Synthesis of a Persistent $1\sigma^3,3\sigma^3$-Diphosphaallyl Cation Featuring a Localized Phosphorus−Carbon Double Bond

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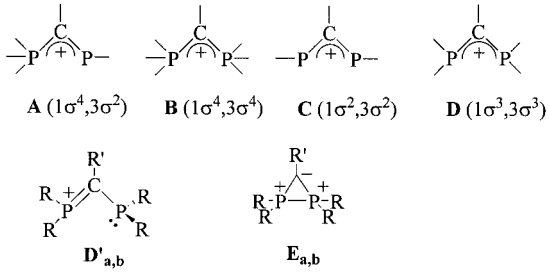
tert-Butyl thiol, 2,6-dimethylthiophenol, 2,6-dimethylphenol, and 2,6-bis(*tert*-butyl)-4-methylphenol cleanly add to the $1\sigma^4,3\sigma^2$-diphosphacumulene **1** to afford the corresponding *C*-phosphanyl phosphorus ylides **2a–d**. Treatment of **2a** with gallium trichloride quantitatively leads to the *C*-phosphonio phosphaalkene **3**, resulting from the1,3-migration of the sulfido group. Under the same experimental conditions, cleavage of the arylthio and aryloxy groups of **2b** and **2c** leading to the *C*-phosphonio phosphaalkene **4** is observed. In the case of the sterically most crowded derivative, **2d**, abstraction of the chloride ion affords the $1\sigma^3,3\sigma^3$-diphosphaallyl cation **5**, which is stable for several weeks in dichloromethane at –20 °C, but decomposes after a few minutes at above 0 °C. Compound **5** reacts at low temperatures with an excess of acetonitrile or benzaldehyde to afford quantitatively and regioselectively the corresponding five-membered heterocycles **6** and **7**. The NMR spectroscopy data and reactivity suggest that **5** features a localized double bond with a planar diamino-substituted phosphorus center, and a single bond with a pyramidalized (amino)(aryloxy)phosphanyl group.

Introduction

The stability of the 1,3-diphosphaallylic cations **A**−**D** is strongly dependent on the coordination number of the phosphorus atoms. Compounds **A**[1] and **B**,[2] featuring one or two σ^4-P atoms, have been isolated, whereas cations of type **C**[1a,3] and **D**,[4] which feature two σ^2-P and two σ^3-P atoms, respectively, have only been postulated as transient intermediates. Interestingly, derivatives **D** are the phosphorus analogues of the well-known and highly stable amidinium salts.[5] This striking difference between nitrogen and phosphorus chemistry lies in the superior ability of nitrogen to achieve a planar configuration and therefore to act as a π-donor.[6] In the case of diaminocarbocations, both amino substituents are involved in the stabilization of the positive charge, while calculations[6b−6d] predict that for **D** only one phosphorus atom acts as a π-donor, while the second one remains pyramidal. Therefore **D** is best described as (phosphanylmethylene)phosphonium ion **D′** that bears simultaneously a nucleophilic and an electrophilic center. This ambivalence underlines the synthetic potential of this species, but it also explains their apparent instability, especially with respect to ring-closure reactions. Indeed, a theoretical study by Schoeller[4] demonstrated that, depending on the nature of the phosphorus and carbon substituents, the energy-minimum structure could either be the open form **D** or the cyclic three-membered heterocycle valence isomer **E**. We have already reported the isolation of the cyclic isomer $\mathbf{E_b}$,[4] and here we report the synthesis and characterization of the first persistent $1\sigma^3,3\sigma^3$-diphosphaallyl cation of type **D**, as well as its reactivity towards dipolarophiles.



a: R = NH_2, R′ = SiH_3: $\varepsilon_{(D)} - \varepsilon_{(E)} = 5.8$ kcal·mol^{-1}
b: R = N(*i*Pr)$_2$, R′ = $SiMe_3$: $\varepsilon_{(D)} - \varepsilon_{(E)} = -6.1$ kcal·mol^{-1}

