C-Phosphoniophosphaalkenes as Precursors of $1\sigma^4,3\sigma^2$-Diphosphaallenes: Scope and Limitations

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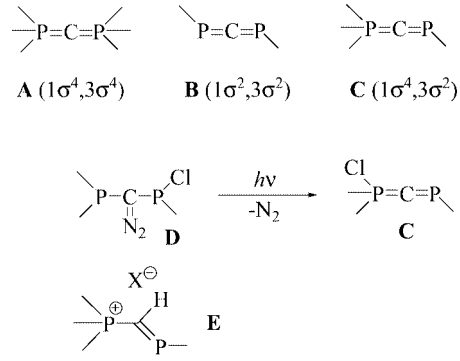
The study of a general synthetic route to $1\sigma^4,3\sigma^2$-diphosphaallenes involving the reaction of LiHMDS with *C*-phosphoniophosphaalkenes is reported. The choice of the base is critical since the precursors are highly electrophilic species that react cleanly with methyl-, butyl-, mesityl-, or *tert*-butyllithium to afford *C*-phosphanylphosphonium ylides. The role of the substituents at the σ^4-phosphorus centre has also been studied. The resulting phosphaallenes react cleanly with a Lewis acid and undergo [3+2] cycloaddition with azides to afford a five-membered heterocycle in a three-step process.

Introduction

Among the possible neutral heterocumulenes featuring the PCP sequence, $1\sigma^4,3\sigma^4$-diphosphaallenes (carbodiphosphoranes) **A**[1] and $1\sigma^2,3\sigma^2$-diphosphaallenes **B**[2] have been known for many years. Recently, we reported the synthesis and characterisation of the first $1\sigma^4,3\sigma^2$-diphosphaallene **C** (Scheme 1), which features two different types of phosphorus–carbon "double" bonds.[3,4] Derivative **C** was prepared by elimination of N_2 from the phosphanyl(chlorophosphanyl)diazomethane **D**, which first leads to the corresponding transient carbene that then undergoes a 1,3-chlorine shift from one phosphorus to the other. However, the scope of this synthetic strategy is very limited in terms of starting materials (diazo precursors and chlorine migrating group).

Although phosphoniophosphaalkenes **E** can be readily prepared in high yields,[5] their reactivity has not been explored in detail. In particular, *C*-hydrogenophosphoniophosphaalkenes could afford the desired heterocumulene **C** by a simple deprotonation. Herein, we describe our results concerning this new and more general synthetic way to $1\sigma^4,3\sigma^2$-diphosphaallenes.



Scheme 1.

Results and Discussion

Phosphoniophosphaalkenes **3** were prepared in two steps by the method described by Grützmacher et al.[5] Two equivalents of phosphonium ylides **1** react with bis(diisopropylamino)chlorophosphane to give the corresponding *C*-phosphanyl phosphorus ylides **2**, with one equivalent of ylide **1** acting as a base to deprotonate the transiently formed *C*-phosphanylphosphonium salts. In the second step, the heterolytic cleavage of a P–N bond is achieved by addition of two equivalents of $BF_3{\cdot}OEt_2$, which affords the corresponding phosphoniophosphaalkenes **3** in good yields (72–95%) (Scheme 2). In the ^{31}P NMR spectra, compounds **3** display an AX system, with a low-field signal ($\delta \approx$ 300 ppm) characteristic of the phosphaalkene moiety, and a phosphorus–phosphorus coupling constant of about 130 Hz. In the ^{13}C NMR spectra, the signal for the PCP carbon atom appears as a doublet of doublets, with chemical shifts in the range δ = 95–100 ppm.

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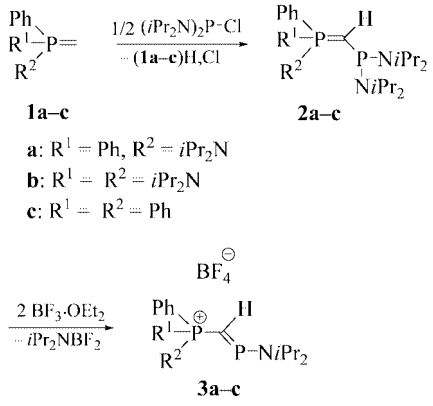
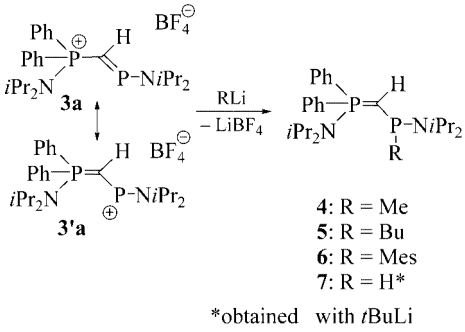


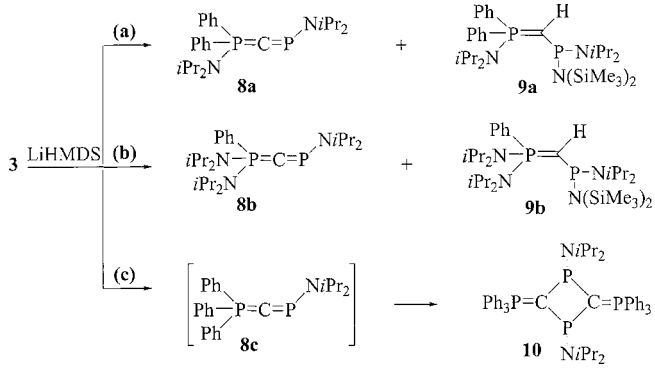
Scheme 2.

