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# Comparative Reactivity of the (Trimethylsilyl)phosphines $(Me_3Si)_{3-n}PH_n$ ($n = 1,2$) in Radical Reactions

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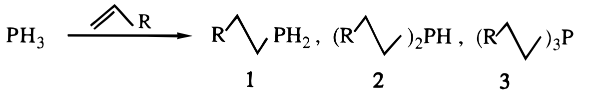
Radical reactions have been studied between $Me_3SiPH_2$ or $(Me_3Si)_2PH$ and selected mono- and dialkenes, cyclohexene, 1-hexene, $Ph_2PCH{=}CH_2$, 1,5-octadiene, norbornadiene, and 1,4-pentadiene, a series chosen for their range of reactivities. The $Me_3SiPH_2$/alkene reactions [alkene in brackets] yield the following: [1-hexene], $Me_3SiP(H)(n\text{-}C_6H_{13})$ (**8**), $Me_3SiP(n\text{-}C_6H_{13})_2$ (**9**); [$Ph_2PCH{=}CH_2$], $(Ph_2PCH_2CH_2)_2PSiMe_3$ (**12**); [1,4-pentadiene], $Me_3SiP(CH_2)_5$ (**14**); [norbornadiene], $Me_3SiP(H)C_7H_9$ (**16A/16B**). The $(Me_3Si)_2PH$/alkene reactons [alkene in brackets] yield the following: [$Ph_2PCH{=}CH_2$], $Ph_2PCH_2CH_2P(SiMe_3)_2$ (**18**); [norbornadiene], $(Me_3Si)_2PC_7H_9$ (**20**). A new synthesis for $(Me_3Si)_2PH$ using a $LiAlH_4/PH_3$ phosphinating reagent is described. Solvolysis of **8**, **9**, **12**, **14**, **16A/16B, 18**, and **20** yields $H_2P(n\text{-}C_6H_{13})$ (**10**), $HP(n\text{-}C_6H_{13})_2$ (**11**), $(Ph_2PCH_2CH_2)_2PH$ (**13**), $(CH_2)_5PH$ (**15**), $H_2PC_7H_9$ (**17**), and $Ph_2PCH_2CH_2PH_2$ (**19**). New compounds are characterized by spectral ($^{31}P$, $^{13}C$, and $^1H$ NMR, IR, and MS) data. Relative reactivities of phosphines in the $(Me_3Si)_{3-n}PH_n$ ($n = 1-3$) series toward alkenes decrease as $PH_3 > Me_3SiPH_2 > (Me_3Si)_2PH$. Origins of these reactivity differences are discussed.

## Introduction

Radical reactions of alkenes with P−H bond containing phosphines can efficiently form phosphorus−carbon bonds[2−11] thereby providing a synthetic route to various organophosphorus products. However, if the phosphine contains more that one P−H bond, e.g. as in $PH_3$, reactions can yield unwanted mixtures of primary (**1**), secondary (**2**), and tertiary (**3**) products.[4,5] We showed previously that this problem can be avoided in part using (trimethylsilyl)phosphine ($Me_3SiPH_2$), whose radical reactions yield products resulting from involvement of one or two P−H bonds without involvement of the Si−P bond (**4** or **5**).[12−15]



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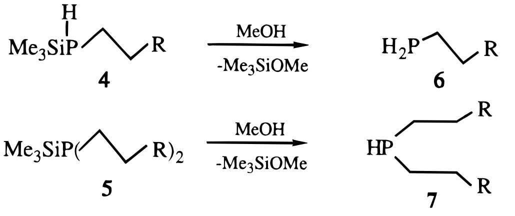

(2a)
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These reactions can yield both acyclic and cyclic silyl(organo)-phosphines, compounds which because they contain easily cleaved silicon−phosphorus bonds are synthons to primary (**6**) or secondary (**7**) organophosphines (eq 2).[12−17] Thus, the $Me_3Si$ group functions as a protecting group for phosphine P−H bonds.

Even though the $Me_3Si$ moiety protects one P−H bond in the radical reactions of $Me_3SiPH_2$, it still can be difficult to prevent formation of di- (**5**) rather than mono- (**4**) substituted products. However, by replacing a second hydrogen with a $Me_3Si$ group, as in $(Me_3Si)_2PH$, it should be possible to obtain further reaction selectivity and to obtain synthons exclusively for primary phosphines. Also, it is of interest to determine how replacement of hydrogen atoms by $Me_3Si$ groups affects P−H bond reactivity, i.e., to compare the reactivity of the $(Me_3Si)_{3-n}PH_n$ ($n = 1-3$) series. To this end we now report studies of $(Me_3Si)_2PH$ and $Me_3SiPH_2$ radical reactions with a series of selected mono- and dialkenes which allow these comparisons to be made. Several of the $Me_3SiPH_2$/alkene reactions below were reported by us in preliminary form earlier.[12]

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## Experimental Section

**Apparatus and Materials.** All manipulations were carried out in a standard vacuum line apparatus or in a $N_2$-flushed glovebag.[18] Infrared spectra were obtained on an IBM FTIR (IR/32 Type 9132), Perkin-Elmer Model 467 grating spectrophotometer, or Hewlett-Packard 5965A IR detector-equipped spectrophotometer. The detector was connected to a Hewlett-Packard 5890A gas chromatograph; the system was thermostated at 250 °C. Mass spectral data were obtained using a VG Analytical 7070 EQ-HF, Varian MAT CH-5 or Hewlett-Packard 5988A GC/MS spectrometer. $^1H$ NMR spectra were obtained using Varian Model EM 390 and JEOL FX-90Q (90.0 MHz) and Bruker WM250 (250 MHz) spectrometers equipped with multinuclear probe accessories. $^{13}C$ and $^{31}P$ NMR spectra were obtained using a JEOL PFT-100 or JEOL FX-90Q spectrometer. $^1H$ and $^{13}C$ chemical shifts are reported relative to $Me_4Si$. $^{31}P$ chemical shifts were measured relative to external 85% $H_3PO_4$. Chemical shifts downfield from the standard are given as positive ($+\delta$).

