Tetrahedron: *Asymmetry* 19 (2008) 2353–2358

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Understanding the π-facial diastereoselectivity in the addition of chiral diaminophosphino(silyl)carbenes to activated olefins

Ona Illa [a], Xavier Bagan [a], Antoine Baceiredo [b,*], Vicenç Branchadell [a,*], Rosa M. Ortuño [a,*]

[a] *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*
[b] *Laboratoire Hétérochimie Fondamentale et Appliquée, UMR 5069, Université Paul Sabatier, 118 Route de Narbonne, 31062 Toulouse cedex 09, France*

ARTICLE INFO

Article history:
Received 30 July 2008
Accepted 23 October 2008
Available online 20 November 2008

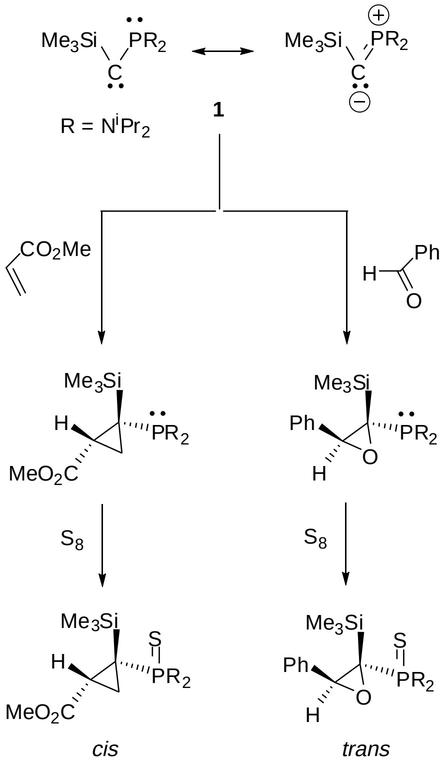
ABSTRACT

The synthesis of a new chiral diaminophosphino(silyl)carbene, based on the use of (*R*,*R*)-cyclohexane-*trans*-1,2-diamine, is described. Its reaction with methyl acrylate afforded a cyclopropane derivative as a single diastereomer. The diastereoselectivity in the addition reactions between olefins and chiral carbenes derived from C_2-symmetric diamines has also been studied by theoretical calculations, which establish that it has a steric origin; we report a rationale to predict the absolute configuration of the adducts.

1. Introduction

Chiral and polyfunctional cyclopropanes are useful compounds either by themselves or as potent scaffolds in the preparation of sophisticated molecules with cyclic or acyclic skeletons.[1] The cyclopropane subunit is present in natural and designed compounds, while chiral cyclopropanes play an important role in bio-organic chemistry.[2] Therefore, the search for efficient and stereoselective synthetic methods for their preparation is a very active field. The most common methods used for the asymmetric synthesis of cyclopropane derivatives are the Simmons–Smith reaction[3] and metal-catalyzed decomposition of diazo compounds in the presence of alkenes.[4] Nevertheless, these methods, albeit highly enantioselective, usually provide low diastereoselection.

Bis(diisopropylamino)phosphino(trimethylsilyl)carbene **1** is a stable singlet carbene,[5] which adds to activated olefins with total *syn*-diastereoselectivity to afford cyclopropanes with a *cis*-stereochemistry with respect to the phosphanyl group.[6] This stereoselectivity is opposite to that observed in the addition of this carbene to aldehydes providing oxiranes with a *trans*-configuration[7] (Scheme 1). The predominant formation of *cis*-cyclopropanes has been interpreted on the basis of theoretical calculations, which state that these cyclopropanation reactions proceed via asynchronous concerted mechanisms involving early transition structures with a significant charge transfer from the carbene to the alkene moiety. The geometric features of these transition structures preclude a significant overlap between the orbitals required for secondary orbital interactions between the reactants, and the diastereoselectivity observed experimentally stems from favorable electrostatic and steric interactions between the reactants leading to diastereoisomers, in which the phosphanyl and carbonyl or aryl groups are *cis* to each other.[8]

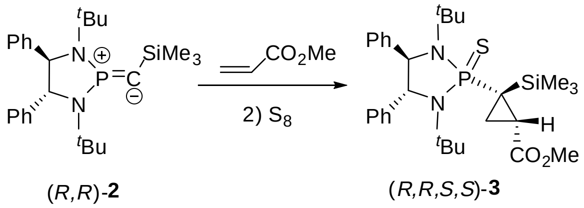


Scheme 1.

---

[*] Corresponding authors. Tel.: +34 93 5811602; fax: +34 93 5811265 (R.M.O.).
E-mail addresses: baceired@chimie.ups-tlse.fr (A. Baceiredo), vicenc.branchadell@uab.es (V. Branchadell), rosa.ortuno@uab.es (R. M. Ortuño).

0957-4166/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2008.10.021

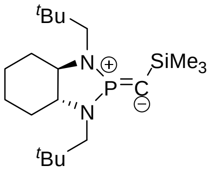


Scheme 2.