Phosphoniophosphaalkenes **3** are highly electrophilic species; they can be regarded as phosphenium salts substituted by a phosphonium ylide fragment (**3′**). Addition of methyl-, *n*-butyl- and mesityllithium to **3a** did not lead to the expected cumulenes; instead, the quantitative formation of the *C*-phosphanylphosphonium ylides **4**–**6** was observed (Scheme 3). This was indicated by the NMR spectroscopic data, in particular the disappearance of the characteristic low-field signal for the σ^2-phosphorus atom of compounds **3a** in the ^{31}P NMR spectrum. When the more sterically demanding *tert*-butyllithium was used, the *C*-phosphanylphosphonium ylide **7**,[6] featuring a P–H bond, was obtained in near quantitative yield. In the ^{31}P ^{1}H-coupled NMR spectrum, derivative **7** presents a characteristic doublet of doublets ($^2J_{P,P}$ = 160, $^1J_{P,H}$ = 220 Hz) at high-field (δ = –18 ppm) for the σ^3-phosphorus atom.



Scheme 3.

In order to prevent the nucleophilic attack at the σ^2-phosphorus atom we turned our attention to the bulky, but not reducing, lithium hexamethyldisilazide (LiHMDS). Addition of one equivalent of this strong base to a THF solution of **3a** afforded a mixture of compounds **8a** and **9a** in a 70:30 ratio (Scheme 4). The spectroscopic data for **9a** are again indicative of a phosphanylphosphonium ylide structure resulting from the addition of LiHMDS to the σ^2-phosphorus atom of **3a**. However, the major compound **8a** displays an AX system at δ = 313 and 41 ppm ($^2J_{P,P}$ = 190 Hz) in the ^{31}P NMR spectrum, the low-field signal being characteristic of a phosphaalkene moiety (Table 1). This new diphosphaallene **8a** was isolated as yellow crystals from a pentane solution in 55% yield, and its structure was unambiguously established by a single-crystal X-ray diffraction study (Figure 1).



Scheme 4.

Table 1. ^{31}P and ^{13}C NMR spectroscopic data (δ in ppm and J in Hertz), and selected structural parameters [bond lengths (pm) and bond angles (°)] for derivatives **8a**, **8b** and **8d**.[4]

	$\delta_{^{31}P}$ ($J_{P,P}$)	$\delta_{^{13}C}$ ($J_{P,C}$)	(σ^4)P–C	(σ^2)P–C	P–C–P
8a	313, 41 (190)	167 (37, 14)	168.4	164.1	115.0
8b	295, 59 (166)	163 (70)	166.9	162.9	125.3
8d	303, 61 (240)	170 (37, 10)	165.0	164.3	120.9

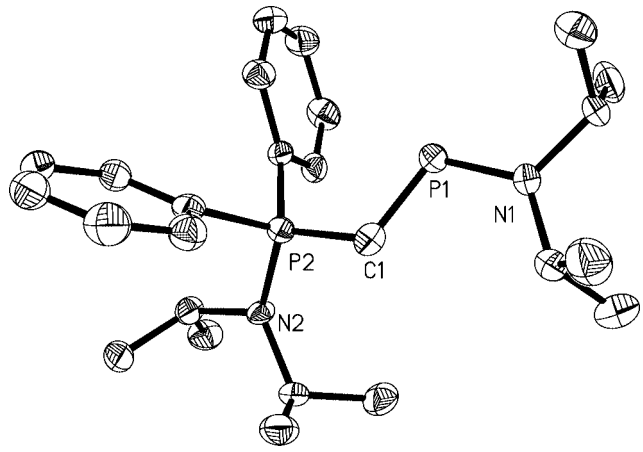


Figure 1. Structure of diphosphaallene **8a** (thermal ellipsoids drawn at 50% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

Taking this result into account, one equivalent of LiHMDS was added to phosphoniophosphaalkene **3b**, in which one phenyl group has been replaced by a diisopropylamino substituent, as one would expect to have a more stabilized phosphonium fragment, and thus a less electrophilic σ^2-phosphorus centre. However, similar results were observed, and we isolated the phosphacumulene **8b** and the phosphanylphosphonium ylide **9b** in a 40:60 ratio (Table 1). Diphosphaallene **8b** was crystallised from a cold pentane solution, and its structure was established by an X-ray dif-

fraction study (Figure 2). With the more acidic phosphoniophosphaalkene **3c**, in which the σ^4-phosphorus atom is substituted by three phenyl groups, we did not observe any addition reaction. However, the expected cumulene **8c** was also not detected, even at low temperature, and the four-membered ring **10**[3] was characterised in solution. In this case the steric protection is probably not sufficient, and **8c** undergoes a head-to-tail dimerisation to afford heterocycle **10**,[3] as demonstrated by the presence of an A_2X_2 spin system at δ = 49 and 9 ppm ($^2J_{P,P}$ = 120 Hz) in the ^{31}P NMR spectrum.

