Phosphorus Cage Compounds

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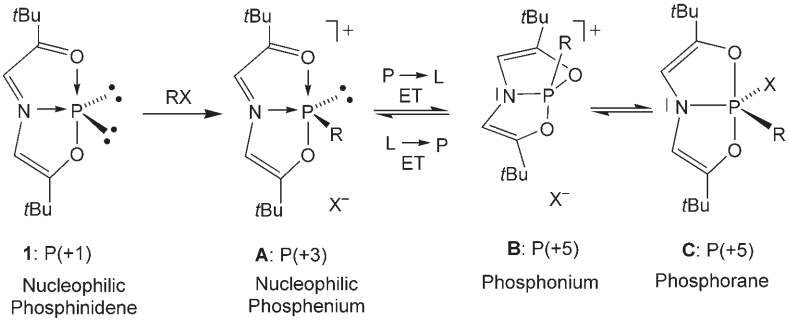
Formation of a Bowl-Shaped, Pentacyclic Phosphonium Cage by Methylation of a Nucleophilic Phosphinidene

Matthias Driess, Nicoleta Muresan, Klaus Merz, and Michael Päch*

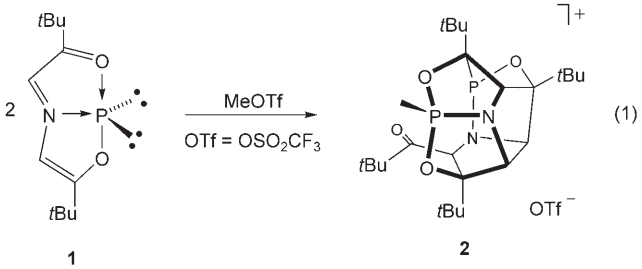
Dedicated to Professor Gottfried Huttner on the occasion of his 68th birthday

Phosphinidenes, that is, carbene-analogous compounds of monovalent phosphorus (phosphanylidenes, R–P) represent a simple class of valuable electrophilic building blocks in organophosphorus chemistry, which are usually highly reactive transients and therefore difficult to isolate.[1] However, one simple chemical trick that aids the preparation of a room-temperature stable phosphinidene is the intra- or intermolecular addition of a donor group D to the initially electron-deficient phosphorus atom (D→PR); this affords an electron-rich (nucleophilic) phosphinidene, having eight or more valence electrons at the phosphorus center. Several types of donor-stabilized phosphinidenes have already been isolated and used as versatile precursors for the preparation of "free" phosphinidenes such as phospha-Wittig reagents ($R_3P=PR'$)[2] and related phosphinidene metal complexes ($L_nM=PR$).[3] The intramolecular donor-stabilization of a P(+1) atom is also the reason for the intriguing stability of the nucleophilic phosphinidene **1** (Scheme 1), which has a planar, T-shaped three-coordinate phosphorus atom with 10 valence electrons (10-P-3 system).[4] Although **1** is a promising versatile building block for the synthesis of novel electronically tunable organophosphorus ligands, its reactivity has only been sparingly investigated.[5] The relatively high nucleophilicity at the P atom prompted us to investigate whether alkylation of phosphorus with classical alkylation reagents RX (R = alkyl; X = anionic leaving group) leads to a nucleophilic phosphenium salt **A**, phosphonium species **B**, or neutral phosphorane **C** as possible valence isomers, depending on the electronic nature and steric demand of R and X, respectively (Scheme 1).

Here we report the surprising formation of the unusual phosphonium cage cation in **2**, which results from a domino cyclization of two molecules of **1** in the presence of methyl trifluoromethylsulfonate (MeOTf). When a solution of MeOTf in CH_2Cl_2 was added to a solution of **1** in CH_2Cl_2 in the molar ratio of 1:1 at 20 °C, a rapid reaction occurs (^{31}P NMR monitoring), affording the unexpected phosphonium salt **2** [Eq. (1)]. The latter is insoluble in hydrocarbon solvents and other nonpolar solvents and can be isolated in



Scheme 1. The possible valence isomers **A**, **B**, and **C** formed by alkylation of **1** with RX (R = alkyl, X = anionic leaving group; ET = electron transfer.



(1)

the form of a colorless solid in 35% yield. The yield can be increased up to 78% by changing the molar ratio of the starting materials MeOTf and **1** to 1:2. Interestingly, compound **2** results also exclusively even if a solution of **1** in CH_2Cl_2 is slowly added to a very large molar excess or even by using neat MeOTf at room temperature or below (–10 °C).

