DOI: 10.1002/ejic.201100098

Investigating the Phospholylcarbene to Phosphinine Conversion

Hui Chen,[a] Jin Li,[a] Huaiqiu Wang,[a] Hui Liu,[a] Zheng Duan,*[a] and François Mathey*[a,b]

Keywords: Heterocycles / Phosphorus / Arsenic / Carbenes / Density functional calculations

A DFT study suggests that the conversion of arsolylcarbenes into arsenines as described by Märkl proceeds via arsabenzvalenes. A similar conversion does not work with phospholylcarbenes. However, we have found that, in some cases, 1-diazoalkylphosphole sulfides are converted into phosphinine sulfides whose in situ reduction by triphenylphosphite affords the dicoordinate phosphinines.

The discovery that phosphinines can play a significant role in homogeneous catalysis[1] has reignited the interest in their synthesis and chemistry.[2] In this context, our attention was drawn to an early work of Märkl describing the conversion of arsolylcarbenes into arsenines.[3] We were puzzled by the fact that this chemistry has no reported equivalent for nitrogen and phosphorus. As a first step, we decided to study this transformation by DFT computations at the B3LYP/6-311+G(d,p) level[4] in order to get a better understanding of the reaction pathway. The singlet arsolylcarbene has a planar structure with a As=C double bond (1.773 Å) and is closely related to the structure of phosphanylcarbenes.[5] Its structure forbids any interaction between the carbene and the diene orbitals. The triplet arsolylcarbene has a pyramidal arsenic atom (sum of the angles 293.5°) and a single As–C bond (1.888 Å). The plane of the carbene is orthogonal to the plane of the arsole. This triplet state lies only 3.7 kcal mol^{-1} above the singlet. This structure is similar to the structure of cyclopentadienylcarbene that yields benzvalene by intramolecular [1+4] carbene + diene cycloaddition.[6] Thus, we suggest that this easily accessible triplet is readily converted into arsabenzvalene. Computations show that this arsabenzvalene is a genuine local minimum (no negative frequency), more stable than the triplet arsolylcarbene by 55 kcal mol^{-1}. It is transformed into arsenine via a transition state (one negative frequency) that is 35.3 kcal mol^{-1} higher in energy. Both the arsabenzvalene and the transition state are shown in Figure 1. Our data on arsabenzvalene (structure and energy) are close to those computed by Sastry.[7]

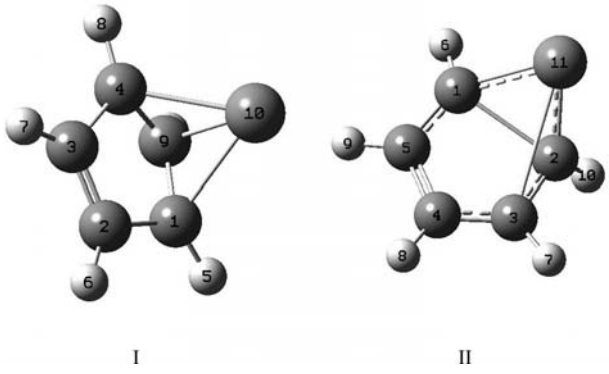


Figure 1. Computed structure of arsabenzvalene I and the transition state II between I and arsenine. Significant distances [Å] and angles [°]: I: As–C1 2.168, As–C9 1.972, C1–C9 1.473, C4–C3 1.482, C3–C2 1.348; C1–As–C4 62.69, C1–As–C9 41.36. II: As–C1 2.023, As–C2 1.861, As–C3 2.836, C1–C2 2.082, C2–C3 1.483, C3–C4 1.353, C4–C5 1.434, C5–C1 1.367; C1–As–C2 64.67, C1–As–C3 60.85, C2–As–C3 28.16.

The case of nitrogen is different. The triplet pyrrolylcarbene is higher in energy than the singlet by 21.8 kcal mol^{-1} and, thus, difficult to reach. Besides, its structure is different. The plane of the carbene is orthogonal to the plane of the ring, as in the arsenic case, but nitrogen is planar (sum of angles at N 359.8°), therefore blocking its transformation into azabenzvalene.

As expected, the situation for phosphorus lies halfway between those for nitrogen and arsenic. The triplet phospholylcarbene is pyramidal at P (sum of angles 313.2°) and lies higher in energy than the singlet by 12.8 kcal mol^{-1}. It is, of course, difficult to predict whether its transformation into phosphabenzvalene is possible. Our structural data are

[a] Chemistry Department, International Phosphorus Laboratory, Zhengzhou University,
Zhengzhou 450052, P. R. China
[b] Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences,
Nanyang Technological University,
21 Nanyang Link, 637371 Singapore
E-mail: duanzheng@zzu.edu.cn
fmathey@ntu.edu.sg

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201100098.