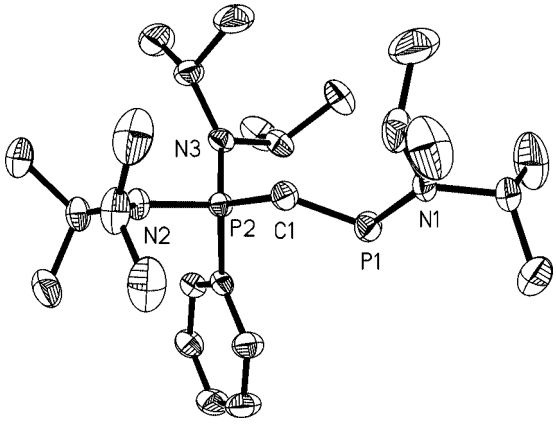
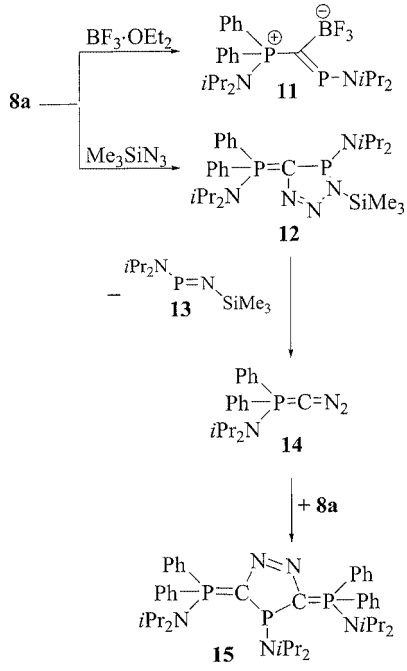


Figure 2. Structure of diphosphaallene **8b** (thermal ellipsoids drawn at 50% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

Derivatives **8a** and **8b** present very similar NMR spectroscopic data (Table 1) to those observed for the already known diphosphacumulene **8d**, which features two diisopropylamino and a chloro group bonded to the σ^4-phosphorus atom.[4] Their molecular structures are also very similar, with very short (σ^2)P–C bond lengths (162.9–164.1 pm); the values of the PCP angles (115.0–125.3°) are in good agreement with an sp^2-hybridized carbon atom.

Thanks to its ylidic character, compound **8a** readily reacts with Lewis acids, such as BF_3, to afford the corresponding complex **11**, which was characterised by multinuclear NMR spectroscopy. Of particular interest is the quadruplet observed in the ^{19}F NMR spectrum at δ = –49 ppm ($^1J_{F,B}$ = 40 Hz), which is characteristic of alkylfluoroborate complexes (Scheme 5).[7] On the other hand, the P=C π-bond of **8a** acts as a dipolarophile upon treatment with trimethylsilyl azide to afford the [3+2]-cycloadduct **12**, which was detected by ^{31}P NMR spectroscopy at low temperature (δ = 110 and 31 ppm, $J_{P,P}$ = 200 Hz). Above –20°C, compound **12** undergoes a clean fragmentation into iminophosphane **13** ($\delta_{^{31}P}$ = 283 ppm)[8] and diazomethylenephosphorane **14** ($\delta_{^{31}P}$ = 23 ppm; IR: $\tilde{\nu}$ = 2200 cm^{-1}).[9] Note that **14** can also act as a 1,3-dipole for the diphosphacumulene **8a** to afford heterocycle **15**,[10] which was isolated as a deep-red oil in 80% yield. In the ^{31}P NMR spectrum, compound **15** displays a doublet of doublets at δ = 5.9 ppm ($^2J_{P,P}$ = 157 and 148 Hz) for the phosphane fragment and two doublets centred at δ = 30 ppm for the two inequivalent phosphonium ylides. The absence of symmetry is probably due to the pyramidalisation of both the phosphane and the ylidic carbons, which appear as doublets of doublets at δ = 94 ppm ($J_{P,C}$ = 137 and 23 Hz) in the ^{13}C NMR spectrum. Heterocycle **15** was also obtained (75%) when half an equivalent of trimethylsilyl azide was added to **8a**.



Scheme 5.