Results and Discussion

According to the theoretical study, a decrease of the steric hindrance should favor the open cation **D** over its cyclic isomer **E**. However, our previous experimental work[4b] demonstrated that in order to observe **D**, it is not

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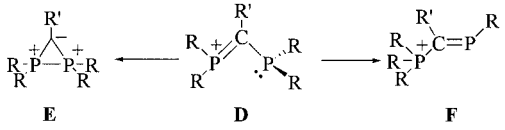
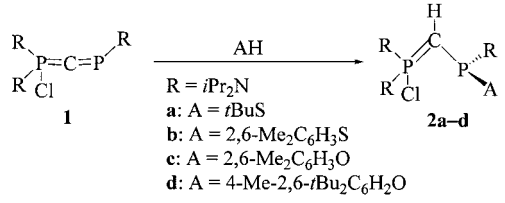
only necessary to avoid the ring closure to **E**, but also to prevent the 1,3-migration of a phosphorus substituent, which gives the far more stable phosphoniophosphaalkene isomer **F** (see Scheme 1). Since small substituents at phosphorus atoms favor the 1,3-migration process, we decided to keep bulky substituents on both phosphorus atoms and to decrease the size of the C substituent (R′); H was the best candidate.



E **D** **F**

Scheme 1

Abstraction of chloride from *P*-chloro phosphorus ylides is a known method to obtain the corresponding methylenephosphonium salts;[7] thus, *P*-chloro-*C*-phosphanyl phosphorus ylides **2** appeared to be potential precursors for the desired $1\sigma^3,3\sigma^3$-diphosphaallyl cation **D**. However, the classical routes to ylides are not applicable for the synthesis of **2a**−**d** and therefore we investigated several original approaches. We found that the recently discovered $1\sigma^4,3\sigma^2$-diphosphacumulene **1**[8] cleanly reacts with acidic compounds of type A−H to afford the desired ylides **2a**−**d** (see Scheme 2). Reactions take place at low temperatures except in the case of the very crowded 2,6-di-*tert*-butyl-4-methylphenol, which requires an additional hour at room temperature. All compounds were obtained as orange oils, and were unequivocally characterized by multinuclear NMR spectroscopy. In the ^{31}P NMR spectra, the addition of A−H resulted in the disappearance of the characteristic low-field signal for the σ^2-phosphorus atom of cumulene **1**, and ylides **2a**−**d** appeared as AX systems with a rather large phosphorus−phosphorus coupling constant ($^2J_{P,P} \approx$ 200 Hz). The PCP carbon atoms give doublet of doublets, with chemical shifts in the range δ = 30−50 ppm, as expected for ylides of this type.



1 **2a–d**

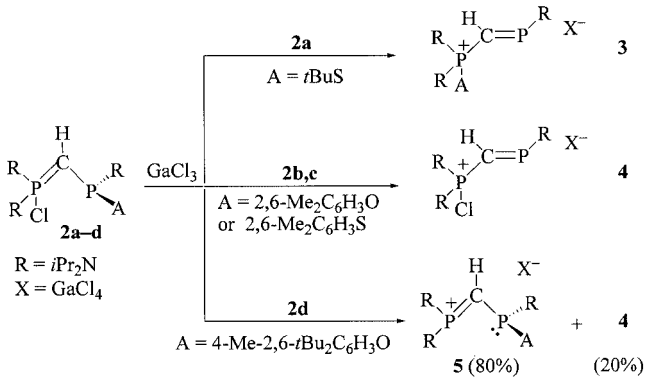
Scheme 2

Addition at −78 °C of 1 equiv. of gallium trichloride to the sterically least hindered ylide, **2a**, quantitatively afforded the (*E*)-*C*-phosphoniophosphaalkene **3**,[9] resulting from the 1,3-migration of the sulfido group. This compound displays an AX system at δ = 305 and 67 ppm ($^2J_{P,P}$ = 137 Hz), the low-field ^{31}P signal being characteristic of the phosphaalkene moiety. Therefore, it can be concluded that the steric demand of the *t*BuS group is not large enough and the σ^4,λ^4-phosphorus atom in **3** is able to accommodate two diisopropylamino and the alkylthio groups.

