(Trimethylsilyl)phosphine as a Versatile Reagent for Syntheses of New 4-Sila- and 4-Phosphaphosphorinanes

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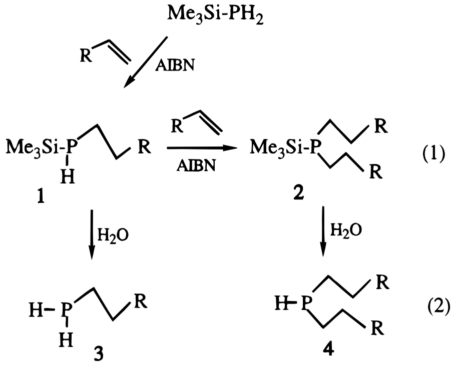
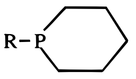
(Trimethylsilyl)phosphine (Me_3SiPH_2) undergoes radical P−H bond addition to vinylphosphines and -silanes to form new 4-phospha- and 4-silaphosphorinanes [vinyl reagent]: [$PhP(CH{=}CH_2)_2$], $PhP(C_2H_4)_2PSiMe_3$ diastereomers (**9A/9B**); [$Et_2NP(CH{=}CH_2)_2$], $Et_2NP(C_2H_4)_2PSiMe_3$ (**11**); [$Me_2Si(CH{=}CH_2)_2$], $Me_2Si(C_2H_4)_2PSiMe_3$ (**14**); [$Si(CH{=}CH_2)_4$], $(CH{=}CH_2)_2Si(C_2H_4)_2PSiMe_3$ (**16**) and [$Me_3SiP(C_2H_4)_2]_2Si$ (**17**). Reactions are accompanied by formation of only small quantities of the Markovnikov addition product phospholanes. Methanolysis of the new silylphosphines yields $PhP(C_2H_4)_2PH$ diastereomers (**10A/10B**), $Me_2Si(C_2H_4)PH$ (**15**), $(CH{=}CH_2)_2Si(C_2H_4)_2PH$ (**18**), and $[HP(C_2H_4)_2]_2Si$ (**19**). Stepwise methanolysis of **11** yields the phosphorinanes $Et_2NP(C_2H_4)_2PH$ (**12**) and $MeOP(C_2H_4)_2PH$ (**13**). Oxidation of **15** and **14** with O_2 or O_2/H_2O, respectively, yields the phosphine oxide $Me_2Si(C_2H_4)_2P(O)H$ (**20**) and the phosphinic acid $Me_2Si(C_2H_4)_2P(O)OH$ (**21**). New compounds were characterized by spectral (^{31}P, ^{1}H, and ^{13}C NMR, IR, and MS) data. **21** was further characterized by a single-crystal X-ray analysis: monoclinic, $P2_1/c$, $a = 10.416(2)$ Å, $b = 6.817(1)$ Å, $c = 14.237(3)$ Å, $\beta = 106.32(2)°$, $Z = 4$, $V = 970.3(3)$ Å^3. The ring of **21** adopts a chair conformation with the P=O bond in an equatorial position. From spectral data, tentative isomeric and conformational structural assignments are made for the new phosphorinanes in solution.

Introduction

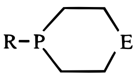
(Trimethylsilyl)phosphine (Me_3SiPH_2) was shown previously[2−4] to be an effective reagent in radical reactions with alkenes for synthesis of primary (**1**) and secondary (**2**) silyl(organo)phosphines (eq 1). Since these reactions occur without involvement of the Si−P bond, and because this bond is later readily cleaved by protic reagents (ROH),[2−4,5−7] these silyl(organo)phosphines can be converted easily to new primary (**3**) and secondary (**4**) phosphines (eq 2). In this sequence the Me_3Si group acts as a protecting group for a P−H bond, a bond which also offers useful functionality.



Reaction of 1,4-pentadiene with Me_3SiPH_2 was particularly efficient at forming the six-membered-ring Me_3Si-substituted phosphorinane **5**, which was subsequently converted by MeOH solvolysis to the parent **6**.[2a,3] Given this strong tendency to react with 1,4-dienes and previous evidence that Me_3SiPH_2 addition to activated alkenes such as $Ph_2PCH{=}CH_2$ is especially facile,[4] we have further explored use of this reaction for synthesis of phosphorus (**7**) and silicon (**8**) ring-substituted phosphorinanes, compound types which could be useful as ligands and have interesting conformational and isomer properties.[8,9] The results of our study are described below; a preliminary report of some of this work has appeared.[2]



(**5**, R = Me_3Si)
(**6**, R = H)



(**7**, E = PR)
(**8**, E = SiR_2)

Experimental Section

Materials and Apparatus. Me_3SiPH_2[5,10] and $Et_2NP(CH{=}CH_2)_2$[11] were prepared as described previously. $PhP(CH{=}CH_2)_2$ (Alfa Inorganics), $Me_2Si(CH{=}CH_2)_2$, and $Si(CH{=}CH_2)_4$ (Petrarch) were placed over activated Linde 4 Å molecular sieves *in vacuo* before use. Methanol (Aldrich) and AIBN [2,2′-bis(isobutyronitrile), Aldrich Chemical Co.] were used as obtained. Benzene and toluene were

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distilled from Na/Pb alloy and stored *in vacuo* over activated 4 Å molecular sieves.

Infrared spectra were obtained on Perkin-Elmer Model 467, Beckman IR 4250, and HP 59970 IRD ChemStation/HP 5965 IR Detector spectrometers. Mass spectra (EI) were measured on Varian MAT CH5 and V. G. Analytical 7070 EQ-HF/HP5988A GC/MS spectrometers. ^{31}P NMR spectra were obtained at 40.5 and 102.7 MHz using JEOL PFT-100 and Bruker WM-250 FT NMR spectrometers, respectively. ^{1}H NMR spectra were obtained at 90.0 and 250.0 MHz using Varian EM-390 and Bruker WM-250 spectrometers. ^{13}C NMR spectra were obtained at 25.1 and 62.90 MHz using JEOL FX-90Q, JEOL PFT-100, Bruker WM-250, and Varian VXR 300S spectrometers. Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P NMR spectra are assigned positive ($+\delta$) values. Elemental analyses were conducted by Huffman Laboratories, Inc., Wheatridge, CO.

