Reaction of lithium (2,4,6-tri-*tert*-butylphenyl)silylphosphides with haloforms

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Dedicated to Professor Anthony J. Arduengo, III on the occasion of his 60th birthday

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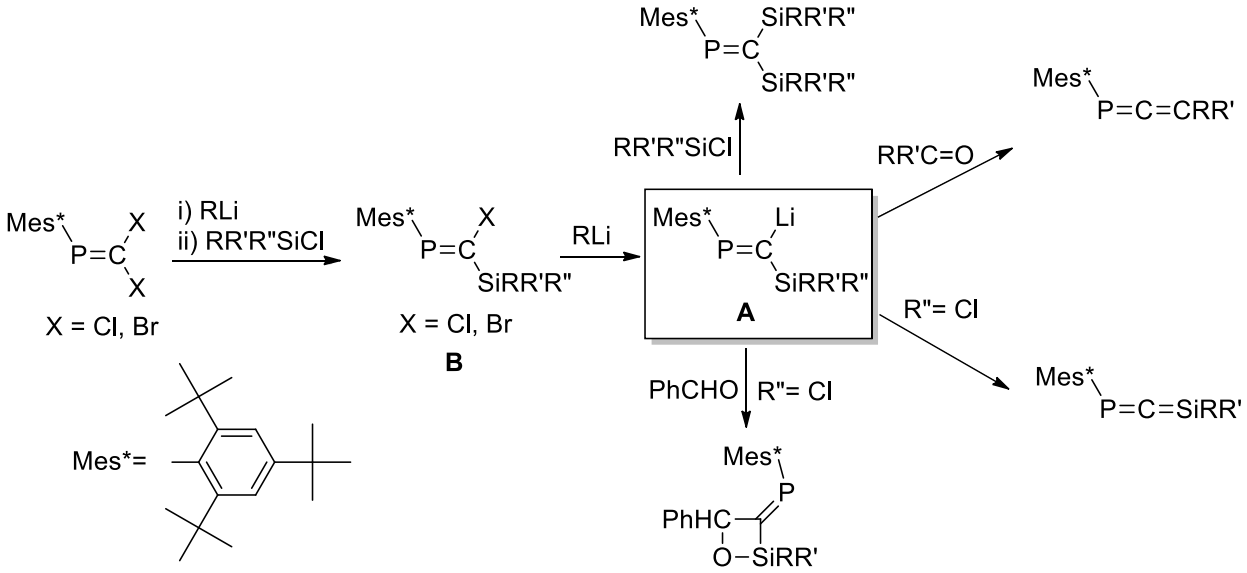
Abstract
The reaction of lithium (*tert*-butyldimethylsilyl)(2,4,6-tri-*tert*-butylphenyl)phosphide with chloroform afforded (*Z*)-2-(*tert*-butyldimethylsilyl)-2-chloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene. The NMR study revealed a secondary phosphine resulting from a formal insertion of a dichlorocarbene to the P-Si bond as a reaction intermediate. The reaction is specific to the reactants and substrates. The use of bromoform gave a bromosilylphosphine and a 2-bromo-1-phosphaethene. A less hindered trimethylsilylphosphide afforded bis(2,4,6-tri-*tert*-butylphenyl)diphosphene.

Keywords: Silylphosphide, haloform, dichlorocarbene, phosphaethene

Introduction

The sterically protected 2-phospha-1-silylethenyllithium **A** is a convenient reagent for the introduction of the phosphaethenyl and phosphaethenylene moieties (Scheme 1).[1] The lithium reagents are prepared *in situ* from the corresponding chloro- or bromophosphaethenes **B** by halogen metal exchange and can react with various electrophiles. The reactions with ketones or aldehydes lead to 1,3-rearrangement of the silyl group followed by elimination to give phosphaallenes.[1b,1c,1d] The 2-phospha-1-silylethenyllithiums bearing a leaving group on the silicon are employed to the synthesis of phosphasilaallene[1e] and phosphinidene oxasiletane.[1f] The precursors, 2-halo-1-phospha-2-silylethenes **B**, are generally synthesized by the metallation of 2,2-dihalo-1-phosphaethene followed by the reaction with silyl halides.[1a,1b,1c] Herein, we report

