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Phosphavinylidene(oxo)phosphorane Mes*P(O)=C=PMes*: A Diphosphaallene Featuring $\lambda^5\sigma^3$- and $\lambda^3\sigma^2$-Phosphorus Atoms

Raluca Septelean,[a] Henri Ranaivonjatovo,*[b] Gabriela Nemes,[a] Jean Escudié,*[b] Ioan Silaghi-Dumitrescu,[a] Heinz Gornitzka,[b] Luminita Silaghi-Dumitrescu,[a] and Stéphane Massou[c]

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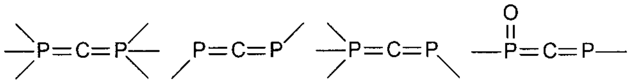
Bis(2,4,6-tri-*tert*-butylphenyl)phosphavinylidene(oxo)phosphorane (**1**) (Mes* = 2,4,6-tri-*tert*-butylphenyl), the first $1\lambda^5\sigma^3,3\lambda^3\sigma^2$-diphosphaallene, has been synthesised by addition of the phosphaalkenyllithium Mes*P=C(Li)Cl to dichlorophosphane oxide Mes*P(O)Cl$_2$. Compound **1** is stable in the solid-state but undergoes a slow intramolecular cyclisation in solution by addition of a C–H bond of an *ortho-tert*-butyl group to the σ^3-P=C double bond. Water adds chemoselectively and regioselectively to the $\lambda^5\sigma^3$-P=C bond, which appears to be more reactive than the $\lambda^3\sigma^2$-P=C bond. This leads to the hydrolysis compound **8** which has been structurally characterised. The new bis(phosphane oxide)methylene **9** formed from the successive cyclisation of an *ortho-tert*-butyl group to the $\lambda^5\sigma^3$-P=C bond and addition of water to the $\lambda^3\sigma^2$-P=C bond has also been structurally characterised.

Introduction

The high utility of ketenes, allenes and cumulenes has been well established in organic synthesis.[1] Phosphaallene derivatives, namely compounds with P=C=C or P=C=P skeletons, are phosphorus congeners of allenes and can thus be expected to be useful starting materials for new organophosphorus compounds.

Among the possible neutral heterocumulenes featuring the P=C=P sequence, $1\sigma^4,3\sigma^4$-diphosphaallenes **I**[2] and $1\sigma^2,3\sigma^2$-diphosphaallenes **II**[3,4] have been known for many years. More recently $1\sigma^4,3\sigma^2$-diphosphaallenes **III** have been isolated.[5]



I **II** **III** **IV**

Here we report the synthesis and the first aspects of the chemical behaviour of a hitherto unknown $1\sigma^3,3\sigma^2$-diphosphaallene **IV**. Despite continuing efforts over the past two decades to synthesise low-coordinate multiply bonded phosphorus compounds, such a functionalised molecule has never been described even as an intermediate. Moreover, such a structure is comprised of a methylene(oxo)phosphorane unit of which only two stable –P(O)=C< representatives have been reported to date.[6]

Results and Discussion

Mes*P(O)=C=PMes*, bis(2,4,6-tri-*tert*-butylphenyl)phosphavinylidene(oxo)phosphorane **1** (Mes* = 2,4,6-tri-*tert*-butylphenyl), was obtained by addition, at –80 °C, of one equiv. of phosphaalkenyllithium **2**[7] to a solution of dichlorophosphane oxide **4**.[8] ^{31}P NMR spectroscopic analysis of the crude mixture showed the presence of **3**, **4** and **1** in a ratio of 1:1:1. The one-pot preparation of **1** probably involves the preliminary formation of phosphaalkenylphosphane oxide **5** followed by a rapid CCl/CLi exchange with phosphaalkenyllithium **2** leading to the starting dichlorophosphaalkene **3** and intermediate **6**. The latter loses LiCl to afford the title compound **1** (Scheme 1), which could be easily obtained as a yellow powder from the reaction mixture by precipitation with pentane. The structure of **1** was unambiguously determined by sophisticated ^{1}H, ^{13}C and ^{31}P NMR spectroscopic studies (1D selective ^{31}P decoupling experiments and 2D HSQC, HMBC) (see supporting information). The ^{31}P NMR spectrum of **1** displays an AX system at δ = 261.4 (σ^2-P) and 117.3 ppm (σ^3-P) with a coupling constant $^{2}J_{P,P}$ of 30.5 Hz. A large high-frequency shift of 120 ppm can be observed for the $\lambda^3\sigma^2$-P in comparison with the value reported for the diphosphaallene Mes*P=C=PMes* (δ^{31}P = 140 ppm[4b]). The signal of the

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[a] Babes-Bolyai University,
Kogalniceanu 1, 400084 Cluj-Napoca, Romania
[b] Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse cedex 9, France
[c] Structure Fédérative Toulousaine en Chimie Moléculaire, FR 2599, Université Paul Sabatier,
118 route de Narbonne, 31062 Toulouse cedex 9, France

