# Reactions of a Stable (Phosphanyl)(silyl)carbene with Aliphatic Aldehydes: [2+1] versus [2+2] Addition to a Carbonyl Group

**Ona Illa,[a] Heinz Gornitzka,[b] Vicenç Branchadell,*[a] Antoine Baceiredo,[b] Guy Bertrand,[c] and Rosa M. Ortuño*[a]**

**Keywords:** Carbenes / Cycloadditions / Oxiranes / Phosphorus

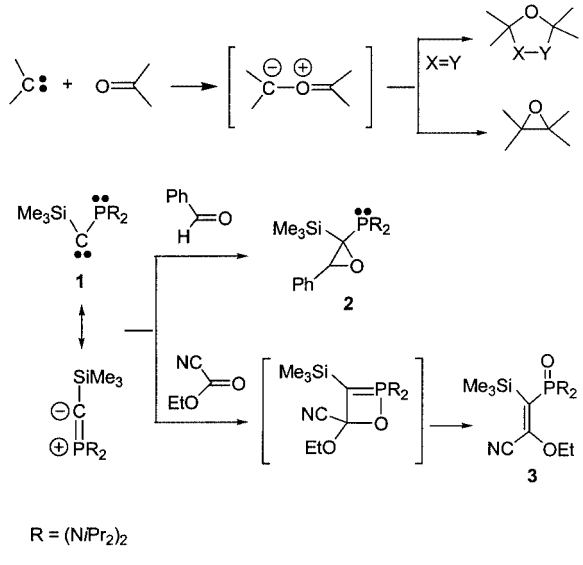
The reactions between the stable (phosphanyl)(silyl)carbene **1** and different aliphatic aldehydes have been investigated for the first time. Results reveal that two competitive processes take place. The kinetically most favorable one is a concerted [2+1] cycloaddition to carbonyl leading to oxiranes as single diastereomers, with the trans arrangement of the alkyl and phosphoranyl groups, as the major products. Simultaneously, a [2+2]-like addition provides short-lived oxaphosphetene intermediates that rapidly evolve to the corresponding olefins with *E* stereochemistry, which are the thermodynamically most stable compounds. DFT calculations establish the mechanism for both processes and a rationale for the observed diastereoselectivity.



## Introduction

Apart from the various chemical transformations[1] of epoxides, which make them among the most useful synthetic intermediates, they have a notable biological significance.[2] The discovery of phosphomycin, (1*R*,2*S*)-epoxypropylphosphonic acid,[3] which is a clinically useful antibiotic, has generated an ongoing interest in the chemistry of C-phosphorylated oxiranes.[4]

In principle, one direct method for the preparation of epoxides would be the reaction of a carbene with a carbonyl group (Scheme 1). However, electrophilic transient carbenes are known to react with carbonyl derivatives through the oxygen lone pair to give transient carbonyl ylides[5] which can be trapped by [3+2]-cycloaddition reactions;[6a] occasionally, those 1,3-dipoles undergo cyclization to give small amounts of the corresponding oxiranes.[6b] Moreover, most of the nucleophilic carbenes, including the stable N-heterocyclic carbenes,[7] catalyze the benzoin condensation.[8] In marked contrast, early studies had shown that the [bis(diisopropylamino)phosphanyl](trimethylsilyl)-carbene (**1**)[9] readily reacted with benzaldehyde affording the corresponding oxirane **2** as only one diastereomer,[10] while for the electron-poor carbonyl group of ethyl cyanoformate a phosphorylated olefin **3** was formed. The ambivalent reactivity of the stable (phosphanyl)(silyl)carbene **1** with carbonyl derivatives, is certainly due to its vinyl ylide form (Scheme 1), and therefore the reactions leading to **2** and **3** are related to the well-known Corey−Chaykovski[11] and Wittig reactions,[12] respectively.




Scheme 1

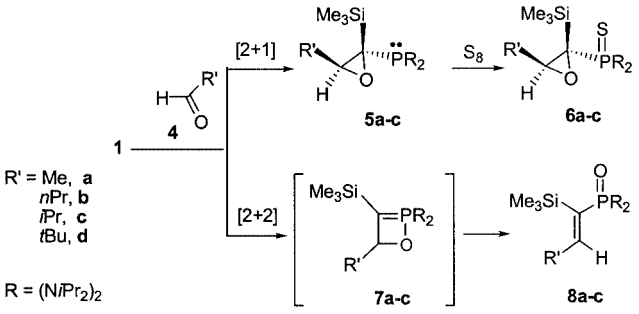
Herein, we report a detailed study on the first reactions of **1** with aliphatic aldehydes bearing a primary, secondary,

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain
E-mail: vicenc@klingon.uab.es; rosa.ortuno@uab.es
[b] Laboratoire Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse cedex 04, France
E-mail: baceired@chimie.ups-tlse.fr
[c] UCR-CNRS Joint Research Chemistry Laboratory, UMR 2282, Department of Chemistry, University of California, Riverside, CA 92521−0403, USA
E-mail: gbertran@mail.ucr.edu
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

and tertiary carbon at the α-carbonyl position. Special attention has been devoted to the nature of the products, as well as to the stereoselectivity of the reactions. The experimental results have been rationalized by DFT calculations.

