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Phosphines Bearing Alkyne Substituents: Synthesis and Hydrophosphination Polymerization

Sharonna Greenberg and Douglas W. Stephan*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

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A synthetic route is described for a series of phosphines bearing pendant alkyne substituents, from the conversion of $BrC_6H_2R_2C{\equiv}CR'$ (R = Me, *i*-Pr; R′ = Ph, $SiMe_3$) to $[(\mu\text{-Br})Cu(Et_2N)_2PC_6H_2R_2C{\equiv}CR']_2$ and subsequently to $Cl_2PC_6H_2R_2C{\equiv}CR'$ and $H_2PC_6H_2R_2C{\equiv}CR'$. Lithiation and subsequent alkylation yield the secondary phosphines $R(H)PC_6H_2(i\text{-}Pr)_2C{\equiv}CPh$ (R = CH_2*i*-Pr, CH_2Ph). Intermolecular hydrophosphination−polymerization is used to prepare the polymeric species $[RPC_6H_2(i\text{-}Pr)_2CH{=}CPh]_n$, which can then be sulfurized to give $[RP(S)C_6H_2(i\text{-}Pr)_2CH{=}CPh]_n$. The polymeric products were characterized by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry and gel permeation chromatography. These data indicate a degree of polymerization (DP_n) of up to 60. Discussion of the mechanism is augmented with gas-phase density functional theory calculations.

Introduction

Phosphines are ubiquitous as ligands in homogeneous catalysis. More recently, the incorporation of organophosphorus fragments into polymers has also drawn attention.[1−4] These efforts are motivated by recognized properties of phosphorus-based compounds, including inherent thermal and oxidative stability as well as flame retardancy.[5] Perhaps the most successful phosphorus-based polymers to date are poly(phosphazene)s and poly(heterophosphazene)s,[5] which have been commercialized. In comparison to their phosphorus(V) counterparts, phosphorus(III) polymers are less well-developed but offer attractive applications as catalyst supports and π-conjugated materials.[1,4] Toward such targets, Manners and co-workers have established thermal and living anionic polymerization routes to poly(ferrocenylphosphine)s,[6,7] as well as ring-opening polymerization of strained cyclic phosphirenes.[8] Gates and co-workers have extensively studied the addition polymerization of phosphaalkenes to prepare poly(methylenephosphine)s,[9,10] which can also occur in a living fashion.[11,12] In parallel studies, Gates *et al.* and Protasiewicz *et al.* examined the condensation polymerization of bifunctional phosphines with acyl chlorides or aldehydes to give π-conjugated poly(*p*-phenylenephosphaalkene)s,[13−15] the phosphorus analogue of poly(phenylenevinylene). Finally, poly(arylphosphine)s are prepared by metal-catalyzed cross-coupling reactions of primary phosphines and dihaloarenes.[16]

Catalytic activation of P−H bonds presents another strategy to phosphorus-containing materials. For example, linear and unique cyclic P−P-bonded oligomers are obtained by metal-catalyzed dehydrocoupling of P−H bonds,[17,18] while phosphorus- and boron-containing polymers are synthesized by dehydrocoupling of primary phosphine−borane adducts.[19−21] Catalytic P−H bond activation can also be

*To whom correspondence should be addressed. E-mail: dstephan@chem.utoronto.ca.

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used to create new P−C bonds, by hydrophosphination of organic unsaturates.[22,23] In this regard, a variety of catalysts designed to mediate such hydrophosphinations have been explored, including bases,[24,25] transition metals,[25−27] lanthanides,[28] group II elements,[29] radical initiators[30−35] and radiation.[31,32,36]

Targeting the use of hydrophosphination as a vehicle to phosphorus-containing polymers, we noted that maximal polymerization via a step-growth process requires precise control of the stoichiometry. This dependence is illustrated by the Carothers equation (eq 1), where even if the extent of the reaction (p) is high, the number-average degree of polymerization (DP_n) is dramatically reduced when the stoichiometric ratio (r) deviates from unity.

$$DP_n = \frac{1+r}{1+r-2rp} \quad (1)$$

This consideration prompted interest in bifunctional precursors that incorporate secondary phosphine and alkyne fragments because such materials provide precise 1:1 stoichiometry of the two reacting functional groups. While bifunctional phosphine−alkynes have been utilized for intramolecular hydrophosphination−cyclization,[28,37] we sought to develop this chemistry as a route towards polymers and therefore targeted molecules where only intermolecular reactivity is possible. In this manuscript, the synthesis of secondary arylphosphines with *para*-substituted alkyne fragments is detailed. Catalytic hydrophosphination of these materials is examined experimentally and the discussion is augmented with density functional theory (DFT) calculations. A preliminary communication of this chemistry has appeared.[38]

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques or a Vacuum Atmospheres inert-atmosphere glovebox. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{7}Li{^{1}H}, and ^{29}Si NMR spectra were acquired on a Bruker Avance 300 MHz spectrometer, a Varian Mercury 300 MHz spectrometer, or a Varian Mercury 400 MHz spectrometer. ^{1}H NMR resonances were referenced internally to the residual protonated solvent resonances. ^{13}C NMR resonances were referenced internally to the deuterated solvent resonances. ^{31}P NMR resonances were referenced externally to H_3PO_4. ^{7}Li resonances were referenced externally to LiCl. ^{1}H−^{29}Si NMR heteronuclear multiple-bond correlation experiments were carried out using conventional pulse sequences and referenced externally to $SiMe_4$. Mass spectra were recorded with a VG 70-250S mass spectrometer in positive ion electron impact (EI) mode. IR spectra were recorded using a Perkin-Elmer Spectrum One Fourier transform IR (FT-IR) spectrometer at 25 °C, either as a Nujol mull or deposited onto the NaCl plate from a CH_2Cl_2 or C_6D_6 solution. Elemental analyses were performed using a Perkin-Elmer 2400 C/H/N analyzer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired using a Waters Micromass MALDI micro MX. Spectra were acquired using the following conditions: positive-polarity mode, reflectron flight path, 12 kV flight tube voltage, 10 Hz laser firing rate, 10 shots per spectrum, pulse 1950 V, and detector 2350 V. The instrument was calibrated using poly(ethylene glycol). The matrix solution consisted of 6 mg of cyano-4-hydroxycinnamic acid in 1 mL of a 6:3:1 mixture of MeCN/MeOH/H_2O plus 1 drop of CF_3COOH. The analyte solution consisted of 3−5 mg/mL of polymer in tetrahydrofuran (THF). The sample was prepared using the layer method,[39] by spotting 1 μL of matrix onto the sample plate followed by 1 μL of the analyte. Polymer molecular weights were determined by gel permeation chromatography (GPC) using one of two instruments. (1) Absolute and relative molecular weights were determined by triple-detection GPC using a Waters liquid chromatograph equipped with a Waters 515 HPLC pump, a Waters 717 plus autosampler, Waters Styragel columns (4.6 × 300 mm), HR2 × 2 and HR4, a Waters 2410 differential refractometer (refractive index detector, λ = 940 nm), a Wyatt tristar miniDAWN (laser light scattering detector, λ = 690 nm), and a Wyatt ViscoStar viscometer. A flow rate of 0.5 mL/min was used, and samples were dissolved in THF (*ca.* 2 mg/mL) and prepared in air. (2) Relative molecular weights were determined using a Waters liquid chromatograph equipped with a Waters 1515 HPLC pump, Waters Styragel columns (4.6 × 300 mm), HR 4E × 3, and a Waters 2414 differential refractometer (refractive index detector, ν = 690 nm). A flow rate of 1.0 mL/min was used, and samples were dissolved in THF (*ca.* 2 mg/mL) and prepared in air. Polystyrene standards were purchased from Polymer Laboratories, with molecular weights varying between 580 and 283 300 g/mol.

Materials. Anhydrous solvents including toluene, pentane, hexanes, diethyl ether, THF, and dichloromethane were purchased from Aldrich and purified using Grubbs-type column systems manufactured by Innovative Technology.[40] C_6D_6 and THF-d_8 were purchased from Cambridge Isotopes Laboratories, vacuum-distilled from sodium/benzophenone, and freeze−pump−thaw-degassed (×3). Diethylamine was purchased from Aldrich and degassed by sonication prior to use. Hyflo Super Cel (Celite) was purchased from Aldrich and dried for at least 12 h in a vacuum oven or on the Schlenk line prior to use. Molecular sieves of 4 Å were purchased from Aldrich and dried at 100 °C under vacuum. *trans*-$Pd(PPh_3)_2Cl_2$ was purchased from Strem; all other reagents were purchased from Aldrich. Phenylacetylene was vacuum-distilled from CaH_2 and stored in the dark at −35 °C. *n*-BuLi (1.6 M hexanes) and *t*-BuLi (1.7 M pentane) were titrated for concentration determination prior to use.[41] All other starting materials were used as received.