AIBN [2,2′-azobis(isobutyronitrile)] (Eastman Kodak), $Ph_2PCH{=}CH_2$ (Alfa Inorganics), $PH_3$ (Scientific Gas Products), and $Si(CH{=}CH_2)_4$ (Petrarch Systems) were used as obtained. $Me_3SiPH_2$ was prepared as described previously.[19] Hexene (Eastman Organic Chemicals), cyclohexene (Aldrich), and norbornadiene (Frinton Labs) were distilled under $N_2$ and stored under vacuum. Tetraglyme (tetraethylene glycol dimethyl ether) (Aldrich Chemical Co.) was vacuum distilled over $CaH_2$. Toluene was distilled from a Na/Pb alloy immediately prior to use. Benzene-$d_6$ and toluene-$d_8$ (Aldrich Chemical Co.) were stored under nitrogen over activated molecular sieves.

*The organophosphines described below are highly malodorous and probably highly toxic. Great care should be excercised in their handling*!

**General Procedures.** Reactions between $Me_3SiPH_2$ or $(Me_3Si)_2PH$ and alkenes were carried out by condensing volatile reagents and solvent into a 10 mL reaction vessel containing degassed AIBN (*ca.* 1−4 mmol % based on phosphorus). 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 75−85 °C. After heating, the vessel was opened and the products were separated as described below. In cases where reaction progress was followed by $^1H$ and/or $^{31}P$ NMR spectroscopy, the same procedure was employed using sealed 5 or 10 mm NMR tubes. Solvolysis reactions occurred rapidly and quantitatively upon mixing benzene or toluene solutions of organo(silyl)phosphine reaction products with 0.5 or 1.0 molar equiv of deoxygenated water or methanol, respectively, under an inert atmosphere.

**Synthesis of $(Me_3Si)_2PH$.** $(Me_3Si)_2PH$[20] was obtained by modification of a method used to synthesize $Me_3SiPH_2$.[19] $LiAlH_4$ (0.95 g; 25 mmol), tetraglyme (5 mL), and a stirbar were freeze−thaw−degassed three times in a 1-L flask. $PH_3$ (380 Torr, 1.44 L; 30 mmol) was condensed in, and the mixture was allowed to stir at 25 °C. After 8 h, $H_2$ (300 Torr, 2.44 L; 45 mmol) was removed at −196 °C. Additional $PH_3$ (380 Torr, 1.44 L; 30 mmol) was condensed in and allowed to react. After 8 h, $H_2$ (338 Torr, 2.44 L; 40 mmol) was removed. The reaction was stirred for an additional 12 h, after which all volatiles, $PH_3$ (111 Torr, 1.32 L; 8 mmol) and $H_2$ (65 Torr, 1.12 L; 4 mol), were removed. $Me_3SiCl$ (15 × 36 Torr, 2.04 L; 60 mmol) was added at −196 °C, the reaction mixture was warmed to 25 °C, and the mixture was stirred vigorously. After 3.5 h, volatiles were removed and separated by high-vacuum column distillation[18] to yield $PH_3$ and $Me_3SiH$ (90 Torr, 2.044 L; 10 mmol), $Me_3SiPH_2$ (220 Torr, 1.83 L; 22 mmol), $(Me_3Si)_2PH$ (29 × 4 Torr, 2.04 L; 13 mmol) and $(Me_3Si)_3P$ (0.26 g; 1 mmol).[20]

**$Me_3SiPH_2$ Reactions. (A) With 1-Hexene. $Me_3SiPH(n\text{-}C_6H_{13})$ (8), $Me_3SiP(n\text{-}C_6H_{13})_2$ (9), $H_2P(n\text{-}C_6H_{13})$ (10), and $HP(n\text{-}C_6H_{13})_2$ (11).** $Me_3SiPH_2$ (20 Torr, 1.83 L; 2.0 mmol), 1-hexene (50 Torr, 1.83 L; 5.0 mmol), benzene (0.3 mL), and AIBN (10 mg; 0.06 mmol) were heated at 85 °C for 6 h ($Me_3SiPH_2$ conversion, 60%; **8** and **9** yields, 50 and 40%). The reaction mixture was trap-to-trap distilled; pure **8** (0.10 g; 0.5 mmol) condensed at 0 °C. **9**, a low volatility oil, remained in the reaction vessel (0.19 g; 0.7 mmol). **8**: $^{31}P$ NMR ($C_6D_6$) $\delta$ −154.0 (d, $J_{PH}$ = 187 Hz). $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ −0.6 (d, 3C, $^2J_{PC}$ = 10.2 Hz; $SiMe_3$), 14.7 (s, 1C; $CH_3$), 14.8 (d, 1C, $J_{PC}$ = 9.9 Hz; $PCH_2$), 23.4 (s, 1C; $CH_2$), 31.3 (d, 1C, $J$ = 9.9 Hz; $CH_2$), 32.3 (s, 1C; $CH_2$), 32.6 (d, 1C, $J_{PC}$ = 11.7 Hz; $CH_2$). $^1H$ NMR ($C_6D_6$) $\delta$ 0.2 (d, 9H, $J_{PH}$ = 4.5 Hz; $SiMe_3$), 0.7−1.9 (compl mult, 13H; alkyl H), est. 2.0 (d of mult, 1H, $J_{PH}$ = 187 Hz; PH). IR (KBr, $cm^{-1}$) 2980−2828 (vs), 2279 (vs; $\nu_{PH}$), 1470 (vs), 1418 (s), 1380 (m), 1249 (s), 1198 (w), 1110 (w), 840 (s), 745 (m), 690 (m), 627 (m), 498 (m). **9**: $^{31}P$ NMR ($C_6D_6$) $\delta$ −101.5 (s); $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ −1.0 (compl mult, 3C, $^2J_{PC}$ = 10.8 Hz; $SiMe_3$), 14.9 (s, 2C; $CH_3$), 12.7 (d, 2C, $J_{PC}$ = 16.6 Hz; $CH_2$), 23.5 (s, 2C, $CH_2$), 30.2 (d, 2C, $J_{PC}$ = 15.4 Hz; $CH_2$); 31.9 (d, 2C, $J_{PC}$ = 11.5 Hz; $CH_2$), 32.6 (s, 2C; $CH_2$). $^1H$ NMR ($C_6D_6$) $\delta$ 0.2 (d, 9H, $J_{PH}$ = 4.5 Hz; $SiMe_3$), 0.8 −2.3 (compl mult, 26H). IR (KBr, $cm^{-1}$) 2860−2975 (vs), 1470 (vs), 1420 (vs) 1380 (s), 1252 (vs), 840 (vs), 748 (s), 692 (s), 628 (s), 496 (m); MS ($M^+$) *m*/*e* 347. Increasing the hexene:$Me_3SiPH_2$ reactant ratio had little effect on reaction outcome.

