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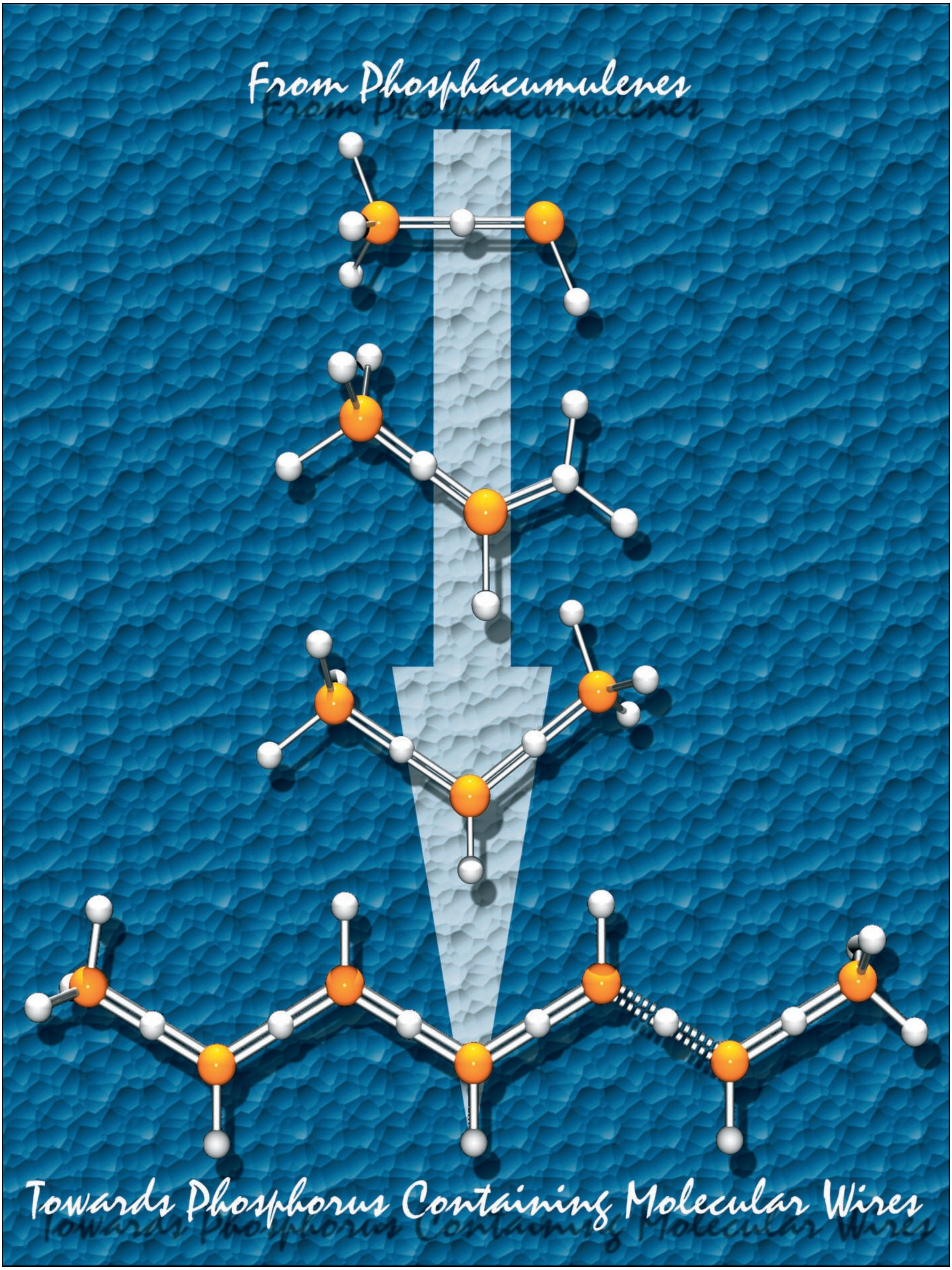


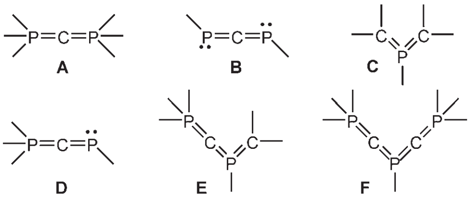
Synthesis of Extended Polyphosphacumulenes

David Martin,[a, b] **Fook S. Tham,**[a] **Antoine Baceiredo,***[b] **and Guy Bertrand***[a]

Abstract: Addition of two equivalents of $(Me_3Si)_2CLiCl$ to the *C*-[(diphenyl)(diisopropylamino)phosphonio]-*P*-(diisopropylamino)phosphaalkene **2** affords the $1\sigma^4,3\sigma^3$-diphosphabuta-1,2,3-triene **E1** in 55 % yield. Derivative **E1** was fully characterized, including a single-crystal X-ray diffraction study. Alkylation of **E1** with methyl trifluoromethanesulfonate gives rise to the first *C*-phosphonio-bis(methylene)phosphorane **5**, which was isolated in 84 % yield. Because the second carbon center is also nucleophilic, cumulene **E1** reacts as a "pincer" with $BF_3{\cdot}OEt_2$, leading to the formation of a novel four-membered PCBC heterocycle **6** with a betaine-like structure. Addition of three equivalents of *P*-[diphenyl(diisopropylamino)]methylene phosphorane to (diisopropylamino)dichlorophosphane, followed by addition of one equivalent of CCl_4, and subsequent deprotonation with lithium hexamethyldisilazide gave rise to $1\sigma^4,3\sigma^3,5\sigma^4$-triphosphapenta-1,2,3,4-tetraene **F1**, which was isolated in 62 % yield.

Keywords: bis(methylene)phosphoranes • cumulenes • phosphacumulenes • phosphorus • ylides

Although all-carbon cumulenes $[R_2C{=}(C{=})_nCR_2]$ have been extensively studied,[1] the construction of stable phosphorus-containing cumulenes remains very challenging. This is partly due to the weakness of phosphorus–carbon multiple bonds,[2] but also to the lack of synthetic methodologies. So far, cumulenes exclusively based on phosphorus–carbon double bonds[3] are limited to $1\sigma^4,3\sigma^4$-diphosphaallenes (carbodiphosphoranes) **A**,[4] $1\sigma^2,3\sigma^2$-diphosphaallenes **B**,[3c,5] bis(methylene)phosphoranes **C**,[6] and the recently discovered $1\sigma^4,3\sigma^2$-diphosphaallenes **D**[7,8] (Scheme 1). Here, we report the synthesis of the first representatives of phosphorus/carbon cumulenes featuring three[9] (**E**) and even four phosphorus–carbon "double bonds" (**F**) (Scheme 1).



