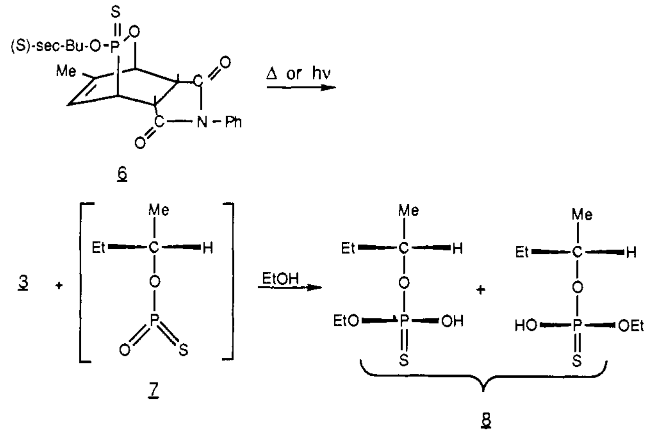
the ^{31}P NMR ($CDCl_3$) spectrum, which consisted of two signals of equal intensity at δ 61.03 and 61.10 on a 300-MHz spectrometer. This product composition is that expected from planar metathiophosphate **7**; no other process (e.g., formation of a P(V) adduct by attack of ethanol on **6** followed by fragmentation) can be visualized that would give this stereochemical result. Furthermore, we obtained exactly the same stereochemical result when ester **6** was fragmented photochemically in the presence of ethanol, which constitutes proof that the same planar species **7** was generated in both the thermal and photochemical processes. Direct observation of a metathiophosphate remains desirable, however, and appropriate experiments are in progress.



Acknowledgment. This work was supported by grants from the Army Research Office and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Synthesis, Reactivity, and Crystal Structure of the First Methylenephosphonium Ion: A Severely Twisted Valence Isoelectronic Olefin

Alain Igau,[†] Antoine Baceiredo,[†] Hansjorg Grützmacher,[‡] Hans Pritzkow,[‡] and Guy Bertrand*[,†]

Laboratoire de Chimie de Coordination du CNRS
205, route de Narbonne
31077 Toulouse Cêdex, France
Anorganische Chemisches Institut der Universität
Im Neuenheimer Feld 270
D-6900 Heidelberg, West Germany

Received March 13, 1989

In the course of the development of low coordinated heavier main group element chemistry, several types of phosphorus–carbon double-bonded derivatives (A,[1] B,[2] C,[3] D[4]) and of phosphorus cations (F,[5] G) have been structurally characterized. In contrast, no X-ray data are available concerning tricoordinated phosphorus cation H.[6] Methylenephosphonium ions (I) have only been postulated as transient intermediates[7] but never isolated.[8,9] This new class of phosphorus cation is of special interest since they are valence isoelectronic to olefins and have been computed to be planar with a short phosphorus–carbon bond length.[10] Here we wish to report the first example of an isolable methylenephosphonium salt, a molecule containing a short but strongly distorted phosphorus–carbon double bond.

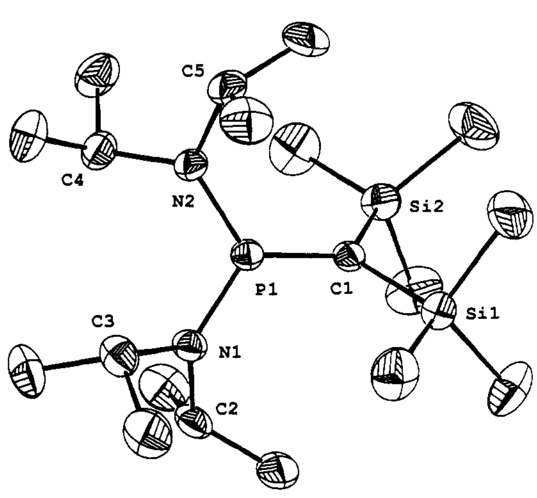
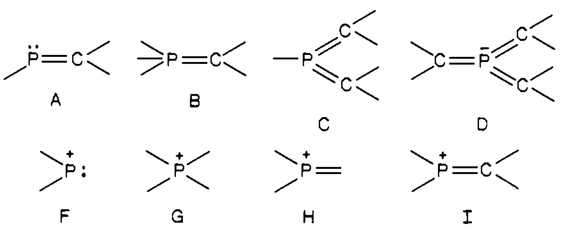