Taking this result into account, the *tert*-butylthio group was replaced by a larger 2,6-dimethylphenylthio substituent, and ylide **2b** was treated with 1 equiv. of $GaCl_3$ at low temperature. Here again, the expected diphosphaallyl cation was not observed. We obtained in near-quantitative yield the phosphonio phosphaalkene **4**,[9] resulting from the cleavage of the phenylthio group. The cation **4** (X = CF_3SO_3) can also be synthesized by simply adding at low temperature 1 equiv. of trifluoromethanesulfonic acid to a dichloromethane solution of **1** and therefore was unequivocally identified. In the same way, when ylide **2c**, featuring the 2,6-dimethylphenyloxy instead of the -phenylthio group, was treated with 1 equiv. of $GaCl_3$ at low temperature, the phosphonio phosphaalkene **4** was obtained in nearly quantitative yield.

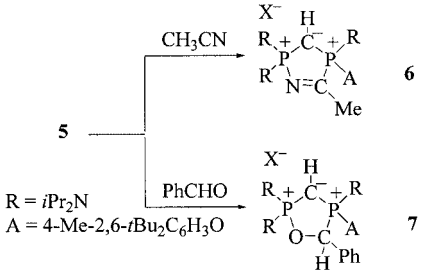
These results might be rationalized by the complexation of the oxygen and sulfur atom by the Lewis acid that enhances their leaving-group ability. In an attempt to protect these heteroatom centers and favor the abstraction of chloride, the steric hindrance at the *ortho* positions of the phenyloxy substituent was increased by using *tert*-butyl instead of methyl groups; 1 equiv. of $GaCl_3$ was added at low temperature to a dichloromethane solution of ylide **2d**. The formation of a mixture of **4** and a new compound **5** was observed in a 20:80 ratio. The ^{31}P NMR spectrum of **5** displays an AX system at δ = 134 and 122 ppm ($^2J_{P,P}$ = 134 Hz). These signals are by far at too low a field for a cyclic structure of type **E**, and at too high a field for the phosphaalkene structure of type **F**. In the ^{13}C NMR spectrum, a CH signal appears as a doublet of doublets at δ = 91.4 ppm ($^1J_{P,C}$ = 146 and 84 Hz) and in the ^{1}H NMR spectrum, the signal for the corresponding proton is also a doublet of doublets at δ = 5.58 ppm ($^2J_{PH}$ = 11 and 4 Hz), demonstrating that the PCHP sequence is preserved. ^{1}H and ^{13}C NMR spectra, obtained while selectively irradiating one phosphorus center, demonstrated that two diisopropylamino groups are linked to the phosphorus atom with signal at δ = 134 ppm, and one amino and the phenoxide group are linked to the phosphorus center with signal at δ = 122 ppm. Clearly, derivative **5** is the desired cation, featuring two σ^3-phosphorus centers. The ^{31}P NMR chemical shifts are in the range for a bis(diisopropylamino)(methylene)phosphonium salt[10] and an (alkyl)(amino)(phenyloxy)phosphane; therefore, as predicted by the calculations, this "$1\sigma^3,3\sigma^3$-diphosphaallylic cation" features a localized double bond involving the diamino-substituted phosphorus atom and a single bond. In other words, the molecule is probably highly unsymmetrical, the phenyloxy-substituted phosphorus atom remains pyramidal. Although **5** is stable in dichloromethane at −20 °C for several weeks, it decomposes above 0 °C after a few minutes, preventing its isolation and an X-ray diffraction study.

