Synthesis and Structures of Cyclic Ethynylphosphine Ligands

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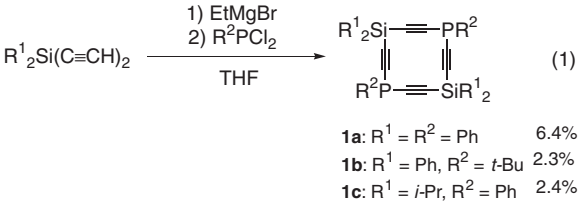
Twelve-membered cyclic diethynylphosphine derivatives $(R^1{}_2SiC{\equiv}C{-}R^2PC{\equiv}C)_2$ (**1a**: $R^1 = R^2 =$ Ph; **1b**: $R^1 =$ Ph, $R^2 = t$-Bu; **1c**: $R^1 = i$-Pr, $R^2 =$ Ph) have been synthesized as a novel cyclic phosphine ligand including potentially reactive acetylene and silane moieties. Compounds **1a** and **1b** were formed as a mixture of *cis*- and *trans*-isomers, while an only *trans*-isomer was obtained for **1c**. X-ray structural analysis revealed planar skeletal structures of the *trans*-isomers of **1a–c**.

Recently cyclic compounds containing ethynylphosphine units, $(t\text{-BuPC}{\equiv}C)_n$ ($n = 3$, 4),[1] and ethynylsilylene units, $(R_2SiC{\equiv}C)_n$ (R = Ph, $n = 4$, 6; R = Me, $n = 3$–6),[2] have been synthesized. Ethynylphosphines are potentially multifunctional ligands because both phosphine and acetylene are capable of coordination.[3] These multifunctional compounds would play an important role in constructing supramolecules.[4] We report here the synthesis and structures of twelve-membered cyclic diethynylphosphine derivatives $(R^1{}_2SiC{\equiv}C{-}R^2PC{\equiv}C)_2$ as new ethynylphosphine ligands.

As shown in Eq 1, treatment of diethynylsilanes, $R^1{}_2Si(C{\equiv}CH)_2$ ($R^1 =$ Ph and *i*-Pr),[2f,5] with 2 equiv. of EtMgBr in THF, followed by a reaction with dichlorophosphines, R^2PCl_2 ($R^2 =$ Ph and *t*-Bu), gave the desired compounds $(R^1{}_2SiC{\equiv}C\text{-}R^2PC{\equiv}C)_2$ (**1a**: $R^1 = R^2 =$ Ph, 6.4%; **1b**: $R^1 =$ Ph, $R^2 = t$-Bu, 1.9%; **1c**: $R^1 = i$-Pr, $R^2 =$ Ph, 2.4%) as main products.[6] Although the yields were low at this stage, and polymeric side products [e.g. $(R^1{}_2SiC{\equiv}C\text{-}R^2PC{\equiv}C)_n$ ($n \geq 6$)] were produced, **1a–c** were easily isolated by gel permeation chromatography.



These compounds were fully characterized by spectroscopic methods, elemental analysis, and X-ray crystallography. The ^{13}C, ^{29}Si, and ^{31}P NMR spectral data of **1** are summarized in Table 1. In the ^{31}P NMR spectra of **1a** and **1b**, two signals appeared, attributed to the *cis*- and *trans*-isomers. The ratios of these isomers were dependent on the phosphine substitution. For **1a**, the *trans*-isomer was predominant and the *cis*-isomer was trace, whereas for **1b**, *trans*- and *cis*-isomers were present in a 1:1 ratio. In the ^{31}P NMR spectra of **1c**, only one signal appeared, assigned to the *trans*-isomer. In the Raman spectra of **1a–c**, strong peaks due to C≡C stretching vibration modes appeared near 2100 cm^{-1}. These compounds were air-stable, and phosphine oxides (P=O) were not formed for several weeks in the air.

Table 1. ^{13}C, ^{29}Si, ^{31}P NMR, and Raman spectral data for **1**

Compounds	**1a**	**1b**	**1c**
^{13}C NMR δ			
SiC_{sp}	109.7[a]	109.2, 109.2	109.7[a]
PC_{sp}	109.2[a]	109.4, 109.5	108.3[a]
^{29}Si NMR δ	−49.7[a]	−50.1, −50.3	−23.7[a]
^{31}P NMR δ	−61.2[a], −61.4[b]	−35.8[a], −36.5[b]	−61.7[a]
Raman υ/cm^{-1}	2103 (C≡C)	2101 (C≡C)	2095 (C≡C)