Figure 1. Thermal ellipsoid diagram (30% probability) of methylenephosphonium **2** showing the atom numbering scheme. Pertinent bond lengths (Å) and bond angles (deg) are as follows: P1-C1 1.620 (3), C1-Si1 1.875 (3), P1-N1 1.615 (3), C1-Si2 1.913 (3), P1-N2 1.610 (3); N1-P1-C1 123.4 (1), C2-N1-P1 121.0 (2), N2-P1-C1 124.4 (1), C3-N1-P1 123.1 (2), N2-P1-N1 112.2 (1), C2-N1-C3 115.6 (2), Si1-C1-P1 121.7 (1), C4-N2-P1 120.2 (2), Si2-C1-P1 119.3 (1), C5-N2-P1 124.4 (2), Si2-C1-Si1 119.1 (1), C4-N2-C5 115.1 (2).



Starting from the recently reported stable nucleophilic phosphinocarbene **1**,[11] a novel entry to the desired ion I was apparent. Addition of trimethylchlorosilane to **1** led to phosphorus ylide **3**[11a] suggesting that the use of silyl derivative containing a non-nucleophilic anion would afford **2**. Reaction of [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene (**1**) with trimethylsilyl triflate at room temperature gave clean conversion to methylenephosphonium ion **2** (yellow crystals extremely air sensitive, mp 80 °C dec, 70% yield).[12]

[†] Laboratoire de Chimie de Coordination du CNRS.

[‡] Anorganische Chemisches Institut der Universität.

(1) For reviews see: (a) Markovski, L. N.; Romanenko, V. D.; Rouban, A. V. *Acyclic Dicoordinated Phosphorus Derivatives*; Kiev-Science, 1988. (b) Lochschmidt, S.; Schmidpeter, A. *Phosphorus Sulfur* **1986**, *29*, 73. (c) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

(2) For a review see for example: Bestmann, H. J.; Zimmermann, R. *Methoden der organischenchemie* (*Houben-Weyl*); Band E1, Thieme, Stuttgart, 1982.

(3) See for example: Appel, R.; Gaitzsch, E.; Dunker, K. H.; Knoch, F. *Chem. Ber.* **1986**, *119*, 535.

(4) Appel, R.; Gaitzsch, E.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 589.

(5) For a review see: Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.

(6) See for examples: (a) Rahil, J.; Haake, P. *J. Org. Chem.* **1981**, *46*, 3048. (b) Michalski, J.; Radziejewski, C.; Skrypczynski, Z.; Dabrowski, W. *J. Am. Chem. Soc.* **1980**, *102*, 1974. (c) Maier, L. *Z. Anorg. Allg. Chem.* **1966**, *345*, 29. (d) Marre, M. R.; Sanchez, M.; Wolf, R. *Phosphorus Sulfur* **1982**, *13*, 327. (e) Sanchez, M.; Marre, M. R.; Brazier, J. F.; Bellan, J.; Wolf, R. *Ibid.* **1983**, *14*, 331. (f) Mulliez, M.; Majoral, J. P.; Bertrand, G. *J. Chem. Soc., Chem. Commun.* **1984**, 284.

(7) Van der Knaap, Th. A.; Bickelhaupt, E. *Tetrahedron Lett.* **1982**, *23*, 2037.

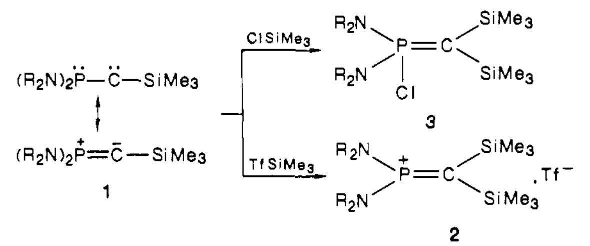
(8) Abstraction of chloride by $AlCl_3$ from a *P*-chloromethylenephosphorane was claimed by Appel et al.[9] to give a methylenephosphonium ion as characterized by ^{31}P NMR and elemental analysis. However, the relatively high field ^{31}P chemical shift of the product makes this assignment unlikely.

(9) Appel, R.; Schmitz, R. *Chem. Ber.* **1983**, *116*, 3521.

(10) Lohr, L. L.; Schlegel, H. B.; Morokuma, K. *J. Phys. Chem.* **1984**, *88*, 1981.

(11) (a) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463. (b) Igau, A.; Baceiredo, A.; Trinquier, G.; Bertrand, G. *Angew. Chem.* **1989**, *101*, 617.

