Experimental Section

General Procedures. All manipulations of air and/or water sensitive compounds were performed under pre-purified nitrogen (Praxair, 99.998%) using standard high vacuum or Schlenk techniques or in an Innovative Technology Inc. glovebox. $^1$H, $^{31}$P, $^{13}$C, $^{29}$Si NMR spectra were recorded on Bruker Avance 300 MHz or Bruker Avance 400 MHz spectrometers. Chemical shifts are reported relative to: CHCl$_3$ or HC$_6$D$_5$ ($\delta$=7.24 and 7.15 for $^1$H); 85% H$_3$PO$_4$ as an external standard ($\delta$=0.0 for $^{31}$P); CDCl$_3$ or C$_6$D$_6$ ($\delta$=77.0 and 128.0 for $^{13}$C). $^{29}$Si NMR spectra were recorded utilizing a DEPT pulse sequence (proton decoupled) with a $^2$J$_{Si-H}$ coupling constant of 7.0 Hz and referenced externally to SiMe$_4$ in CDCl$_3$ ($\delta$ 0.0 for $^{29}$Si). Infrared spectra were obtained as thin films between NaCl plates using a Bomen MB-series instrument. UV/Vis spectra were recorded on a Unicam UV2 spectrophotometer. Mass Spectra were acquired using Kratos MS 50 instrument. Thermogravimetric analyses of 3 were carried out on a TA Instruments 2000 instrument, heating under dry helium at 10 °C/min from 20 °C to 800 °C. Elemental analyses were performed by Mr. P. Borda in the Department Microanalysis Facility.

Materials. Diethyl ether, hexanes, and dichloromethane were dried by passing through activated alumina columns.$^{[1]}$ Tetrahydrofuran was distilled from sodium/benzophenone immediately prior
to use; C₆D₆ (CIL) was degassed and dried over activated 3 Å molecular sieves; and CDCl₃ (CIL) distilled from P₂O₅ and degassed. 1,4-dibromobenzene, durene, 2-bromomesitylene, bromine, PCl₃, Me₃SiCl, Mg, SOCl₂, LiAlH₄, MeLi (1.6 M in ethyl ether), and 'BuLi (1.7 M in pentane) were purchased from Aldrich and used as received. Et₂NH, PhPCl₂ were purchased from Aldrich and distilled prior to use. Mesitylene-2-carboxylic acid chloride,[2] dibromodurene,[3] 1,4-diphosphinobenzene,[4] bis(trimethylsilyl)phenylphosphine,[5] were prepared following the literature procedures.

NMR Assignments. All assignments of ¹³C and ¹H NMR spectra reported for 1, 2, and 3 were made with the aid of COSY, APT, HMQC and HMBC experiments. For a discussion of NMR spectra of phosphaalkenes see, E. Fluck In *Topics in Phosphorus Chemistry*, Wiley: New York; 1980, Vol. 10, p. 193, and references therein. See also, refs. 11 and 12 of the present work.

Preparation of 1,4-dicarboxylic acid-2,3,5,6-tetramethylbenzene: To a stirred solution of 1,4-dibromo-2,3,5,6-tetramethylbenzene (17.62 g, 60.3 mmol) in Et₂O (250 mL) was added 'BuLi (149 mL, 1.7 M, 253 mmol) at –78 °C. After 1.5 h at –78 °C, dry CO₂ was bubbled through the reaction mixture for 30 min. The resulting mixture was extracted with aqueous hydrochloric acid (0.5 M), and the aqueous layer extracted with Et₂O (3 x 175 mL), dried with MgSO₄, and the solvent removed in vacuo yielding a colorless powder (11.9 g, 89%).

¹H NMR (CD₃C(O)CD₃, 300.1 MHz): δ=11.48 (s, 1H; COOH), 2.16 ppm (s, 6H; CH₃)

Preparation of 4. 1,4-dicarboxylic acid-2,3,5,6-tetramethylbenzene (11.89 g, 53.5 mmol) was suspended in thionyl chloride (100 mL) and heated to reflux overnight over which time all the
solid dissolved forming a brown solution. SOCl₂ was removed in vacuo, leaving a pale brown solid. Colorless crystals (12.0 g, 90%) were isolated after vacuum sublimation (50 °C; 0.1 mmHg).

¹H NMR (CDCl₃, 300.1 MHz): δ=2.28 ppm (s, CH₃); Elem. Anal.: C₁₂H₁₂Cl₂O₂: calcd. C 55.62, H 4.67, found C 55.44, H 4.75.

Preparation of 5. To a stirred solution of 1,4-diphosphinobenzene (1.00 g, 7.04 mmol) in Et₂O (50 mL) was added MeLi in Et₂O (18.5 mL, 1.6 M, 29.6 mmol) at -78° C. The reaction mixture was stirred at -78 °C for ca. 30 min, and the yellow suspension allowed to warm to room temperature and stirred for ca. 1 h. After cooling to -78° C, Me₃SiCl (3.21 g, 29.6 mmol) was added resulting in the immediate formation of a white precipitate (presumably LiCl). After warming to room temperature and removing the solvent in vacuo, the residue was extracted with hexanes (2 x 50 mL) and filtered. The solvent was removed in vacuo leaving a pale yellow crystalline solid. 5 (1.74 g, 60%) was isolated as colorless crystals after vacuum sublimation (100 °C, 0.1 mmHg).

³¹P NMR (C₆D₆, 121.5 MHz): δ=-138.0 (s); ¹H NMR (C₆D₆, 400.1 MHz): δ=7.27 (dd, 4H, ³J(P,H)=5.0 Hz, ⁴J(P,H)=3.5 Hz; C₆H₄), 0.22 (d, 36H, ³J(P,H)=5.0 Hz; Si(CH₃)₃); ¹³C NMR (CDCl₃, 75.5 MHz): δ=136.1 (dd, ³J(P,C)=14.8 Hz, ³J(P,C)=7.2 Hz; o-C₆H₄), 131.3 (d, ¹J(P,C)=16.1 Hz; i-C₆H₄), 1.1 (d, ³J(P,C)=12.7 Hz, Si(CH₃)₃); ²⁹Si NMR (C₆D₆, 79.5 MHz): δ=1.9 (d, ¹J(P,Si)=24 Hz); MS (EI, 70 eV): m/z (%) 434, 433, 432, 431, 430 (1, 2, 3, 11) [M⁺]; 208, 207 (1, 2, 3, 11) [M⁺-PSi₂(CH₃)₃H]; 75, 74, 73 (3, 8, 100) [SiCH₃]; Elem. Anal.: C₁₈H₄₀P₂Si₄: calcd. C 50.18, H 9.36, found C 49.87, H 9.32.
References