## Results and Discussion

Carbene **1** reacts instantaneously with aldehydes **4a−c** (Scheme 2) in pentane solution at temperatures ranging from 20 to −60 °C. Pivalaldehyde, **4d**, remained unaltered under the reaction conditions probably because of the excessive steric hindrance of the *tert*-butyl group. After thiolation with elemental sulfur, oxiranes **6a−c** (30−40% yield) and olefins **8a−c** (6−11% yield) were readily isolated by column chromatography. Total yields as well as the oxirane/olefin ratio proved not to be temperature or solvent dependent. Moreover, all attempts to isomerize oxiranes **5** into olefins **8** failed. All of these compounds were obtained as single stereoisomers, demonstrating the excellent diastereoselectivity of these reactions. The trans arrangement of the R′ and thioxophosphoranyl groups has been determined by X-ray analysis of compounds **6a** and **6c**, as shown in Figure 1.[13] The same relative configuration was also determined by $^1$H NMR for olefins **8a−c** since significant NOE enhancements were observed on the isopropyl protons when the vinyl proton was selectively irradiated.




Scheme 2

The concomitant production of the oxiranes and olefins suggests that Corey−Chaykovski-like and Wittig-like processes compete throughout the reaction between carbene **1** and aliphatic aldehydes. The excellent stereoselectivity observed for the formation of epoxides **5** suggest a concerted [2+1] cycloaddition mechanism. On the other hand, a [2+2]-like addition would afford highly strained oxaphosphetene derivatives **7**, which would rapidly evolve towards the corresponding olefin. However, even at low temperature, all attempts to characterize such cyclic intermediates spectroscopically failed.

In order to rationalize these results, density functional calculations have been carried out. We have studied the reaction between acetaldehyde and [bis(dimethylamino)phosphanyl](silyl)carbene (**1′**), which is a simplified model for carbene **1**. We have not considered simpler models, since it has been established that the structure and reactivity of

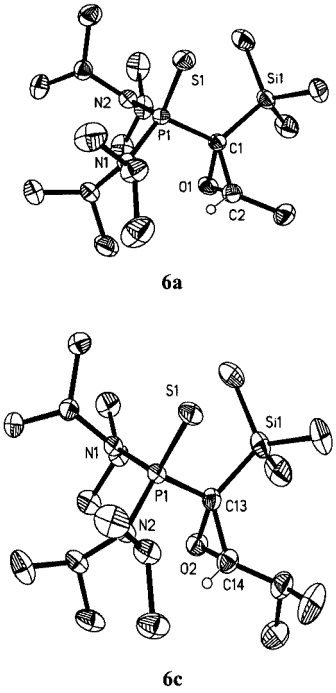



Figure 1. Thermal ellipsoid diagram (30% probability) of **6a** and **6c** showing the atom numbering scheme

(phosphanyl)(silyl)carbenes is strongly dependent on the phosphorus substituents.[14]

Figure 2 presents the structures of **1′** and of the stationary points corresponding to the [2+1] cycloaddition leading to the formation of oxirane **5′a**. We have considered the formation of two different isomers *cis*-**5′a** and *trans*-**5′a**, defined by the relative arrangement of the phosphanyl and methyl groups. Figure 3 presents the structures of the stationary points associated with the [2+2]-like addition. The relative energies and Gibbs energies of all these structures are presented in Table 1. We can observe that solvation has a minor effect on the Gibbs energies obtained in the gas phase.

The optimized geometry of **1′** is in good agreement with the crystal structure of a similar substrate.[15,16] The environment around P is planar and the C−P bond is shorter than the C−Si bond. The value of the Si−C−P bond angle is smaller than the 175.9° computed for $(H_2N)_2PCSiH_3$ from Hartree−Fock calculations.[14a] We have optimized the geometry of this system at the B3LYP level of calculation and have obtained an energy minimum with a Si−C−P bond angle of 151.4° and a nearly linear structure (Si−C−P = 178.5°) corresponding to a transition state associated to Si−C−P bending and placed only 0.2 kcal·mol$^{-1}$ above the minimum.

