Stereoselectivity and Stereospecificity of Cyclopropanation Reactions with Stable (Phosphanyl)(silyl)carbenes

Stéphanie Goumri-Magnet, Tsuyoshi Kato, Heinz Gornitzka, Antoine Baceiredo, and Guy Bertrand*

Contribution from the Laboratoire d'Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France

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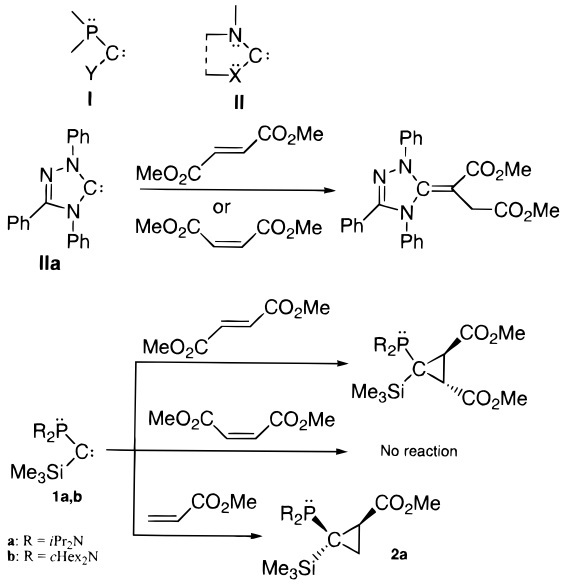
Abstract: The stable (phosphanyl)(silyl)carbenes **1a,b** react efficiently with various electron-poor alkenes [methyl acrylate, 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene, styrene, (*Z*)- and (*E*)-2-deuteriostyrene, (*E*)-*t*-BuOC(O)CH=CHC(O)OEt, and (*E*)-$Me_2NCOCH{=}CHCO_2Me$] giving the corresponding cyclopropanes in good yields. The stereochemical outcome was such that all monosubstituted alkenes gave exclusively the syn isomer (with respect to the phosphanyl group), and the addition of disubstituted alkenes was totally stereospecific. The high stereoselectivity observed was ascribed to a secondary orbital interaction ($LUMO_{carbene}-HOMO_{alkene}$) similar to that explaining the endo-rule in Diels−Alder reactions.

Introduction

In a recent paper,[1] Krogh-Jespersen, Yan, and Moss wrote: "The addition of a carbene to an alkene with the formation of a cyclopropane is perhaps the most fundamental of cycloaddition reactions, as well as a basic component of the synthetic armamentarium." Indeed, cyclopropanation reactions involving transient carbenes[2] or even transition metal carbene complexes have been widely studied.[3] Both singlet and triplet transient carbenes undergo cyclopropanation reactions, although with a totally different mechanism, which is apparent from the stereochemistry of the reaction: with singlet carbenes the stereochemistry about the original carbon−carbon double bond is maintained, while with triplet carbenes the stereochemical information is lost.[4] Additionally, for all types of carbene, including transition metal−carbene complexes, intermolecular cyclopropanation usually occurred in poor to moderate diastereoselectivity (syn- versus anti-attack).[5]

To date, two types of stable singlet carbene are known:[6] the phosphanylcarbenes **I** and the aminocarbenes **II**. For derivatives of type **II**, no cyclopropanation reactions have been reported, most probably because of the strong donation of the amino substituent, which makes the vacant orbital too high in energy.[7] For example, the 1,2,4-triazol-5-ylidene **IIa** reacts with diethyl fumarate and diethyl maleate to give methylenetriazoline derivatives and not the corresponding cyclopropanes.[8] In contrast, we have already shown that the (phosphanyl)(silyl)-carbenes **1a,b** react with dimethyl fumarate with retention of the stereochemistry about the double bond to give the corresponding *trans*-cyclopropane.[9] However, since **1** does not react with dimethyl maleate no conclusion could be drawn on the stereospecificity of the reaction (Scheme 1). The difference in reactivity between cis and trans alkenes toward carbenes has

Scheme 1



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(7) This is well illustrated by the structure of the radical anion **IIa**$^{\bullet-}$ obtained by reduction of the corresponding stable carbene **IIa**. According to ESR spectroscopy and ab initio calculations, the additional electron is not located at the carbene carbon atom but delocalized into the PhCN fragment: Enders, D.; Breuer, K.; Raabe, G.; Simonet, J.; Ghanimi, A.; Stegmann, H. B.; Teles, J. H. *Tetrahedron Lett.* **1997**, *38*, 2833.

(8) Enders, D.; Breuer, K.; Raabe, G.; Runsink, J.; Teles, J. H.; Melder, J. P.; Ebel, K.; Brode, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021.

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Table 1. Crystallographic Data for Cyclopropanes **2a**, **6b**, **7a**, **7b**, **8a**, and **15a**