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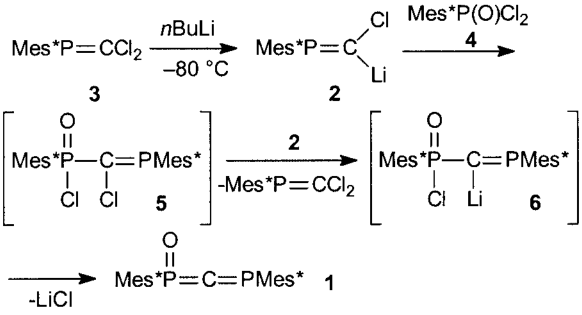
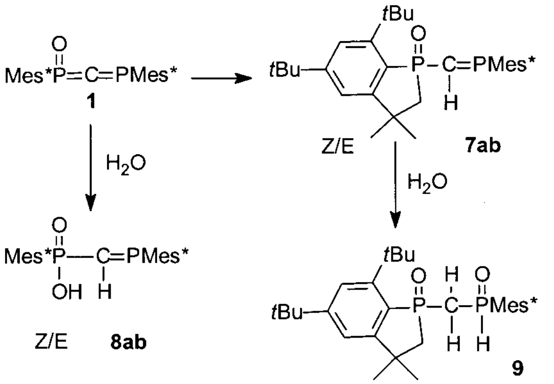
$\lambda^5\sigma^3$-phosphorus atom is slightly lower in frequency in relation to those observed for Mes*P(O)=C(R)SiMe$_3$ [δ^{31}P = 153.7 ppm (R = Ph),[6a] 161.1 ppm (R = Me$_3$Si)[6b]]. The sp hybridised carbon atom gives rise to a doublet of doublets at δ = 229.1 ppm ($^1J_{C,P(O)}$ = 177.4, $^1J_{C,P}$ = 46.8 Hz). The ^{1}H NMR spectrum at room temperature shows slow rotation of the Mes* group bonded to the $\lambda^3\sigma^2$-phosphorus atom. Dynamic ^{1}H NMR spectroscopy was performed between 213 and 328 K and the coalescence temperatures for the *o*-*t*Bu groups and for the aromatic protons on the Mes* group bonded to the $\lambda^3\sigma^2$-P are 268 and 253 K, respectively, giving a rotation barrier of 12.2 kcal mol^{-1}. Similar values have been reported for the rotation barriers of Mes* groups in the phosphaarsaallene Mes*P=C=AsMes* (13.6 kcal mol^{-1})[9] and in the diphosphaallene Mes*P=C=PMes* (14.0 kcal mol^{-1}).[10] Hindered rotation can be observed for the Mes* group bonded to the P(O) moiety even at 328 K (two singlets for the *o*-*t*Bu groups and two doublets of doublets for the aromatic protons). A molecular ion peak can be observed in the mass spectrum of **1** with the expected fragments at *m*/*z* = 565 [M – Me]$^+$ and 523 [M – *t*Bu]$^+$.



Scheme 1. Synthesis of Mes*P(O)=C=PMes* (**1**).

Compound **1** is stable for months at room temperature in the solid-state but attempts to crystallise it in various solvents at low temperatures did not afford satisfactory single crystals for X-ray diffraction studies. Compound **1** slowly rearranges within one day at room temperature in solution. The rearrangement affords the phosphaalkenylphosphane oxides **7a** and **7b** in near quantitative yield in the form of two geometric isomers in the ratio of 85:15 (Scheme 2). B3LYP/6-31G(d)//ONIOM B3LYP/6-31G(d):PM3 calculations support this easy isomerisation and **7** was found to be lower in energy than **1** by about 54 kcal mol^{-1}.

The ^{31}P NMR spectra of **7a** and **7b** exhibit signals in the typical range for phosphalkenes[11a–11d] [δ^{31}P for P=C in **7a** at δ = 339.1 ppm (dd, $^2J_{P,P}$ = 70.2 Hz, $^2J_{P,H}$ = 24.4 Hz) and in **7b** at δ = 353.0 ppm (dd, $^2J_{P,P}$ = 73.3 Hz, $^2J_{P,H}$ = 21.4 Hz, P=C)] and phosphane oxides[11e] [δ^{31}P for P(O) in **7a** at δ = 49.3 ppm (d, $^2J_{P,P}$ = 70.2 Hz) and in **7b** at δ = 38.7 ppm (d, $^2J_{P,P}$ = 73.3 Hz)]. Similar chemical shifts at 327 and 10 ppm have been reported for Mes*P=CH–P(O)HMes*.[12] The *E* structure has been tentatively assigned to the major isomer **7a** on the basis of the $^2J_{P,H}$ coupling constant. For example, in the Mes*P=CHR system, the larger coupling constant always corresponds to the *E* isomer [18 Hz (*Z*) and 24.7 Hz (*E*) in Mes*P=C(H)SiMe$_3$].[7a] Moreover ONIOM B3LYP/6-31G(d):PM3 geometry optimisations of **7** place the *Z* isomer higher in energy by 3.63 kcal mol^{-1}.



Scheme 2. Rearrangement reaction and hydrolysis of **1**.

This intramolecular cyclisation results from the addition of a C–H bond of an *ortho*-*tert*-butyl substituent of a supermesityl group to the σ^3-P=C double bond.[13] This rearrangement shows that the methylene(oxo)phosphorane moiety is much less stable than the phosphane oxide one. In contrast to bis(methylene)phosphoranes RP(=CR′$_2$)$_2$ which isomerise into phosphiranes,[14] the O=P=C unit in **1** does not undergo a similar cyclisation (which would lead to the three-membered ring oxaphosphirane).