Scheme 1. Schematic representations of the known P,C-containing cumulenes **A**–**D**, and of those reported herein **E** and **F**.

Bis(methylene)phosphoranes **C** are classically prepared by addition of a carbenoid to a phosphaalkene.[6,10] However, according to ^{31}P NMR spectroscopy, addition of $1\sigma^4,3\sigma^2$-diphosphaallene **1** to lithium bis(trimethylsilyl)chloromethanide (**3**)[11] led to a complex mixture of products, with no signals corresponding to the desired cumulene **E1.** To enhance the electrophilicity of the phosphorus center, we turned our attention to the protonated form **2**[7,12] of the diphosphaallene **1** (Scheme 2). When one equivalent of carbenoid **3** was used, the desired nucleophilic addition to the phosphorus center, as well as the subsequent 1,2-Cl shift[13] occurred, but instead of obtaining the *P*-chloro compound **4**, we observed the quantitative formation of the fluoro derivative **4′**. All attempts to eliminate HF from **4′** failed. To prevent the halogen exchange, phosphonio phosphaalkene **2** was added to two equivalents of **3** (one for the addition reaction and one as a base to eliminate HCl from **4**) at −100 °C, and $1\sigma^4,3\sigma^3$-diphosphabuta-1,2,3-triene **E1** was isolated as yellow crystals in 55 % yield.

In the $^{31}P\{^1H\}$ NMR spectrum, compound **E1** displays an AX system at $\delta_P = 124$ and 24 ppm ($^2J_{P,P} = 200$ Hz) for the

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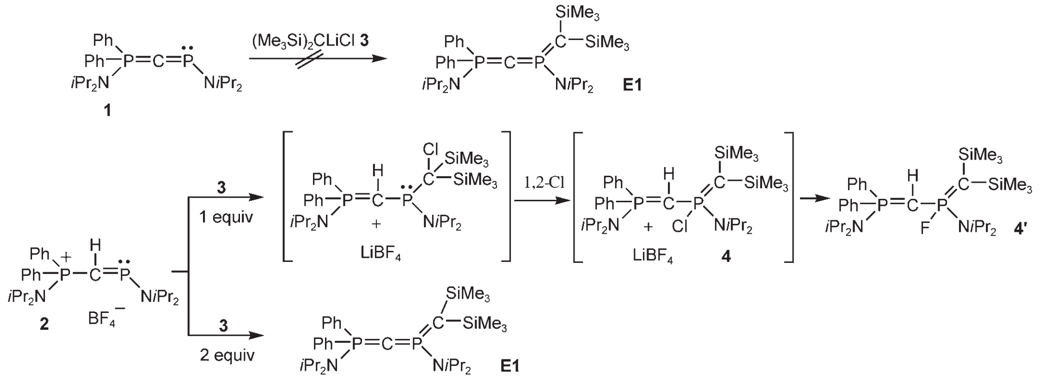


Scheme 2. Towards the synthesis of **E1**.

σ^3,λ^5-P and σ^4,λ^5-P atoms, respectively. In the ^{13}C NMR spectrum, the quaternary carbon atoms appear as a doublet of doublets at $\delta_C = 93$ ppm ($J_{P,C} = 154$ and 133 Hz), and as a doublet at $\delta_C = 27$ ppm ($J_{P,C} = 60$ Hz). All these NMR signals are strongly shifted to higher field compared to those for cumulenes **D**[7] and bis(methylene)phosphoranes **C**.[6] According to a single-crystal X-ray diffraction study (Figure 1), the σ^3,λ^5-phosphorus atom P1 is in a trigonal-planar environment (sum of the angles: 359.68°), the P1–C1 (167 pm) and P1–C2 (161 pm) bond lengths are short, and the C2-P1-C1-Si2 dihedral angle is very pronounced (51°). All these features are very similar to those found in classical bis(methylene)phosphoranes **C**.[6] The P2-C2-P1 skeleton is also similar to that of cumulenes of type **D**, with a P2-C2-P1 bond angle of 127° and a short P2–C2 bond length (167 pm).

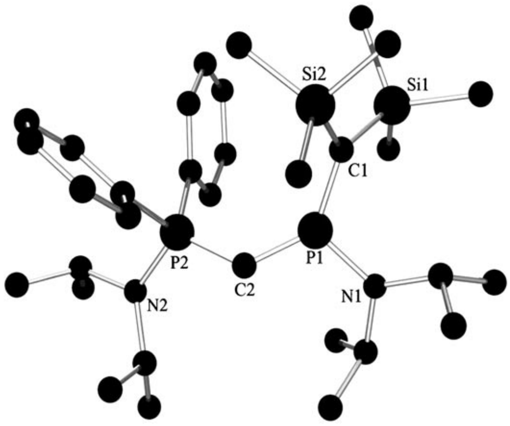
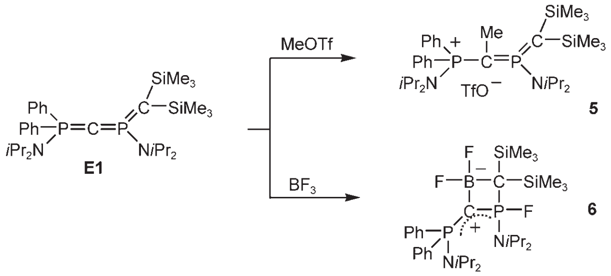


Figure 1. Molecular view of the crystal structure of **E1**. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.6725(13), P1–C2 1.6123(14), P1–N1 1.6597(10), P2–C2 1.6675(13), Si1–C1 1.8469(13), Si2–C1 1.8403(13); C2-P1-N1 113.59(6), C2-P1-C1 132.69(7), N1-P1-C1 113.40(6), P1-C1-Si2 117.20(7), P1-C1-Si1 121.85(7), Si2-C1-Si1 120.95(7), P1-C2-P2 127.52(8).

Carbon C2 can be viewed as a dianionic center, since it is part of the ylidic function and of the bis(methylene)phosphorane fragment, which is isoelectronic to an allylic anion. Not surprisingly, a very clean alkylation reaction was observed with methyl trifluoromethanesulfonate (Scheme 3). The corresponding *C*-phosphonio-bis(methylene)phosphorane **5** was isolated in 84 % yield. A single-crystal X-ray diffraction analysis (Figure 2) confirms the regioselective alkylation at the C2 position. The central phosphorus atom (P1) remains in a trigonal-planar environment (sum of the angles: 359.5°), with a short P1–C1 (163 pm) bond length,



Scheme 3. Reactivity of **E1**.