Hydrolysis of **8**, followed by repeated passage of the hydrolysate through −23 °C and −45 °C traps, gave **10** in the −45 °C trap. $^{31}P$ NMR ($C_6D_6$): $\delta$ −139.0 (t, $J_{PH}$ = 190.0 Hz). $^1H$ NMR ($C_6D_6$): $\delta$ 0.7−1.7 (compl mult, 13H; alkyl H), 2.9 (d of mult., 2H, $J_{PH}$ = 180; $PH_2$). MS ($M^+$) (rel. int.): *m*/*e* 118 (2).

Volatile components of the **9** hydrolysis were removed *in vacuo* leaving **11** as a colorless oil. $^{31}P$ NMR ($C_6D_6$): $\delta$ −69.8 (d, $J_{PH}$ = 191 Hz). $^1H$ NMR ($C_6D_6$): $\delta$ 0.7−1.7 (compl mult, 26H; alkyl H), 2.9 (d of mult, 1H, $J_{PH}$ = 191 Hz; PH). MS ($M^+$): *m*/*e* 202. Anal. Calcd for $C_{12}H_{27}P$: C, 71.23; H, 13.45; P, 15.32. Found: C, 71.46; H, 12.98; P, 15.44.

**(B) With $Ph_2PCH{=}CH_2$. $(Ph_2PCH_2CH_2)_2PSiMe_3$ (12) and $HP(CH_2CH_2PPh_2)_2$ (13).** $Me_3SiPH_2$ (20 Torr, 1.83 L; 2.0 mmol), $Ph_2PCH{=}CH_2$ (0.87 g; 4.1 mmol), toluene (0.5 mL), and AIBN (10 mg; 0.06 mmol) were heated at 85 °C for 3 h ($Me_3SiPH_2$ conversion, 100%; yield, 90%). Volatile materials were removed *in vacuo*. **12** remained as a colorless oil. $^{31}P\{^1H\}$ NMR ($C_7D_8$): $\delta$ −13.38 (d, 2P, $^3J_{PP}$ = 28.3; $PPh_2$), −85.9 (t, 1P; $PSiMe_3$). $^1H$ NMR ($C_7D_8$): $\delta$ 0.10 (d, 9H, $J_{PH}$ = 4.5 Hz; $SiMe_3$), 1.4−2.5 (compl mult, 8H; $CH_2$), 7.0−7.7 (compl mult, 20H; $C_6H_5$). $^{13}C\{^1H\}$ NMR ($C_7D_8$): $\delta$ 16.7 (d of d, 1C, $J_{PC}$ = 14.8 Hz, $J_{PC}$ = 14.7 Hz; $CH_2PH$), 27.0 (d of d, 1C, $J_{PC}$ = 15.5 Hz, 9.4 Hz; *C*$H_2PPh_2$), 128.5 (s), 128.8 (s), 139.1 (d of d, $J_{PC}$ = 18.6 Hz, 1.8 Hz). IR (KBr, $cm^{-1}$): 3065 (s), 3049 (s), 3009 (m), 2998 (m), 2938 (m), 2893 (m), 1952 (w), 1832 (w), 1808 (w), 1759 (w), 1582 (m), 1478 (s), 1431 (vs), 1305 (m), 1244 (s), 1182 (m), 1156 (m), 1092 (s), 1068 (m), 1025 (s), 998 (m), 982 (m), 838 (s), 739 (vs), 694 (vs). Anal. Calcd for $C_{31}H_{37}P_3Si$: C, 70.7; H, 7.15. Found: C, 71.0; H, 7.42.

Hydrolysis of **12**, followed by removal of volatiles *in vacuo* at 80 °C, left **13** as a low-volatility colorless oil. $^{31}P\{^1H\}$ NMR ($C_7H_8$): $\delta$ −58.1 (t, 1P, $^3J_{PP}$ = 22.0 Hz, broad with $^1H$ coupling, $^1J_{PH}$ = ca. 190 Hz; PH), −14.0 (d, 2P, $PPh_2$). $^{13}C\{^1H\}$ NMR ($C_7D_8$): $\delta$ 16.7 (d of d, 1C, $J_{PC}$ = 14.8 Hz, $J_{PC}$ = 14.7 Hz; $CH_2PH$), 27.0 (d of d, 1C, $J_{PC}$ = 15.5 Hz, 9.4 Hz; $CH_2PPh_2$), 128.5 (s), 128.8 (s), 139.1 (d of d, $J_{PC}$ = 18.6 Hz, 1.8 Hz). IR (KBr, $cm^{-1}$): 3062 (s), 2902 (m), 2304 (s, $\nu_{PH}$), 1952 (w), 1898 (w), 1818 (w), 1698 (m), 1487 (vs), 1442 (vs), 1182 (m), 1100 (s), 1082 (m), 1022 (s), 998 (s), 770 (vs), 715 (vs), 498 (s). MS ($M^+$) *m*/*e*: 458 ($^{12}C_{28}H_{29}P_3{}^+$). Anal. Calcd for $C_{28}H_{29}P_3$: C, 73.34; H, 6.37. Found: C, 72.88; H, 6.45.