Conclusions

In conclusion, we have demonstrated that phosphoniophosphaalkenes **3** are convenient precursors for $1\sigma^4,3\sigma^2$-diphosphaallenes of type **C**. The presence of bulky substituents at the σ^4-phosphorus centre is required to prevent dimerisation. Future work will focus on the preparation of new types of cumulenes using the potential reactivity of the σ^2-phosphorus atom of these phosphoniophosphaalkenes.

Experimental Section

General Remarks: All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AC80, AC200, WM250 or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. ^{19}F chemical shifts are reported in ppm relative to F_3CCO_2H as external standard. IR spectra were recorded on a Perkin–Elmer spectrometer.

Preparation of *C*-Phosphanyl Phosphorus Ylides 2a,c: In a typical experiment, a THF solution of bis(diisopropylamino)chlorophosphane (0.2 g, 1 mmol) was added dropwise at –78 °C to a THF solution of two equivalents of ylide **1a**,**c**. The mixture was then warmed to room temperature. After stirring overnight, the solvent

was removed under vacuum and the product was extracted with pentane. Compounds **2a,c** were purified by recrystallisation from hot acetonitrile.

2a: Yield: 0.47 g (89%), orange crystals, m.p. 98–100 °C. ^{1}H NMR (C_6D_6): δ = 1.90 (dd, $^2J_{P,H}$ = 4, $^2J_{P,H}$ < 1 Hz, 1 H, PC*H*P), 1.06 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.12 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.28 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 3.6 (d sept, $^2J_{P,H}$ = 7, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 4.0 (sept, $^3J_{H,H}$ = 7 Hz, 2 H, NC*H*), 7.80 (m, 4 H, H_{aro}), 7.12 (m, 6 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 20.1 (dd, $^1J_{C,P}$ = 134 and 13 Hz, P*C*P), 24.2 (d, $^3J_{C,P}$ = 3 Hz, NCH*C*H$_3$), 25.0 (d, $^3J_{C,P}$ = 5 Hz, NCH*C*H$_3$), 46.0 (d, $^2J_{C,P}$ = 11 Hz, N*C*H), 127.8 (s, *C*H$_p$), 130.0 (d, $^3J_{C,P}$ = 3 Hz, *C*H$_m$), 132.9 (dd, $^2J_{C,P}$ = 93, $^4J_{C,P}$ = 3 Hz, *C*H$_o$), 134.0 (dd, $^1J_{C,P}$ = 100, $^3J_{C,P}$ = 3 Hz, *C*$_i$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 50 and 35 (d, $^2J_{P,P}$ = 190 Hz).

2b: Yield: 0.53 g (96%), yellow powder, m.p. 113–115°C. ^{1}H NMR (C_6D_6): δ = 1.12 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.24 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.28 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.40 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.8 (dd, $^2J_{P,H}$ = 9 and 2 Hz, 1 H, PC*H*P), 3.86 (d sept, $^2J_{P,H}$ = 6, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 4.13 (d sept, $^2J_{P,H}$ = 13, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 7.1 (m, 2 H, H_{aro}), 8.0 (m, 3 H, H_{aro}) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): AB system centred at 56.0 ($^2J_{P,P}$ = 137 Hz).

2c: Spectroscopic data were identical to those reported in the literature.[5]

Preparation of *C*-Phosphoniophosphaalkenes 3a,c: In a typical experiment, a freshly distilled BF_3·OEt_2 solution (2 equiv.) was added dropwise at –78 °C to a CH_2Cl_2 solution of ylide **2a,c** (1 mmol). The mixture was warmed to room temperature and the volatile materials were removed under vacuum. The crude product was dissolved in CH_2Cl_2 and precipitated by vigorous stirring with Et_2O. The resulting powder was washed with Et_2O and dried under vacuum. Compounds **3a,c** were recrystallised from a CH_2Cl_2/Et_2O mixture at –30 °C.

3a: Yield: 0.37 g (72%), yellow crystals, m.p. 168 –170 °C. ^{1}H NMR ($CDCl_3$): δ = 1.24 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 3.6 (d sept, $^2J_{P,H}$ = 16, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 6.75 (dd, $^2J_{P,H}$ = 12, $^2J_{P,H}$ = 4 Hz, 1 H, PC*H*P), 7.80 (m, 10 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.4 (broad, NCH*C*H$_3$), 49.2 (d, $^2J_{C,P}$ = 6 Hz, N*C*H), 95.5 (dd, $^1J_{C,P}$ = 105 and 56 Hz, P*C*P), 124.5 (dd, $^1J_{C,P}$ = 106, $^3J_{C,P}$ = 5 Hz, *C*$_i$), 129.8 (dd, $^2J_{C,P}$ = 13 Hz, *C*H$_{aro}$), 133.2 (d, $^3J_{C,P}$ = 10 Hz, *C*H$_{aro}$), 134.2 (s, *C*H$_p$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 308 and 40 (d, $^2J_{P,P}$ = 133 Hz).