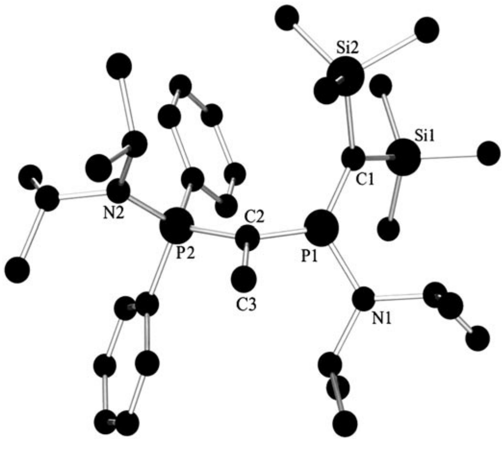
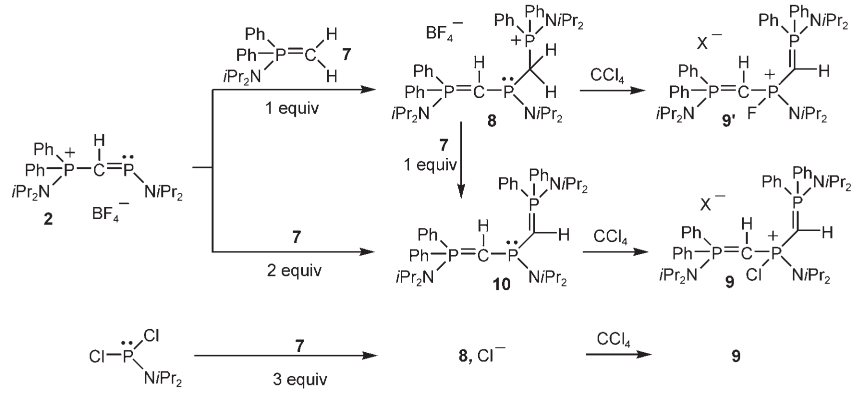


Figure 2. Molecular view of the crystal structure of **5**. The compound is statistically mixed with an impurity, which is not represented. Triflate anions and H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.629(8), P1–N1 1.641(3), P1–C2 1.698(4), C1–Si2 1.878(7), C1–Si1 1.885(5), P2–C2 1.742(4), C2–C3 1.531(4); C1-P1-N1 120.1(3), C1-P1-C2 127.6(3), N1-P1-C2 111.73(16), P1-C1-Si2 118.7(3), P1-C1-Si1 122.8(4), Si2-C1-Si1 118.0(4), C3-C2-P1 117.3(2), C3-C2-P2 118.3(2), P1-C2-P2 122.3(2).

which indicates that **5** has to be viewed as the first example of a phosphonio-substituted bis(methylene)phosphorane. This is confirmed by the $^{31}P\{^{1}H\}$ NMR spectrum, an AX system at $\delta_P = +166$ and +50 ppm ($^{2}J_{P,P} = 70$ Hz) in the range expected for both of these fragments.

Because the second carbon center is also nucleophilic, compound **E1** was expected to react as a "pincer". Indeed, the addition of one equivalent of a $BF_3{\cdot}OEt_2$ led to the formation of the novel four-membered heterocycle **6** with a betaine-like structure (Scheme 3). This compound results formally from the substitution of a fluorine atom of BF_3 by the electron-rich C2 atom, followed by complexation of the Lewis acid by the second carbon (C1) and addition of fluoride to P1. Both enantiomers crystallized together from a pentane/THF solution and their structures were obtained from an X-ray diffraction study (Figure 3).[9]

The next goal was the synthesis of longer cumulenes, and we chose to prepare a derivative of type **F**. First, based on the synthetic strategy used for preparing **E1**, one equivalent of phosphorus ylide **7** was added to the phosphonio phosphaalkene **2**, and the resulting adduct **8** was treated immediately with carbon tetrachloride. However, as observed for the preparation of **4**, a halogen exchange occurred and the fluorinated phosphonio bis(ylide) **9′** was obtained as shown by the $^{31}P\{^{1}H\}$ NMR ($\delta_P = +72$, td, $J_{P,P} = 30$ Hz, $J_{P,F} = 920$ Hz; $\delta_P = +37$, dd, $J_{P,P} = 30$ Hz, $J_{P,F} = 13$ Hz) and ^{19}F NMR spectra ($\delta_F = -66$, td, $J_{P,F} = 13$ and 920 Hz). Since the dehydrofluorination could not be achieved, compound **9′** was not characterized further. To prevent the exchange reaction, two equivalents of ylide **7** were used, and indeed the phosphino bis(ylide) **10** was isolated in 40% yield. Treatment with CCl_4 gave rise to the expected phosphonio bis(ylide) **9**, although in low yield. The symmetry of derivative **9** was indicated by an AX_2 system in the $^{31}P\{^{1}H\}$ NMR spectrum ($\delta_P = +63$ (t) and +38 (d) $^{2}J_{P,P} = 24$ Hz), the two ylidediyl fragments being equivalent. This was confirmed by the ^{13}C NMR spectra, since the two ylidic carbon atoms appeared as a single doublet of doublets at $\delta_C = 30.3$ ($J_{P,C} = 52$ and 73 Hz). A better method to prepare **9** is the direct treatment of (diisopropylamino)dichlorophosphane with three equivalents of ylide **7**, followed by addition of one equivalent of CCl_4. By this route **9** was isolated in 80% yield (Scheme 4).



Scheme 4. Towards the precursor **9** of **F1**.

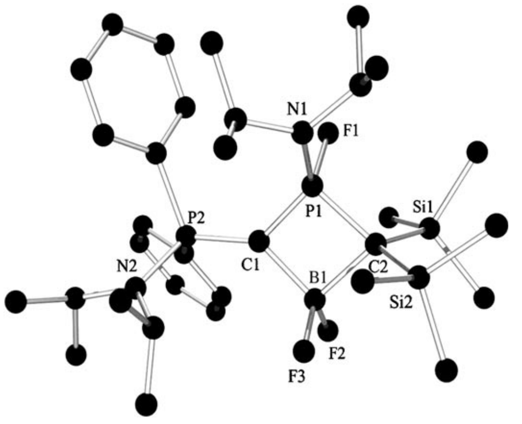
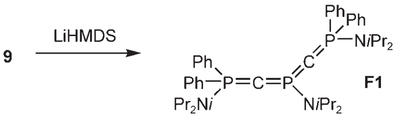


Figure 3. Molecular view of the crystal structure of **6**. Only one enantiomer is represented. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–F1 1.6005(17), P1–N1 1.651(2), P1–C1 1.667(3), P1–C2 1.765(3), Si1–C2 1.896(3), Si2–C2 1.886(3), B1–C2 1.756(4), B1–C1 1.669(4), B1–F2 1.393(4), B1–F3 1.408(4), P2–C1 1.702(3); C1-P1-C2 94.49(14), C1-B1-C2 94.8(2), P1-C1-B1 88.15(18), P1-C1-P2 135.03(18), B1-C1-P2 136.0(2), B1-C2-P1 82.44(17).

