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Silylphosphide Reagents in Synthetic Routes to Cyclophosphines

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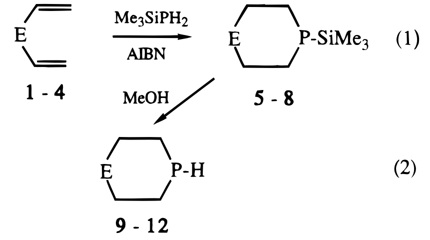
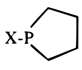
Introduction

We demonstrated previously that radical reactions of (trimethylsilyl)phosphine (Me$_3$SiPH$_2$) with acyclic 1,4- and 1,5-dienes (e.g., **1−4**) efficiently yield six- and seven-membered cyclic organo(silyl)phosphines (**5−8**).[2−4] In these reactions, the favored products are the result of anti-Markovnikov addition to the diene. Subsequently, **5−8** can be converted to the parent P−H bond containing phosphines (**9−12**) by methanolysis,[2−4] taking advantage of the readily cleaved silicon−phosphorus bond.[5−7] However, analogous reactions between Me$_3$SiPH$_2$ and allene or 1,3-butadiene do not yield the smaller four- and five-membered rings, phosphetanes (**13a**) or phospholanes (**14a**). These reactions yield only mixtures of acyclic propenyl- and butenylphosphine isomers, Me$_3$SiP(H)C$_3$H$_5$ and Me$_3$SiP(H)-C$_4$H$_7$.[8]

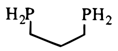


1, **5**, **9**; E = CH$_2$: **2**, **6**, **10**; E = PPh:
3, **7**, **11**; E = Me$_2$Si: **4**, **8**, **12**; E = CH$_2$CH$_2$

13a (X = Me$_3$Si)
13b (X = H)



14a (X = Me$_3$Si)
14b (X = H)



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In an attempt to further determine the usefulness of silylphosphines Me$_3$SiPH$_2$ and Me$_2$Si(PH$_2$)$_2$ in cyclic phosphine synthesis, and to obtain viable routes to several potential phosphine ligands containing P−X functional bonds, we now have examined some prototype reactions between silylphosphides and alkenyl halides (i) as routes to subsequently cyclizable alkenylphosphine intermediates or (ii) as routes directly to new cyclophosphines. Our results are reported below.

Experimental Section

Materials and Apparatus. Trimethylsilylphosphine (Me$_3$SiPH$_2$)[9] and Me$_2$Si(PH$_2$)$_2$[9] were prepared as described previously. The 3-bromopropene (Aldrich) and monoglyme (Eastman Kodak) were distilled from CaH$_2$ and stored over molecular sieves. The 1,3-dibromopropane (Aldrich) was distilled from P$_4$O$_{10}$. The 4-bromo-1-butene (Pfaltz and Bauer), MeI (Aldrich), *n*-BuLi (Aldrich; standardized, 1.6 M in hexanes), AIBN [2,2′-bis(isobutyronitrile)], and MeOH (Aldrich) were used as obtained. Benzene and toluene were distilled from Na/Pb alloy. Tetrahydrofuran was distilled over sodium benzophenone immediately before use.

All manipulations were made in standard high-vacuum systems or an inert atmosphere apparatus.[10] Infrared spectra were obtained on IBM (IR/32 Type 9132) or Hewlett-Packard 5965 IR detector spectrometers. Mass spectra (EI) were measured on VG Analytical 7070 EQ-HF and Hewlett-Packard 5988 GC/MS spectrometers. ^{31}P (36.2 and 121.4 MHz) and ^{1}H (89.9 and 250 MHz) NMR spectra were obtained using JEOL FX-90Q and Bruker WM-250 FT NMR spectrometers. ^{13}C NMR spectra were obtained at 22.5 and 75.4 MHz using JEOL FX 90Q and Varian VXR300S spectrometers. Chemical shifts downfield from Me$_4$Si for ^{1}H and ^{13}C NMR spectra and from H$_3$PO$_4$ for ^{31}P NMR spectra are assigned positive ($+\delta$) values.