The structure of **1** was also established unambiguously from its hydrolysis products. The $\lambda^5\sigma^3$-P=C double bond is much more reactive than the $\lambda^3\sigma^2$-P=C bond since one equiv. of water adds only to this double bond to afford the two geometric isomers **8a** and **8b** (Scheme 2). Again, ONIOM B3LYP/6-31G(d):PM3 optimisations show that **8b** (*E* isomer) is lower in energy by 5.27 kcal mol^{-1}.

The ^{31}P NMR spectra of **8a** and **8b** exhibit characteristic signals of phosphaalkenes [δ^{31}P **8a** = 305.5 ppm (dd, $^2J_{P,P}$ = 47.3 Hz, $^2J_{P,H}$ = 24.4 Hz, P=C), **8b** = 335.4 ppm (dd, $^2J_{P,P}$ = 68.5 Hz, $^2J_{P,H}$ = 24.4 Hz, P=C] and phosphinic acids [δ^{31}P **8a** = 24.6 ppm {d, $^2J_{P,P}$ = 47.3 Hz, P(O)}; **8b** = 34.9 ppm {d, $^2J_{P,P}$ = 68.5 Hz, P(O)}].

This addition is regioselective and gives, as expected, the derivative with the hydrogen atom bonded to the central sp^2 carbon atom. However, since the reaction of water with **1** is slow in solution (about one day in pentane at room temperature), the competitive cyclisation products **7a**,**b** are also formed. Compounds **7** and **8** are obtained in the ratio **7a** (25%), **7b** (5%), **8a** (20%) and **8b** (50%). The X-ray structure of the *Z* isomer **8b** has been determined (Figure 1) and displays standard bond lengths and angles.

Addition of water to the *Z*/*E* mixture of **7** afforded, after one week, the new bis(phosphane oxide)methylene **9** in the form of only one diastereoisomer, which was isolated as pale yellow crystals in 85% yield. The ^{31}P NMR spectrum of **9** displays two doublets at δ = 52.1 and 4.8 ppm (small coupling constant $^2J_{P,P}$ of 2.7 Hz). In the nondecoupled ^{31}P NMR spectrum, derivative **9** exhibits a doublet of doublets

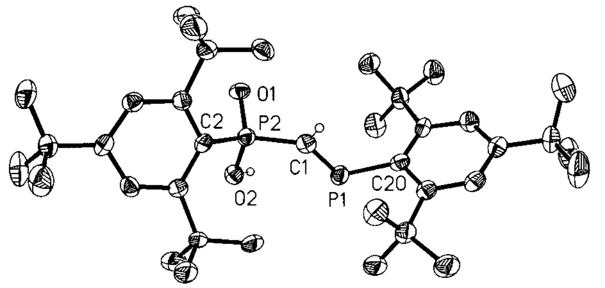


Figure 1. Structure of **8** (*E*) (50% probability level). Selected bond lengths [Å] and angles [°]: P1–C1 1.650(4), P2–C1 1.822(3), P2–C2 1.828(4), P1–C20 1.847(5), P2–O1 1.510(3), P2–O2 1.550(3), P1–C1–P2 122.3(3), O1–P2–C1 108.72(17), O2–P2–C1 107.32(18), O1–P2–C2 108.39(17), O2–P2–C2 105.60(18), C1–P2–C2 116.26(19), C20–P1–C1–P2 168.0.

of triplets for the signal at 4.8 ppm ($^1J_{P,H}$ = 517.4 Hz, $^2J_{P,H}$ = 2.8 Hz, $^2J_{P,P}$ = 2.7 Hz), the very large $^1J_{P,H}$ coupling constant being characteristic of a hydrogen bonded to a $\lambda^5\sigma^4$-phosphorus atom. The ^{1}H and ^{13}C NMR spectra display hindered rotation of the Mes* group. Dynamic ^{1}H NMR spectroscopy was performed between 253 and 323 K. The coalescence temperatures for the *o*-*t*Bu groups and for the aromatic protons on the Mes* group bonded to the P(H) atom are 288 K in both cases, corresponding to a rotation barrier of 14.2 kcal mol^{-1} which is 2 kcal mol^{-1} higher than that of the Mes* group bonded to the $\lambda^3\sigma^2$-phosphorus atom in **1**.

The X-ray structure of **9** (Figure 2) displays standard bond lengths and angles.

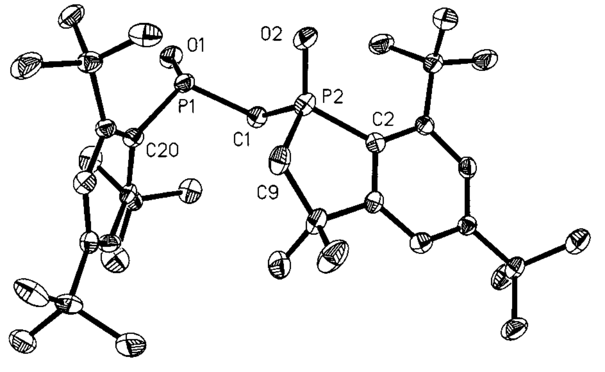


Figure 2. Structure of **9** (50% probability level). Selected bond lengths [Å] and angles [°]: P1–C1 1.827(3), P2–C1 1.822(3), P2–C2 1.819(3), P2–C9 1.794(4), P1–C20 1.818(4), P1–O1 1.482(2), P2–O2 1.481(2), P1–C1–P2 115.14(18), O1–P1–C1 112.78(15), O2–P2–C1 111.13(14), O2–P2–C2 119.96(16), O1–P1–C20 120.11(14).