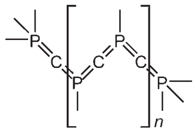
Finally, the desired 1σ^4,3σ^3,5σ^4-triphosphapenta-1,2,3,4-tetraene **F1** was obtained by dehydrochlorination of the phosphonio bis(ylide) **9** at −78 °C using two equivalents of lithium hexamethyldisilazide (LiHMDS) (Scheme 5). Compound **F1** was extracted with pentane and isolated as a yellow powder after evaporation of the volatiles. All attempts to obtain single crystals suitable for an X-ray diffraction study failed. However, the symmetrical cumulenic structure of **F1** was established from the spectroscopic data. In the $^{31}P\{^{1}H\}$ NMR spectrum the central σ^3,λ^5 phosphorus nucleus appeared as a triplet at $\delta_P = +74$ ppm ($J_{P,P} = 107$ Hz), and the other two equivalent σ^4,λ^5 phosphorus centers as a doublet at $\delta_P = +10$ ppm ($J_{P,P} = 107$ Hz). As expected, these chemical shifts are at higher field compared to those of the corresponding "non-cumulenic" bis(methylene)phosphor-



Scheme 5. Synthesis of **E1**.

anes **C** and phosphonium ylides. Moreover, in the ^{31}P NMR spectrum, the signal for the σ^3,λ^5-P atom is a well-defined triplet of triplets due to the additional large coupling constant ($^3J_{\mathrm{P,H}}=18$ Hz) with the two CH protons of the *i*Pr$_2$N substituents. This unusual value is characteristic of a (diisopropylamino)bis(methylene) phosphorane moiety.[6] In addition, only one set of ^{1}H and ^{13}C NMR signals was observed for the four phenyl groups, which is consistent with a trigonal-planar geometry around the central phosphorus atom; it must also be noted that the same groups are inequivalent in the precursor **9**, for which the central phosphorus atom is prochiral. For the two quaternary carbon atoms, the observed chemical shift (pseudo-triplet $\delta_{\mathrm{C}}=52$ ppm, $J_{\mathrm{P,C}}=160$ Hz) also lies at higher field in comparison with **E1**.

In conclusion, we have synthesized, isolated and characterized the first phosphacumulenes featuring a bis(methylene)phosphorane fragment. These compounds can be obtained in good yields, through simple and short syntheses. The generalization of the synthetic methodology to the preparation of longer cumulenic molecules, featuring bis(methylene)phosphorane fragments, such as molecular wires of type **G**, is currently under investigation.



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Experimental Section

General remarks: All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Tetrachloromethane was dried by elution through a dry basic alumina column. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Varian Inova 300 and 500, and Bruker Avance 300 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me$_4$Si as external standard. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H$_3$PO$_4$. ^{19}F chemical shifts are reported in ppm relative to FCCl$_3$ as external standard.

Bis(ylide) 4′: One equivalent of *n*-BuLi in hexane (1.35 mL, 2.15 mmol) was added dropwise over a period of ten minutes to a solution of bis(trimethylsilyl)dichloromethane (0.5 g, 2.15 mmol) in THF (5 mL)/Et$_2$O (1 mL)/pentane (1 mL) at −110 °C. After the reaction mixture was stirred for 3 h at −100 °C, a solution of phosphonio phosphaalkene **2** (1.12 g, 2.17 mmol) in THF (5 mL) was added dropwise. The mixture was allowed to warm up to −80 °C over a period of 1.5 h, and then to room temperature. After evaporation of the volatiles under vacuum, the residue was extracted with pentane, and derivative **4′** was obtained as yellow crystals in 51% yield from the pentane solution at −30 °C. m.p.: 112–114 °C; ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta=$ 83 (dd, $J_{\mathrm{P,P}}=26$ Hz), $J_{\mathrm{P,F}}=910$ Hz), 38 ppm (dd, $J_{\mathrm{P,P}}=26$ Hz, $J_{\mathrm{P,F}}=12$ Hz); ^{19}F NMR (C$_6$D$_6$): $\delta=$ −71 ppm (d broad, $^1J_{\mathrm{P,F}}=910$ Hz); ^{1}H NMR (C$_6$D$_6$) $\delta=$ 0.29 (s, 9H; SiCH$_3$), 0.46 (s, 9H; SiCH$_3$), 1.01 (d, $^3J_{\mathrm{H,H}}=6$ Hz, 6H; CHCH_3), 1.03 (d, $J_{\mathrm{H,H}}=6$ Hz, 6H; CHCH_3), 1.17 (d, $J_{\mathrm{H,H}}=7$ Hz, 6H; CHCH_3), 1.20 (d, $J_{\mathrm{H,H}}=7$ Hz, 6H; CHCH_3), 1.49 (dd, $J_{\mathrm{P,H}}=11$ Hz and 4 Hz, 1H; PCHP), 3.95 (sept, $J_{\mathrm{H,H}}=7$ Hz, 2H; NCH), 4.40 (d sept, $J_{\mathrm{H,H}}=6$ Hz, $J_{\mathrm{P,H}}=12$ Hz, 2H; NCH), 7.10 (m, 4H; H_{aro}), 7.81 ppm (m, 6H; H_{aro}); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta=$ 5.9 (s, SiCH$_3$), 15.9 (dd, $J_{\mathrm{P,C}}=127$ Hz, $J_{\mathrm{C,F}}=17$ Hz; PCSi), 16.4 (ddd, $J_{\mathrm{P,C}}=132$ and 162 Hz, $J_{\mathrm{C,F}}=27$ Hz; PCHP), 24.1 (s, CHCH$_3$), 24.3 (s, CHCH$_3$), 25.2 (s, CHCH$_3$), 47.0 (broad, NCH), 48.5 (d, $J_{\mathrm{P,C}}=6$ Hz, NCH), 128.6 (s, C_{aro}H), 131.4 (d, $J_{\mathrm{P,C}}=9$ Hz; C_{aro}H), 133.1 (s, C_{aro}H), 133.0 (d, $J_{\mathrm{P,C}}=18$ Hz; C_{aro}H), 132.1 ppm (d, $J_{\mathrm{P,C}}=25$ Hz; C_{ipso}).