Caution! The silylphosphines and organo(silyl)phosphines studied are malodorous, sometimes flammable in air, and probably highly toxic. Extreme care should be exercised in their handling.

Me$_3$SiP(H)Me (16). Tetrahydrofuran (THF) (2 mL) in a 5-mL vessel with a stir bar was triply freeze−thaw−degassed. Me$_3$SiPH$_2$ (10.3 Torr, 1.8 L, 22 °C; 1.0 mmol) was condensed in, and the mixture was warmed to −78 °C and stirred. The flask was filled with N$_2$ before *n*-BuLi (0.63 mL, 1.0 mmol) was slowly added via syringe. The solution turned dull yellow as it warmed to 25 °C over 1.5 h. The contents were freeze−thaw−degassed, MeI (0.28 g, 2.0 mmol) was condensed into the flask, and the reaction was allowed to warm first to −78 °C and then to 25 °C over 1.8 h. Volatile materials were removed. ^{31}P spectral analysis showed **16** (65%) along with lesser amounts of MePH$_2$ (17%) and Me$_2$PH (18%). Fractional condensation through traps at −45 and −63 °C, followed by column distillation[10] of the −63 °C trap condensate, gave pure **16**. ^{31}P NMR (C$_6$D$_6$); δ −175.0 (d, $^{1}J_{\mathrm{PH}}$ = 187.5 Hz); in agreement with earlier report.[11] ^{1}H NMR (C$_6$D$_6$): δ 1.97 (d of mult, 1H, $^{1}J_{\mathrm{HP}}$ = 180 Hz), 0.85 (d of d, 3H, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, $^{2}J_{\mathrm{HP}}$ = 2.8 Hz), 0.11 (d, 6H, $^{3}J_{\mathrm{HP}}$ = 4.1 Hz). IR (gaseous, cm^{-1}): 2963(s), 2917(m), 2283(s, PH), 1427(w), 1255(s), 988(m), 845(vs). MS (GC, EI^{+}; M^{+}, *m/e*): 120 [^{12}C$_4$H$_{13}$PSi^{+}].

Me$_3$SiP(H)CH$_2$CH═CH$_2$ (17). THF (2 mL), monoglyme (0.5 mL) and a spin bar in a 5-mL reactor were triply freeze−thaw−degassed. Me$_3$SiPH$_2$ (10.4 Torr, 1.8 L, 22 °C; 1.0 mmol) was condensed in and the reaction was warmed to −78 °C and stirred. N$_2$ was added before *n*-BuLi (0.63 mL, 1.0 mmol) was slowly added via syringe. The solution turned light yellow. The reaction was allowed to warm to room temperature over 2 h; then the contents were freeze−thaw−degassed, and H$_2$C═CHCH$_2$Br (15 Torr, 1.8 L; 1.5 mmol) was condensed in. The contents were allowed to warm to −78 °C and then to 25 °C over 0.5 h. Volatile materials were removed; a ^{31}P NMR spectrum of the mixture showed both **17** (90%)[12] and H$_2$C═CHCH$_2$-PH$_2$ (10%).[13] Passage of the mixture through traps at −45, −63, and

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−196 °C followed by column distillation[10] of the −45 and −63 °C condensates yielded **17** (25.0 °C, vapor pressure = 1 Torr). ^{31}P NMR (C_6D_6): δ −148.8 (d, $^1J_{PH}$ = 189 Hz). ^{13}C NMR (C_6D_6): δ 138.5 (d, $^2J_{CP}$ = 4.9 Hz), 114.2 (d, $^3J_{CP}$ = 9.3 Hz), 19.6 (d, $^1J_{CP}$ = 14.3 Hz), 0.0 (d, $^2J_{CP}$ = 9.9 Hz). IR (gaseous, cm^{-1}): 3087(w), 2962(s), 2906(m), 2283(s; PH), 1821(w), 1636(w), 1413(w), 1255(vs), 1201(w), 1075(w), 990(w), 909(s), 845(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 146 [$^{12}C_4H_{13}PSi^+$]. ^{1}H NMR data had been reported previously.[12] Neat samples of **17** in vacuo at 25 °C were stable for periods of hours. Reaction of **17** with excess MeOH produced $CH_2{=}CHCH_2PH_2$[13] quantitatively.

