [m, P(O)OH], 1170 (P=O); MS, M^+, 178 ($^{12}C_6H_{16}{}^{28}SiPO_2{}^+$).

14 Single crystal X-ray data for 7 were collected at 294–296 K using a Syntex $\bar{P}1$ automated diffractometer [Mo-K_α radiation, λ 0.71073 Å] equipped with a graphite monochromator. Crystal data: $C_6H_{15}PSiO_2$, f.w. 178.24 amu, monoclinic, $P2_1/c$, a 10.4167(20) Å, b 6.8171(13) Å, c 14.2379(29) Å, β 106.326(15) deg, V 970.3(3) Å^3, $Z = 4$, Intensity data. θ–wθ scan mode, 3.0–55.0 deg, 9215 reflections measured (2246 unique) of which 1653 were observed. Data were reduced using Syntex and SHELXTL computing routines. Refinement converged at $R = 0.038$, $R_w = 0.052$.

15 (a) L.D. Quin, A.T. McPhail, S.O. Lee, and K.D. Onan, Tetrahedron Lett., 38 (1974) 3473.

16 (a) R.O. Day, W.G. Bentrude, K.C. Yee, W.N. Setzer, J.A. Dexters and R.R. Holmes, J. Am. Chem. Soc., 106 (1984) 103; (b) A.W. Cordes, P.F. Schubert, and R.T. Oakley, Can. J. Chem., 57 (1979) 174.

17 P.F. Brandt, M.L.J. Hackney, A.D. Norman, submitted for publication.