As transient $1\sigma^3,3\sigma^3$-diphosphaallylic cations are known to undergo 1,3-dipolar cycloaddition,[4b] we tested the reactivity of **5** with two different dipolarophiles. Compound **5** reacts at low temperature with an excess of acetonitrile or



Scheme 3

benzaldehyde to afford quantitatively and regioselectively the five-membered heterocycles **6** and **7**, respectively.[11] The observed regioselectivity reinforced the hypothesis of the diamino-substituted P center acting as the electrophilic part of the molecule. Indeed, it is quite likely that the reaction proceeds stepwise: complexation of the heteroatom of the dipolarophile to the planar phosphorus atom, followed by nucleophilic attack of the phosphane center at the activated carbon atom of the nitrile and aldehyde groups.



Scheme 4

Conclusion

$1\sigma^3,3\sigma^3$-diphosphaallylic cations are thermodynamically stable species but they are highly reactive. The presence of bulky substituents at both phosphorus centers is required in order to prevent 1,3-shift, and the presence of a small substituent on the carbon atom is necessary to favor the open form and to therefore prevent the ring closure that leads to the three-membered heterocyclic isomer. At least for nonsymmetrically substituted compounds, there is no delocalization of the π system. We are currently investigating the possibility of preparing symmetrical, isolable $1\sigma^3,3\sigma^3$-diphosphaallylic cations, by including such species in a cyclic system.

Experimental Section

General Remarks: All manipulations were performed under argon using standard Schlenk techniques. Dry, oxygen-free solvents, freshly distilled thiol, thiophenol and freshly sublimed phenols were employed. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded with 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.

Preparation of *P*-Chloro-*C*-Phosphanyl Phosphorus Ylides 2a−d: In a typical experiment, a toluene solution (0.6 mL) of 1 equiv. of thiol, thiophenol or phenols was added to a toluene solution (1 mL) of cumulene **1** (0.11 mmol) at −78 °C. The reaction was monitored by ^{31}P NMR spectroscopy. Ylides **2a−c** were readily obtained after the solution mixture was warmed to room temperature. In the case of the more crowded ylide **2d**, the reaction was complete after 1 h at room temperature. After removal of the solvent under vacuum, derivatives **2a−d** were obtained as orange oils. They are formed in nearly quantitative yields and are used without further purification.

2a: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 58.5 and 57.5 ($^2J_{P,P}$ = 200 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.20 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.23 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.31 (d, $^3J_{H,H}$ = 6 Hz, 12 H, CHCH_3), 1.36 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.39 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.60 (s, 9 H, SCCH_3), 2.6 (pseudo t, $^2J_{PH}$ = 6 Hz, 1 H, PCHP), 3.68 (m, 2 H, NCH), 3.80 (m, 2 H, NCH), 4.07 (m, 2 H, NCH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 23.0 (d, $J_{P,C}$ = 2 Hz, SCCH_3), 24.0 (d, $J_{P,C}$ = 3 Hz, CHCH_3), 24.2 (d, $J_{P,C}$ = 3 Hz, CHCH_3), 24.7 (d, $J_{P,C}$ = 3 Hz, CHCH_3), 33.9 (pseudo t, $J_{P,C}$ = 140 Hz, P*C*P), 44.4 (d, $J_{P,C}$ = 6 Hz, S*C*CH$_3$), 46.9 (br., NCH), 47.0 (br., NCH), 47.6 (br., NCH), 48.7 (br., NCH) ppm.

