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Synthesis of Stable Multifunctional *C*-Phosphonio Phosphorus Vinyl Ylides

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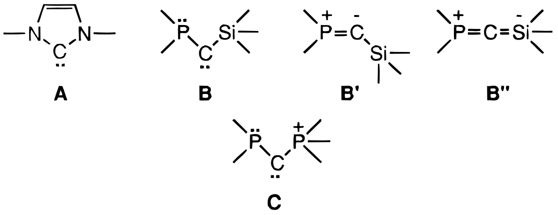
Trifluoromethanesulfonic acid reacts at 240 K with bis[bis(diisopropylamino)phosphino]diazomethane, **1**, affording the corresponding cationic (phosphino)(*P*-hydrogenophosphonio)diazomethane derivative **2**, which eliminates dinitrogen above 250 K, leading to (phosphino)(phosphonio)carbene **3** isolated in 76% yield (mp 88 °C). Bis(diisopropylamino)phosphenium salt **5a** adds at 240 K to *P*-chlorodiazomethylenephosphorane **4** giving (phosphino)(*P*-chlorophosphonio)diazo derivative **6a**, which leads, after N_2 elimination, to the corresponding carbene **7a**. Addition of potassium *tert*-butoxide to **3** gives rise to the transient diphosphinocarbene **8**, which rearranges into phosphaalkene **9**. Sodium tetrafluoroborate, *tert*-butyllithium, and tributyltin hydride react with **3** to afford *P*-fluoro-*P*′-hydrogenocarbodiphosphorane **10**, *P*,*P*′-dihydrogenocarbodiphosphorane **12**, and stannyl-substituted methylene salt **15**, respectively. *tert*-Butyl isocyanide reacts with phosphoniocarbene **3** giving heterocycle **19**, whereas with carbene **7** phosphonioketeneimine **18** and bis(diisopropylamino)phosphinonitrile are obtained.

Introduction

The synthesis of stable carbenes has long been an important goal for chemists from both synthetic and theoretical view points. Recently two types of carbene have been isolated at room temperature: the 1,3-dialkylimidazol-2-ylidenes **A**[1] and the (phosphanyl)(silyl)carbenes **B**.[2] The stability of Arduengo's carbenes **A** is due to the presence of the two adjacent nitrogen atoms and of the CC double bond which considerably increases the electron density at the carbene centre and therefore prevents dimerization or the attack by any nucleophiles.[1e] On the other hand, calculations[2e,f] led to the conclusion that phosphinocarbenes **B** are best described as vinyl ylides **B′** or even as cumulenes **B″**; the silyl group partially releases the negative charge of the carbon atom. As phosphonio and silyl groups possess similar electronic properties, the possibility of obtaining stable (phosphino)(phosphonio)carbenes **C** was thus considered[3] (Chart 1).

Here we report the preparation, using two different synthetic routes, and low temperature multinuclear NMR characterization of several (phosphino)(phosphonio)diazo derivatives, which are the precursors of carbenes of type **C**. One of these carbenes has been isolated as crystals, while the others have been characterized in solution. The reactivity of these intriguing species is also presented.

Chart 1



Results and Discussion

Since (phosphino)(silyl)diazomethane derivatives have proven to be excellent precursors for carbenes **B**,[2a−d,4] we chose to prepare (phosphino)(phosphonio) analogues as starting materials for carbenes **C**. Two synthetic routes appeared to be successful (Scheme 1).

The first route involves the protonation of bis[bis(diisopropylamino)phosphino]diazomethane, **1**. One equivalent of trifluoromethanesulfonic acid was added to a $CDCl_3$ solution of **1**[5] at 193 K, and the sample was gradually warmed in approximately 10 K steps, while monitoring the reaction by ^{31}P NMR spectroscopy. At 240 K a new set of signals (+70.71 ppm, broad d, $J_{PP} = 97$ Hz; +12.01 ppm, ddq, $J_{PP} = 97$ Hz, $J_{PH} = 578$ and 17.2 Hz) appeared. The value of the PP coupling constant is typical of a $\sigma^3P{-}C{-}\sigma^4P$ containing fragment,[6] while the presence of a large J_{PH} proved that the σ^4-phosphorus atom is directly bound to a hydrogen atom. We attributed this system to the formation of the desired (phosphino)(phosphonio)diazomethane **2**. The nature of **2** was further confirmed by the

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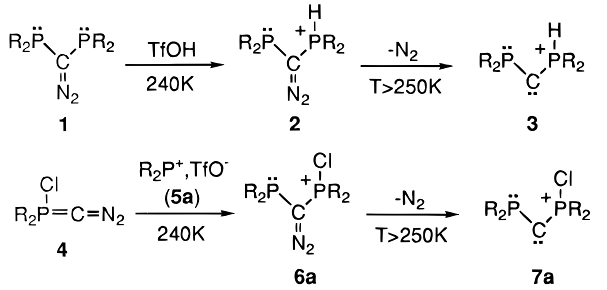
Scheme 1



R: *i*-Pr$_2$N; Tf: CF$_3$SO$_2$; counter anion: CF$_3$SO$_3^-$

Table 1. Comparison of Selected NMR Spectral Data for the Intermediate Diazo Compounds **2** and **6a** and the Carbenes **3** and **7a**−**c**[a]

compound	δ ^{31}P(ppm) (J_{PP} Hz)	δ ^{13}C(ppm) (J_{PC} Hz)
2[b]	+70.71, +12.01 (97.3)	+35.76 (143.7, 99.9)
6a[c]	+73.86, +63.95 (123.6)	+40.82 (160.6, 101.4)
3	+27.16, +3.14 (120.8)	+98.90 (143.4, 157.9)
7a	+51.94, +35.05 (71.4)	+103.85 (127.8, 153.7)
7b	+53.82, +34.28 (75.9)	
7c	+49.53, +36.17 (73.6)	

[a] **2**, **6a**, **3** and **7a** chemical shifts reported in CDCl$_3$; **7b** and **7c** shifts recorded in DCE. [b] Spectra recorded at 240 K. [c] Spectra recorded at 235 K.