formation of 2-chloro-1-phospha-2-silylethene **B** by the reaction of a lithium silylphosphide with chloroform. The reaction was unexpectedly found in the course of the synthetic study of phosphaalkenes by the reaction of the lithium silylphosphides with carbonyl compounds. The phosphaethene **B** was found in the samples mixed with $CDCl_3$ for the NMR monitoring of the reaction. Further investigation revealed that the reaction is specific to the substrate and the reactant, but the NMR study allowed observation of a reaction intermediate, which deepened understanding of the reaction mechanism.

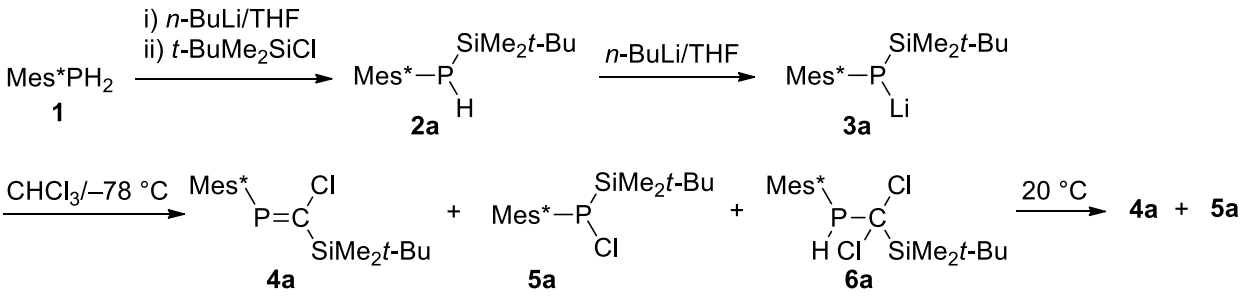


Scheme 1. Reactions of 2-phospha-1-silylethenyllithium.

Results and Discussion

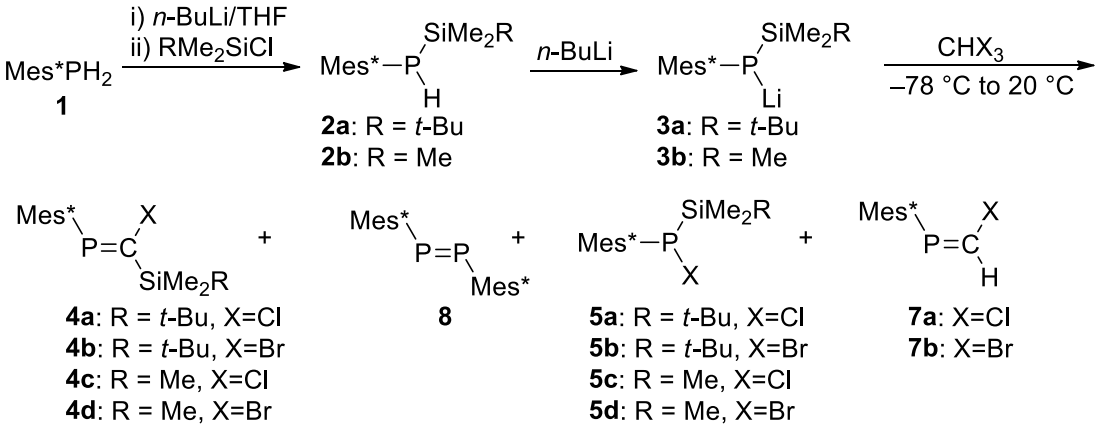
The lithiation of the sterically protected primary phosphine **1**[2] followed by the addition of *tert*-butylchlorodimethylsilane gave silylphosphine **2a** (Scheme 2).[3] The lithium silylphosphide **3a**[3] was generated by the lithiation of **2a** with butyllithium and was allowed to react with chloroform at –78 °C. The ^{31}P NMR spectrum of the sample taken from the cold reaction mixture indicated to consist of **4a** (δ_P 297.0 (s))/**5a** (33.8(s))/**6a** (–21.9 (d, $^1J_{PH}$ 231.9 Hz))/**2a** (–137.5 (d, $^1J_{PH}$ 207.5 Hz)) in a ratio of 3/2/9/10. The compound of δ_P –21.9, which was assigned as a secondary phosphine **6a** based on J_{PH} value and the reaction mechanism (*vide infra*, Scheme 5), gradually disappeared during the measurement with the growing signal intensity of **4a**. Thus, the mixture was warmed to 20 °C for the completion of the reaction and butyllithium was added to the mixture at –78 °C for the regeneration of the silylphosphide from **2a**. The ^{31}P NMR spectrum of the cold sample consisted of the four compounds **4a**/**5a**/**6a**/**2a** in a ratio of 10/3/5/5 and **6a** was again converted to **4a**. The mixture was warmed and purified to give **4a** in 47%. The structure of **4a** was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR and mass spectroscopy. The geometry of **4a** was