2b: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 79.0 and 62.0 ($^2J_{P,P}$ = 196 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.16 (d, $^3J_{H,H}$ = 5 Hz, 12 H, CHCH_3), 1.22 (d, $^3J_{H,H}$ = 4 Hz, 12 H, CHCH_3), 1.25 (d, $^3J_{H,H}$ = 5 Hz, CHCH_3), 12 H, 2.86 (s, 6 H, $C_{arom.}CH_3$), 3.22 (septd, $^3J_{H,H}$ = 4, $^3J_{PH}$ = 7 Hz, 2 H, NCH), 3.66 (septd, $^3J_{H,H}$ = 5, $^3J_{PH}$ = 7 Hz, 4 H, NCH), 6.9 (m, 3 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 22.7 (d, $J_{P,C}$ = 11 Hz, CHCH_3), 23.4 (s, $C_{arom.}CH_3$), 23.5 (m, CHCH_3), 23.9 (d, $J_{P,C}$ = 9 Hz, CHCH_3), 44.8 (dd, $J_{P,C}$ = 160 and 34 Hz, PCP), 48.2 (d, $J_{P,C}$ = 8 Hz, NCH), 48.4 (d, $J_{P,C}$ = 8 Hz, NCH), 45.9 (d, $J_{P,C}$ = 6 Hz, NCH), 126.2 (s, $C_{arom.}H$), 128.3 (d, $J_{P,C}$ = 5 Hz, $C_{arom.}H$), 143.3 (s, $C_{arom.}$), 144.0 (d, $J_{P,C}$ = 9 Hz, $C_{arom.}$) ppm.

2c: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 128 and 67 ($^2J_{P,P}$ = 187 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.05 (d, $^3J_{H,H}$ = 6 Hz, 6 H, CHCH_3), 1.16 (d, $^3J_{H,H}$ = 6 Hz, 12 H, CHCH_3), 1.18 (d, $^3J_{H,H}$ = 6 Hz, 6 H, CHCH_3), 1.33 (d, $^3J_{H,H}$ = 8 Hz, 6 H, CHCH_3), 1.54 (d, $^3J_{H,H}$ = 8 Hz, 6 H, CHCH_3), 2.27 (s, 6 H, $C_{arom.}CH_3$), 2.77 (dd, $^2J_{PH}$ = 3 and 4 Hz, 1 H, PCHP), 3.55 (septd, $^3J_{H,H}$ = 6, $^3J_{PH}$ = 16 Hz, 4 H, NCH), 3.65 (m, 2 H, NCH), 6.79 (t, $^2J_{H,H}$ = 10 Hz, 1 H, $H_{arom.}$), 6.94 (d, $^2J_{H,H}$ = 10 Hz, 2 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 16.8 (s, $C_{arom.}CH_3$), 22.9 (d, $J_{P,C}$ = 6 Hz, CHCH_3), 23.9 (d, $J_{P,C}$ = 6 Hz, CHCH_3), 24.6 (d, $J_{P,C}$ = 4 Hz, CHCH_3), 46.0 (d, $J_{P,C}$ = 11 Hz, NCH), 46.2 (dd, $J_{P,C}$ = 127 and 35 Hz, PCP), 48.0 (d, $J_{P,C}$ = 8 Hz, NCH), 48.6 (d, $J_{P,C}$ = 11 Hz, NCH), 121.7 (d, $J_{P,C}$ = 2 Hz, $C_{arom.}H$), 124.3 (s, $C_{arom.}$), 128.9 (d, $J_{P,C}$ < 1 Hz, $C_{arom.}H$), 131.9 (d, $J_{P,C}$ = 2 Hz, $C_{arom.}$) ppm.

2d: $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 140 and 68 ($^2J_{P,P}$ = 180 Hz) ppm. ^{1}H NMR (C_6D_6): δ = 1.11 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.17 (d, $^3J_{H,H}$ = 5 Hz, 6 H, CHCH_3), 1.19 (d, $^3J_{H,H}$ = 5 Hz, 6 H, CHCH_3), 1.37 (d, $^3J_{H,H}$ = 6 Hz, 12 H, CHCH_3), 1.46 (d, $^3J_{H,H}$ = 7 Hz, 6 H, CHCH_3), 1.74 (s, 18 H, CCH_3), 2.30 (s, 3 H, $C_{arom.}CH_3$), 3.65 (sept d, $^3J_{H,H}$ = 6, $^3J_{PH}$ = 16 Hz, 2 H, NCH), 3.79 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ = 16 Hz, 2 H, NCH), 4.02 (septd, $^3J_{H,H}$ = 5,