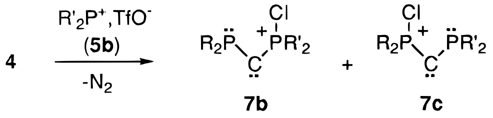
^{13}C{^{1}H} NMR spectrum; the diazo carbon atom appearing as expected as a doublet of doublets at 35.7 ppm ($^1J_{PC}$ = 143.7 and 99.9 Hz) (Table 1).

The method used for the synthesis of the phosphoniodiazo compound **2** appears specific to the H-substituted derivative. Attempts to prepare the methyl analogue using methyl triflate instead of triflic acid failed. Direct substitution of the proton itself has also proved impossible; therefore, we investigated a totally different synthetic route.

We have already shown that diazomethylenephosphorane **4**[7] reacts with Lewis acids giving the corresponding phosphoniodiazo derivatives.[8] On treating cumulene **4** with 1 equiv of bis(diisopropylamino)phosphenium trifluoromethanesulfonate, **5a**,[9] the (phosphino)(*P*-chlorophosphonio)diazo derivative **6a** is readily formed at low temperature as demonstrated by ^{31}P{^{1}H} NMR (AX system at +73.86 and +63.95 ppm, J_{PP} = 123.3 Hz) and ^{13}C NMR spectroscopy (C=N$_2$: 40.82 ppm, dd, J_{PC} = 101.2 and 160.6 Hz) (Table 1, Scheme 1).

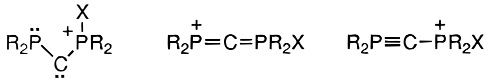
In marked contrast with most of the (phosphino)(silyl)-diazomethane derivatives, both (phosphino)(phosphonio)diazo compounds **2** and **6a** appeared to be unstable with respect to dinitrogen elimination, which began at 250 K. *P*-Hydrogenophosphoniocarbene **3** was obtained as extremely air sensitive yellow crystals (mp 88 °C; 76% yield), stable in the solid state for months at room temperature. Compound **3** was fully characterized including by an X-ray diffraction study.[3a] The σ^3-phosphorus atom is planar and the P−C−P angle (165 °) much larger than expected for a singlet carbene (typically 102−105 °).[1,10] Furthermore the σ^3P−C bond of approximately 1.548 Å is comparable with a σ^1P−C triple bond,[11] while the σ^4P−C distance of approximately 1.7 Å is too short to be considered a single bond (implying a degree of ylide character). From this X-ray analysis, as well as from calculations,[12] it is reasonable to invoke a certain degree of charge delocalization throughout the molecule, and thus compound **3** is best regarded as **3′**.

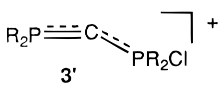
Scheme 2



R: *i*-Pr$_2$N; R′: *c*-Hex$_2$N; Tf: CF$_3$SO$_2$; counter anion: CF$_3$SO$_3^-$

Chart 2





3′

In the same way, the *P*-chloro analogue **7a** was formed in nearly quantitative yield from **6a** (typically 80−90% according to ^{31}P NMR spectroscopy), although the reaction is critically dependent on the purity of all reactants and on precise reaction conditions. Despite being stable in solution at room temperature for a period of days, all attempts to isolate **7a** (including by exchange of the counteranion) failed; thus **7a** was only characterized spectroscopically. As apparent in Table 1, the ^{31}P and ^{13}C NMR data obtained for **7a** and **3** are quite comparable, suggesting a very similar structure.

In an attempt to isolate a compound of type **7**, we chose to synthesise the unsymmetrical carbene **7b** by treating diazomethylenephosphorane **4** with 1 equiv of the bis(dicyclohexylamino)phosphenium salt **5b**.[13] The ^{31}P{^{1}H} NMR spectrum of the reaction mixture revealed the formation of two AX systems at +53.82, +34.28 ppm (J_{PP} = 75.9 Hz) and +49.53, +36.17 ppm (J_{PP} = 73.6 Hz) in a ratio of 4:1, respectively. Since the chemical shifts and the coupling constants are very similar to those observed for **7a** (Table 1), it is quite likely that these signals can be attributed to carbenes **7b** and **7c** (Scheme 2). This result can be explained by the relatively facile migration of the chlorine atom between the two phosphorus centers. The lability of the chlorine substituent may explain the problems experienced in isolating compounds **7**.

Depending on the way we look at derivatives **3** and **7**, they can be considered as possessing several functionalities: a reactive substituent at the phosphonio group (H or Cl), a methylenephosphonium arrangement, a phosphorus ylide moiety, a phosphorus−carbon triple bond, and a carbenic center (Chart 2). Indeed, these species show interesting and diverse reactivity.

