# The Inferior p-Donor Ability of Phosphanyl versus Amino Substituents: Consequences on the Stability and Reactivity of Phosphanyl- and Aminocarbenes

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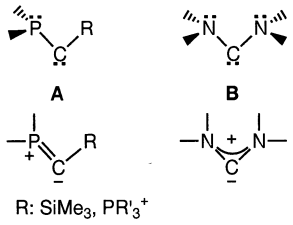
Bis(diisopropylamino)(trimethylstannyl)phosphane (**2**) reacts with the (chloromethylene)diisopropylammonium salt **1** affording the *C*-phosphanyl-substituted iminium salt **3** (67 % yield), which features a short C–N (1.284 Å) and a long P–C bond (1.850 Å), a planar iminium nitrogen atom and a pyramidalized phosphorus atom. Deprotonation of **3** leads to the enamine **8** (92 % yield), while addition of sodium methoxide followed by thermolysis of the resulting hemiaminal **9** (90 % yield) gives rise to the azaphosphetane **10** (85 % yield), by intramolecular CH insertion of the transiently formed (amino)(phosphanyl)carbene **6**.

## Introduction

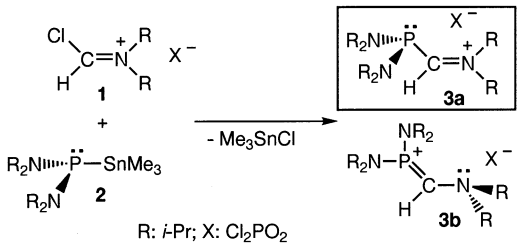
The genuine carbene nature of stable phosphanylcarbenes **A**[1] and diaminocarbenes **B**[2] is still a debatable topic.[3] Part of the debate relates to the role of the heteroatom substituents. Indeed, in the ground state, both **A** and **B** feature a heteroatom−carbon multiple-bond character.[4] In a recent paper, Schleyer et al[5] mentioned that "the *inherent* p donor capabilities of the heavier elements are as large as or larger than their second row counterparts" but add that "the superior ability of nitrogen compared to phosphorus to act as a p donor is due to the ease in achieving the optimum planar configurations with $sp^2$ hybridization". Here we report our preliminary results concerning the synthesis of an "(amino)(phosphanyl)carbenium salt",[6][7] and the generation of an (amino)(phosphanyl)carbene.




## Results and Discussion

The "[bis(diisopropylamino)phosphanyl](diisopropylamino)carbenium salt" **3** was obtained in 67% yield, along with chlorotrimethylstannane, on reaction of the (chloromethylene)ammonium salt **1**[8a] with the stannylphosphane **2**[9] (Scheme 1). Only one signal is observed in the $^1$H- and $^{13}$C-NMR spectra for the four CH groups of the amino substituents bonded to the phosphorus atom, while two signals are detected for the two CH groups of the amino group directly bonded to the carbon atom. Thus, in solution, derivative **3** has to be regarded as *C*-phosphanyl-substituted iminium salt **3a**. Single crystals of **3** suitable for an X-ray diffraction study were grown from a dichloromethane/ether solution at −20°C. The molecular structure of **3** along with pertinent geometric parameters are shown on Figure 1. The C(1) and N(1) atoms are planar (sum of the angles: 359.9 and 359.8°, respectively) while the phosphorus atom is strongly pyramidalized (sum of the angles: 308.48°). The C(1)−P (1.850 Å) and the C(1)−N(1) (1.284 Å) bond lengths are in the range expected for C−P single and C=N double bonds, respectively. Therefore, in solution and in the solid state, derivative **3** has to be regarded as *C*-phosphanyl-substituted iminium salt **3a**, and not as (*C*-aminomethylene)phosphonium salt **3b**,[10] clearly demonstrating the superior p donor ability of the nitrogen compared to the phosphorus atom toward carbenium centers.