The asymmetric version of this cyclopropanation reaction was first undertaken by a [1+2] cycloaddition of **1** to olefins bearing a chiral auxiliary. In this case, asymmetric inductions up to 87% de were observed, although with low chemical yields.[9] The next alternative way explored consisted of the use of chiral carbenes.

Phosphino(silyl)carbenes are best described as phosphorus vinyl ylides with a planar phosphorus atom;[8,10] only those bearing amino substituents at the phosphorus atom are stable.[5c] This feature was taken into account to introduce chirality by using a cyclic diamino C_2-symmetric system at phosphorus. Thus, the first stable, chiral phosphino(silyl)carbenes **2** (both enantiomers) were designed and reacted with methyl acrylate to afford cyclopropanes with total *syn*-diastereoselectivity and excellent enantioselectivity (Scheme 2). The stereochemistry of these compounds was confirmed by X-ray structural analysis,[11] while the enantioselectivity was justified by considering steric effects exerted by the phenyl groups.

Nevertheless, the synthetic route to **2** is long and difficult. During the course of those studies, the results obtained demonstrated that the stability of these carbenes is strongly related to the steric bulk of the amino substituents at phosphorus. Herein, we report on the synthesis and reactivity of a new type of chiral phosphino(silyl)carbenes exemplified by carbene **4**. In addition, we provide a rationale, based on theoretical calculations, to understand and predict the enantioselectivity of the reactions between olefins and chiral carbenes **2** and **4**.



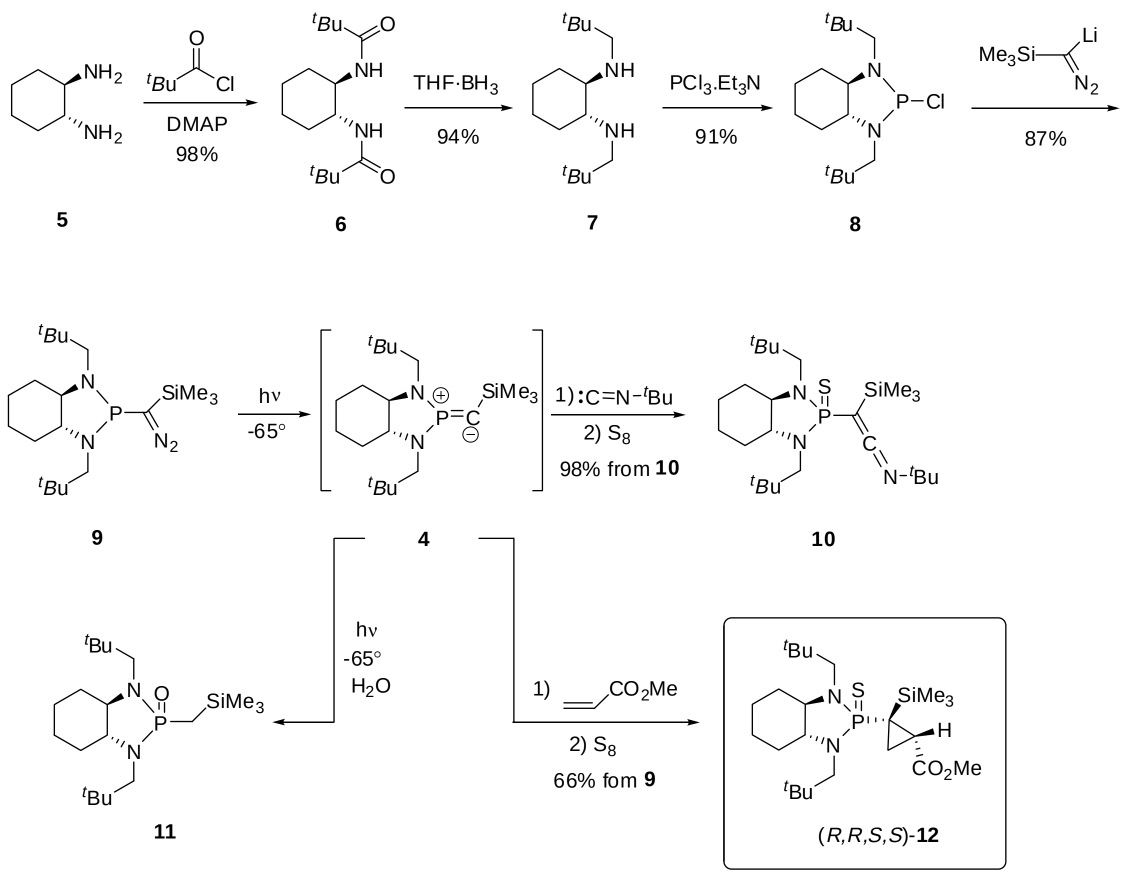
4

2. Results and discussion

2.1. Synthesis and reactivity of carbene 4 toward methyl acrylate

Carbene **4** bears bulky substituents in which the *tert*-butyl groups are spacered from nitrogen by intercalating a methylene group to confer more flexibility on the molecule. The contribution of the *N*-alkyl groups to the stereoselectivity was expected. The synthesis of **4** relies on the use of C_2-symmetric cyclohexane-*trans*-1,2-diamine, which is commercially available in both enantiomeric forms. The (*R*,*R*)-enantiomer **5** was used in this work for the preparation of **4**; details on the synthetic sequence leading to this carbene are provided in Scheme 3.