Since compound **3** features a proton on the phosphonio group, it was tempting to remove it, which was achieved using potassium *tert*-butoxide. The subsequent bis(phosphanyl)-carbene **8** is transiently formed but rapidly rearranges *via* a classical 1,2-migration affording the corresponding phosphaalkene **9**. Note that **9** can also be obtained by photolysis of the

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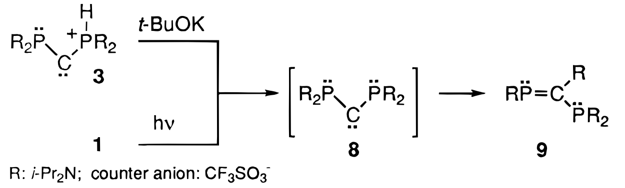
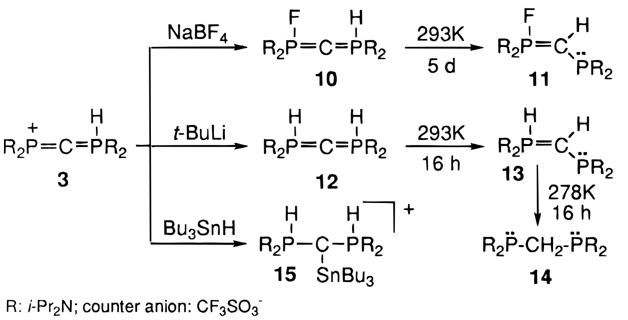
Scheme 3



Scheme 4



corresponding diazo compound **1**[5a] (Scheme 3). This result clearly demonstrates that phosphanylcarbenes are only stable when they are substituted by an electron-withdrawing group.

Phosphonium salts do not usually react with nucleophiles (except by anion exchange); however, since one of the forms of compounds **3** and **7** features a strongly electrophilic methylenephosphenium moiety ($\rangle P^+{=}C\langle$),[14] the reaction with fluoride anion was investigated. Indeed, compound **3** reacts with sodium tetrafluoroborate leading to carbodiphosphorane **10**, which was isolated in 70% yield. This result also demonstrates the strong Lewis acid character of the three-coordinate phosphorus center of **3**. This compound is thermally stable in the solid state (mp 116 °C), but in solution, at room temperature, it rearranges after 1 week into the isomeric phosphorus ylide **11** (Scheme 4). Note, that **10** can also be directly obtained by addition of tetrafluoroboric acid to diphosphinodiazomethane **1**.

Taking into account the surprising stability[15] of **10**, since no example of a carbodiphosphorane with a P−H bond was known, it was tempting to prepare a carbodiphosphorane featuring two P−H bonds. Reactions of **3** with *tert*-butyllithium gave the desired compound **12**, which was characterized in solution. Rearrangement occurs at room temperature over the course of about 16 h to give the phosphorus ylide **13**. Again, **13** featuring a P−H bond is not stable and was completely transformed overnight into diphosphinomethane **14** (Scheme 4).

Unsaturated substrates readily undergo hydrometalloaddition with certain metal hydrides.[16] Thus to probe the phosphorus−carbon multiple bond character, indicated by the X-ray molecular structure, **3** was treated with 1 equiv of (n-Bu)$_3$SnH (Scheme 4). Indeed, this cleanly afforded a new adduct **15**, which gave a single resonance in the ^{31}P{^{1}H} NMR spectrum at +34.7 ppm and showed a coupling to tin of $J_{PSn} = 33.3$ Hz, confirmed by the ^{119}Sn NMR spectrum which displayed a triplet at −6.5 ppm.

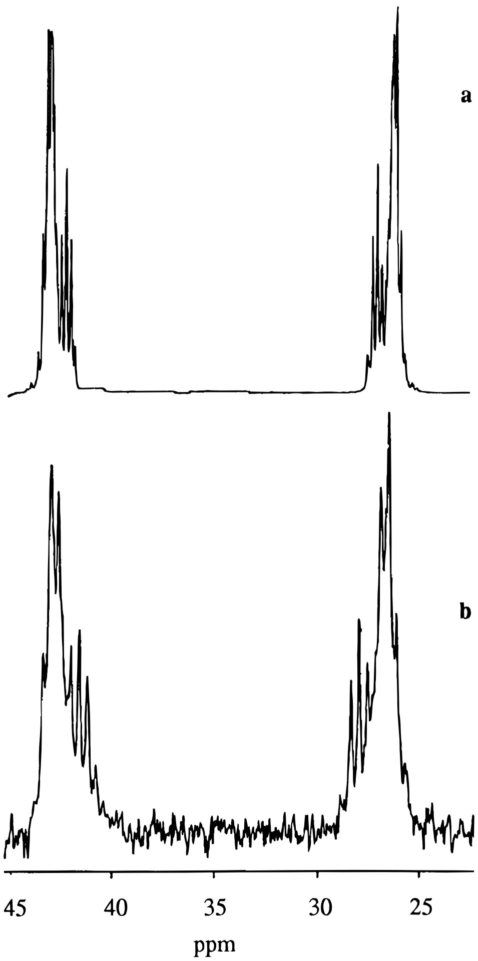


Figure 1. Calculated (a) and experimental (b) ^{31}P NMR spectra (32.438 MHz) of stannyl derivative **15**.