	2a	**6b**	**7a**	**7b**	**8a**	**15a**
formula	$C_{20}H_{43}N_2O_2SiP$	$C_{36}H_{61}N_2SiP(C_7H_8)_{0.5}$	$C_{24}H_{45}N_2SiPS$	$C_{36}H_{61}N_2SiPS$	$C_{26}H_{53}N_2O_4SiP$	$C_{23}H_{48}N_3O_3SiPS$
formula wt	402.62	627	452.74	612.99	516.76	505.76
cryst system, space group	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/n$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, $Pna2_1$
a, Å	15.147(8)	10.013(2)	10.293(2)	12.552(1)	36.818(5)	10.233(1)
b, Å	9.852(4)	10.937(2)	13.027(2)	16.173(2)	9.5963(12)	17.265(2)
c, Å	18.554(8)	17.832(3)	19.551(3)	17.548(1)	18.765(2)	16.354(2)
α, deg		79.51(2)				90
β, deg	114.04(2)	76.75(2)	94.96(2)	97.72(1)	104.749(6)	90
γ, deg		89.38(2)				90
V, Å^3	2529(2)	1868.1(6)	2611.7(8)	3530.0(6)	6411.5(15)	2889.3(6)
Z	4	2	4	4	8	4
d(calcd), Mg/m^3	1.058	1.115	1.151	1.153	1.071	1.163
absorp coeff, mm^{-1}	0.171	0.134	0.244	0.198	0.152	0.236
no of total reflcns	22045	10001	20109	28238	14359	23935
no of unique reflcns	3403	5065	3875	5328	5699	4580
R_1 ($I > 2\sigma(I)$)	0.0523	0.0385	0.0331	0.0354	0.994	0.0395
wR2[a] (all data)	0.1392	0.1021	0.0825	0.0875	0.2832	0.0913
$(\Delta/\rho)_{max}$ [eÅ^{-3}]	0.204 and −0.163	0.190 and −0.248	0.250 and −0.264	0.235 and −0.365	0.443 and 0.401	0.175 and −0.132

[a] $wR2 = \{[\Sigma w(Fo^2 - Fc^2)^2]/[\Sigma w(Fo^2)^2]\}^{1/2}$.

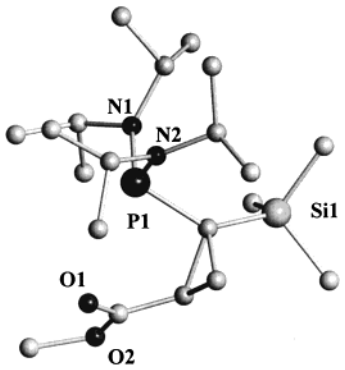


Figure 1. Solid-state structure of cyclopropane **2a**.

already been noted by Moss et al. with the methoxy(phenyl)-carbene.[10] On the other hand, we have reported that **1a** reacted with methyl acrylate to give the corresponding cyclopropane as only one diastereomer **2a**.[9] However, the total selectivity of the reaction was quite surprising, and the structure only based on questionable NMR data.

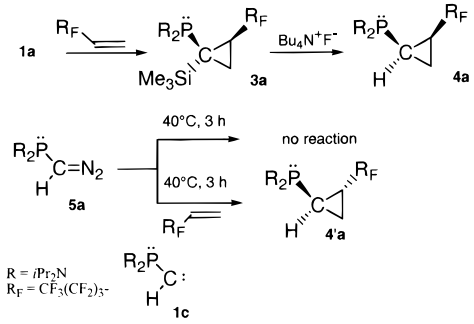
Here, we report a detailed study of the reactions of the stable (phosphanyl)(silyl)carbenes **1a** and **1b** with various electron-poor alkenes, focusing particularly on their diastereoselectivity (syn- versus anti-attack) and diastereospecificity.

Results

We first reproduced the synthesis of the phosphanylcyclopropane **2a**[9] by addition of methyl acrylate to the carbene **1a** (Scheme 1).[11a] The total syn-selectivity (with respect to the phosphanyl group), according to NMR spectroscopy, was confirmed by a single-crystal X-ray diffraction study (Figure 1, Table 1).

According to multinuclear NMR spectroscopy, the (phosphanyl)(silyl)carbene **1a** quantitatively reacts with 3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene, affording the cyclopropane **3a** as a single diastereomer (Scheme 2). The total syn-selectivity was suggested

Scheme 2



by the large $^4J_{PF}$ coupling constant (178.5 Hz), which cannot readily be explained without involving a through space coupling.[12] Treatment of a thf solution of **3a** with a stoichiometric amount of hydrated tetrabutylammonium fluoride gave rise to the *syn*-cyclopropane **4a** (95% yield) which also showed a large $^4J_{PF}$ coupling constant (145.9 Hz).

The phosphanylcarbene **1c** is unavailable because of its instability.[11a] Its diazo precursor **5a** is stable toward dinitrogen elimination on heating at 40 °C for 3 h. Interestingly, under the same experimental conditions, but in the presence of the perfluoroalkyl-substituted alkene, cyclopropane **4′a** was obtained in 95% yield (Scheme 2). The anti-configuration was apparent from the ^{31}P and ^{19}F NMR spectra: no J_{PF} coupling constants were observed.

The reaction of carbene **1a** with styrene was monitored by ^{31}P NMR spectroscopy. After 30 min at room temperature, the reaction was over, and two new signals at +73 and +61 ppm in a 90/10 ratio were observed, arguing for the presence of two diastereomers. A white solid was obtained after treatment with elemental sulfur, and purification by column chromatography. Although one single spot was apparent on the TLC, two signals (+93 and +86 ppm; 60/40 ratio) were observed in the ^{31}P NMR spectrum of a $CDCl_3$ solution of the solid. The ^{1}H and ^{13}C NMR spectra confirmed the presence of two species, but the similarities of their spectroscopic data (Table 2) were surprising for two diastereomers. Slow evaporation of a pentane solution of the solid gave single crystals suitable for an X-ray diffraction study. The molecular structure of the molecule is depicted in

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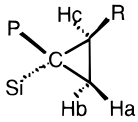
Table 2. Selected ^{1}H NMR Resonance Values and Coupling Constants for Cyclopropanes **7a**, **10a**, **12a**, and **15a**