On the basis of a previously described methodology,[12] chiral diamine **5** was reacted with pivaloyl chloride in the presence of



Scheme 3.

DMAP to afford diamide **6** in 98% yield. Reduction of the diamide was carried out by reaction with BH_3·THF for 3 days at room temperature followed by stirring in the presence of HCl (pH 2) to destroy the amine-boron complex. The previously known diamine **7** was thus obtained in 94% yield. Subsequent reaction with PCl_3 in the presence of two equivalents of triethylamine afforded the new chlorophosphine **8** in 91% yield. In the next step, commercial trimethylsilyldiazomethane was treated with butyllithium, and the resultant lithium salt was reacted with **8** to provide diazophosphine **9** in 87% yield.

Carbene **4** was then generated by photolysis via irradiation of **9** in THF at −65 °C for 18 h. The reaction was monitored by ^{31}P NMR spectroscopy following the disappearance of the peak at $\delta = 127.0$, but any defined new signal was not observed, suggesting that carbene **4**, if formed, must not be stable under these experimental conditions. However, the transient carbene **4** could be trapped when photolysis was performed in the presence of *tert*-butylisonitrile, and the formation of the corresponding keteneimine ($\delta = 133.7$) was observed. The IR spectrum provided further information of the reaction progress since the absorption of the diazophosphine at 2027 cm^{-1} changed to a band at 1982 cm^{-1}, which is typical of the cumulene.

After completion, elemental sulfur was added to stabilize the phosphine by thiolation giving thioxo(phosphino)keteneimine **10,** which was isolated in almost quantitative yield. Although the preparative work was performed under an inert atmosphere, and freshly dried solvents and reagents were used, carbene **4** is very sensitive to the presence of traces of water in the reaction medium and phosphonodiamide **11** always resulted in variable amounts when precursor diazocompound **9** was irradiated.

Bis(*tert*-butyl) carbene **4** was generated and reacted in situ with methyl acrylate to provide, after thiolation, cyclopropane (*R*,*R*,*S*,*S*)-**12** in 66% yield as a single stereoisomer. This compound was obtained as an oil, and therefore was not suitable for X-ray structural analysis. Otherwise, attempts to correlate it with a derivative of **3** failed. The relative *cis*-stereochemistry with respect to the phosphine group was assumed by comparison with other previous results on the reactions between similar phosphino(silyl)carbenes and olefins.[6] The absolute configuration was assigned on the basis of theoretical calculations as described below. Since the precursor diamine (*S*,*S*)-**5** is also available, the preparation of the enantiomeric cyclopropane (*S*,*S*,*R*,*R*)-**12** is guaranteed.

2.2. Theoretical calculations

Theoretical calculations were carried out in order to investigate the origin of the diastereoselectivity observed in the [1+2] cycloaddition reactions involving carbenes **2** and **4**, and methyl acrylate. Achiral carbene **1** was also considered for comparison. Figure 1 shows the optimized structures of the studied carbenes. The cyclic carbenes **2** and **4** present shorter P–C and C–Si bonds than the acyclic **1**. Regarding the P–C–Si bond angle, the values vary within a wide range (145–173°). The largest value was observed in the case of carbene **2**, where the cyclic nitrogen atoms are substituted by bulky *tert*-butyl groups.

Atomic spheres represent atoms in the first layer in ONIOM calculations.

For each carbene, we studied the cycloadditon reaction with methyl acrylate. Since experimentally only *trans*-adducts were observed,[6,8] we only considered the formation of this type of adducts.