3b: Yield: 0.51 g (95%), colourless powder, m.p. 176–178 °C. ^{1}H NMR ($CDCl_3$): δ = 1.28 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.40 (d, $^3J_{H,H}$ = 7 Hz, 6 H, NCC*H*$_3$), 3.7 (d sept, $^2J_{P,H}$ = 16, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 3.9 (broad, 4 H, NC*H*), 6.22 (dd, $^2J_{P,H}$ = 12 and 6 Hz, 1 H, PC*H*P), 7.7 (m, 10 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 23.6 (d, $^2J_{C,P}$ = 3 Hz, NC*C*H$_3$), 24.2 (broad, NCH*C*H$_3$), 48.7 (d, $^2J_{C,P}$ = 5 Hz, N*C*H), 50.0 (broad, N*C*H), 99.8 (dd, $^1J_{C,P}$ = 119 and 50 Hz, P*C*P), 124.2 (dd, $^1J_{C,P}$ = 125, $^3J_{C,P}$ = 3 Hz, *C*$_i$), 129.3 (d, $^2J_{C,P}$ = 14 Hz, *C*H$_{aro}$), 133.3 (d, $^3J_{C,P}$ = 6 Hz, *C*H$_{aro}$), 134.4 (s, *C*H$_{aro}$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 303 and 53 (d, $^2J_{P,P}$ = 125 Hz).

3c: Spectroscopic data were identical to those reported in the literature.[5]

General Procedure for the Synthesis of Adducts 4–7: In a typical experiment, one equivalent of organolithium derivative (**4**: MeLi; **5**: *n*BuLi; **6**: MesLi; **7**: *t*BuLi;) in solution in hexanes was added to a THF solution of the phosphaalkene **3a** (0.43 g, 1 mmol) at –78 °C. The mixture was warmed to room temperature and the solvent was removed under vacuum. The resulting product was extracted with pentane and dried under vacuum. Derivatives **4**–**7** were obtained as orange oils and used without further purification.

4: Yield: 0.43 g (97%). ^{1}H NMR (C_6D_6): δ = 1.01 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHC*H*$_3$), 1.05 (d, $^3J_{H,H}$ = 6 Hz, 6 H, CHC*H*$_3$), 1.14 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHC*H*$_3$), 1.16 (d, $^3J_{H,H}$ = 5 Hz, 6 H, CHC*H*$_3$), 1.43 (d, $J_{P,H}$ = 7 Hz, 3 H, PC*H*$_3$), 1.65 (dd, $J_{P,H}$ = 9 and 3 Hz, 1 H, PC*H*P), 3.5 (m, 4 H, NC*H*), 7.1 (m, 6 H, H$_{aro}$), 7.7 (m, 4 H, H$_{aro}$) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 22.8 (dd, $^1J_{P,C}$ = 131 and 10 Hz, P*C*P), 23.0 (dd, $J_{P,C}$ = 14 and 20 Hz, P*C*H$_3$), 23.4 (s, CH*C*H$_3$), 23.7 (d, $J_{P,C}$ = 2 Hz, CH*C*H$_3$), 24.6 (s, CH*C*H$_3$), 24.8 (s, CH*C*H$_3$), 44.6 (d, $J_{P,C}$ = 8 Hz, N*C*H), 47.0 (d, $J_{P,C}$ = 5 Hz, N*C*H), 127.7 (s, *C*$_{aro}$H), 130.0 (dd, $J_{P,C}$ = 6 and 2 Hz, *C*$_{aro}$H), 132.0 (d, $J_{P,C}$ = 8 Hz, *C*$_{aro}$H), 132.9 (dd, $J_{P,C}$ = 9 and 2 Hz, *C*$_{aro}$H), 135.0 (dd, $J_{P,C}$ = 92 and 3 Hz, *C*$_i$) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 35 and 6 (d, $^2J_{P,P}$ = 107 Hz).

5: Yield: 0.44 g (90%). ^{1}H NMR (C_6D_6): δ = 0.8–1.1 (m, 33 H, butyl and CH$_3$), 2.57 (dd, $J_{P,H}$ = 9 and 8 Hz, 1 H, PC*H*P), 3.40 (d sept, $J_{H,H}$ = 8 Hz and $J_{P,H}$ = 10 Hz, 2 H, NC*H*), 3.60 (m, 2 H, NC*H*), 7.1 (m, 4 H, H_{aro}), 7.8 (m, 6 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ = 14.4 (s, CH$_3$), 21.7 (dd, $J_{P,C}$ = 114 and 16 Hz, P*C*HP), 23.3 (broad, NCH*C*H$_3$), 23.7 (s, NCH*C*H$_3$), 24.7 (s, CH$_2$), 29.5 (d, $J_{P,C}$ = 17 Hz, CH$_2$), 36.9 (dd, $J_{P,C}$ = 17 and 7 Hz, PCH$_2$), 44.8 (d, $J_{P,C}$ = 8 Hz, N*C*H), 47.0 (d, $J_{P,C}$ = 5 Hz, N*C*H), 127.7 (s, *C*$_{aro}$H), 130.1 (dd, $J_{P,C}$ = 9 and 3 Hz, *C*$_{aro}$H), 132.6 (d, $J_{P,C}$ = 9 Hz, *C*$_{aro}$H), 134.2 (dd, $J_{P,C}$ = 103 and 8 Hz, *C*$_{ipso}$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 38 and 15 (d, $^2J_{P,P}$ = 150 Hz).