[a]*trans*-isomer, [b]*cis*-isomer

trans-Isomers of the ethynylphosphines **1a–c** were characterized by X-ray crystal structure analysis (Figure 1).[7] The asymmetric unit of the crystal of **1b** contains two crystallographically independent molecules A and B, which were nearly identical. The 12-membered rings of **1** were almost planar, analogous to $(Ph_2SiC{\equiv}C)_4$.[2b] In **1a** and **1c**, the dihedral angles between the P1–Si1–P2 and the P1–Si2–P2 mean planes were 177.6 and 176.4°, respectively. Since **1b** has a symmetric center in the middle of the molecule, the corresponding angle was 180°. The average bond lengths of are Si–C(sp), P–C(sp), and C≡C were 1.821, 1.773, and 1.197 Å, respectively, similar to the reported values for $Ph_2Si(C{\equiv}CH)_2$ (Si–C(sp); 1.821 and 1.803 Å, C≡C; 1.210 and 1.204 Å)[5] and $P(C{\equiv}CH)_3$ (P–(sp); 1.757 Å, C≡C;

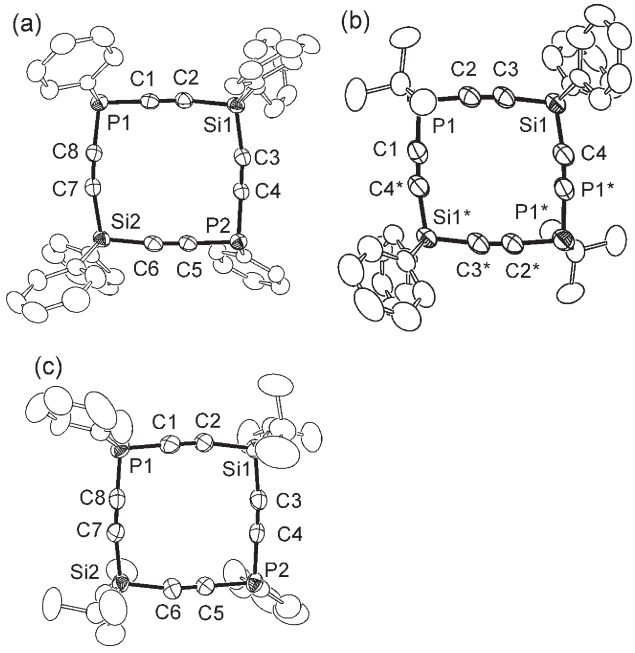


Figure 1. ORTEP drawings of compounds **1** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. (a) **1a**, (b) **1b**, (c) **1c**.

1.168 Å).[8] The average bond angles of Si–C≡C and C(sp)–Si–C(sp) were 171.0 and 103.2°, respectively, which are similar to the reported angles for $(Ph_2SiC{\equiv}C)_4$ (172.7 and 104.3°),[2b] yet smaller than those of the starting material $Ph_2Si(C{\equiv}CH)_2$ (Si–C≡C; 178.04° and 176.74°, C(sp)–Si–C(sp); 108.7°).[5] The average bond angle of C(sp)–P–C(sp) was 96.6°, which was also smaller than those of the model compound $P(C{\equiv}CH)_3$ (102 and 99°).[8] The average bond angle of P–C≡C was 174.5°, similar to those of the model compound $P(C{\equiv}CH)_3$ (169 and 172°).[8] The small angles of C(sp)–Si–C(sp) and C(sp)–P–C(sp) and the deviation from linearity of Si–C≡C and P=C≡C reduce the ring strain.