The composition and constitution of **2** was established by EI-FAB and ESI (electrospray ionization) mass spectrometry

[*] Prof. Dr. M. Driess, Dr. N. Muresan, Dr. M. Päch
Institute of Chemistry: Metalorganics and Inorganic Materials
Technical University of Berlin
Strasse des 17. Juni 135, Sekr. C2, 10623 Berlin (Germany)
Fax: (+49) 303-142-2168
E-mail: matthias.driess@tu-berlin.de
Dr. K. Merz
Fakultät für Chemie der Ruhr-Universität Bochum
Universitätsstrasse 150, 44801 Bochum (Germany)

(m/z 497), correct combustion analyses (C,H,N,P), and NMR spectroscopy (^{1}H, ^{13}C, ^{31}P). The ^{31}P NMR spectrum of **2** in CD_2Cl_2 shows two multiplets at $\delta = 107.4$ and 112.8 ppm without scalar ^{31}P–^{31}P coupling. Since the connectivity of **2** was difficult to interpret based exclusively on the NMR spectra, its structure was unequivocally established by an single-crystal X-ray diffraction analysis (Figure 1).[6] The latter revealed that **2** is an ion pair that consists of a bowl-shaped phosphonium cage with a λ^3-pyramidal and a λ^4-tetrahedral coordinate phosphorus atom, and a "non-coordinating" triflate anion.

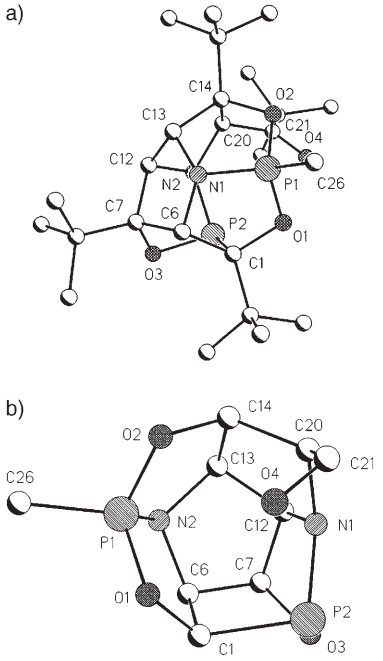
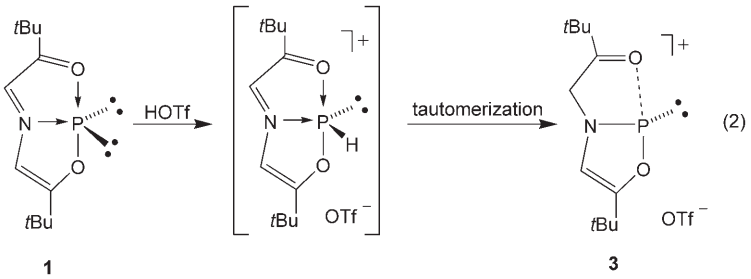


Figure 1. a) Molecular structure of the cation in **2**; b) core of the cage in **2**, including the terminal methyl carbon atom (C26) at the *phosphonium* P atom; hydrogen atoms are omitted for clarity. Selected distances [pm] and angles [°]: P1–O1 155.3(4), P1–O2 156.1(4), P1–N2 164.0(5), P1–C26 175.8(6), P2–O3 165.1(5), P2–N1 171.7(5), P2–C1 191.2(5); O2-P1-O1 117.0(2), O2-P1-C26 106.8(3), N2-P1-C26 121.8(3), O3-P2-N1 89.5(2), C20-N1-C12 106.6(4), C20-N1-P2 132.4(4), C12-N1-P2 111.1(3), C13-N2-C6 110.6(4), C13-N2-P1 108.6(3), C6-N2-P1 108.7(3).