determined to be (*Z*)-form by comparison with NMR data of (*E*)- and (*Z*)-forms of the trimethylsilyl derivatives **4c**.[1a,1b] ^{1}H and ^{13}C NMR signals of the $SiCH_3$ groups of (*Z*)-**4a** and (*Z*)-**4c** showed the coupling with ^{31}P nucleus typical of those *cis* to the lone pair of the low coordinated phosphorus,[4] which are not observed for (*E*)-**4c** ((*Z*)-**4a**. ^{1}H NMR δ 0.26 (d, J_{PH} 1.5 Hz), ^{13}C NMR δ –4.7 (d, J_{PC} 11.0 Hz). (*Z*)-**4c**. ^{1}H NMR δ 0.26 (d, J_{PH} 1.10 Hz). ^{13}C NMR δ–1.27 (d, J_{PC} 9.16 Hz)).



Scheme 2. Reaction of lithium (*tert*-butyldimethylsilyl)(2,4,6-tri-*tert*-butylphenyl)phosphide with chloroform.

To gain further insight into the reaction, we investigated a similar reaction with different substrates (Scheme 3, Table 1). The reaction of the phosphide **3a** with bromoform gave bromophosphine **5b** as a main product with small amount of phosphaethene **7b**.[1a,5] The reaction of the less hindered trimethylsilylphosphide **3b**[6] with chloroform or bromoform gave diphosphene **8**[7] as a main isolable product with a trace amount of **4**. The reaction was substrate-specific rather than general. The phosphaethene **4a** gives phosphaethenyl anion by halogen metal exchange similarly to the trimethylsilyl derivative **4c** and **4d**, or by desilylation catalyzed by fluoride ion, and thus **4a** is expected to be a potential source of the Mes*PC unit (Scheme 4).

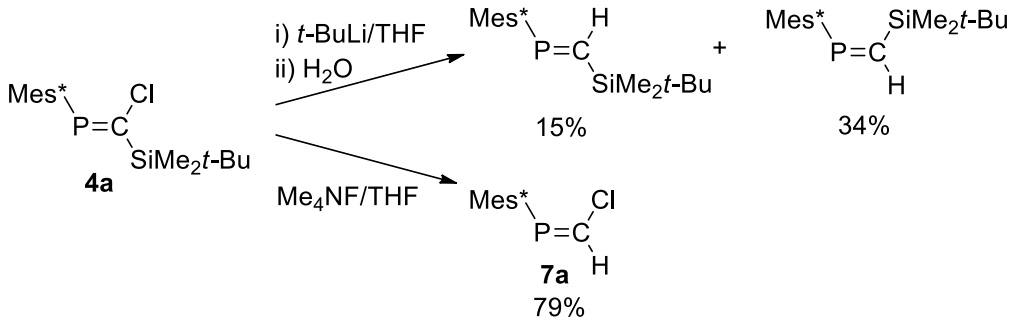


Scheme 3. Reaction of the silylphosphides with haloforms.