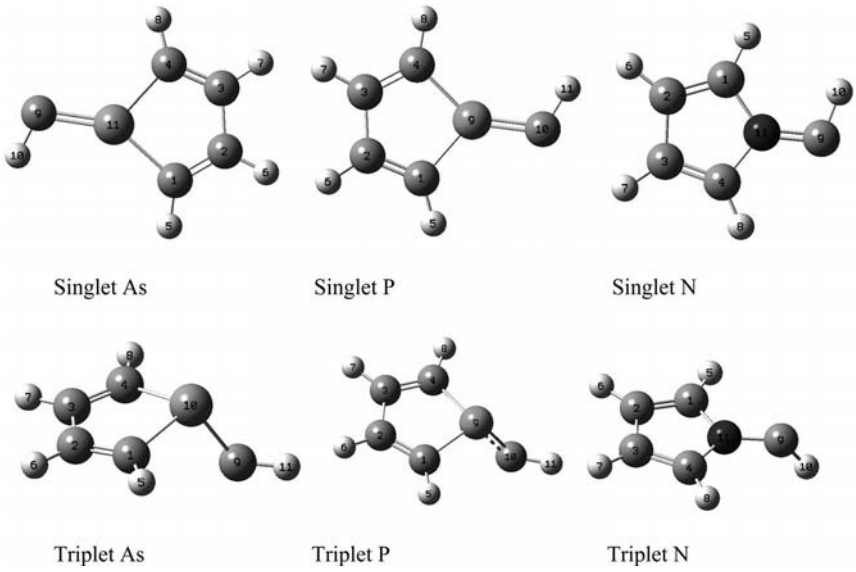
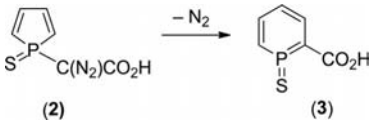
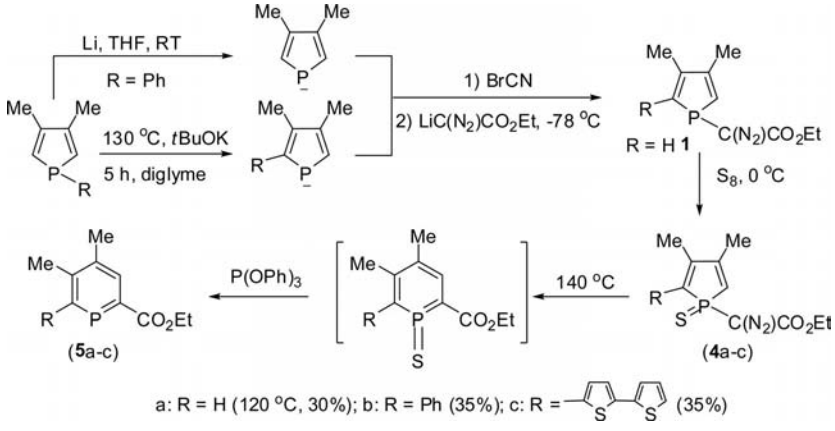


Figure 2. Computed structures of singlet and triplet heterolylcarbenes. Significant distances [Å] and angles [°]: Singlet As: As–C4 1.899, As–C1 1.931, As–C9 1.773; C1–As–C4 89.81, As–C9–H10 107.91. Singlet P: P–C1 1.778, P–C4 1.799, P–C10 1.642; C1–P–C4 94.11, P–C10–H11 114.40. Singlet N: N–C4 1.419, N–C1 1.426, N–C9 1.332; C1–N–C4 106.98, N–C9–H10 105.65. Triplet As: As–C1=As–C4 1.954, As–C9 1.888; C1–As–C4 86.03, C1–As–C9=C4–As–C9 103.74, As–C9–H11 131.30. Triplet P: P–C1=P–C4 1.808, P–C10 1.741; C1–P–C4 91.36, C1–P–C10=C4–P–C10 110.90, P–C10–H11 132.43; Triplet N: N–C1=N–C4 1.399, N–C9 1.365; C1–N–C4 108.08, C1–N–C9=C4–N–C9 125.86, N–C9–H10 127.30.