The pentacyclic cation consists of a $C_7O_3N_2P_2$ skeleton with "globular-fused" five-membered rings. The core of the cation can be simply described as a cycloadduct of two molecules of **1**. The P–O and P–N distances are shorter than those in **1** but similar to the values for related *phosphane*-P–O and -P–N systems[7] and corresponding *phosphonium*-P–O[8] and -P–N systems,[9] respectively. The terminal P1–C26 distance of the *phosphonium*-P atom (175.8(6) pm) is significantly shorter than the other P–C distances within the cation core and in other phosphonium cations with P–CH_3 bonds.[10] This is probably due to the relatively high positive partial charge at the phosphorus center and the resulting σ-bond polarity of the P1–C26 bond. Because of the steric congestion around the N1 atom, it adopts an almost trigonal-planar configuration (sum of bond angles $\Sigma = 350.2°$); this is in contrast to the coordination geometry around the N2 atom which displays a less distorted pyramidal configuration ($\Sigma = 328°$). The structural parameters have been consistently reproduced by density functional theory (DFT) calculations[11] on the model cation **2′**, in which the *t*Bu groups were replaced by Me groups: The values for the distances and angles differ by less than 3 pm and 2°, respectively. The formation of **2** is in strong contrast to the result of the related protonation of **1** with HOTf, which, surprisingly, leads to the nucleophilic phosphenium ion in **3** as the sole product [Eq. (2)].[12] Since the molecular structure of the cation in **3**



was hitherto unknown, we carried out a single-crystal X-ray diffraction analysis (Figure 2).[6] The phosphenium cation consists of a planar, five-membered C_2NOP ring, which has close structural and electronic similarities to other related cyclic phosphenium ions.[13]

The P1–N1 distance of 165.1(3) pm is slightly longer than that in the acyclic phosphenium ion $[P(NiPr_2)_2]^+$ (161.3(4) pm)[14] but similar to the values in related cyclic phosphenium ions.[13] The relatively long P–O distances of 282

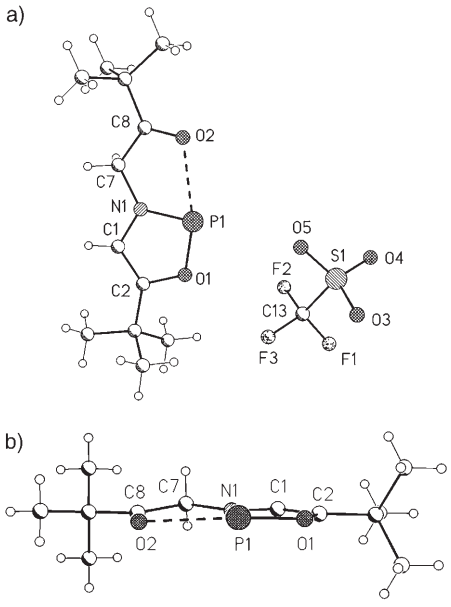
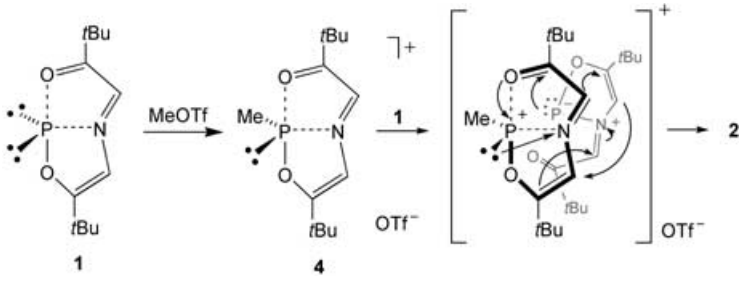


Figure 2. a) Molecular structure of **3**; b) side view of the cation in **3**. Selected distances [pm] and angles [°]: P1–O1 163.1(3), P1–N1 165.1(3), O1–C2 137.7(4), N1–C1 139.2(5), N1–C7 146.5(4), O2–C8 122.4(4), C7–C8 149.0(5), C1–C2 134.3(5), P1–O2 250.1(1); O1-P1-N1 90.65(1), O1-P1-O2 165.2(2), C2-O1-P1 115.0(2), C1-N1-C1 118.9(3, C1-N1-P1 112.4(2), C7-N1-P1 128.6(2).

and 285 pm of two oxygen atoms of neighboring OTf groups reflect the very weak donor–acceptor interactions between the phosphorus atom and the counterion. Thus, it is peculiar that the low-coordinate P atom is only weakly stabilized by intramolecular coordination of the carbonyl oxygen atom as indicated by the relatively long O2–P1 distance of 250.1(1) pm. Surprisingly, the carbonyl oxygen atom approaches the P atom in the ONP plane and not perpendicular to it, as usually observed for other donor adducts of phosphenium ions.[13] This is confirmed by DFT calculations of the respective model compound **3C**, which show that instead of the vacant p_z orbital at the phosphorus center, the P1–O1 σ* orbital serves as the acceptor orbital.[11] The respective geometry optimizations of the corresponding isomers **3A**–**3C** clearly confirm the preference for **3C** by 10.6 (**3A**) and 37.5 kcal mol^{-1} (**3B**) (Figure 3). The nature of the phosphorus atoms in **3A** and **3B** should be quite different: While **3A** possesses a P(+3) atom with a lone pair of electrons and the atom is coordinated by a monobasic, tridentate ketoimino-enolate, **3B** has a P(+5) atom of the "classical" phosphonium type, coordinated by a tribasic, tridentate bis(enolate)amido ligand. How can one explain the formation of the cation in **2**? Apparently, the reaction implies a remarkable domino-cycloaddition reaction between the hitherto unknown P-methylated cationic species **4** and **1**, which involves the formation of one new P–C and three additional C–C bonds. However, the structural analogue of **3c**, that is, the donor-stabilized phosphenium ion **4c** (see Figure 3), can be excluded as the key intermediate for the formation of **2**. Since no intermediate could be observed, we performed DFT calculations[11] of the respective model systems **4A**, **4B**, and **4C**