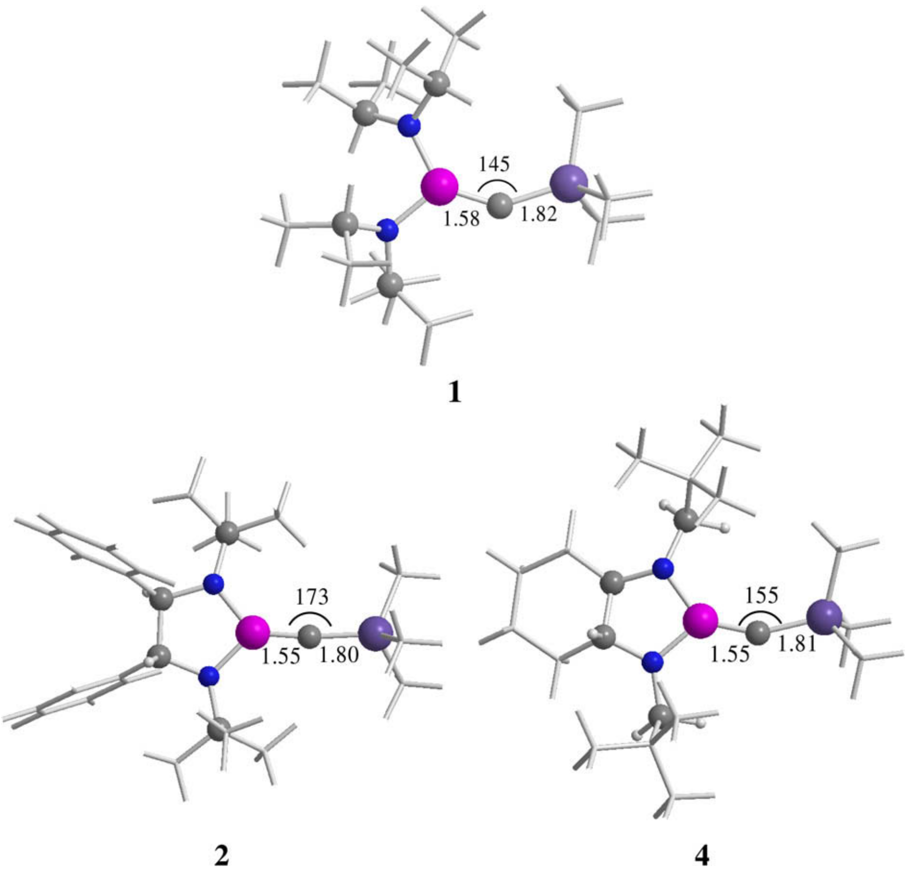


Figure 1. Structures of carbenes **2** and **4** optimized at the ONIOM(B3LYP/6-31G(d):AM1) level of calculation. Bond distances in Å and bond angle in °. Atomic spheres represent atoms in the first layer in ONIOM calculations.

Table 1
Lengths of the forming bonds[a] at the transition states and potential energy barriers[b] computed for the reactions between carbenes and methyl acrylate

Carbene	Diastereomer	r_1	r_2	$\Delta E^{\ddagger}$	
				ONIOM[c]	B3LYP[d]
1		2.191	2.894	6.4	7.8 (13.7)
2	*R,R,S,S*	2.179	2.785	8.2	13.4 (19.1)
	R,R,R,R	2.144	2.788	12.2	19.1 (23.9)
4	*R,R,S,S*	2.109	2.769	7.4	8.4 (12.7)
	R,R,R,R	2.093	2.756	10.4	14.1 (18.6)

[a] In Å. See Fig. 2.
[b] In kcal mol^{-1}.
[c] ONIOM(B3LYP/6-31G(d):AM1) level of calculation.
[d] B3LYP//ONIOM(B3LYP/6-31G(d):AM1) level of calculation. Values corrected for basis set superposition error are given in parentheses.

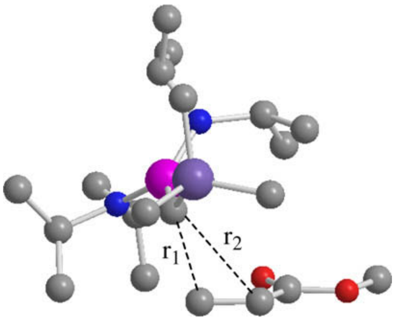


Figure 2. Structure of the transition state corresponding to the reaction between carbene **1** and methyl acrylate. Hydrogen atoms have been omitted for clarity.

For the reactions involving chiral carbenes, we have studied the formation of two possible diastereomers. The results are summarized in Table 1, and the structures of the transition states are shown in Figures 2 and 3.

Table 1 shows that the lengths of the forming C–C bonds (r_1 and r_2) are lower for the transition states of the reactions of carbenes **2** and **4** than that for the non-chiral carbene **1**. The differences are the largest ones for the (*R*,*R*,*R*,*R*)-transition states.

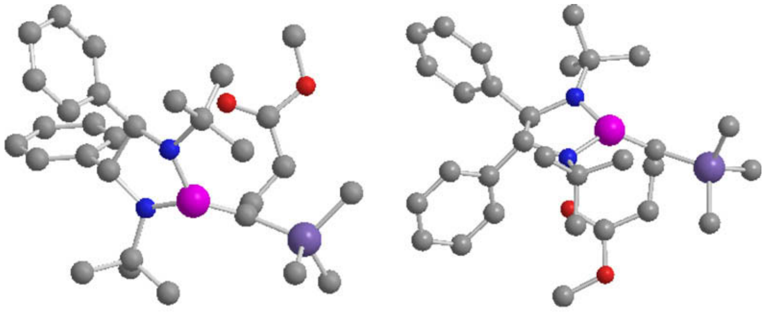
For carbene **2**, our results predict that the (*R*,*R*,*S*,*S*)-diastereomer of cyclopropane **3** is kinetically the most favorable one; this is in excellent agreement with the experimental results. From the potential energy barriers computed at the B3LYP level including correction for basis set superposition error, the ratio between the rates of formation of (*R*,*R*,*S*,*S*)- and (*R*,*R*,*R*,*R*)-diastereomers is predicted to be around 3300 at 25 °C.