1σ^4,3σ^3-diphospha-1,2,3-butatriene E1: One equivalent of *n*-BuLi in hexane (2.7 mL, 4.3 mmol) was added, dropwise over a period of ten minutes to a solution of bis(trimethylsilyl)dichloromethane (1.0 g, 4.3 mmol) in THF (10 mL)/Et$_2$O (1 mL)/pentane (1 mL) at −110 °C. After the reaction mixture was stirred for 3 h at −100 °C, a solution of phosphonio phosphaalkene **2** (1.12 g, 2.17 mmol) in THF (5 mL) was added dropwise. The mixture was allowed to warm up to −80 °C over a period of 1.5 h, and then to room temperature. After evaporation of the volatiles under vacuum, the residue was extracted with pentane, and compound **E1** was obtained as yellow crystals from the pentane solution at 4 °C. Yield 0.7 g (55%); m.p. 99–101 °C; ^{31}P{^{1}H} NMR (C$_6$D$_6$): $\delta=$ 124 and 24 ppm ($J_{\mathrm{P,P}}=200$ Hz); ^{1}H NMR (C$_6$D$_6$): $\delta=$ 0.23 (s, 18H; SiCH_3), 1.10 (d, $J_{\mathrm{H,H}}=6$ Hz, 12H; CHCH_3), 1.35 (d, $J_{\mathrm{H,H}}=7$ Hz, 12H; CHCH_3), 3.79 (d sept, $J_{\mathrm{H,H}}=6$ Hz, $^3J_{\mathrm{P,H}}=14$ Hz, 2H; NCH), 4.58 (d sept, $J_{\mathrm{H,H}}=7$ Hz, $J_{\mathrm{P,H}}=15$ Hz, 2H; NCH), 7.18 (m, 6H; H_{aro}), 7.98 ppm (m, 4H; H_{aro}); ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta=$ 3.0 (d, $J_{\mathrm{P,C}}=22$ Hz; SiCH$_3$), 21.8 (s, CHCH$_3$), 22.3 (s, CHCH$_3$), 27.5 (d, $J_{\mathrm{P,C}}=60$ Hz; PC_qSi), 45.6 (d, $J_{\mathrm{P,C}}=7$ Hz, NCH), 47.4 (d, $J_{\mathrm{P,C}}=7$ Hz; NCH), 92.5 (dd, $J_{\mathrm{P,C}}=154$ and 133 Hz; PC$_{\mathrm{q}}$P), 126.8 (s, C_{para}H), 128.9 (d, $J_{\mathrm{P,C}}=2$ Hz; C_{meta}H), 131.0 (d, $J_{\mathrm{P,C}}=10$ Hz; C_{ortho}H), 133.5 ppm (dd, $J_{\mathrm{P,C}}=101$ and 8 Hz; C_{ipso}H).

Phosphonio bis(methylene)phosphorane 5: Freshly distilled methyltrifluoromethanesulfonate (0.1 mL, 1.2 mmol) was added to a solution of **E1** (480 mg, 0.82 mmol) in pentane (5 mL) at −80 °C. After the mixture was allowed to warm up to room temperature, a yellow solid appeared. The solution was filtered and the resulting powder was washed with diethyl ether (3×10 mL) and dried under vacuum. Crystals of **5**, suitable for an X-ray diffraction study, were obtained by layering Et$_2$O over a solution of **5** in CH$_2$Cl$_2$ at room temperature. Yield 0.52 g (84%); m.p. 130–132 °C; ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta=$ 166 (d, $J_{\mathrm{P,P}}=70$ Hz), 50 ppm (d, $^2J_{\mathrm{P,P}}=70$ Hz); ^{1}H NMR (CDCl$_3$): $\delta=-0.06$ (s, 9H; SiCH$_3$), −0.04 (s, 9H; SiCH$_3$), 1.20 (d, $J_{\mathrm{H,H}}=4$ Hz, 12H; CHCH_3), 1.25 (d, $J_{\mathrm{H,H}}=8$ Hz, 6H; CHCH_3), 1.27 (d, $J_{\mathrm{H,H}}=7$ Hz, 6H; CHCH_3), 1.36 (d, $J_{\mathrm{H,H}}=8$ Hz, 6H; CHCH_3), 1.39 (d, $J_{\mathrm{H,H}}=8$ Hz, 6H; CHCH_3), 2.02 (dd, $J_{\mathrm{P,H}}=13$ Hz and 20 Hz, 3H; PC(CH_3)P), 3.84 (broad, 4H; NCH), 4.30 (broad, 2H; NCH), 7.62 (m, 6H; H$_{\mathrm{aro}}$), 7.73 ppm (m, 4H; H$_{\mathrm{aro}}$); ^{13}C{^{1}H} NMR (CDCl$_3$):?$\delta=$ 2.6 (d, $J_{\mathrm{P,C}}=6$ Hz; SiCH$_3$), 3.6 (d, $J_{\mathrm{P,C}}=6$ Hz; SiCH$_3$), 22.0 (dd, $J_{\mathrm{P,C}}=8$ and 54 Hz; H$_3$$C$CP), 24.2 (s, H$_3$$C$CN), 24.2 (s, H$_3$$C$CN), 24.7 (s, H$_3$$C$CN), 25.6 (s, H$_3$$C$CN), 34.4 (dd, $J_{\mathrm{P,C}}=47$ and 54 Hz; PCP), 49.1 (broad, HCN), 49.4 (d, $J_{\mathrm{P,C}}=5$ Hz; HCN), 74.6 (d, $J_{\mathrm{P,C}}=80$ Hz; PCSi), 129.3 (d, $J_{\mathrm{P,C}}=12$ Hz; CH$_{\mathrm{aro}}$), 131.0 (dd, $J_{\mathrm{P,C}}=10$ and 102 Hz; C$_{\mathrm{aro}}$), 132.9 (d, $J_{\mathrm{P,C}}=11$ Hz; CH$_{\mathrm{aro}}$), 134 ppm (s, CH$_{\mathrm{aro}}$).