**(C) With 1,4-Pentadiene. $Me_3SiP(CH_2)_5$ (14) and $HP(CH_2)_5$ (15).** Typically $Me_3SiPH_2$ (36 Torr, 2.04 L; 4.0 mmol), 1,4-pentadiene (70 Torr, 1.95 L; 7.5 mmol), benzene (0.5 mL), and AIBN (10 mg; 0.06 mmol) were heated at 85 °C for 4.5 h ($Me_3SiPH_2$ conversion, 70%; **14** and $(Me_3Si)_2PH$[21] yields, 95% and 5%). $^{31}P$ NMR analysis showed only traces (ca. 5%) of products at $\delta$ −153.8 and −237.5. The mixture was passed *in vacuo* through 0 and −23 °C traps; pure liquid **14** (2.6 mmol) condensed at −23 °C. $^{31}P$ NMR ($C_6D_6$): $\delta$ −107.8 (s). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ −2.5 (d, 3C, $J_{PC}$ = 11.0 Hz; $SiMe_3$), 18.4 (d, 2C, $^2J_{PC}$ = 14.6 Hz; $CH_2$), 27.1 (d, 2C, $^1J_{PC}$ = 3.7 Hz; $CH_2$), 28.7 (d, 1C, $^3J_{PC}$ = 9.9 Hz; $CH_2$). $^1H$ NMR ($C_6$ $D_6$): $\delta$ 0.3 [d, $J_{PH}$ = 4.5 Hz; $Si(CH_3)_3$], 2.3 (compl mult, 10H). IR (KBr, cm $^{-1}$): 2948 (s), 2920 (vs), 2850 (s), 2818 (m), 1447 (s), 1420 (m), 1247 (vs), 1200 (m), 942

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(m), 838 (vs), 742 (m), 690 (m), 622 (m), 445 (m). MS: *m/e* 174 ($^{12}C_8H_{19}{}^{29}SiP^+$, $M^+$), 175 ($M + 1^+$). Anal. Calcd for $C_8H_{19}SiP$: C, 55.13; H, 10.99; P, 17.77. Found: C, 55.04; H, 10.81; P, 18.16.

Hydrolysis of **14**, followed by high-vacuum, low-temperature column distillation[18] gave pure **15**.[21] $^{31}P$ NMR ($C_6D_6$): $\delta$ −66.0 (d, $J_{PH}$ = 190 Hz). $^1H$ NMR ($C_6D_6$): 0.40−0.95 (compl mult, 10H; $CH_2$), 3.1 (d of t, 1H, $^1J_{PH}$ = 190 Hz, $^3J_{PH}$ = 12.9 Hz; PH). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 17.2 (d, 2C, $^2J_{PC}$ = 11 Hz), 26.4 (s, 1C), 27.8 (d, 2C, $^2J_{PC}$ = 2 Hz). IR (gas, $cm^{-1}$); 2962 (s), 2923 (s), 2287 (vs, $\nu_{PH}$), 1446 (s), 1398 (m), 1380 (m), 1259 (s), 1145 (m), 1074 (m), 850 (m), 758 (m). MS: *m/e* 102 ($^{12}C_5H_{11}P^+$, $M^+$), 103 ($M + 1^+$).

**(D) With Norbornadiene. $Me_3SiP(H)C_7H_9$ (16A/16B) and $H_2PC_7H_9$ (17).** $Me_3SiPH_2$ (2 × 38 Torr; 8.0 mmol), norbornadiene (0.43 g; 4.0 mmol), benzene (0.4 mL), and AIBN (10 mg; 0.06 mmol) were heated at 85 °C for 4.5 h. Equal-area $^{31}P$ NMR resonances at $\delta$ −149.3 (d, *J* = 191 Hz) and −152.5 (d, *J* = 191 Hz) (**16A/16B**) were seen ($Me_3SiPH_2$ conversion, 50%; yield of **16**, 60%). The mixture was fractionated through a 0 °C trap. **16A/16B** (3.3 mmol) condensed at 0 °C. Small quantitites of a nonvolatile, yellow oil remained in the reaction vessel. **16**: $^{31}P$ NMR ($C_6D_6$) $\delta$ −149.3 (d, $J_{PH}$ = 191 Hz; **16A**), −152.5 (d, $J_{PH}$ = 191; **16B**); $^1H$ NMR ($C_6D_6$) $\delta$ 0.1 (d, $J_{PH}$ = 4.5 Hz, 9H; $SiMe_3$), 0.25 (d, 9H, $J_{PH}$ = 4.5 Hz; $SiMe_3$), 0.8−2.2 (compl mult, 18H), 2.0 (d of mult, 2H, $J_{PH}$ = 191 Hz; PH); IR (KBr, $cm^{-1}$) 3075 (m), 2960 (vs), 2911 (m), 2889 (s), 2279 (s, $\nu_{PH}$), 1445 (m), 1418 (m), 1323 (m), 1245 (vs), 1204 (m), 1178 (m), 820 (vs), 798 (s), 740 (m), 690 (m), 620 (m); MS, after brief exposure to air required for transfer to the spectrometer, cutoff observed at *m/e* 230, due to the oxidation product $(Me_3SiO)PH(O)C_7H_9$. Anal. Calcd for $C_{10}H_{19}SiP$: C, 60.56; H, 9.66; P, 15.62. Found: C, 60.24; H, 9.55; P, 15.86.

The **16A/16B** hydrolysis products were fractionated repeatedly through a −45 °C trap, into which **17** condensed. $^{31}P$ NMR ($C_6D_6$) $\delta$ −142.7 (t, $J_{PH}$ = 190 Hz). $^{13}C\{^1H\}$ NMR ($C_6D_6$) $\delta$ 8.60 (s, 1C; CH), 11.21 (d, 1C, $J_{PH}$ = 4.6 Hz; CH), 16.69 (d, 1C, *J* = 5.4 Hz; CH), 28.40 (d, 1C, *J* = 5.8 Hz; CH), 30.60 (d, 1C, $J_{PC}$ = 8.0 Hz; CH), 33.82 (d, 1C, 5.0 Hz; $CH_2$), 34.47 (d, 1C, $J_{PC}$= 8.8 Hz; $CH_2$). $^1H$ NMR ($C_6D_6$) $\delta$ 0.9−1.8 (compl mult, 9H; alkyl H), 2.95 and 2.18 (2H, d of AB mult split into d, $^1J_{PH}$ = 192 Hz, $^2J_{PH}$ = 12.7 Hz, $^3J_{PH}$ = 6.4 Hz; PH). IR (gas, $cm^{-1}$) 2973 (s), 2290 (vs, $\nu_{PH}$), 1448 (m), 1408 (w), 1152 (m), 1080 (vs), 915 (m), 856 (s), 762 (m), 695 (w), 622 (m). MS: *m/e* 126 ($^{12}C_7H_{11}P^+$, $M^+$). Anal. Calcd for $C_7H_{11}P$: C, 66.44; H, 8.79. Found: C, 67.10; H, 8.84.