For the reaction of carbene **4**, the formation of the (*R*,*R*,*S*,*S*)-diastereomer is also predicted to be the most favorable one. In this case, the ratio between diastereomeric reaction rates at room temperature is around 21,000. From this result, the only product experimentally obtained may be assigned as the (*R*,*R*,*S*,*S*)-diastereomer.

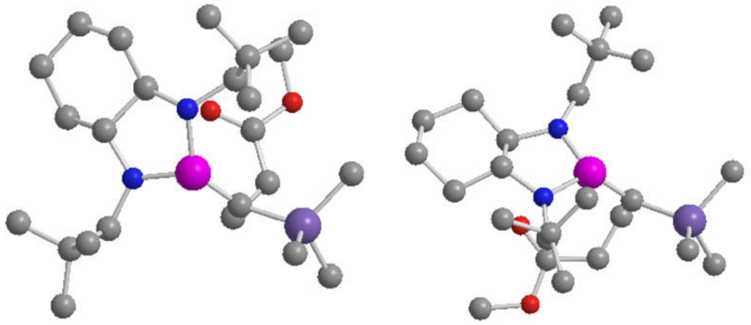
The results obtained up to now show that chiral carbenes **2** and **4** lead to the formation of enantiomerically pure chiral cyclopropanes. The origin of this high diastereoselectivity may be analyzed through a partition analysis of the potential energy barriers. The potential energy barrier ($\Delta E^{\ddagger}$) for a cycloaddition reaction between a carbene and methyl acrylate can be partitioned into several terms

$$\Delta E^{\ddagger} = E_{\text{prep}} + E_{\text{Pauli}} + E_{\text{elstat}} + E_{\text{orb}}$$

The preparation energy, E_{prep}, is the energy necessary to distort the reactant molecules from their equilibrium geometries to the geometries they have at the transition state. E_{Pauli} is the Pauli repulsion term associated to closed-shell repulsions between carbene and methyl acrylate fragments at the transition state. E_{elstat} is the electrostatic interaction energy arising from the interaction between both fragments, each one having the electron density that it would have in the absence of the other fragment. The orbital



2- TS *(R,R,S,S)* **2**- TS *(R,R,R,R)*



4- TS *(R,R,S,S)* **4**- TS *(R,R,R,R)*

Figure 3. Structures of the transition states for the reactions of chiral carbenes with methyl acrylate. Hydrogen atoms have been omitted for clarity.

interaction term, E_{orb}, arises when the electron densities of both fragments are allowed to relax, and it accounts for charge transfer and polarization.

If we compare the contribution of each term to the energy barriers of all reactions (Table 2), we can observe that the largest variation takes place in the preparation energy term. This contribution is lower than 10 kcal mol^{-1} for carbene **1**, whereas it reaches much larger values for carbenes **2** (both transition states) and **4** [(*R,R,R,R*)-transition state]. The contribution of the Pauli repulsion term varies within a range of 10.1 kcal mol^{-1}, while the electrostatic and orbital interaction terms vary only in 4.9 and 5.2 kcal mol^{-1}, respectively.

Table 2

Partition[a] of the potential energy barriers[b] for the reactions between carbenes and methyl acrylate

Carbene	Diastereomer	E_{prep}	E_{Pauli}	E_{elstat}	E_{orb}	$\Delta E^{\ddagger}$
1		9.8	91.7	−47.0	−43.5	11.0
2	(*R,R,S,S*)	18.3	81.6	−42.1	−39.9	17.9
	(*R,R,R,R*)	22.4	86.5	−42.7	−43.1	23.1
4	(*R,R,S,S*)	11.7	85.1	−42.9	−42.4	11.5
	(*R,R,R,R*)	17.1	89.2	−44.1	−45.1	17.0

[a] See text for definitions.
[b] All values in kcal mol^{-1}.

For carbenes **2** and **4**, the major contribution to the differences between diastereomeric energy barriers comes both from the preparation energy and from the Pauli repulsion terms. These terms account for the steric requirements associated with the formation of the (*R,R*)-diastereomer. Geometry distortion of the carbene may partly relieve the steric repulsion through a slight increase of electrostatic and orbital stabilization.

Therefore, from the analysis of the different contributions to the energy barriers, we can state that the diastereoselectivity in the reactions between chiral diaminophosphino(silyl)carbenes and methyl acrylate has a steric origin.

3. Conclusions

From these studies we can conclude that chiral diaminophosphino(silyl)carbenes add to olefins with total diastereoselectivity, which includes *cis*/*trans*-stereoselectivity and (*R*/*S*) asymmetric induction. Theoretical calculations afford a rationale to understand the origin of the optical diastereoselectivity, which lies on the steric effects provoked by the bulky substituents linked to the amino groups, and allow us to predict the absolute configuration of the resultant cyclopropane derivatives.