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1-Bromo-2,6-dimethyl-4-iodobenzene,[42] 1-bromo-2,6-diisopropyl-4-iodobenzene,[43] and $ClP(NEt_2)_2$[44] were synthesized according to literature procedures.

Synthesis of $BrC_6H_2R_2C{\equiv}CR'$ (1, R = Me, R′ = Ph; 2, R = *i*-Pr, R′ = Ph; 3, R = *i*-Pr, R′ = $SiMe_3$). All compounds were prepared in a similar manner; thus, only the synthesis of **2** is reported. To a solution of 1-bromo-2,6-diisopropyl-4-iodobenzene (4.440 g, 12.10 mmol) in 100 mL of $HNEt_2$ was added 2.5 mol % *trans*-$Pd(PPh_3)_2Cl_2$ (211 mg, 0.301 mmol) and 1 mol % CuI (24 mg, 0.13 mmol). The yellow mixture was stirred for 10 min, and 1.3 equiv of freshly distilled HC≡CPh (1.602 g, 15.68 mmol) was added by syringe. The mixture was allowed to stir at room temperature overnight, and then the solvent was removed *in vacuo* and the residue extracted with Et_2O, filtered through Celite, and evacuated once again.

1. Yield: 99%. ^{1}H NMR (C_6D_6): δ 7.57−7.54 (m, 2H, *o*-Ph), 7.11 (s, 2H, C_6H_2), 7.06−7.00 (m, 3H, *m*- and *p*-Ph), 2.13 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.1 (*ipso*-*C*), 133.1 (Ar), 132.2 (Ar), 131.9 (Ar), 129.6 (Ar), 129.1 (Ar), 124.3 (Ar), 122.6 (Ar), 90.7 (C≡C), 89.9 (C≡C), 24.0 (Me). EI-MS (*m*/*z*): 286 and 284 (100% and 97%) $[M]^+$; 205 (15%) $[M]^+ - Br$. HRMS: $C_{16}H_{13}{}^{79}Br$ mass 284.0200; calcd mass 284.0201 (fit −0.4 ppm). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2213 cm^{-1} (weak). Anal. Calcd for $C_{16}H_{13}Br$: C, 67.39; H, 4.59. Found: C, 67.74; H, 4.91.

2. Yield: 98%. ^{1}H NMR (C_6D_6): δ 7.58−7.54 (m, 2H, *o*-Ph), 7.46 (s, 2H, C_6H_2), 7.02−6.99 (m, 3H, *m*- and *p*-Ph), 3.50 (septet, 2H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 1.07 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 148.6 (*ipso*-*C*), 131.9 (Ar), 128.8 (Ar), 128.6 (Ar), 127.4 (Ar), 123.8 (Ar), 123.3 (Ar), 90.2 (C≡C), 90.1 (C≡C), 33.9 (*i*-Pr), 22.8 (*i*-Pr). EI-MS (*m*/*z*): 342 and 340 (100% and 99%) $[M]^+$; 327 and 325 (48% and 52%) $[M]^+ - Me$. HRMS: $C_{20}H_{21}{}^{79}Br$ mass 340.0829; calcd mass 340.0827 (fit 0.6 ppm). FT-IR (Nujol mull): ν(C≡C) 2210 cm^{-1} (weak). Anal. Calcd for $C_{20}H_{21}Br$: C, 70.39; H, 6.20. Found: C, 70.31; H, 6.17. Crystals suitable for X-ray crystallography were obtained from the oil upon standing.

3. Yield: 91%, ^{1}H NMR (C_6D_6): δ 7.42 (s, 2 H, C_6H_2), 3.44 (septet, 2H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 0.99 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 0.26 (s, 9H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 148.6 (*ipso*-*C*), 123.2 (Ar), 105.9 (*C*≡CSiMe$_3$), 94.7 (C≡*C*SiMe$_3$), 33.9 (*i*-Pr), 22.7 (*i*-Pr), 0.0 ($SiMe_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −17.8 (s). EI-MS (*m*/*z*): 338 and 336 (32% and 33%) $[M]^+$; 323 and 321 (95% and 100%) $[M]^+ - Me$. HRMS: $C_{17}H_{25}{}^{79}BrSi$ mass 336.0910; calcd mass 336.0909 (fit 0.3 ppm). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2160 cm^{-1} (sharp). Anal. Calcd for $C_{17}H_{25}BrSi$: C, 60.52; H, 7.47. Found: C, 60.38; H, 7.40.

Synthesis of $[(\mu\text{-}Br)Cu(Et_2N)_2PC_6H_2R_2C{\equiv}CR']_2$ (4, R = Me, R′ = Ph; 5, R = *i*-Pr, R′ = Ph; 6, R = *i*-Pr, R′ = $SiMe_3$). All compounds were prepared in a similar manner; thus, only the synthesis of **5** is reported. A dark-red solution of **2** (6.154 g, 18.03 mmol) in 300 mL of THF was cooled to −78 °C, and 1.9 equiv of *t*-BuLi (1.7 M pentane, 20.2 mL, 34.34 mmol) was added via syringe over ca. 30 min, yielding a dark-brown mixture. The mixture was stirred at −78 °C for 3 h, then the cold bath was removed, and the dark-purple mixture was stirred at room temperature for 1 h. CuCl (2.142 g, 21.64 mmol, 1.2 equiv) was added at room temperature, and the mixture was then cooled again to −78 °C, whereupon $ClP(NEt_2)_2$ was added (3.80 g, 18.0 mmol) via syringe over ca. 15 min. The mixture was stirred overnight while warming to room temperature. All volatile materials were removed *in vacuo* to give a green-brown residue, which was extracted with 100 mL of toluene and filtered through Celite, and all volatiles were removed *in vacuo*. The residue was washed with 50 mL of toluene to give a beige solid, which was isolated and dried on a frit. An additional portion was isolated from the filtrate by removing the toluene *in vacuo* and adding 20 mL of pentane.

4. Yield: 24%. ^{1}H NMR (C_6D_6): δ 7.60−7.57 (m, 2H, *o*-Ph), 7.21 (m, 2H, C_6H_2), 7.03−7.00 (m, 3H, *m*- and *p*-Ph), 2.96−2.86 (m, 8H, $N(CH_2Me)_2$), 2.55 (s, 6H, Me), 0.95 (t, 12H, $N(CH_2Me)_2$, $^3J_{H-H}$ = 7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 86.2. $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 140.9 (d, *ipso*-*C*, $^1J_{P-C}$ = 13 Hz), 133.5 (s, Ar), 132.0 (s, Ar), 128.7 (s, Ar), 124.2 (s, Ar), 124.0 (s, Ar), 91.0 (s, C≡C), 90.1 (s, C≡C), 44.2 (d, $P(N(CH_2Me)_2)_2$, $^2J_{P-C}$ = 11 Hz), 22.6 (d, $P(N(CH_2Me)_2)_2$, $^3J_{P-C}$ = 11 Hz), 14.9 (s, Me). EI-MS (70 eV, *m*/*z*): 380 (35%) $[M]^+$, 308 (90%) $[M - N(CH_2Me)_2]^+$, 237 (100%) $[M - (N(CH_2Me)_2)_2 + H]^+$. HRMS (70 eV, EI): calcd for $C_{24}H_{33}N_2P$ 380.2381; found 380.2389 (fit 2.1 ppm). FT-IR (Nujol mull): ν(C≡C) 2210 cm^{-1} (weak). Anal. Calcd for $C_{24}H_{33}BrCuN_2P$: C, 55.02; H, 6.35; N, 5.35. Found: C, 54.87; H, 6.54; N 5.26. Crystals suitable for X-ray diffraction were obtained from the oil upon standing.

