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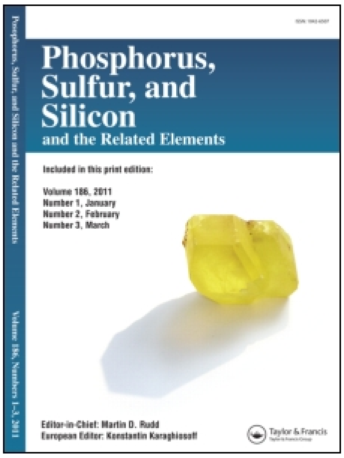

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SILYLPHOSPHINE - ALKENE REACTION ROUTES TO ACYCLIC AND CYCLIC ORGANOPHOSPHINES

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SILYLPHOSPHINE - ALKENE REACTION ROUTES TO ACYCLIC AND CYCLIC ORGANOPHOSPHINES*

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Radical reactions of Me_3SiPH_2, $(Me_3Si)_2PH$, $Me_2Si(PH_2)_2$ and PH_3 with selected alkenes have been examined as routes to new organo(silyl)phosphines. The Me_3SiPH_2/1,5-hexadiene reaction initiated by AIBN yields the phosphepane $Me_3SiP(CH_2)_6$ (**11a**) and acyclic $Me_3SiP[(CH_2)_4CH{=}CH_2]_2$ (**12**); the Me_3SiPH_2/1,3-butadiene reaction yields only acyclic butenyl phosphines $Me_3SiP(H)C_4H_7$ (**14A – C**) and $Me_3SiP(C_4H_7)_2$ (**15A – D**). Reactions of Me_3SiPH_2 with $P(CH{=}CH_2)_3$ and $MeSi(CH{=}CH_2)_3$ yield the vinyl-substituted *cis-* and *trans*-phosphorinanes $(CH_2{=}CH)P(C_2H_4)_2PSiMe_3$ (**18A/18B**) and $Me(CH_2{=}CH)Si(C_2H_4)_2PSiMe_3$ (**20A/20B**). $(Me_3Si)_2PH/Me_2Si(CH{=}CH_2)_2$ reaction produces only the acyclic $(CH_2{=}CH)Me_2SiC_2H_4P(SiMe_3)_2$ (**22**) and $Me_2Si[C_2H_4P(SiMe_3)_2]_2$ (**25**). The $Me_2Si(PH_2)_2$/1,4-pentadiene reaction yields phosphorinanyl derivatives $Me_2Si(PH_2)[P(CH_2)_5]$ (**27**) and $Me_2Si[P(CH_2)_5]_2$ (**28**); no large-ring products form. The AIBN initiated reaction of $CH_2{=}CHCH_2PH_2$ has been reinvestigated; the known bicyclic $[(CH_2)_3]_2P_2$ is obtained instead of the previously reported tricyclic $[(CH_2)_3]_3P_2$. The $PH_3/Me_2Si(CH{=}CH_2)_2$reaction yields mixtures of tentatively characterized $Me_2Si(C_2H_4)_2PC_2H_4SiMe_2(CH{=}CH_2)$ (**29**) and $[Me_2Si(C_2H_4)_2PC_2H_4]_2SiMe_2$ (**30**). Solvolysis (with MeOH or H_2O) of silylphosphines **11a**, **27** (or **28**), **12**, **14A–C, 15A–D, 18A/18B**, **20A/20B**, **22** and **25** yields phosphorinanes $(CH_2)_5PH$ (**7**) and $Me_2Si(C_2H_4)_2PH$ (**9**), the new phosphepane $(CH_2)_6PH$ (**11b**), $HP[(CH_2)_4CH{=}CH_2]_2$ (**13**), $H_2PC_4H_7$ (**16A–C**), $HP(C_4H_7)_2$ (**17A–D**), the *cis-* and *trans*-$(CH_2{=}CH)P(C_2H_4)_2PH$ (**19A/19B**) and $Me(CH_2{=}CH)Si(C_2H_4)_2PH$ (**21A/21B**), $(CH_2{=}CH)Me_2SiC_2H_4P(H)SiMe_3$ (**23**), $(CH_2{=}CH)Me_2SiC_2H_4PH_2$ (**24**) and $Me_2Si(C_2H_4PH_2)_2$ (**26**). Attempts to obtain new tricyclic or large-ring cyclic phosphines by radical ring closure of **19A/19B** and **21A/21B** or cyclooligomerization of **23** or **24** were unsuccessful. New compounds are characterized by spectral (^1H, ^{13}C, and ^{31}P NMR, MS and IR) data.

Keywords: phosphines; silylphosphines; phosphorinanes; phosphepane; phosphination

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* Dedicated to Professor Robert Wolf on the occasion of his 70th birthday.

† Corresponding author.

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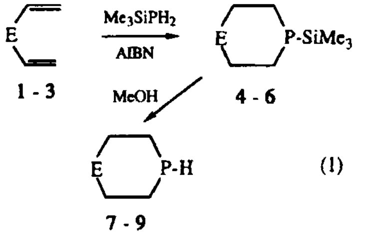
INTRODUCTION

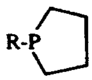
Trimethylsilylphosphine (Me_3SiPH_2) and $(Me_3Si)_2PH$ undergo radical reactions with olefins to produce a variety of new silyl-substituted cyclic and acyclic organophosphines.[2-4] Upon hydrolysis or alcoholysis, these readily undergo silicon-phosphorus bond cleavage and conversion to the parent primary and secondary organophosphines. Reactions in many cases are high yielding, making them useful synthetic routes to new compound classes. This is especially true for six-membered ring cyclic phosphines, where not only the parent phosphorinane (**4**, **7**) but also 4-phospha- (eg. **5**, **8**) and 4-sila- (eg. **6**, **9**) phosphorinanes can be prepared in good yields.[4,5]



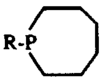
(1)

1, 4, 7; E = CH_2; 2, 5, 8; E = PPh;
3, 6, 9; E = $SiMe_2$

Given that silylphosphine/alkene reactions are highly effective for phosphorinane synthesis, it becomes a question of what other cyclic phosphines might be obtained from silylphosphine/alkene reactions. To this end, we have conducted a study of reactions between Me_3SiPH_2, $(Me_3Si)_2PH$ and $Me_2Si(PH_2)_2$ and selected alkenes, which have the potential to yield phosphorus-containing five- (**10**), seven- (**11**) and larger, eg. eight- or twelve-membered rings, or tricyclic molecules. The results of this study are described below.



10a, **10b**



11a, **11b**

(a = Me_3Si, b = H)

EXPERIMENTAL SECTION

Materials and Apparatus

Trimethylsilylphosphine (Me_3SiPH_2),[6,7] $(Me_3Si)_2PH$[6,7] $Me_2Si(PH_2)_2$,[7] $CH_2{=}CHCH_2PH_2$[8] and $Me_2Si(C_2H_4)_2PH$ (**9**)[5] were prepared as described previously. $PhP(CH{=}CH_2)_2$(Strem Chemicals) and 1,5-hexadiene (Aldrich Chem. Co.) were placed over activated Linde 4Å molecular sieves *in vacuo* before use. 1,3-Butadiene (Matheson Gases, Inc.), AIBN [2,2'-bis(isobutyronitrile)] (Aldrich Chem. Co.), $Me_2Si(CH{=}CH_2)_2$ (Petrarch Systems), $(CH_2{=}CH)_3P$ (Alfa Inorganics), $(CH_2{=}CHCH_2)_3P$ (Alfa Inorganics), $MeSi(CH_2CH{=}CH_2)_3$ (Petrarch Systems), $MeSi(CH{=}CH_2)_3$ (Petrarch Systems), PH_3 (Scientific Gas Products) and MeOH were used as obtained. Benzene and toluene were distilled from Na-Pb alloy and stored *in vacuo* over activated 4Å molecular sieves.