6: Yield: 0.54 g (98%). ^{1}H NMR (C_6D_6): δ = 0.88 (d, $^3J_{H,H}$ = 8 Hz, 6 H, CHC*H*$_3$), 0.95 (d, $^3J_{H,H}$ = 8 Hz, 6 H, CHC*H*$_3$), 1.03 (d, $^3J_{H,H}$ = 5 Hz, 6 H, CHC*H*$_3$), 1.08 (d, $^3J_{H,H}$ = 5 Hz, 6 H, CHC*H*$_3$), 2.15 (s, 3 H, C$_{aro}$C*H*$_3$), 2.16 (s, 6 H, C$_{aro}$C*H*$_3$), 2.48 (dd, $J_{P,H}$ = 9 and 7 Hz, 1 H, PC*H*P), 3.4 (d sept, $J_{H,H}$ = 7, $J_{P,H}$ = 14 Hz, 2 H, NC*H*), 3.7 (m, 2 H, JC*H*), 6.8 (s, 2 H, H_{aro}), 7.1 (m, 6 H, H_{aro}), 7.8 (m, 4 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 21.6 (dd, $J_{P,C}$ = 151 and 47 Hz, P*C*P), 23.6 (s, CH*C*H$_3$), 24 (m, *C*H$_3$), 46.9 (d, $J_{P,C}$ = 5 Hz, N*C*H), 47.0 (d, $J_{P,C}$ = 5 Hz, N*C*H), 47.4 (d, $J_{P,C}$ = 10 Hz, N*C*H), 127.3 (s, *C*$_{aro}$H), 127.4 (s, *C*$_{aro}$H), 130.7 (s, *C*$_{aro}$H), 132.8 (d, $J_{P,C}$ = 8 Hz, *C*$_{aro}$H), 129.9 (d, $J_{P,C}$ < 1 Hz, *C*$_{aro}$H), 134 (m, *C*$_{aro}$), 136.0 (s, *C*$_{aro}$), 141.3 (d, $J_{P,C}$ = 18 Hz, *C*$_{aro}$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 39 and 18 (d, $^2J_{P,P}$ = 202 Hz).

7: Yield: 0.41 g (95%) ppm. ^{1}H NMR (C_6D_6): δ = 1.06 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHC*H*$_3$), 1.11 (d, $^3J_{H,H}$ = 6 Hz, 6 H, CHC*H*$_3$), 1.13 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHC*H*$_3$), 1.19 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHC*H*$_3$), 2.00 (pseudo t, $J_{P,H}$ = 9 Hz, 1 H, PC*H*P), 3.4 (m, 4 H, NC*H*), 6,01 (ddd, $J_{P,H}$ = 220, $J_{H,H}$ = 8 Hz, 1 H, P*H*), 7.1 (m, 6 H, H_{aro}), 7.7 (m, 4 H, H_{aro}) ppm. ^{13}C{^{1}H} NMR(C_6D_6): δ = 20.0 (dd, $J_{P,C}$ = 126 and 16 Hz, P*C*P), 23.3 (s, CH*C*H$_3$), 23.4 (s, CH*C*H$_3$), 24.0 (s, CH*C*H$_3$), 24.1 (s, CH*C*H$_3$), 24.2 (s, CH*C*H$_3$), 24.3 (s, CH*C*H$_3$), 47.7 (d, $J_{P,C}$ = 5 Hz, N*C*H), 49.2 (d, $J_{P,C}$ = 8 Hz, N*C*H), 128.4 (s, *C*$_{aro}$H), 130.7 (s, *C*$_{aro}$H), 132.8 (d, $J_{P,C}$ = 8 Hz, *C*$_{aro}$H), 133.1 (dd, $J_{P,C}$ = 7 and 2 Hz, *C*$_{aro}$H), 134.5 (dd, $J_{P,C}$ = 53 and 4 Hz, *C*$_i$) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 38 and –18 (d, $^2J_{P,P}$ = 160 Hz).

Reaction of LiMHDS with Phosphoniophosphaalkenes 3a,c: THF (6 mL) was added to a solid mixture of phosphaalkene **3a**,**c** (1.9 mmol) and LiHMDS·Et_2O (1.9 mmol), at –90 °C, and the solution was warmed to room temperature. The solvent was removed under vacuum and the crude product was immediately extracted with pentane.