General Procedures. All manipulations were made in standard high-vacuum systems or inert-atmosphere apparatus.[12] Reactions between Me_3SiPH_2 and olefins were carried out by condensing volatile reagents and solvent into a 10 mL reaction vessel containing degassed AIBN. Low-volatility reagents, $PhP(CH{=}CH_2)_2$, $Et_2NP(CH{=}CH_2)_2$, and $Si(CH{=}CH_2)_4$, were added by syringe and degassed prior to addition of volatile materials. The reaction vessel was sealed *in vacuo*, the contents were warmed to room temperature and mixed, and then the vessel was heated to 75−85 °C. After heating, the vessel was opened and the products were separated as described below. Often it was desirable to follow reaction progress by ^{1}H and/or ^{31}P NMR spectroscopy. In these cases, the same procedure was employed using sealed 5 mm or 10 mm NMR tubes. Product yields reported below are given as a percentage of the Me_3SiPH_2 converted to products, as determined by ^{31}P NMR spectral analysis. Solvolysis reactions occurred rapidly and quantitatively upon mixing benzene or toluene solutions of organo(silyl)phosphine reaction products with one or more molar equivalents of deoxygenated H_2O or MeOH under a N_2 atmosphere.

Caution! The silyl(organo)- and (organo)phosphines prepared in this study are malodorous and likely to be highly toxic. Great care should be exercised in their handling.

Me_3SiPH_2 Reactions. (A) With $PhP(CH{=}CH_2)_2$. $PhP(C_2H_4)_2PSiMe_3$ (9A/9B) and $PhP(C_2H_4)_2PH$ (10A/10B). $PhP(CH{=}CH_2)_2$ (0.39 mL, 2.4 mmol), Me_3SiPH_2 (26 Torr, 1.9 L, 24 °C; 2.5 mmol), and AIBN (8 mg, 0.05 mmol) in benzene (0.4 mL) were heated at 85 °C for 4.5 h (Me_3SiPH_2 conversion > 95%). Removal of volatiles *in vacuo* left the oil **9A**/**9B** (yield > 90%). ^{31}P{^{1}H} NMR (C_6D_6): δ −8.7 (s) and −84.6 (s) [**9A**], −11.7 (d) and −82.3 (d, $^3J_{PP}$ = 20.2 Hz) [**9B**]; **9A**:**9B** ~ 1:2.3. ^{1}H NMR (C_6D_6): δ 0.30 (d, 9H, J_{PH} = 4.5 Hz; $SiMe_3$), 1.3−2.4 (compl. mult., 8H; CH_2), 7.1−7.7 (compl. mult., 5H; C_6H_5). MS (*m/e*, M$^+$): 268 ($^{12}C_{13}H_{22}SiP_2^+$). Anal. Calcd for $C_{13}H_{22}SiP_2$: C, 58.18; H, 8.27. Found: C, 58.22; H, 8.34.

9A/**9B** was allowed to react with excess MeOH. Volatiles were removed from the hydrolysate. Molecular distillation of the remaining oil from a 100 °C trap to a 0 °C trap yielded pure **10A**/**10B** (90% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ −27.4 (d, $^4J_{PP}$ = 3.3 Hz; br d in ^{1}H coupled spectrum, J_{PH} = 190 Hz), −63.1 (d) [**10A**], −33.4 (d, J_{PP} = 4.0 Hz; br d in ^{1}H coupled spectrum, J_{PH} = 190 Hz) and −58.3 (d) [**10B**]; **10A**:**10B** ~ 1:2. ^{1}H NMR (C_6D_6): δ 1.3−2.4 (compl. mult., 8H; CH_2), 7.1−7.7 (compl. mult., 5H; C_6H_5), and 3.0 (d, 1H, J_{PH} = 191 Hz; PH). ^{13}C{^{1}H} NMR (C_6D_6): δ 12.51 (d of d, 2C, J_{PC} = 11.4 Hz, J_{PC} = 1.5 Hz), 28.96 (d of d, 2C, J_{PC} = 12.3 Hz, J_{PC} = 2.3 Hz) [**10A**], 17.14 (d of d, J = 14.1 Hz, J_{PC} = 11.1 Hz), 23.19 (d, J_{PC} = 16.2 Hz) [**10B**], 126.5−131.0 (compl. mult.; C_6H_5; **A** and **B**). IR (KBr, cm^{-1}): 2280 (s, ν_{PH}). MS (*m/e*, M$^+$): 196 ($^{12}C_{10}H_{14}P_2^+$). Anal. Calcd for $C_{10}H_{14}P_2$: C, 61.22; H, 7.19. Found: C, 61.42; H, 7.24.

(B) With $Et_2NP(CH{=}CH_2)_2$. $Et_2NP(C_2H_4)_2PSiMe_3$ (11), $Et_2NP(C_2H_4)_2PH$ (12), and $MeOP(C_2H_4)_2PH$ (13A/B). Me_3SiPH_2 (81 Torr, 920 mL, 23 °C; 4.0 mmol), $Et_2NP(CH{=}CH_2)_2$ (0.72 g, 4.6 mmol), and AIBN (10 mg, 0.06 mmol) in C_6D_6 (10 mmol) were heated to 85 °C for 3.5 h (Me_3SiPH_2 conversion, ca. 65%). Product ^{31}P NMR resonances occurred at δ 49.2 (d) and −100.2 (d) (**11**), 55 to 54 and −145.9 to −146.8 (overlapped unresolved resonances), −236.9 [$(Me_3Si)_2PH$],[13] and −252.6 [$(Me_3Si)_3P$][5] and −241.0 (PH_3).[14] High-volatility materials were removed in vacuo. Additional AIBN and C_6H_6 were added to the residual material followed by heating an additional 2 h at 85 °C. Removal of high-volatility materials, followed by repeated distillation of the low-volatility fraction at 55 °C to a 0 °C trap yielded pure **11**. ^{31}P{^{1}H} NMR (C_6D_6): δ 49.2 (d, ^{1}H, J_{PP} = 20.5; Et_2NP) and −100.2 (d, 1P; $PSiMe_3$). ^{1}H NMR (C_6D_6): δ 0.08 (d, 9H, J_{PH} = 4.1 Hz; $SiMe_3$), 0.93 (t, 6H, J_{HH} = 7.01 Hz; CH_2CH_3), 1.8−2.4 (compl mult., 8H; ring CH_2), 2.9 (d of q, 4H, J_{PH} = 9.4 Hz, J_{HH} = 7.0 Hz; NCH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ −1.9 (d, 3C, J_{PC} = 10.9 Hz; $SiMe_3$), 16.4 (d, 2C, J_{PC} = 3.7; CH_2CH_3), 17.7 [t, 2C, J_{PC} = 14.7 Hz; ring CH_2], 29.5 (d of d, 2C, J_{PC} = 6.1 Hz, J_{PC} = 15.9 Hz; ring CH_2], 44.0 (d, 2C, J_{PC} = 13.4; NCH_2CH_3). MS (*m/e*, M$^+$): 263 ($C_{11}H_{27}NP_2Si^+$). Anal. Calcd for $C_{11}H_{27}NP_2Si$: C, 50.16; H, 10.33; N, 5.32; P, 23.52. Found: C, 50.06; H, 10.18; N, 5.11; P, 24.71.