	δ ^{31}P (ppm)	δ H_a ($^2J_{HH}$, $^3J_{(HH)trans}$, $^3J_{PH}$)	δ H_b ($^2J_{HH}$, $^3J_{(HH)cis}$, $^3J_{PH}$)	δ H_c ($^2J_{(HH)cis}$, $^3J_{(HH)trans}$, $^3J_{PH}$)
7a	85.9 major	1.73 (4.2, 7.3, 19.6)	not observed	2.53 (7.8, 7.3, 17.6)
	93.2 minor	2.43 (3.9, 8.6, 20.6)		2.69 (8.0, 8.6, 17.2)
10a	85.9 major		not observed	2.52 (7.8, −, 17.6)
	93.0 minor			2.69 (8.5, −, 16.8)
12a	85.9 major	1.71 (−, 7.3, 19.4)		2.50 (−, 7.3, 18.6)
	93.1 minor	2.42 (−, 8.0, 22.4)		2.68 (−, 7.9, 16.8)
15a	90.8	2.9 (−, 5.4, 18.8)		3.35 (−, 5.4, 16.4)

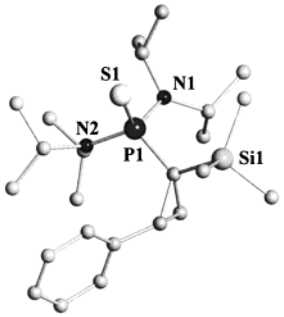


Figure 2. Solid-state structure of cyclopropane **6b**.

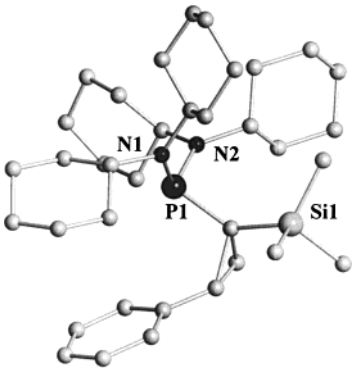


Figure 3. Solid-state structure of cyclopropane **7a**.

Scheme 3

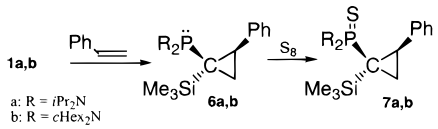


Figure 2. In the unit cell, the two enantiomers corresponding to the *syn*-cyclopropane **7a** were observed, suggesting that a diastereoselective crystallization occurred. However, the room temperature ^{31}P NMR spectrum of a $CDCl_3$ solution of the single crystal showed the two signals previously observed at +93 and +86 ppm in the same 60/40 ratio! On cooling this solution to 240 K only the signal at +86 ppm was observed, while heating at $T > 363$ K led to the decomposition of the product. These results as a whole strongly suggest that a stereoselective syn-cyclopropanation occurred leading to **6a**, which exists as two rotamers in a slow equilibrium (Scheme 3).

Very similar results were observed using the [bis(dicyclohexylamino)phosphanyl](silyl)carbene **1b**.[11b] However, in this case, single crystals of both the phosphanyl-substituted cyclopropane **6b** and thioxophosphoranyl-substituted cyclopropane **7b**, suitable for analysis by X-ray diffraction, were obtained (Figures 3 and 4). These studies confirmed the exclusive formation of the syn-cyclopropanes **6b** and **7b** and that unexpected isomerization does not occur in the sulfuration process (Scheme 3).

The phosphanylcarbene **1a** also reacts with the unsymmetrically substituted olefin (*E*)-*t*-BuOC(O)CH═CHC(O)OEt to give a 9/1 mixture of cyclopropanes **8a** and **8′a**. The major isomer **8a** was isolated by selective recrystallization as colorless crystals in 40% yield. An X-ray diffraction study (Figure 5) unambiguously established the anti-position of the *tert*-butyl group with respect to the phosphanyl group.

Addition at room temperature of 3 equiv of (*Z*)- and (*E*)-2-deuteriostyrene to the carbene **1a** afforded the cyclopropanes **9a** and **11a**, respectively. Addition of elemental sulfur, followed by column chromatography gave rise to the thioxophosphoranyl

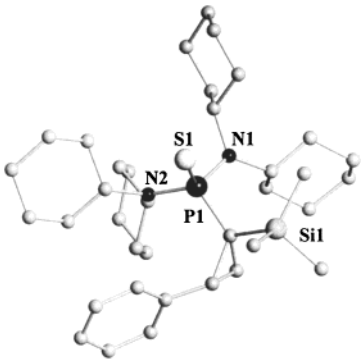


Figure 4. Solid-state structure of cyclopropane **7b**.

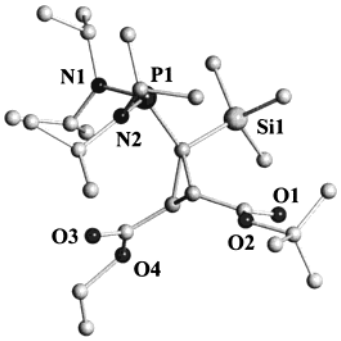
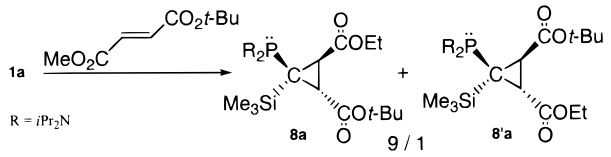


Figure 5. Solid-state structure of cyclopropane **8a**.

analogues **10a** and **12a** in 95 and 96% yield, respectively (Scheme 5). Again, in both cases two rotamers were observed. The relative configuration of the three stereogenic centers of **10a** and **12a** was determined based on the ^{1}H NMR spectra of cyclopropanes **7a**, **10a**, and **12a** (Table 2). By comparing the spectra of **7a** and **10a**, it is clear that H_a has been substituted by a deuterium atom: its signal is not present and the $J_{H_aH_c}$