4. Experimental

4.1. Computational details

Calculation has been carried out using the GAUSSIAN-03 program.[13] The structures have been fully optimized using the multilayer ONIOM method with two layers.[14] The first layer includes methyl acrylate, and the carbene atoms are represented by spheres in Figure 1. For this first layer, the B3LYP density functional[15] with the 6-31G(d) basis set has been used.[16] For the second layer, we have used the semi-empirical AM1 method.[17] All stationary points have been characterized through the calculation of harmonic vibrational frequencies at this level of calculation. The energies of stationary points have been recomputed at the B3LYP/6-31G(d) level of calculation. Basis set superposition error on potential energy barriers has been estimated through the counterpoise method.[18] Finally, potential energy barriers of the reactions have been analyzed through the energy partition scheme[8] implemented in the ADF program[19] using the B3LYP density functional[15,20] and a triple-zeta plus polarization basis set.

4.2. General experimental

All manipulations were performed under an inert atmosphere of nitrogen by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4.

4.3. (3a*R*,7a*R*)-2-Chloro-1,3-dineopentylperhydro-1,3,2-benzodiazaphosphole, 8

Freshly distilled PCl_3 (0.28 mL, 3.2 mmol) and TEA (1.3 mL, 9.5 mmol) were successively added to an ice-cooled solution containing diamine **7** (0.8 g, 3.2 mmol), prepared according to the literature,[12] in dry THF (10 mL) under a nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 2 h. Solvent was removed under reduced pressure and pentane (15 mL) was added to the residue. The precipitated salts were filtered and rinsed with pentane. The combined organic solutions were evaporated under vacuo to afford chlorophosphine **8** (0.9 g, 91% yield) as a rather unstable yellowish dense oil, which was identified by its spectroscopic data. ^1H NMR (250 MHz, benzene-d_6): δ 0.90–1.05 (m, 18H), 1.20–2.05 (m, 8H), 2.30–3.40 (m, 6H). ^{13}C NMR (62.5 MHz, benzene-d_6): δ 24.4, 24.5, 28.2 (6C), 29.8, 30.0, 31.5, 33.2, 55.2 (d, $^2J_{P-C}$ = 20.5 Hz), 56.0 (d, $^2J_{P-C}$ = 20.5 Hz), 64.1 (d, $^2J_{P-C}$ = 8.6 Hz), 65.5 (d, $^2J_{P-C}$ = 5.2 Hz). HRMS (CI) $C_{16}H_{32}ClN_2P$ (M^+) requires: 318.1992, found: 318.1983.

4.4. (3a*R*,7a*R*)-2-[Diazo(trimethylsilyl)methyl]-1,3-dineopentylperhydro-1,3,2-benzodiazaphosphole, 9

At first, 2.0 M trimethylsilyldiazomethane in hexane (1.4 mL, 2.9 mmol) was dissolved in anhydrous THF (10 mL) and cooled into a liquid nitrogen–ethyl acetate bath. Subsequently, 1.6 M BuLi in hexane (2.0 mL, 3.2 mmol) was added and the mixture was stirred for 30 min under a nitrogen atmosphere. Then, a solution of chlorophosphine **8** (0.9 g, 2.9 mmol) in 8 mL of anydrous THF was added via canula. The mixture was allowed to reach room temperature and stirred for 3 h. Solvents were removed under reduced pressure, and anhydrous pentane (15 mL) was added. The precipitated salts were removed and washed with pentane. Finally, the solvent was evaporated to afford diazophosphine **9** (1.0 g, 87% yield) as an unstable red dense oil that was identified by its spectroscopic data. IR: 2027.2 cm^{-1}. ^1H NMR (250 MHz, benzene-d_6): δ 0.25 (s, 9H), 1.12 (s, 9H), 1.14 (s, 9H), 0.90–1.80 (m, 8H), 2.05–3.25 (m, 6H). ^{13}C NMR (62.5 MHz, benzene-d_6): δ -0.3 (3C), 24.9, 25.2, 28.7 (6C), 30.8 (d, $^2J_{P-C}$ = 77.2 Hz), 31.7, 34.2, 32.9 (2C), 65.1, 65.6, 67.1 (d, $^2J_{P-C}$ = 7.8 Hz), 71.8 (d, $^2J_{P-C}$ = 5.9 Hz). HRMS (CI) $C_{20}H_{41}N_4PSi$ (M^+) requires: 396.6256, found: 396.6242.

4.5. (3a*R*,7a*R*)-2-(2′-*tert*-Butylimino-1′-trimethylsilylethen-1′-yl-1,3-dineopentylperhydro-1,3,2-λ^5-benzodiazaphosphol-2-thione, 10