5. Yield: 76%. ^{1}H NMR (C_6D_6): δ 7.65−7.64 (m, 2H, C_6H_2), 7.60−7.57 (m, 2H, *o*-Ph), 7.01−6.98 (m, 3H, *m*- and *p*-Ph), 4.30−4.24 (m, 2H, (*i*-Pr), 3.15−2.95 (m, 8H, $N(CH_2Me)_2$), 1.31 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 1.01 (t, 12H, $N(CH_2Me)_2$, $^3J_{H-H}$ = 7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 88.9. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.3 (d, *ipso*-*C*, $^1J_{P-C}$ = 12 Hz), 132.0 (s, Ar), 131.6 (s, Ar), 128.7 (s, Ar), 128.5 (s, Ar), 127.2 (s, Ar), 125.3 (s, Ar), 124.0 (s, Ar), 91.0 (s, C≡C), 90.4 (s, C≡C), 43.4 (d, $P(N(CH_2Me)_2)_2$, $^2J_{P-C}$ = 12 Hz), 30.2 (s, *i*-Pr), 28.4 (d, $P(N(CH_2Me)_2)_2$, $^3J_{P-C}$ = 13 Hz), 25.8 (s, *i*-Pr). EI-MS (*m*/*z*): 436.3 (7%) $[M]^+ - CuBr$; 364.2 (100%) $[M]^+ - CuBr - NEt_2$; 292.1 (28%) $[M]^+ - CuBr - 2NEt_2$; 175.1 (37%) $[P(NEt_2)_2]^+$. HRMS: $C_{28}H_{41}N_2P$ mass 436.3010; calcd mass 436.3007 (fit 0.7 ppm). FT-IR (Nujol mull): ν(C≡C) 2209 cm^{-1} (weak). Anal. Calcd for $C_{28}H_{41}BrCuN_2P$: C, 57.98; H, 7.12; N, 4.83. Found: C, 58.35; H, 7.08; N, 5.24. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution.

6. Yield: 20%. ^{1}H NMR (C_6D_6): δ 7.57 (d, 2H, C_6H_2, $^4J_{P-H}$ = 3 Hz), 4.18 (d of septets, 2H, (*i*-Pr, $^3J_{H-H}$ = 7 Hz, $^4J_{P-H}$ = 3 Hz), 3.10−2.91 (m, 8H, $N(CH_2Me)_2$), 1.21 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 0.98 (t, 12H, $N(CH_2Me)_2$, $^3J_{H-H}$ = 7 Hz), 0.28 (s, 9H, $Si(Me)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 85.0. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.1 (d, *ipso*-*C*, $^1J_{P-C}$ = 13 Hz), 132.2 (s, Ar), 131.9 (s, Ar), 125.0 (s, Ar), 106.3 (s, *C*≡CSiMe$_3$), 95.2 (s, C≡*C*SiMe$_3$), 43.3 (d, $P(N(CH_2Me)_2)_2$, $^2J_{P-C}$ = 11 Hz), 28.3 (d, *i*-Pr, $^3J_{P-C}$ = 13 Hz), 25.6 (s, *i*-Pr), 14.5 (s, $P(N(CH_2Me)_2)_2$), 0.0 (s, $SiMe_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −17.8. EI-MS (70 eV; *m*/*z*): 432 (7%) $[M]^+$, 360 (100%) $[M - N(CH_2Me)_2]^+$, 330 (12%) $[M - N(CH_2Me)_2 - MeCH_2 - H]^+$, 287 (39%) $[M - (N(CH_2Me)_2)_2 - H]^+$, 175 (19%) $[P(N(CH_2Me)_2)_2]^+$. HRMS (70 eV, EI): calcd for $C_{25}H_{45}N_2PSi$ 432.3090; found 432.3097 (fit 1.6 ppm). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2157 cm^{-1} (sharp). Anal. Calcd for $C_{25}H_{45}BrCuN_2PSi$: C, 52.12; H, 7.78; N, 4.86. Found: C, 52.14; H, 7.89; N 4.91.

Synthesis of $Cl_2PC_6H_2R_2C{\equiv}CR'$ (7, R = Me, R′ = Ph; 8, R = *i*-Pr, R′ = Ph; 9, R = *i*-Pr, R′ = $SiMe_3$). All compounds were prepared in a similar manner; thus, only the synthesis of **8** is reported. A yellow solution of **5** (9.161 g, 15.79 mmol) in 150 mL of Et_2O/toluene was cooled in an ice−water bath, and HCl(g) was bubbled through the solution for 15−20 min, during which time a fine white precipitate was generated. The yellow solution was filtered through a Schlenk frit containing Celite, 75 mL of toluene was added to the original flask, and the suspension was bubbled with HCl(g) for a further 3 min. This solution was also filtered through the Schlenk frit, and the precipitate was extracted with a further 50 mL of toluene. All volatiles were removed *in vacuo*, yielding a yellow oil or solid.

7. Yield: 81%. ^{1}H NMR (C_6D_6): δ 7.56−7.52 (m, 2H, *o*-Ph), 7.06−7.00 (m, 5H, C_6H_2 and *m*- and *p*-Ph), 2.40 (d, 6H, Me,

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$^3J_{P-C}$ = 4 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 165.2. $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 143.7 (d, *ipso-C*, $^1J_{P-C}$ = 26 Hz), 132.8 (s, Ar), 132.1 (s, Ar), 129.0 (s, Ar), 128.8 (s, Ar), 123.3 (s, Ar), 92.7 (s, C≡C), 89.1 (s, C≡C), 21.3 (d, Me, $^3J_{P-C}$ = 26 Hz). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2212 cm^{-1} (sharp). Anal. Calcd for $C_{16}H_{13}Cl_2P$: C, 62.57; H, 4.27. Found: C, 63.23; H, 4.79. Crystals suitable for X-ray diffraction were obtained from the oil upon standing.

8. Yield: 89%. ^1H NMR (C_6D_6): δ 7.56−7.52 (m, 4H, *o*-Ph and C_6H_2), 6.99−6.97 (m, 3H, *m*- and *p*-Ph), 4.12−4.06 (m, 2H, *i*-Pr), 1.12 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 162.7. $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 155.1 (d, *ipso-C*, $^1J_{P-C}$ = 23 Hz), 135.6 (s, Ar), 134.6 (s, Ar), 132.1 (s, Ar), 129.1 (s, Ar), 128.8 (s, Ar), 123.2 (s, Ar), 92.6 (s, C≡C), 89.6 (s, C≡C), 30.9 (d, *i*-Pr, $^3J_{P-C}$ = 27 Hz), 24.4 (s, *i*-Pr). EI-MS (*m*/*z*): 362.1 (27%) $[M]^+$; 327.1 (100%) $[M]^+ - Cl$. HRMS: $C_{20}H_{21}Cl_2P$ mass 362.0753; calcd mass 362.0758 (fit −1.4 ppm). FT-IR (Nujol mull): ν(C≡C) 2209 cm^{-1} (sharp). Anal. Calcd for $C_{20}H_{21}Cl_2P$: C, 66.13; H, 5.83. Found: C, 66.32; H, 5.90. Crystals suitable for X-ray diffraction were obtained from the oil upon standing.

9. Yield: 91.3%. ^1H NMR (C_6D_6, 25 °C, 300 MHz): δ 7.48 (d, 2H, C_6H_2, $^4J_{P-H}$ = 3 Hz), 4.03 (m, 2H, *i*-Pr), 1.02 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 0.26 (s, 9H, $Si(Me)_3$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 162.5. $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 155.2 (d, *ipso-C*, $^1J_{P-C}$ = 22 Hz), 129.3 (s, Ar), 125.7 (s, Ar), 105.3 (s, C≡C), 97.4 (s, C≡C), 30.9 (d, *i*-Pr, $^3J_{P-C}$ = 27 Hz), 24.3 (s, *i*-Pr), −0.09 (s, $Si(Me)_3$. $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −17.4 (s). EIMS (70 eV; *m*/*z*): 358 (48%) $[M]^+$, 343 (79%) $[M-Me]^+$, 323 (100%) $[M-Cl]^+$, 307 (35%) $[M-Me-Cl-H]^+$. HRMS (70 eV, EI): calcd for $C_{17}H_{25}Cl_2PSi$ 358.0840; found 358.0823 (fit −4.7 ppm). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2160 cm^{-1} (sharp). Anal. Calcd for $C_{17}H_{25}Cl_2PSi$: C, 56.82; H, 7.01. Found: C, 56.85; H, 6.93.

Synthesis of $H_2PC_6H_2R_2C{\equiv}CR'$ (10, R = Me, R′ = Ph; 11, R = *i*-Pr, R′ = Ph; 12, R = *i*-Pr, R′ = $SiMe_3$). All compounds were prepared in a similar manner; thus, only the synthesis of **11** is reported. An orange solution of **8** (1.760 g, 4.845 mmol) in 20 mL of Et_2O and 20 mL of toluene was added dropwise via cannula over 30 min to a −78 °C slurry of $LiAlH_4$ (1.014 g, 26.72 mmol, 5.5 equiv) in 70 mL of Et_2O. The mixture was stirred overnight while warming to 25 °C. The brown mixture was cooled again in an ice−water bath, and 10 mL of degassed water was added dropwise, resulting in gas formation. The organic layer was transferred by cannula to a flask containing $MgSO_4$. The aqueous layer was extracted with two portions of 20 mL of Et_2O, and all organic portions were combined in the flask containing $MgSO_4$. The yellow solution was then transferred via cannula to a Schlenk frit and filtered. Upon removal of all volatiles *in vacuo*, a yellow residue was obtained.