$^3J_{PH}$ = 12 Hz, 2 H, NCH), 7.11 (s, 2 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 21.3 (s, $C_{arom.}CH_3$), 23.9 (br., $CHCH_3$), 24.6 (d, $J_{P,C}$ = 6.3 Hz, $CHCH_3$), 25.1 (d, $J_{P,C}$ = 4.2 Hz, $CHCH_3$), 30.2 (s, CCH_3), 34.3 (s, CCH_3), 42.5 (dd, $J_{P,C}$ = 161 and 44 Hz, PCP), 47.3 (d, $J_{P,C}$ = 11.6 Hz, NCH), 48.0 (d, $J_{P,C}$ = 5.2 Hz, NCH), 48.3 (d, $J_{P,C}$ = 9.1 Hz, NCH), 48.4 (d, $J_{P,C}$ = 4 Hz, NCH), 125.8 (s, $C_{arom.}H$), 136 (s, $C_{arom.}$), 142 (d, $J_{P,C}$ = 2 Hz, $C_{arom.}$), 152 (d, $J_{P,C}$ = 40 Hz, $C_{arom.}$) ppm.

Abstraction of Chloride from Ylides 2a−d: In a typical experiment, a CH_2Cl_2 solution (0.8 mL) of ylide **2** (0.1 mmol) was added to a CH_2Cl_2 solution (0.3 mL) of 1 equiv. of $GaCl_3$ at −78 °C. The solution mixture was warmed to room temperature. The solvent was removed under vacuum and the residue was characterized without further purification. In the case of **5**, which is not stable above 0 °C, $CDCl_3$ was used as the solvent and the solution mixture was spectroscopically characterized at −40 °C.

3: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 305 and 67 ($^2J_{P,P}$ = 137 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.40 (d, $^3J_{H,H}$ = 7 Hz, 24 H, $CHCH_3$), 1.45 (d, $^3J_{H,H}$ = 6 Hz, 12 H, $CHCH_3$), 1.59 (d, $^3J_{H,H}$ = 1 Hz, 9 H, $SCCH_3$), 3.9 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ = 14 Hz, 4 H, NCH), 4.2 (br., 2 H, NCH), 6.0 (dd, $^2J_{PH}$ = 12 and 7 Hz, 1 H, PCHP) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 23.4 (d, $J_{P,C}$ = 2 Hz, $CHCH_3$), 24.6 (d, $J_{P,C}$ = 2 Hz, $CHCH_3$), 33.7 (d, $J_{P,C}$ = 6 Hz, $SCCH_3$), 49.6 (d, $J_{P,C}$ = 6 Hz, NCH), 50.2 (d, $J_{P,C}$ = 4 Hz, NCH), 56.7 (d, $J_{P,C}$ = 6 Hz, $SCCH_3$), 100.0 (dd, $J_{P,C}$ = 118 and 55 Hz, PCP) ppm.

4: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 309 and 60 ($^2J_{P,P}$ = 161 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.37 (d, $^3J_{H,H}$ = 7 Hz, 12 H, $CHCH_3$), 1.38 (d, $^3J_{H,H}$ = 6 Hz, 12 H, $CHCH_3$), 1.42 (d, $^3J_{H,H}$ = 7 Hz, 12 H, $CHCH_3$), 3.9 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ = 21 Hz, 4 H, NCH), 4.4 (m, 2 H, NCH), 6.4 (dd, $^2J_{PH}$ = 11 and 4 Hz, 1 H, PCHP) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 22.5 (d, $J_{P,C}$ = 12 Hz, $CHCH_3$), 26.6 (br., $CHCH_3$), 49.5 (d, $J_{P,C}$ = 4 Hz, NCH), 54 (d, $J_{P,C}$ = 13 Hz, NCH), 101 (dd, $J_{P,C}$ = 142 and 57 Hz, PCP) ppm.