0002-7863/89/1511-6853$01.50/0



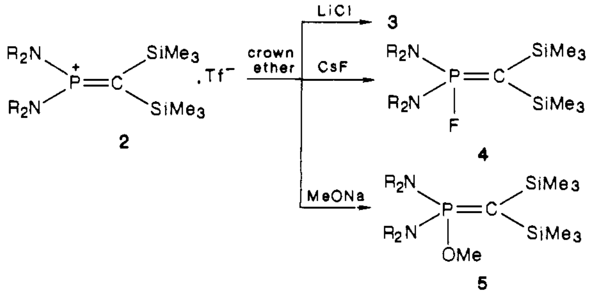
R = iPr; Tf = CF$_3$SO$_3$

In contrast to P-halogenated ylide **3**, derivative **2** is poorly soluble in nonpolar solvent. The ^{31}P chemical shift (+130.8 ppm) and the ^{13}C chemical shift of the tricoordinated carbon (+76.51 ppm, J_{PC} = 87.6 Hz), as expected for a cationic species, are significantly deshielded compared with those of related phosphorus ylides.[13] The ionic structure of **2** was unambiguously determined by an X-ray crystal structure analysis.[14] The thermal ellipsoid diagram of the molecule is shown in Figure 1 as well as the pertinent metric parameters.

Several aspects of the structure merit discussion. No interaction with the triflate is observed, demonstrating the ionic character of **2**. The positive charge is delocalized onto the nitrogen atoms, indicative of a PN partial double bond character, as shown by their planar geometry[15] and the short P-N bond lengths (1.61 vs 1.68 Å in H_2PNH_2).[16] The structural parameters for the framework atoms (P1 and C1) are as expected for a valence isoelectronic olefin: (i) the P-C distance of 1.62 Å is short, even compared to that in phosphaalkenes (1.64-1.69 Å),[1] and in good agreement with that from a theoretical study on the parent compound (1.624 Å);[10] (ii) the geometry at both P1 and C1 is strictly planar (±0.01 Å). However, the dihedral angle between these two planes corresponds to a twist of the double bond by 60°! This value is significantly larger than that reported by Sakurai (50.2°) for the "most crowded olefin".[17]

In order to rationalize the simultaneous existance of the short P-C bond and the large twist angle, a model developed by Trinquier[18] to describe the bonding in phosphorus ylides can be employed. This involves the interaction of a phosphenium ion with a p_π^2 closed-shell singlet excited carbene. The energy required for reaching the p_π^2 configuration from a n_σ^2 configuration is largely compensated by the building of the ylidic bond which is basically a dative bond (phosphenium lone pair → carbene empty n_σ) plus a partial back-donation (carbene occupied p_π → phosphenium empty d_π).

All attempts to involve the P-C double bond of **2** in reactions failed. However, in the presence of crown ether, substitution reactions occur with lithium chloride, cesium fluoride, and sodium methoxide, yielding the corresponding phosphorus ylides **3-5**.



R = iPr ; Tf = CF$_3$SO$_3$

Acknowledgment. Thanks are due to Drs. G. Trinquier and G. Gillette for helpful discussions and to the CNRS (GRECO basses coordinences) for financial support of this work.

Supplementary Material Available: Tables of bond distances and angles with estimated standard deviations and atomic coordinates and thermal parameters (5 pages); listing of structure factors (10 pages). Ordering information is given on any current masthead page.

---

[12] To an ether solution (10 mL) of carbene **1** (0.2 g, 0.6 mmol), a slight excess of trimethylsilyl triflate (0.12 mL, 0.7 mmol) was added dropwise at room temperature. Methylenephosphonium salt **2** precipitated from the solution as a yellow powder. After filtration, **2** was recrystallized at −10 °C from a dichloromethane/toluene solution. ^{31}P NMR (CD_2Cl_2) +130.8; ^{13}C NMR (CD_2Cl_2) 2.93 (d, J(PC) = 7.1 Hz, SiCH$_3$), 24.55, 24.72 (s, CH_3CH), 48.88 (d, J(PC) = 6.1 Hz, CHCH$_3$), 76.51 (d, J(PC) = 87.6 Hz, P=C), 124.23 (q, J(CF) = 321.1 Hz, CF$_3$SO$_3$); ^{1}H NMR (C_6D_6) 0.32 (d, J(PH) = 0.6 Hz, 18 H, SiCH$_3$), 1.47 (d, J(HH) = 6.9 Hz, 24 H, CH_3CH), 4.16 (sept d, J(HH) = 6.9 Hz, J(PH) = 12.8 Hz, 4 H, CHCH$_3$); ^{29}Si NMR (C_6D_6) −0.24 (s); ^{19}F NMR (C_6D_6) −3.37 (s).