Table 1 shows that the formation of *trans*-oxirane **5′a** is favored compared to that of the *cis*-isomer both kinetically and thermodynamically. More importantly, although the alternative path, i.e. the [2+2] cycloaddition leading to the formation of oxaphosphetene intermediate **7′a**, is thermodynamically more favorable, this process involves a larger

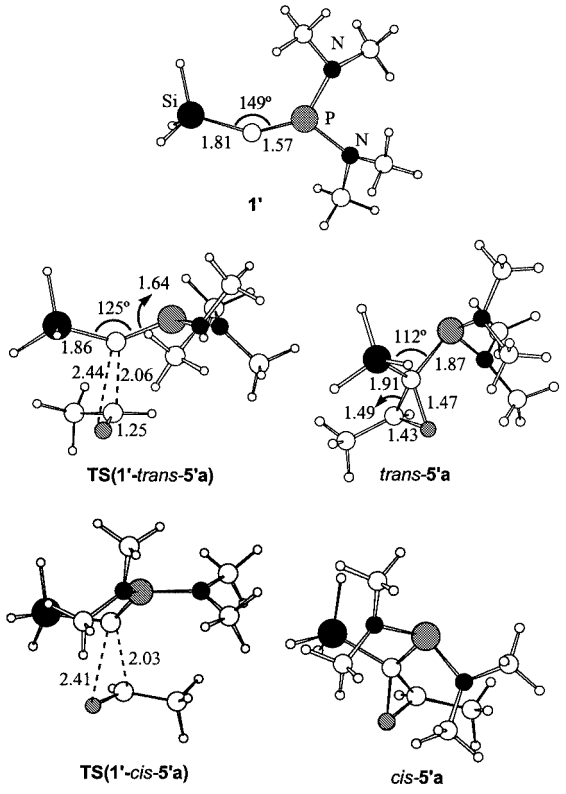



Figure 2. Structure of carbene **1′** and of the stationary points corresponding to its [2+1] cycloaddition to acetaldehyde; interatomic distances in Å and bond angles in degrees

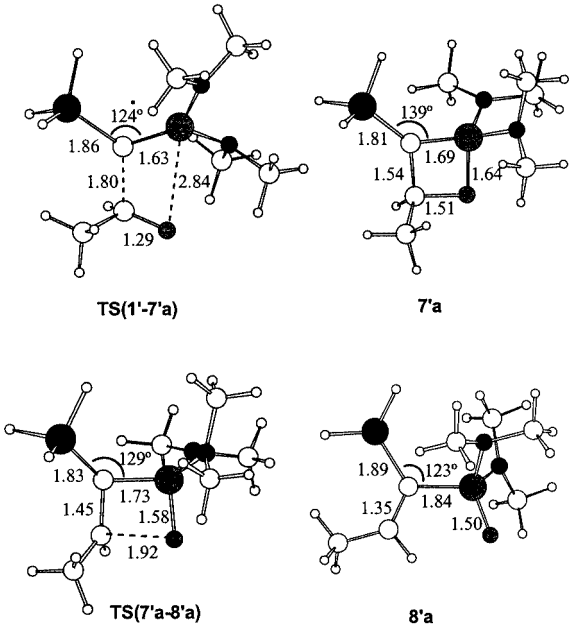



Figure 3. Structure of the stationary points corresponding to the [2+2] cycloaddition between **1′** and acetaldehyde; interatomic distances in Å and bond angles in degrees

Gibbs activation energy ($\Delta G^{\ddagger}$ = 26.0 kcal·mol$^{-1}$) than the formation of *trans*-**5′a**.

The heterocycle **7′a** is unstable with respect to ring opening and easily isomerizes to olefin **8′a** (the most stable product of the whole process) with a Gibbs activation energy of only 8.2 kcal·mol$^{-1}$ in the gas phase and 7.4 kcal·mol$^{-1}$ in solution. We have also located a transition state for the rearrangement of *trans*-**5′a** to **7′a** (see Figure 4) but it involves a gas-phase Gibbs activation energy of 47.3 kcal·mol$^{-1}$, notably larger than the 38.9 kcal·mol$^{-1}$ corresponding to the cycloreversion of *trans*-**5′a** to the reactants (see Table 1). These values nicely explain the absence of isomerization of **5** into **8**.

Table 1. Energies and Gibbs energies (kcal·mol$^{-1}$) relative to reactants for the stationary points (see Figures 2 and 3) corresponding to the reactions between **1′** and acetaldehyde

| | $\Delta E$[a] | $\Delta E$[b] | $\Delta G$[b] [c] | |
|---|---|---|---|---|
| TS(1′-*trans*-5′a) | 7.9 | 11.1 | 25.2 | (25.6) |
| *trans*-**5′a** | −39.5 | −31.8 | −13.7 | (−13.9) |
| TS(1′-*cis*-5′a) | 8.2 | 11.4 | 26.5 | (28.2) |
| *cis* −**5′a** | −38.4 | −30.5 | −12.2 | (−11.1) |
| TS(1′-7′a) | 10.1 | 10.8 | 26.0 | (26.0) |
| 7′a | −46.3 | −44.0 | −25.6 | (−23.2) |
| TS(7′a-8′a) | −35.4 | −34.7 | −17.4 | (−15.8) |
| 8′a | −82.3 | −81.7 | −64.3 | (−64.0) |

[a] B3LYP/6-31G(d). [b] B3LYP/cc-pVTZ//B3LYP/6-31G(d). [c] At 1 atm and 298.15 K. In parentheses values in heptane solution.