Scheme 1




Recently, the bis(diisopropylamino)carbene **5** has been obtained by a reaction of the corresponding formamidinium chloride **4** with LDA.[8a] However, this synthetic method appeared inappropriate to generate the (amino)-

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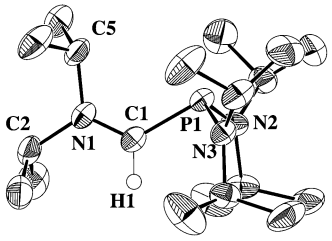
Figure 1. Molecular structure of **3**[a]




[a] Selected bond lengths [Å] and angles [°]: C(1)−N(1) 1.284(4), C(1)−P(1) 1.850(3), C(1)−H(1) 0.99(4); N(2)−P(1)−N(3) 113.90(12), N(3)−P(1)−C(1) 97.93(13), N(2)−P(1)−C(1) 96.65(13), N(1)−C(1)−P(1) 124.6(2), N(1)−C(1)−H(1) 115.6(2.2), P(1)−C(1)−H(1) 119.7(2.2), C(1)−N(1)−C(2) 121.3(3), C(1)−N(1)−C(5) 120.2(7), C(2)−N(1)−C(5) 118.3(7), N(1)−C(2)−C(3) 110.3(3), N(1)−C(2)−C(4) 110.3(3).

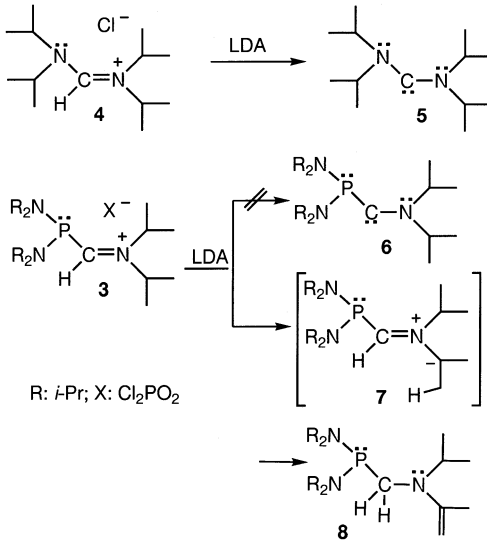
(phosphanyl)carbene **6**. Indeed, LDA reacts with **3**, but leads to the enamine **8** (92% yield), probably through the transient formation of the azomethine ylide **7**, followed by a prototropic rearrangement (Scheme 2).

In order to generate the (amino)(phosphanyl)carbene **6**, the synthetic method developed by Enders et al. was used.[11] Compound **3** was first treated with sodium methoxide affording the hemiaminal **9** in 90% yield, which was subsequently thermolyzed at 160°C under vacuum. Instead of the desired carbene **6**, the azaphosphetane **10** was obtained in 85% yield. The formation of heterocycle **10** clearly results from a regio- and stereoselective intramolecular insertion of the transient carbene **6** into a methine C−H bond of an isopropylamino group bonded to P. The same regio- and stereoselectivity have already been observed with the diphosphanylcarbene **11**.[12] Note that CH insertions are typical reactions for transient singlet carbenes, but have never been observed with diaminocarbenes[13] (Scheme 3).

## Conclusion

For cationic species, the experimental results reported here clearly corroborate the theory:[5] an amino substituent has a better p-donor ability than a phosphanyl substituent. For carbenes with comparable steric hindrance, it was already known that the diaminocarbenes are stable,[8b] while the diphosphanylcarbenes are only transient intermediates;[12] the (amino)(phosphanyl)carbenes seem also to be unstable. Therefore, from these results and those previously

Scheme 2




reported in the literature, it seems clear that the stabilization of singlet[14] carbenes can at least be achieved by two strong p-donor substituents *which can easily adopt a planar configuration*, and by the combination of a weak p donor with a p-acceptor substituent,[15] such as in **A**.