10. Yield: 44%. ^1H NMR (C_6D_6): δ 7.58−7.56 (m, 2H, *o*-Ph), 7.21 (s, 2H, C_6H_2), 7.04−6.98 (m, 3H, *m*- and *p*-Ph), 3.50 (d, 2H, PH_2, $^1J_{P-H}$ = 207 Hz), 2.03 (d, 6H, Me, $^4J_{P-H}$ = 9 Hz). ^{31}P NMR (C_6D_6): δ −153.8 (t, $^1J_{P-H}$ = 207 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 141.0 (d, *ipso*-C, $^1J_{P-C}$ = 11 Hz), 131.9 (s, Ar), 130.9 (s, Ar), 124.1 (s, Ar), 122.7 (s, Ar), 90.2 (s, C≡C), 22.9 (d, Me, $^3J_{P-C}$ = 10 Hz). EI-MS (*m*/*z*): 238.1 (100%) $[M]^+$; 223.1 (60%) $[M]^+-Me$. HRMS: $C_{16}H_{15}P$ mass 238.0911; calcd mass 238.0902 (fit −3.8 ppm). FT-IR (Nujol mull): ν(C≡C) 2211 cm^{-1} (weak), ν(P−H) 2306 cm^{-1} (sharp). Despite repeated attempts, suitable elemental analysis could not be obtained.

11. Yield: 70% ^1H NMR (C_6D_6): δ 7.60−7.57 (m, 2H, *o*-Ph), 7.54 (d, 2H, C_6H_2, $^4J_{P-H}$ = 2 Hz), 7.00−6.89 (m, 3H, *m*- and *p*-Ph), 3.77 (d, 2H, PH_2, $^1J_{P-H}$ = 206 Hz), 3.23 (d of septets, 2H, *i*-Pr, $^3J_{H-H}$ = 7 Hz, $^4J_{P-H}$ = 3 Hz), 1.08 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz). ^{31}P NMR (C_6D_6): δ −156.3 (t, $^1J_{P-H}$ = 207 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 152.2 (d, *ipso-C*, $^1J_{P-C}$ = 9 Hz), 132.0 (s, Ar), 128.7 (s, Ar), 126.5 (s, Ar), 124.1 (s, Ar), 123.9 (s, Ar) 90.9 (s, C≡C), 90.3 (s, C≡C), 33.1 (d, *i*-Pr, $^3J_{P-C}$ = 11 Hz), 23.4 (s, *i*-Pr). EI-MS (*m*/*z*): 294.2 (100%) $[M]^+$; 251.1 (83%) $[M]^+ - i$-Pr. HRMS: $C_{20}H_{23}P$ mass 294.1542; calcd mass 294.1537 (fit 1.74 ppm). FT-IR (25 °C, Nujol mull): ν(C≡C) 2209 cm^{-1} (weak), ν(P−H) 2315 cm^{-1} (br). Anal. Calcd for $C_{20}H_{23}P$: C, 81.60; H, 7.88. Found: C, 81.10; H, 8.12. Crystals suitable for X-ray diffraction could be obtained from the oil upon standing.

12. Yield: 55%. ^1H NMR (C_6D_6): δ 7.50 (d, 2H, C_6H_2, $^4J_{P-H}$ = 2 Hz), 3.72 (d, 2H, PH_2, $^1J_{P-H}$ = 207 Hz), 3.23 (d of septets, 2H, *i*-Pr, $^3J_{H-H}$ = 7 Hz, $^4J_{P-H}$ = 3 Hz), 1.01 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 0.28 (s, 9H, $Si(Me)_3$). ^{31}P NMR (C_6D_6): δ −156.2 (t, $^1J_{P-H}$ = 207 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 152.1 (d, *ipso-C*, $^1J_{P-C}$ = 9 Hz), 128.3 (s, Ar), 126.7 (s, Ar), 123.7 (s, *quat*-Ar), 106.7 (s, *C*≡CSiMe$_3$), 94.5 (s, C≡*C*SiMe$_3$), 33.1 (d, *i*-Pr, $^3J_{P-C}$ = 11 Hz), 23.3 (s, *i*-Pr), 0.127 (s, $Si(Me)_3$). $^{29}Si\{^1H\}$ NMR (C_6D_6): δ −18.2 (s). EI-MS (70 eV; *m*/*z*): 290 (100%) $[M]^+$, 275 (72%) $[M-Me]^+$. HRMS (70 eV, EI): calcd for $C_{17}H_{27}P$ 290.1620; found 290.1606 (fit −4.8 ppm). FT-IR (evaporation of a CH_2Cl_2 solution): ν(C≡C) 2158 cm^{-1} (sharp), ν(P−H) 2320 cm^{-1} (br). Anal. Calcd for $C_{17}H_{27}PSi$: C, 70.30; H, 9.37. Found: C, 70.58; H, 8.73.

Generation of Compound $Li(THF)_xHPC_6H_2$-*i*-$Pr_2C{\equiv}CPh$ (13). Compound **11** (200 mg, 0.680 mmol) was placed in a 20 mL scintillation vial inside a brass plate designed to surround the bottom and walls of the vial. A total of 10 mL of THF was added, and the entire assembly was cooled to −35 °C. *n*-BuLi in pentane (0.44 mL of 1.7 mol/L, 0.75 mmol, 1.1 equiv) was added with stirring, generating a red solution. The entire assembly was warmed to room temperature over 4 h, and then all volatiles were removed *in vacuo*, giving a red residue. Yield: 350 mg (95%). ^1H NMR (C_6D_6): δ 7.58−7.54 (m, 4H, *o*-Ph and C_6H_2), 7.03−6.94 (m, 3H, *m*- and *p*-Ph), 3.90 (m, 2H, *i*-Pr), 3.52 (m, ca. 7.6H, THF), 2.92 (d, 2H, PH_2, $^1J_{P-H}$ = 182 Hz), 1.41 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 7 Hz), 1.37 (m, ca. 7.6H, THF). ^{31}P NMR (C_6D_6): δ −162.5 (d, $^1J_{P-H}$ = 182 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.8 (d, *ipso-C*, $^1J_{P-C}$ = 6 Hz), 132.0 (s, Ar), 131.7 (s, Ar), 127.3 (s, Ar), 125.5 (s, Ar), 124.9 (s, Ar), 114.4 (s, Ar), 93.8 (s, C≡C), 88.2 (s, C≡C), 68.1 (THF), 33.0 (d, *i*-Pr, $^3J_{P-C}$ = 14 Hz), 25.7 (THF), 23.9 (s, *i*-Pr). $^7Li\{^1H\}$ NMR (C_6D_6): δ −0.7.

Synthesis of $R(H)PC_6H_2$(*i*-$Pr)_2C{\equiv}CPh$ [R = CH_2*i*-Pr (14), CH_2Ph (15)]. These compounds were prepared in a similar manner; thus, only the synthesis of **14** is reported. Compound **13** was generated as above. The entire assembly was warmed to 25 °C over 4 h, then $BrCH_2$*i*-Pr (88 mg, 0.64 mmol, 1.0 equiv), as well as 4 mL of toluene, was added dropwise, and the reaction mixture was stirred overnight. The orange-brown mixture was filtered through Celite, and all volatiles were removed *in vacuo*, yielding a brown oil.