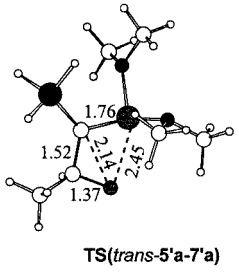



Figure 4. Structure of the transition state corresponding to the direct rearrangement of *trans*-**5′a** to **7′a**; interatomic distances in Å

Figure 5 shows the two highest molecular orbitals and the LUMO of **1′**. The sub-HOMO and LUMO are the C−P π and π* orbitals resulting from the mixing of the out-of-plane non-bonding 2p orbital of C and the P lone pair.

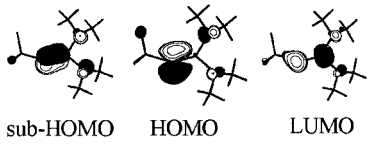



Figure 5. Selected molecular orbitals of **1′**

Figure 6 shows the interactions between fragment frontier orbitals at the [2+1] and [2+2] transition states. The most important interaction at the initial stage of the reaction involves electron donation from the HOMO of the carbene to the π* orbital of acetaldehyde.[17]

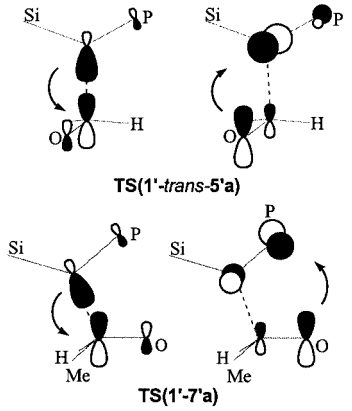



Figure 6. Schematic representation of orbital interactions between the HOMO of **1**′ and π* of **4a** (left side) and between π of **4a** and LUMO of **1**′ (right side) at the transition states

The [2+1] transition state corresponds mainly to the formation of the C−C bond. A remarkable degree of pyramidalization is observed for P so that the C−P π bond is partially broken. At the transition state the carbene is tilted by about 30° with respect to the plane perpendicular to the C−O axis. In this way electron back donation from the π orbital of acetaldehyde to the LUMO of the carbene is possible. Moreover, the carbene turns around the C−C axis (see Figure 7) in such a way that the silyl group moves away from methyl and P moves towards H. This motion relieves steric repulsion between the silyl and methyl groups, but it also favors the interaction between the carbene HOMO and the π* orbital of acetaldehyde. For the cis transition state, rotation around the C−C axis also relieves the steric repulsion between $PR_2$ and methyl, but the orbital interaction becomes less favorable, so that the cis transition state has a higher energy than the trans one.

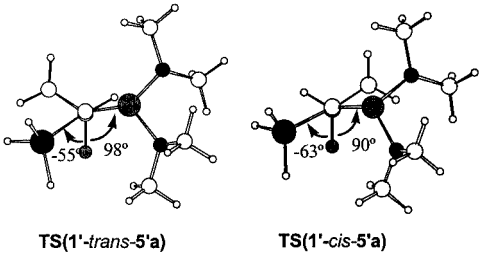



Figure 7. Top view of the transition states corresponding to the formation of oxiranes **5**′**a**; O−C−C−Si and O−C−C−P dihedral angles in degrees

The [2+2] transition state also corresponds to the formation of the C−C bond and the value of the C−C distance shows that it appears later on the reaction coordinate than the [2+1] transition states. The carbonyl group and the carbene are nearly coplanar, with the C−O axis rotated by 10° with respect to the carbene plane. The environment of P is planar and the $PR_2$ group has rotated about 18° around the C−P bond. In this way, back donation between the π orbital of acetaldehyde and the LUMO of the **1**′ is possible. Formation of the P−O bond takes places after the transition state and involves a pyramidalization around P. **7**′**a** presents a weak C−O bond, so that ring opening is feasible. This process is accompanied by a rotation of 90° around the C−C bond and a rearrangement of the P environment from a trigonal pyramid to a tetrahedron.

## Concluding Remark

The results obtained in this work suggest that carbene **1** reacts with aliphatic aldehydes according to two competitive processes: a concerted [2+1] addition leading to oxiranes, which is the kinetically most favored, and a [2+2] addition providing transient oxaphosphetenes. The short life of the latter intermediates prevents their detection since they rapidly evolve to olefinic derivatives that are the thermodynamically most stable products (Figure 8). On the basis of calculations, the high stereoselectivity in the production of oxiranes has been justified as a result of the kinetic control of the whole process.