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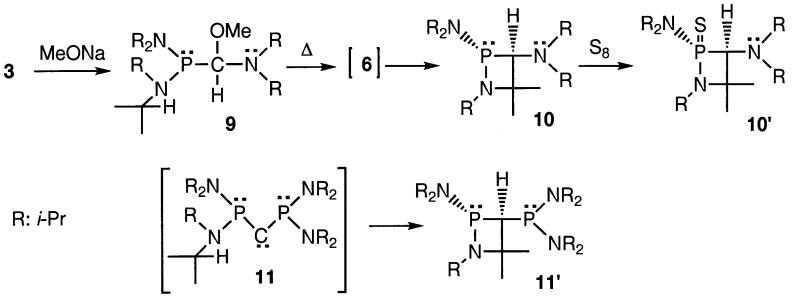
## Experimental Section

*General:* All experiments were performed under dry argon. Melting points are uncorrected. $^1$H-, $^{13}$C-, and $^{31}$P-NMR spectra were recorded with Brucker 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% $H_3PO_4$. Mass spectra were obtained with a Ribermag R10 10E instrument. Conventional glassware was used.

**3**: To a $CH_2Cl_2$ solution (5 ml) of (chloromethylene)ammonium salt **1** (0.28 g, 1 mmol) was added at −78°C one equivalent of [bis(diisopropylamino)]trimethylstannylphosphane (**2**) (0.39 g, 1 mmol). The solution was allowed to warm to room temperature (r.t.) and stirred for a further 30 min. After evaporation of the solvent under vacuum, the residue was dissolved in a minimum of $CH_2Cl_2$. Compound **3** was precipitated as a yellow solid (0.32 g, 67%) by adding $Et_2O$. M.p. 153°C. − $^{31}$P NMR (32 MHz, $CDCl_3$):

Scheme 3



δ = 32.3 ($N_2P$), −10.3 ($PO_2$). − $^1$H NMR (200 MHz, $CDCl_3$): δ = 9.78 (s, 1 H; CH), 5.22 [sept, $^3J$(H,H) = 6.6 Hz, 1 H, CNCH], 4.21 [sept d, $^3J$(H,H) = 6.7 Hz, $^4J$(P,H) = 2.3 Hz, 1 H, CNCH], 3.80 [sept d, $^3J$(H,H) = 6.6 Hz, $^3J$(P,H) = 5.9 Hz, 4 H, PNCH], 1.61 [d, $^3J$(H,H) = 6.6 Hz, 6 H, CNCHC$H_3$], 1.46 [d, $^3J$(H,H) = 6.7 Hz, 6 H, CNCHC$H_3$], 1.28 [d, $^3J$(H,H) = 6.6 Hz, 12 H, PNCHC$H_3$], 1.16 [d, $^3J$(H,H) = 6.6 Hz, 12 H, PNCHC$H_3$]. − $^{13}$C NMR (50 MHz, $CDCl_3$): δ = 183.6 [d, $^1J$(P,C) = 21.7 Hz, P-C], 59.6 [d, $^3J$(P,C) = 32.9 Hz, CN*C*H], 54.9 (s, CN*C*H), 49.0 [d, $^2J$(P,C) = 12.3 Hz, PNCH], 25.0 [d, $^3J$(P,C) = 6.2 Hz, PNC$CH_3$], 23.6 [d, $^3J$(P,C) = 6.6 Hz, PNC$CH_3$], 23.0 (s, CNC$CH_3$), 19.1 (s, CNC$CH_3$). − $C_{19}H_{43}Cl_2N_3O_2P_2$ (477.2): calcd. C 47.70, H 9.06, N 8.78; found C 47.41, H 9.50, N 8.57.