A mixture containing diazophosphine **9** (400 mg, 0.1 mmol) and *tert*-butylisonitrile (23 μL, 0.2 mmol) in 0.4 mL of anhydrous THF, cooled at −65 °C, was irradiated for 18 h. Then excess of elemental sulfur was added and the mixture was stirred at room temperature for 30 min. Solvent was removed under reduced pressure and non-reacted sulfur was filtered off to afford compound **10** (47 mg, 98% yield) as an oil. $[\alpha]_D = -42.9$ (*c* 0.89, CH_2Cl_2). ^{31}P NMR (101.2 MHz, $CDCl_3$): δ 98.1. ^1H NMR (250 MHz, $CDCl_3$): δ 0.24 (s, 9H), 0.92 (s, 9H), 0.96 (s, 9H), 1.18–1.27 (m, 4H), 1.33 (s, 9H), 1.78 (m, 2H), 1.95 (m, 2H), 2.24 (dd, $^{3}J_{P-H}$ = 17.4 Hz, $^{2}J_{H-H}$ = 14.3 Hz, 1H), 2.33 (dd, $^{2}J_{H-H}$ = 15.0 Hz, $^{3}J_{P-H}$ = 12.0 Hz, 1H), 2.57 (m, 1H), 2.71 (m, 1H), 3.09 (dd, $^{3}J_{P-H}$ = 20.0 Hz, $^{2}J_{H-H}$ = 15.0 Hz, 1H), 3.78 (dd, $^{3}J_{P-H}$ = 21.1 Hz, $^{2}J_{H-H}$ = 14.5 Hz, 1H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 1.3 (3*C*), 24.4, 25.0, 28.8–32.1 (13*C*), 49.8 (d, $^{1}J_{P-C}$ = 91.6 Hz), 56.7, 58.3, 58.6, 65.5 (d, $^{2}J_{P-C}$ = 3.8 Hz), 66.9 (d, $^{2}J_{P-C}$ = 2.9 Hz), 160.8. ESI-MS (*m*/*z*): 506.3 (M+Na$^+$). HRMS (CI) $C_{25}H_{50}N_3PSSi$ (M$^+$) requires: 483.3232, found: 483.3241.

4.6. (3a*R*,7a*R*)-2-[(Trimethylsilyl)methyl]-1,3-dineopentylperhydro-1,3,2-λ^5-benzodiazaphosphol-2-one, 11

This compound was obtained as an oil under irradiation of diazophosphine **9** as described above but in the presence of water. $[\alpha]_D = -38.2$ (*c* 2.20, CH$_2$Cl$_2$). ^{31}P NMR (101.2 MHz, CDCl$_3$): δ 48.11. ^{1}H NMR (250 MHz, CDCl$_3$): 0.13 (s, 9H), 0.89 (2 s, 18H), 1.14–1.31 (m, 6H), 1.87 (m, 1H), 1.98 (m, 1H), 2.22 (m, 2H), 2.41 (m, 1H), 2.62 (dd, $^{3}J_{P-H} = {}^{2}J_{H-H}$ = 14.7 Hz, 1H), 2.74 (m, 1H), 3.29 (dd, $^{3}J_{P-H}$ = 15.9 Hz, $^{2}J_{H-H}$ = 14.7 Hz, 1H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 0.8 (3*C*), 18.6 (d, $^{1}J_{P-C}$ = 99.6 Hz), 24.5, 24.8, 28.4 (3*C*), 28.7 (3*C*), 29.7–32.53 (4*C*), 54.4, 57.2, 63.5 (d, $^{2}J_{P-C}$ = 10.0 Hz), 66.0 (d, $^{2}J_{P-C}$ = 5.7 Hz). ESI-MS (*m*/*z*): 387.3 (M+H)$^+$, 409.3 (M+Na)$^+$. HRMS (CI) $C_{20}H_{43}N_2OPSi$ (M$^+$) requires: 386.2882, found: 386.2880.

4.7. (3a*R*,7a*R*,1′*S*,2′*S*)-2-(2′-Methoxycarbonyl-1′-trimethylsilylcycloprop-1′-yl)-1,3-dineopentylperhydro-1,3,2-λ^5-benzodiazaphosphol-2-thione, (*R*,*R*,*S*,*S*)-12

A mixture of diazophosphine 9 (350 mg, 0.9 mmol) and freshly distilled methyl acrylate (0.08 mL, 0.9 mmol) in anhydrous THF (4 mL) was cooled at −65 °C, and irradiated for 18 h. Excess elemental sulfur was then added and the mixture was allowed to reach room temperature and stirred for 30 min. Solvent was removed at reduced pressure and the residue was chromatographed on silica gel (9:1 hexane–ethyl acetate) to afford cyclopropane (*R*,*R*,*S*,*S*)-12 as an oil (247 mg, 66% yield). $[\alpha]_D = -33.3$ (*c* 2.20, CH$_2$Cl$_2$). ^{31}P NMR (101.2 MHz, CDCl$_3$): δ 102.79. ^{1}H NMR (250 MHz, CDCl$_3$): δ 0.15 (s, 9H), 0.81–1.00 (m, 3H,), 0.92–1.04 (2 s, 2 × 9H), 1.2–3.2 (complex absorption, 14H), 3.68 (s, 3H). ^{13}C NMR (62.5 MHz, CDCl$_3$): δ 0.8 (3*C*), 14.2, 18.6 (d, $^{1}J_{P-C}$ = 195 Hz), 25.0, 25.8, 28.0 (3*C*), 30.8 (3*C*), 28.0–34.1 (5*C*), 52.5, 54.8, 55.0, 65.2 (d, $^{2}J_{P-C}$ = 9.1 Hz), 66.2 (d, $^{2}J_{P-C}$ = 5.7 Hz), 171.5. ESI-MS (*m*/*z*): 509.3 (M+Na)$^+$. HRMS (CI) $C_{24}H_{47}N_2O_2PSSi$ (M$^+$) requires: 486.2865, found: 486.2859.