8a: Yield: 0.45 g (55%), yellow needles from pentane/THF at 4 °C, m.p. 64–66 °C. ^{1}H NMR (C_6D_6): δ = 1.23 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.33 (br. d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 3.5 (d sept,

$^2J_{P,H}$ = 16, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 7.0 (m, 6 H, H_{aro}), 7.9 (m, 4 H, H_{aro}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.3 (s, NCH*C*H$_3$), 47.6 (d, $^2J_{C,P}$ = 4 Hz, N*C*H), 128.1 (s, *C*H$_p$), 130.0 (d, $^3J_{C,P}$ = 3 Hz, *C*H$_m$), 132.1 (dd, $^2J_{C,P}$ = 12, $^4J_{C,P}$ < 1 Hz, *C*H$_o$), 135.0 (dd, $^1J_{C,P}$ = 93, $^3J_{C,P}$ = 3 Hz, C_i), 166.5 (dd, $^1J_{C,P}$ = 37 and 14 Hz, P*C*P) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 313 and 41 (d, $^2J_{P,P}$ = 190 Hz) ppm. $C_{54}H_{84}N_4OP_4$: calcd. C 69.80, H 9.11, N 6.03; found C 69.75, H 9.04, N 6.10.

9a: Yield: 0.28 g (25%). ^1H NMR (C_6D_6): δ = 0.22 (s, 9 H, SiCH$_3$), 0.41 (s, 9 H, SiCH$_3$), 1.03 (d, $^3J_{H,H}$ = 6 Hz, 12 H, NCC*H*$_3$), 1.07 (d, $^3J_{H,H}$ = 6 Hz, 12 H, NCC*H*$_3$), 1.13 (d, $^3J_{H,H}$ = 6 Hz, 12 H, NCC*H*$_3$), 2.39 (dd, $^2J_{P,H}$ = 12 and 2 Hz, 1 H, PCHP), 3.73 (d sept, $^2J_{P,H}$ = 7, $^3J_{H,H}$ = 6 Hz, 4 H, NC*H*), 3.80 (d sept, $^2J_{P,H}$ = 14, $^3J_{H,H}$ = 6 Hz, 2 H, NC*H*),7.2 (m, 6 H, H_{aro}), 7.6 (m, 4 H, H_{aro}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.22 (s, Si*C*H$_3$), 4.48 (s, Si*C*H$_3$), 23.2 (s, NCH*C*H$_3$), 23.8 (s, NCH*C*H$_3$), 47.0 (d, $^2J_{C,P}$ = 5 Hz, N*C*H), 47.8 (d, $^2J_{C,P}$ = 4 Hz, N*C*H), 127.8 (d, $J_{C,P}$ = 6 Hz, *C*H$_{aro}$), 129.8 (dd, $J_{C,P}$ = 15 and 3 Hz, *C*H$_{aro}$), 130.0 (d, $J_{C,P}$ = 2 Hz, *C*H$_{aro}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 80 and 40 (d, $^2J_{P,P}$ = 200 Hz) ppm.

8b: Yield: 0.14 g (17%), yellow needles from pentane/THF, m.p. 80–82°C. ^1H NMR (C_6D_6): δ = 1.20 (d, $^3J_{H,H}$ = 7 Hz, 24 H, NCC*H*$_3$), 1.35 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 4.0 (m, 6 H, NC*H*), 7.1 (m, 6 H, H_{aro}), 8.0 (m, 4 H, H_{aro}) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.9 (s, NCH*C*H$_3$), 24.5 (s, NCH*C*H$_3$), 45.5 (broad, N*C*H), 46.8 (d, $^2J_{C,P}$ = 5 Hz, N*C*H), 127.6 (s, *C*H$_{aro}$), 129.5 (dd, $^3J_{C,P}$ = 8 and 2 Hz, *C*H$_{aro}$), 132.4 (dd, $^2J_{C,P}$ = 10, $^4J_{C,P}$ < 1 Hz, *C*H$_{aro}$), 136.0 (d, $^1J_{C,P}$ = 125 Hz, C_i), 162.4 (d, $^1J_{C,P}$ = 70 Hz, P*C*P) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 295 and 59 (d, $^2J_{P,P}$ = 166 Hz) ppm. $C_{25}H_{47}N_3P_2$: calcd. C 66.49, H 10.49, N 9.30; found C 66.55, H 10.53, N 9.27.

9b: Yield: 0.46 g (40%), yellow needles from pentane/THF, m.p. 121–122 °C. ^1H NMR (C_6D_6): δ = 0.53 (s, 9 H, SiCH$_3$), 0.55 (s, 9 H, SiCH$_3$), 1.06 (d, $^3J_{H,H}$ = 8 Hz, 12 H, NCC*H*$_3$), 1.15 (d, $^3J_{H,H}$ = 8 Hz, 12 H, NCC*H*$_3$), 1.24 (d, $^3J_{H,H}$ = 7 Hz, 6 H, NCC*H*$_3$), 1.26 (d, $^3J_{H,H}$ = 7 Hz, 6 H, NCC*H*$_3$), 1.79 (dd, $^2J_{P,H}$ = 9 and 2 Hz, 1 H, PCHP), 3.7–4.2 (m, 6 H, NC*H*), 7.2 (m, 3 H, H_{aro}), 8.1 (m, 2 H, H_{aro}) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 83 and 54 ($^2J_{P,P}$ = 170 Hz) ppm.