*Crystal-Structure Determination of* **3**: $C_{19}H_{43}Cl_2N_3O_2P_2$, $M$ = 478.40, monoclinic, $P2_1/c$, $a$ = 15.205(2) Å, $b$ = 10.3700(10) Å, $c$ = 17.201(3) Å, β = 90.91(2)°, $V$ = 2711.8(6) Å$^3$, $Z$ = 4, $\rho_c$ = 1.172 Mg m$^{-3}$, $F$(000) = 1032, λ = 0.71073 Å, $T$ = 173(2) K, μ(Mo-$K_\alpha$) = 0.375 mm$^{-1}$, crystal size 0.6 × 0.4 × 0.3 mm, 2.29° < θ < 23.26°, 17995 reflections (3686 independent, $R_{int}$ = 0.0425, completness 88.7%) were collected with a STOE-IPDS diffractometer. The structure was solved by direct methods (SHELXS-97)[16] and 381 parameters were refined with 191 restraints using the least-squares method on $F^2$.[17] Largest electron density residue: 0.635 e Å$^{-3}$, $R_1$ [for $F > 2\sigma(F)$] = 0.0432 and $wR_2$ = 0.1174 (all data) with $R_1 = \Sigma\, F_o - F_c / \Sigma\, F_o$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$. A disorder of the anion was refined anisotropically on two positions with the occupancy 0.85/0.15, and a disorder of the two isopropyl groups was also refined anisotropically on two positions with the occupancies 0.61/0.39 and 0.59/0.41 using ADP and distance restraints. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-101971. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

**8**: To a THF solution (5 ml) of the *C*-phosphanyl-substituted iminium salt **3** (0.48 g, 1 mmol) was added one equivalent of LDA (0.11 g, 1 mmol) in THF solution (4 ml) at −78°C. The reaction mixture was allowed to warm to r.t. and stirred for a further 30 min. After evaporation of the solvent in vacuo, the residue was extracted with pentane (10 ml). After filtration and evaporation of pentane, compound **8** was obtained as a yellow oil (0.31 g, 92%). − $^{31}$P NMR (32 MHz, $CDCl_3$): δ = 45.8. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 4.57 [d, $^5J$(P,H) = 2.4 Hz, 1 H, =$CH_2$], 4.55 [dd, $^2J$(P,H) = 0.8 Hz, $^5J$(P,H) = 0.8 Hz, 1 H, =$CH_2$], 3.71 [sept, $^3J$(H,H) = 6.7 Hz, 1 H, CNCH], 3.40 [sept d, $^3J$(H,H) = 6.6 Hz, $^3J$(P,H) = 10.2 Hz, 4 H, PNCH], 3.26 [d, $^2J$(P,H) = 10.3 Hz, 2 H, P$CH_2$], 1.94 [m, $^4J$(H,H) = 0.7 Hz, $^5J$(P,H) = 1.0 Hz, 3 H, $CH_3$C=], 1.34 [d, $^3J$(H,H) = 6.6 Hz, 12 H, PNCHC$H_3$], 1.31 [d, $^3J$(H,H) = 6.6 Hz, 12 H, PNCHC$H_3$], 1.17 [d, $^3J$(H,H) = 6.7 Hz, 6 H, NCHC$H_3$]. − $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 149.2 [d, $^3J$(P,C) = 2.6 Hz, >C=], 94.8 [d, $^4J$(P,C) = 13.5 Hz, =$CH_2$], 49.9 [d, $^3J$(P,C) = 5.1 Hz, CNCH], 47.6 [d, $^2J$(P,C) = 10.9 Hz, PNCH], 44.5 (s, P-$CH_2$), 25.4 [d, $^3J$(P,C) = 6.8 Hz, PNC$CH_3$], 24.7 [d, $^3J$(P,C) = 6.8 Hz, PNC$CH_3$], 23.0 (s, $CH_3$C=), 19.5 (s, NC$CH_3$). − MS ($NH_3$, CI); *m/z*: 344 [M + 1].