11 reacted with HCl below −78 °C to produce only intractable products. Neat **11** was heated at 200 °C for 24 h; the ^{31}P NMR spectrum showed no change.

Reaction of **11** in benzene with slightly less than 1 equiv of MeOH for 15 min at 25 °C, followed by fractional condensation of the mixture into a −23 °C trap, yielded **12** (>95% pure). ^{31}P{^{1}H} NMR (C_6D_6): δ −58.2 (d, 1P, J_{PP} = 4.4 Hz; J_{PH} = 193.2 Hz in ^{1}H coupled spectrum) and 49.2 (br s, 1P). ^{1}H NMR (C_6D_6): δ 0.88 (t, 6H; CH_3), 1.75 (compl. mult., 8H; ring CH_2), 2.85 (compl. mult., 4H; CH_2N), and 3.1 (d, 1P, 190 Hz; PH). ^{13}C{^{1}H} NMR (C_6D_6): δ 16.4 (d, 2C, J_{PC} = 3.7 Hz; CH_3), 19.0 [t, 2C, J_{PC} = 14.7 Hz; ring CH_2], 32.8 (d of d, 2C, J_{PC} = 14.7 Hz, J_{PC} = 2.4 Hz; ring CH_2), 43.8 [d, 2C, J_{PC} = 14.6 Hz; $Et_2N(CH_2)_2$]. MS (*m/e*, M$^+$): 191 ($C_8H_{19}NP_2^+$). IR (thin film, cm^{-1}); 2250 (m, ν_{PH}). Anal. Calcd for $C_8H_{19}P_2N$: C, 50.24; H, 10.01. Found: C, 50.41; H, 10.28.

Reaction of **11** in benzene with 2 equiv of MeOH for 12 h at 25 °C, followed by fractional condensation of the reaction mixture into a −23 °C trap, yielded **13A**/**13B** (80% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 118.3 (d, 1P, J_{PP} = 7.3 Hz; CH_3OP) and −59.9 (d, 1P; PH) (**13A**), 119.9 (d, 1P, J_{PP} = 3.7 Hz; CH_3OP) and −66.3 (d, 1P; PH) (**13B**); **13A**:**13B** = 3:2. ^{1}H NMR (C_6D_6): δ 1.3 (compl. mult., 4H; ring CH_2), 1.9 (compl mult., 4H; ring CH_2), 3.30 (d, 3H, $^3J_{PH}$ = 13.3 Hz; CH_3OP), 3.26 (d, 1H, J_{PH} = 188 Hz; PH). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.8 (d of d, 2C, J_{PC} = 12.2, J_{PC} < 2 Hz; ring CH_2), 29.4 (d of d, 2C, J_{PC} = 23.2, J_{PC} = 3.7 Hz; ring CH_2), 32.6 (d, 1C, J_{PC} = 18.3 Hz; $POCH_3$). MS (*m/e*, M$^+$): 150 ($C_5H_{12}OP_2^+$). Samples of **13** routinely contained traces (<5%) of unidentified impurities, which could not be removed by molecular distillation.

(C) With $Me_2Si(CH{=}CH_2)_2$. $Me_2Si(C_2H_4)_2PSiMe_3$ (14) and $Me_2Si(C_2H_4)_2PH$ (15). $Me_2Si(CH{=}CH_2)_2$ (0.26 g, 2.3 mmol), Me_3SiPH_2 (40 Torr, 920 mL, 24 °C; 2.0 mmol), and AIBN (10 mg, 0.06 mmol) in benzene-d_6 (0.4 mL) were heated at 85 °C. After 1 h, ^{31}P NMR resonances appeared at δ −95.0 (s; **14**) and −139.8 (d, $^2J_{PH}$ = 181.7 Hz). Reaction was complete after 3 h (Me_3SiPH_2, 90% consumed). The final reaction mixtures typically contained **14** (85%) and minor ^{31}P resonances at δ −70.9 (s), −139.8 (d), and −237.3 [$(Me_3Si)_2PH$].[13] High-vacuum column distillation[12] yielded **14** (>95% pure). ^{31}P{^{1}H} NMR (C_6D_6): δ −95.0 (s). ^{1}H NMR (C_6D_6): δ −0.04 (s, 3H; $SiCH_3$) and 0.01 (s, 3H; $SiCH_3$), 0.11 [d, $^3J_{PH}$ = 3.4 Hz, 9H; $PSi(CH_3)_3$], 0.85 (compl. mult., 4H; ring CH_2), 1.65 (compl. mult., 4H; ring CH_2). ^{13}C{^{1}H} NMR (C_6D_6): δ 16.4 (d, J_{PC} = 15.2 Hz, 2C; ring CH_2), 14.6 (d, J_{PC} = 12.2 Hz, 2C; ring CH_2), −2.3 [d, J_{PC} = 10.7 Hz, 3C; $Si(CH_3)_3$], −1.7 (s, 1C, $SiCH_3$), −4.1 (s, 1C; $SiCH_3$). MS (*m/e*, M$^+$): 218 ($^{12}C_9H_{23}P^{28}Si_2^+$). Anal. Calcd for $C_9H_{23}PSi_2$: C, 49.49; H, 10.6l; P, 14.18. Found: C, 49.26; H, 10.48; P, 13.90.