Scheme 4



Scheme 5

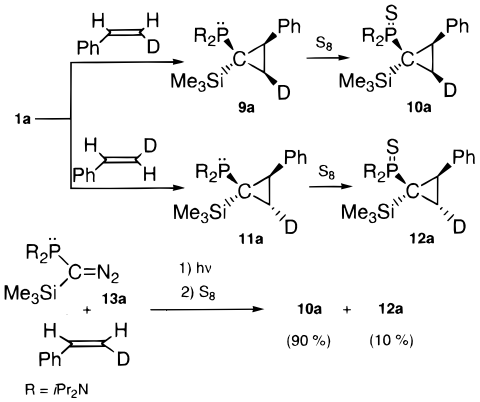
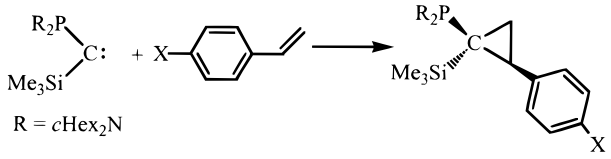
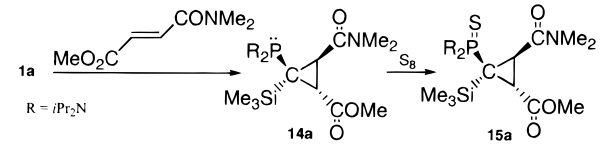


Table 3. Philicity of Phosphino(silyl)carbene **1b** toward Styrenes



X	X	k_X/k_H
CH_3O	H	0.88
H	H	1
F	H	1.7
CF_3	H	7

Scheme 6



coupling constant is not observed. In the spectrum of **12a**, the signals of both H_a and H_c are present, but no coupling constants with H_b are observed. In both cases, no trace of other isomers was detected.

Interestingly, photolysis at 300 nm of the diazo precursor **13a** in the presence of (*Z*)-2-deuteriostyrene led after sulfuration to a 9/1 mixture of cyclopropanes **10a** and **12a** (Scheme 5). However, we have checked that irradiation of (*Z*)-2-deuteriostyrene under the same experimental conditions (during the same period of time) gave a 9/1 mixture of (*Z*)- and (*E*)-2-deuteriostyrene.

Competitive reactions of phosphinocarbene **1b** with various para-substituted styrenes have been carried out, and the results are summarized in Table 3.

The carbene **1a** also readily reacts at room temperature with (*E*)-$Me_2NCOCH{=}CHCO_2Me$ to give the corresponding cyclopropane **14a**, in near quantitative yield. Treatment with elemental sulfur gave the corresponding thioxophosphoranyl derivative **15a** (45% yield) (Scheme 6), which was fully characterized including by an X-ray diffraction study (Figure 6). Interestingly,

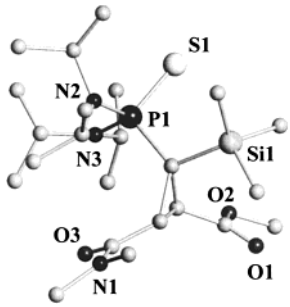


Figure 6. Solid-state structure of cyclopropane **15a**.

we obtained exclusively the isomer featuring the amido and phosphanyl substituents syn to one another.

Discussion

The total syn-stereoselectivity (with respect to the phosphanyl group) observed in the reaction of the carbenes **1** with methyl acrylate, styrene, and the perfluoroalkene was quite surprising (Schemes 1, 2, and 3). Indeed, looking at the molecular structures (Figures 1−4), it is hard to believe that steric factors could govern the observed selectivity since the bis(amino)-phosphanyl group appears to be roughly as sterically demanding as the trimethylsilyl group. The definitive proof that the phosphanyl group is in fact more sterically demanding than the trimethylsilyl group is given by the results observed with the alkene substituted by the ethyl and *tert*-butyl ester groups: the major isomer **8a** features the bulkier ester group anti with respect to the phosphanyl group.

Since the syn-selectivity observed with the carbenes **1** is not due to steric factors, the obvious other possibility is to invoke orbital-controlled reactions. Thus, it was first necessary to check that the cyclopropanation reactions were concerted (or at least quasiconcerted). Although the total stereospecificity observed in the reaction of **1a** with (*Z*)- and (*E*)-2-deuteriostyrene is not a definitive proof for the concerted nature of the cyclopropanation reactions, this is a strong argument[13] (Scheme 5).

Before drawing a reasonable hypothesis to explain the observed syn-selectivity, it was necessary to check whether carbenes **1** are nucleo- or electrophilic in character.[2a] Indeed, although their nucleophilic character appears from the calculations,[14] we recently reported that **1b** reacted with phosphines to give the correspnding phosphorus ylides,[15] which suggests that **1b** features an accessible vacant orbital and therefore could behave as an electrophile. The results observed with different styrene derivatives (Table 3) leave no doubt that the carbenes **1** are the nucleophilic partners in the cycloaddition reaction with olefins. For example, using the same set of styrene derivatives, but the electrophilic H−C−CO_2Et carbene generated by copper-catalyzed decomposition of the corresponding ethyl diazoacetate,

(13) The stereochemical results are most compatible with concerted addition of **1a** to styrene, in accord with typical singlet carbene behavior, and with the lack of theoretical prohibition of concerted nucleophilic carbene−olefin [1+2] cycloadditions. However, there is no spin-inversion barrier to rapid closure of a 1,3-dipole, so that a two-step singlet carbene addition is not as certain to occur nonstereospecifically as in a triplet carbene addition, which proceeds via a triplet 1,3-diradical. Moss, R. A.; Huselton, J. K. *J. Chem. Soc., Chem. Commun.* **1976**, 950.