**9**: To a THF solution (15 ml) of the *C*-phosphanyl-substituted iminium salt **3** (0.48 g, 1 mmol) was added at r.t. one equivalent of MeONa (0.05 g, 1 mmol). The reaction mixture was stirred for 30 min. After evaporation of the solvent in vacuo, the residue was extracted with pentane (20 ml). After filtration and evaporation of the solvent, compound **9** was obtained as a yellow powder (0.34 g, 90%). M.p. 189−190°C. − $^{31}$P NMR (32 MHz, $CDCl_3$): δ = 60.6. − $^1$H NMR (250 MHz, $C_6D_6$): δ = 4.38 [d, $^2J$(P,H) = 3.5 Hz, 1 H, P-CH],3.56 (m, 6 H, NCH), 3.23 (s, 3 H, $OCH_3$), 1.24-1.11 (m, 36 H, $CH_3$). − $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 94.8 [d, $^1J$(P,C) = 7.5 Hz, P-CH], 54.7 (s, $OCH_3$), 48.5 [d, $^2J$(P,C) = 11.9 Hz, PNCH], 48.0 [d, $^2J$(P,C) = 8.8 Hz, PNCH], 45.3 [d, $^3J$(P,C) = 3.6 Hz, NCH], 24.6, 24.5, 24.4, 23.4 (s, $CH_3$). − $C_{20}H_{46}N_3OP$ (375.3): calcd C 63.96, H 12.34, N 11.19; found C 62.98, H 12.95, N 10.68.

**10**: 0.1 g (0.27 mmol) of neat hemiaminal **9** was heated at 160°C in vacuo. During this process, methanol was evolved and compound **10**, a yellow oil, was obtained as the distillate (0.09 g, 85%) and characterized by $^{31}$P-NMR spectroscopy (32 MHz, $C_6D_6$): δ = 111.3.

**10′**: A THF solution of **10** (0.08 g) was stirred for 3 h at r.t. with an excess of elemental sulfur. After filtration and evaporation of the solvent, **10′** (0.09 g, 95%) was isolated by column chromatography on silica gel (hexane/ether, 98:2, $R_F$ = 0.4). M.p. 79−80°C. − $^{31}$P NMR (162 MHz, $CDCl_3$): δ = 86.1. − $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.87 (m, 3 H, CHNP), 3.49 [sept, $^3J$(H,H) = 6.7 Hz, 2 H, CHNCP], 3.48 [d, $J$(P,H) = 20.3 Hz, 1 H, $CH_{ring}$], 1.43 (s, 3 H, $CH_{3ring}$), 1.40 [d, $^3J$(H,H) = 7.3 Hz, 6 H, C$H_3$CHNP], 1.38 [d, $^3J$(H,H) = 8.6 Hz, 6 H, C$H_3$CHNP], 1.36 [d, $^3J$(H,H) = 6.8 Hz, 3 H, C$H_3$CHNC], 1.25 [d, $J$(P,H) = 1.1 Hz, 3 H, $CH_{3ring}$], 1.21 [d, $^3J$(H,H) = 6.4 Hz, 3 H, C$H_3$CHN], 1.10 [d, $^3J$(H,H) = 6.4 Hz, 6 H, C$H_3$CHNC], 1.01 [d, $^3J$(H,H) = 6.4 Hz, 6 H, C$H_3$CHNC]. − $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 70.7 [d, $J$(P,C) = 62.9 Hz, $CH_{ring}$], 62.7 [d, $J$(P,C) = 19.3 Hz, $C_{ring}$], 46.9 [d, $^2J$(P,C) = 1.0 Hz, PNCH], 45.8 (s broad, PNCH), 45.1 (s, NCH), 31.1 [d, $J$(P,C) = 27.6 Hz, $CH_3$], 24.3 [d, $J$(P,C) = 6.5 Hz, *C*$H_3$CHNP], 23.9 (s, *C*$H_3$CHN), 23.7 [d, $J$(P,C) = 2.9 Hz, *C*$H_3$CHNP], 23.4 (s, *C*$H_3$CHN), 23.2 [d, $J$(P,C) = 5.5 Hz, *C*$H_3$CHN], 21.6 (s, *C*$H_3$CHN). − $C_{19}H_{42}N_3PS$ (375.3): calcd. C 60.76, H 11.27, N 11.19; found C 60.32, H 10.94, N 10.62. − The relative configuration of the chiral phosphorus and carbon atoms has been established by comparison of the NMR data of **10′** with those of the thioxo derivative **11′**.[12]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