The structure of **15** was confirmed by the ^{31}P proton-coupled NMR which gave a second order spectrum, AA′XX′. The spectrum could adequately be simulated using the PANIC program (Figure 1). The stannyl derivative **15** proved to be relatively stable in solution at room temperature yet all attempts to isolate it resulted in decomposition.

The reactivity reported so far involved either the cationic or the multiple bond character of phosphoniocarbenes, and of course it was of primary importance to find some carbenic reactivity. In contrast to the related (phosphino)(silyl)carbenes **B**, no cyclopropanation reaction was observed on reacting **3** or **7** with alkenes, possibly because of the excessive steric hindrance around the carbenic center. However, when two equivalents of *tert*-butyl isocyanide were added to **3** at low temperature a clean reaction occurred leading to heterocycle **19** (Scheme 5). The involvement of two *t*-BuNC and the elimination of diisopropylamine are clear from the mass spectrum. A cyclic structure for **19** is evident from the ^{13}C NMR spectrum which features a doublet of doublets for each of the two ring carbon atoms at 41.6 ppm ($J_{PC} = 30.2$ and 107.0 Hz) and 173.89 ppm ($J_{PC} = 51.0$ and 104.2 Hz). The high field signal is in the range expected for a keteneimine arrangement [confirmed by a second signal for the sp-hybridized carbon at 140.53 ppm ($J_{PC} = 9.7$ and 22.8 Hz) and an IR absorption at 2086 cm^{-1}], while the low field signal argues for the presence of an imine. Furthermore, the ^{13}C NMR spectrum shows that one of the phosphorus centers is chiral and bears two diastereotopic isopropyl C−H groups, as signified by their greatly differing chemical shifts (54.12 and 44.29 ppm). This was

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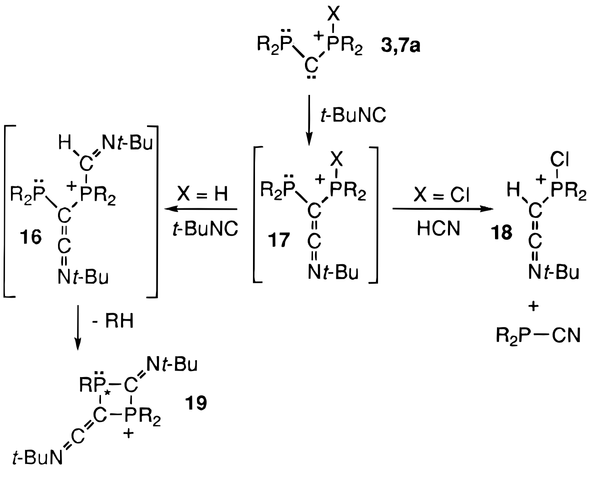
Scheme 5



R: i-Pr_2N; counter anion: $CF_3SO_3^-$

confirmed by both heteronuclear correlated NMR spectra and by ^{13}C NMR spectra with selective phosphorus decoupling.

It is believed that the initial coupling product **17** rapidly inserts a further equivalent of isocyanide into the P–H bond (using 1 equiv of isocyanide left 50% of **3** unreacted). This type of insertion has been observed previously by Hoffmann.[17] The intermediate **16** then undergoes rapid elimination of (i-$Pr)_2NH$ with subsequent formation of **19** (Scheme 5).

To verify that the formation of **19** did actually result from the insertion of a second equivalent of *tert*-butyl isocyanide into the P–H bond of **17**, the reaction was repeated using the *P*-chlorophosphoniocarbene **7a**. Two singlets appeared on the ^{31}P NMR spectrum, indicating the formation of a mixture of two products in a ratio of 1:1. The same result was observed if 2 equiv of isocyanide were used. The peak at +53.48 ppm (doublet of quintets, $J_{PH} = 7.9$ and 22.2 Hz), has been attributed to the formation of the phosphonioketeneimine **18**. This is consistent with the observation of a band at 2091 cm^{-1} in the infrared spectrum, and of two doublets at 150.36 ppm ($J_{PC} = 3.5$; C=*C*=N) and 38.42 ppm ($J_{PC} = 175.1$ Hz; *C*=C=N) in the ^{13}C NMR spectrum. All attempts to isolate **18** failed and thus all characterization was performed spectroscopically. The second product (+31.30 ppm, $J_{PH} = 12.6$ Hz) is the (bis(diisopropylamino)phosphino)nitrile,[4] which was isolated as the thioxophosphoranyl analogue[18] after treatment with elemental sulfur. It is believed that these two products result from the reaction of the intermediate coupling product **17** with residual HCN, inherently present in the t-BuNC (Scheme 5).