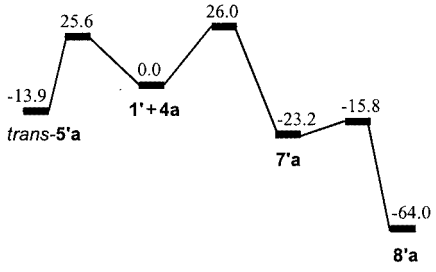



Figure 8. Gibbs energy diagram for the reactions between **1**′ and acetaldehyde in heptane solution; relative Gibbs energies at 1 atm and 298.15 K in kcal·mol$^{-1}$

## Experimental Section

**General Remarks:** All manipulations were performed under an inert atmosphere of nitrogen using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Carbene **1** was prepared according to reference.[10a] Aldehydes **4a**−**c** were purchased from Aldrich and distilled before each reaction. 250-MHz $^1$H, 62.5-MHz $^{13}$C, and 101.2-MHz $^{31}$P NMR spectra were recorded on a Bruker Avance 250 spectrometer. $^{31}$P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% $H_3PO_4$. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer. High-resolution mass spectra were obtained on a VG AutoSpec (Micromass Inst) spectrometer. Microanalyses were performed with a Carlo Erba Instruments EA-1108 apparatus.

**Computational Details:** Calculations have been done using the Gaussian-98 program.[18] Molecular geometries and harmonic vibrational frequencies have been determined using the B3LYP[19] functional with the 6-31G(d) basis set.[20] Single point calculations have been done on these geometries using the cc-pVTZ basis set[21] in order to reduce the basis set superposition error. The reported energies do not include the zero-point correction. The Gibbs energies at 1 atm and 298.15 K have been computed from the B3LYP/

cc-pVTZ energies and from B3LYP/6-31G(d) vibrational frequencies. The solvent effect has been estimated for the gas-phase stationary points at the B3LYP/6-31G(d) level of calculation using the conductor-like screening model[22] implemented in the Gaussian-98 program. We have considered heptane ($\varepsilon = 1.92$) as solvent to model pentane ($\varepsilon = 1.8$) used in the experiments.

**General Procedure for the Reactions of Carbene 1 with Aldehydes 4a−c:** Aldehyde **4a−c** (3 equiv.) was added to a 0.1 M pentane solution of carbene **1** at room temperature. The resulting mixture was stirred at room temperature, and the progress of the reaction was monitored by $^{31}$P-NMR spectroscopy. When the reaction was complete, an excess of elemental sulfur was added and the mixture was stirred for 2 h. The solvent was then evaporated under vacuum. Oxiranes **6a−c** and olefins **8a−c** were purified by column chromatography on silica gel (hexane/ether, 9:1).

**Oxirane 6a:** Crystals (341 mg, 30% yield). Mp 128−130 °C (from methanol). $^1$H NMR ($CDCl_3$): δ = 0.35 [s, 9 H, Si(C$H_3$)$_3$], 1.27−1.47 [m, 27 H, (C$H_3$)$_2$CHN- and C$H_3$], 3.38 (dq, $^3J_{H,P}$ = 8.8, $^3J_{H,H}$ = 5.8 Hz, 1 H, H$_{ring}$), 3.93 [m, 4 H, (CH$_3$)$_2$C$H$N-] ppm. $^{13}$C NMR ($CDCl_3$): δ = 1.61 [Si($CH_3$)$_3$], 16.31 (d, $^3J_{C,P}$ = 1.9 Hz; $CH_3$), 23.91−25.20 [($CH_3$)$_2$CHN-], 47.52 [d, $^2J_{C,P}$ = 5.7 Hz; (CH$_3$)$_2$$C$HN-], 49.00 [d, $^2J_{C,P}$ = 5.7 Hz, (CH$_3$)$_2$$C$HN-], 57.80 (d, $^1J_{C,P}$ = 73.4 Hz; P$C$Si), 58.07 ($CH_{ring}$) ppm. $^{31}$P NMR ($CDCl_3$): δ = 84.80 ppm. HRMS (EI) calcd. for $C_{18}H_{41}N_2OSiPS$: 392.2446, found 392.2441.