Infrared spectra were obtained on Perkin-Elmer Model 467 or Beckman IR 4250 spectrometers. Mass spectra (EI^+) were measured on a Varian MAT CH5 spectrometer. ^{31}P NMR spectra were obtained at 40.5 MHz 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 MHz and 250 MHz using Varian EM-390 and Bruker WN-250 spectrometers, respectively. ^{13}C NMR spectra were obtained at 25.1 MHz and 62.90 MHz using JEOL PFT-100 and Bruker WM-250 spectrometers. Chemical shifts (in ppm) downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and 85 % H_3PO_4 for ^{31}P NMR spectra are assigned positive ($+\delta$) values. Elemental analyses were conducted by Huffman Laboratories, Inc., Wheatridge, Colorado.

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General Procedures

All manipulations were made in standard high-vacuum systems or inert atmosphere apparatus.[9] Reactions of Me_3SiPH_2, $(Me_3Si)_2PH$, or $Me_2Si(PH_2)_2$ with olefins were carried out by condensing volatile reagents and solvent into the reaction vessel containing degassed AIBN. Nonvolatile reagents, 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 the reaction temperature. In some cases reaction progress was followed by ^{1}H and/or ^{31}P NMR spectroscopy. Here, the same procedure was employed using sealed 5 mm or 10 mm NMR tubes. Organo(silyl)phosphines were converted to parent organophosphines by their reaction with deareated MeOH or H_2O in an inert atmosphere.

The organo(silyl)- and organo-phosphines prepared in this study are malodorous, likely highly toxic and sometimes spontaneously flammable. Great care should be exercised in their handling.

Me_3SiPH_2 Reaction

(A) With 1,5-Hexadiene. $Me_3SiP(CH_2)_6$ (11a), $Me_3SiP[(CH_2)_4CH=CH_2]_2$ (12), $HP(CH_2)_6$ (11b), and $HP[(CH_2)_4CH=CH_2]_2$ (13).

Me_3SiPH_2 (0.16 g, 1.5 mmol), 1,5-hexadiene (0.12 g, 1.4 mmol), toluene (0.6 mL) and AIBN (10 mg, 0.06 mmol) were heated at 85 °C for 6 h (Me_3SiPH_2 conversion, 71 %; **11a** and **12** yields, 46 % and 42 %). The mixture was separated by fractional condensation through traps at 0 °C and –23 °C. **11a** (0.75 mmol) condensed at –23 °C; **12** (ca. 0.2 mmol) remained in the reaction vessel as a nonvolatile, colorless oil. **11a**: ^{31}P NMR (toluene-d_8): δ –105.8 (s). ^1H NMR (toluene-d_8):δ 0.2 (d, 9H, J_{PH} = 4.5 Hz; $SiMe_3$), 1.1–1.9 (compl. mult., 12H; CH_2). ^{13}C NMR (benzene-d_6): δ –2.0 (d, 3C, J = 11.5 Hz; $SiMe_3$), 20.1 (d, 2C, J = 22.0 Hz; CH_2), 28.8 (d, 2C, J = 3.5 Hz; CH_2), 30.4 (d, 2C, J = 4.2 Hz; CH_2). MS (EI^+), m/e: 188 ($^{12}C_9H_{21}SiP^+$, M^+). **12**: ^{31}P NMR (toluene-d_8): δ –101.8 (s). ^1H NMR (toluene-d_8): δ 0.2 (d, 9H, J_{PH} = 4.5 Hz; $SiMe_3$), 1.0 – 2.3 (compl. mult., 16H; CH_2), 4.8 – 6.0 (ABX mult.,[10] 6H; olefinic H). MS (EI^+), m/e: 270 ($^{12}C_{15}H_{31}{}^{28}SiP^+$, M^+). **12** could not be freed of traces (< 5%) of non-volatile products.

The **11a** hydrolysate was separated by repeated passage through –23 °C and –45 °C traps. **11b** condensed at –45 °C. ^{31}P NMR (toluene-d_8): δ –65.5 (d, $^1J_{PH}$ = 190 Hz). ^1H NMR (benzene-d_6): δ 1.35 – 1.65 (compl. mult., 12H; CH_2), 3.24 (d of mult., 1H, $^1J_{PH}$ = 190 Hz, $^3J_{PH}$ – 3.5 Hz; PH). $^{13}C\{^1H\}$ NMR (toluene-d_8); δ 21.2 (d, 2C, J_{PC} = 19.0 Hz), 29.0 (d, 2C, J_{PC} = 2.0 Hz), 29.3 (d, 2C, J_{PC} = 3.0 Hz). IR (gas, cm^{-1}): 2997 (vs), 2981(s), 2324 (vs, ν_{PH}), 1476 (m), 1323 (m), 1298 (m), 1046 (m), 953 (m), 858 (m), 794 (w), 758 (w), 681 (w). MS (EI^+), m/e: 116 [$^{12}C_6H_{13}P^+$, M^+].

Volatile materials were removed from the **12** hydrolysis mixture *in vacuo*, leaving **13** as a nonvolatile colorless oil. ^{31}P NMR (toluene-d_8) : δ –69.7 (d, J_{PH} = 191 Hz). ^1H NMR (toluene-d_8) δ 1.0 – 2.3 (compl. mult., 16H; alkyl H), 3.1 (d of mult., 1H, J_{PH} = 191 Hz; PH), 4.8 – 6.0 (ABX mult.,[10] 6H; olefinic H). IR (thin film, cm^{-1}): 3078 (m), 2929 (vs), 2858 (vs), 2280 (s, ν_{PH}), 1641 (s), 1455 (s), 1415 (m), 1175 (s), 992 (m), 991 (m), 802 (w), 778 (w), 723 (2). MS, m/e: 198 [$^{12}C_{12}H_{23}P^+$, M^+]. *Anal.* Calcd. for $C_{12}H_{23}P$: C, 72.68; H, 11.69. Found: C, 73.22; H, 11.38.

(B) With 1,3-Butadiene. $Me_3SiP(H)C_4H_7$ (14), $Me_3SiP(C_4H_7)_2$ (15), $H_2PC_4H_7$ (16), and $HP(C_4H_7)_2$ (17).

Me_3SiPH_2 (0.34 g, 3.2 mmol), butadiene (0.54 g, 10.0 mmol), benzene (1 mL) and AIBN (15 mg, 0.09 mmol) were heated at 85 °C for 16 h (Me_3SiPH_2 conversion, 60 %; **14** and **15** yields, 36 and 64 %). The reaction mixture was fraction-

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ally distilled through 0 °C and –23 °C traps; **14** (0.33 mmol) condensed at –23 °C and **15** (ca. 0.6 mmol) remained in the reaction vessel. **14**: ^{31}P NMR (benzene-d_6): δ –147.4 (d, J_{PH} = 188.0 Hz) [**14A**], –148.3 (d, J_{PH} = 188.0 Hz) [**14B**], –150.5 (d, J_{PH} = 188 Hz) [**14C**]; **14A:14B:14C** mole ratio ≅ 4:1.5:1. ^1H NMR (benzene-d_6): δ 0.1-0.3 (compl. group of d, 9H, J_{PH} = ca. 5 Hz; $SiMe_3$), 1.4 – 2.5 (compl. mult., ca. 4.5H; CH_2), 5.3 – 5.6 (superposition of AB and ABX mult.,[10]ca. 2.5H; olefinic H). MS (EI^+), m/e: 161 [$C_7H_{17}PSi^+$, M^+]. **15**: ^{31}P NMR (benzene-d_6): δ-94.1 (s) [**15A**], –96.3 (s) [**15B**], –97.7 (s) [**15C**], –97.9 [**15D**]; **15A:15B:15C:15D** mole ratio = 6:10:1:3. ^1H NMR (benzene-d_6): δ 0.1-0.3 (compl. group of d, 9H, J_{PH} = 4.5; $SiMe_3$), 1.4 – 2.5 (compl. mult., 8H), 5.3 – 5.6 (superposition of AB and ABX mult.,[10] ca. 5H).