Conclusion

Surprisingly, (phosphino)(phosphonio)carbenes are stable at room temperature and can even in some cases be isolated as crystals, while their diazo precursors are only observable at low temperature. This new family of "carbenes" are in fact best described as phosphorus vinyl ylides with some delocalization of the positive charge over the whole molecule. They are useful synthetic precursors to a range of new products. Due to the presence of an electrophilic center, the synthesis of the first carbodiphosphoranes featuring P–H bonds can be achieved. 1,2-Addition reactions with tin hydrides are possible due to their phosphorus–carbon multiple bond character, and "carbene–carbene" coupling reactions are also observed with isonitriles. In other words, these so-called carbenes react in a number of unclassical ways.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry argon using standard vacuum line and Schlenk techniques or in an argon-filled Braun drybox. Solvents were dried prior to use and distilled from molten sodium (toluene), sodium/benzophenone (ether, THF), P_2O_5 (pentane, dichloromethane, 1,2-dichloromethane), and calcium hydride (acetonitrile). n-Bu_3SnH (Aldrich) was used as received. Trifluoromethanesulfonic acid (Aldrich) was degassed prior to use. *tert*-Butyl isocyanide (Aldrich) was dried over 4-Å molecular sieves and degassed. Bis[bis(diisopropylamino)phosphino]diazomethane, **1**,[5] chlorodiazomethylenephosphorane, **4**,[7] bis(diisopropylamino)phosphenium trifluoromethanesulfonate, **5a**,[9] and bis(dicyclohexylamino)phosphenium trifluoromethanesulfonate, **5b**,[13] were prepared according to published procedures. ^1H, ^{13}C, ^{31}P and ^{119}Sn NMR spectra were recorded on Bruker AC80, AC200, WM250, and AMX400 spectrometers at ambient probe temperatures unless otherwise stated. C_6D_6 and $CDCl_3$ were distilled from P_2O_5 and degassed prior to use. ^1H and ^{13}C chemical shifts in ppm were referenced using the partially deuterated solvent as internal reference. ^{31}P and ^{119}Sn downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and Me_3SnCl, respectively. Coupling constants and line widths are reported in Hz. Infrared spectra were obtained in a solution cell with KBr windows on a Perkin-Elmer FT-IR 1725X spectrometer. Mass spectra were recorded on a Ribermag R10 10E instrument and are reported in *m*/*z*.

Synthesis of (Phosphino)(phosphonio)carbene 3. To a dichloromethane solution (4 mL) of diazo derivative **1** (0.40 g, 0.8 mmol) was added a stoichiometric quantity of trifluoromethanesulfonic acid (70 μL, 0.8 mmol) dropwise at −40 °C. After the mixture was warmed to room temperature, solvent was removed *in vacuo*, and the resulting solid washed with ether (3 × 5 mL), **3** was obtained as a yellow powder (0.38 g, 76%): mp 87–89 °C dec; ^1H (200.13 MHz, $CDCl_3$) 7.56 (dd, $^1J_{PH} = 530.3$ Hz, $^3J_{PH} = 7.2$ Hz, 1H, PH), 3.70 (m, 8H, $CH(CH_3)_2$), 1.32 (d, $^3J_{HH} = 6.7$ Hz, 24H, $CH(CH_3)_2$), 1.22 (d, $^3J_{HH} = 6.9$ Hz, 12H, $CH(CH_3)_2$), 1.19 (d, $^3J_{HH} = 6.9$ Hz, 12H, $CH(CH_3)_2$); ^{13}C (50.32 MHz, $CDCl_3$) 120.4 (q, $^1J_{CF} = 320.0$ Hz, CF_3), 98.9 (dd, $^1J_{PC} = 143.4$ Hz and 157.9 Hz, PCP), 49.7 (d, $^2J_{PC} = 2.6$ Hz, σ^3-PNCH), 45.8 (d, $^2J_{PC} = 6.2$ Hz, σ^4-PNCH), 23.0 (d, $^3J_{PC} = 15.1$ Hz, σ^4-P-$NCH(CH_3)_2$), 22.5 (s, σ^3-P-$NCH(CH_3)_2$); ^{31}P (81.01 MHz, $CDCl_3$) +27.16 (ddq, $^2J_{PP} = 120.8$ Hz, $^3J_{PH} = 7.2$ and 19.2 Hz), +3.14 (ddq, $^2J_{PP} = 120.8$ Hz, $^1J_{PH} = 530.3$ Hz, $^3J_{PH} = 17.4$ Hz).

Synthesis of Carbene 7a. To a 1,2-dichloroethane (DCE) solution (3 mL) of **4** prepared from [bis(diisopropylamino)phosphanyl](trimethylsilyl)diazomethane (0.225 g, 0.65 mmol) and CCl_4 (63 μL, 0.65 mmol), a DCE solution (3 mL) of **5a** was added at 0 °C. Darkening of the solution occured on warming to room temperature, ^{31}P NMR indicating nearly quantitative conversion to the carbene **7a**. Isolation of **7a** proved impossible due to facile decomposition and was thus characterized in solution without further purification: ^1H NMR (400.13 MHz, 273 K, $CDCl_3$) 3.81 (m, 8 H, $CH(CH_3)_2$) 1.38 (d, $^3J_{HH} = 6.7$ Hz, 12H, $CH(CH_3)_2$), 1.31 (d, $^3J_{HH} = 6.0$ Hz, 12 H, $CH(CH_3)_2$), 1.29 (d, $^3J_{HH} = 6.0$ Hz, 12 H, $CH(CH_3)_2$), 1.23 (d, $^3J_{HH} = 6.8$ Hz, 12 H, $CH(CH_3)_2$); ^{13}C NMR (100.62 MHz, 273 K, $CDCl_3$) 120.35 (q, $^1J_{CF} = 320.2$ Hz, $CF_3SO_3^-$), 103.85 (dd, $^1J_{CP} = 127.8$ and 153.7 Hz, P=*C*=P), 50.35 (s, $CH(CH_3)_2$), 49.09 (d, $^2J_{CP} = 11.0$ Hz, $CH(CH_3)_2$), 48.07 (d $^2J_{CP} = 5.3$ Hz, $CH(CH_3)_2$), 23.53 (d, $^2J_{CP} = 8.3$ Hz, $CH(CH_3)_2$), 23.06 (s, $CH(CH_3)_2$), 22.82 (s, $CH(CH_3)_2$), 22.23 (s, $CH(CH_3)_2$); ^{31}P NMR (161.98 MHz, 273 K, $CDCl_3$) +51.94 (qd, $^2J_{PP} = 70.7$, $^3J_{PH} = 16.5$ Hz, σ^4-P), +35.05 (m br, $^2J_{PP} = 71.4$ Hz, σ^3-P).