**Oxirane 6b:** Crystals (204 mg, 39% yield). Mp 113−114 °C (from pentane). $^1$H NMR ($CDCl_3$): δ = 0.33 [s, 9 H, Si(C$H_3$)$_3$], 0.99 (broad t, $^3J_{H,H}$ = 7.2 Hz, 3 H, C$H_3$CH$_2$CH$_2$-), 1.01−1.43 [m, 28 H, (C$H_3$)$_2$CHN- and CH$_3$C$H_2$C$H_2$-], 3.26 (dt, $^3J_{H,P}$ = 13.0, $^3J_{H,H}$ = 3.9 Hz, 1 H, H$_{ring}$), 3.82−4.06 [m, 4 H, (CH$_3$)$_2$C$H$N-] ppm. $^{13}$C NMR ($CDCl_3$): δ = 1.54 [Si($CH_3$)$_3$], 13.95 ($CH_3$CH$_2$CH$_2$-), 20.79 (CH$_3$$CH_2$CH$_2$-), 23.93−25.16 [($CH_3$)$_2$CHN-], 32.33 (CH$_3$CH$_2$$CH_2$-), 47.57 [d, $^2J_{C,P}$ = 5.3 Hz; (CH$_3$)$_2$$C$HN-], 49.06 [d, $^2J_{C,P}$ = 5.3 Hz, (CH$_3$)$_2$$C$HN-], 57.46 (d, $^1J_{C,P}$ = 73.9 Hz; P$C$Si), 62.20 (CH$_{ring}$) ppm. $^{31}$P NMR ($CDCl_3$): δ = 85.42 ppm. HRMS (EI) calcd. for $C_{20}H_{45}N_2OSiPS$: 420.2759, found 420.2755.

**Oxirane 6c:** Crystals (411 mg, 40% yield). Mp 94−97 °C (from methanol). $^1$H NMR ($CDCl_3$): δ = 0.32 [s, 9 H, Si(C$H_3$)$_3$], 1.04 [s, 3 H, (C$H_3$)$_2$CH-], 1.07 [s, 3 H, (C$H_3$)$_2$CH-], 1.29−1.42 [m, 24 H, (C$H_3$)$_2$CHN-], 2.97 (dd, $^3J_{H,P}$ = 9.9, $^3J_{H,H}$ = 9.0 Hz, 1 H, H$_{ring}$), 3.85−4.09 [m, 5 H, (CH$_3$)$_2$C$H$N- and (CH$_3$)$_2$C$H$-] ppm. $^{13}$C NMR ($CDCl_3$): δ = 1.44 [Si($CH_3$)$_3$], 19.66 [($CH_3$)$_2$CH-], 20.03 [($CH_3$)$_2$CH-], 22.97−28.05 [($CH_3$)$_2$CHN-], 46.09 [d, $^3J_{C,P}$ = 5.8 Hz; (CH$_3$)$_2$$C$H-], 47.61 [d, $^2J_{C,P}$ = 5.7 Hz; (CH$_3$)$_2$$C$HN-], 49.05 [d, $^2J_{C,P}$ = 5.7 Hz; (CH$_3$)$_2$$C$HN], 58.67 (d, $^1J_{C,P}$ = 71.5 Hz; P$C$Si), 67.81 ($CH_{ring}$) ppm. $^{31}$P NMR ($CDCl_3$): δ = 86.19 ppm. HRMS (EI) calcd. for [MH$^+$] $C_{20}H_{46}N_2OSiPS$: 421.2838, found 421.2829.

**Olefin 8a:** Oil (70 mg, 7% yield). $^1$H NMR ($CDCl_3$): δ = 0.28 [s, 9 H, Si(C$H_3$)$_3$], 1.16−1.25 [m, 24 H, (C$H_3$)$_2$CHN-], 1.92 (dd, $^4J_{H,P}$ = 3.1, $^3J_{H,H}$ = 0.7 Hz, 3 H, C$H_3$), 3.55 [m, 4 H, (CH$_3$)$_2$C$H$N-], 6.92 (dq, $^3J_{H,P}$ = 32.6, $^3J_{H,H}$ = 7.2 Hz, 1 H, C$H$) ppm. $^{13}$C NMR ($CDCl_3$): δ = 1.76 [Si($CH_3$)$_3$], 18.94−23.13 [($CH_3$)$_2$CHN-], 23.78 ($CH_3$), 46.35 [(CH$_3$)$_2$$C$HN-], 138.97 (d, $^2J_{C,P}$ = 110.6 Hz; P$C$Si), 152.93 (=$C$H) ppm. $^{31}$P NMR ($CDCl_3$): δ = 36.22 ppm. HRMS (EI) calcd. for $C_{18}H_{41}N_2OSiP$: 360.2726, found 360.2680; calcd. for [M$^+$ − CH$_3$] $C_{17}H_{38}N_2OSiP$: 345.2491, found 345.2467.