The **14** hydrolysate was fractionally condensed through –23 °C and –78 °C traps. **16** condensed at –78 °C. ^{31}P NMR (benzene-d_6): δ –132.8 (t, J_{PH} = 190 Hz; **16A**), –135.0 (t, J_{PH} = 190 Hz; **16B**), –140.0 (t, J_{PH} = –190 Hz; **16C**); **16A:16B:16C** ratio = 4:1.5:1. ^1H NMR (benzene-d_6): δ 1.1 – 2.2 (compl. mult., ca. 4.5H; alkyl H), 2.4 – 2.9 (compl. mult., 2H; PH_2), 4.8 – 5.7 (superposition of AB and ABX[10]; m, ca. 2.5H). MS (EI^+), m/e: 88 [$C_4H_9P^+$, M^+].

The **15** hydrolysate was repeatedly fractionated through 0 °C and –23 °C traps. **17** collected at –23°C. ^{31}P NMR (benzene-d_6); δ –66.7 (d, J_{PH} = 190 Hz; **17A**), – 67.2 (d, J_{PH} = 190 Hz; **17**), – 68.9 (d, J_{PH} = 190 Hz; **17C**), – 69.4 (d, J_{PH} = 190 Hz; **17D**); **17A:17B:17C:17D** ratio = 6:10:1:3. ^1H NMR (benzene-d_6): δ 1.1 – 2.2 (compl. mult., 9H), 2.4 – 2.9 (compl. mult., 1H), 4.5 – 5.7 (superposition of AB and ABX mult.;[10] 5H). MS (EI^+), m/e: 142 [$C_8H_{15}P^+$, M^+]. Since **16** and **17** were isomer mixtures, no IR and ^{13}C NMR data were obtained.

(C) With $(CH_2{=}CH)_3P$. $(CH_2{=}CH)P(C_2H_4)_2PSiMe_3$ (18A/18B) and $(CH_2{=}CH)P(C_2H_4)_2PH$ (19A/19B).

Me_3SiPH_2 (0.16 g, 1.5 mmol), $(CH_2{=}CH)_3P$ (0.17 g, 1.5 mmol) and AIBN (10 mg, 0.06 mmol) in an NMR tube in toluene (6 mmol) were heated at 85 °C. After 3 h, the reaction mixture exhibited, besides the singlet from unreacted Me_3SiPH_2 (20 %), resonance pairs at δ –102.2 [s, 1P; $PSiMe_3$] and –31.2 (s, 1P; $PCH{=}CH_2$) (**18A**; 30 %) and –99.0 (d, 1P, J = 18.3 Hz; $PSiMe_3$] and –32.9 (d, 1P; $PCH{=}CH_2$) (**18B**, 45 %) and several unassigned singlets (< 5 %). **18A/18B** were too non-volatile to be removed from the tube in vacuo and further purified.

The **18A/18B** mixture was allowed to react with H_2O, after which volatile materials could be removed and separated by fractional condensation through a –23 °C trap into a –196 °C trap. PH_3, $(CH_2{=}CH)_3P$, and $(Me_3Si)_2O$ condensed at –196 °C. The –23°C liquid condensate contained **19** and it exhibited major (>90 area %) ^{31}P NMR resonances (benzene-d_6) at δ –34.7 (d, 1P, $^3J_{PP}$ = 7.6 Hz; $CH_2CH\underline{P}$) and – 62.6 (d, 1P, $^3J_{PP}$ = 7.6 Hz, $\underline{P}H$; $^1J_{PH}$= 196.8 Hz in ^1H coupled

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spectrum) (**19A**) and –37.4 (d, 1P, Jpp = 3.1 Hz, $CH_2CH\underline{P}$) and – 60.3 (d, 1P, $^3J_{PP}$ = 3.1 Hz, $\underline{P}H$; $^1J_{PH}$ = 192.3 Hz in ^1H coupled spectrum) (**19B**) (**19A/19B** = 1.5:1) along with minor approximately equal-area (< 10 %) singlets at δ 5.9 and –18.6. MS (EI^+), m/e, M^+: 146 [$^{12}C_6H_{12}P_2$+]. **19A** and **19B** could not be separated from each other or even completely from the singlet δ 5.9 and –18.6 compounds, hence unambiguous IR and ^1H NMR data were precluded.

(D) With $MeSi(CH{=}CH_2)_3$. $Me(CH_2{=}CH)Si(C_2H_4)_2PSiMe_3$ (20A/20B) and $Me(CH_2{=}CH)Si(C_2H_4)_2PH$ (21A/21B).

Me_3SiPH_2 (0.16 g, 1.5 mmol), $MeSi(CH{=}CH_2)_3$ (0.20 g, 1.6 mmol), and AIBN (10 mg, 0.06 mmol) in benzene-d_6 (0.5 mL) were heated at 85° C for 6.8 h (Me_3SiPH_2 conversion, 75 %). ^{31}P NMR analysis of the volatile reaction products showed major resonances (70 %) due to **20A/20B** and minor resonances at δ – 69.8, –70.0, –140.0 and –237.1 [$(Me_3Si)_2PH$].[11] Volatile materials were fractionally distilled through traps at –23 °C and –196 °C; the **20A/20B** mixture condensed at – 23 °C. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –95.0 (s) (**20A**) and –95.4 (s) (**20B**); **20A:20B** mole ratio = 1:1. ^1H NMR (benzene-d_6): δ 0.01 (s, 3H; $SiCH_3$), 0.10 [d, J_{PH} = 3.9 Hz, 9H; $PSi(CH_3)_3$], 1.05 (comp. mult., 4H, ring CH_2), 1.70 (compl. mult., 4H; CH_2), and 5.85 (compl. mult., 3H; $SiCHCH_2$). IR (thin film, cm^{-1}): 3050 (w), 2948 (s), 2902 (s), 2868 (s), 1402 (m), 1248 (vs), 1085 (w), 1008 (m), 952 (m), 889 (w), 840 (vs), 798 (vs), 726 (m), 625 (m), 523 (w), 397 (m). MS (EI^+), m/e: 230 [$^{12}C_{10}H_{23}P^{28}Si_2$+, M^+]. *Anal.* Calcd. for $C_{10}H_{23}PSi_2$: C, 52.12; H, 10.06; P, 13.44. Found: C, 51.47; H, 9.83; P, 13.35.

MeOH solvolysis of **20A/20B** mixture followed by molecular distillation into a –23° C trap, yielded isomer mixture **21A/21B**; **21A:21B** mole ratio = 1:1. ^{31}P NMR (benzene-d_6): δ –53.3 (J_{PH} = 192.3 Hz; PH) (**21A**) and –54.1 (d, J_{PH} = 192.3 Hz; PH) (**21B**). ^1H NMR (C_6D_6): δ –0.5 (s, 3H; $SiCH_3$), 0.3 (s, 3H; $SiCH_3$), 0.8 (compl. mult., 8H; CH_2), 1.4 (compl. mult., 9H; CH_2 and upfield PH), 3.8 (t, J_{aa} = 10.0 Hz, J_{ae} = 2.0 Hz, 0.5H, 1/2 PH), 4.2 (t of t, J_{aa} = 10.0 Hz, J_{ae} = 2.0 Hz, 0.5H; 1/2 PH), 6.0 (compl. mult., 6H; $SiCHCH_2$). MS (EI^+), m/e: 158 [$^{12}C_7H_{15}P^{28}Si^+$, M^+].

(E) $Me_2Si(CH_2CH{=}CH_2)_2$ or $(CH_2{=}CHCH_2)_3P$.

$Me_2Si(CH_2CH{=}CH_2)_2$ (0.22 g, 1.6 mmol) or $(CH_2{=}CHCH_2)_3P$ (0.20 g, 1.3 mmol) with Me_3SiPH_2 (0.17 g, 1.6 mmol) and AIBN (5 mg, 0.03 mmol) in benzene-d_6 (0.6 mL) were heated at 80 – 85 °C.° After 2 h, ^{31}P NMR spectral analysis showed no reaction.