$Me_3SiP(H)CH_2CH_2CH{=}CH_2$ (18) and $(Me_3Si)_2PCH_2CH_2CH{=}CH_2$ (19). THF (4.0 mL), monoglyme (2.0 mL), and a stir bar in a 10-mL flask were triply freeze−thaw−degassed. Me_3SiPH_2 (61 Torr, 920 mL, 23 °C; 3.0 mmol) was added, and the reactants were warmed to −78 °C. N_2 and then *n*-BuLi (1.9 mL, 3.0 mmol) were slowly added via syringe. The solution turned bright yellow. The solution was allowed to warm to 25 °C over 2 h, after which the solution was cooled to −78 °C and $CH_2{=}CHCH_2CH_2Br$ (0.50 mL, 5.0 mmol) was slowly syringed in. During 30 min the solution was warmed to room temperature. Volatile materials were removed and distilled through traps at −23, −45, and −196 °C. Approximately 30% of the material, **19**, was too nonvolatile to transfer from the reaction vessel. The −45 °C trap contained a mixture of **18** and $H_2PCH_2CH_2CH{=}CH_2$.[13] Distillation of the −23 °C fraction yielded pure **18**: ^{31}P NMR (C_6D_6); δ −154.4 (d, $^1J_{PH}$ = 188 Hz). ^{13}C NMR (C_6D_6): δ 138.9 (d, $^4J_{CP}$ = 9.9 Hz), 114.8 (s), 36.1 (d, $^2J_{CP}$ = 12.1 Hz), 13.9 (d, $^1J_{CP}$ = 13.2 Hz), −0.1 (d, $^2J_{CP}$ = 9.9 Hz). ^{1}H NMR (C_6D_6): δ 5.8 (compl mult, 1H), 5.0 (compl mult, 2H), 2.35 (compl mult, 0.5H), 2.17 (compl mult, 2H), 1.52 (compl mult, 2.5H), 0.13 (d, 9H, $^3J_{HP}$ = 4.1 Hz). IR (gaseous, cm^{-1}): 3087(m), 2961(s), 2909(m), 2280(s, PH), 1834(w), 1641(w), 1417(w), 1316(w), 1254(s), 992(m), 915(m), 845(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 160 [$^{12}C_7H_{17}PSi^+$]. Anal (EI$^+$, exact mass MS). Calcd for $C_7H_{17}PSi$: 160.0837. Found: 160.0814. Extraction of nonvolatile materials in the reaction vessel with benzene followed by removal of benzene in vacuo yielded **19**. ^{31}P NMR (C_6D_6): δ −175.4 (s). ^{13}C NMR (C_6D_6): δ 139.4 (d, $^4J_{CP}$ = 13.2 Hz), 114.6 (s), 36.7 (d, $^2J_{CP}$ = 18.1 Hz), 15.0 (d, $^1J_{CP}$ = 15.4 Hz), 1.1 (d, $^2J_{CP}$ = 11.5 Hz). ^{1}H NMR (C_6D_6): δ 5.85 (compl mult, 1H), 5.0 (compl mult, 2H), 2.27 (compl mult, 2H), 1.65 (t of d, 2H, $^2J_{HP}$ = 2.7 Hz, $^3J_{HH}$ = 8.1 Hz), 0.30 (d, 18H, $^3J_{HP}$ = 4.1 Hz). IR (gaseous, cm^{-1}): 3087(m), 2960(s), 2905(s), 1641(w), 1407(w), 1253(vs), 1066(w), 992(w), 913(m), 838(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 232 [$^{12}C_{10}H_{25}PSi_2^+$]. Anal (EI$^+$, exact mass MS). Calcd for $C_{10}H_{25}PSi_2$: 232.1232. Found: 232.1212. Reaction of **18** and **19** with excess MeOH produced $CH_2{=}CHCH_2CH_2PH_2$[13] quantitatively.