[13] ^{31}P NMR: **3** +72.1; **4** +70.3; **5** +71.0 ppm. ^{13}C NMR (C=): **3** 12.35 (J_{PC} = 151.5 Hz); **4** 7.25 (J_{PC} = 149.2 Hz); **5** 5.45 (J_{PC} = 135.6 Hz) ppm.

[14] A single crystal of **2** was grown from a dichloromethane/toluene solution, at −10 °C. **2** crystallizes in the monoclinic space group $P2_1/c$, a = 11.323 (6) Å, b = 9.432 (5) Å, c = 28.070 (20) Å; β = 90.67 (5)°; V = 2998 Å^3; Z = 4. The 3331 observed data ($I > 2\sigma I$) were collected by using Mo Kα radiation in the ω-scan mode and were used in the least-squares refinement to yield R = 0.050; R_w = 0.031 for 465 variables. The hydrogen atoms were refined isotropically in observed positions except for 4 methyl groups which were refined as rigid groups. Tables of bond lengths, bond angles, atomic coordinates, thermal parameters, and structure factors are given in the supplementary material.

[15] The geometry of the $(R_2N)_2P$ fragment is quite similar to that reported for the corresponding phosphenium ion: Cowley, A. H.; Cushner, M. C.; Szobota, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 7784.

[16] Cowley, A. H.; Mitchell, D. J.; Whangbo, M. H.; Wolfe, S. *J. Am. Chem. Soc.* **1979**, *101*, 5224.

[17] Sakurai, H.; Ebata, K.; Kabuto, C.; Nakadaira, Y. *Chem. Lett.* **1987**, 301.

[18] Trinquier, G.; Malrieu, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 5303.

Pericyclic Reactions of Cyclopropylcarbene-Chromium Complexes

James W. Herndon* and Leonard A. McMullen

Department of Chemistry and Biochemistry
University of Maryland
College Park, Maryland 20742

Received March 13, 1989

Recently, we reported that cyclopropylcarbene-chromium complexes react with alkynes to give highly substituted cyclopentenones.[1] Two mechanisms were proposed for this reaction, one of which involves ring expansion of the cyclopropylcarbene complex **1** to a chromacyclopentene (**2**) (Scheme I) as the initial step of the reaction. The penultimate product of the reaction is the cyclopentadienone **3**, which is reduced to the cyclopentenone **4** under the conditions of the reaction.[2] Rearrangement of a cyclopropylcarbene-transition metal complex to a metallacyclopentene is not precedented,[3] but this step can be viewed as an analogue of the vinylcyclopropane rearrangement.[4] We have studied the thermal chemistry of cyclopropylcarbene-chromium complexes[5] as a probe for the viability of this step. Herein we report our preliminary results of this study.

Carbene complex **1** was unchanged after 1 h when heated to reflux in benzene or p-dioxane. Since the reaction between carbene complex **1** and alkynes typically proceeded rapidly at 65 °C, the unreactivity of carbene complex **1** under the above conditions would seem to rule out the mechanism in Scheme I, provided that the conversion of **1** to **2** is not strongly influenced by the presence of alkyne ligands at chromium. In the all-carbon system, vinylcyclopropane rearrangements typically require a great deal of activation energy and usually proceed only at high temperatures.[4]

---

[1] Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334-3335.

[2] Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 295-296.

[3] For other examples of the reactivity of cyclopropylcarbene-metal complexes, see: (a) Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2119-2124. (b) Brookhart, M.; Studabaker, W. B.; Husk, R. G. *Organometallics* **1985**, *4*, 943-944. (c) Brookhart, M.; Studabaker, W. B.; Husk, R. G. *Organometallics* **1987**, *6*, 1141-1145. (d) Hegedus, L. S.; de Weck, G.; D'Andrea, S. *J. Am. Chem. Soc.* **1988**, *110*, 2122-2126.

[4] Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247-335.

[5] For studies on the thermolysis of the corresponding acylate complex, see: Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77-86.

0002-7863/89/1511-6854$01.50/0 © 1989 American Chemical Society