summarized in Figure 2. The structures of the triplets follow the same trend as those of the corresponding heteroles (exocyclic CH replaced by CH_3), while the increasing pyramidal inversion barrier of the heteroatom from N to As reduces the singlet–triplet gap. The high tendency of As to be pyramidal logically destabilizes the planar singlet state. In order to check the fate of phospholylcarbenes, we prepared a diazo precursor **1**, as shown in Scheme 1. This precursor proved to be unstable upon standing at room temperature, but its decomposition does not yield the corresponding phosphinine. Only a mixture of ill-defined decomposition products was observed. On the contrary, the corresponding P-sulfide is stable and has been fully characterized. At this point, our attention was drawn to a paper of Divisia[8] reporting the thermal conversion of $Ph_2P(S)$–$C(N_2)$–C(O)Ph into PhP(S)=C(Ph)–C(O)Ph by migration of Ph from phosphorus to the carbene center. DFT computations showed us that the decomposition of a phosphole sulfide, such as **2**, cannot yield the corresponding carbene, which does not correspond to a local minimum on the potential energy surface. The product is, in fact, the corresponding phosphinine sulfide **3** [Equation (1)], whose structure is shown in Figure 3.



(1)



Scheme 1.

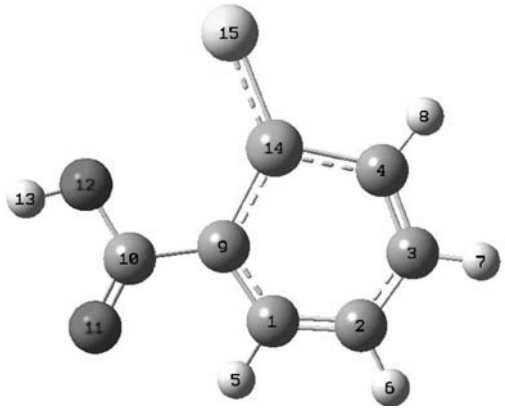


Figure 3. Computed structure of phosphinine sulfide **3**. Significant distances [Å] and angles [°]: P–S 1.936, C4–P 1.723, C3–C4 1.384, C2–C3 1.401, C1–C2 1.386, C1–C9 1.405, C9–P 1.741, C9–C10 1.487; C4–P–C9 105.84.

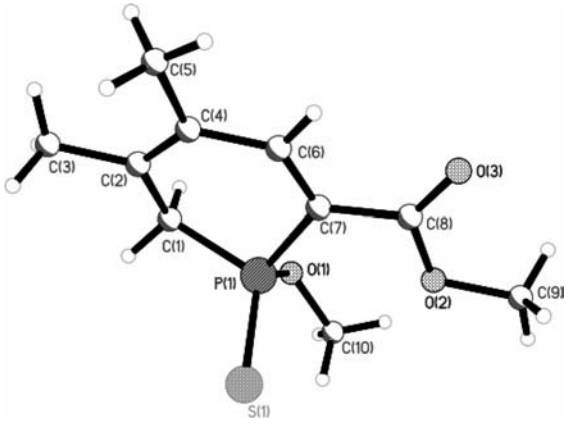
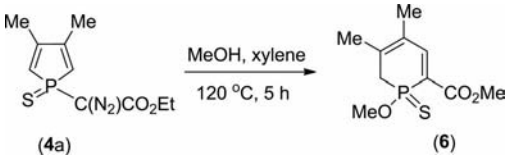


Figure 4. X-ray crystal structure of dihydrophosphinine sulfide **6**. Significant distances [Å] and angles [°]: C1–P1 1.798(3), C1–C2 1.497(4), C2–C4 1.340(4), C4–C6 1.448(4), C6–C7 1.347(4), C7–P1 1.790(3), P1–O1 1.587(2), P1–S1 1.9321(12); C1–P–C7 101.48(14).

Phosphinine sulfides are highly reactive species that cannot be isolated except when stabilized by bulky substituents.[9] The practical use of this transformation needed the addition of a mild reducing agent whose role would be to reduce only the phosphinine sulfide without altering the phosphole sulfide precursor. We were happy to find that triphenyl phosphite is able to perform this task (but triethyl phosphite is not effective) (Scheme 1).