Four-membered heterocycle 6: A stoichiometric amount of BF$_3$·Et$_2$O was added to a solution of **E1** in hexane at −78 °C. The resulting mixture was stirred at room temperature for 2 h. A solid precipitated. After filtration, the yellow powder was dried under vacuum, and recrystallized from a pentane/THF mixture at −30 °C. Heterocycle **6** was obtained as yellow crystals. Yield 0.5 g (65%); m.p. 77–75 °C; ^{31}P{^{1}H} NMR ([D$_8$]THF): $\delta=$ 74 (d broad, $J_{\mathrm{P,F}}=1090$ Hz), 32 ppm (broad); ^{19}F NMR ([D$_8$]THF): $\delta=$ −48 (d broad, $J_{\mathrm{P,F}}=1090$ Hz), −67 ppm (broad); ^{1}H NMR ([D$_8$]THF): $\delta=$ −0.31 (s, 9H; SiCH$_3$), −0.20 (s, 9H; SiCH$_3$), 0.37 (d, $J_{\mathrm{H,H}}=6$ Hz, 6H; NCCH$_3$), 0.64 (d, $J_{\mathrm{H,H}}=7$ Hz, 6H; NCCH$_3$), 0.71 (d, $J_{\mathrm{H,H}}=6$ Hz, 6H; NCCH$_3$), 0.89 (d, $J_{\mathrm{H,H}}=6$ Hz, 6H; NCCH$_3$), 3.25 (m, 2H; NCH), 3.82 (sept broad, $J_{\mathrm{H,H}}=6$ Hz, 2H; NCH), 7.10 (m, 4H; H$_{\mathrm{aro}}$), 7.46 ppm (m, 6H; H$_{\mathrm{aro}}$); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta=$ 4.2 (s, SiCH$_3$), 4.8 (s, SiCH$_3$), 24.4 (s, NCCH$_3$), 24.6 (s, NCCH$_3$), 24.9 (d, $J_{\mathrm{P,C}}=3$ Hz, NCCH$_3$), 25.0 (s, NCCH$_3$), 48.6 (d, $J_{\mathrm{P,C}}=8$ Hz, NCH), 49.0 (d, $J_{\mathrm{P,C}}=5$ Hz, NCH), 128.6 (pseudo t, $J_{\mathrm{P,C}}=10$ Hz; CH$_{\mathrm{aro}}$), 129.3 (d, $J_{\mathrm{P,C}}=11$ Hz; CH$_{\mathrm{aro}}$), 129.6 (d, $J_{\mathrm{P,C}}=10$ Hz; CH$_{\mathrm{aro}}$), 129.6 ppm (dd, $J_{\mathrm{P,C}}=52$ Hz and 5 Hz; C$_{\mathrm{aro}}$).

Addition of phosphorus ylide 7 (1 equiv) to phosphonio phosphaalkene 2: One equivalent of phosphorus ylide **7** was added to a solution of **2** in THF at −78 °C. After warming to room temperature, the mixture was stirred for 1 h. The solvent was removed under vacuum and the residue was washed with ether and dried under vacuum to give **8** in about 80% purity. ^{31}P{^{1}H} NMR: $\delta=$ 50 (d, $J_{\mathrm{P,P}}=90$ Hz), 39 (d, $J_{\mathrm{P,P}}=184$ Hz), 20 ppm (dd, $J_{\mathrm{P,P}}=90$ and 184 Hz). One equivalent of CCl$_4$ was then added to a solution of **8** in THF at −78 °C. After the mixture had been warmed to room temperature, multinuclear NMR spectroscopy indicated the quantitative formation of the fluorinated derivative **9′**. ^{31}P{^{1}H} NMR

([D$_8$]THF): δ= 72 (td, $J_{P,P}$=30 Hz, $J_{P,F}$=920 Hz), 37 ppm (dd, $J_{P,P}$=30 Hz, $J_{P,F}$=13 Hz); ^{19}F NMR ([D$_8$]THF): δ= −66 ppm (td, $J_{P,F}$=13 and 920 Hz).

Addition of phosphorus ylide 7 (2 equiv) to phosphonio phosphaalkene 2: Two equivalents of phosphorus ylide **7** were added to a solution of **2** in THF at −78 °C. After warming up to room temperature, the mixture was stirred overnight. The solvent was removed under vacuum and the product was extracted with pentane. The evaporation of the volatiles afforded **10** as an orange oil; ^{31}P{^{1}H} NMR (C_6D_6): δ= 7.0 (dd, $J_{P,P}$=147 and 154 Hz), 29.9 (d, $J_{P,P}$=147 Hz), 29.9 ppm (d, $J_{P,P}$=154 Hz); ^{1}H NMR (C_6D_6): δ= 1.03 (d, $J_{H,H}$=7 Hz, 6H; H_3CCN), 1.11 (d, $J_{H,H}$=6 Hz, 12H; H_3CCN), 2.0 (dd, $J_{P,H}$=6 and 2 Hz, 2H; PCHP), 3.66 (d sept, $J_{H,H}$=6 Hz, $J_{P,H}$=9 Hz, 2H; HCN), 3.78 (sept, $J_{H,H}$=7 Hz, 4H; HCN), 7.1 (m, 12H; H_{aro}), 7.2 (m, 4H; H_{aro}), 7.8 ppm (m, 4H; H_{aro}); ^{13}C{^{1}H} NMR (C_6D_6): δ= 23.7 (s, H_3CCN), 23.9 (s, H_3CCN), 24.0 (s, H_3CCN), 24.1 (s, H_3CCN), 30 (dt, $J_{P,C}$=18 and 124 Hz; PCP), 45.4 (d, $J_{P,C}$=9 Hz; HCN), 46.2 (d, $J_{P,C}$=4 Hz; HCN), 127.0 (s, CH_{aro}), 127.2 (s, CH_{aro}), 128.8 (s, CH_{aro}), 129.3 (s, CH_{aro}), 132.1 (d, $J_{P,C}$=8 Hz; CH_{aro}), 133.2 (d, $J_{P,C}$=8 Hz; CH_{aro}), 135.3 ppm (dd, $J_{P,C}$=3 and 110 Hz; C_{aro}).

Addition of phosphorus ylide 7 (3 equiv) to dichlorodiisopropylaminophosphine: The aminodichlorophosphine (1.45 mL, 8 mmol) was added to a solution of phosphorus ylide **7** (24 mmol) in THF (20 mL) at −78 °C. After warming to room temperature, the solution was stirred overnight. The solution was filtered and the product was extracted from the solid residue with THF (3×20 mL). The volatiles of the combined THF solutions were removed under vacuum. The resulting white powder was washed with diethyl ether (3×30 mL) and dried under vacuum. This sample contained a small amount of methyl(diisopropylamino)diphenyl phosphonium chloride, but can be used without any further purification. **8:** Yield: 6.0 g (80 %); the ^{31}P NMR data are identical to those described above for the tetrafluoroborate salt.