$Me_2Si(PH_2)(PHMe)$ (20) and $Me_2Si(PHMe)_2$ (21). THF (4 mL), monoglyme (1 mL), and a spin bar were added to a 5-mL reaction vessel, and the mixture was triply freeze−thaw−degassed. $Me_2Si(PH_2)_2$ (20 Torr, 920 mL, 24 °C; 1.0 mmol) was condensed into the vessel, the contents were warmed to −78 °C, and the mixture was stirred. Under N_2, *n*-BuLi (1.3 mL, 2.0 mmol) was slowly added. The solution turned yellow immediately. The reaction was stirred for 5 min and then quickly cooled to −196 °C. MeI (31 Torr, 1.8 L, 22 °C; 3.0 mmol) was condensed into the reaction vessel, and the contents were warmed to −78 °C for 5 min, until effervesence ceased. Volatile materials were removed. The ^{31}P NMR spectrum showed peaks attributed to PH_3 (δ −245.0, 12%),[14] **20**, **21**, and $MePH_2$ (δ −163.0, 26%).[14] Volatile materials were fractionally condensed through traps at −45, at −63, and into −196 °C. Compounds **20** and **21** condensed at −63 and −45 °C, respectively. Compound **20**: ^{31}P{^{1}H} NMR (C_6D_6): δ −238.8 (d, $^2J_{PP}$ = 11.5 Hz, PH_2), −165.9 (d, $^2J_{PP}$ = 11.5 Hz, PHMe). ^{31}P NMR (C_6D_6): δ −238.8 (t of mult, $^1J_{PH}$ = 184 Hz), −165.9 (d of mult, $^1J_{PH}$ = 189 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 1.2 (t, $^2J_{CP}$ = 9.9 Hz, MeSi), 0.8 (t, $^2J_{CP}$ = 10.2 Hz, MeSi), −3.4 (d of d, $^1J_{CP}$ = 16.2 Hz, $^3J_{CP}$ = 3.0 Hz, MeP). ^{1}H NMR (C_6D_6): δ 2.10 (d of q of d, 1H, $^1J_{HP}$ = 190 Hz, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 3.7 Hz, P*H*Me), 1.37 (d of d, 2H, $^1J_{HP}$ = 184 Hz, $^3J_{HP}$ = 3.7 Hz, PH_2), 0.84 (d of d, 3H, $^2J_{HP}$ = 3.2 Hz, $^3J_{HH}$ = 7.3 Hz, PH*Me*), 0.24 (t, 3H, $^3J_{HP}$ = 4.15 Hz, Me_2Si), 0.22 (t, 3H, $^3J_{HP}$ = 4.15 Hz, Me_2Si). IR (gaseous, cm^{-1}): 2968(m), 2921(w), 2290(vs, PH), 1423(w), 1254(s), 1060(m), 988(m), 836(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 138 [$^{12}C_3H_{12}P_2Si^+$]. Compound: **21**: ^{31}P{^{1}H} NMR (C_6D_6): δ −177.7 (s), −176.2 (s). ^{31}P NMR (C_6D_6): δ −177.7 (d, $^1J_{PH}$ = 191 Hz), −176.2 (d, $^1J_{PH}$ = 189 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ −1.5 (t, 1C, $^2J_{CP}$ = 10.2 Hz, MeSi), −1.8 (t, 2C, $^2J_{CP}$ = 11.0 Hz, Me_2Si),-2.0 (t, 1C, $^2J_{CP}$ = 9.9 Hz, MeSi), −3.8 (compl mult, MeP). ^{1}H NMR (C_6D_6): δ 2.11 (d of mult, 2H, $^1J_{HP}$ = 190 Hz, P*H*Me), 0.87 (d of d, 3H, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 3.2 Hz, PH*Me*), 0.85 (d of d, 3H, $^2J_{HP}$ = 3.2 Hz, $^3J_{HH}$ = 7.3 Hz, PH*Me*), 0.20−0.24 (compl mult, 6H, Me_2Si). IR (gaseous, cm^{-1}): 2969(s), 2926(s), 2283(vs, PH), 1429(w), 1253(s), 988(s), 816(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 152 [$^{12}C_4H_{14}P_2Si^+$]. Anal (EI$^+$, exact mass MS). Calcd for $C_4H_{14}P_2Si$: 152.0340. Found: 152.0357.