Table 1. Reaction of the silylphosphides with haloforms

Entry	R	X	Yield/%				
			4	**5**	**7**	**8**	**1**
1	*t*-Bu	Cl	47	+ [a]	+ [a]	0	18
2	*t*-Bu	Br	0	+ [a]	7	0	0
3	Me	Cl	trace	0	trace	23	trace
4	Me	Br	trace	0	0	15	10

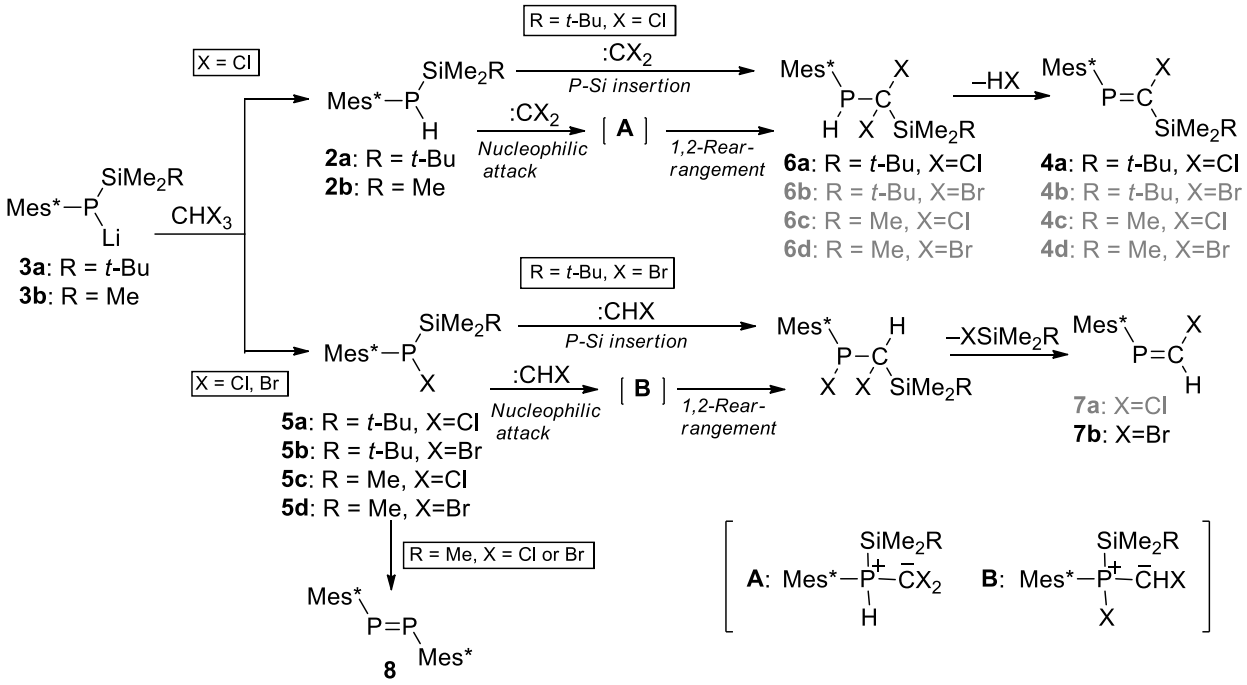
[a]Observed, but not isolated.