14. Yield: 179 mg. ^1H NMR (C_6D_6): δ 7.62−7.57 (m, 4H, *o*-Ph and C_6H_2), 7.03−6.97 (m, 3H, *m*- and *p*-Ph), 4.36 (ddd, 1H, P*H*, $^1J_{P-H}$ = 212 Hz, $^3J_{H-H}$ = 9 Hz, $^3J_{H-H}$ = 6 Hz), 3.78−3.67 (m, 2H, Ar-*i*-Pr), 1.86−1.76 (m, 1H, PCH_aH_b), 1.74−1.64 (m, 1H, PCH_2-*i*-Pr), 1.49−1.37 (m, 1H, PCH_aH_b), 1.20 (d, 6H, $ArCH(Me)_a(Me)_b$, $^3J_{H-H}$ = 7 Hz), 1.13 (d, 6H, $ArCH(Me)_a(Me)_b$, $^3J_{H-H}$ = 7 Hz), 0.97 (d, 3H, $PCH_2CH(Me)_a(Me)_b$, $^3J_{H-H}$ = 4 Hz), 0.94 (d, 3H, $PCH_2CH(Me)_a(Me)_b$, $^3J_{H-H}$ = 4 Hz). ^{31}P NMR (C_6D_6): δ −99.0 (d, $^1J_{P-H}$ = 212 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 153.5 (d, *ipso-C*, $^1J_{P-C}$ = 11 Hz), 133.9 (s, Ar), 133.6 (s, Ar), 132.0 (s, Ar), 128.7 (s, Ar), 126.9 (s, Ar), 124.6 (s, Ar), 124.1 (s, Ar), 90.9 (s, C≡C), 90.4 (s, C≡C), 34.2 (d, PCH_2-*i*-Pr, $^1J_{P-C}$ = 13 Hz), 33.0 (d, Ar-*i*-Pr, $^3J_{P-C}$ = 13 Hz), 28.4 (d, PCH_2-*i*-Pr, $^2J_{P-C}$ = 12 Hz), 24.7 (s, $ArCH(Me)_a(Me)_b$), 24.3 (s, $ArCH(Me)_a(Me)_b$), 23.94 (s, PCH_2-*i*-Pr), 23.86 (s, PCH_2-*i*-Pr). EI-MS (*m*/*z*): 350.2 (37%) $[M]^+$; 293.1 (100%) $[M]^+-CH_2$-*i*-Pr. HRMS: $C_{24}H_{31}P$ mass 350.2164; calcd mass 350.2163 (fit 0.3 ppm). FT-IR (Nujol mull): ν(C≡C) 2209 cm^{-1} (sharp), ν(P−H) 2320 cm^{-1} (br). Despite repeated attempts, suitable elemental analysis could not be obtained.

15. Yield: 50%. ^1H NMR (C_6D_6): δ 7.58−7.56 (m, 4H, Ar*H*), 7.03−6.91 (m, 8H, Ar*H*), 4.54 (dt, 1H, P*H*, $^1J_{P-H}$ = 214 Hz, $^3J_{H-H}$ = 7 Hz), 3.50−3.44 (m, 2H, *i*-Pr), 2.89 (m, 2H, PCH_2Ph), 1.09 (d, 12H, *i*-Pr, $^3J_{H-H}$ = 6 Hz). ^{31}P NMR (C_6D_6): δ −80.9 (d, $^1J_{P-H}$ = 214 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, partial): δ 153.6 (d, *ipso-C*,

$^1J_{P-C}$ = 11 Hz), 139.9 (s, Ar), 132.0 (s, Ar), 129.3 (s, Ar), 128.7 (s, Ar), 126.8 (s, Ar), 126.1 (s, Ar), 125.7 (s, Ar), 124.8 (s, Ar), 124.0 (s, Ar), 90.9 (s, C≡C), 90.5 (s, C≡C), 32.9 (d, *i*-Pr, $^3J_{P-C}$ = 13 Hz), 31.6 (d, P*C*H$_2$Ph, Ar-*i*-Pr, $^1J_{P-C}$ = 16 Hz), 24.4 (s, ArCH(Me)$_a$(Me)$_b$), 24.1 (s, ArCH(Me)$_a$(Me)$_b$). EI-MS (*m*/*z*): 384.2 (51%) $[M]^+$; 293.1 (100%) $[M]^+ - CH_2Ph$. HRMS: $C_{27}H_{29}P$ mass 384.2013; calcd mass 384.2007 (fit 1.6 ppm). FT-IR (Nujol mull): ν(C≡C) 2208 cm^{-1} (sharp), ν(P−H) 2313 cm^{-1} (br). Despite repeated attempts, suitable elemental analysis could not be obtained.

Synthesis of [RPC$_6$H$_2$(*i*-Pr)$_2$CH=CPh]$_n$ [R = CH$_2$-*i*-Pr (16), CH$_2$Ph (17)]. These compounds were prepared in a similar manner; thus, only the synthesis of **16** is reported. Compound **14** (0.999 g, 2.85 mmol) and 3 mL of THF were placed in a 20 mL scintillation vial, to which freshly titrated *n*-BuLi in hexanes (0.365 mL of 1.578 mol/L, 0.576 mmol, 0.200 equiv) was added with stirring. The resultant dark-brown mixture was stirred overnight and then precipitated into a vortex of hexanes. The brown supernatant was decanted to give a dark-brown gummy residue, which was then dissolved in 2 mL of THF and reprecipitated into hexanes. This step was repeated (three or four precipitations in total). The dark-brown gummy residue was then dried under vacuum to give a dark-brown solid.

16. Yield: 38%. ^{1}H NMR (THF-d_8, 25 °C): δ 7.7−5.9 (br, 7H, ArH), 4.1−3.6 (br, 2H, ArC*H*Me$_2$), 1.6−0.5 (br, 21H, PCH$_2$C*H*Me$_2$ and ArCH*Me*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ −20 (br). ^{13}C{^{1}H} NMR (C$_6$D$_6$, partial): δ 156 (br, Ar), 148 (br, Ar), 143 (br, Ar), 130 (b, Ar), 129 (br, Ar), 126 (br, Ar), 37 (br, alkyl), 35.6 (s, alkyl), 33 (br, alkyl), 32.7 (s, alkyl), 30.1 (s, alkyl), 29 (br, alkyl), 25 (br, alkyl), 24.6 (s, alkyl), 19.1 (s, alkyl), 14.6 (s, alkyl), 10.4 (s, alkyl). FT-IR (25 °C, deposited from a THF solution): no peaks between 2700 and 2000 cm^{-1}. GPC (viscosity): M_n 3600 g/mol, M_w 9200 g/mol. GPC (RI): M_n 3300 g/mol, M_w 13 800 g/mol. GPC (LS): M_n 21 000 g/mol, M_w 25 000 g/mol.

17. Yield: 48%. ^{1}H NMR (C$_6$D$_6$, 25 °C): δ 7.4−6.7 (br, 12H, Ar*H*), 4.1−3.9 and 3.3−3.1 (br, 4H, ArC*H*(CH$_3$)$_2$ and C*H*$_2$Ph), 1.2−0.8 (br, 12H, ArCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ −8.2 (br). ^{13}C{^{1}H} NMR (C$_6$D$_6$ and THF-d_8, partial): δ 157 (br, Ar), 147 (br, Ar), 142 (br, Ar), 140 (br, Ar), 130 (br, Ar), 126 (br, Ar), 33 (br, alkyl). FT-IR (25 °C, deposited from a THF solution): no peaks between 2700 and 2000 cm^{-1}. GPC (refractive index detection, vs polystyrene standards): M_n 2300 g/mol, M_w 10 800 g/mol.

Synthesis of [RCH$_2$P(S)C$_6$H$_2$(*i*-Pr)$_2$CH=CPh]$_n$ [R = CH$_2$-*i*-Pr (18), CH$_2$Ph (19)]. These compounds were prepared in a similar manner; thus, only the synthesis of **18** is reported. Compound **16** (50 mg, 0.14 mmol) and 4 mL of THF were placed in a 20 mL scintillation vial, to which elemental sulfur was added (6 mg, 0.19 mmol). The reaction was stirred overnight at 25 °C. The brown solution was precipitated into a vortex of hexanes, and the resulting beige solid was isolated from the supernatant by decanting and dried under vacuum.

18. Yield: 82%. ^{1}H NMR (THF-d_8, 25 °C): δ 7.9−6.5 (br, 7H, ArH), 4.3−4.0 (br, 2H, ArC*H*Me$_2$), 2.3−0.3 (br, 21H, PCH$_2$C*H*Me$_2$ and ArC*H*Me$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ 46.2 (br). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C, partial): δ 157 (br, Ar), 139 (br, Ar), 133 (br, Ar), 131 (b, Ar), 129 (br, Ar), 128 (br, Ar), 36 (s, alkyl), 33 (s, alkyl), 31 (br, alkyl), 30 (s, alkyl), 28 (s, alkyl), 24 (s, alkyl), 21 (s, alkyl), 14 (s, alkyl), 12 (s, alkyl). GPC (RI): M_n 3000 g/mol, M_w 9600 g/mol.