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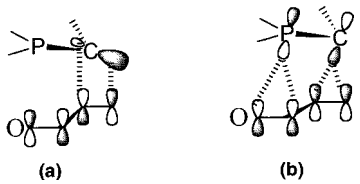


Figure 7. Schematic representation of the cycloaddition of phosphino-(silyl)carbene to acroleine.

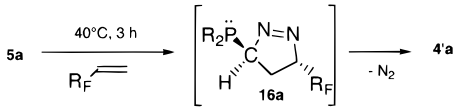
the reverse relative rate of cyclopropanation has been observed.[16] It is important to note that in the latter case a range of syn/anti isomers from 1:1 to 1:15 was obtained.[16]

At this point, it seems clear that the (phosphanyl)(silyl)-carbenes have to be compared with methoxymethylcarbene[17] for which the nucleophilic character is strongly expressed but its electrophilicity not totally suppressed (as observed for the dimethoxycarbene).[18] Therefore, in the transition state, the more dominant orbital interaction is between the $HOMO_{carbene}$ and the $LUMO_{alkene}$ (Figure 7a), but this set of orbitals does not explain the observed syn-selectivity. However, in the course of computational and experimental[19] work on the addition of carbenes to alkenes the significance of a second pair of orbital interactions in the addition geometry has been pointed out. Thus, our hypothesis was that the secondary orbital interaction $LUMO_{carbene}-HOMO_{alkene}$ (Figure 7b) should explain the selectivity observed. Due to donation of the phosphorus lone pair, the $LUMO_{carbene}$ has some π^*(PC) character and shows significant bonding overlap between the phosphorus center and the alkene substituent, as indicated schematically in Figure 7b. In other words, like the endo selectivity in the Diels−Alder reaction,[20] the high stereoselectivity observed could be rationalized on the basis of favorable "secondary orbital interactions".

The effectiveness of the secondary orbital interactions on the selectivity of cyclopropanation reactions is demonstrated by the exclusive formation of **14a** (Scheme 6). Not surprisingly, simple Hückel calculations show that the highest coefficient of the HOMO of the alkene is located at the amido group, and thus despite the smaller steric demand of the ester group, the amido substituent lies syn with respect to the phosphanyl group.

On the other hand, the synthetic importance of having stable carbenes is nicely illustrated by the reaction of the phosphanyldiazomethane **5a** with the perfluoro-substituted alkene, which leads to the *anti*-cyclopropane **4′a**, while desilylation of **3a** affords the *syn*-cyclopropane **4a** (Scheme 2). Since in the absence of olefin the diazo derivative **5a** is stable toward nitrogen elimination, it is quite clear that the formation of **4′a** does not involve the carbene **1c** but results from a [3+2]-cycloaddition process giving the transient pyrazoline **16a**, which undergoes a classical nitrogen elimination[21] (Scheme 7). Note also that when the carbene **1a** is generated under irradiation in the presence of (*Z*)-2-deuteriostyrene, a mixture of *cis*- and *trans*-cyclopropanes **9a** and **11a** is obtained due to the photoisomerization of the alkene, while using the stable carbene **1a**, only **9a** is formed.

Scheme 7



Conclusion

These results present convincing evidence for the concerted nature of cyclopropanation reaction and therefore the genuine singlet carbene nature of stable phosphanylsilylcarbenes. To date, the observed diastereoselectivity (where present) of cyclopropanation reactions involving transient nucleophilic singlet carbenes has been rationalized by steric factors.[22] Here, we demonstrate that the diastereoselectivity is due to second-order orbital interactions, in a manner analogous to the well-known endo rule for the Diels−Alder reaction. These reactions allow the diastereoselective synthesis of various cyclopropanes with simultaneous control of two or even three stereogenic centers. The enantioselective version of this reaction is under active investigation.

Experimental Section

All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Brucker AC80, AC200, WM250, or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P and ^{19}F NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 and CF_3CO_2H, respectively. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1725 X. Mass spectra were obtained on a Ribermag R10 10E instrument.

Preparation of the Carbenes 1a,b. In a typical experiment, phosphanyl(silyl)carbenes **1a,b** were obtained by irradiation (300 nm, 8 h) of a pentane solution (3 mL) of the corresponding phosphanyl-(silyl)diazomethane[11] (0.30 mmol). According to ^{31}P NMR spectroscopy the reactions were quantitative and the carbenes **1a,b** were used without any further purification.

General Procedure for Cycloaddition Reactions with the Carbenes 1a,b. To a pentane solution (3 mL) of the carbene **1** (0.3 mmol) was added at room temperature 3 equiv of alkene. The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. After the reaction was complete (1−3 h), volatile components were removed under reduced pressure, and the phosphanylcyclopropanes were analyzed without any further purification. Treatment of a thf solution of phosphanylcyclopropanes with an excess of elemental sulfur gave the corresponding thioxophosphoranyl derivatives, which were purified as indicated for each compound by column chromatography on silica gel.

3a: Yellow oil. ^{31}P{^{1}H} NMR ($CDCl_3$) δ 78.2 (d, $^4J_{PF}$ = 178.5 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$: δ −51.3 and −46.0 (m, $CF_3-CF_2-CF_2-$), −34.2 (dd, $^2J_{FF}$ = 265.1 Hz, $^2J_{PF}$ = 178.5 Hz, CF_2-CH), −25.9 (s, CF_2-CH), −5.0 (t, $^3J_{FF}$ = 9.0 Hz, CF_3).