**Olefin 8b:** Oil (30 mg, 6% yield). $^1$H NMR ($CDCl_3$): δ = 0.27 [s, 9 H, Si(C$H_3$)$_3$], 0.93 (m, 3 H, C$H_3$CH$_2$CH$_2$-), 1.18−1.28 [m, 24 H, (C$H_3$)$_2$CHN-], 1.45 (m, 2 H, CH$_3$C$H_2$CH$_2$-), 2.26 (m, 2 H, CH$_3$CH$_2$C$H_2$-), 3.39−3.65 [m, 4 H, (CH$_3$)$_2$C$H$N-), 6.84 (dt, $^3J_{H,P}$ = 3.1, $^3J_{H,H}$ = 7.4 Hz, 1 H, C$H$) ppm. $^{13}$C NMR ($CDCl_3$): δ = 0.77 [Si($CH_3$)$_3$], 14.01 ($CH_3$$CH_2$CH$_2$-), 23.11−24.01 [($CH_3$)$_2$CHN- and $CH_3$CH$_2$$CH_2$-], 29.67 (CH$_3$CH$_2$$CH_2$-), 45.95 [d, $^3J_{C,P}$ = 5.7 Hz, (CH$_3$)$_2$$C$HN-], 46.48 [d, $^3J_{C,P}$ = 5.7 Hz, (CH$_3$)$_2$$C$HN-], 137.52 (d, $^2J_{C,P}$ = 110.4 Hz, P$C$Si), 158.30 (=$C$H) ppm. $^{31}$P NMR ($CDCl_3$): δ = 37.09 ppm. HRMS (EI) calcd. for $C_{20}H_{45}N_2OSiP$: 388.3039, found 388.3018; calcd. for [M$^+$ − CH$_3$] $C_{19}H_{42}N_2OSiP$: 373.2804, found 373.2838.

**Olefin 8c:** Oil (104 mg, 11% yield). $^1$H NMR ($CDCl_3$): δ = 0.27 [s, 9 H, Si(C$H_3$)$_3$], 0.96 [s, 3 H, (C$H_3$)$_2$CH-], 0.98 [s, 3 H, (C$H_3$)$_2$CH], 1.20−1.26 [m, 24 H, (C$H_3$)$_2$CHN-], 2.76 [m, 1 H, (CH$_3$)$_2$C$H$-], 3.57 [sept, $^2J_{H,P}$ = 6.9 Hz, 4 H; (CH$_3$)$_2$C$H$N-], 6.61 (dd, $^3J_{H,P}$ = 32.8, $^3J_{H,H}$ = 10.6 Hz, 1 H; C$H$) ppm. $^{13}$C NMR ($CDCl_3$): δ = 2.11 [Si($CH_3$)$_3$], 21.93−24.10 [($CH_3$)$_2$CHN- and ($CH_3$)$_2$CH-], 31.91 [(CH$_3$)$_2$$C$H-] 46.51 [(CH$_3$)$_2$$C$HN-], 134.26 (d, $^2J_{C,P}$ = 109.7 Hz, P$C$Si), 164.17 (=$C$H) ppm. $^{31}$P NMR ($CDCl_3$): δ = 37.65 ppm. HRMS (EI) calcd. for $C_{20}H_{45}N_2OSiP$: 388.3039, found 388.3004; calcd. for [M$^+$ − CH$_3$] $C_{19}H_{42}N_2OSiP$: 373.2804, found 373.2828.

**Crystal Data for 6a and 6c. Compound 6a:** $C_{18}H_{41}N_2OSiPS$, $M$ = 392.65, orthorhombic, *Pbca*, $a$ = 17.169(2), $b$ = 14.149(1), $c$ = 18.955(2) Å, $V$ = 4604.7(7) Å$^3$, $Z$ = 8, $T$ = 193(2) K, 13609 reflections (3859 independent, $R_{int}$ = 0.0566), largest electron density residue: 0.405 e·Å$^{-3}$, $R_1$ [for $I > 2\sigma(I)$] = 0.0447 and $wR_2$ = 0.1141 (all data) with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

**Compound 6c:** $C_{20}H_{45}N_2OSiPS$, $M$ = 420.7, orthorhombic, *Pbca*, $a$ = 13.211(1), $b$ = 19.307(1), $c$ = 20.151(1) Å, $V$ = 5139.9(5) Å$^3$, $Z$ = 8, $T$ = 173(2) K, 28852 reflections (5262 independent, $R_{int}$ = 0.0272), largest electron density residue: 0.490 e·Å$^{-3}$, $R_1$ [for $I > 2\sigma(I)$] = 0.0356 and $wR_2$ = 0.0986 (all data).

Data for both structures were collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with Mo-$K\alpha$ radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97)[23] and all non-hydrogen atoms were refined anisotropically using the least-squares method on $F^2$.[24]

CCDC-201584 and -201585 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving/html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; (fax: +44−1223/336-033; or E-mail: deposit@ccdc.cam.com.ac.uk).

## Acknowledgments

O.I. thanks the DGU for a predoctoral fellowship. Financial support through the projects BQU2001-1907 (MCyT) and ACI 2001-35, 2001SGR 00182 (DURSI, Generalitat de Catalunya) (Spain), and from CNRS (France) is gratefully acknowledged.

[1] For a review on the reactivity of epoxides, see: M. Bartek, K. L. Lang, in: *The Chemistry of Functional Groups, Supplement E* (Ed.: S. Patai) Wiley, New York, **1980**, p. 609.