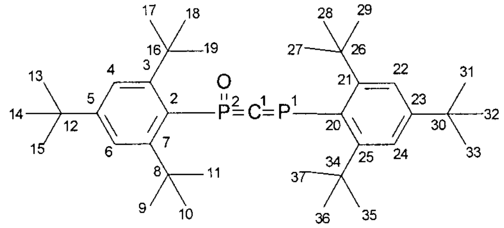
In conclusion, the first phosphavinylidene(oxo)phosphorane **1**, a derivative with three "cumulated formal double bonds", was obtained as a stable compound in the solid-state in a one-pot procedure. The ability of **1** to form transition metal complexes is now under investigation.

Experimental Section

General: All experiments were carried out in flame-dried glassware under an argon atmosphere using high-vacuum-line techniques. Solvents were dried and freshly distilled from sodium benzophenone ketyl and carefully deoxygenated on a vacuum line by several "freeze-pump-thaw" cycles. NMR spectra were recorded in $CDCl_3$ on the following spectrometers: ^{1}H, Bruker Avance 300 (300.13 MHz) and Avance 400 (400.13 MHz); $^{13}C\{^1H\}$, Bruker Avance 300 (75.47 MHz) and Avance 400 (100.62 MHz) (reference TMS); ^{31}P, Bruker AC200 (81.02 MHz) and Avance 400 (162.04 MHz) (reference H_3PO_4). Melting points were determined on a Wild Leitz-Biomed apparatus. Mass spectra were obtained on a Hewlett–Packard 5989A spectrometer by EI at 70 eV.

Synthesis of Mes*P(O)=C=PMes* (1): To a solution of Mes*P=CCl_2 **3** (3.15 g, 8.67 mmol) in THF (20 mL) cooled to –80 °C was added a solution of *n*-butyllithium (5.7 mL, 1.6 M in hexane, 9.1 mmol). After stirring for 1 h, the solution of Mes*P=C(Cl)Li was transferred by cannula to a solution of Mes*P(O)Cl_2 **4** (3.00 g, 8.67 mmol) in THF (30 mL) at –80 °C. The reaction mixture became dark brown and after 15 min stirring and subsequent warming to –20 °C, the solvent was removed under vacuum. Pentane (30 mL) was added to the residue and **3** and **4** dissolved. However **1** and LiCl precipitated due to both being very poorly soluble in pentane. After filtration, **1** was extracted with CH_2Cl_2. Removal of the solvent gave a pale yellow powder of **1** (2.01 g, 40%, m.p. 125 °C, dec.).

The carbon and phosphorus atoms are numbered as follows:



1

In order to assign all the signals observed in the ^{1}H and ^{13}C NMR spectra, HSQC, HMBC and selective ^{31}P decoupling experiments were performed. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 213 K): δ = 1.10 (s, 9 H, H on C27–29), 1.23 (s, 9 H, H on C17–19), 1.34 (s, 9 H, H on C13–15), 1.36 (s, 9 H, H on C31–33), 1.65 (s, 9 H, H on C35–37), 1.79 (s, 9 H, H on C9–11), 7.27 (broad s, 1 H, H on C22), 7.37 (broad d, $^4J_{H,P}$ = 5.2 Hz, 1 H, H on C6), 7.46 (broad s, 1 H, H on C24), 7.48 (broad d, $^4J_{H,P}$ = 6.1 Hz, 1 H, H on C4) ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz): δ = 31.3 (C13–15), 31.5 (C31–33), 32.8 (C17–19), 33.1 (d, $^4J_{C,P1}$ = 6.5 Hz, C27–29), 33.3 (C9–11), 33.9 (C35–37), 35.2 (C30), 35.5 (C12), 37.4 (C26), 38.1 (d, $^3J_{C,P2}$ = 3.1 Hz, C16), 38.5 (C34), 38.7 (d, $^3J_{C,P2}$ = 3.6 Hz, C8), 119.7 (d, $^1J_{C,P2}$ = 127.5 Hz, C2), 121.7 (C22), 122.6 (d, $^3J_{C,P2}$ = 13.8 Hz, C6), 122.7 (C24), 122.9 (d, $^3J_{C,P2}$ = 15.6 Hz, C4), 138.3 (dd, $^1J_{C,P1}$ = 74.6 Hz, $^3J_{C,P2}$ = 28.5 Hz, C20), 150.3 (C23), 152.0 (C21), 153.6 (d, $^2J_{C,P2}$ = 6.7 Hz, C7), 153.9 (C25), 154.2 (d, $^2J_{C,P2}$ = 11.0 Hz, C3), 154.6 (d, $^4J_{C,P2}$ = 2.9 Hz, C5), 227.3 (dd, $^1J_{C,P1}$ = 47.1 Hz, $^1J_{C,P2}$ = 184.7 Hz, C1) ppm.