Synthesis of carbenes 7b and 7c. A similar experimental procedure was used as for the preparation of **7a**.

Synthesis of Phosphaalkene 9. To a solution of **3** (0.62 g, 1 mmol) in THF (5 mL) was added at −78 °C an equimolar amount of t-BuOK. When the solution was warmed to room temperature, the solvent was removed under vacuum, and the residue was extracted with pentane (10 mL). Evaporation of the solvent afforded **9** as a viscous oil (45%).[5a]

Synthesis of Carbodiphosphorane 10. To a solution of **3** (0.62 g, 1.0 mmol) in dichloromethane (5 mL) was added 1 equiv of $NaBF_4$

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(18) Sicard, G.; Baceiredo, A.; Crocco, G.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 301–302.

(0.11 g, 1.0 mmol). After the mixture was stirred at room temperature for 2 h, the solvent was removed *in vacuo*. Subsequent washing with ether (3 × 5 mL) afforded **10** as a white powder: yield 0.35 g (70%); mp 114−118 °C; ^{1}H NMR (200.13 MHz, 295 K, CDCl$_3$) 7.20 (m, $^{1}J_{PH}$ = 524.2 Hz, $^{3}J_{PH}$ = 4.0 Hz, $^{4}J_{HF}$ = 4.0 Hz, 1H, P−H), 3.70 (m, $^{3}J_{HH}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 1.25 (d, $^{3}J_{HH}$ = 6.8 Hz, 48H, CH(C*H*$_3$)$_2$); ^{13}C NMR (50.32 MHz, 273 K, CDCl$_3$) 48.06 (dd, $^{2}J_{PC}$ = 5.7 Hz, $^{3}J_{CF}$ = 2.5 Hz, *C*H(CH$_3$)$_2$), 46.40 (d, $^{2}J_{PC}$ = 4.4 Hz, *C*H(CH$_3$)$_2$), 22.94 (d, $^{3}J_{PC}$ = 2.6 Hz, CH(*C*H$_3$)$_2$), 22.65 (s, CH(*C*H$_3$)$_2$), 17.90 (ddd, $^{1}J_{PC}$ = 143.8 and 195.0 Hz, $^{2}J_{PF}$ = 24.8 Hz, =C=); ^{31}P NMR (32.44 MHz, 273 K, CDCl$_3$) +59.5 (dddq, $^{1}J_{PF}$ = 951.8 Hz, $^{2}J_{PP}$ = 32.9 Hz, $^{3}J_{PH}$ = 4.0 and 17.8 Hz, PF), +9.2 (dddq, $^{1}J_{PH}$ = 524.2 Hz, $^{3}J_{PH}$ = 16.1 Hz, $^{2}J_{PP}$ = 32.9 Hz, $^{3}J_{PF}$ = 15.3 Hz, PH). Carbodiphosphorane **10** can also be obtained by treating a solution of the diazo **1** (0.50 g, 1 mmol) in dichloromethane (5 mL) at −40 °C with a stoichiometric quantity of tetrafluoroboric acid−diethyl ether complex (0.20 g, 1 mmol). After this was stirred at room temperature for 2 h, the solvent was removed *in vacuo*. Subsequent washing with ether (3 × 5 mL) afforded **10** as a white powder, yield 0.38 g (75%).

Synthesis of Phosphorus Ylide 11. A solution of **10** (0.49 g, 1.0 mmol) in THF (5 mL) was stirred at room temperature for 1 week. After removal of solvent under reduced pressure, **11** was obtained as a viscous oil: yield 0.44 g (90%); ^{1}H NMR (200.13 MHz, 295 K, CDCl$_3$) 3.90 (dsept, $^{3}J_{PH}$ = 17.3 Hz, $^{3}J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 3.44 (dsept, $^{3}J_{PH}$ = 12.8 Hz, $^{3}J_{HH}$ = 6.6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.75 (ddd, $^{2}J_{PH}$ = 16.8 and 5.4 Hz, $^{3}J_{FH}$ = 10.9 Hz, 1H, C*H*), 1.42 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.35 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.21 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$), 1.11 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, CH(C*H*$_3$)$_2$); ^{13}C NMR (50.32 MHz, 295 K, CDCl$_3$) 49.00 (pseudo-t, $^{2}J_{PC}$ and $^{3}J_{FC}$ < 2 Hz, FP(NCH)), 47.60 (d, $^{2}J_{PC}$ = 12.1 Hz, *C*H(CH$_3$)$_2$), 28.10 (ddd, $^{1}J_{PC}$ = 99.6 and 44.5 Hz, $^{2}J_{FC}$ = 15.3 Hz, *C*H), 23.90 (d, $^{2}J_{PC}$ = 6.8 Hz, CH(*C*H$_3$)$_2$), 23.80 (d, $^{2}J_{PC}$ = 7.1 Hz, CH(*C*H$_3$)$_2$), 23.2 (s, CH(*C*H$_3$)$_2$), 22.70 (s, CH(*C*H$_3$)$_2$); ^{31}P NMR (32.44 MHz, 310 K, CDCl$_3$) +71.2 (dddq, $^{2}J_{PP}$ = 81.1 Hz, $^{1}J_{PF}$ = 1015.4 Hz, $^{2}J_{PH}$ = 16.8 Hz, $^{3}J_{PH}$ = 17.3 Hz, PF), +39.3 (ddq, $^{2}J_{PP}$ = 81.1 Hz, $^{3}J_{PH}$ = 12.8 Hz, $^{2}J_{PH}$ = 5.4 Hz, σ^3-P). Anal. Calcd for $C_{25}H_{57}N_4P_2$: C, 63.10; H, 12.10; N, 11.78. Found: C, 63.00; H, 11.90; N, 11.70.