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6 **1a**: mp ca. 200 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.83 (m, Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 109.2 (d, $^1J_{PC}$ = 17 Hz, SiC≡*C*P of *trans*-**1a**), 109.7 (s, Si*C*≡CP of *trans*-**1a**), 128.2, 130.2, 130.6, 135.0 (Si–Ph of *trans*-**1a**), 128.9 (d, $^3J_{PC}$ = 8.9 Hz, *m*-Ph on P of *trans*-**1a**), 130.2 (s, *p*-Ph on P of *trans*-**1a**), 133.0 (d, $^2J_{PC}$ = 23 Hz, *o*-Ph on P of *trans*-**1a**); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −49.7 (*trans*-**1a**); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −61.2 (*trans*-**1a**), −61.4 (*cis*-**1a**); MS (EI, 70 eV) *m*/*z* 676 (M^+, 37), 520 (M^+–PhP(C≡C)$_2$, 9), 105 (M^+–$Ph_2Si[PhP(C{\equiv}C)_2]_2$–Ph, 100); Raman (cm^{-1}, 532 nm, 36 m·W) 2103 (s), 1578 (m), 989 (m); Anal. Found: C, 78.27; H, 4.63%. Calcd for $C_{44}H_{30}P_2Si_2$ C, 78.08; H, 4.47%. **1b**: mp ca. 200 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26, 1.28 (d, $^3J_{PH}$ = 15 Hz, 18H, *t*-Bu), 7.39–7.42, 7.69–7.71 (m, 20H, Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 27.3, 27.4 (d, $^2J_{PC}$ = 16 Hz, C(CH_3)$_3$), 32.2, 32.2 (s, *C*(CH_3)$_3$), 109.2, 109.2 (d, $^1J_{PC}$ = 5.1 Hz, Si*C*≡CP), 109.4, 109.5 (d, $^1J_{PC}$ = 25 Hz, SiC≡*C*P), 128.1, 130.4, 130.6, 130.9, 131.5, 134.8, 135.0 (Ph of *cis*-**1b**), 128.1, 130.5, 131.2, 134.9 (Ph of *trans*-**1b**); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −50.1, −50.3; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −35.8 (*trans*-**1b**), −36.5 (*cis*-**1b**); MS (FAB, Xe, *m*-NBA) *m*/*z* 637 (M^++1, 37), 105 (M^+–$Ph_2Si[^tBuP(C{\equiv}C)_2]_2$–Ph, 100); Raman (cm^{-1}, 532 nm, 36 m·W) 2101 (s), 1581 (m), 991 (m); Anal. Found: C, 75.51; H, 5.97%. Calcd for $C_{40}H_{38}P_2Si_2$ C, 75.44; H, 6.01%. **1c**: mp ca. 180 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97–1.08 (overlap, *i*-Pr), 7.40–7.42, 7.77–7.83 (m, 10H, Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 11.7, 17.8 (s, *i*-Pr), 108.3 (d, $^1J_{PC}$ = 14 Hz, SiC≡*C*P), 109.7 (s, Si*C*≡CP), 129.0 (d, $^3J_{PC}$ = 8.6 Hz, *m*-Ph), 130.2 (s, *p*-Ph), 130.6, 133.2 (d, $^2J_{PC}$ = 23 Hz, *o*-Ph); ^{29}Si NMR (59.6 MHz, $CDCl_3$) δ −23.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ −61.8; MS (EI, 70 eV) *m*/*z* 540 (M^+, 45), 324 (M^+–Ph–^{i}Pr$_2$Si(C≡C), 100); Raman (cm^{-1}, 532 nm, 36 m·W) 2095 (s), 1576 (m), 989 (m); Anal. Found: C, 70.90; H, 7.19%. Calcd for $C_{32}H_{38}P_2Si_2$ C, 71.07; H, 7.08%.

7 Single crystals of **1a**–**c** were grown from chloroform-methanol solvent mixtures at room temperature. Intensity data was collected on a Bruker SMART 1000 CCD system[9] using graphite-monochromatized Mo *K*α radiation (λ = 0.71073 Å). Integration was performed using the program SAINT,[10] and absorption correction was calculated empirically using the program SADABS.[11] Subsequent calculations were carried out using SHELXTL.[12] Crystal data for **1a**: $C_{44}H_{30}P_2Si_2$, *M*r = 676.80, triclinic, space group $P\bar{1}$, a = 8.7245(17) Å, b = 14.192(3) Å, c = 15.927(3) Å, α = 70.452(4)°, β = 77.841(4)°, γ = 75.974(4)°, V = 1784.8(6) Å^3, Z = 2, D_{calcd} = 1.259 Mg/m^3, R = 0.0563, R_w = 0.1335 based on 4142 observed reflections [$I > 2\sigma(I)$] and 433 variable parameters. Crystal data for **1b**: $C_{40}H_{38}P_2Si_2$, *M*r = 636.82, monoclinic, space group $P2_1/c$, a = 11.559(5) Å, b = 17.842(8) Å, c = 16.739(7) Å, β = 91.088(8)°, V = 3451(3) Å^3, Z = 4, D_{calcd} = 1.226 Mg/m^3, R = 0.0548, R_w = 0.1335 based on 2250 observed reflections [$I > 2\sigma(I)$] and 403 variable parameters. Crystal data for **1c**: $C_{32}H_{38}P_2Si_2$, *M*r = 540.74, monoclinic, space group $P2_1$, a = 8.512(3) Å, b = 19.841(6) Å, c = 9.772(3) Å, β = 97.803(5)°, V = 1635.3(9) Å^3, Z = 2, D_{calcd} = 1.098 Mg/m^3, R = 0.0746, R_w = 0.1713 based on 4084 observed reflections [$I > 2\sigma(I)$] and 333 variable parameters. Crystallographic data obtained by structural analysis for **1a**–**c** has been submitted to the Cambridge Crystallographic Data Centre (CCDC No. 191173-191175). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 (1223) 336-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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