**(E) With Cyclohexene.** Cyclohexene (0.26 g; 3.2 mmol), $Me_3SiPH_2$ (33.5 Torr, 982 mL; 1.8 mmol), and AIBN (8 mg; 0.05 mmol) in benzene (0.4 mL) when heated at 80 °C for 8 h underwent no reaction.

**Reactions of $(Me_3Si)_2PH$. (A) With $Ph_2PCH{=}CH_2$. $Ph_2PCH_2CH_2P(SiMe_3)_2$ (18) and $Ph_2PCH_2CH_2PH_2$ (19).** $(Me_3Si)_2PH$ (0.53 g; 3 mmol), $Ph_2PCH{=}CH_2$ (0.53 g; 2.5 mmol), AIBN (5 mg; 0.3 mmol) and benzene (1 mL) were allowed to react as above for 4 h at 80 °C [$(Me_3Si)_2PH$ conversion, 35% (0.46 g); yield of **18**, >95%]. After second and third additions of AIBN and heating for an additional 8 h, $(Me_3Si)_2PH$ conversion reached 60%. After removal of volatiles by heating in vacuo at 80 °C, only nonvolatile **18** remained. $^{31}P$ NMR ($C_6D_6$): $\delta$ −166.3 [d, 1P, $^3J_{PP}$ = 31.8 Hz; $P(SiMe_3)_2$], −13.6 (d, 1P; $Ph_2P$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 139.4 (d, 1C, $^1J_{CP}$ = 15.2 Hz; $PCC_5H_5$), 133.2 (d, 2C, $^2J_{CP}$ = 18.5 Hz; *o*-C), 128.7 (s, 1C; p-C), 128.5 (d, 2C, $^3J_{PC}$ = 6.1 Hz; *m*-C), 31.5 (d of d, 1C, $J_{CP}$ = 19.0 Hz, $J_{CP}$ = 15.6 Hz; $CH_2PPh_2$), 11.1 [d of d (appears as t), 1C, $^2J_{CP}$ = 17.4 Hz; $CH_2PSi(Me_3)_2$], 0.7 (d, 3C, $^2J_{CP}$ = 11.4 Hz; $SiMe_3$). $^1H$ NMR ($C_6D_6$) $\delta$ 7.0−7.5 (broad unresolved mult, 10H; $C_6H_5$), 1.6−2.4 (broad unresolved mult, 4H; $CH_2$), 0.13 (d, $^3J_{HP}$ = 4.10 Hz, 18H; $P(SiMe_3)_2$). IR (NaCl, $cm^{-1}$) 3071 (s), 3056 (s), 2952 (vs), 2897 (s), 1482 (s), 1433 (s), 1402 (s), 1246 (vs), 1096 (s), 1026 (s), 833 (vs), 745 (vs), 696 (vs), 625 (vs). MS ($EI^+$) ($M^+$) [*m/e* (rel. int.)]: 390(16) [$^{12}C_{20}H_{32}P_2Si_2{}^+$]. Anal. Calcd for $C_{20}H_{32}P_2Si_2$: 390.1518. Found ($EI^+$, exact mass MS): 390.1524.

Hydrolysis of **18**, followed by removal of high volatility materials *in vacuo*, yields the previously reported **19** (ca. 50% yield).[22]

**(B) With Norbornadiene. $(Me_3Si)_2PC_7H_9$ (20).** $(Me_3Si)_2PH$ (0.53 g; 3 mmol), norbornadiene, (10 Torr; 1.83 L; 1 mmol), toluene-$d_8$ (8 mmol), and AIBN (10 mg; 0.06 mmol) were heated at 85 °C for 16 h. Volatile materials were removed *in vacuo*. Unreacted $(Me_3Si)_2PH$ was recovered from the volatile fraction. All norbornadiene was consumed. **20** remained as a colorless, low-volatility liquid. $^{31}P$ NMR ($C_6D_6$): $\delta$ −171.3 (s). $^1H$ NMR ($C_7H_8$): 0.9−2.2 (broad unresolved mult, 9H; $C_7H_9$), 0.3 [d, $^3J_{HP}$ = 4.5 Hz, 18H, $P(SiMe_3)_2$]. IR (KBr, $cm^{-1}$): 3093 (m), 3067 (m), 2970 (vs), 2909 (s), 2889 (s), 1461 (m), 1445 (m), 1407 (m), 1306 (s), 1297 (m), 1249 (vs), 1213(m), 1164 (m), 1010 (m), 924 (m), 849 (vs), 771 (s), 751 (s), 690 (s), 634 (s), 474 (m), 441 (m). MS ($EI^+$): after the brief exposure to air required for introduction of samples into the spectrometer, an envelope appeared at *m/e* 318 (5%) attributed to $M^+$ of the oxidation product $(Me_3SiO)_2P(O)C_7H_9$. Reaction of **20** with $H_2O$ yields **17** quantitatively.

**(C) With 1-Hexene and 1,4-Pentadiene.** Reactions of 1-hexene and 1,4-pentadiene with $(Me_3Si)_2PH$ and AIBN at 75 °C in NMR tubes for up to 22 h resulted only in the decomposition of $(Me_3Si)_2PH$. Traces of $[(Me_3Si)_2P]_2$[23] appeared.