[2] [2a] S. Hatakeyama, N. Ochi, S. Takano, *Chem. Pharm. Bull.* **1993**, *41*, 1358. [2b] D. M. Jerina, J. W. Daly, *Science* **1974**, *185*, 573. [2c] A. R. Becker, J. M. Janusz, T. C. Bruice, *J. Am. Chem. Soc.* **1979**, *101*, 5679. [2d] F. Sato, Y. Kobayashi, *Synlett* **1992**, 849.

[3] [3a] D. Hendlin, E. O. Stapley, M. Jackson, H. Wallick, A. K. Miller, F. J. Wolf, T. W. Miller, L. Chaier, F. M. Kahan, E. L. Foltz, H. B. Woodruff, J. M. Mata, S. Hernandez, S. Mochales,

*Science* **1969**, *166*, 122. [3b] T. Hori, M. Horiguchi, A. Hayashi, *Biochemistry of Natural C-P Compounds*, Maruzen, Kyoto Branch Publishing Service, **1984**.

[4] [4a] For a review on the synthesis of 1,2-epoxyalkylphosphonates, see: B. Iorga, F. Eymery, P. Savignac, *Synthesis* **1999**, 207. [4b] F. Hammerschmidt, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 341. [4c] P. Liu, K. Murakami, T. Seki, X. He, S.-M. Yeung, T. Kuzuyama, H. Seto, H.-W. Liu, *J. Am. Chem. Soc.* **2001**, *123*, 4619.

[5] For a review on ylide formation from transient carbenes, see: A. Padwa, S. F. Hornbuckle, *Chem. Rev.* **1991**, *91*, 263.

[6] [6a] P. De March, R. Huisgen, *J. Am. Chem. Soc.* **1982**, *104*, 4952. [6b] M. Regitz, *Synthesis* **1972**, 351.

[7] For recent reviews on N-heterocyclic carbenes, see: [7a] A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913. [7b] D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39. [7c] W. A. Herrmann, T. Weskamp, V. P. W. Bohm, *Adv. Organomet. Chem.* **2001**, *48*, 1. [7d] L. Jafarpour, S. P. Nolan, *Adv. Organomet. Chem.* **2001**, *46*, 181. [7e] Herrmann, W. A, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.

[8] D. Enders, U. Kallfass, *Angew. Chem. Int. Ed.* **2002**, *41*, 1743.

[9] [9a] A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.* **1988**, *110*, 6463. [9b] For a review on stable phosphanyl(silyl)carbenes, see: G. Bertrand, in: *Carbene Chemistry from Fleeting Intermediates to Powerful Reagents*, Marcel Dekker, New York, **2002**, p. 177.

[10] [10a] A. Igau, A. Baceiredo, G. Trinquier, G. Bertrand, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 621. [10b] G. R. Gillette, A. Igau, A. Baceiredo, G. Bertrand, *New J. Chem.* **1991**, *15*, 393.

[11] [11a] A.-H. Li, L.-X. Dai, V. K. Aggarwal, *Chem. Rev.* **1997**, *97*, 2341. [11b] V. K. Aggarwal, *Synlett* **1998**, 329.

[12] [12a] B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863. [12b] O. L. Kolodiazhnyi, *Phosphorus Ylides. Chemistry and Application in Organic Synthesis*; Wiley-VCH: Weinheim, **1999**.

[13] In the case of benzaldehyde the corresponding thioxophosphoranyl oxirane has also been crystallized, and an X-ray diffraction study showed the same diastereoselectivity, contrary to the first attribution based on the NMR spectroscopic data.[10]

[14] [14a] D. A. Dixon, K. D. Dobbs, A. J. Arduengo III, G. Bertrand, *J. Am. Chem. Soc.* **1991**, *113*, 8782. [14b] L. Nyulászi, D. Szieberth, J. Réffy, T. Veszprémi, *J. Mol. Struct. THEOCHEM* **1998**, *453*, 91. [14c] W. W. Schoeller, A. J. B. Rozhenko, A. Alijah, *J. Organomet. Chem.* **2001**, *617–618*, 435.

[15] P–C = 1.532 Å, C–Si = 1.795 Å, P–C–Si = 152.6°. See ref.[16]

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

[17] The energies of the HOMO and LUMO of **2′** are −0.1905 and −0.0151 a. u, whereas the energies of acetaldehyde π and π* orbitals are −0.3644 and −0.0218 a. u., respectively.

[18] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh PA, **1998**.

[19] [19a] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. [19b] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[20] [20a] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724. [20b] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257. [20c] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209. [20d] M. S. Gordon, *Chem. Phys. Lett.* **1980**, *76*, 163. [20e] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[21] R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796.

[22] [22a] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* **1993**, 799. [22b] V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.

[23] M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

[24] SHELXL-97, *Program for Crystal Structure Refinement*, G. M. Sheldrick, University of Göttingen, **1997**.

Received April 11, 2003