Scheme 2. Proposed domino-cyclization for the formation of **2**.

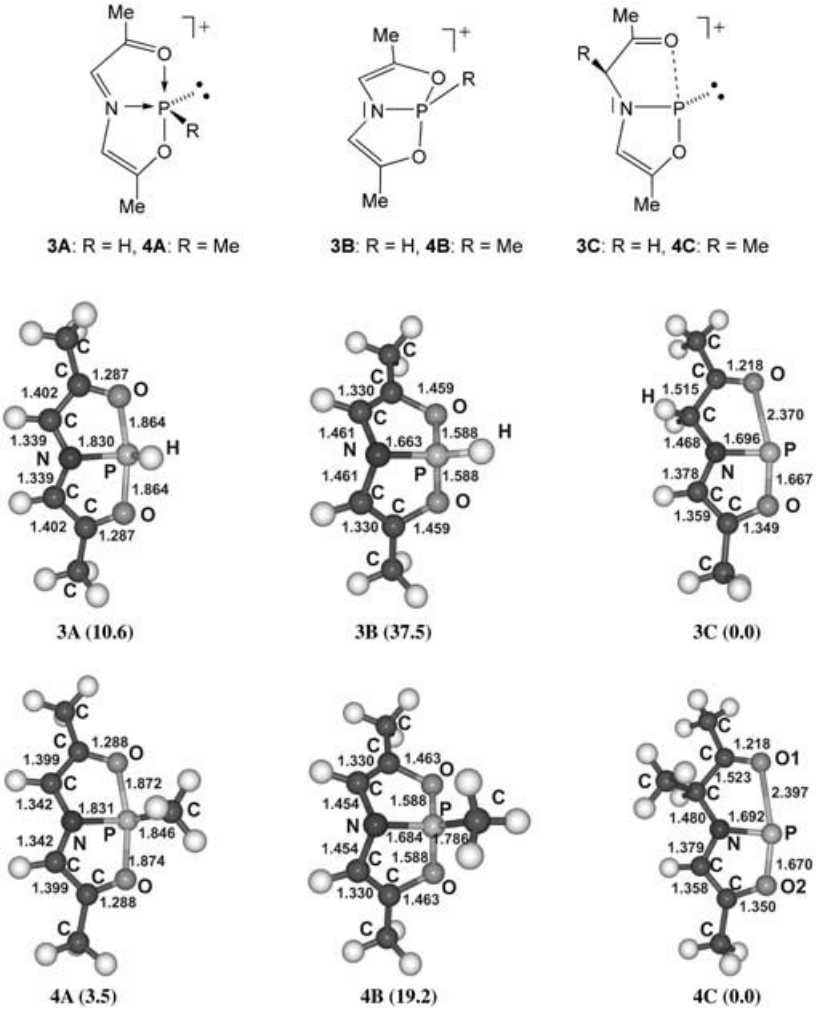


Figure 3. B3LYP/6-311+G(d)-optimized structures of **3A**–**3C** and **4A**–**4C**.[11] Relative energies in parentheses [kcal mol^{-1}]; distances in Å.