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$(Me_3Si)_2PH$ Reaction

(A) With $Me_2Si(CH{=}CH_2)_2$ (1:3 Ratio). $(CH_2{=}CH)Me_2SiC_2H_4P(SiMe_3)_2$ (22), $(CH_2{=}CH)Me_2SiC_2H_4P(H)SiMe_3$ (23) and $(CH_2{=}CH)Me_2SiC_2H_4PH_2$ (24).

$(Me_3Si)_2PH$ (0.41 g, 2.0 mmol), AIBN (39 mg, 0.24 mmol), benzene (1 mL) and a stirbar were triply freeze-thaw degassed. $Me_2Si(CH{=}CH_2)_2$ (0.55 mL, 6.0 mmol) was condensed in and the solution was heated to 75 °C for 3.5 h [$(Me_3Si)_2PH$ conversion, 30 %; **22** yield, 95 %]. Volatile materials were fractionally condensed through traps at 0 °C and –78 °C; **22** condensed at 0 °C. ^{31}P NMR (benzene-d_6): δ –163.4 (s). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 138.7 (s, 1C; $\underline{C}HCH_2$), 132.1 (s, 1C; $CH\underline{C}H_2$), 18.9 (d, 1C, J_{CP} = 11.0 Hz; CH_2), 9.4 (d, 1C, J_{CP} = 17.1 Hz; CH_2), 1.3 (d, 3C, J_{CP}= 12.2 Hz; $SiMe_3$), –3.4 (s, 2C, $SiMe_2$). ^1H NMR (C_6D_6): δ 5.8 (compl. mult., 3H; $CHCH_2$), 1.6 – 1.9 (broad unresolved mult,. 2H; PCH_2), 0.7 – 1.1 (broad unresolved mult., 2H; $SiCH_2$), 0.25 [d, $^3J_{HP}$ = 4.1 Hz, 18H; $P(SiMe_3)_2$], 0.09 (s, 6H; Me_2Si). IR (thin film, cm^{-1}): 3050(s), 2959(vs), 2902(vs), 1407(s), 1253(vs), 1158(s), 1011(s), 952(s), 845(vs), 762(m), 692(s), 668(s), 624(vs), 474(vs). MS (EI^+), M^+, m/e: 290 [$^{12}C_{12}H_{31}PSi_3$+]. *Anal.* Calcd. for $C_{12}H_{31}PSi_3$: 290.1471. Found (EI^+), exact mass MS: 290.1458.

Reaction of **22** with one equivalent of MeOH, followed by passage of volatile materials through –23 and –45 °C traps, yielded **23** (along with minor amounts of **24** from which it could not be separated) at –23 °C. ^{31}P NMR (benzene-d_6): δ –140.1 (d, J_{PH} = 191 Hz). Because **23** was not obtained pure, satisfactory ^1H NMR data were not obtained. IR and MS (EI^+) data for **23** were obtained using gas chromatography/coupled IR and MS spectral apparatus. IR (gas, cm^{-1}): 3056 (m), 2962 (vs), 2905 (m), 2275 (s, ν_{PH}), 1408 (m), 1255 (vs), 1009 (m), 953 (m), 840 (vs); MS, M^+, m/e: 218 [$^{12}C_9H_{23}PSi_2{}^+$].

Reaction of **22** with excess MeOH, followed by removal of excess MeOH and $MeOSiMe_3$, left **24** as a colorless oil. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –122.8 (s). ^{31}P NMR (benzene-d_6): δ –122.8 (t of t of t, $^1J_{PH}$ = 188 Hz, $^2J_{PH}$ = 7 Hz, $^3J_{PH}$ = 4 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 138.4 (s, 1C, $\underline{C}HCH_2$), 132.1 (s, 1C, $CH\underline{C}H_2$), 19.2 (d, 1C, J_{CP} = 3.66 Hz; CH_2), 8.2 (d, 1C, J_{CP} = 8.55 Hz; CH_2), –3.7(s, 2C, $SiMe_2$). ^1H NMR (benzene-d_6): δ 5.8 (compl. mult., 2H; $CHCH_2$), 2.77 (d of t, 2H, $^1J_{HP}$ = 190 Hz, $^2J_{PH}$ = 6.8 Hz; PH_2), 1.3 – 2.5 (unresolved broad mult., 4H; CH_2CH_2), –0.04 (s, 6H; Me_2Si). IR (thin film, cm^{-1}): 3057(s), 2963(vs), 2910(s), 2294(vs, ν_{PH}), 1409(s), 1259(s), 1163(s), 1086(s), 1011(s), 955(s), 829(vs). MS (EI^+), M^+, m/e: 146 [$^{12}C_6H_{15}PSi^+$]. *Anal.* Calcd. for $C_6H_{15}PSi$: 146.0681. Found (EI^+, exact mass MS): 146.0696.

(F) With $Me_2Si(CH{=}CH_2)_2$ (3:1). $Me_2Si[C_2H_4P(SiMe_3)_2]_2$ (25) and $Me_2Si(C_2H_4PH_2)_2$ (26).

$(Me_3Si)_2PH$ (1.2 mL, 6 mmol), AIBN (39 mg, 0.24 mmol), benzene (1 mL) and $Me_2Si(CH{=}CH_2)_2$ (0.17 g, 2.0 mmol) were heated to 80 °C. After 4 h, ^{31}P NMR spectra of reaction mixtures showed **22** and **25**, respectively [70 % and 30 % yields, $(Me_3Si)_2PH$ conversion = 70 %]. Further additions of AIBN and heating for 4 h gave increased yields of both products. Volatiles at 25 °C were removed *in vacuo* leaving the nonvolatile oil **25**. ^{31}P NMR (benzene-d_6): δ –163.2 (s). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 18.7 (d, 2C, J_{CP} = 11.0 Hz; CH_2), 9.5 (d, 2C, J_{CP} = 17.1 Hz; CH_2), 1.3 (d, 12C, J_{CP} = 11.0 Hz; $SiMe_3$), –3.5 (s, 2C; $SiMe_2$). ^1H NMR (benzene-d_6): δ 1.6 – 1.9 (broad unresolved mult., 2H; PCH_2), 0.7 – 1.1 (broad unresolved mult., 2H; $SiCH_2$), 0.28 [d, $^3J_{HP}$ = 4.1 Hz, 18H; $P(SiMe_3)_2$], 0.06 (s, 3H; Me_2Si). IR (thin film, cm^{-1}): 2953(vs), 2897(vs), 1406(s), 1246(vs), 1152(s), 1073(s), 997(s), 835(vs), 752(vs), 691(vs), 625(vs), 463(s), 411(s). MS (EI^+), M^+, m/e: 468 [$^{12}C_{18}H_{50}P_2Si_5{}^+$]. *Anal.* Calcd. for $C_{17}H_{47}P_2Si_5$: 453.1999. Found (EI^+, exact mass MS): 453.1920 (for M – $CH_3{}^+$).

Reaction of **25** with excess MeOH, followed by removal of Me_3SiOMe and excess MeOH in vacuo yields **26**. $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –122.9 (s). ^{31}P NMR (benzene-d_6): δ –122.8 (t of t of t, $^1J_{PH}$ = 188.1 Hz, $^2J_{PH}$ = 7.0 Hz, $^3J_{PH}$ = 4.0 Hz). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 18.6 (d, $^2J_{CP}$ = 3.7 Hz; PCH_2), 8.1 (d, $^1J_{CP}$ = 8.6 Hz; $SiCH_2$), –4.0 (s, $SiMe_2$). ^1H NMR (benzene-d_6): δ 2.79 (d of t, 4H, $^1J_{PH}$ = 187.8 Hz, $^2J_{PH}$ = 6.8 Hz; PH_2), 1.3 – 2.5 (broad unresolved mult., 8H: CH_2CH_2), –0.19 (s, 6H; Me_2Si). IR (thin film, cm^{-1}): 2959(vs), 2904(vs), 2294(vs, PH) 1416(s), 1259(vs), 1165(s), 1087(vs), 1006(s), 827(vs). MS (EI^+), M^+, m/e: 180 [$^{12}C_6H_{18}P_2{}^{28}Si^+$]. *Anal.* Calcd. for: $C_6H_{18}P_2Si$: 180.0653. Found (EI^+ exact mass MS): 180.0638.

