

Charged Phosphiranes

Synthesis, Structure, and Reactivity of a Stabilized Phosphiranylium Salt**

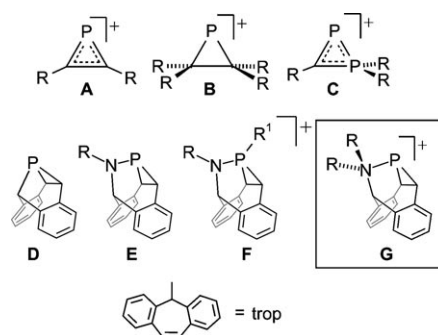
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In memory of Pascal Le Floch

Phosphiranes with a three-membered PC₂ ring have unique electronic properties.^[1] Although their ring strain is smaller than that in cyclopropanes, they are highly reactive and display remarkable chemistry, such as [2+1] cycloreversions to olefins and phosphinidenes [R–P],^[2] cationic ring-opening polymerization to poly(ethylenephosphine),^[3] and special properties as ligands in transition-metal complexes for catalysis.^[4] Positively charged species are even more reactive. Species such as **A** (phosphirenylium ion) or **B** (phosphiranylium ion), which may be viewed as π -complexes of P⁺ to alkynes or alkenes,^[5] respectively (Scheme 1), have never been isolated.^[6] A notable exception is the crystalline diphosphirenium ion **C**.^[7]

The dibenzo[*a,d*]cycloheptatrienyl (trop) platform was used for the synthesis of the highly strained dibenzophosphasemibullvalene **D**,^[8] very robust aminophosphiranes (BABAR-Phos) **E**,^[9] and the phosphiranium ion **F** (R = *i*Pr, R¹ = *t*Bu; Scheme 1).^[10] Isolated examples of the latter are likewise rare.^[11]

Because the lone pair at phosphorus has a very high *s*-orbital character,^[10] phosphiranes are generally reluctant to be alkylated, oxygenated, or sulfurated, and with bulky substituents R in **E** these reactions are suppressed. However,

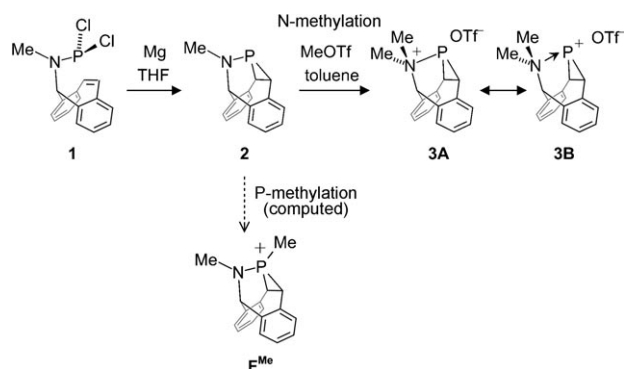


Scheme 1. Cationic three-membered phosphorus heterocycles (**A–C**) and BABAR-Phos derivatives **D–G**.

transition-metal ions (Pt^{II}, Rh^I) bind to the phosphorus center, albeit very weakly.^[4b]

We now report on the synthesis of a sterically unshielded BABAR-Phos derivative that reacts with methyl triflate, a “hard” alkylation reagent, at the “hard” nitrogen center, to give the cation **G**, which can be described as an intramolecular amine complex of the elusive phosphiranylium ion **B**.

The synthesis of the ^{Me}BABAR-Phos **2** is straightforward, as is shown in Scheme 2 (see the Supporting Information for details). As previously reported,^[4a] the reduction of the amino(dichloro)trop phosphane **1** with magnesium turnings (room temperature, 3 h) results in the rather clean formation of ^{Me}BABAR-Phos **2** (73 %; $\delta_{31\text{P}} = -149.0$ ppm) as a result of the spatial proximity of the PCl₂ unit and the olefin. The characteristic low-frequency shifts of the ¹H and ¹³C resonances of the HCCH_{trop} unit and the *J*(H,P) and *J*(C,P) couplings in **2** ($\delta_{\text{H}} = 2.55$ ppm (²*J*(H,P) = 18.3 Hz); $\delta_{13\text{C}} =$



Scheme 2. Synthesis of **2** and **3**.

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24.1 ppm ($^1J(\text{C,P}) = 41.7$ Hz)) clearly indicate its formation (vs. $\delta_{\text{H}} = 6.83$ ppm and $\delta_{\text{C}} = 130.9$ ppm in **1**).