MeOH solvolysis of **14** yielded **15** quantitatively. **15** was trap-to-trap distilled and collected at −23 °C. ^{31}P NMR (C_6D_6): δ −52.8 (d, J_{PH} = 193 Hz). ^{1}H NMR (C_6D_6): δ −0.08 (s, 3H; $SiCH_3$), −0.04 (s, 3H; $SiCH_3$), 0.65 and 0.88 (AB mult., 4H; CH_2), 1.48 and 1.87 (AB mult., 4H; CH_2), 3.18 (d of t of t, 2H, J_{PH} = 193.0 Hz, $^3J(HPCH_{ax})$ = 10.8 Hz, $^3J(HPCH_{eq})$ = 1.8 Hz; PH). ^{13}C{^{1}H} NMR (C_6D_6): δ −1.73 (s, 1C; CH_3), −3.90 (s, 1C; CH_3), 16.5 (s, 2C; CH_2), 17.0 (d, 2C; CH_2;

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${}^2J_{PC}$ = 12.2 Hz). IR (KBr, cm^{-1}): 2260 (s, ν_{PH}). MS (m/e, M$^+$): 146 (${}^{12}C_6H_{15}PSi^+$). Anal. Calcd for $C_6H_{15}SiP$: C, 49.26; H, 10.33; P, 21.19. Found: C, 49.80; H, 10.02; P, 21.38.

(D) With $Si(CH{=}CH_2)_4$. $(CH_2{=}CH)_2Si(C_2H_4)_2PSiMe_3$ (16), $[Me_3SiP(C_2H_4)_2]_2Si$ (17), $(CH_2{=}CH)_2Si(C_2H_4)_2PH$ (18), and $[HP(C_2H_4)_2]_2Si$ (19). Approximately equimolar quantities of Me_3SiPH_2 (72 Torr, 1.8 L, 23 °C; 7.0 mmol), $Si(CH{=}CH_2)_4$ (1.0 g, 7.3 mmol), and AIBN (15 mg, 0.090 mmol) in toluene (3 mL) were heated at 90 °C. After 2.7 h, reaction was complete (Me_3SiPH_2, 90% consumed); in addition to **16**, small resonances (<10%) at δ −237.5 [$(Me_3Si)_2PH$],[13] δ −23.7 to −25.3 (comp. mult.), and δ −139.6 (d, ${}^1J_{PH}$ = 191 Hz) are present. Pure **16**, as a colorless oil, was collected by trap-to-trap distillation into a 0 °C trap (75% yield). ${}^{31}P\{{}^1H\}$ NMR (C_6D_6): δ −95.3 (s). ${}^1H$ NMR: δ 0.06 [d, J_{PH} = 3.87 Hz, 9H; $PSiCH_3)_3$], 1.35 (comp. mult., 8H; CH_2), 5.85 [comp. mult., 6H; $Si(CHCH_2)_2$]. ${}^{13}C\{{}^1H\}$ NMR: δ 137.0 (s, 1C; $SiCHCH_2$), 135.8 (s, 1C; $SiCHCH_2$, 134.8 (s, 1C; $SiCHCH_2$), 134.2 (s, 1C; $SiCHCH_2$), 16.7 (d, J_{PC} = 14.6 Hz, 2C; CH_2), 12.3 (d, J_{PC} = 11.0 Hz, 2C; CH_2), −1.7 [d, J_{PC} = 9.7 Hz, 3C; $Si(CH_3)_3$]. MS (m/e, M$^+$): 242 (${}^{12}C_{11}H_{23}PSi_2$). Anal. Calcd for $C_{11}H_{23}PSi_2$: C, 54.49; H, 9.56; P, 12.78. Found: C, 54.23; H, 9.53; P, 12.85.

Using a higher Me_3SiPH_2:$Si(CH{=}CH_2)_4$ reactant ratio (3.1:1.4 mmol), the reactants with AIBN (0.06 mmol) in benzene-d_6 were heated at 85 °C for 4 h. Volatile materials were removed in vacuo leaving a colorless oil **17**. ${}^{31}P\{{}^1H\}$ NMR (C_6D_6): δ −94.3 (s). ${}^1H$ NMR (C_6D_6): δ 0.06 [d, J_{PH} = 3.9 Hz, 18H; Si $(CH_3)_3$], 0.9 (comp. mult., 8H; CH_2), 1.6 (comp. mult., 8H; CH_2). ${}^{13}C\{{}^1H\}$ NMR (C_6D_6): δ 16.6 (d, J_{PC} = 14.7 Hz, 4C; PCH_2), 13.7 (d, J_{PC} = 11.1 Hz, 2C $SiCH_2$), 10.6 (d, J_{PC} = 12.2 Hz, 2C, $SiCH_2$), −1.8 [d, J_{PC} = 9.8 Hz, 6C, $Si(CH_3)_3$]. MS (m/e, M$^+$): 348 (${}^{12}C_{14}H_{34}P_2{}^{28}Si_3^+$). Anal. Calcd for $C_{14}H_{34}P_2Si_3$: C, 48.23; H, 9.83; P, 17.77. Found: C, 48.47; H, 9.47; P, 17.63. Samples of **17** were generally contaminated with small quantitites (<10%) of uncharacterized nonvolatile products from which they could not be separated.