5: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 233 K): δ_A = 134 and δ_B = 122 ($^2J_{P,P}$ = 134 Hz) ppm. ^1H NMR ($CDCl_3$, 233 K): δ = 1.19 (d, $^3J_{H,H}$ = 6 Hz, $CHCH_3$), 6 H, 1.22 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.28 (d, $^3J_{H,H}$ = 6 Hz, 12 H, $CHCH_3$), 1.39 (d, $^3J_{H,H}$ = 6 Hz, 12 H, $CHCH_3$), 1.45 (s, 18 H, CCH_3), 2.31 (s, 3 H, $C_{arom.}CH_3$), 3.41 (septd, $^3J_{H,H}$ = 6, $^3J_{PAH}$ = 7 Hz, 2 H, NCH), 3.94 (br., coupled with P_A, 2 H, NCH), 4.0 (br., coupled with P_B, 2 H, NCH), 5.58 (dd, $^2J_{PAH}$ = 11 Hz and $^2J_{PBH}$ = 4 Hz, 1 H, PCHP), 7.06 (s, 2 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 233 K): δ = 21.6 (s, $C_{arom.}CH_3$), 22.3 (br., coupled with P_A, $CHCH_3$), 23.3 (d, J_{PAC} = 4 Hz, $CHCH_3$), 24.5 (br., coupled with P_B, $CHCH_3$), 24.7 (br., coupled with P_A, $CHCH_3$), 30.6 (s, CCH_3), 31.8 (s, $C_{arom.}CCH_3$), 46 (br., NCH), 48 (br., NCH), 49 (br., NCH), 91.4 (dd, J_{PAC} = 146 Hz and J_{PBC} = 84 Hz, PCP), 125.9 (s, $C_{arom.}H$), 135.7 (s, $C_{arom.}$), 131.2 (d, J_{PBC} = 2 Hz, $C_{arom.}$), 148.4 (d, J_{PBC} = 10 Hz, $C_{arom.}$) ppm.

Five-Membered Heterocycles 6 and 7: A CH_2Cl_2 solution (0.8 mL) of ylide **2d** (0.1 mmol) was added to a CH_2Cl_2 solution (0.3 mL) of 1 equiv. of $GaCl_3$ at −78 °C. The formation of **5** was monitored by ^{31}P NMR spectroscopy at −40 °C. Then an excess of dried acetonitrile or benzaldehyde was added and the reaction mixture was warmed to room temperature. The solvent was removed under vacuum. The residue was washed with Et_2O and the resulting yellow powder was dried under vacuum.

6: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 63 and 55 (AB system, $^2J_{P,P}$ = 229 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 1.02 (dd, $^2J_{PH}$ = 9, 7 Hz, 1 H, PC*H*P), 1.22 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.29 (d, $^3J_{H,H}$ = 7 Hz, 12 H, $CHCH_3$), 1.39 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.43 (d, $^3J_{H,H}$ = 5 Hz, 6 H, $CHCH_3$), 1.43 (s, 18 H, CCH_3), 1.45 (d, $^3J_{H,H}$ = 5 Hz, 6 H, $CHCH_3$), 2.26 (s, 3 H, $C_{arom.}CH_3$), 2.82 (d, $^2J_{PH}$ = 6 Hz, 3 H, N=CCH_3), 3.37 (septd, $^3J_{H,H}$ = 5, $^3J_{P\tilde{H}}$ 1 Hz, 2 H, NCH), 3.70 (septd, $^3J_{H,H}$ = 7, $^3J_{P\tilde{H}}$ 1 Hz, 2 H, NCH), 3.90 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ = 15 Hz, 2 H, NCH), 6.97 (s, 2 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.8 (dd, $J_{P,C}$ = 163 and 167 Hz, PCP), 20.9 (s, $C_{arom.}CH_3$), 21.7 (d, $J_{P,C}$ = 5 Hz, $CHCH_3$), 22.8 (d, $J_{P,C}$ = 5 Hz, $CHCH_3$), 23.0 (d, $J_{P,C}$ = 5 Hz, $CHCH_3$), 23.3 (d, $J_{P,C}$ = 4 Hz, $CHCH_3$), 23.4 (d, $J_{P,C}$ = 6 Hz, $CHCH_3$), 29.7 (s, CCH_3), 30.3 (s, CCH_3), 48.1 (d, $J_{P,C}$ = 7 Hz, NCH), 48.6 (d, $J_{P,C}$ = 5 Hz, NCH), 49.6 (d, $J_{P,C}$ = 5 Hz, NCH), 125.5 (s, $C_{arom.}H$), 134.0 (s, $C_{arom.}$), 135.7 (s, $C_{arom.}$), 141.8 (d, $J_{P,C}$ = 9 Hz, $C_{arom.}$), 187 (d, $J_{P,C}$ = 64 Hz, C=N) ppm.