^{31}P NMR ($CDCl_3$, 81.02 MHz, 298 K): δ = 117.3 (d, $^2J_{P,P}$ = 30.5 Hz, P2), 261.4 (d, $^2J_{P,P}$ = 30.5 Hz, P1) ppm. MS (EI = 70 eV): *m*/*z* (%) = 580 (1) $[M]^+$, 565 (3) $[M - Me]^+$, 523 (20) $[M - tBu]^+$, 467 (5) $[M - 2\,tBu + 1]^+$, 335 (30) $[M - Mes^*]^+$, 57 (100) $[tBu]^+$. $C_{37}H_{58}OP_2$ (580.81): calcd. C 76.51, H 10.07; found C 76.76, H 9.75. At 253 K, the signals of C21, 22, 24–26, 27–29, 34, and 35–37 (^{13}C NMR) and the signals of H on C22, 24, 27–29, 35–37 (^{1}H NMR) are too broad to be observed. At 328 K, the free rotation of Mes* bonded to P1 occurs and the following signals may be observed: 33.8 (C27–29 and C35–37), 37.8 (C26 and C34), 121.9 (C22 and C24) and 153.2 ppm (C21 and C25) in the ^{13}C NMR spectrum; 1.39 (s, C27–29 and C35–37) and 7.32 ppm (s, C22 and C24) in the ^{1}H NMR spectrum.

Synthesis of Cyclisation Products 7a and 7b: A solution of Mes*-P(O)=C=PMes* **1** (1.20 g, 2.01 mmol) in toluene (10 mL) was heated at 80 °C for 1 h. NMR analysis showed the conversion of **1** into **7a** and **7b** in the ratio 85:15. Removal of solvent in vacuo led to a powder of **7a**,**b**. Attempts at fractional crystallisation in various solvents (pentane, Et_2O, $CHCl_3$) did not allow the complete separation of the two isomers **7a** and **7b**. Selective ^{31}P decoupled ^{1}H and ^{13}C NMR experiments were performed. At 283 K, signals of some *t*Bu groups were too broad to be observed by ^{1}H NMR spectroscopy.

7a [(*E*) isomer]: ^{1}H NMR ($CDCl_3$, 400.13 MHz, 283 K): δ = 1.31, 1.48 and 1.56 (3s, 27 H, H from *t*Bu groups), 2.36 [ddd, $^{2}J_{\mathrm{H,H}}$ = 15.0 Hz, $^{2}J_{\mathrm{H,P2}}$ = 19.3 Hz, $^{4}J_{\mathrm{H,P1}}$ = 3.9 Hz, 1 H, H on C9 (carbon atom bonded to P2)], 2.50 (dd, $^{2}J_{\mathrm{H,H}}$ = 15.0 Hz, $^{2}J_{\mathrm{H,P2}}$ = 7.1 Hz, 1 H, H on C9), 7.16, 7.28, 7.36 and 7.40 (4 broad s, 4 × 1 H, arom H), 7.58 (dd, $^{2}J_{\mathrm{H,P1}}$ = 22.3 Hz, $^{2}J_{\mathrm{H,P2}}$ = 13.8 Hz, 1 H, H on C1) ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz, 283 K): δ = 31.2, 31.3 and 32.5 (C13–15, C17–19, C31–33), 34.2 (d, $^{4}J_{\mathrm{C,P1}}$ = 7.0 Hz, C27–29, C35–37), 37.5 (C30), 38.3 (C26, C34), 39.0 (d, $^{2}J_{\mathrm{C,P2}}$ = 5.8 Hz, C8), 40.0 (d, $J_{\mathrm{C,P2}}$ = 2.8 Hz) and 40.8 (d, $J_{\mathrm{C,P2}}$ = 3.6 Hz) (C12, C16), 43.7 (dd, $^{1}J_{\mathrm{C,P2}}$ = 75.9 Hz, $^{3}J_{\mathrm{C,P1}}$ = 6.0 Hz, C9), 118.7 (d, $^{3}J_{\mathrm{C,P2}}$ = 13.8 Hz) and 122.8 (d, $^{3}J_{\mathrm{C,P2}}$ = 10.0 Hz, C4, C6), 122.2 (C22, C24), 127.1 (d, $^{1}J_{\mathrm{C,P2}}$ = 95.6 Hz, C2), 138.8 (dd, $^{1}J_{\mathrm{C,P1}}$ = 67.5 Hz, $^{3}J_{\mathrm{C,P2}}$ = 17.7 Hz, C20), 150.1 (C23), 153.4 (C21, C25), 154.2 (d, $^{2}J_{\mathrm{C,P2}}$ = 7.2 Hz) and 157.0 (d, $^{2}J_{\mathrm{C,P2}}$ = 20.2 Hz, C3, C7), 155.7 (d, $^{4}J_{\mathrm{C,P2}}$ = 2.5 Hz, C5), 165.3 (dd, $^{1}J_{\mathrm{C,P2}}$ = 74.8 Hz, $^{1}J_{\mathrm{C,P1}}$ = 63.2 Hz, C1) ppm. ^{31}P NMR ($CDCl_3$, 81.02 MHz, 298 K): δ = 49.3 (d, $^{2}J_{\mathrm{P,P}}$ = 70.2 Hz, P2), 339.1 (dd, $^{2}J_{\mathrm{P,P}}$ = 70.2 Hz, $^{2}J_{\mathrm{P,H}}$ = 24.4 Hz P1) ppm. MS (EI = 70 eV): *m*/*z* (%) = 565 (8) $[M - 15]^+$, 523 (15) [M – *t*Bu]$^+$, 335 (100) [M – Mes*]$^+$, 57 (90) [*t*Bu]$^+$.