4a: To a thf solution (3 mL) of the cyclopropane **3a** (0.1 g, 0.18 mmol) was added at room temperature 1 equiv of Bu_4NF (0.05 g, 0.18 mmol). The reaction was monitored by ^{31}P NMR spectroscopy, and the cyclopropane **4a** was obtained after 3 h in near-quantitative yield (according to NMR spectroscopy). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 44.1 (d, $^4J_{PF}$ = 145.9 Hz); ^{19}F{^{1}H} NMR ($CDCl_3$) δ −49.7 and −47.1 (m, $CF_3-CF_2-CF_2-$), −43.1 (dd, $^2J_{FF}$ = 268.1 Hz, $^2J_{PF}$ = 145.9 Hz, CF_2-CH), −28.7 (s, CF_2-CH), −5.1 (m, CF_3).

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4′a: A pentane solution (3 mL) of the diazo compound **5a**[11a] (0.1 g, 0.37 mmol) and nonafluoro-1-hexen (193 μL, 1.11 mmol) was heated at 40 °C. The reaction was monitored by ^{31}P NMR spectroscopy, and the cyclopropane **4′a** was obtained after 2 h in near-quantitative yield (according to the NMR spectroscopy). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 50.6; $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −50.1 and −46.2 (m, $CF_3-CF_2-CF_2-$), −35.4 (m, CF_2-CH), −5.0 (t, $^3J_{FF}$ = 8.7 Hz, CF_3).

6a: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 76.6 and +61.0 ppm (2 rotamers, 90/10 ratio).

7a: (pentane/ether, 98/2, R_F = 0.6). (0.12 g; 90%). Mp 163−164 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 85.9 and 93.2 (2 rotamers, 60/40); ^{1}H NMR (C_6D_6) **major rotamer** δ 0.33 (s, 9 H, $SiCH_3$), 0.50 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, $CHCH_3$), 1.13 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 1.29−1.50 (m, 12 H, $CHCH_3$), 1.73 (ddd, $^2J_{HH}$ = 4.2 Hz, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 19.6 Hz, 1 H, CH_2), 2.53 (td, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 17.6 Hz, 1 H, CH), 3.54−4.11 (m, 4 H, $CHCH_3$), 7.17−7.61 (m, 5 H, H_{arom}), one of the CH_2 protons was not observed, **minor rotamer** δ 0.30 (s, 9 H, $SiCH_3$), 1.27−1.51 (m, 24 H, $CHCH_3$), 2.43 (ddd, $^2J_{HH}$ = 3.9 Hz, $^3J_{HH}$ = 8.6 Hz, $^3J_{PH}$ = 20.6 Hz, 1 H, CH_2), 2.69 (td, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 17.2 Hz, 1 H, CH), 3.54−4.11 (m, 4 H, $CHCH_3$), 7.17−7.61 (m, 5 H, H_{arom}), one of the CH_2 protons was not observed; $^{13}C\{^1H\}$ NMR (C_6D_6)- **major rotamer** δ 0.6 (s, $SiCH_3$), 15.1 (d, $^2J_{PC}$ = 5.1 Hz, CH_2), 21.0 (d, $^1J_{PC}$ = 91.6 Hz, PC), 23.7 (d, $^3J_{PC}$ = 6.9 Hz, $CHCH_3$), 24.0 (s, $CHCH_3$), 25.5 (s, $CHCH_3$), 26.6 (d, $^3J_{PC}$ = 1.2 Hz, $CHCH_3$), 29.6 (d, $^2J_{PC}$ = 5.9 Hz, CH), 48.2 (d, $^2J_{PC}$ = 6.0 Hz, CHN), 126.9 (d, $^4J_{PC}$ = 17.4 Hz, C_o), 128.2 (s, C_p), 130.8 (d, $^4J_{PC}$ = 8.5 Hz, C_m), 137.5 (s, C_i). Anal. Calcd for $C_{24}H_{45}N_2SiPS$: C, 63.67; H, 10.02; N, 6.19. Found: C, 64.01; H, 10.15; N, 5.98.

6b: Yellow crystals from a pentane solution at −20 °C (0.16 g, 95%). Mp 210−211 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.4 and +67.4 ppm (2 rotamers, 95/5 ratio). Anal. Calcd for $C_{36}H_{61}N_2SiP$: C, 70.43; H, 10.58; N, 4.82. Found: C, 70.23; H, 10.45, N, 4.65.

7b (hexane/ether, 95/5, R_F = 0.8): Pale yellow crystals were obtained by slow evaporation of a pentane solution (0.16 g; 90%). Mp 196−197 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 84.4. Anal. Calcd for $C_{36}H_{61}N_2SiPS$: C, 70.54; H, 10.03; N, 4.57. Found: C, 70.14; H, 9.83, N, 4.71.