Acknowledgments

Financial support from the Ministerio de Educación y Ciencia (CTQ2007-61704/BQU), the Generalitat de Catalunya (2005SGR-103, LEA-LTPMM) (Spain), and the CNRS (France) (LEA-368) is gratefully acknowledged.

References

1. (a) Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73; (b) Wong, H. N. C.; Hon, M.-Y.; Tse, C.-W.; Yip, Y.-C.; Tanko, J.; Hudlicky, T. *Chem. Rev.* **1989**, *89*, 165; (c) de Meijere, A.; Wessjohan, L. *Synlett* **1990**, 20; (d) Hudlicky, T.; Fan, R.; Reed, J. W.; Gadamasetti, K. G. *Org. React.* **1992**, *41*, 1; (e) Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977.
2. (a) Suckling, C. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 537; (b) Salaün, J.; Baird, M. S. *Curr. Med. Chem.* **1995**, *2*, 511; (c) Pietruszka, J. *Chem. Rev.* **2003**, *103*, 1051; (d) Wessjohann, L. A.; Brandt, W.; Thiemann, T. *Chem. Rev.* **2003**, *103*, 1625.
3. (a) Charette, A. B.; Marcoux, J. F. *Synlett* **1995**, 1197; (b) Charrette, A. B.; Juteau, H.; Lebel, H.; Molinaro, C. *J. Am. Chem. Soc.* **1998**, *120*, 11943; (c) Charrette, A. B.; Beauchemin, A. *Org. React.* **2001**, *58*, 1; (d) Denmark, S. E.; Beutner, G. In *Cycloaddition Reactions in Organic Synthesis*; Kobayashi, S., Jorgensen, K. A., Eds.; Wiley-CVH Verlag GmbH & Co. KgaA: Weinheim, Germany, 2002; p 85.
4. (a) Iwasa, S.; Takezawa, F.; Tuchiya, Y.; Nishiyama, H. *Chem. Commun.* **2001**, 59. *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, Ed.; Springer: London, 2000.; (b) Doyle, M. P.; Protopopova, M. N. *Tetrahedron* **1998**, *54*, 7919; (c) Maas, G. *Chem. Soc. Rev.* **2004**, *33*, 183; (d) Doyle, M. P. *J. Org. Chem.* **2006**, *71*, 9253.
5. (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., Int. Ed.* **1989**, *28*, 621; (c) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
6. Goumri-Magnet, S.; Kato, T.; Gornitzka, H.; Baceiredo, G. *J. Am. Chem. Soc.* **2000**, *122*, 4464.
7. (a) Illa, O.; Gornitzka, H.; Branchadell, V.; Baceiredo, A.; Betrand, G.; Ortuño, R. M. *Eur. J. Org. Chem.* **2003**, 3147; (b) Illa, O.; Gornitzka, H.; Baceiredo, A.; Bertrand, G.; Branchadell, V.; Ortuño, R. M. *J. Org. Chem.* **2003**, *68*, 7707; (c) Illa, O.; Álvarez-Larena, Á.; Baceiredo, A.; Branchadell, V.; Ortuño, R. M. *Tetrahedron: Asymmetry* **2007**, *18*, 2617; (d) Fernández, D.; Illa, O.; Avilés, F. X.; Branchadell, V.; Vendrell, J.; Ortuño, R. M. *Bioorg. Med. Chem.* **2008**, *16*, 4823.
8. Lecea, B.; Ayerbe, M.; Arrieta, A.; Cossio, F. P.; Branchadell, V.; Ortuño, R. M.; Baceiredo, A. *J. Org. Chem.* **2007**, *72*, 357.
9. Krysiak, J.; Kato, T.; Gornitzka, H.; Baceiredo, A.; Mikolajczyk, M.; Bertrand, G. *J. Org. Chem.* **2001**, *66*, 8240.
10. Kato, H.; Gornitzka, H.; Baceiredo, A.; Savin, A.; Bertrand, G. *J. Am. Chem. Soc.* **2000**, *122*, 998.
11. Krysiak, J.; Lyon, C.; Baceiredo, A.; Gornitzka, H.; Mikolajczyk, M.; Bertrand, G. *Chem. Eur. J.* **2004**, *10*, 1982.
12. Cermak, D. M.; Du, Y.; Wiemer, D. F. *J. Org. Chem.* **1999**, *64*, 388.
13. GAUSSIAN 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.
14. Vreven, T.; Morokuma, K. *J. Comput. Chem.* **2000**, *21*, 1419.
15. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648; (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785; (c) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
16. Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.
17. Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.
18. Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.
19. (a) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931; (b) ADF2007.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
20. Watson, M. A.; Handy, N. C.; Cohen, A. J. *J. Chem. Phys.* **2003**, *119*, 6475.