Synthesis of the phosphonio bis(ylide) 9: A suspension of **8** (2.8 g, 3.7 mmol) in THF (30 mL) was stirred vigorously at room temperature, and freshly dried CCl_4 (0.5 mL, 5 mmol) was added dropwise. After 30 minutes, the volatiles were removed under vacuum. The resulting yellow powder was washed with Et_2O (3×20 mL) and dried under vacuum. Yield: 2.5 g (84 %); ^{31}P{^{1}H} NMR ($CDCl_3$): δ= 63 (t, $J_{P,C}$=24 Hz), 38 ppm (d, $J_{P,C}$=24 Hz); ^{1}H NMR ($CDCl_3$): δ= 0.91 (d, $J_{H,H}$=7 Hz, 12H; H_3CCN), 0.94 (d, $J_{H,H}$=7 Hz, 12H; H_3CCN), 1.05 (d, $J_{H,H}$=7 Hz, 12H; H_3CCN), 1.44 (dt, $J_{P,H}$=2 and 7 Hz, 2H; PCHP), 3.53 (pseudo oct, $J_{P,H}$=$J_{H,H}$=7 Hz, 4H; HCN), 3.75 (d sept, $J_{P,H}$=9 Hz, $J_{H,H}$=7 Hz, 2H; HCN), 7.46 (m, 10H; H_{aro}), 7.64 (m, 5H; H_{aro}), 7.82 ppm (m, 5H; H_{aro}); ^{13}C{^{1}H} NMR ($CDCl_3$): δ=22.6 (d, $J_{P,C}$=4 Hz; H_3CCN), 23.2 (s, H_3CCN), 30.3 (dd, $J_{P,C}$=52 and 73 Hz; PCP), 47.8 (d, $J_{P,C}$=6 Hz; HCN), 48.2 (d, $J_{P,C}$=3 Hz; HCN), 127.3 (dd, $J_{P,C}$=3 and 58 Hz; C_{aro}), 128.2 (d, $J_{P,C}$=11 Hz; HC_{aro}), 128.7 (dd, $J_{P,C}$=3 and 57 Hz; C_{aro}), 128.7 (d, $J_{P,C}$=13 Hz; CH_{aro}), 129.5 (d, $J_{P,C}$=14 Hz; CH_{aro}), 130.0 (d, J_{PC}=14 Hz; CH_{aro}), 130.4 (d, $J_{P,C}$=12 Hz; CH_{aro}), 132.4 (s, CH_{aro}), 132.6 (s, CH_{aro}), 133.1 (d, $J_{P,C}$=11 Hz; CH_{aro}), 134.0 ppm (d, $J_{P,C}$=13 Hz; CH_{aro}).

$1\sigma^4,3\sigma^3,5\sigma^4$-triphosphapenta-1,2,3,4-tetraene F1: Two equivalents of a LiHMDS solution (1.2 g, 5 mmol) in THF (10 mL) was added at −78 °C to a suspension of bis-ylide **9** (2.0 g, 2.5 mmol) in THF (20 mL). After the mixture was allowed to warm to room temperature, the volatile materials were removed under vacuum, and the residue was extracted with pentane. Derivative **F1** precipitated from a concentrated pentane solution at −30 °C as a yellow powder. Yield 1.12 g (62 %); ^{31}P NMR (C_6D_6): δ= 74 (tt, $J_{P,P}$=107 Hz, $J_{P,H}$=18 Hz), 10 ppm (d, $J_{P,P}$=107 Hz); ^{1}H NMR (C_6D_6): δ= 1.16 (d, $J_{H,H}$=7 Hz, 24H; H_3CCN), 1.34 (d, $J_{H,H}$=6 Hz, 12H; H_3CCN), 3.68 (d sept, $J_{P,H}$=15 Hz, $J_{H,H}$=7 Hz, 4H; HCN), 4.33 (d sept, $J_{P,H}$=18 Hz, $J_{H,H}$=6 Hz, 2H; HCN), 7.08 (m, 8H; H_{aro}), 7.78 ppm (m, 12H; H_{aro}); ^{13}C{^{1}H} NMR (C_6D_6): δ= 23.6 (s, $NCCH_3$), 24.2 (s, $NCCH_3$), 47.3 (d, $J_{P,C}$=6 Hz; NCH), 47.5 (d, $J_{P,C}$=8 Hz; NCH), 51.1 (t, $J_{P,C}$=160 Hz; PCP), 128.0 (d, $J_{P,C}$=12 Hz; CH_{aro}), 129.4 (s, CH_{aro}), 132.8 (d, $J_{P,C}$=12 Hz; -CH_{aro}), 138.4 ppm (dd, $J_{P,C}$=100 and 4 Hz; C_{aro}).