Synthesis of Carbodiphosphorane 12. To a solution of **3** (0.62 g, 1.0 mmol) in [D$_8$]THF (5 mL) at −78 °C was added *t*-BuLi (0.63 mL, 1.6 M, 1.0 mmol). This resulted in the formation of **12** as indicated by ^{31}P NMR spectroscopy. Due to its reactive nature **12** was characterized in solution without further purification: ^{31}P NMR (32.44 MHz, 310 K, CDCl$_3$) −8.0 ($AA'XX'M_4M_4'$ system $^{1}J_{PH}$ = 465 Hz, $^{3}J_{PH}$ = 1 Hz, $^{2}J_{PP}$ = 158 Hz, $^{4}J_{HH}$ = 0, $^{3}J_{PH(CH)}$ = 15 Hz).

Synthesis of 13. After 16 h at room temperature the carbodiphosphorane **12** underwent a near quantitative rearrangement in [D$_8$]THF, affording **13**, according to ^{31}P NMR spectroscopy: ^{31}P NMR (32.44 MHz, 310 K, CDCl$_3$) +49.5 (broad d, $^{2}J_{PP}$ = 174.7 Hz), +13.1 (broad dd, $^{2}J_{PP}$ = 174.7 Hz, $^{1}J_{PH}$ = 486.3 Hz).

Synthesis of 14. After 16 h at room temperature **13** in [D$_8$]THF underwent a rearrangement to quantitatively afforded **14**. The solvent was removed *in vacuo* and the resulting solid recrystallized from pentane/toluene at −20 °C to afford **14** as colorless crystals: yield 0.40 g (85%); mp 167−168 °C; MS *m*/*z* 477 ($M + H^+$); ^{1}H NMR (200.13 MHz, 295 K, CDCl$_3$) 3.40 (d sept, $^{3}J_{PH}$ = 7.0 Hz, $^{3}J_{HH}$ = 6.6 Hz, 8H, C*H*(CH$_3$)$_2$), 2.10 (t, $^{2}J_{PH}$ = 5.0 Hz, 2H, C*H*$_2$), 1.17 (d, $^{3}J_{HH}$ = 6.6 Hz, 24H, CH(C*H*$_3$)$_2$), 1.15 (d, $^{3}J_{HH}$ = 6.6 Hz, 24H, CH(C*H*$_3$)$_2$); ^{13}C NMR (50.32 MHz, 295 K, CDCl$_3$) 46.31 (pseudo-t, $^{2}J_{PC}$ = 5.0 Hz, *C*H(CH$_3$)$_2$), 30.27 (t, $^{1}J_{PC}$ = 21.9 Hz, *C*H$_2$), 24.56 (s, CH(*C*H$_3$)$_2$), 24.55 (d, $^{2}J_{PC}$ = 10.7 Hz, CH(*C*H$_3$)$_2$), 24.18 (s, CH(*C*H$_3$)$_2$), 24.16 (d, $^{2}J_{PC}$ = 3.3 Hz, CH(*C*H$_3$)$_2$); ^{31}P NMR{^{1}H} (32.44 MHz, 310 K, CDCl$_3$) +44.0 (s). Anal. Calcd for $C_{25}H_{58}N_4P_2$: C, 62.97; H, 12.29; N, 11.75. Found: C, 62.90; H, 12.01; N, 11.60.

Synthesis of the *C*-Bis[bis(diisopropylamino)phosphonio]-*C*-[tris(*n*-butyl)stannyl]methylene Cation, 15. To a THF solution (10 mL) of **3** at −40 °C was added neat *n*-BuSnH (0.29 g, 1 mmol). Due to the facile decomposition of **15**, all characterization was performed spectroscopically: ^{1}H (200.13 MHz, 295 K, CDCl$_3$) 7.02 (d, $^{1}J_{PH}$ = 526.2 Hz, 2 H, P*H*), 3.71 (dsept, $^{3}J_{PH}$ = 13.8 Hz, $^{3}J_{HH}$ = 6.9 Hz, 8 H, C*H*(CH$_3$)$_2$), 1.31 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.29 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 1.07 (m, 6 H, CH$_3$(C*H*$_2$)$_3$Sn), 0.85 (m, 3 H, C*H*$_3$(CH$_2$)$_3$Sn); ^{13}C (50.32 MHz, 295 K, CDCl$_3$) 120.4 (q, $^{1}J_{CF}$ = 320.4 Hz, *C*F$_3$SO$_3$), 47.50 (s, *C*H(CH$_3$)$_2$), 28.9 and 27.1 (s, CH$_3$*C*H$_2$*C*H$_2$Sn), 24.25 (s, CH(*C*H$_3$)$_2$), 23.80 (s, CH(*C*H$_3$)$_2$), 13.32 (s, *C*H$_3$(CH$_2$)$_3$Sn), 13.10 (s, $^{1}J_{C^{119}Sn}$ = 352.6, $^{1}J_{C^{117}Sn}$ = 330.0 Hz, CH$_3$CH$_2$CH$_2$*C*H$_2$Sn); ^{31}P (32.44 MHz, 310 K, CDCl$_3$) see Figure 1; ^{119}Sn (29.88 MHz, 310 K, CDCl$_3$) −6.47 (t, $^{2}J_{PSn}$ = 34.1 Hz).