19. Yield: 65%. ^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 7.8−6.7 (br, 12H, Ph), 4.6−4.3, 3.8−3.6, and 3.4−3.2 (br, 5H, ArC*H*(CH$_3$)$_2$, PCH$_2$Ph, and alkene), 1.2−0.8 (br, ArCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, 25 °C, 121.5 MHz): δ 45.4 (br). ^{13}C{^{1}H} NMR (C$_6$D$_6$ and THF-d_8, partial): δ 132 (Ar), 129 (Ar), 115 (C=C), 35 (alkyl), 31 (alkyl), 23 (alkyl), 14 (alkyl). GPC (refractive index detection, vs polystyrene standards): M_n 2300 g/mol, M_w 11 900 g/mol.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, oxygen-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data (4.5° < 2θ < 45−50.0°) were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of the reflections within these frames showed no statistically significant change over the duration of the data collection. The data were processed using the *SAINT* and *SHELXTL* processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement were performed using the *SHELXTL* solution package.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[45] The heavy-atom positions were determined using direct methods employing the *SHELXTL* direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $w(F_o - F_c)^2$, where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively (see Table 1). In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C−H bond length of 0.95 Å. Hydrogen-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon-atom to which they are bonded. The hydrogen-atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

Computational Methods. Optimizations were performed with the *Gaussian* (*G03*) suite.[47] Gas-phase relative energies were calculated at the B3LYP/6-31G(d) level of theory for the reagents, products, and proposed transition states. Examination of the optimized structures by analytical frequency analysis at this level demonstrated that they were minima (no imaginary frequencies), or transition states (one imaginary frequency).

Results and Discussion

Synthesis of Phosphines Bearing Alkyne Substituents. Sonogashira coupling[46] of an aryl iodide and a terminal alkyne affords a series of compounds Br(C$_6$R$_2$H$_2$)(C≡CR′) in excellent yields (**1**, R = Me, R′ = Ph; **2**, R = *i*-Pr, R′ = Ph; **3**, R = *i*-Pr, R′ = SiMe$_3$). X-ray crystallographic studies confirmed the nature of products **1** and **2**. The Br−C$_{ipso}$ bond distance in compound **1** is similar to those reported for BrC$_6$H$_4$C≡CR (R = Ph, 1.884(4) Å; C$_6$H$_4$Br, 1.891(6) Å;[47] C$_6$H$_2$Br$_2$C≡CC$_6$H$_4$Br, 1.887(4) Å[48]), whereas for compound **2**, the corresponding Br−C distance of 1.907(3) Å is slightly longer. This is attributed to the presence of the electron-donating *i*-Pr substituents.

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Table 1. Crystallographic Data[a]

	2	4	5	7	8	11
formula	$C_{20}H_{21}Br$	$C_{48}H_{66}Br_2Cu_2N_4P_2$	$C_{56}H_{82}Br_2Cu_2N_4P_2$	$C_{16}H_{13}Cl_2P$	$C_{20}H_{21}Cl_2P$	$C_{20}H_{23}P$
formula wt	341.28	1047.88	1160.10	307.13	363.24	294.35
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
a (Å)	12.984(3)	10.2751(16)	12.210(3)	7.7142(14)	10.696(2)	12.8438(18)
b (Å)	10.408(2)	13.845(2)	12.162(3)	8.2249(15)	9.761(2)	10.7033(15)
c (Å)	13.080(3)	17.689(3)	20.067(5)	12.280(2)	18.094(4)	13.4456(19)
α (deg)				81.541(2)		
β (deg)	104.12(3)	92.000(2)	104.265(4)	82.734(2)	90.33(3)	103.084(2)
γ (deg)				86.607(2)		
V (Å^3)	1714.2(6)	2515.0(7)	2888.2(13)	763.8(2)	1889.0(7)	1800.4(4)
Z	4	2	2	2	4	4
T (°C)	−150	25	25	25	−150	25
d(calc) (g/cm^3)	1.322	1.384	1.334	1.335	1.277	1.086
abs coeff, μ (cm^{-1})	2.390	2.533	2.213	0.513	0.425	0.145
data collected	12 780	23 493	27 122	7340	11 697	16 748
R_{int}	0.0770	0.0533	0.0600	0.0270	0.0525	0.0236
data $F_o^2 > 3\sigma(F_o^2)$	3009	4418	5090	2683	4286	3177
variables	190	257	298	172	208	198
R1[b]	0.0401	0.0629	0.0505	0.0439	0.0584	0.0523
wR2[c]	0.0939	0.2220	0.1532	0.1239	0.1454	0.1610
GOF	1.018	1.033	1.009	1.048	1.027	1.032

[a] Data were collected with Mo Kα radiation ($\lambda = 0.710\,69$ Å). [b] $R1 = \sum(F_o - F_c)/\sum F_o$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o)^2]\}^{1/2}$.

Compounds **1**−**3** undergo lithium−bromide exchange using *t*-BuLi,[49] and treatment with $ClP(NEt_2)_2$ in the presence of CuCl affords the compounds $[(\mu\text{-Br})Cu(Et_2N)_2PC_6H_2R_2C{\equiv}CR']_2$ (**4**, R = Me, R′ = Ph; **5**, R = *i*-Pr, R′ = Ph; **6**, R = *i*-Pr, R′ = $SiMe_3$; Scheme 1). Halide exchange accounts for isolation of the CuBr adducts **4**−**6**. High-resolution mass spectral data for these compounds are consistent with the liberation of the free phosphine from CuBr to give $(NEt_2)_2P(C_6H_2R_2)(C{\equiv}CR')$ in the gas phase. Related copper(I) monophosphine complexes with sterically unencumbered phosphines are known to adopt cubane or stepped tetrameric geometries,[50,51] while those with sterically demanding phosphines are more commonly dimeric or even monomeric in the solid state.[52−54] Species **4** and **5** were confirmed unambiguously to be dimeric CuBr adducts by X-ray crystallography (Figure 1). The copper centers in **4** and **5** are planar, while the Cu−Br distances were found to be 2.3886(15) and 2.4055(13) Å in **4** and 2.3930(10) and 2.4470(10) Å in **5**. The corresponding P−Cu bond distances are 2.1944(19) and 2.2059(13) Å, respectively. The Br−Cu−Br bond angles were found to be 98.66(4)° and 101.52(3)° in **4** and **5**, respectively, while the P−Cu−Br angles were 133.05(7)° and 128.24(7)° in **4** and 133.17(4)° and 125.28(5)° in **5**. These metrical parameters about Cu in **4** and **5** are comparable to those previously reported for the dimeric species $[(o\text{-tol})_3P)Cu(\mu\text{-Br})]_2$[55,56] and $[(Ph_2MesP)Cu(\mu\text{-Br})]_2$.[57] The P−N bond distances and N−P−N angles in **4** and **5** are typical of other bisamidophosphines.[26,58,59] As expected, the alkyne fragment adopts an approximately linear geometry.

The treatment of compounds **4**−**6** with gaseous HCl generates dichlorophosphines $Cl_2PC_6H_2R_2C{\equiv}CR'$ with the loss of $[H_2NEt_2]Cl$ (**7**, R = Me, R′ = Ph; **8**, R = *i*-Pr, R′ = Ph; **9**, R = *i*-Pr, R′ = $SiMe_3$; Scheme 1). The observed downfield shift to approximately 163 ppm in the $^{31}P\{^1H\}$ NMR spectra is typical of dichloroarylphosphines.[60] In addition, the formulations of **7** and **8** were confirmed crystallographically (Figure 2). The P−Cl distances were found to be 2.0593(12) and 2.0641(11) Å in **7** and 2.0655(13) and 2.0724(14) Å in **8**, typical of dichloroarylphosphines.[61−65]

Subsequent reduction with $LiAlH_4$ yields the primary phosphines $H_2PC_6H_2R_2C{\equiv}CR'$ (**10**, R = Me, R′ = Ph; **11**, R = *i*-Pr, R′ = Ph; **12**, R = *i*-Pr, R′ = $SiMe_3$; Scheme 1). Compounds **10**−**12** exhibit a corresponding upfield shift in the ^{31}P NMR spectrum to about −155 ppm and a P−H coupling constant of 207 Hz, typical of primary phosphines.[66] The P−H stretch is also evident in the IR spectrum at 2305−2320 cm^{-1}. The retention of the alkynyl