$Me_2Si[(H)P(CH_2)_3P(H)]$ (22). THF (2.0 mL) and monoglyme (2.0 mL) in a 10-mL reaction flask were triply freeze−thaw−degassed. $Me_2Si(PH_2)_2$ (17 × 2 Torr, 920 mL, 22 °C; 1.7 mmol) was condensed in, and the flask was warmed to −95 °C and stirred. *n*-BuLi (2.1 mL, 3.4 mmol) was slowly syringed in, and the mixture was stirred for 5 min. To the resulting yellow solution, $Br(CH_2)_3Br$ (0.18 mL, 1.8 mmol) was slowly added, and the mixture was warmed to 25 °C. Column distillation of volatile materials yielded **22** (yield, 40%). ^{31}P{^{1}H} NMR (C_6D_6): δ −155.6 (s), −136.6 (s). ^{31}P NMR (C_6D_6): δ −155.6 (d, $^1J_{PH}$ = 184 Hz), −136.5 (d, $^1J_{PH}$ = 191 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 32.7 (t, 1C, $^2J_{CP}$ = 4.4 Hz), 29.3 (s, 1C), 15.4 (d, 2C, $^1J_{CP}$ = 16.5 Hz), 14.8 (d, 2C, $^1J_{CP}$ = 14.3 Hz), −0.4 (compl mult, 3C), −1.5 (t, 1C, $^2J_{CP}$ = 20.3 Hz). ^{1}H NMR (C_6D_6): δ 2.3 (d of mult, 4H, $^1J_{HP}$ = 190 Hz), 1.0−1.8 (compl mult, 8H), 0.88 (t, 4H, *J* = 7.3 Hz), 0.28−0.35 (compl mult, 9H, Me_2Si), 0.21 (t, 3H, $^3J_{HP}$ = 4.1 Hz). IR (gaseous, cm^{-1}): 2964(m), 2922(vs), 2854(m), 2278(vs, PH), 1430(w), 1253(s), 1012(w), 840(vs), 804(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 164 [$^{12}C_5H_{14}P_2Si^+$]. Anal (EI$^+$, exact mass MS). Calcd for $C_5H_{14}P_2Si$: 164.0340. Found: 164.0325. Compound **22** reacted with an excess of MeOH to form the previously reported $H_2P(CH_2)_3PH_2$[15] quantitatively.

Cyclization of 17 and 18. $Me_3SiP(CH_2)_4$ (14a) and $HP(CH_2)_4$ (14b). Compound **18** (16.5 mg, 0.10 mmol), AIBN (5 mg, 0.03 mmol), and benzene-*d*$_6$ (0.55 mL) in a sealed NMR tube were heated at 75 °C for 3 h (conversion, 80%; yield of **14a**, 85%). Repeated fractional condensation into a −45 °C trap yielded **14a**. ^{31}P NMR (C_6D_6): δ −101.3 (s). ^{13}C NMR (C_6D_6): δ 30.4 (d, 2C, $^2J_{CP}$ = 2.7 Hz; CH_2), 19.5 (d, 2C, $^1J_{CP}$ = 14.3 Hz; CH_2), −1.8 (d, 3C, $^2J_{CP}$ = 11.5 Hz; $SiMe_3$). ^{1}H NMR (C_6D_6): δ 1.6 (compl mult, 8H; CH_2), 0.08 (d, 9H, $^3J_{HP}$ = 4.1 Hz; $SiMe_3$). IR (GC, gas; cm^{-1}): 2950(vs), 2869(w), 1442(w), 1253(s), 840(vs). MS (GC, EI$^+$; M$^+$, *m/e*): 160 [$^{12}C_7H_{17}PSi^+$). Anal (EI$^+$, exact mass MS). Calcd for $C_7H_{17}PSi$: 160.0837. Found: 160.0836. Reaction of **14a** with excess MeOH yielded phospholane $HP(CH_2)_4$ (**14b**) quantitatively.[2,16]

Compound **17** (0.1 mmol) with AIBN (4 mg, 0.02 mmol) in benzene was sealed in an NMR tube and heated to 75 °C for 4 h. The solution turned bright yellow. The ^{31}P NMR spectra showed decomposition to mainly $(Me_3Si)_2PH$;[17,18] product was identified as $(CH_2{=}CHCH_2)_2PH$ and several undetermined species. No resonance was exhibited clearly attributable to the phosphetane (**13a**, R = Me_3Si).