MeOH solvolysis of **16** or **17** formed **18** or **19**, respectively, quantitatively. Trap-to-trap distillation yielded **18** (in −23 °C condensate); removal of volatiles in vacuo from mixtures yielded **19**. **18**: ${}^{31}P$ NMR (C_6D_6) δ −53.6 (d, J_{PH} = 192 Hz); ${}^1H$ NMR (C_6D_6) δ 0.9 (comp. mult., 4H; CH_2), 1.1 (comp. mult., 4.5H; CH_2 + $^1/_2$ PH), 4.2 (t of t, J_{aa} = 10.4 Hz, J_{ae} = 1.9 Hz, 0.5H; $^1/_2$ PH, upfield $^1/_2$ was obscured by ring CH_2 resonances), 5.9 [comp. mult., 6H, $Si(CH{=}CH_2)_2$]; ${}^{13}C\{{}^1H\}$ NMR (C_6D_6) δ 140.3 (s, 1C), 136.6 (s, 1C), 134.9 (s, 1C), 134.2 (s, 1C), 13.7 (s, 2C; CH_2), 16.7 (d, J_{PC} = 12.2 Hz, 2C; CH_2). **19**: ${}^{31}P$ NMR δ −53.0 (d, J_{PH} = 192 Hz); ${}^1H$ NMR (C_6D_6) δ 0.5−2.0 (comp. mult., 17H; CH_2 + $^1/_2$ PH's), 4.2 (t of t, J_{aa} = 10.2 Hz, J_{ae} = 2.2 Hz, 1H; $^1/_2$ PH's, upfield $^1/_2$ obscured by CH_2 resonances); ${}^{13}C\{{}^1H\}$ NMR (C_6D_6) δ 12.2 (s, 2C; CH_2), 14.6 (s, 2C; CH_2), 16.6 (br s, J_{PC} = 12.2 Hz, 4C; CH_2). MS (m/e, M$^+$) 204 (${}^{12}C_8H_{18}P_2{}^{28}Si^+$). Anal. Calcd for $C_8H_{15}SiP$: C, 56.43; H, 8.88. Found. C, 57.00; 8.65.

Oxidation of 14 and 15. (A) 15 with O_2. $Me_2Si(C_2H_4)_2P(O)H$ (20). Oxygen (O_2) was bubbled into a toluene solution of **15** at 25 °C. After 24 h, solvent was removed in vacuo and the product **21** was vacuum distilled at 55 °C (75% yield). ${}^{31}P$ NMR (C_6D_6): δ 30.6 (d of mult., J_{PH} = 443 Hz). ${}^1H$ NMR: δ −0.3 (s, 3H; $SiCH_3$), −0.2 (s, 3H; $SiCH_3$), 0.2−1.0 (comp. mult., 4H; CH_2), 1.6−2.1 (comp. mult., 4H; CH_2), 6.5 (d, J_{PH} = 443 Hz, 1H; PH). ${}^{13}C\{{}^1H\}$ NMR (C_6D_6): δ −3.8 (s, 1C; $SiCH_3$), −3.4 (s, 1C; $SiCH_3$), 7.5 (s, 2C; CH_2), 24.2 (d, J_{PC} = 63 Hz, 2C; CH_2). IR (KBr, cm^{-1}): 2340 (m, ν_{PH}). MS [m/e (rel. int.)]: 163 (23) [M + 1$^+$], 162 (5), [${}^{12}C_6H_{15}OSiP^+$, M$^+$].

(B) 14 with H_2O/O_2. $Me_2Si(C_2H_4)_2P(O)OH$ (21). *Caution! Reactions of **14** with O_2/H_2O are difficult to control and sometimes occur explosively; therefore, these reactions should be performed only with great care.* Water-saturated O_2 was bubbled slowly through a toluene solution of **14** at 25 °C. After 11 h, a viscous oil remained. Sublimation at 70 °C yielded **21**. ${}^{31}P\{{}^1H\}$ NMR (C_6D_6): δ 49.5 (s); ${}^1H$ coupled, pentet, ${}^2J_{PCH}$ = 18.3 Hz. ${}^1H$ NMR (C_6D_6): δ −0.2 [s, 6H; Si $(CH_3)_2$], 0.9 (comp. mult., 4H; CH_2), 1.9 (comp. mult., 4H, CH_2). The OH proton resonance was not observed. MS (m/e, M$^+$): 178 (${}^{12}C_6H_{16}O_2SiP^+$).

X-ray Analysis of 21. Crystals of **21**, obtained by sublimation, were mounted on glass fibers using epoxy resin. Crystal data for **21** are given in Table 1. The structure was solved using direct methods and refined using blocked-cascade least-squares techniques.[15] In the final model non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. Final refined parameters for the non-hydrogen atoms are given in Table 2.

Table 1. Crystal Data for $Me_2Si(C_2H_4)_2P(O)OH$ (**21**)

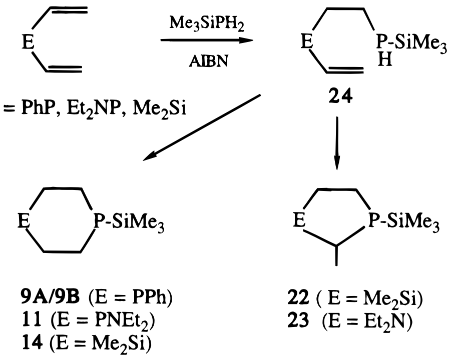
formula	$C_6H_{15}SiPO_2$	fw	178.24
a, Å	10.416(2)	space group	$P2_1/c$
b, Å	6.817(1)	temp, K	294−296
c, Å	14.237(3)	λ, Å	Mo Kα (0.710 73)
β, deg	106.32(2)	d_c, g/cm^3	1.22
V, Å^3	970.3(3)	(Mo Kα), cm^{-1}	3.48
Z	4	R	0.038
transm coeff	0.912, 0.850	R_w	0.052

Table 2. Final Positional Parameters (×10^4) and Isotropic Thermal Parameters for the Non-Hydrogen Atoms of $Me_2Si(C_2H_4)_2P(O)OH$ (**21**)

atom	x/a	y/b	z/c	U^a
P	1119.1(6)	1937.0(8)	2465.6(4)	502(2)
Si	3178.6(6)	3535.6(9)	1133.6(4)	491(2)
O(1)	1763(2)	−142(3)	2672(1)	672(7)
O(2)	−3(2)	2244(3)	2913(1)	651(7)
C(1)	2486(3)	3575(4)	2936(2)	568(8)
C(2)	3653(2)	3248(4)	2493(2)	555(8)
C(3)	1667(3)	1956(4)	649(2)	582(9)
C(4)	571(2)	2289(4)	1164(2)	555(8)
C(5)	4606(4)	2710(5)	681(2)	761(12)
C(6)	2747(3)	6131(5)	801(3)	704(12)

[a] U (Å^2 × 10^4) defined as one-third the trace of the orthogonalized **U** tensor.