Scheme 4. Reaction of **4a.**

The ^{31}P NMR spectra of the reaction mixture strongly suggest the secondary phosphine **6a** as a reaction intermediate to **4a**. Taking the structure of the product **4a** and the reaction condition into consideration, the reaction intermediate is **6a** and the formation of **4a** can be explained as shown in scheme 5. The phosphide **3a** deprotonates chloroform to give silylphosphine **2a** and trichloromethyllithium. Trichloromethyllithium works as a carbenoid or is converted to dichlorocarbene to give the P-Si insertion product **6a** by the direct insertion or by the formation of the phosphonium salt followed by silyl migration. The formal insertion of carbenes to the P-H bond of sterically protected primary phosphine has been reported.[1a,5] The dehydrochlorination of **6a** under the basic condition gives **4a**. The silylphosphide **3a** prefers the halogen-metal exchange to the deprotonation in the reaction with bromoform because of the lower acidity of the C-H and higher reactivity of the C-Br bond. The formation of phosphaethene **7b** can be rationalized by the formal insertion of the bromocarbene to the P-Si bond of **5b** followed by the elimination of the bromotrimethylsilane. The P-Si bond or phosphorus lone pair of **5b** is less reactive toward the vacant orbital of the electrophilic carbene than that of silylphosphine **2a** because of the inductive effect of the bromo group. Actually, the reaction of **3a** with carbon tetrachloride gave chlorophosphine **5a** as the sole product without formation of phosphaalkenes. Phosphine **5a** is more inert to the carbene as expected from higher electronegativity of chlorine. The absence of the silyl substituted phosphaethene **4b** excludes the formation of **7b** by the desilylation of **4b**. A less hindered trimethylsilylphosphide **3b** undergoes halogen-metal exchange to give

chlorosilylphosphine **5c** or bromosilylphosphine **5d**. **5c** and **5d** are more reactive than the more hindered *tert*-butyldimethylsilyl derivatives **5a** and **5b** to give diphosphene **8** as reported.[8]



Scheme 5. A plausible reaction mechanism. Minor or missing products are shown in faint fonts.

The reason for the reactivity difference between the *tert*-butyldimethylsilyl and the trimethylsilyl derivatives is not clear so far. It is not plausible that the difference of the silyl groups leads to marked difference of the ratio between the chlorinated and the protonated products. In the course of the various reactions of the trimethylsilylphosphide, we often encountered the desilylated products which do not appear in the similar reaction of the *tert*-butyldimethylsilyl derivative. Thus, it seems the *tert*-butyl group on the silicon hinders nucleophilic attack on the silicon, so that the *tert*-butyldimethylsilyl derivative exhibits unique reactivity, while the trimethylsilyl derivatives undergo desilylation and various reactions. As for the reactivity difference within haloforms, the relative acidities can give an explanation for the diversity of the reaction products.

Conclusions

We found a unique reaction of a silylphosphide with a carbene or carbenoid to afford 2-chloro-2-silyl-1-phosphaethene. The reaction is specific to *tert*-butyldimethylsilyl derivative **3a** and

chloroform because this combination only affords the nucleophilic silylphosphine that is reactive to the carbene. The reaction is unique not only because of the direct formation of the synthetically useful 2-chloro-2-silyl-1-phosphaethene, but also because of the observation of the reaction intermediate. The reaction itself suffers from severe limitation of the substrates; the behavior of the series of the substrates shown in this report is suggestive of the development of a broad range of the reactions having analogous mechanism.

Experimental Section

General. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on a JEOL FX90Q spectrometer. ^{1}H and ^{13}C NMR chemical shifts are expressed as δ from external tetramethylsilane and calibrated to the residual proton of the deuterated solvents (δ 7.25 for chloroform-*d*) or the carbon of the deuterated solvent (δ 77.0 for chloroform-*d*). ^{31}P NMR chemical shifts are expressed as δ from external 85% H_3PO_4. Mass spectra were measured on a JEOL D-300 spectrometer. Fuji Silysia BW-300 was used for the flash column chromatography. All reactions were carried out under argon unless otherwise specified. Anhydrous tetrahydrofuran was distilled from sodium diphenylketyl under argon just prior to use.