7b [(*Z*) isomer]: ^{1}H NMR ($CDCl_3$, 400.13 MHz, 283 K): δ = 7.82 (dd, $^{2}J_{\mathrm{H,P2}}$ = 212.0 Hz, $^{2}J_{\mathrm{H,P1}}$ = 17.6 Hz, 1 H, CH=P) ppm (other ^{1}H signals and ^{13}C signals of the minor isomer could not be assigned unambiguously). ^{31}P NMR ($CDCl_3$, 81.02 MHz, 298 K): δ = 38.7 (d, $^{2}J_{\mathrm{P,P}}$ = 73.3 Hz, PO), 353.0 (dd, $^{2}J_{\mathrm{P,P}}$ = 73.3 Hz, $^{2}J_{\mathrm{P,H}}$ = 21.4 Hz P=C) ppm.

Hydrolysis of 7a and 7b. Synthesis of 9: An excess of degassed water was added to the mixture of **7a**,**b** (0.60 g, 1.04 mmol) in Et_2O. After stirring for a week at room temperature, NMR analysis showed the formation of **9**. Et_2O was removed under vacuum and recrystallisation from pentane afforded pure **9** as pale yellow crystals (0.48 g, 78 %, m.p. 203 °C). HSQC, HMBC, NOESY and selective ^{31}P decoupled ^{1}H and ^{13}C NMR experiments were performed. ^{1}H NMR ($CDCl_3$, 400.13 MHz, 253 K): δ = 0.46 (dd, $^{2}J_{\mathrm{H,P2}}$ = 6.2 Hz, $^{2}J_{\mathrm{H,H}}$ = 15.3 Hz, 1 H, H on C9, carbon atom bonded to P2), 0.90 and 1.21 (2s, 2 × 3 H, H on C10,11), 1.30 (s, 9 H, H on C13–15), 1.38 (s, 9 H, H on C31–33), 1.52 and 1.65 (2s, 2 × 9 H, H on C27–29 and C35–37), 1.53 (s, 9 H, H on C17–19), 1.54 (dd, $^{2}J_{\mathrm{H,P2}}$ = 20.4 Hz, $^{2}J_{\mathrm{H,H}}$ = 15.3 Hz, 1 H, H on C9), 2.43 (dddd, $^{2}J_{\mathrm{H,P1}}$ = 15.0 Hz, $^{2}J_{\mathrm{H,P2}}$ = 7.2 Hz, $^{2}J_{\mathrm{H,H}}$ = 15.3 Hz, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 1 H, H on C1), 3.30 (dt, $^{2}J_{\mathrm{H,P1}}$ and $^{2}J_{\mathrm{H,P2}}$ = 16.6 Hz, $^{2}J_{\mathrm{H,H}}$ = 15.3 Hz, 1 H, H on C1), 7.07 (dd, $^{4}J_{\mathrm{H,P2}}$ = 2.0 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.0 Hz, 1 H, H on C4), 7.41 (dd, $^{4}J_{\mathrm{H,P2}}$ = 5.2 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.0 Hz, 1 H, H on C6), 7.45 (dd, $^{4}J_{\mathrm{H,P1}}$ = 2.0 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.0 Hz, 1 H, H on C22), 7.54 (dd, $^{4}J_{\mathrm{H,P1}}$ = 4.1 Hz, $^{4}J_{\mathrm{H,H}}$ = 1.0 Hz, 1 H, H on C24), 8.52 (ddd, $^{1}J_{\mathrm{H,P1}}$ = 517.4 Hz, $^{3}J_{\mathrm{H,P2}}$ = 2.8 Hz, $^{3}J_{\mathrm{H,H}}$ = 7.1 Hz, 1 H, H on P1) ppm. ^{13}C NMR ($CDCl_3$, 100.62 MHz, 253 K): δ = 31.2 (C13–15), 31.4 (C31–33), 31.9 and 33.5 (C10–11), 32.2 (C17–19), 33.6 and 34.3 (C27–29 and C35–37), 35.3 (C30), 35.4 (C12), 37.7 (C16), 38.7 (d, $^{2}J_{\mathrm{C,P2}}$ = 6.2 Hz, C8), 39.2 (C26 and C34), 39.6 (d, $^{1}J_{\mathrm{C,P2}}$ = 72.1 Hz, C9), 40.6 (dd, $^{1}J_{\mathrm{C,P1}}$ = 55.1 Hz, $^{1}J_{\mathrm{C,P2}}$ = 50.5 Hz, C1), 118.9 (d, $^{3}J_{\mathrm{C,P2}}$ = 14.4 Hz, C4), 123.3 (d, $^{3}J_{\mathrm{C,P2}}$ = 10.2 Hz, C6), 123.6 (d, $^{3}J_{\mathrm{C,P1}}$ = 11.9 Hz) and 124.1 (d, $^{3}J_{\mathrm{C,P1}}$ = 13.4 Hz) (C22 and C24), 125.2 (dd, $^{1}J_{\mathrm{C,P2}}$ = 96.5 Hz, $^{3}J_{\mathrm{C,P1}}$ = 3.9 Hz, C2), 128.2 (d, $^{1}J_{\mathrm{C,P1}}$ = 99.0 Hz, C20), 153.6 (d, $^{4}J_{\mathrm{C,P1}}$ = 3.1 Hz, C23), 154.2 (d, $^{2}J_{\mathrm{C,P2}}$ = 8.1 Hz, C7), 156.0 (d, $^{2}J_{\mathrm{C,P1}}$ = 5.7 Hz, C21), 156.3 (d, $^{2}J_{\mathrm{C,P2}}$ = 33.0 Hz, C3), 156.6 (d, $^{4}J_{\mathrm{C,P2}}$ = 2.4 Hz, C5), 157.4 (d, $^{2}J_{\mathrm{C,P1}}$ = 11.9 Hz, C25) ppm. ^{31}P NMR ($CDCl_3$, 81.02 MHz, 298 K): δ = 4.8 (ddt, $^{2}J_{\mathrm{P,P}}$ = 2.7 Hz, $^{1}J_{\mathrm{P,H}}$ = 517.4 Hz, $^{2}J_{\mathrm{P,H}}$ = 2.8 Hz, P1), 52.1 (d, $^{2}J_{\mathrm{P,P}}$ = 2.7 Hz, P2) ppm. MS (EI = 70 eV): *m*/*z* (%) = 599 (2) $[M + 1]^+$, 581 (1) $[M - O - 1]^+$, 541 (100) [M – *t*Bu]$^+$, 353 (85) [M – Mes*]$^+$, 57 (70) [*t*Bu]$^+$ $C_{37}H_{60}O_2P_2$ (598.82): calcd.C 74.21, H 10.10; found C 74.56, H 9.85.