Scheme 1



Results and Discussion

(Trimethylsilyl)phosphine (Me_3SiPH_2) undergoes radical reactions with $PhP(CH{=}CH_2)_2$, $Et_2NP(CH{=}CH_2)_2$, $Me_2Si(CH{=}CH_2)_2$, and $Si(CH{=}CH_2)_4$ in toluene in the presence of the AIBN initiator. Reactions involving $PhP(CH{=}CH_2)_2$, $Me_2Si(CH{=}CH_2)_2$, and $Si(CH{=}CH_2)_4$ are suprisingly clean. These yield mainly the 4-phosphaphosphorinane diastereomeric mixture **9A/9B** and the monoisomeric 4-silaphosphorinanes **14**, **16**, and **17** (Schemes 1 and 2), the result of terminal addition of P−H bonds to the alkene units,[16] respectively. The reactions with $Et_2NP(CH{=}CH_2)_2$ and $PhP(CH{=}CH_2)_2$ could yield both *cis* and *trans* isomer products; however, the former does not. Only one isomer is seen. In the $Me_3SiPH_2/Si(CH{=}CH_2)_4$ reaction, a 1:1 reactant mole ratio yields mainly **16**; however, in the 2:1 ratio reactions the spirocyclic bis(phosphine) **17** predominates. The $Me_3SiPH_2/Et_2NP(CH{=}CH_2)_2$ reaction is less

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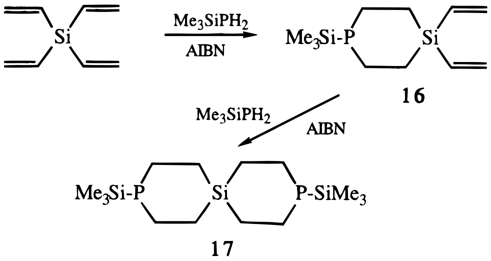
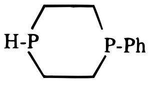
Scheme 2



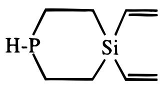
clean, although it produces phosphorinane **11** in moderate yield (ca. 15%). The reaction proceeds with greater difficulty; i.e., multiple AIBN additions and heating cycles are needed and the reactions yield significant amounts of higher molecular weight, intractable products. The latter are presumed to be oligomeric/polymeric although further characterization was not attempted. Reaction with $Me_2Si(CH{=}CH_2)_2$ also yields small quantities of what from ^{31}P NMR[14,17] and mass spectral data is characterized tentatively as the five-membered phospholane ring **22**. The Me_3SiP group ^{31}P NMR resonance for **22** occurs at δ −70.9 in a region characteristically downfield from the phosphorinane **14**. The $Me_3SiPH_2/Et_2NP(CH{=}CH_2)_2$ reaction may also produce minor amounts of phospholane **23**; however, the spectral regions where these should occur were too complex to interpret unambiguously. Not suprisingly, separation of the phosphorinanes from trace phospholane(s) is difficult and requires repeated fractional distillation. Diastereomers **9A**/**9B** were not separable by fractional distillation.

The Me_3SiPH_2/diene reaction products are all presumed to form via acyclic intermediates such as **24**, and in the $Me_3SiPH_2/Me_2Si(CH{=}CH_2)_2$, $Et_2NP(CH{=}CH_2)_2$, and $Si(CH{=}CH_2)_4$ reactions the species were tentatively identified. When the reactions were monitored by ^{31}P NMR spectral analysis, small doublet resonances at δ −139.8, −139.6, and −146.9 appeared ($^2J_{PH} = 180-200$ Hz) in the chemical shift region characteristic of Me_3Si-substituted primary organophosphines.[18] As reactions progress, final products dominate and the intermediates decrease or disappear. Even in reactions in which the Me_3SiPH_2:diolefin ratio was high (ca. 10:1), only small quantities (<5%) of the intermediates were detected. Apparently, in all cases intramolecular addition of the $Me_3SiP(H)$ group P−H bond to the alkenyl group of **24** to form the final phosphorinanes is very fast compared to the initial reaction of Me_3SiPH_2 with the alkenes.

Silylphosphines **9A**/**9B**, **11**, **14**, **16**, and **17** undergo rapid and clean solvolysis with 1 equiv of alcohol to form the new P−H-containing phosphorinanes **10A**/**10B**, **12**, **15**, **18**, and **19**.



10A/10B



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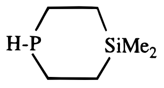

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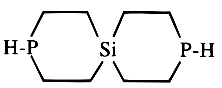

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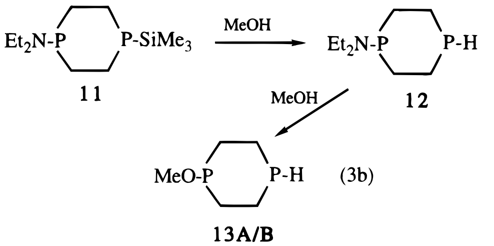
Solvolysis of **11** is somewhat unique in that it, and its first solvolysis product **12**, contain oppositely polarized, i.e. $P(-\delta)-Si(+\delta)$ [or P−H] and $P(+\delta)-N(-\delta)$, P-substituent bonds. Thus, **11** with 1 equiv of MeOH is converted first to the diethylamino derivative **12** (eq 3), but with additional MeOH,



it reacts further to the methoxy-substituted diastereomers **13A**/**13B** (eq 3b). Such reactions, because of the opposite bond polarity feature, offer interesting opportunities for further synthetic use.

The new 4-phospha- and 4-silaphosphorinanes were not crystallizable, hence, their characterization is based on spectral data. All show mass spectral parent ions and the expected mass spectral fragmentation patterns. The Me_3Si-substituted phosphorinanes exhibit ^{31}P NMR resonances in the δ −107.8 to −94.3 range, characteristic of silyl-substituted secondary phosphines.[4,18] As expected, the P−H phosphorus resonances in **10A**/**10B**, **12**, **13A**/**13B**, **15**, **18**, and **19** appear as doublets ($^1J_{PH} \sim 190$ Hz) in the δ −52.8 to −66.0 range.[14] The Ph-P resonances in **9A**/**9B** and **10A**/**10B** (δ −8.7 to −33.0) and the Et_2N-P resonances of **11** and **12** (δ 49.2) are in the chemical shift regions expected for aryl-[14,19,20] and alkylamino-substituted[11,14,21] phosphorinanes. Phosphorinanes **11**, **12**, **14**, and **16**−**19** are formed as single isomers; hence, all exhibit single $P-SiMe_3$, P−H, or $P-NEt_2$ ^{31}P and ^1H NMR resonances. In contrast, **9A**/**9B**, its derived **10A**/**10B**, and the methoxyphosphaphosphorinane **13A**/**13B** exist as mixtures of two, presumably *cis* and *trans*, isomers. Each contains two sets of ^{31}P NMR resonances, one from each diastereomer. Isomers **9A** and **9B** form in an approximate 1:2.3 ratio, a ratio which is essentially maintained when **9A**/**9B** are converted to **10A**/**10B**. Phosphorinanes **13A** and **13B** occur in a 3:2 mole ratio. Interestingly, isomers **9A**/**9B** show significantly different $^3J_{PP}$ coupling between the ring phosphorus atoms—the observed couplings are 20.2 and <2 Hz. A similar situation has been reported by King for the diastereomers of $Et_2NP(C_2H_4)_2PPh$, where $^3J_{PP}$ couplings of 17 and <2 Hz (the reported resolution limit) were seen.[11]