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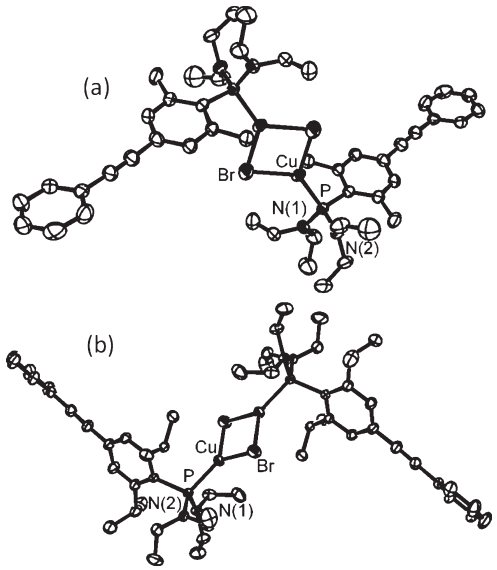
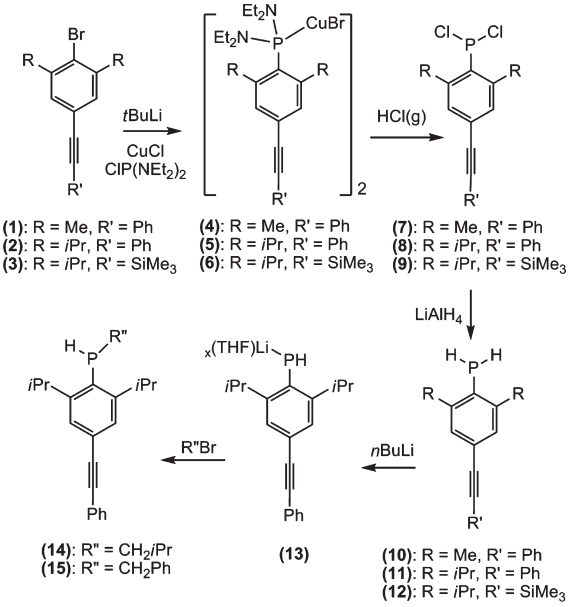


Figure 1. ORTEP drawings of (a) **4** and (b) **5**. Selected bond distances (Å) and angles (°) for **4**: Cu−P 2.1944(19), Cu−Br 2.3886(15), Cu−Br′ 2.4055(13), P−N(1) 1.667(6), P−N(2) 1.679(7), C(9)−C(10) 1.169(11); P−Cu−Br′ 133.05(7), P−Cu−Br 128.24(7), Br−Cu−Br′ 98.66(4), Cu−Br−Cu′ 81.34(4), N(1)−P−N(2) 107.2(3), N(1)−PC(1) 101.0(3), N(2)−P−C(1) 113.9(3), N(1)−P−Cu 115.6(2), N(2)−P−Cu 108.8(2). C(1)−P−Cu 110.3(2). Selected bond distances (Å) and angles (°) for **5**: Br−Cu 2.3930(10), Br′−Cu 2.4470(10), Cu−P 2.2059(13), P−N(2) 1.672(4), P−N(1) 1.701(4), C(13)−C(14) 1.187(7); Cu−Br−Cu′ 78.48(3), P−Cu−Br′ 133.17(4), P−Cu−Br 125.28(5), Br−Cu−Br′ 101.52(3), N(2)−P−N(1) 107.7(2), N(2)−P−C(1) 103.1(2), N(1)−P−C(1) 109.8(2), N(2)−P−Cu 116.59(15), N(1)−P−Cu 109.20(14), C(1)−P−Cu 110.13(14).

Scheme 1. Synthesis of Compounds **1**−**15**



fragment in these products is evidenced by the $^{13}C\{^1H\}$ NMR signals between 90 and 105 ppm, and the alkyne stretch observed in the IR spectrum at 2160−2210 cm^{-1}. In the case of **11**, this formulation was further confirmed by X-ray diffraction (Figure 3). The geometry about P

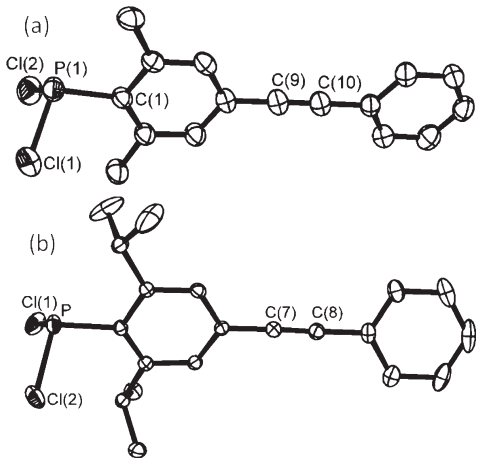


Figure 2. ORTEP drawings of (a) **7** and (b) **8**. Selected bond distances (Å) and angles (°) for **7**: P−C(1) 1.822(2), P−Cl(1) 2.0593(12), P−Cl(2) 2.0641(11), C(9)−C(10) 1.194(4); C(1)−P−Cl(1) 102.56(9), C(1)−P−Cl(2) 102.40(9), Cl(1)−P−Cl(2) 100.43(5). Selected bond distances (Å) and angles (°) for **8**: P−C(1) 1.832(3), P−Cl(1) 2.0655(13), P−Cl(2) 2.0724(14), C(8)−C(7) 1.202(4); C(1)−P−Cl(1) 101.84(10), C(1)−P−Cl(2) 101.73(10), Cl(1)−P−Cl(2) 101.62(5).

and the P−C and P−H bond lengths in **11** are typical of primary phosphines.[65,67,68]

The primary phosphine **11** is deprotonated by reaction with *n*-BuLi or *t*-BuLi to give $Li(THF)_xHPC_6H_2$-*i*-$Pr_2C{\equiv}CPh$ (**13**; Scheme 1). Although this species was not isolated analytically pure, it was completely characterized by ^1H, ^{13}C, ^{31}P, and ^7Li NMR spectroscopy. Subsequent reaction with isobutyl bromide or benzyl bromide yields $R(H)PC_6H_2$(*i*-Pr)$_2C{\equiv}CPh$ [R = CH_2-*i*-Pr (**14**) and CH_2Ph (**15**)], respectively, both of which are viscous oils (Scheme 1). The ^{31}P NMR spectrum of each compound shows a doublet downfield of **13**. The configurational rigidity at P in **14** results in the observation of diastereotopic methyl protons for the isopropyl groups on the arene ring and in the isobutyl substituent.

Hydrophosphination−Polymerization

Polymerization of monomer **14** was achieved by treatment with 0.2 equiv of *n*-BuLi in THF (Scheme 2). The formation of the resulting polymer **16** was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After 1.5 h at 25 °C, nearly all of the starting material was consumed, and a new signal at −20 ppm emerged. To ensure complete reaction, the mixture was allowed to stand for 18 h; repeated precipitation into hexanes resulted in a gummy residue (**16**). This product exhibited a broad $^{31}P\{^1H\}$ NMR signal at −20 ppm. No signal in the $^{31}P\{^1H\}$ NMR spectrum was attributable to an end group, suggesting that the product is cyclic. This view is also supported by the absence of a C≡C stretch or a P−H stretch in the IR spectrum of **16**. In the ^1H NMR spectrum of **16**, the very broad resonances attributable to the alkene proton suggest variations in the regiochemistry of the addition and the stereochemistry at P.

The molecular weight of polymer **16** was examined using MALDI-TOF mass spectrometry and GPC. The MALDI-TOF mass spectrum shows patterns of peaks spaced by *m*/*z* 350 units, the mass of one monomer fragment, from *m*/*z* 1050

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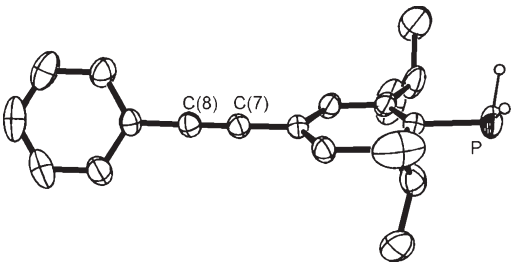
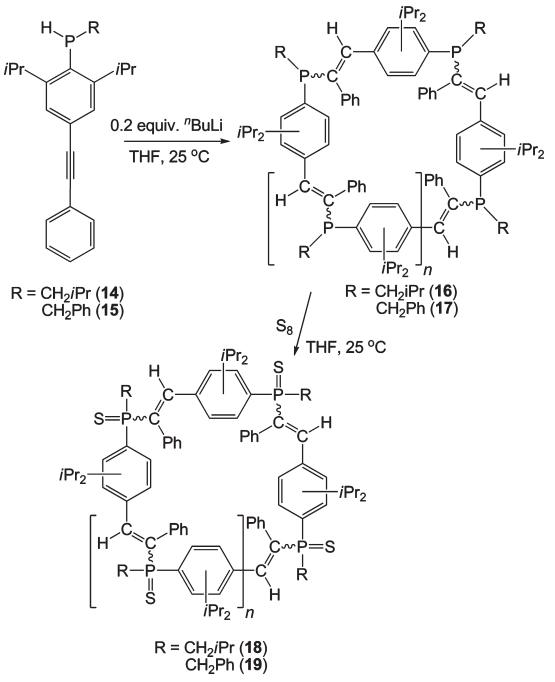


Figure 3. ORTEP drawing of **11**. Selected bond distances (Å): P−C(1) 1.838(2), C(8)−C(7) 1.192(3).