(G) With $P(CH{=}CH_2)_3$ or $MeSi(CH{=}CH_2)_3$.

$P(CH{=}CH_2)_3$ (0.17 g, 1.5 mmol) or $MeSi(CH{=}CH_2)_3$ (0.19 g, 1.5 mmol) with $(Me_3Si)_2PH$ (0.24 g, 1.6 mmol) and AIBN (10 mg, 0.06 mmol) heated at 75° – 85 °C in an NMR tube resulted only in $(Me_3Si)_2PH$ decomposition.[4]

Reactions of $Me_2Si(PH_2)_2$ with 1,4-Pentadiene. $Me_2Si(PH_2)[P(CH_2)_5]$ (27) and $Me_2Si[P(CH_2)_5]_2$(28).

$Me_2Si(PH_2)_2$ (0.25 g, 2.0 mmol), 1,4-pentadiene (0.41 g, 6.0 mmol), benzene (1.0 mL) and AIBN (10 mg, 0.06 mmol) were heated at 85°C for 4.5 h. Volatile reaction components were passed repeatedly through a 0°C trap. **27** (ca. 1.0 mmol) condensed in the 0°C trap; **28** (ca. 1.0 mmol) remained as a nonvolatile, colorless liquid. **27**: $^{31}P\{^1H\}$ NMR (benzene-d_6): δ –103.1 (d, J_{PP} = 14.0 Hz, –247.0 (d, J_{PP} = 14.0 Hz; with ^1H coupling, $^1J_{PH}$ = 190 Hz). ^1H NMR (ben-

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zene-d$_6$): δ 0.1 (d of d, $^3J_{PH}$ = 4.0 Hz, 6H), 1.1 (d of d, $^1J_{PH}$ = 190 Hz, $^3J_{PH}$= 4.0 Hz; 2H), 0.8 – 2.2 (compl. mult., 10H). **28**: ^{31}P NMR (benzene-d$_6$): δ –106.2 (s). ^{1}H NMR (benzene-d$_6$): δ 0.4 (t, $^3J_{PH}$ = 4.0 Hz, 6H), 0.8 – 2.2 (compl. mult., 20H). Hydrolysis of **28** or **27** quantitatively yields (CH$_2$)$_5$PH (**7**) or **7** and PH$_3$, respectively, as the only phosphorus-containing hydrolysis products.

Reactions of PH$_3$

(A) With Me$_2$Si(CH=CH$_2$)$_2$, Me$_2$Si(C$_2$H$_4$)$_2$PC$_2$H$_4$-SiMe$_2$ (CH=CH$_2$) (29) and [Me$_2$Si(C$_2$H$_4$)$_2$PC$_2$H$_4$]$_2$SiMe$_2$ (30).

Reactions were conducted in a 25-cm long sublimation tube connected to a Fischer-Porter valve with a ball joint for vacuum line connection. The tube bottom was widened and elongated to accomodate the volume of the reactants. AIBN (15 mg, 0.09 mmol), toluene (1 mL) and a spinbar in the above apparatus were triply freeze-thaw degassed. Me$_2$Si(CH=CH$_2$)$_2$ (0.41 g, 3.7 mmol) and PH$_3$ (3 mmol) were added. After a 2-3 h reaction at 80 °C, high volatility material (PH$_3$, 1.1 mmole) was removed and the low volatility material which remained in the reaction tube was sublimed. A light yellow oil (ca. 50% of total) sublimed at 70 °C (fraction A) and a second light yellow oil (ca. 35%) sublimed at 170 °C (fraction B). The remaining product was a hard, brown intractable wax. Repeated molecular distillation of fraction A resulted in product enriched to ca. 75 % **29**. Spectral data for a 75:25 **29/30** mixture: ^{31}P NMR (benzene-d$_6$): δ -24.6. ^{13}C {^{1}H} NMR (benzene-d$_6$): δ 138.8 (s, $\underline{C}$H=CH$_2$), 132.1 (s, CH=$\underline{C}$H$_2$), 22.5 (d, $^1J_{CP}$ = 14.6 Hz; ring CH$_2$), 21.3 (d, $^1J_{CP}$ = 14.6 Hz; CH$_2$), 11.0 (d, $^2J_{CP}$ = 7.3 Hz; CH$_2$), 10.6 (d, $^2J_{CP}$ = 8.0 Hz; ring CH$_2$), -2.3 (s, SiMe$_2$), -3.4 (s, ring SiMe$_2$). ^{1}H NMR (benzene-d$_6$, areas given as % of total area) : δ 5.8 (area 7.2, compl. mult., CH=CH$_2$), 1.1 – 2.1 (area 23.9, unresolved broad, CH$_2$'s), 0.3 – 1.1 (area 28.9, unresolved broad, CH$_2$'s), 0.08 (broad s, area 17.8, SiMe$_2$), –0.02 (s, area 11.1, ring SiMe$_2$), –0.05 (s, area 11.1, ring SiMe$_2$). MS (EI$^+$, 70 °C): Parent ion envelopes (EI$^+$) at m/e: 404 [^{12}C$_{18}$H$_{42}$P$_2$Si$_3$+] and 258 [^{12}C$_{12}$H$_{27}$P^{28}Si$_2$+].

Fraction B exhibited ^{31}P NMR spectral resonances at: δ -30.6, -24.6, -23.1 and 12.7, along with numerous other very small peaks. Owing to the inhomogeneity of this fraction and our inability to separate it, additional spectral data were not obtained.

Excess PH$_3$ and Me$_2$Si(CH=CH$_2$)$_2$(10:1 mole ratio) were combined and heated with AIBN for 2-3 h. PH$_3$ was recovered in vacuo. ^{31}P NMR spectral analysis of the reaction mixtures showed six peaks in the region δ –22.1 to –24.7 for the most volatile fraction (sublimed at 70 °C) and nine peaks between δ –23.8 and –24.6 for a lower volatility fraction (sublimed at 170 °C). Further characterization of these fractions or the sublimation residue was not attempted.

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$Me_2Si(CH=CH_2)_2$ – $Me_2Si(C_2H_4)_2PH$ (9) Reaction.

$Me_2Si(CH=CH_2)_2$ and **9** were allowed to react in 2:1, 1:1 and 1:4 mole ratios. Typically **9** (0.25 g, 1.7 mmol) was syringed into the toluene (3 mL) and AIBN (12 mg, 0.10 mmol) solution. The solution was triply freeze-thaw degassed. $Me_2Si(CH=CH_2)_2$ (0.19 g, 1.7 mmol) was added and the solution heated to 80 °C. After 3 h, traces of high volatility materials were removed and the remaining low volatility oil was distilled. Fractions were collected at 70 °C (fraction A, 50%) and 170 °C (fraction B, 35 %). An intractable brown wax remained behind. Spectral data for fraction A was virtually superimposable with that for **29/30**, above.

Fraction B and the nonvolatile residue appeared to have the same general makeup as fraction B from the $PH_3/Me_2Si(CH=CH_2)_2$ reaction and was not characterized further.

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$Me_2Si(C_2H_4)_2P(S)C_2H_4SiMe_2(CH=CH_2)$ (31) and $[Me_2Si(C_2H_4)_2P(S)C_2H_4]_2SiMe_2$ (32).