The conformational and isomeric structural properties of the new phosphorinanes are of interest. Detailed studies of 1,3,2-dioxo- and 1,3,2-oxaza- phosphorinanes, rings in which O or O and N atoms are adjacent to the phosphorus atoms, have shown they can exist as both *cis* and *trans* isomers and in chair, twist-chair, and boat forms, depending largely on the subtituents present on phosphorus and/or the other ring atoms.[8,9,22−25] In contrast, phosphorinanes which contain heteroatoms in the

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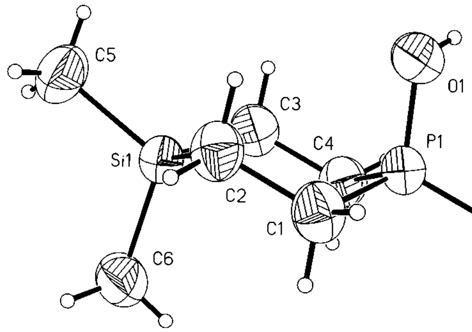
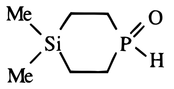


Figure 1. Structure and numbering system for $Me_2Si(C_2H_4)_2P(O)OH$ (**21**). Thermal ellipsoids are shown at the 50% level.

4-position are less studied. There are only limited examples of ring 4-phospha substitution.[19,26] From X-ray crystallographic and solution NMR studies of alkyl- and aryl-substituted phosphorinanes[20,27−29] and $PhP(C_2H_4)_2PPh$,[19] it has been determined that the rings adopt chair conformations and that small to modest-sized P-substituents (e.g. Me and Ph) prefer axial bonding positions.[28,29] In contrast, no conformational information about 4-sila-substituted phosphorinanes has been reported. Unfortunately, none of the new 4-silaphosphorinanes, **14**−**19**, were crystallizable; however, we have been able through oxidation to derivatize **14** and thereby obtain a crystallizable phosphinic acid derivative **21**.

Reaction of **15** with ambient O_2 yields the phosphine oxide **20**, which is readily purified by fractional distillation. Its



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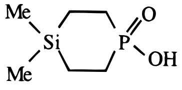


21

spectral properties are as expected; its ^{31}P NMR resonance occurs at δ 30.6 in the region characteristic of secondary phosphine oxides.[14] Even when the sample is allowed to stand in air for several hours, no significant further oxidation is seen. However, if **14** is treated with a O_2/H_2O mixture, more complete oxidation occurs. When a O_2/H_2O mixture is bubbled through a toluene solution of **14** at 25 °C, reaction occurs during 11 h to form **21** which can be purified by sublimation and recrystallized from toluene for X-ray analysis.

The X-ray crystal structure of **21** is shown in Figure 1; metrical data are given in Table 3. The molecule consists of a chair-form six-membered ring of approximate C_s molecular symmetry. The interplane dihedral angles between the C(1)/C(2)/C(3)/C(4) plane and the P/C(1)/C(4) and Si/C(2)/C(3) planes are 51 and 45°, respectively. The P=O bond is equatorially oriented. The ring mean Si−C (1.87 Å), C−C (1.54 Å), and C−P (1.79 Å) bond distances and the bond angles are as expected. Angles around Si are close to tetrahedral; only the C(3)−Si−C(5) angle is somewhat large at 111.7°. Angles around the P atom are also close to tetrahedral; the 113.2° O(1)−P−(O2) angle is largest. In order to accommodate the larger P and Si atoms in the six-membered ring, bond angles around ring carbons C(1), C(2), C(3), and C(4) are greater than tetrahedral, 113.1, 113,6, 113.6, and 114.2°, respectively.

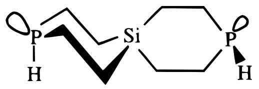
Table 3. Selected Structural Parameters for $Me_2Si(C_2H_4)_2P(O)OH$ (**21**)

(a) Bond Distances (Å)			
P−O(1)	1.560 (2)	Si−C(3)	1.872 (3)
P−O(2)	1.495 (2)	Si−C(5)	1.867 (4)
P−C(1)	1.785 (3)	Si−C(6)	1.854 (3)
P−C(4)	1.795 (2)	C(1)−C(2)	1.534 (4)
Si−C(2)	1.869 (2)	C(3)−C(4)	1.537 (4)
(b) Bond Angles (deg)			
O(1)−P−O(2)	113.2 (1)	C(1)−C(2)−Si	113.6 (1)
O(1)−P−C(1)	104.0 (1)	C(4)−C(3)−Si	113.6 (1)
O(1)−P−C(4)	108.1 (1)	C(2)−Si−C(3)	105.7 (1)
O(2)−P−C(1)	112.9 (1)	C(2)−Si−C(5)	108.8 (1)
O(2)−P−C(4)	111.2 (1)	C(2)−Si−C(6)	109.8 (1)
C(1)−P−C(4)	107.0 (1)	C(3)−Si−C(5)	111.7 (1)
P−C(1)−C(2)	113.3 (1)	C(3)−Si−C(6)	109.6 (1)
P−C(4)−C(3)	114.2 (1)	C(5)−Si−C(6)	111.0 (2)