Crystal structure determination of compounds E1, 5, and 6: The Bruker SMART-1000 X-ray diffractometer[14a] with Mo-radiation was used for data collection of compounds **E1**, **5**, and **6**. All data frames were collected by using the ω-scan mode (hemisphere reflections for **5**, sphere of reflections for **E1** and **6**) and integrated by using the Bruker SAINTPLUS software package.[14b] The intensity data were corrected for Lorentzian polarization, and absorption corrections were performed by using the SADABS program incorporated in the SAINTPLUS software package. The Bruker SHELXTL software package[14c] was used for direct methods of phase determination and structure refinement. Atomic coordinates, as well as isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of the three compounds were refined by means of a full-matrix least-squares procedure on F^2. All H atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. **E1**: dimensions 0.46×0.40×0.18 mm^3, triclinic, space group $P\bar{1}$, a=9.2941(7), b=10.6288(8), c=19.6356(15) Å, α=84.765(2)°, β=83.516(2)°, γ=68.7100(10)°, V=1793.1(2) Å^3, ρ_{calcd}=1.087 g cm^{-3}, $2\theta_{max}$=56.56°, Mo radiation (λ=0.71073 Å), low temperature=223(2) K, total reflections collected=18601, independent reflections=8853 (R_{int}=0.0210, R_{sig}=0.0252), 7714 (87.2 %) reflections were greater than 2σ(I), index ranges $-12\leq h\leq 12$, $-14\leq k\leq 13$, $-26\leq l\leq 26$, absorption coefficient μ=0.210 mm^{-1}; max/min transmission=0.9632/0.9096, 410 parameters were refined and converged at $R1$=0.0393, $wR2$=0.1102, with intensity $I>2\sigma(I)$, the final difference map was 0.455/−0.238 e Å^{-3}. **5**: dimensions 0.38×0.21×0.13 mm^3, monoclinic, space group $P2(1)/c$, a=11.055(2), b=20.816(4), c=18.375(4) Å, β=98.323(5)°, V=4183.9(15) Å^3, ρ_{calcd}=1.199 g cm^{-3}, $2\theta_{max}$=56.56°, Mo radiation (λ=0.71073 Å), low temperature=218(2) K, total reflections collected=58364, independent reflections=10386 (R_{int}=0.0451, R_{sig}=0.0316), 7624 (73.4 %) reflections were greater than 2σ(I), index ranges $-14\leq h\leq 14$, $-27\leq k\leq 27$, $-24\leq l\leq 24$, absorption coefficient μ=0.258 mm^{-1}; max/min transmission=0.9672/0.9082, 841 parameters were refined and converged at $R1$=0.0540, $wR2$=0.1431, with intensity $I>2\sigma(I)$, the final difference map was 0.353/−0.208 e Å^{-3}. **6**: dimensions 0.48×0.22×0.03 mm^3, monoclinic, space group $P\bar{1}$, a=9.8703(9), b=16.1740(14), c=23.333(2) Å, α=86.084(2)°, β=80.160(2)°, γ=88.468(2)°, V=3661.1(6) Å^3, ρ_{calcd}=1.188 g cm^{-3}, $2\theta_{max}$=49.42°, Mo radiation (λ=0.71073 Å), low temperature=223(2) K, total reflections collected=28876, independent reflections=12490 (R_{int}=0.0457, R_{sig}=0.0690), 8268 (66.2 %) reflections were greater than 2σ(I), index ranges $-11\leq h\leq 11$, $-19\leq k\leq 19$, $-27\leq l\leq 27$, absorption coefficient μ=0.223 mm^{-1}; max/min transmission=0.9933/0.9004, 897 parameters were refined and converged at $R1$=0.0490, $wR2$=0.1173, with intensity $I>2\sigma(I)$, the final difference map was 0.378/−0.304 e Å^{-3}. CCDC-610973 (**E1**), CCDC-610974 (**5**), and CCDC-610975 (**6**) 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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[1] See for example: a) B. Bildstein, M. Schweiger, H. Angleitner, H. Kopacka, K. Wurst, K.-H. Ongania, M. Fontani, P. Zanello, *Organometallics* **1999**, *18*, 4286; b) H. Hopf in *The Chemistry of Ketenes, Allenes, and Related Compounds* (Ed.: S. Patai), Wiley, Chichester, **1980**, Chapter 20.

[2] a) *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, **1990**; b) K. B. Dillon, F. Mathey, J. F. Nixon, *Phosphorus: The Carbon Copy*, Wiley, Chichester, **1998**.

[3] Other cumulenes based on carbon and phosphorus are known, but they contain C−C double bonds, see for example: a) G. Märkl, P. Kreitmeier, *Angew. Chem.* **1988**, *100*, 1411; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1360; b) H. J. Bestmann, D. Hadawi, H. Behl, M. Bremer, F. Hampel, *Angew. Chem.* **1993**, *105*, 1198; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1205; c) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639, and references therein.

[4] a) O. I. Kolodiazhnyi, *Phosphorus Ylides*, Wiley-VCH, Weinheim, **1999**; b) A. W. Johnson, W. C. Kaska, K. A. O. Starzewski, D. A. Dixon, in *Ylides and Imines of Phosphorus* (Ed.: A. W. Johnson), Wiley-Interscience, New York, **1993**; c) H. J. Bestmann, R. Zimmermann in *Comprehensive Organic Synthesis Vol. 6* (Eds.: B. M. Trost, I. Fleming, E. Winterfeldt), Pergamon, Oxford, **1991**, p. 171.

[5] a) M. Gouygou, M. Koenig, J. Escudié, C. Couret, *Heteroat. Chem.* **1991**, *2*, 221; b) M. Yoshifuji, K. Toyota, N. Inamoto, *J. Chem. Soc. Chem. Commun.* **1984**, 689; c) H. H. Karsh, H. U. Reisacher, G. Müller, *Angew. Chem.* **1993**, *96*, 619; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 618.

[6] a) R. Appel, J. Peters, A. Westerhaus, *Angew. Chem.* **1982**, *94*, 76; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 80; b) R. Appel in *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme, New York, **1990**; c) R. Pietschnig, M. Nieger, E. Niecke, K. Airola, *J. Organomet. Chem.* **1997**, *541*, 237; d) T. Baumgartner, P. Moors, M. Nieger, H. Hupfer, E. Niecke, *Organometallics* **2002**, *21*, 4919.

[7] a) T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *Angew. Chem.* **2000**, *112*, 3457; *Angew. Chem. Int. Ed.* **2000**, *39*, 3319; b) D. Martin, H. Gornitzka, A. Baceiredo, G. Bertrand, *Eur. J. Inorg. Chem.* **2005**, *13*, 2619.

[8] The synthesis of cumulene **D** in the coordination sphere of a transition metal has been reported earlier: W. V. Konze, V. G. Young, Jr., R. J. Angelici, *Organometallics* **1998**, *17*, 1569.

[9] A cumulene of type **E**, but with a terminal imino instead of a methylene group has already been reported: W. Schilbach, V. von der Gönna, D. Gudat, M. Nieger, E. Niecke, *Angew. Chem.* **1994**, *106*, 1037; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 982.

[10] E. Niecke, W. Flick, *Angew. Chem.* **1974**, *86*, 128; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 134.

[11] D. Seyferth, E. M. Hanson, F. M. Armbrecht Jr., *J. Organomet. Chem.* **1970**, *23*, 361.

[12] H. Grützmacher, H. Pritzkow, *Angew. Chem.* **1989**, *101*, 768; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 740.

[13] The tautomeric equilibrium between α-chlorophosphanes and the corresponding chloro-ylides is well documented. See for example: a) O. I. Kolodiazhnyi, *Russ. Chem. Rev.* **1997**, 66, 225; b) R. Appel, M. Huppertz, A. Westerhaus, *Chem. Ber.* **1983**, *116*, 114.

[14] a) Software Reference Manual, Version 5.054, Bruker Analytical X-Ray System, Inc., Madison, WI 1997–**1998**; b) SAINTPLUS Software Reference Manual, Version 6.02 A, Bruker Analytical X-Ray System, Inc., Madison, WI **1997–1998**; c) SHELXTL Software Reference Manual, Version 6.10, December 5th, **2000**, Bruker Analytical X-Ray System, Inc., Madison, WI.

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