A **29/31** mixture (74:26) was allowed to react with excess S_8 under N_2. White crystals, **31/32**, formed immediately. Neither fractional crystallization nor thin layer chromatography on silica plates achieved separation of the reaction mixture. ^{31}P NMR (benzene-d_6): δ 47.4. $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 137.4 (s, $\underline{C}H=CH_2$), 132.3 (s, $CH\underline{C}H_2$), 26.7 (d, J_{CP} = 48.8 Hz, CH_2), 26.3 (d, J_{CP} = 50.0 Hz; ring CH_2), 7.7 (d, J_{CP} = 2.5 Hz; ring CH_2), 6.5 (d, J_{CP}= 6.1 Hz; CH_2), –3.1 (s, ring SiMe), –3.8 (s, $SiMe_2$), –4.5 (s, ring SiMe) ^1H NMR (benzene-d_6, areas given as % of total): δ 5.8 (compl. mult., area 7.1; $CHCH_2$), 0.1 – 2.0 (broad unresolved mult., area 52.7; CH_2's), 0.02 (s, area 18.4; $SiMe_2$), –0.10 (s, area 10.9; ring $SiMe_2$), –0.20 (s, area 10.9; ring $SiMe_2$). MS (EI^+) M^+, m/e: parent ions at 468 [$^{12}C_{18}H_{42}P_2S_2{}^{28}Si_3$+] and 290 [$^{12}C_{12}H_{27}PS_{28}Si_2$+].

Cyclization Reactions of: (A) 23 and 24.

Typically, **24** (0.12 mL, 0.80 mmol) was allowed to react with AIBN (40 mg, 0.24 mmol) in toluene at 80 °C for 2.5 hr. The ^{31}P NMR spectrum exhibited resonances at δ –53.5 (**9**, 60 %)[5] in addition to minor resonances at δ –24.8, –25.5, –70.0 and –122.5 (unreacted **24**). Separation adequate to allow further characterization was not achieved.

Under similar reaction conditions, a **23/24** mixture (5:1 ratio) when heated with AIBN yielded a mixture which exhibited a major ^{31}P NMR resonance at –53.4 (**9**, 54 %), minor resonances at –70.8, –95.2 (**6**), –122.4 (**24**) and δ –140.3 (**23**), and minor unassigned resonances in the δ –20 to –30 region.

(B) 19A/19B.

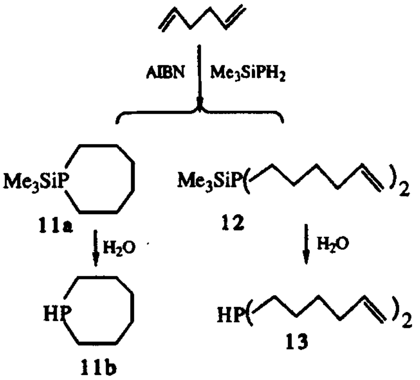
Treatment of the **19A/19B** mixture (0.23 g, 1.6 mmol) with AIBN (10 mg, 0.06 mmol) in benzene-d_6 (2 mL) at 85 °C resulted in the disappearance of **19A/19B** resonances and the appearance of major singlets at δ 5.9 and -18.6. The product mixture showed a strong mass spectral ion at m/e 146 along with low intensity ion envelopes at higher mass. Attempts to separate the reaction mixture failed.

(C) $CH_2{=}CHCH_2PH_2$. $P_2(CH_2)_3$ *(33).*

$CH_2{=}CHCH_2PH_2$ (0.11g, 1.5 mmol) and benzene-d_6 were condensed into an NMR tube with AIBN (10 mg, 0.06 mmol). The reaction was heated at 85 °C for 2 – 3 h. Repeated high-vacuum column distillation[9] of the volatile reaction materials yielded **33.**[12] ^{31}P NMR (benzene-d_6): δ -28.2(s). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 30.41(t, 4C, $J_{CP} = 16.0$ Hz), 29.99 (t, 2C, $J_{CP} = 4.6$ Hz). MS (EI$^+$), M$^+$, m/e: 148 [$C_6H_{12}P_2$+]. Anal. Calcd. for $C_6H_{12}P_2$: C, 49.32; H, 8.28; P, 42.40. Found. C, 49.61; H, 8.26; 41.99. The ^1H NMR (benzene-d_6) spectrum agreed closely with that reported recently by Alder and coworkers.[12,13]

RESULTS AND DISCUSSION

Reactions of Me_3SiPH_2 with 1,5-hexadiene and 1,3-butadiene in the presence of AIBN initiator were examined as potential routes to 7-membered phosphepane (**11**) and 5-membered, phosphetane (**10**) rings, respectively. With 1,5-hexadiene, reaction occurs smoothly at 85 °C in toluene to form cyclic **11a** (Scheme 1) along with acyclic **12**. Phosphorus-31 NMR spectral analysis of the reaction mixture shows mainly strong singlets at δ -105.8 and -101.8, in the region characteristic



SCHEME 1

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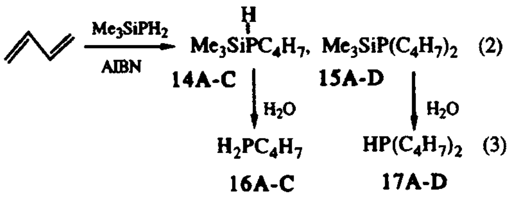
of secondary silylphosphines.[14,15] Only traces of 6-membered phosphorinanes were seen. Yields of **11a** and **12** are typically 45 – 50 % and 35 – 45 %, respectively. Even using other than 1:1 reactant ratios, both products are observed. Although **11a** is favored under dilute reaction conditions, in none of the experiments were significant amounts of higher molecular weight oligomers or polymers seen. Even though a phosphorinane product might be more stable and could be expected as a reaction product, the tendency of the silylphosphinyl radical to add anti-Markovnikov to olefins dominates.[4,5] In contrast, the analogous reaction between Me_3SiPH_2 and 1,3-butadiene yields no detectable 5-membered ring phosphetane (**10a**). Instead the reaction yields both mono- (**14A-C**) and bis- (**15A-D**) butenyl products (eqn 2). The reaction mixture shows three distinct ^{31}P NMR resonances from **14A-C** in the δ −147.7 to −150.5 region expected for primary silylphosphines.[14,15] All three show characteristic $^1J_{PH}$ coupling of 180 – 190 Hz[16] in the ^1H coupled spectrum. Likewise, isomers **15A – D** show ^{31}P NMR singlets at δ −94.1 to −97.7 as expected for secondary alkyl(silyl)phosphines.[14,15] Silylphosphines **11a, 12, 14A-C** and **15A-D** all are quantitatively hydrolyzed to the parent phosphines **11b, 13, 16A-C** and **17A-D**, and were readily characterized by spectral data. To our knowledge, the parent phosphepane $(CH_2)_6PH$ (**11b**) appears previously unprepared, although phosphorus alkyl- and aryl- substituted derivatives are known.[16] The ^1H NMR spectrum is especially interesting since it shows only a single doublet P-H ($^1J_{PH}$ = 190 Hz) of quintets ($^3J_{HP}$ = 3.5 Hz). This pattern indicates nearly equal vicinal coupling of the P-H proton to the four α-CH_2 protons, due possibly to rapid interconversions between various possible conformations of the 7-membered ring. This contrasts with behavior seen for the 6-member phosphorinane $(CH_2)_5PH$ (**7**) where ^1H NMR data show clear preference for the P-H being in an axial position.[17]



The Me_3SiPH_2/1,3-butadiene reaction yields mixtures of isomeric products. If we assume that, as in the Me_3SiPH_2 reactions with 1,4-pentadiene and 1,5-hexadiene,[4,5] addition of the $Me_3SiPH\cdot$ radicals to terminal olefin positions is preferred, the three observed monobutenylphosphines (**14A-C**) can be the result of both 1,2- and 1,4- addition to the butadiene (**I – III**, below). However, formation of the bis(butenyl)phosphine shows a degree of regioselectivity, since we

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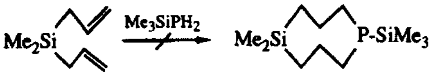
observe only four (**15A-D**) of the possible six isomers. Unfortunately, our spectral data do not allow the specific assignment of NMR resonances to particular isomers and they allow no reasonable assumptions about the isomer composition of **14** and **15** or their hydrolysis products **16** and **17**.