## Results and Discussion

**$(Me_3Si)_2PH$ Synthesis.** Although $(Me_3Si)_2PH$ syntheses have been reported previously,[20,24] we wished to determine if the $LiAlH_4/PH_3$ phosphinating system[25,26] might provide a higher-yielding route. It was shown earlier that $LiAlH_4$ reacts with excess $PH_3$ in a 1:4 ratio in glyme ethers to form $LiAl(PH_2)_4$[25,26] which is a highly effective $PH_2$-unit phosphinating reagent (eq 3).[25−27] We now find that if the reaction is carried out using a

$$LiAlH_4 + 4PH_3 \rightarrow 4\,H_2 + LiAl(PH_2)_4 \tag{3}$$

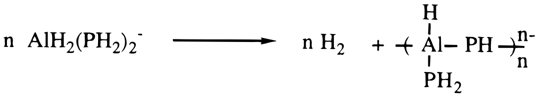
deficiency of $PH_3$, e.g. a $LiAlH_4$:$PH_3$ ratio of 1:2, a product mixture of different composition attains. From the outset $H_2$ is evolved as $PH_3$ is consumed; however as the reaction proceeds, the molar quantity of $H_2$ evolution exceeds the $PH_3$ consumption. Typically, after 28 h the $H_2$ produced:$PH_3$ consumed ratio approaches a 2:1 molar ratio. Treatment of the resulting reaction mixture with $Me_3SiCl$ results in phosphination; the products $Me_3SiPH_2$, $(Me_3Si)_2PH$, and $(Me_3Si)_3P$[20] are produced in approximately 40%, 25%, and 2% yields, respectively. Although $Me_3SiPH_2$ is still the major product, this method represents a good route to $(Me_3Si)_2PH$.

The relatively high yield of $(Me_3Si)_2PH$ obtained from the 2:1 $PH_3/LiAlH_4$ phosphinating mixtures allows tentative conclusions about the composition of the phosphinating mixture. It is assumed that $PH_3$ reacts with $LiAlH_4$ stepwise replacing hydrogens by $PH_2$ groups, as in eq 4a,b. After reaction with 2

$$PH_3 + AlH_4{}^- \rightarrow H_2 + AlH_3(PH_2)^- \tag{4a}$$

$$PH_3 + AlH_3(PH_2)^- \rightarrow H_2 + AlH_2(PH_2)_2{}^- \tag*{(4a)}$$

mol of $PH_3$, a species is formed of average composition corresponding to the $AlH_2(PH_2)_2{}^-$ ion. However, in the absence of excess $PH_3$ further condensation apparently occurs between initially-formed phosphinoaluminate species. For example, intermolecular condensation of $AlH_2(PH_2)_2{}^-$ ions might result in $H_2$ elimination and formation of phosphido−bridged (−PH−) oligomeric/polymeric phosphinoaluminate species of general type **21**. Such species, formally a source of $PH_2{}^-$ and $PH^{2-}$



$$n\ AlH_2(PH_2)_2{}^- \longrightarrow n\,H_2 + \left( \overset{H}{\underset{PH_2}{Al}} - PH \right)_n^{n-} \tag{5}$$

**21**

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**Chart 1**

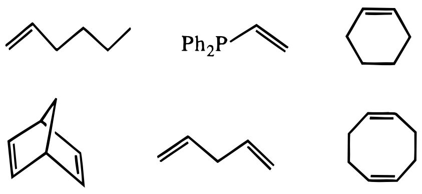
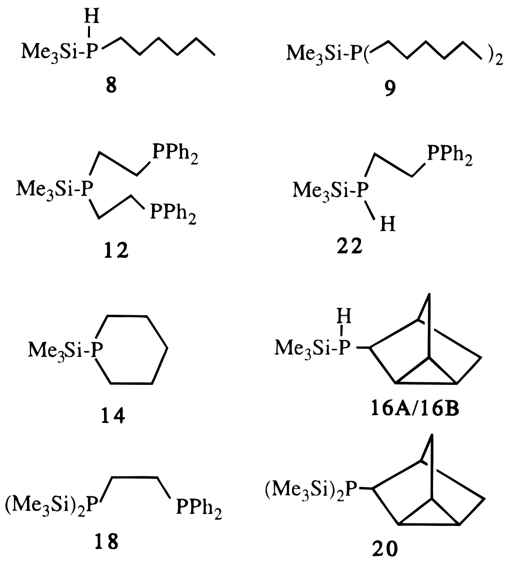


**Chart 2**



ions, upon reaction with $Me_3SiCl$ would produce both $Me_3SiPH_2$ and $(Me_3Si)_2PH$. It appears that more complex condensation processes, of sorts that would yield triply bridging (=P−) phosphido groups, do not occur to a high degree since under the reaction conditions used only small amounts of $(Me_3Si)_3P$ appear. At this time structural details of new phosphinoaluminate oligomers are not known; the system is being studied further.

**Comparative Reactions with Alkenes.** The alkenes 1-hexene, diphenyl(vinyl)phosphine, cyclohexene, norbornadiene, 1,4-pentadiene, and 1,5-cyclooctadiene (Chart 1) were selected for studies of their reactivity toward $Me_3SiPH_2$ and $(Me_3Si)_2PH$. These mono- and dialkenes offer a range of reactivity toward radical species;[27] reactions of several of these with $PH_3$ have already been reported.[2,3,6,7]

Although monoalkenes, e.g. 1-octene[5] and cyclohexene,[2,6] readily undergo radical reactions with $PH_3$, there are distinct differences with respect to their reactivity toward $Me_3SiPH_2$ and $(Me_3Si)_2PH$. Neither $Me_3SiPH_2$ nor $(Me_3Si)_2PH$ reacts with cyclohexene even after extended periods at 80 °C. By comparison, the more reactive terminal 1-hexene reacts with $Me_3SiPH_2$ but not with $(Me_3Si)_2PH$. $^{31}P$ NMR spectral analysis of the hexene/$Me_3SiPH_2$ reactions shows early formation of the monosubstituted anti-Markovnikov[27] addition product **8** ($\delta$ −154.0) (Chart 2). Later a second resonance appears due to disubstituted **9** ($\delta$ −101.5); reaction is complete after 6 h. There were only minor resonances which might be attributed to a Markovnikov addition product; hence both steps in the bis-substitution process are highly regiospecific. No products are observed which would be attributed to Si−P bond cleavage or participation in competing reactions.

Only the most reactive monoalkene of the series, the vinylphosphine $Ph_2PCH{=}CH_2$, which reacts readily with $Me_3SiPH_2$, is sufficiently activated to react with $(Me_3Si)_2PH$. The $Me_3SiPH_2/Ph_2PCH{=}CH_2$ reaction proceeds quantitatively in 3 h at 85 °C to **12**. Even at shorter reaction times significant quantities of the monophosphination product **22** were not observed. In contrast, the $(Me_3Si)_2PH/Ph_2PCH{=}CH_2$ reaction is significantly slower, clearly demonstrating the much higher selectivity of the $(Me_3Si)_2P^{\bullet}$ radical. Only after heating for several 4 h periods at 80 °C was it possible to obtain a 65% conversion of $(Me_3Si)_2PH$ to diphosphine **18**. Attempts to drive the reaction to completion by further additions of AIBN and additional heating resulted mostly in reactant decomposition.