BF_3 Complex 11: One equivalent of $BF_3{\cdot}OEt_2$ was added to a THF solution (5 mL) of cumulene **8a** (0.8 g, 2 mmol) at room temperature. After stirring the mixture for 1 h, the solvent was removed under vacuum and the crude product was extracted with Et_2O. The solvent was removed under vacuum, and complex **11** was obtained as a yellow powder (0.6 g, 62%). M.p. 89–91 °C. ^1H NMR ($CDCl_3$): δ = 1.14 (br. d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 1.17 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCC*H*$_3$), 3.6 (br. m, 4 H, NC*H*), 4.0 (d sept, $^2J_{P,H}$ = 14, $^3J_{H,H}$ = 7 Hz, 4 H, NC*H*), 7.0 (m, 6 H, H_{aro}), 7.9 (m, 4 H, H_{aro}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.2 (s, NCH*C*H$_3$), 49 (d, $^2J_{C,P}$ = 6 Hz, N*C*H), 128.1 (d, $J_{C,P}$ = 20 Hz, *C*H$_{aro}$), 129.0 (dd, $^1J_{C,P}$ = 115, $^3J_{C,P}$ = 8 Hz, C_i), 131.9 (s, *C*H$_{aro}$), 135.0 (d, $J_{C,P}$ = 10 Hz, *C*H$_{aro}$) ppm. ^{19}F NMR ($CDCl_3$): δ = –49 (q, $^1J_{B,F}$ = 40 Hz) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 326 (d, $^2J_{P,P}$ = 195 Hz), 57 (dq, $^2J_{P,P}$ = 195, $^3J_{P,F}$ = 8 Hz) ppm.

Heterocycle 15: Freshly distilled Me_3SiN_3 (13 μL, 0.1 mmol) was added to a THF solution (1 mL) of cumulene **8a** (80 mg, 0.2 mmol) at –78 °C. After warming to room temperature, the volatile materials were removed under vacuum to give compound **15** as a deep-red oil (110 mg (80%). ^1H NMR (C_6D_6): δ = 1.07 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCCH$_3$), 1.30 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCCH$_3$), 1.60 (d, $^3J_{H,H}$ = 7 Hz, 12 H, NCCH$_3$), 3.8 (d sept, $^2J_{P,H}$ = 16, $^3J_{H,H}$ = 7 Hz, 4 H, NCH), 7.0 (m, 6 H, CH$_{aro}$), 8.0 (m, 4 H, CH$_{aro}$), 8.4 (m, 4 H, CH$_{aro}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 24.1 (s, CH$_3$), 24.8 (s, CH$_3$), 47.6 (d, $J_{P,C}$ = 5 Hz, NCH), 94.0 (dd, $J_{P,C}$ = 137 and 23 Hz, PCP), 130.1 (s, HC$_{aro}$), 130.8 (s, HC$_{aro}$), 133.0 (dd, $J_{P,C}$ = 108 and 75 Hz, C$_i$), 134.8 (d, $J_{P,C}$ = 50 Hz, HC$_{aro}$), 134.9 (d, $J_{P,C}$ = 60 Hz, HC$_{aro}$) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 30.0 (dd, $^2J_{P,P}$ = 157 and 148 Hz), 5.9 (dd, $^2J_{P,P}$ = 157 and 148 Hz) ppm.

Crystallographic Data for 8a: $C_{54}H_{84}N_4OP_4$, M = 929.13, monoclinic, $P2_1/c$, a = 23.882(2), b = 7.920(1), c = 28.678(2) Å, β = 94.061(1)°, V = 5410.6(6) Å^3, Z = 4, T = 173(2) K. 22828 Reflections (7276 independent, R_{int} = 0.0698) were collected. Largest electron density residue: 0.305 e Å^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0641 and wR_2 = 0.1519 (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Crystallographic Data for 8b: $C_{25}H_{47}N_3P_2$, M = 451.60, triclinic, $P\bar{1}$, a = 8.158(1), b = 12.372(2), c = 15.531(2) Å, α = 112.822(2)°, β = 95.436(2)°, γ = 102.054(2)°, V = 1385.8(4) Å^3, Z = 2, T = 193(2) K. 9920 Reflections (5404 independent, R_{int} = 0.0336) were collected. Largest electron density residue: 0.377 e Å^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0457 and wR_2 = 0.1180 (all data).

All data for both structures were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97)[11] and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2.[12]

CCDC-259732 (for **8a**) and -259733 (for **8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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