(Me groups instead of *t*Bu groups in **4**) to learn whether the phosphenium cation **4A** or the symmetric phosphonium valence isomer **4B** is the preferred initial product of the oxidative addition of a methyl cation. Interestingly, the geometry optimizations revealed that even in the series **4A**–**4C**, the O→P stabilized phosphenium analogue **4C** (O→P distance 237.0 pm) is slightly favored over **4A** by 3.5 kcal mol^{-1} but is 19.2 kcal mol^{-1} lower in energy than **4B** (ΔE (**4B**–**4A**) = 15.7 kcal mol^{-1}). DFT calculations of the possible experimental systems **4** (**A**-type and **C**-type with *t*Bu groups) at a lower level of theory (BLYP/6-31G*) revealed that the **A**-type is now slightly favored over the **C**-type by about 2 kcal mol^{-1} due to steric hindrance.[11] Accordingly, the formation of the unexpected phosphonium cage cation in **2** as the sole "self-trapping" product during the methylation of **1** clearly suggests the preferred population of the **4A**-type compound as the reactive intermediate. Since the latter phosphenium cation possesses a highly electrophilic backbone, it gets easily attacked by the electron-rich phosphinidene **1**, which initiates the tandem-cyclization (Scheme 2).

Further investigations in the presence of other competing trapping reagents are currently underway to explore the use of the strong electrophilic phosphenium transient **4** as a novel building block for other polycyclic phosphonium ions.

Experimental Section

2: MeOTf (0.432 g, 2.65 mmol) was added to a stirring solution of **1** (1.27 g, 5.31 mmol) in dichloromethane (50 mL). The resulting clear solution was stirred at room

temperature and then concentrated to 10 mL. The desired product was precipitated by addition of diethyl ether (10 mL), filtered, and dried under vacuo to yield a white solid (1.32 g; 78%). Slow diffusion of diethyl ether in a solution of **2** in dichloromethane afforded crystals suitable for an X-ray structure analysis. M.p.: 205–207 °C (decomp); ^{1}H NMR (CD_2Cl_2): $\delta = 1.27$ (s, 9H; *t*Bu), 1.32 (s, 9H; *t*Bu), 1.35 (s, 9H; *t*Bu), 1.49 (s, 9H; *t*BuCO), 2.62 (d, $^2J(^1H,^{31}P) = 17.3$ Hz, 3H; MeP), 3.62–3.65 (m, 2H; HC-N), 4.92 ppm (d, $^3J(^1H,^{31}P) = 17.0$ Hz, 1H; HC-N); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 107.4$ (s), 112.8 ppm (s); EI-FAB: *m*/*z* (%): 497 ($[M-OTf]^+$, 5), 57 ($t Bu^+$, 100); ESI-MS (CH_2Cl_2): *m*/*z*: 497 ($[M-OTf]^+$, 100); elemental analysis (%) calcd. for $C_{26}H_{46}F_3N_2O_7P_2S$ (649.67): C 48.06, H 7.13, N 2.15, P 9.54; found: C 47.65, H 7.15, N 2.08, P 9.33.

3: The compound was prepared as reported by Arduengo et al. and the NMR data (^{1}H, ^{31}P) of the sample were identical with the reported values.[12]

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[6] Crystal structure analysis: A crystal of **2** and **3** were each mounted on a glass capillary in perflourinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker axs area detector ($Mo_{K\alpha}$ radiation), $\lambda = 0.71073$ A, ω scan) at −60 °C. **2** ($C_{28}H_{47}Cl_4F_3N_2O_7P_2S$): triclinic, $P\bar{1}$, $a = 12.49(2)$, $b = 13.22(2)$, $c = 14.99(2)$ Å, $\alpha = 100.05(5)$, $\beta = 102.58(7)$, $\gamma = 114.80(8)^o$, $V = 2092(6)$ Å^3, $Z = 2$, $\mu = 0.462$ mm^{-1}. A total of 8652 reflections were collected ($2\theta_{max} = 50°$), 6694 independent, 3828 observed ($F_o > 4\sigma(F_o)$), 424 parameters; $R1 = 0.0722$, $wR2$ (all data) $= 0.1977$. **3** ($C_{13}H_{21}F_3NO_5PS$): monoclinic, $P2_1/n$, $a = 6.612(3)$, $b = 22.88(1)$, $c = 12.710(6)$ Å, $\beta = 102.163(8)^o$, $V = 1879(1)$ Å^3, $Z = 4$, $\mu = 0.307$ mm^{-1}. A total of 9002 reflections were collected ($2\theta_{max} = 50°$), 3288 independent, 1901 observed ($F_o > 4\sigma(F_o)$), 217 parameters; $R1 = 0.0573$, $wR2$ (all data) $= 0.1604$. Structure solutions by direct methods (SHELXS 97), refinement against F^2 with all measured reflections (SHELXTL 97). The positions of the H atoms were calculated and considered isotropically according to a riding model. CCDC 274136 (**2**) and 274167 (**3**) 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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