Results and Discussion

Silylphosphines Me_3SiPH_2 and $Me_2Si(PH_2)_2$ react readily with *n*-BuLi at −78 °C to form silylphosphides, which subsequently react with alkyl and alkenyl halides, as shown in Schemes 1 and 2. The *n*-BuLi reaction with Me_3SiPH_2 yields the monolithiophosphide. However, with $Me_2Si(PH_2)_2$ the reaction yields both mono- and bislithio products, even when using only 1 equiv of the butyl lithium reagent. Apparently, deprotonation of $Me_2Si(PH_2)_2$ and $Me_2Si(PH_2)(PHLi)$ occur at comparable rates, indicating that the electronic effect of deprotonating the first PH_2 group is not strongly transmitted to the second.

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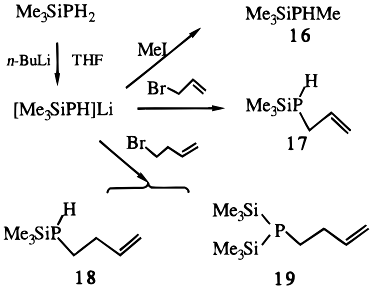
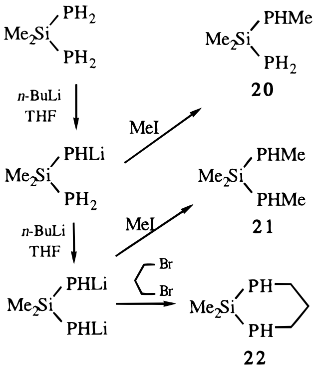
Scheme 1



Scheme 2



Reactions of the lithiosilylphosphides with MeI yield the known methylated derivative **16**[11] and the bisphosphines **20** and **21**. These reactions also produced small quantities of Me_2PH and $MePH_2$, perhaps the result of alkyl(silyl)phosphine redistribution, e.g., for **16** according to eq 3. Similar redistributions

$$2Me_3SiPHMe \rightarrow (Me_3Si)_2PH + Me_2PH \qquad (3)$$

of unsymmetrically substituted alkylphosphines such as $MeP(H)CH_2CH{=}CH_2$ have been previously established.[19] Similarly, $[Me_3SiPH]Li$ reacts with $CH_2{=}CHCH_2Br$ and $CH_2{=}CHCH_2CH_2Br$ to form the alkenyl(silyl)phosphines **17**[12] and the new **18**, respectively. Formation of **18** is also accompanied by significant amounts of **19**, likely to be the result of redistribution of **18** in the reaction medium. Reaction of 1,3-dibromopropane with $Me_2Si(PHLi)_2$, prepared by reaction of $Me_2Si(PH_2)_2$ with greater than 2 equiv of *n*-BuLi, occurs cleanly to form **22**. Only small amounts of products were attributable to $Me_2Si(PH_2)(PHLi)$/1,3-dibromopropane reaction or reaction of $Me_2Si(PHLi)_2$ with more than 1 equiv of 1,3-dibromopropane. These minor products were not characterized.

The methylated silylphosphine **16**[11,20] has been prepared previously from KPHMe or $LiAl(PHMe)_4$ reactions with trimethylsilyl halides, although, from the $LiAl(PHMe)_4/Me_3SiCl$ reaction, **16** underwent rapid redistribution to $(Me_3Si)_2PH$ and $MePH_2$. Small quantitities of $MePH_2$ also are obtained from our $[Me_3SiPH]Li$/MeI reaction; however, the product once purified is thermally stable. Compound **21** is claimed from the $Me_2SiCl_2/(MePH)Li$ reaction, but only as an intermediate to the observed trimer $(Me_2SiPMe)_3$.[21] In our system, similar high thermal instability of **21** was not observed. Phosphorus-substituted derivatives of **22** have been reported.[22] However, little of their chemistry is known.