I

II (*cis*-), III (*trans*-)

Radical initiated reactions of Me_3SiPH_2 with $Me_2Si(CH_2CH{=}CH_2)_2$ or the triallyl- and trivinyl- compounds $P(CH_2CH{=}CH_2)_3$, $P(CH{=}CH_2)_3$ and $MeSi(CH{=}CH_2)_3$ were examined as potential routes to 8-membered, or possibly larger, cyclic silicon atom-containing phosphines (eg. **34**, eqn 4) or to allyl- or



(4)

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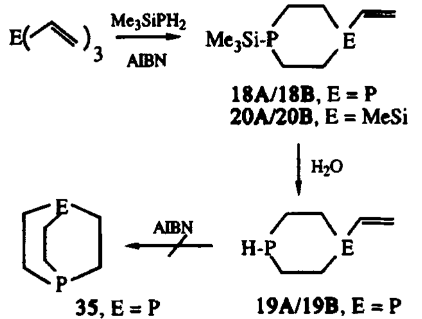
vinyl- substituted 8- or 6-membered phosphorus-containing rings (eg. **18** or **19**, Scheme 2). These rings, after hydroysis to the parent phosphines and further reaction with AIBN, might ring close to tricyclic cages, as **35** or **36** for the vinyl systems shown in Scheme 2.



18A/18B, E = P
20A/20B, E = MeSi

35, E = P
36, E = MeSi

19A/19B, E = P
21A/21B, E = MeSi

SCHEME 2

Unfortunately Me_3SiPH_2 with AIBN at 85 °C showed no reaction with $Me_2Si(CH_2CH{=}CH_2)_2$ or $P(CH_2CH{=}CH_2)_3$. This is somewhat surprising, since Issleib and coworkers[18] have reported that the allyl(silyl)phosphine $RSi(PH_2)(CH_2CH{=}CH_2)_2$ (R = Me, Ph) undergoes AIBN initiated intramolecu-

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lar closure to the bicyclic RSi[$(CH_2)_3]_2P$ product. However, P$(CH=CH_2)_3$ and MeSi$(CH=CH_2)_3$ do react with Me_3SiPH_2yielding the desired phosphorinane intermediates, **18A/18B** and **20A/20B**, respectively. In addition, the MeSi$(CH=CH_2)_3$ reaction shows minor ^{31}P NMR singlets at δ –69.8 and –70.0 presumed to be from diastereomeric 5-membered phospholane[15,19] byproducts and at δ –140.0 from the acyclic intermediate $(CH_2=CH)_2MeSiC_2H_4P(H)SiMe_3$ which preceeds **20A/20B**.[4] Isomers **18A/18B** yield characteristic ^{31}P NMR two-doublet resonance spectral patterns; **20A/20B** exhibit singlets. In both cases the isomer mixtures are low in volatility, precluding their complete purification by fractional distillation. However, they were characterized as mixtures and, secondarily, as their hydrolysis products **19A/19B** and **21A/21B**.

Spectral characterization of **19A/19B** and **21A/21B** show them to be vinyl-substituted 4-phospha and 4-silaphosphorinanes, respectively. Both show two sets of ^{31}P NMR resonances, because they are present as both *cis* and *trans* isomers.[5,20] Since **19A/19B** are diphosphorus molecules, each isomer exhibits two pairs of coupled doublets, one in the P-H region at δ –62.6 and –60.3 and the other in the alkylphosphorinane phosphorus region[5,21] at δ –34.7 and –37.4. Isomers **21A/21B** exhibit the expected two singlets at δ –53.5 and –54.0, in the phosphorinane region. Both show characteristic ^1H NMR vinyl AB_2 multiplet resonances, however, because they are isomer mixtures the multiplets are overlapped, broadened and poorly resolved.

Heating **19A/19B** and **21A/21B** at 77 – 85 °C in toluene in the presence of AIBN resulted in reaction, but not clearly to formation of **35** or **36**. Although **35** has been reported,[22] no spectral data were given. Our data show no quantifiable difference in *cis*- and *trans*- isomer reactivity. In both cases reactant resonances disappeared as product resonances appeared. In the **19A/19B** reaction, the major ^{31}P NMR resonances were singlets at δ 5.9 and –18.6; the volatile products from the product mixture displayed a mass spectral (EI^+) highest mass peak at m/e 146, consistent with the presence of **35** or one of several possible structural isomers. In the **21A/21B** reaction a series of small resonances appear between δ –20 and –25. These products were too non-volatile to separate by fractional distillation, suggesting oligomer/polymer rather than cage formation. Since spectral data for the target tricyclic molecules have not been reported, unambiguous characterization awaits finding better methods for product isolation.

We have found in this study that the allylsilanes and allylphosphines are unreactive towards silylphosphinyl radicals; in contrast we observed earlier[23] that allylphosphine $(CH_2=CHCH_2PH_2)$ in the presence of AIBN underwent reaction to a tricyclic compound characterized as **37**. This reactivity difference, the possiblilty that at higher dilution a $CH_2=CHCH_2PH_2$ radical reaction might yield an 8- membered ring product, and the recent report [12,24] that the spectral properties

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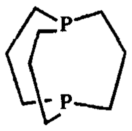

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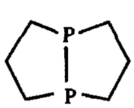
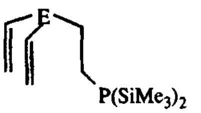


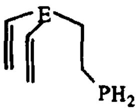
38

we reported for **37** were more consistent with the bicyclic **38** reported earlier by Issleib et. al.,[25] prompted us to reinvestigate the $CH_2{=}CHCH_2PH_2$ radical initiated reaction. Allylphosphine and AIBN in toluene were heated at 85 °C to effect reaction. The low-volatility product oil was repeatedly distilled. From this we obtained a product whose spectral properties, except for the MS data, are closely similar to those reported before.[24] We previously reported a highest mass ion at m/e 154, attributed to the $^{12}C_9H_{15}P^+$ ion, ie. the parent $P[(CH_2)_3]_3P^+$ minus a PH_3 molecule. However, with improved purification, the highest-mass peak is observed at m/e 146, consistent instead with **38**. Thus, we conclude that the main product of the reaction is in fact **38**, and that our first report was in error because of an unrecognized impurity.

In an alternate approach to tricyclic phosphines of type **35** or **36**, AIBN initiated reactions of $(Me_3Si)_2PH$ with $P(CH{=}CH_2)_3$ or $MeSi(CH{=}CH_2)_3$ were examined to determine the possibility of mono-phosphination to **39**, followed by its hydrolysis to **40** and ultimately cyclization to **35**/**36**. However, neither $P(CH{=}CH_2)_3$ nor $MeSi(CH{=}CH_2)_3$ reacted with $(Me_3Si)_2PH$ when heated at 80 – 85 °C for up to 5 h in toluene; only $(Me_3Si)_2PH$ decomposition is observed. Clearly, the lowered reactivity of the $(Me_3Si)_2P\cdot$ radical is a limiting factor in syntheses of this type.