Dialkene reactions with $Me_3SiPH_2$ could yield either or both cyclic and acylic products; however, $(Me_3Si)_2PH$, because it contains only a single P−H bond, is expected to be selective for formation of acylic phosphines. Reaction of 1,4-pentadiene with $Me_3SiPH_2$ yields the six-membered ring phosphorinane **14** in high yield. Attempts to control the reaction and limit it to monosubstitution, i.e. formation of $Me_3SiP(H)(CH_2)_3CH{=}CH_2$ (**22**), failed. Only small quantitites of the acyclic intermediate **22** and $(Me_3Si)_2PH$, which show weak resonances at $\delta$ −153 and −237.5, respectively, are seen. Resonances attributable to five-membered ring phospholanes were not evident. Thus, as with the $Me_3SiPH_2$/monoalkene reactions, reactions with dialkenes appear to be highly regioselective favoring addition to terminal alkene carbon atoms. Since norbornadiene is known to be highly susceptible to radical additions, it is not suprising that it reacts with $Me_3SiPH_2$. After only 4.5 h at 85 °C, product **16A/16B** is formed, an approximately 1:1 mixture of mono-$Me_3SiP(H)$-substituted diastereomers. Reaction is accompanied by formation of large amounts of high molecular weight, possible polymeric, materials. There was no evidence for formation of the bis-substituted product $Me_3SiP(C_7H_9)_2$. If it is present, it is so low in volatility that we were unable to isolate it from the reaction mixture. Apparently, the $Me_3SiP(H)^{\bullet}$ radical adds to norbonadiene to form a carbon-centered radical which after rearrangement and H abstraction yields the nortricylene structure **16**. Analgous reactions are known involving sulfur-basd ($RS^{\bullet}$) free radicals.[28]

In contrast to the facile reactivity toward 1,4-pentadiene and norbornadiene shown by $Me_3SiPH_2$, $(Me_3Si)_2PH$ is much less reactive. No reaction is observed between $(Me_3Si)_2PH$ and 1,4-pentadiene or 1,5-cyclooctadiene even during reaction times of up to 22 h. Small amounts of the diphosphine $[(Me_3Si)_2P]_2$[23] are seen after extended periods of heating, presumably from coupling of $(Me_3Si)_2P^{\bullet}$ radicals. However, with the more active norbornadiene, the product **20** forms in high yield in 16 h. In contrast to the $Me_3SiPH_2$/1,4-pentadiene reaction, the reaction is cleaner, yielding relatively little polymeric material.

Solvolysis of the silylphosphines[29] **8**, **9**, **12**, **14**, **16A/16B**, **18**, and **20** by their reaction with excess water yield quantitatively the phosphines **10**, **11**, **13**, **15**, **17**, and **19** (Chart 3). Compounds **15**[21] and **19**[22] were reported previously, although **15** lacked complete characterization. Compounds **12**, **13**, **18**, and **19** are of particular interest because they contain not only multiple phosphorus(III) coordination sites[9,22,30−33] but also P−H or P−$SiMe_3$ bonds whose functionality can be used in subsequent derivatization reactions.

The silyl(organo)- and organophosphines prepared in this

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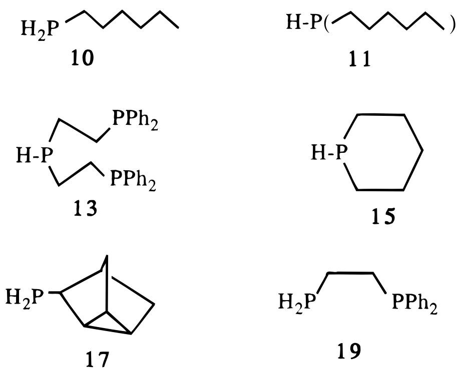
**Chart 3**



study are low-volatility pale yellow oils with properties generally characteristic of primary or secondary phosphines. All are highly malodorous and readily oxidized in ambient air. The new phosphines were characterized by spectral data. All exhibited expected mass spectral patterns,[34−36] although because of hydrolysis in the mass spectrometer source the silylphosphines generally showed background peaks due to the hydrolyzed species. The silyl(organo)phosphines showed strong fragment ions that result from loss of $Me_3Si$ and $Me_3SiP$ units. Compounds **16** and **20** appeared to be exceptionally oxidatively reactive and invariably showed, instead of the parent ions, highest mass ions at *m*/*e* 230 and 318, respectively, attributed to the oxidation products $(Me_3SiO)PH(O)C_7H_9$ and $(Me_3SiO)_2P(O)C_7H_9$. Infrared spectra of the silyl(organo)phosphines are relatively uninformative; however, all the primary and secondary phosphines show characteristic P−H stretching absorptions in the 2250−2300 $cm^{-1}$ region.[37]