Reaction of lithium silylphosphide (3a) with chloroform

To a solution of 2,4,6-tri-*tert*-butylphenylphosphine **1** (559 mg, 2.01 mmol) in tetrahydrofuran (30 mL) was added butyllithium (2.41 mmol in hexane) and the mixture was stirred for 10 min. To the mixture was added a solution of *tert*-butylchlorodimethylsilane (503 mg, 3.33 mmol) in tetrahydrofuran (7 mL) and the mixture was stirred for 90 min, and butyllithium (2.81 mmol in hexane) was added. The mixture was stirred for 10 min, cooled to –78 °C, and chloroform (0.321 mL, 4.02 mmol) was added. After being stirred for 12 h at –78 °C, an aliquot was removed from the cold solution and the ^{31}P NMR spectrum indicated that the mixture consisted of **4a** (δ_P 297.0 (s))/**5a** (33.8(s))/**6a** (–21.9 (d, $^{1}J_{PH}$ 231.9 Hz))/**2a** (–137.5 (d, $^{1}J_{PH}$ 207.5 Hz)) in a ratio of 3/2/9/10 and the conversion of **6a** to **4a** was observed. The mixture was warmed to 20 °C, cooled to –78 °C, and butyllithium (1.61 mmol in hexane) was added. After being stirred for 10 min at –78 °C, ^{31}P NMR spectrum of the sample taken from the cold solution consisted of **4a**/**5a**/**6a**/**2a** in a ratio of 10/3/5/5 and the conversion of **6a** to **4a** was again observed. The mixture was warmed to 20 °C, concentrated under reduced pressure, and purified by flash column chromatography (SiO_2/pentane) to give **4a** (410 mg, 0.934 mmol, 47%), **1** (103 mg, 0.369 mmol, 18%), and an inseparable mixture of **4a** and **7a** (82.0 mg).[1a,5] **4a**: colorless oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.40 (2H, d, $^{4}J_{PH}$ 1.3 Hz, arom), 1.47 (18H, s, *o*-*t*-Bu), 1.33 (9H, s, *p*-*t*-Bu), 0.99 (9H, s, Si-*t*-Bu), 0.26 (6H, d, $^{3}J_{PH}$ 1.5 Hz, Si-Me). ^{13}C NMR (22.5 Hz, $CDCl_3$) δ 173.6 (d, $^{1}J_{PC}$ 84.2 Hz, P=C), 153.1 (d, $^{2}J_{PC}$ = 2.4 Hz, *o*-arom), 150.4 (s, *p*-arom), 136.2 (d, $^{1}J_{PC}$ 64.7 Hz, *ipso*-arom), 121.8 (s, *m*-arom), 37.8 (s, *o*-*C*Me$_3$), 35.1 (s, *p*-*C*Me$_3$), 32.8 (d, $^{4}J_{PC}$ 7.3 Hz, *o*-C*C*H$_3$), 31.4 (s, *p*-C*C*H$_3$), 27.0 (s, SiC*C*H$_3$), 18.2 (d, $^{3}J_{PC}$ 4.9 Hz, Si*C*CH$_3$), –4.7 (d, $^{3}J_{PC}$ 11.0 Hz, Si*C*H$_3$). ^{31}P NMR

($CDCl_3$) δ 296.1 (s). FDMS *m*/*z* (intensity) 441.0 (M^++3, 15), 444.0 (M^++2, 43), 439.0 (M^++1, 36), 438.0 (M^+, 100).