The phosphinine **5**a was purified by chromatography and identified by comparison of its spectroscopic data with those reported in the literature.[10] Our attempts to generalize this reaction met with a mixed success. The replacement of the CO_2Et substituent by $SiMe_3$ proved to be a failure. The trimethylsilyl analogue of **1** displays a better stability but its sulfide does not yield the corresponding phosphinine when following the procedure in Scheme 1. On the contrary, we can modify the substitution pattern of the ring carbons. The necessary precursors are synthesized as shown in Scheme 1. The [1,5] shift of R is a classical reaction of phosphole chemistry.[11] We also wanted to establish the intermediacy of the phosphinine sulfides as proposed in Equation (1). This was achieved by heating **4**a in the presence of methanol as shown in Equation (2).



(2)

The structure of **6** was established by X-ray analysis (Figure 4).

Although the phosphinine yields are modest, interesting substitution patterns can be obtained and the procedure is simple. This approach is thus a valuable addition to the phosphinine synthetic toolbox.

Experimental Section

Synthesis of 2-Ethoxycarbonyl-4,5-dimethylphosphinine (5a): A solution containing ethyl diazoacetate (105 μL) in dry Et_2O (6 mL) and dry THF (2 mL) was cooled to –110 °C, and *n*BuLi (1 mmol, 0.35 mL of a 2.8 M solution) was added dropwise to the mixture. After stirring for 30 min, a solution containing 1-cyanol-3,4-dimethyl phosphole (108 mg, 1 mmol) [12] in dry THF (2 mL) was added to the mixture at –78 °C, which was then warmed to 0 °C (phosphole **1** is not stable at room temperature, even under argon). Sulfurization was performed overnight by addition of sulfur powder (38.4 mg, 1.2 mmol) at 0 °C. After elimination of the solvent under vacuum, the residue was chromatographed with petroleum ether/CH_3CO_2Et (5:1) as the eluent to yield a yellow solid, **4a** (192 mg, 75%) [δ^{31}P ($CDCl_3$) = 36.0 ppm].

A mixture of **4a** (192 mg, 0.75 mmol) and triphenyl phosphite (263 μL, 0.75 mmol) in xylene was heated for 5 h at 120 °C. After elimination of the solvent under vacuum, the residue was chromatographed with hexane/CH_2Cl_2 (3:1) as the eluent to give a colorless solid, **5a** (45 mg, 30%).

Spectral Characterization of Phosphinines (5b,c)

5b: ^{31}P NMR ($CDCl_3$): δ = 205.2 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.40 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, Me), 2.26 (d, $^5J_{HP}$ = 1.8 Hz, 3 H, C^4-Me), 2.50 (d, $^4J_{HP}$ = 3.3 Hz, 3 H, C^5-Me), 4.41 (q, $^3J_{HH}$ = 7.2 Hz, 2 H, OCH_2), 7.13–7.33 (m, 5 H, Ph), 8.42 (d, $^3J_{HP}$ = 4.2 Hz, 1 H, C^3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.04 (s, Me), 17.86 (s, Me), 22.13 (s, Me), 60.09 (s, OCH_2), 125.94 (CH Ph), 126.75 (CH Ph), 128.22 (d, J_{CP} = 9.0 Hz, CH Ph), 136.80 (d, J_{CP} = 13.3 Hz), 139.35 (d, J_{CP} = 13.7 Hz), 141.49 (d, J_{CP} = 26.6 Hz), 143.53 (d, J_{CP} = 10.9 Hz), 152.48 (d, $^1J_{CP}$ = 51.0 Hz, C_α), 166.96 (d, $^2J_{CP}$ = 24.2 Hz, CO_2), 170.30 (d, $^1J_{CP}$ = 49.1 Hz, C_α) ppm. MS (ESI): *m*/*z* = 272.8 (M^+).

5c: ^{31}P NMR ($CDCl_3$): δ = 209.3 ppm. ^{1}H NMR ($CDCl_3$): δ = 1.41 (t, $^3J_{HH}$ = 7.1 Hz, 3 H, Me), 2.48 (m, 6 H), 4.42 (q, $^3J_{HH}$ = 7.1 Hz, 2 H, OCH_2), 6.90–7.20 (m, 5 H, Th), 8.40 (d, $^3J_{HH}$ = 4.2 Hz, 1 H, C^3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 13.28 (s, Me), 18.37 (s, Me), 22.44 (d, J_{CP} = 2.0 Hz, Me), 60.43 (s, OCH_2), 122.71 (CH-Th), 122.86 (CH-Th), 123.48 (CH-Th), 126.83 (CH-Th), 127.33 (d, J_{CP} = 10.1 Hz, CH-Th), 136.00 (s), 137.51 (d, $^2J_{CP}$ = 13.1 Hz, C^3), 137.68 (s), 139.77 (d, J_{CP} = 13.1 Hz), 141.85 (d, J_{CP} = 31.4 Hz), 145.41 (d, J_{CP} = 10.7 Hz), 153.10 (d, $^1J_{CP}$ = 51.5 Hz, C_α), 161.09

(d, $^1J_{CP}$ = 49.9 Hz, C_α), 166.86 (d, $^2J_{CP}$ = 23.9 Hz, CO_2) ppm. MS (ESI): *m*/*z* = 360.7 (M^+).