Scheme 2. Synthetic Routes to **16**−**19**



to 2800 (Figure 4a). These data suggest the presence of oligomeric products with at least eight repeat units, although an analysis of the molecular weight and distribution is not possible by MALDI-TOF because of the broad polydispersity of the sample.[69] Instead, molecular weight data were obtained using GPC relative to polystyrene standards with refractive index detection. These experiments indicated M_n = 3600 g/mol and M_w = 9200 g/mol, corresponding to a number-average degree of polymerization of 10. These values may be underestimated,[10] because GPC employing light-scattering detection suggests higher molecular weights of M_n = 21 000 g/mol and M_w = 25 000 g/mol. Together, these data indicate that **16** is a mixture of cyclic oligomers with 8−60 repeat units. It should be noted that cyclic species are expected to have smaller hydrodynamic volumes than their linear counterparts with exactly the same molecular

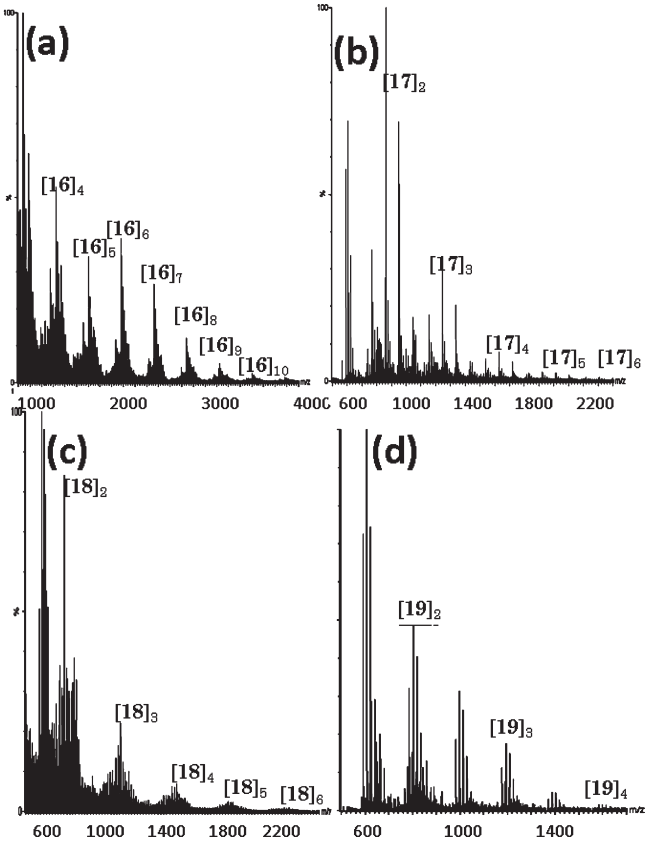


Figure 4. MALDI-TOF mass spectra of (a) **16**, (b) **17**, (c) **18**, and (d) **19**.

weight.[70−73] This results in an increased retention time by GPC and therefore an underestimate of the molecular weight.[74,75]

Polymer **17** is formed in a manner similar to that of **16**, using monomer **15** and 0.2 equiv of *n*-BuLi in THF. The $^{31}P\{^1H\}$ NMR spectrum of **17** is similar to that of **16**, with a broad peak at −8.2 ppm and no signal attributable to an end group; the IR spectrum also shows no peaks corresponding to P−H or C≡C stretches. These data suggest a cyclic structure similar to that proposed for **16**. GPC data with refractive index detection relative to polystyrene standards indicate M_n = 2300 g/mol and M_w = 10 800 g/mol, which again may be underestimated. The MALDI-TOF mass spectrum of **17** (Figure 4b) reveals independent patterns of peaks spaced by *m*/*z* 384 units, the mass of a single monomer fragment. One of these patterns of peaks corresponds to an integral number of monomer units, while the other patterns are offset from the first by *m*/*z* 91 units. The origin of these other sets of peaks is unclear. Because of the soft ionization offered by MALDI, it is unlikely that fragmentation has occurred. One possible explanation to account for these peaks involves a backbiting mechanism, which has also been proposed for other phosphorus-containing polymers.[76] Another possible explanation involves phosphide abstraction of a benzyl substituent (*m*/*z* 91) as an alternative termination pathway.

Polymer **16** or **17** reacts with elemental sulfur in THF to give **18** or **19**, with a corresponding resonance in the $^{31}P\{^1H\}$ NMR spectrum at 46.2 or 45.4 ppm, respectively. For polymer **18** or **19**, molecular weights were determined

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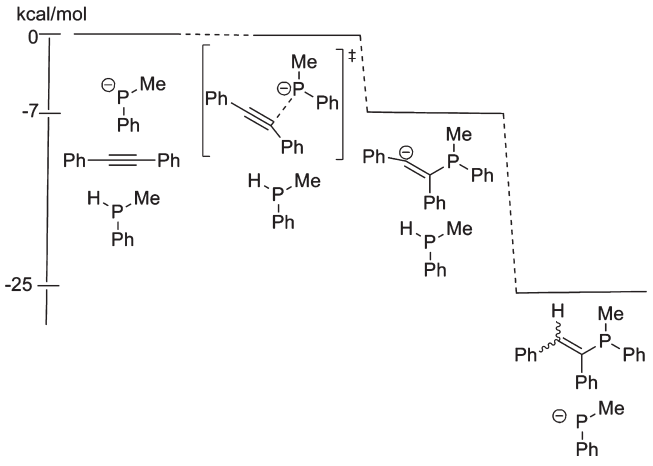

Figure 5. Relative energies of the hydrophosphination of PhCCPh and MePhPH, calculated by DFT methods.

to be M_n = 3000 g/mol, M_w = 9600 or M_n = 2300 g/mol, M_w 11 900 g/mol by GPC relative to polystyrene standards. MALDI-TOF mass spectra show patterns of peaks spaced by m/z 382 units or m/z 416 units for **18** or **19**, respectively (Figure 4c,d). Together these data indicate that the polymer structure is maintained upon sulfurization, without appreciable chain degradation.

Mechanistic Considerations

Mechanistically, the present hydrophosphinations could follow a radical[30,33,34,77] or an ionic[24,25] process. However, the radical pathway is eliminated based on the lack of reactivity with benzoyl peroxide or azobis(isobutyroniltrile) (AIBN). Indeed, monitoring a sample of **14** in benzene-d_6 in the presence of benzoyl peroxide resulted in no change in the $^{31}P\{^1H\}$ NMR spectrum after 3−4 days at room temperature. After 3 weeks at 70 °C, the reaction mixture consisted of only unreacted secondary phosphine and a small amount of phosphine oxide (6%). A similar situation was observed for mixture of **14** with AIBN.

(77) Brandt, P. F.; Schubert, D. M.; Norman, A. D. *Inorg. Chem.* **1997**, *36*, 1728–1731.

As a result, the mechanism of hydrophosphination−polymerization is intuitively thought to follow an ionic route. This view is supported by DFT calculations. For simplification, the phosphine and alkyne were modeled separately. The model compounds were chosen to be methylphenylphosphine and diphenylacetylene. Gas-phase relative energies were calculated at the B3LYP/6-31G(d) level of theory for the reagents, products, and proposed transition states, in order to illustrate the initial steps of the polymerization process. The only reaction pathway found in these computations (Figure 5) involves the exothermic initial attack on the alkyne by the phosphide, giving the transition state in a barrierless process. Subsequent protonation of the alkenylphosphine anion by phosphine is slightly further downhill in energy. Proton transfer from phosphine provides an overall exothermic process for hydrophosphination and regenerates the phosphide for subsequent reaction.

Conclusions

The present results provide routes to primary and secondary phosphines with pendant alkynyl functionalities. These compounds are shown to undergo hydrophosphination−polymerization to give cyclic species, which can be further derivatized to the phosphine sulfides. These studies provide a unique and new approach to phosphorus-containing oligomers, the utility of which is currently being explored. In addition, the viability of this approach for the synthesis of related nitrogen-containing polymers is under investigation. The results of these studies will be reported in due course.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.