39 (E = P, MeSi)



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The radical reaction between $Me_2Si(PH_2)_2$ and 1,4-pentadiene was examined as a potential route to large-ring phosphines, eg. the 12-membered ring that could result from addition of two molecules of diene across the bis(phosphine), eg. **41** as shown in Scheme 4. However, when allowed to react, only the new bis(phosphorinanyl) derviatives **27** and **28** formed along with minor amounts of higher molecular weight material. Compound **27** exhibits characteristic ^{31}P NMR doublet of doublet resonances at δ –247.0 ($^1J_{PH} = 190$ Hz, $^2J_{PP} = 14.0$ Hz) and a doublet pattern at δ –103.1, as expected for the monophosphorinanyl species.[5]

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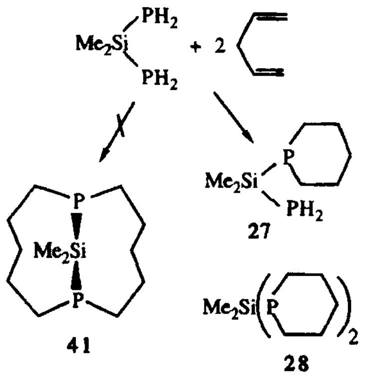
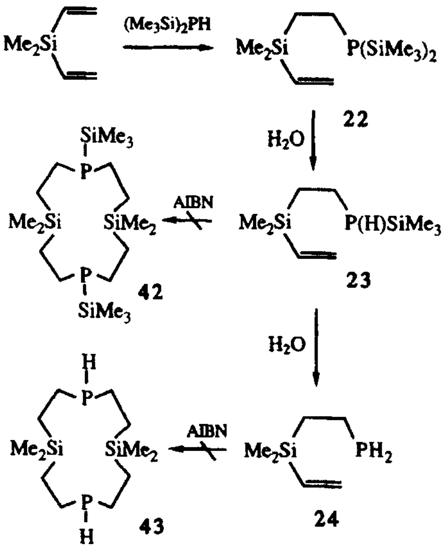


SCHEME 4

Compound **28** shows only a singlet resonance in the silyl(phosphorinane) region at δ –106.1. Both silylphosphines were hydrolyzed quantitatively to the known parent phosphorinane, $(CH_2)_5PH$ (**7**). If a ring product such as **41** formed, it was not identifiable among the minor products.

A second approach to large-ring formation, could involve alkenylphosphine cyclooligomerization (Scheme 5), where an alkenyl silylphosphine such as **23** or **24**, instead of undergoing radical cyclization to phosphorinanes, could cyclodimerize to 12-membered rings such as **42** or **43**. Cyclooligomerization of



SCHEME 5

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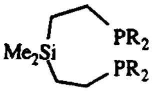
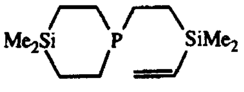
24 might proceed differently from that of **23**, because of the presence of the sterically bulky Me_3Si group on the phosphorus atom. To this end, $(Me_3Si)_2PH$ in the presence of AIBN was allowed to react with $Me_2Si(CH{=}CH_2)_2$, at 1:3 and 3:1 mole ratios. In both cases, reaction proceeds smoothly. In the 1:3 reaction the major product is the desired **22**, however, in the 3:1 reaction both **22** and the bis(silylphosphino) product **25** are attained. Both undergo reaction with MeOH to P-H bond containing products. Compound **22** reacts stepwise with one equivalent of MeOH to yield **23** along with traces of **24** from which it was difficult to fully separate. With two equivalents of MeOH, **22** is converted only to **24**. No attempt was made to solvolyze **25** stepwise, but with more than four equivalents of MeOH it was converted quantitatively to the parent bis(phosphine) **26**. The new compounds, **22** – **26**, were all readily characterized by spectral data. Interestingly, upon cyclization of either **23** or **24** by their thermolysis with AIBN at 85 °C, cyclization occurs primarily to the known 4-silaphosphorinanes **6** and **9**, respectively, along with lesser amounts of the isomeric 5-membered phospholanes. If significant quantities of large rings such as **42** or **43** had formed, their presence in the reaction mixtures could not be unambiguously established.

Although radical reactions of PH_3 with alkenes are known generally to involve all three P-H bonds and the formation of mono-, bis- and tris- alkylated products,[26-28] it remained of interest to determine if PH_3 reaction with a divinyl molecule, eg. $Me_2Si(CH{=}CH_2)_2$, could be controlled sufficiently to allow formation of large ring compounds such as **43** or the tricyclic analog which might result from reaction of a $Me_2Si(CH{=}CH_2)_2$ unit across the P-H bonds of **43**. However, even in dilute solutions, PH_3 reacts with $Me_2Si(CH{=}CH_2)_2$ in the presence of AIBN at 80 °C to yield a complex mixture of low-volatility products which are the result of complete P-H addition to vinyl groups. The highest-volatility products were isolated from the reaction mixture by sublimation of the mixture along a temperature gradient tube under high vacuum. This material was separable into a higher (A) and a lower (B) volatility fraction; a non-volatile wax was left



25, R = Me_3Si
26, R = H



29

30

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behind. Only fraction A could be reasonably well characterized. It was determined by spectral analysis (^{31}P, ^{1}H and ^{13}C{^{1}H} NMR and MS) to be a **29/30** mixture. Mass spectral parent ions at m/e 258 and 404 were clearly visible for **29** and **30**, respectively. Compounds **29** and **30** were not fully separable because they have similar and very low volatilities. However, upon repeated fractional distillation we obtained samples enriched to 75 % in **29**.

Compounds **29** and **30** have very similar NMR spectra, hence spectral analysis of the mixtures was difficult. At 36.2 MHz, the ^{31}P NMR resonances of the two appeared superimposed as one peak at δ –24.6 in the tertiary phosphine region.[16] The compounds show ^{13}C{^{1}H} NMR spectral resonances at δ 138.8 and 132.1, attributable to the vinyl carbon atoms of **29**. The other ^{13}C NMR resonances arise from both **29** and **30**. There are two doublet resonances at δ 22.5 ($^{2}J_{CP}$ = 14.6 Hz) and 21.3 ($^{2}J_{CP}$ = 14.6 Hz) tentatively assigned to CH_2 groups directly bonded to phosphorus centers, two doublets at δ 11.0 ($^{3}J_{CP}$ = 7.3 Hz) and 10.6 ($^{3}J_{CP}$ = 8.0 Hz) from CH_2 groups bonded to Si atoms and singlets at δ –2.3 and –3.4 from non-ring $SiMe_2$ and ring $SiMe_2$ carbon atoms, respectively. Only from ^{1}H NMR spectral data, was it possible to assess relative amounts of **29** and **30**. By comparing the relative area of the vinylic proton multiplet at δ 5.8 (from **29** only) to the total of the closely grouped $SiMe_2$ group resonances at δ 0.08, –0.02, and –0.05 (from both **29** and **30**), it was possible to determine for any mixture the approximate **29/30** ratio. Because distillation did not result fully in their separation, they were converted by S_8 oxidation to the phosphine sulfides **31/32**. These crystallized readily, but even after repeated recrystallizations and thin-layer chromatography, could not be obtained as homogeneous separated samples.

In an attempt to further establish the structures of **29** and **30** and to determine that the products were not large-ring oligomers, their synthesis was accomplished via a second route. The phosphorinane $Me_2Si(CH_2CH_2)_2PH$ (**9**) was allowed to react with $Me_2Si(CH{=}CH_2)_2$ in toluene in the presence of AIBN at 80 °C. The resulting product mixture yielded spectral data for a **29/30** mixture, virtually indentical to those obtained from $PH_3/Me_2Si(CH{=}CH_2)_2$reactions. Also, the S_8 oxidation of this yields product whose spectral data are superimposable to that obtained from oxidation of **29/30**.

Conclusions

The studies reported herein have resulted in formation of several new organo(silyl)phosphines and organophosphines which are of interest as ligands and, because they contain the functional P-Si or P-H bonds, as synthons for the preparation of other organophosphine derviatives. Our studies also show that

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whereas silylphosphine/alkene reactions that can form six- and seven- membered rings will do just that, other situations which might result in larger ring formation generally do not. Whether this is simply a function of the relatively high stability of the six- and seven- membered phosphorus-containing rings relative to eight-, ten- or twelve- membered rings or in part a characteristic of silylphosphines in radical reactions, remains unclear. We plan additional studies to further elucidate these questions.

Acknowledgements

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