Reaction of lithium silylphosphide (3a) with bromoform

To a solution of **1** (156 mg, 0.561 mmol) in tetrahydrofuran (10 mL) was added butyllithium (0.673 mmol in hexane) and the mixture was stirred for 20 min. To the mixture was added a solution of *tert*-butylchlorodimethylsilane (138 mg, 0.916 mmol) in tetrahydrofuran (5 mL) and the mixture was stirred for 120 min, and butyllithium (0.785 mmol in hexane) was added. The mixture was stirred for 20 min, cooled to -78 °C, and bromoform (0.20 mL, 2.29 mmol) was added. After being stirred for 5 min at –78 °C, ^{31}P NMR spectrum of the sample taken from the cold solution consisted of **5b** (δ_P 20.5 (s)). The mixture was warmed to 20 °C, stirred for 12 h. ^{31}P NMR spectrum of the sample taken from the solution showed the formation of **5b** (δ_P 20.5 (s)). The mixture was concentrated under reduced pressure, ^{31}P NMR spectrum of the sample consisted of peaks due to **7b** (δ_P 269.1 (d, $^2J_{PH}$ 42.7 Hz))/(36.0(s))/**5b** (δ_P 23.1 (s)) in a ratio of 7/25/74. The mixture was purified by flash column chromatography (SiO_2/pentane) to give **7b** (15.2 mg, 0.0412 mmol, 7%), and an inseparable mixture of 2,4,6-tri-*tert*-butylphenylphosphine oxide and 2,4,6-tri-*tert*-butylphenylphosphinic acid (80.5 mg).

(*Z*)-2-Bromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (7b). [1a,5] Colorless oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.41 (2H, s, arom), 7.33 (1H, d, $^2J_{PH}$ 44.2 Hz, CH), 1.49 (18H, s, *o*-*t*-Bu), 1.34 (9H, s, *p*-*t*-Bu). ^{31}P NMR ($CDCl_3$) δ 268.9 (d, $^2J_{PH}$ 42.7 Hz).

2,4,6-Tri-*tert*-butylphenylphosphine oxide. ^{31}P NMR ($CDCl_3$) δ –9.9 (t, $^1J_{PH}$ 488.3 Hz).[9]

2,4,6-Tri-*tert*-butylphenylphosphinic acid. ^{31}P NMR ($CDCl_3$) δ 24.6 (d, $^1J_{PH}$ 573.7 Hz).[9]

Reaction of lithium silylphosphide (3b) with chloroform

To a solution of **1** (292 mg, 1.05 mmol) in tetrahydrofuran (10 mL) was added butyllithium (1.15 mmol in hexane) and the mixture was stirred for 10 min. To the mixture was added chlorotrimethylsilane (0.146 mL, 1.15 mmol) and the mixture was stirred for 15 min, and butyllithium (1.15 mmol in hexane) was added. The mixture was stirred for 7 min, cooled to –78 °C, and chloroform (0.117 mL, 1.47 mmol) was added. After being stirred for 10 min at –78 °C, the mixture was warmed to 20 °C. ^{31}P NMR spectrum of the sample mainly consisted of **8** (δ_P 492.5 (s)).[7] The mixture was concentrated under reduced pressure, purified by flash column chromatography (SiO_2/pentane) to give **8** (66.5 mg, 0.120 mmol, 23%), a trace amount of **4c** (δ_P 285.7 (s)),[1a,1b] **7a** (δ_P 249.2 (d, $^2J_{PH}$ 42.7 Hz)),[1a,5] 2,2-dichloro-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (δ_P 232.2 (s)),[10] 1,2-bis(2,4,6-tri-*tert*-butylphenyl)-3,3-dichlorodiphosphirane (δ_P –69.2 (s)),[10,11] 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphane (δ_P –64.6 (s)),[12] butyl(2,4,6-tri-*tert*-butylphenyl)phosphine (δ_P –73.7 (m)),[13] and **1**.