7: $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 72 and 66 (AB system, $^2J_{P,P}$ = 142 Hz) ppm. ^1H NMR ($CDCl_3$): δ = 0.76 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.10 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.23 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 1.40 (d, $^3J_{H,H}$ = 7 Hz, 12 H, $CHCH_3$), 1.43 (s, 18 H, CCH_3), 1.54 (d, $^3J_{H,H}$ = 7 Hz, 6 H, $CHCH_3$), 2.34 (s, 3 H, $C_{arom.}CH_3$), 3.26 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ < 1 Hz, 2 H, NCH), 3.88 (septd, $^3J_{H,H}$ = 7, $^3J_{PH}$ < 1 Hz, 4 H, NCH), 5.9 (dd, $^2J_{H,P}$ = 7, 9 Hz, 1 H, PCHO), 7.2 (m, 3 H, $H_{arom.}$), 7.53 (s, 2 H, $H_{arom.}$), 7.7 (m, 2 H, $H_{arom.}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 15.7 (dd, $J_{P,C}$ = 173 and 152 Hz, PCHP), 20.8 (s, $C_{arom.}CH_3$), 22.8 (br., $CHCH_3$), 23.2 (br., $CHCH_3$), 23.8 (d, $J_{P,C}$ = 5 Hz, $CHCH_3$), 25.6 (br., $CHCH_3$), 29.7 (s, CCH_3), 30.3 (s, CCH_3), 47.6 (d, $J_{P,C}$ = 7 Hz, N*C*H), 49.2 (d, $J_{P,C}$ = 5 Hz, N*C*H), 49.6 (d, $J_{P,C}$ = 5 Hz, NCH), 50.7 (d, $J_{P,C}$ = 5 Hz, NCH), 80.3 (dd, $J_{P,C}$ = 80 and 3 Hz, PCHO), 125.6 (s, $C_{arom.}H$), 128.6 (d, $J_{P,C}$ = 5 Hz, $C_{arom.}H$), 129.3 (d, $J_{P,C}$ = 1 Hz, $C_{arom.}H$), 133.0 (s, $C_{arom.}$), 134.0 (d, $J_{P,C}$ = 2 Hz, $C_{arom.}$), 135.2 (s, $C_{arom.}H$), 141.1 (d, $J_{P,C}$ = 5 Hz, $C_{arom.}$), 142.5 (s, $C_{arom.}$) ppm.

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[9] The (*E*) configuration of phosphaalkenes **3** and **4** was assigned by comparing the J_{PP} values with that observed in a similar compound[1b] which was crystallographically characterized.

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[11] Derivative **4** does not react with benzaldehyde and acetonitrile. The regiochemistry of products **6** and **7** was assigned by comparing the NMR spectroscopy data with that observed in similar compounds.[4b]

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