Synthesis of Heterocycle 19. To a dichloromethane solution (1.5 mL) of **3** (0.49 g, 0.78 mmol) was added a dichloromethane solution (1.5 mL) of *tert*-butyl isocyanide (0.18 mL, 1.56 mmol) at −78 °C. ^{31}P NMR spectroscopy indicated that complete conversion had occurred on warming to room temperature. Dichloromethane was removed *in vacuo* and THF (2 mL) added, the solution then being cooled to −30 °C overnight. Ammonium salts were removed by filtration. Removal of all volatiles under vacuum afforded a yellow/orange oil, which was further purified by washing with ether (5 × 5 mL): ^{1}H NMR (400.14 MHz, 273 K, CDCl$_3$) 3.83 (m, C*H*(CH$_3$)$_2$), 3.56 (m, C*H*(CH$_3$)$_2$), 1.22 (m, CH(C*H*$_3$)$_2$), 1.16 (m, CH(C*H*$_3$)$_2$); ^{13}C NMR (100.62 MHz, 273 K, CDCl$_3$) 173.89 (dd, $^{1}J_{PC}$ = 51.0 and 104.2 Hz, *C*=NC(CH$_3$)$_3$), 140.53 (dd, $^{2}J_{PC}$ = 9.7 and 22.8 Hz, C=*C*=NC(CH$_3$)$_3$), 119.95 (q, $^{1}J_{CF}$ = 319.5 Hz, *C*F$_3$SO$_3$), 64.34 (d, $^{3}J_{PC}$ = 35.2 Hz, *C*(CH$_3$)$_3$), 62.10 (s, *C*(CH$_3$)$_3$), 54.12 (d, $^{2}J_{PC}$ = 13.3 Hz, σ^3-P*C*H(CH$_3$)$_2$), 48.47 (d, $^{2}J_{PC}$ = 3.4 Hz, σ^4-P*C*H(CH$_3$)$_2$), 47.62 (d, $^{2}J_{PC}$ = 4.2 Hz, σ^4-P*C*H(CH$_3$)$_2$), 44.29 (d, $^{2}J_{PC}$ = 22.2 Hz, σ^3-P*C*H(CH$_3$)$_2$), 41.6 (dd, $^{1}J_{PC}$ = 30.2 and 107.0 Hz, *C*=C=N), 22.60 (m, CH(*C*H$_3$)$_2$); ^{31}P NMR (161.98 MHz, 273 K, CDCl$_3$) +83.59 (dt, $^{2}J_{PP}$ = 78.4 Hz, $^{3}J_{PH}$ = 10.5 Hz, σ^3-P), +47.56 (m, σ^4-P).

Synthesis of Phosphonioketene Imine 18. To a DCE solution (2 mL) of carbene **7a** (1.14 mmol) was added neat *tert*-butyl isocyanide (130 μL, 1.14 mmol) at −78 °C. When this was warmed to room temperature, two products were present according to ^{31}P NMR spectroscopy. The reaction mixture was treated with ether (5 mL) and the soluble fraction isolated by filtration, which on removal of volatiles under vacuum afforded (bis(diisopropylamino)phosphino)nitrile.[4] The insoluble fraction contained **18** which was subsequently characterized spectroscopically: ^{1}H NMR (200.13 MHz, 295 K, CDCl$_3$) 4.71 (d, $^{2}J_{PH}$ = 8.0 Hz, 1H, PCH), 3.84 (m, 4H, C*H*(CH$_3$)$_2$), 1.31 (d-broad, $^{3}J_{HH}$ = 6.0 Hz, 24 H, CH(C*H*$_3$)$_2$); ^{13}C NMR (62.90 MHz, 295 K, CDCl$_3$) 150.55 (d, $^{2}J_{PC}$ = 9.7 Hz, C=*C*=N), 61.91 (d, $^{4}J_{PC}$ = 3.5 Hz, *C*CH$_3$), 48.49 (d, $^{2}J_{PC}$ = 4.4 Hz, *C*H(CH$_3$)$_2$), 38.45 (d, $^{1}J_{PC}$ = 175.1 Hz, PCH), 29.28 (s, C*C*H$_3$), 22.65 (d, $^{3}J_{PC}$ = 5.9 Hz, CH(*C*H$_3$)$_2$); ^{31}P NMR (81.02 MHz, 295 K, CDCl$_3$) +53.48 (dq, $^{3}J_{PH}$ = 22.2 Hz, $^{2}J_{PH}$ = 8.0 Hz); IR (CDCl$_3$) 2091 cm^{-1}.

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