CCDC-800546 (compound **6**) contains 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 (see footnote on the first page of this article): Complete experimental section.

Acknowledgments

The authors thank the National Natural Science Foundation of China (No. 20702050, 21072179), the Scientific Research Foundation for the Returned Overseas Chinese, Zhengzhou University and Nanyang Technological University in Singapore for the financial support of this work.

[1] B. Breit, *Chem. Commun.* **1996**, 2071; B. Breit, *J. Mol. Catal. A* **1999**, *143*, 143; B. Breit, R. Winde, K. Harms, *J. Chem. Soc. Perkin Trans. 1* **1997**, *18*, 2681; B. Breit, R. Winde, T. Mackewitz, R. Paciello, K. Harms, *Chem. Eur. J.* **2001**, *7*, 3106; L. Weber, *Angew. Chem.* **2002**, *114*, 583; *Angew. Chem. Int. Ed.* **2002**, *41*, 563; M. T. Reetz, X. Li, *Angew. Chem.* **2005**, *117*, 3022; *Angew. Chem. Int. Ed.* **2005**, *44*, 2962; C. Müller, L. Guarrotxena-Lopéz, H. Kooijman, A. L. Spek, D. Vogt, *Tetrahedron Lett.* **2006**, *47*, 2017; F. Knoch, F. Kremer, U. Schmidt, U. Zennek, P. Le Floch, F. Mathey, *Organometallics* **1996**, *15*, 2713.

[2] A few recent references: J. R. Bell, A. Franken, C. M. Garner, *Tetrahedron* **2009**, *65*, 9368; S. K. Mallissery, D. Gudat, *Dalton Trans.* **2010**, *39*, 4280; S. K. Mallissery, M. Nieger, D. Gudat, *Z. Anorg. Allg. Chem.* **2010**, *636*, 1354; H. Wang, C. Li, D. Geng, H. Chen, Z. Duan, F. Mathey, *Chem. Eur. J.* **2010**, *16*, 10659; Y. Mao, F. Mathey, *Org. Lett.* **2010**, *12*, 3384.

[3] G. Märkl, H. Hauptmann, J. Advena, *Angew. Chem.* **1972**, *84*, 440; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 441; G. Märkl, J. Advena, H. Hauptmann, *Tetrahedron Lett.* **1974**, *15*, 303.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision B.05*, Gaussian, Inc., Pittsburgh PA, **2003**.

[5] T. Kato, H. Gornitzka, A. Baceiredo, A. Savin, G. Bertrand, *J. Am. Chem. Soc.* **2000**, *122*, 998.

[6] T. J. Katz, E. J. Wang, N. Acton, *J. Am. Chem. Soc.* **1971**, *93*, 3782; T. J. Katz, R. J. Roth, N. Acton, E. J. Carnahan, *J. Org. Chem.* **1999**, *64*, 7663. The various H-inward and outward, singlet and triplet cyclopentadienylcarbenes have been studied theoretically: H. F. Bettinger, P. R. Schreiner, H. F. Schaeffer III, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1998**, *120*, 5741.

[7] U. Deva Priyakumar, T. C. Dinadayalane, G. Narahari Sastry, *New J. Chem.* **2002**, *26*, 347.

[8] B. Divisia, *Tetrahedron* **1979**, *35*, 181.

[9] J.-M. Alcaraz, F. Mathey, *J. Chem. Soc., Chem. Commun.* **1984**, 508; A. Moores, T. Cantat, L. Ricard, N. Mézailles, P. Le Floch, *New J. Chem.* **2007**, *31*, 1493.

[10] S. Holand, L. Ricard, F. Mathey, *J. Org. Chem.* **1991**, *56*, 4031.

[11] S. Holand, M. Jeanjean, F. Mathey, *Angew. Chem.* **1997**, *109*, 117; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 98.

[12] S. Holand, F. Mathey, *Organometallics* **1988**, *7*, 1796.

Received: January 28, 2011
Published Online: February 22, 2011