Characterization of the new organo(silyl)phosphines **18**−**22** was readily accomplished by spectral techiniques (^{31}P, ^{1}H, ^{13}C NMR, IR, and MS). Also, ^{1}H NMR spectral data for **16** were remeasured, since we found the reported chemical shift data[11] to be in error. All compounds exhibit unambiguous mass spectral parent ions (M^{+}). Compounds **16**−**18** and **20**−**22** display characteristic IR P−H stretching absorptions[23] at 2278−2290 cm^{-1} and ^{31}P NMR spectral P−H doublets ($^{1}J = 184-190$ Hz) in the δ −154 to −175 region;[14] in addition **20** shows a clear PH_2 group triplet ($^{1}J = 184$ Hz) at δ −238.8. ^{1}H NMR spectra are as expected; the Me_3Si and Me_2Si group protons for the series and the Me group protons of **16**, **20**, and **21** correlate well with those for known methylphosphines and silylphosphines.[17,21,24,25] The resonance patterns for the allyl, propenyl, and trimethylene groups of **17**−**19** and **22**, respectively, are closely similar to those seen in $CH_2{=}CHCH_2PH_2$,[13] $CH_2{=}CHCH_2CH_2PH_2$,[13] and 1,3-$(PH_2)_2C_3H_6$ (**15**).[15]

Alkenyl(silyl)phosphines **17** and **18** were heated in toluene in the presence of a radical initiator, under conditions previously established for radical addition of phosphine P−H bonds to alkenes.[2,3,26,27] After heating **17** in the presence of AIBN for 4 h, no ^{31}P NMR resonances were observed attributable to the phosphetane **13a**. Only peaks due to $(Me_3Si)_2PH$,[17] $(CH_2{=}CHCH_2)_2PH$ and minor uncharacterized species appear. The observed products might result from redistribution, a reaction that becomes competitive in cases where the silylphosphinyl radical does not react readily with the alkene.[2] In contrast, **18** when heated at 75 °C for 3 h in the presence of AIBN yields the silylphospholane $Me_3SiP(CH_2)_4$ (**14a**, X = Me_3Si) in greater than 85% yield. Similar radical intramolecular ring closures to five- and six-membered P-alkyl and P-aryl substituted rings are known;[27,28] perhaps they occur readily, whereas cyclization of **17** does not because of the greater strain associated with the four-membered ring.[29,30]

The organo(silyl)phosphines **16** and **17** and the new **14a** and **18**−**22** are potentially valuable synthons because they contain the readily cleaved $P{-}SiMe_3$ bond.[2,5] Reaction of $CH_2{=}CHCH_2PH_2$ with Me_3SiI in the presence of Et_3N was reported earlier to yield **17**;[12] however, the reaction is less efficient than our new silylphosphide reagent route. Moreover, the silylphosphines are quantitatively converted to the parent organophosphines by reaction with MeOH or H_2O. Solvolysis of **16**, **20**, and **21** yields $MePH_2$ (or $MePH_2$ and PH_3). Compounds **17**−**19** yield the known alkenylphosphines $CH_2{=}CHCH_2PH_2$[13] and

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$CH_2{=}CHCH_2CH_2PH_2$.[13] Most significantly, solvolysis of **22** or **14a** readily yields the 1,3-diphosphinopropane (**15**)[15] and the parent phospholane $(CH_2)_4PH$ (**14b**),[16] both ligands that are not otherwise readily available. Compound **15** has been prepared by reactions of the PH_2^- ion with 1,3-dibromopropane,[15] and phospholane **14b** has been prepared by thermolysis of the adduct $(CH_2)_4P(NMe_2)_2(BH_3)$;[16] however, these reactions are lower-yielding, making our current method based on silylphosphine precusors preferable.

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