Reaction of lithium silylphosphide (3b) with bromoform

To a solution of **1** (206 mg, 0.741 mmol) in tetrahydrofuran (12.5 mL) was added butyllithium (0.815 mmol in hexane) and the mixture was stirred for 5 min and cooled to –78 °C. To the

mixture was added chlorotrimethylsilane (0.113 mL, 0.889 mmol) and the mixture was stirred for 20 min at 20 °C, and butyllithium (0.963 mmol in hexane) was added. The mixture was stirred for 15 min, cooled to –78 °C, and bromoform (0.084 mL, 0.963 mmol) was added. After being stirred for 20 min at –78 °C, the mixture was warmed to 20 °C. ^{31}P NMR spectrum of the sample mainly consisted of **8** (δ_P 492.4 (s))/ butyl(2,4,6-tri-*tert*-butylphenyl)phosphine (δ_P –73.7 (m))/ **2b** (δ_P –129.7 (d, $^1J_{PH}$ 213.6 Hz)/(2,4,6-tri-*tert*-butylphenyl)bis(trimethylsilyl)phosphine (δ_P –143.7 (s)) in a ratio of 26/3/6/4. The mixture was concentrated under reduced pressure and purified by flash column chromatography (SiO_2/pentane) to give **8** (31.3 mg, 0.0566 mmol, 15.3%), **1** (21.3 mg, 0.0765 mmol, 10.3%), **1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphane** (6.8 mg, 0.020 mmol, 3%), and a trace amount of **4d** (δ_P 302.2 (s)).

Lithiation of (4a). To a solution of **4a** (0.107 mmol) in tetrahydrofuran (2 mL) was added *tert*-butyllithium (0.078 mmol in pentane) at –78 °C and the mixture was stirred for 18 min and hydrolyzed with water (0.1 mL). The mixture was warmed to 20 °C, concentrated under reduced pressure, and purified by flash column chromatography (SiO_2/hexane) to give (*Z*)-2-(*tert*-butyldimethylsilyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (34%) and (*E*)-2-(*tert*-butyldimethylsilyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene (15%).

(*Z*)-2-(*tert*-Butyldimethylsilyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene. Colorless oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.81 (1H, d, $^2J_{PH}$ 16.3 Hz, CH), 7.34 (2H, d, $^4J_{PH}$ 1.3 Hz, arom), 1.50 (18H, s, *o*-*t*-Bu), 1.31 (9H, s, *p*-*t*-Bu), 0.79 (9H, s, Si-*t*-Bu), –0.57 (6H, s, Si-Me). ^{31}P NMR ($CDCl_3$) δ 347.8 (d, $^2J_{PH}$ 18.3 Hz). LRMS *m*/*z* 404 (M^+).

(*E*)-2-(*tert*-Butyldimethylsilyl)-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene. Colorless oil. ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.88 (1H, d, $^2J_{PH}$ 24.2 Hz, CH), 7.38 (2H, d, $^4J_{PH}$ 0.4 Hz, arom), 1.49 (18H, s, *o*-*t*-Bu), 1.33 (9H, s, *p*-*t*-Bu), 0.90 (9H, s, Si-*t*-Bu), 0.16 (6H, d, $^3J_{PH}$ 1.1 Hz, Si-Me). ^{31}P NMR ($CDCl_3$) δ 333.5 (d, $^2J_{PH}$ 24.4 Hz). LRMS *m*/*z* 404 (M^+).

Desilylation of (4a). A mixture of **4a** (0.158 mmol) and tetramethylammonium fluoride (0.264 mmol) in tetrahydrofuran (10 mL) was stirred for 24 h, concentrated under reduced pressure, and purified by flash column chromatography (SiO_2/hexane) to give **7a** (0.125 mmol, 79%). **7a**. Colorless solid; mp 85.3–87.1 °C. ^{1}H NMR (90 MHz, $CDCl_3$) δ 7.42 (2H, d, $^4J_{PH}$ 1.5 Hz, arom), 7.10 (2H, d, $^2J_{PH}$ 46.6 Hz, CH), 1.50 (18H, s, *o*-*t*-Bu), 1.34 (9H, s, *p*-*t*-Bu). ^{31}P NMR ($CDCl_3$) δ 249.5 (d, $^2J_{PH}$ 48.8 Hz). LRMS *m*/*z* 326 (M^++2), 324 (M^+).

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