The $^{31}P$ NMR spectral patterns and chemical shift data allow identification of the new phosphines as $(Me_3Si)_2PR$, $Me_3Si(H)PR$, $H_2PR$, $Me_3SiPR_2$, or $HPR_2$ (R = organo moiety) substitutional types. Compounds **8**, **11**, **13**, and **15** show the 1:1 doublet patterns associated with P(III) PH-containing species;[38,39] similarly **10**, **17**, and **19** show 1:2:1 triplets from $PH_2$ groups. In both situations, the $^1J_{PH}$ coupling constants of 187−192 Hz are in the normal range.[38,39] Compound **16A**/**16B**, present as two diastereomers, exhibits the expected two $^{31}P\{^1H\}$ NMR spectral singlet resonances; resonances occur at $\delta$ −149.3 and −152.5. The diphosphines **18** and **19** and triphosphines **12** and **13** exhibit AX equal-area doublet and $AX_2$ doublet−triplet patterns[40] due to the expected $^3J_{PP}$ coupling (15.0−31.5 Hz) between the 1,4-substituted phosphorus-containing moieties.[41] Also, the chemical shifts correlate well with differences in substitution environments. Chemical shifts for the primary organophosphines (**10** and **19**) at $\delta$ −122.8 and −139.0 occur at appreciably higher field than those for secondary phosphines (**11**, **13**, and **15**) at −58.1 to −69.8 ppm.[38] Additionally, substitution of silyl groups for hydrogen consistently causes a shift to higher field; the mono- (**8**, **16A**/**16B**) and bis- (**18** and **20**) silylated primary phosphines occur in the ranges $\delta$ −145 to −154 and −162.2 to −171.3, respectively. For the silylated secondary phosphines (**9**, **12**, and **14**) shifts are upfield by ca. 20 ppm, e.g. in the range of −85.9 to −101.5 ppm. The origin(s) of these shifts is not understood; however, they may arise from both structural and electronic factors.[38,42] As silyl substitution is increased, the geometry around the phosphorus center may go more toward planar, a factor known to be important in determining chemical shifts.[38,39] In addition, more silyl groups on phosphorus could cause increased electronic shielding of the phosphorus nuclei. The degree to which these are important is being studied further.

The $^1H$ and $^{13}C$ NMR spectral data were in every case as expected. All protons of the species are clearly evident in the $^1H$ spectra. The $Me_3Si-$ group singlet (**8**, **9**, **12**, **14**, **16**, **22**), phenyl multiplet (**18**), PH group $^1J_{PH}$ doublets (**11**, **13**, **15**, **16**, **19**), and $PH_2$ group $^1J_{PH}$ doublet (**10**, **17**, **19**) resonances are unmistakable both in pattern and chemical shift; other protons occurred as complex, second-order multiplets.[43,44] The $^1H$ resonances for the $PH_2$ protons in **17** are a characteristic pair of eight-line patterns, because the $PH_2$ protons are diastereotopic and coupled to each other, to the vicinal proton on the attached carbon, and to the $^{31}P$ nucleus. The $^{13}C\{^1H\}$ NMR $Me_3Si$ group resonances in all new compounds occur as doublets ($^2J_{PC}$ = 10.2−12.0 Hz) between $\delta$ −1.0 and 1.3. The $Me_3Si$ carbon atoms are easily distinguished from the $CH_2$ and $CH_3$ carbons of alkyl chains or bridging $CH_2CH_2$ groups, whose resonances are seen at somewhat lower field between $\delta$ 8.0 and 32.3.[43−46] Phenyl carbons of the $Ph_2P$ groups of **12** and **13** occur at much lower field, typically in the $\delta$ 128−140 range.

Bis(trimethylsilyl)phosphine undergoes radical reactions with alkenes, but only with the more activated ones and often to a limited degree. Clearly, $(Me_3Si)_2PH$ is less reactive than $Me_3SiPH_2$, which reacts with all the selected alkenes except for the nonpolar alkenes cyclohexene and 1,5-cyclooctadiene. Both $(Me_3Si)_2PH$ and $Me_3SiPH_2$ are less reactive than $PH_3$, which adds easily to cyclohexene[6] and 1,5-cyclooctadiene.[7] The $(Me_3Si)_2P^{\bullet}$ radicals might be sufficiently sterically bulky to be slowed in their reactivity toward dienes like norbornadiene. With the less active alkenes it typically was necessary to reduce solvent and increase the reaction temperature and AIBN concentration in order to maximize product yields. Under these more rigorous conditions, the reaction solutions turned bright yellow and small quantities of the diphosphine $(Me_3Si)_2PP(SiMe_3)_2$[23] became evident in the $^{31}P$ NMR spectra. This is presumed to arise from coupling of $(Me_3Si)_2P^{\bullet}$ radicals in the system.

On the basis of our results, we conclude that the $(Me_3Si)_{3-n}PH_n$ ($n$ = 1−3) series reactivity in radical reactions toward alkenes is $PH_3 > Me_3SiPH_2 > (Me_3Si)_2PH$. We assume that silylphosphines undergo radical additions to alkenes by the same

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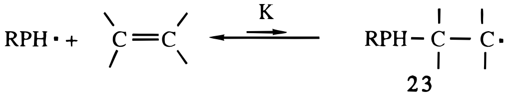
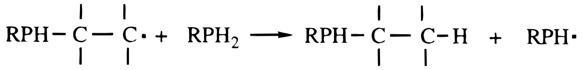
mechanism as the previously studied alkyl phosphines ($RPH_2$).[5] With these, the phosphinyl radicals and alkene react and exist in equilibrium with the addition intermediate radical **23** (eq 6a).



$$\mathrm{RPH}^{\bullet} + \mathrm{C{=}C} \overset{K}{\rightleftharpoons} \underset{\mathbf{23}}{\mathrm{RPH{-}C{-}C}^{\bullet}} \qquad (6a)$$



$$\mathrm{RPH{-}C{-}C}^{\bullet} + \mathrm{RPH_2} \longrightarrow \mathrm{RPH{-}C{-}C{-}H} + \mathrm{RPH}^{\bullet} \qquad (6b)$$

Upon hydrogen abstraction by **23** from additional phosphine, the final phosphino-substituted product (eq 6b) is formed, a phosphinyl radical is regenerated, and the reaction continues. Given this, we expect that the differences in $PH_3$, $Me_3SiPH_2$, and $(Me_3Si)_2PH$ reactivity is in part related to differences in the position of the eq 6a equilibrium reaction and differences in the nucleophilicities of the carbon-based radicals (**23**).[27] Equilbrium 6a would be influenced by the relative stabilities of the $PH_2^{\bullet}$, $Me_3SiPH^{\bullet}$, and $(Me_3Si)_2P^{\bullet}$ radicals; with increasing $Me_3Si$ group subtitution these could become correspondingly more stable because of the increased potential for delocalization of the radical electron. For the same reason, the nucleophilicity of species **23** might be lowered, making the increasingly substituted carbon-centered radicals less reactive. However, the extent to which these or other electronic factors influence silylphosphinyl radical reactivity remains an ongoing problem, which we continue to investigate in our laboratories.

**Acknowledgment.** Support for this work by National Science Foundation Grants CHE-8312856 and CHE-8714951 is gratefully acknowledged.

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