Reaction of $^{\text{Me}}\text{BABAR-Phos}$ **2** with methyl triflate in toluene (room temperature, 2 h) resulted exclusively in N-alkylation (91 %; $\delta_{\text{31P}} = -83.6$ ppm; Scheme 2). The structure of the novel salt **3** was established by X-ray crystal structure determination (Figure 1)^[12] and displays a remarkable long P–N bond (1.845(1) Å) compared with that in the neutral analogues **E** (1.73–1.74 Å)^[4a,13] and phosphiranium ion **F** (1.628(4) Å).^[10]

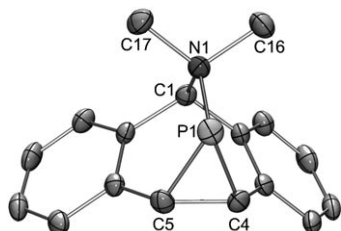


Figure 1. Displacement ellipsoid plot (50% probability) of **3**. The OTf[−] anion is omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 1.8449(14), P1–C4 1.8532(18), P1–C5 1.8593(17), N1–C1 1.541(2), N1–C16 1.509(2), N1–C17 1.510(2), C4–C5 1.523(2); N1–P1–C4 97.68(7), N1–P1–C5 97.95(7), C5–P1–C4 48.44(7); $\Sigma(\text{P})$: 244.1°.

DFT calculations at the B3PW91/6-311 + G(d,p) level of theory were performed to understand and compare the electronic structure and reactivity of **2**, **3**, and the non-observed P-methylated product **F^{Me}**.^[14] The HOMO of **2** (−5.81 eV) is mainly located on the nitrogen atom, while the HOMO−1 (−6.35 eV; Figure 2) can be attributed to the “lone pair” located on the phosphorus atom. This finding is in accord with the preferred alkylation at nitrogen. Further, the N-alkylated cation **3** is 9.5 kcal mol^{−1} more stable than the computed P-alkylated derivative **F^{Me}**.

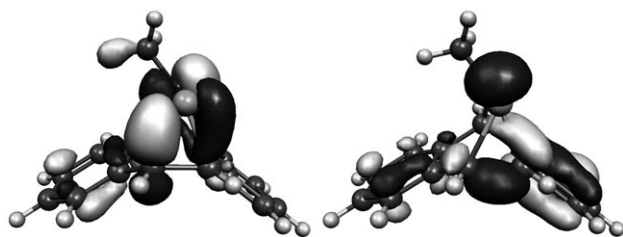


Figure 2. HOMO (left) and HOMO−1 (right) of $^{\text{Me}}\text{BABAR-Phos}$ **2**.

The nature of the P–N bond was studied by analyzing the electron density by using the theory of atoms in molecules (AIM)^[15] to investigate the relative weight of the resonance structures **3A** (ammonium salt with the positive charge on N) and **3B** (intramolecular amino-stabilized phosphiranium cation with the positive charge localized on the PC₂ ring; Scheme 2).^[5e] The atomic charges of the basins for nitrogen Q(N) and phosphorus Q(P) of **2**, **3**, and **F^{Me}** are given in Table 1. As expected, the positive charge at the P atom in phosphonium-type ion **F^{Me}** is the highest (+2.47 *e*). With

Table 1: Characterization of the P–N bond with AIM.^[a]

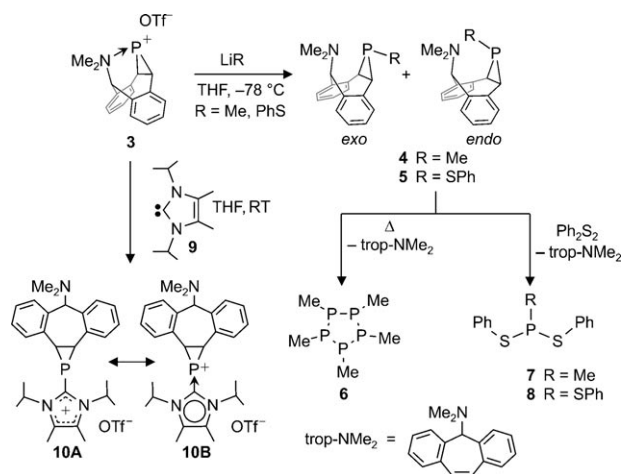
	P–N Bond Length	$H(r_c)^{[b]}$	Q(P)	Q(N)
2	1.727 Å	−0.912	1.34	−1.33
3	1.885 Å	−0.670	1.09	−1.11
F^{Me}	1.660 Å	−1.102	2.47	−1.41

[a] The B3PW91/6-311 + G(d,p) calculated structures were used; [b] the bond critical point r_c corresponds to a saddle point of the electron density in the bonding region.

respect to **2**, N-methylation diminishes both the negative charge at N and the positive charge on P. That is, **3** contains the longest, weakest, and least-polar P–N bond ($\Delta Q(\text{N,P}) = 2.20 e$ [vs. 2.67 *e* (**2**) and 3.88 *e* (**F^{Me}**)].

From the obtained energy densities ($H(r_c)$; Table 1), it can be derived that the P–N bond in **2** and **F^{Me}** has a strong covalent character.^[16] However, the decreased energy density ($H(r_c) = -0.670$ hartree Å^{−3}) of the P–N bond in **3** indicates a significant contribution of resonance structure **3B** to the electronic ground state of **3**, which may be viewed as an intramolecular donor–acceptor N→P complex^[17] of an amino-stabilized phosphiranylium ion (**B**).