8a and 8′a: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 293 K) δ 89.7 very large. By cooling the sample, two rotamers were observed for each compound, $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 223 K) δ 96.5 and 88.0 (major isomer **8a**), 87.8 and 87.0 (minor isomer **8′a**). At 193 K, only one rotamer was detected for each isomer,$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 193 K) δ 88.0 (**8a**),- and 87.8 (**8′a**) (90/10 ratio). The major isomer **8a** precipitated from a pentane solution at −50 °C as colorless crystals (0.04 g; 40%). Mp 147−148 °C; ^{1}H NMR (CD_2Cl_2, 193 K) δ 0.23 (s, 9 H, $SiCH_3$), 1.22 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 1.23 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, $CHCH_3$), 1.29 (d, 3 H, $^3J_{HH}$ = 7.2 Hz, OCH_2CH_3), 1.43 (s, 9H, *t*Bu), 2.56 (t_{like}, $^3J_{HH}$ = $^3J_{PH}$ = 6.1 Hz, 1 H, CH_{ring}), 2.73 (dd, 1 H, $^3J_{HH}$ = 6.0 Hz, $^3J_{PH}$ = 12.2 Hz, CH_{ring}), 3.50 (m, 4 H, $CHCH_3$), 4.00 (dq, 1 H, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 10.8 Hz, OCH_2CH_3), 4.22 (dq, 1 H, $^3J_{HH}$ = 7.2 Hz, $^2J_{HH}$ = 10.8 Hz, OCH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 193 K) δ 0.9 (d, $^3J_{PC}$ = 9.6 Hz, $SiCH_3$), 14.5 (s, OCH_2CH_3), 24.5 (d, $^3J_{PC}$ = 17.5 Hz, $CHCH_3$), 26.9 (d, $^3J_{PC}$ = 15.3 Hz, $CHCH_3$), 28.1 (s, $OC(CH_3)_3$), 34.8 (d, $^2J_{PC}$ = 2.3 Hz, CH_{ring}), 35.7 (d, $^2J_{PC}$ = 9.0 Hz, CH_{ring}), 38.1 (d, $^1J_{PC}$ = 91.8 Hz, PCSi), 45.1 (d, $^2J_{PC}$ = 37.9 Hz, CHN), 51.1 (d, $^2J_{PC}$ = 10.0 Hz, CHN), 61.4 (s, OCH_2CH_3), 81.0 (s, $OC(CH_3)_3$), 172.8 (d, $^3J_{PC}$ = 5.4 Hz, CO), 174.8 (d, $^3J_{PC}$ = 8.0 Hz, CO). Anal. Calcd for $C_{26}H_{53}N_2O_4PSi$: C, 60.43; H, 10.34; N, 5.42; Found: C, 60.22; H, 10.28; N, 5.36.

9a: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 73.5.

10a (pentane/ether, 98/2, R_F = 0.6): Colorless crystals of **10a** were obtained by slow evaporation of a dichloromethane solution (0.13 g; 95%). Mp 161−162 °C; $^{31}P\{^1H\}$ NMR (C_7D_8) δ 85.9 and 93.0 (2 rotamers, 60/40); ^{1}H NMR (C_7D_8) **major rotamer** δ 0.51 (s, 9 H, $SiCH_3$), 1.11 (d, 12 H, $^3J_{HH}$ = 7.0 Hz, $CHCH_3$), 1.13 (d, 12 H, $^3J_{HH}$ = 7.0 Hz, $CHCH_3$), 2.52 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 17.6 Hz, 1 H, CH), the proton of CDH was not observed, 4.32 (m, 4 H, $CHCH_3$), 7.22−7.71 (m, 5 H, H_{arom}), **minor rotamer** δ 2.69 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{PH}$ = 16.8 Hz, 1 H, CH), the proton of CDH was not observed.

11a: $^{31}P\{^1H\}$ NMR (C_6D_6) δ 73.5.

12a (pentane/ether, 98/2, R_F = 0.5): Colorless crystals of **12a** were obtained by slow evaporation of a dichloromethane solution (0.13 g; 95%). Mp 163−164 °C; $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 85.9 and 93.1 (2 rotamers 60/40); ^{1}H NMR ($CDCl_3$) **major rotamer** δ 0.25 (s, 9 H, $SiCH_3$), 1.07−1.54 (m, 24 H, $CHCH_3$), 1.71 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 19.4 Hz, 1 H, CHD), 2.50 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 18.6 Hz, 1 H, CH), 3.85 (m, 4 H, $CHCH_3$), 7.19−7.80 (m, 5 H, H_{arom}), **minor rotamer** 2.42 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{PH}$ = 22.4 Hz, 1 H, CHD), 2.68 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{PH}$ = 16.8 Hz, 1 H, CH).

Reaction of the Diazo 13a in the Presence of (*Z*)-2-Deuteriostyrene. A pentane solution (3 mL) of phosphanyl(silyl) diazomethane (**13a**, 0.10 g, 0.30 mmol) and 3 equiv of (*Z*)-2-deuteriostyrene (0.09 g, 0.90 mmol) was irradiated at 300 nm for 18 h. According to ^{31}P NMR spectroscopy the reaction was quantitative (δ 73.5). Treatment of the solution mixture with an excess of elemental sulfur gave the thioxo-phosphoranyl derivatives **10a** and **12a** in a 90/10 ratio (according to ^{1}H NMR spectroscopy).

14a: Yellow oil. $^{31}P\{^1H\}$ NMR (C_7D_8) δ 94.0; ^{1}H NMR (C_7D_8) δ 0.65 (d, $^4J_{PH}$ = 1.0 Hz, 9 H, $SiCH_3$), 1.45 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 1.49 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 1.55 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 1.71 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $CHCH_3$), 2.81 (s, 3 H, CH_3N), 2.84 (s, 3 H, CH_3N), 3.00 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{PH}$ = 4.8 Hz, 1 H, CH_{ring}), 3.50 (dd, $^3J_{HH}$ = 6.4 Hz, $^3J_{PH}$ = 11.4 Hz, 1 H, CH_{ring}), 3.59 (s, 3 H, CH_3O), 3.80 (sept d, $^3J_{HH}$ = 6.8 Hz, $^3J_{PH}$ = 9.0 Hz, 4 H, $CHCH_3$); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 1.9 (d, $^3J_{PC}$ = 8.8 Hz, $SiCH_3$), 24.8 (d, $^3J_{PC}$ = 4.9 Hz, $CHCH_3$), 24.9 (d, $^3J_{PC}$ = 3.5 Hz, $CHCH_3$), 34.6 (d, $^2J_{PC}$ = 3.4 Hz, CH_{ring}), 35.8 (s, CH_3N), 35.9 (d, $^2J_{PC}$ = 7.2 Hz, CH_{ring}), 36.7 (d, $^1J_{PC}$ = 100.0 Hz, PCSi), 37.5 (s, CH_3N), 51.6 (s, CH_3O), 52.4 (d, $^2J_{PC}$ = 15.9 Hz, CHN), 170.8 (d, $^3J_{PC}$ = 6.5 Hz, CO), 174.1 (d, $^3J_{PC}$ = 5.2 Hz, CO).