Synthesis of 8a and 8b by Hydrolysis of the P(O)=C Double Bond of 1: An excess of degassed water was added to a solution of **1** (1.15 g, 1.98 mmol) in pentane (20 mL). After stirring for 2 d at room temperature, NMR analysis showed the formation of a mixture of **7a**,**b** and **8a**,**b**. Attempts at crystallisation from various solvents did not allow complete separation of the two derivatives and only some single crystals of **8**, suitable for an X-ray structure determination, could be obtained by crystallisation from $CHCl_3$ and cyclohexane. ^{31}P NMR ($CDCl_3$, 81.02 MHz, 298 K) **8a** (30 %), δ = 24.6 (d, $^{2}J_{\mathrm{P,P}}$ = 47.3 Hz, PO), 305.5 ppm (dd, $^{2}J_{\mathrm{P,P}}$ = 47.3 Hz, $^{2}J_{\mathrm{P,H}}$ = 24.4 Hz, P=C) **8b** (70 %), δ = 34.9 ($^{2}J_{\mathrm{P,P}}$ = 68.5 Hz, PO), 335.4 ppm (dd, $^{2}J_{\mathrm{P,P}}$ = 68.5 Hz, $^{2}J_{\mathrm{P,H}}$ = 24.4 Hz, P=C).

X-ray Structure Determinations

Crystal Data for 8 and 9. Compound 8: $C_{43}H_{73}Cl_3O_2P_2$, $M = 790.30$ ($CHCl_3$ and cyclohexane in the lattice), triclinic, $P\bar{1}$, $a = 13.998(2)$, $b = 14.106(2)$, $c = 14.348(2)$ Å, $\alpha = 91.531(4)$, $\beta = 119.170(3)$, $\gamma = 108.678(3)°$, $V = 2285.6(6)$ Å^3, $Z = 2$, $T = 173(2)$ K. 9004 reflections (5491 independent, $R_{\mathrm{int}} = 0.0740$) were collected. Largest electron density residue: 0.341 eÅ^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0565 and $wR_2 = 0.1433$ (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w\ (F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. **Compound 9:** $C_{37}H_{60}O_2P_2$, $M = 598.79$, monoclinic, $P2_1/c$, $a = 10.275(1)$, $b = 25.939(2)$, $c = 14.342(1)$ Å, $\beta = 110.884(2)°$, $V = 3571.4(6)$ Å^3, $Z = 4$, $T = 173(2)$ K. 15676 reflections (5066 independent, $R_{\mathrm{int}} = 0.1213$) were collected. Largest electron density residue: 0.250 eÅ^{-3}, R_1 [for $I > 2\sigma(I)$] = 0.0558 and $wR_2 = 0.0943$ (all data).

All data for structures reported in this paper were collected at low temperature using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97)[15] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2 (SHELXL-97).[16]

CCDC-605519 (for **8**) and -605520 (for **9**) 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.

Supporting Information: (for details see the footnote on the first page of this article): variable temperature ^{1}H NMR, 2D HSQC and 2D HMBC, ^{13}C{^{1}H,^{31}P} and ^{13}C{^{1}H} Jmod spectra of diphosphaallene Mes*P(O)=C=PMes* (**1**), variable-temperature ^{1}H NMR spectra of bis(phosphane oxide)methylene **9**.