The reactivity of the amino phosphiranylium salt **3** was investigated as well. Addition of methyl lithium at −78 °C resulted in P-alkylation under breaking of the P–N bond yielding the P-methyl phosphiranes *endo*-**4** ($\delta_{\text{31P}} = -173.3$ ppm) and *exo*-**4** ($\delta_{\text{31P}} = -205.7$ ppm; 4:1 ratio; Scheme 3) quantitatively.^[18] The reaction of **3** with thiolate [Li(SPh)] gives exclusively the sterically less encumbered isomer *exo*-**5** ($\delta_{\text{31P}} = -132.8$ ppm), which is stable in solution and in the solid state.



Scheme 3. Reactivity of the amino phosphiranylium salt **3**.

Solutions of **4** can be stored at −18 °C for days, but within 24 h at room temperature clean fragmentation to the cyclic phosphinidene oligomer (PMe)₅ (**6**; Scheme 3)^[19] and (5-*H*-dibenzo[*a,d*]cyclohepten-5-yl)-dimethylamine (trop-NMe₂) occurs. Addition of diphenyldisulfide to a freshly prepared solution of the phosphiranes **4** or **5** resulted in the quantitative formation of the phosphonodithious acids **7** ($\delta_{\text{31P}} = 85.2$ ppm)^[20] and **8** ($\delta_{\text{31P}} = 130.8$ ppm),^[21] respectively

(Scheme 3). Formally, these reactions correspond to the expulsion of a phosphinidene $[R-P]$,^[22] but at this stage of our investigations, we assume a $[R-P]$ transfer process without the intermediacy of free phosphinidenes as our calculations predict that this process costs approximately 50 kcal mol⁻¹.

Interestingly, **3** also reacts with neutral nucleophiles such as N-heterocyclic carbenes (NHCs; Scheme 3). Namely, addition of $LiPr_2Me_2$ **9** resulted in the NHC-stabilized phosphiranylium cation **10** ($\delta_{31P} = -214.3$ ppm).^[23,24]

The molecular structure of **10**, established by X-ray crystal structure analysis (Figure 3),^[12] may be viewed as an olefin carbene P^I cation. The sum of bond angles at the phosphorus

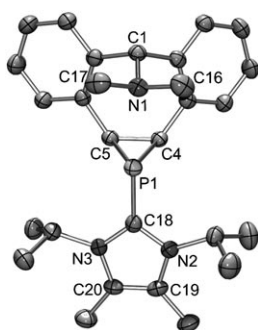


Figure 3. Displacement ellipsoid plot (50% probability) of **10**. Only one of two independent molecules is shown. The OTf⁻ anion and ordered/disordered THF solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–N1 2.581(2), P1–C4 1.908(3), P1–C5 1.896(2), P1–C18 1.881(3), N1–C1 1.478(3), N1–C16 1.467(3), N1–C17 1.466(3), N2–C18 1.350(3), N2–C19 1.384(3), N3–C18 1.351(3), N3–C20 1.391(3), C4–C5 1.500(3), C19–C20 1.354(4); C4–P1–C5 46.43(11), C4–P1–C18 95.32(11), C5–P1–C18 96.22(11), C5–C4–P1 66.36(13), C4–C5–P1 67.21(13), N2–C18–N3 106.8(2); $\Sigma(P)$: 238.0°.

center ($\Sigma(P)$: 238.0°) is small (cf. 244.1° for **3**) despite the sterically demanding substituents. The strength of the P–C_{carbene} interaction in **10** (P1–C18 1.881(3) Å) was investigated with a bond decomposition scheme (ADF on model system **10'** with H for all NHC substituents).^[25] Strong σ -donation of the lone pair of the C center of the carbene to the empty p orbital at the phosphorus atom makes up for 91% (–130 kcal mol⁻¹) of the orbital interaction energy (E^{oi}) to which a small contribution from π -back-donation of the phosphorus lone pair into the empty π^* orbital of the carbene is added (–13 kcal mol⁻¹, 9% of E^{oi}). In contrast, in Macdonald's bis(carbene) P^I cation $[P(LiPr_2Me_2)_2]^+$,^[26] the contribution of the π -back-donation to the interaction energy is significantly higher (–27 kcal mol⁻¹; 13%).^[24] This is reflected in the P–C bond dissociation energies (BDEs), which are much smaller in **10'** (–54.9 kcal mol⁻¹) than in $[P(NHC)_2]^+$ (–105.6 kcal mol⁻¹). Interestingly, the low energy density at the bond critical point of the P–C_{carbene} bond in **10** ($H(r_c) = -0.763$ hartree Å⁻³) is comparable to that of the P–N bond in **3**, which underlines the contribution of resonance structure **10B** (Scheme 3) to the electronic ground state of **10**.

In conclusion, our computational and experimental results indicate that $[N,N$ -dimethyl-BABAR-Phos]OTf **3** and $[(Me_2N-trop)P(LiPr_2Me_2)]OTf$ **10** may be regarded as the first isolated examples of intra- and intermolecular amino- or carbene-stabilized phosphiranylium salts, respectively.

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