Some tentative conclusions can be made concerning isomer structure and the location of substituents in axial vs equatorial positions for the new 4-sila- and 4-phosphaphosphorinanes, assuming that, like previously reported phosphorinanes[19,28,29] and **21**, the compounds prepared in this study assume chair conformations and that NMR data correlations can be made with the known substituted phosphorinanes.[28,29]

The 4-silaphosphorinanes **14**−**19** are all monoisomeric. Compounds **15**, **18** and **19** contain a P−H bond; comparison of their ^{1}H NMR spectral data with those for the parent phosphorinane $(CH_2)_5PH$ (**6**)[4,30] allows tentative conclusions regarding whether the P−H bond is in an axial or an equatorial position. Lambert et al. argued previously,[31,32] on the basis of Karplus dihedral angle−coupling constant correlations,[33] that two distinctly different ^3J couplings between the P−H and α-CH (axial) or α-CH(equatorial) hydrogen atoms are expected if the P−H bond is in an axial position of a chair ring conformation. In contrast, a P−H bond in an equatorial position should display two relatively similar ^3J values. For **6**, where two $^3J(HPCH_\alpha)$ couplings of 17.0 and <2 Hz were observed,[31,32] attributable to $^3J(HPCH_{ax})$ and $^3J(HPCH_{eq})$, respectively, axial P−H bonding was supported. Thus, **15**, **18** and **19** which exhibit ^3J couplings of 10.8 and 1.8 Hz, 10.4 and 1.9 Hz, and 10.2 and 2.2 Hz, are also presumed to contain axial P−H bonds. Furthermore, it seems likely that **14**, **16**, and **17**, from which **15**, **18**, and **19** are derived by solvolysis, would have the large Me_3Si substitutents in equatorial ring positions, although our NMR data do not support a particular assignment.

15 (R = Me)
18 (R = $CH=CH_2$)



19

Structural characterization of the 4-phosphaphosphorinanes **9**−**13** is more complicated because, for each, there are questions of *cis* vs *trans* isomerism in addition to those of axial vs equatorial location of substituent groups. Only with **9A**/**9B**, **10A**/**10B**, and **13A**/**13B** are both isomers observed. Compounds

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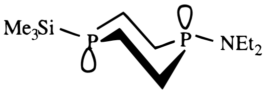
10A/**10B**, **11**, and **13A**/**13B** exhibit ^{1}H NMR P−H resonances not clearly consistent with the P−H bond being in axial positions. The P−H resonances are broad and poorly resolved. These data might indicate that the P−H bonds are predominantly equatorially located as expected if the $^3J(\mathrm{HPCH_{eq}})$ and $^3J(\mathrm{H\text{-}PCH_{ax}})$ coupling constants are closely similar or that they are being averaged for each isomer between the axial and equatorial positions. The question is further complicated by the fact that the P−H resonances are expectedly more complex and broadened because the H-P protons exhibit not only $^1J_{\mathrm{HP}}$ coupling but also $^4J_{\mathrm{HP}}$ coupling to the distant ring phosphorus atoms. Interestingly, phosphorinanes **9A**/**9B** exhibit two distinctly different $^3J_{\mathrm{PP}}$ values, <2 and 20.0 Hz, in contrast to **10A**/**10B** and **13A**/**13B**, which show $^3J_{\mathrm{PP}}$ couplings of 3.3 and 4.0 Hz and 7.3 and 3.7 Hz, respectively. Also the single isomeric **11** shows a large, 20.5 Hz, $^3J_{\mathrm{PP}}$ coupling, whereas for **12** $^3J_{\mathrm{PP}}$ is only 4.4 Hz. Whether this large difference in $^3J_{\mathrm{PP}}$ values is unique to amino-substituted 4-phosphorinanes or if it suggests differences in conformational properties between the **9A**/**9B**, *cis*- and *trans*-$\mathrm{Et_2NP(C_2H_4)_2PPh}$,[11] and **11** compound group versus the **10A**/**10B**, **13A**/**13B**, and **12** compound group is unclear. However, it is possible that diastereomers in the former group are predominantly of one conformational type whereas the others are a mixture. If the large $\mathrm{Me_3Si}$ group prefers the equatorial orientation in both the *cis* and *trans* isomers of **9A**/**9B**, and if the P−Ph group ^{31}P NMR chemical shift for the isomer with the equatorial P−Ph group is upfield from that with the axial P−Ph group, as is the case in previously reported P-substituted phosphorinanes,[20] **9A** and **9B** would be characterized as *cis* and *trans*, respectively. Thus, **9B** has the larger $^3J_{\mathrm{PP}}$ (20.2 Hz) and as expected is the major isomer. Since **11** has a similarly large $^3J_{\mathrm{PP}}$ (20.5 Hz) it might also be the *trans* isomer. For **10A**/**10B**, **12**, and **13A**/**13B**, where intermediate $^3J_{\mathrm{PP}}$ couplings (3.7−7.0 Hz) are seen, it could be that for each isomer axial−equatorial interconversion of the P−H and/or the P−Ph groups occurs. This is not unlikely since neither the H or Ph group is large and therefore might not express a strong preference for either position. Further attempts are being made to resolve these questions through single-crystal X-ray analysis of crystallizable derivatives and will be the subject of a subsequent report.

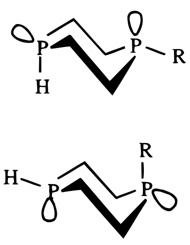
9A (*cis*)

9B (*trans*)



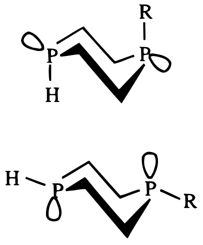
11 (*trans*)

12



(*cis*)

10A (R = Ph)
13A (R = MeO)



(*trans*)

10B (R = Ph)
13B (R = MeO)

Our studies have shown that $\mathrm{Me_3SiPH_2}$ readily undergoes P−H bond addition to 1,4-dienes to form both 4-phospha- and 4-silaphosphorinanes, in reactions that are likely to be general for syntheses of various other compounds in these classes. Both the new silyl(organo)phosphines and the organophosphines to which they can be converted by quantitative solvolysis are of interest for their structural properties and for opportunities they offer in subsequent syntheses.[34]

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Supporting Information Available: Tables of X-ray data, positional and thermal parameters, and bond distances and angles (8 pages). Ordering information is given on any current masthead page.

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