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[1] a) *The Chemistry of Ketenes, Allenes and Related Compounds* (Ed.: S. Patai), **1980**; b) *The Chemistry of Allenes* (Ed.: S. R Landor), **1982**; c) *Allenes in Organic Synthesis* (Eds.: H. F. Schuster, G. M. Coppola), **1984**.

[2] a) F. Ramirez, N. B. Desai, B. Hansen, N. Mc Kelvie, *J. Am. Chem. Soc.* **1961**, *83*, 3539–3540; b) H. J. Bestmann, R. Zimmermann, in: *Methoden der Organische Chemie*, Houben–Weyl, 4th ed., vol. E1, **1982**, pp. 752–758; c) 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**; d) O. I. Kolodiazhnyi, in: *Phosphorus Ylides* (Ed.: O. I. Kolodiazhnyi), Wiley-VCH, Weinheim, **1999**.

[3] For reviews see: a) R. Appel, in: *Multiple Bonds and Low Coordination in Phosphorus Chemistry* (Eds.: M. Regitz, O. J. Scherer), Thieme: Stuttgart, **1990**, p. 157–219; b) J. Escudié, H. Ranaivonjatovo, L. Rigon, *Chem. Rev.* **2000**, *100*, 3639–3696; c) J. Escudié, H. Ranaivonjatovo, M. Bouslikhane, Y. El Harouch, L. Baiget, G. Cretiu-Nemes, *Russ. Chem. Bull.* **2004**, *53*, 1020–1033.

[4] a) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, F. Knoch, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 618–619; b) H. H. Karsch, F. H. Köhler, H.-U. Reisacher, *Tetrahedron Lett.* **1984**, *25*, 3687–3690; c) M. Yoshifuji, K. Toyota, N. Inamoto, *J. Chem. Soc., Chem. Commun.* **1984**, 689–690; d) M. Gouygou, M. Koenig, J. Escudié, C. Couret, *Heteroat. Chem.* **1991**, *2*, 221–227; e) M. Yoshifuji, S. Sasaki, N. Inamoto, *J. Chem. Soc., Chem. Commun.* **1989**, 1732–1733; f) M. Yoshifuji, T. Niitsu, D. Shiomi, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 5433–5436; g) K. Toyota, A. Nakamura, M. Yoshifuji, *Chem. Commun.* **2002**, 3012–3013.

[5] a) U. Krüger, H. Pritzkow, H. Grützmacher, *Chem. Ber.* **1991**, *124*, 329–331; b) H. P. Schrödel, G. Jochem, A. Schmidpeter, H. Nöth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1853–1856; c) T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, *Angew. Chem. Int. Ed.* **2000**, *39*, 3319–3321; d) D. Martin, H. Gornitzka, A. Baceiredo, G. Bertrand, *Eur. J. Inorg. Chem.* **2005**, 2619–2624.

[6] a) R. Appel, C. Casser, *Tetrahedron Lett.* **1984**, *25*, 4109–4112; b) R. Appel, H. Knoch, H. Kunze, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 157–158.

[7] a) S. J. Goede, F. Bickelhaupt, *Chem. Ber.* **1991**, *124*, 2677–2684; b) E. Niecke, M. Nieger, O. Schmidt, D. Gudat, W. W. Schoeller, *J. Am. Chem. Soc.* **1999**, *121*, 519–522; c) M. Yoshifuji, S. Ito, *Top. Curr. Chem.* **2003**, *223*, 67–89.

[8] S. Freeman, M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 1* **1987**, 1399–1406.

[9] H. Ranaivonjatovo, H. Ramdane, H. Gornitzka, J. Escudié, J. Satgé, *Organometallics* **1998**, *17*, 1631–1633.

[10] M. Yoshifuji, S. Sasaki, T. Niitsu, N. Inamoto, *Tetrahedron Lett.* **1989**, *30*, 187–188.

[11] For reviews see: a) S. Lochschmidt, A. Schmidpeter, *Phosphorus Sulfur Silicon Relat. Elem.* **1986**, *29*, 73–109; b) R. Appel, F. Knoll, *Adv. Inorg. Chem.* **1989**, *33*, 259–361; c) L. N. Markovski, V. D. Romanenko, *Tetrahedron* **1989**, *45*, 6019–6090; d) L. Weber, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 271–288; e) *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data* (Ed.: J. C. Tebby), CRC Press, Boca Raton, Florida (USA), **1991**.

[12] H. H. Karsch, H.-U. Reisacher, *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *37*, 241–242.

[13] Such intramolecular cyclisations are well-known in the chemistry of phosphaallenes a) H. H. Karsch, H.-U. Reisacher, *Phosphorus Sulfur Silicon Relat. Elem.* **1988**, *36*, 213–215; b) H. H. Karsch, H.-U. Reisacher, G. Müller, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 454–455; c) M. A. David, J. B. Alexander, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **1997**, *16*, 378–383; d) M. A. David, S. N. Paisner, D. S. Glueck, *Organometallics* **1995**, *14*, 17–19.

[14] a) R. Appel, Th. Gaitzsch, F. Knoch, G. Lenz, *Chem. Ber.* **1986**, *119*, 1977–1985; b) E. Niecke, D. A. Wildbredt, W. Schoeller, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 131–132.

[15] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[16] G. M. Sheldrick, *Program for Crystal Structure Refinement*, University of Göttingen **1997**.

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