15a: White crystals obtained by slow evaporation of a ether solution (0.06 g; 45%). Mp 191−192 °C dec; $^{31}P\{^1H\}$ NMR (C_7D_8) δ 90.8; ^{1}H NMR (C_7D_8) δ 0.76 (s, 9 H, $SiCH_3$), 1.20−2.17 (m, 24 H, $CHCH_3$), 2.90 (dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 18.8 Hz, 1 H, CH_{ring}), 2.89 (s, 3 H, CH_3N), 3.07 (s, 3 H, CH_3N), 3.34 (s, 3 H, CH_3O), 3.35 (dd, $^3J_{HH}$ = 5.4 Hz, $^3J_{PH}$ = 16.4 Hz, 1 H, CH_{ring}), 4.23, 4.44, 4.50, and 4.63 (m, 4 H, $CHCH_3$); $^{13}C\{^1H\}$ NMR (C_7D_8) δ 4.3 (s, $SiCH_3$), 23.0 (s, $CHCH_3$), 23.8 (s, $CHCH_3$), 25.6 (s, $CHCH_3$), 25.8 (s, $CHCH_3$), 25.9 (d, $^3J_{PC}$ = 4.2 Hz, $CHCH_3$), 29.2 (d, $^2J_{PC}$ = 3.1 Hz, CH_{ring}), 33.6 (d, $^2J_{PC}$ = 2.7 Hz, CH_{ring}), 34.9 (d, $^1J_{PC}$ = 79.7 Hz, PCSi), 35.6 (s, CH_3N), 39.3 (s, CH_3N), 53.1 (s, CH_3O), 47.3 (s, CHN), 47.8 (d, $^2J_{PC}$ = 7.4 Hz, CHN), 50.1 (s, CHN), 51.7 (d, $^2J_{PC}$ = 8.2 Hz, CHN), 166.2 (d, $^3J_{PC}$ = 6.6 Hz, CO), 171.9 (d, $^3J_{PC}$ = 4.4 Hz, CO). Anal. Calcd for $C_{23}H_{48}N_3O_3SiPS$: C, 54.62; H, 9.57; N, 8.31. Found: C, 54.83; H, 9.70; N, 8.41.

Competition Experiments (*p*-X−C_6H_4−CH=CH_2 vs C_6H_4−CH=CH_2) Using Carbene 1b. In a typical experiment, 1 equiv of styrene and 1 equvi of para-substituted-styrene (X = CH_3O, F, CF_3) was added at room temperature to a pentane solution (3 mL) of phosphanyl(silyl)-carbene **1b**. When the reaction had reached completion (1−3 h), volatile components were removed in vacuo, and the ratios of the resulting cyclopropanes were determined by ^{1}H NMR spectroscopy without any further purification. The phosphanylcyclopropanes resulting from the reaction of **1b** with the different para-substituted-styrenes were independently prepared**.** X = CH_3O: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.7 and +68.5 (2 rotamers, 90/10 ratio); ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H, $SiCH_3$), 0.53−1.64 (m, 41 H, CH_2 and CH_{ring}), 2.51−2.89 (m, 6 H, CHN and CH_{ring}), 3.64 (s, 3 H, CH_3O), 6.54−7.17 (m, 5 H, CH_{arom}). X = F: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.2 and +67.7 (2 rotamers, 90/10 ratio); ^{1}H NMR ($CDCl_3$) δ 0.12 (s, 9 H, $SiCH_3$), 0.81−1.63 (m, 41 H, CH_2 and CH_{ring}), 2.52−3.04 (m, 6 H, CHN and CH_{ring}), 6.73−7.15 (m, 5 H, CH_{arom}). X = CF_3: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 76.3 and +67.9 (2 rotamers, 90/10ratio); ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H, $SiCH_3$), 0.43−1.99 (m, 41 H, CH_2 and CH_{ring}), 2.56−2.96 (m, 6 H, CHN and CH_{ring}), 7.24−7.39 (m, 5 H, CH_{arom}).

X-ray Crystallographic Studies of Compounds 2a, 6b, 7a, 7b, 8a, and 15a. Crystal data for all structures are presented in Table 1. Data for **6b**, **7a**, **7b**, and **15a** were collected at low temperatures on a Stoe-IPDS diffractometer and data for **2a** and **8a** were collected at room temperature on a Bruker-CCD with Mo Kα (λ = 0.71073 Å). The structures were solved by direct methods by means of SHELXS-97[23]

(23) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

and refined with all data on F^2 by means of SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the molecules were geometrically idealized and refined using a riding model. Refinement of an inversion twin parameter[25] [$x = -0.16(9)$; $x = 0$ for the correct absolute structure and $x = +1$ for the inverted structure] confirmed the absolute structure of **15a**.

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Supporting Information Available: X-ray crystallographic data for compounds **2a**, **6b**, **7a**, **7b**, **8a**, and **15a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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