Stable Optically Pure Phosphino(silyl)carbenes: Reagents for Highly Enantioselective Cyclopropanation Reactions

Jerzy Krysiak,[a, b] Céline Lyon,[a] Antoine Baceiredo,*[a] Heinz Gornitzka,[a] Marian Mikolajczyk,*[b] and Guy Bertrand*[a, c]

Abstract: The stability of phosphino(-trimethylsilyl)carbenes bearing cyclic diamino substituents on phosphorus is strongly dependent on the steric hindrance of the nitrogen substituents. Phosphinocarbenes **3** and **7**, derived from the *trans-N,N′*-diisopropylcyclohexane-1,2-diamine and *N,N′*-diisopropyl-1,2-ethanediamine, are not observed; instead the 1,3-diphosphete **4** and a novel six-membered heterocycle **8**, which results from the dimerization of **3** and the reaction of **7** with its diazo precursor **6**, respectively, have been isolated. In contrast, the phosphino(silyl)carbene **14** derived from *N,N′*-di-*tert*-butyl-1,2-ethanediamine has been isolated in high yield. By using the enantiomerically pure (*S,S*)-, and (*R,R*)-*N,N′*-di-*tert*-butyl-1,2-diphenyl-1,2-ethanediamines, the first optically pure phosphino(sily)carbenes (*S,S*)-**17** and (*R,R*)-**17** have been prepared. They react with methyl acrylate to give the corresponding cyclopropanes (*S,S,R,R*)-**19** and (*R,R,S,S*)-**19** with a total *syn* diastereoselectivity and an excellent enantioselectivity (*de* > 98 %).

Keywords: asymmetric synthesis · carbenes · cycloaddition · diazo compounds · phosphorus

Introduction

The presence of cyclopropane subunits in many natural and synthetic biologically active compounds,[1] as well as the utility of these small rings as synthetic intermediates,[2] has promoted many strategies for their construction. We have previously demonstrated that, in contrast to the other known stable carbenes, namely aminocarbenes,[3,4] singlet nucleophilic phosphino(silyl)carbenes are efficient building blocks for the preparation of cyclopropanes.[5] Notably, reaction with monosubstituted olefins affords three-membered rings with a total *syn* diastereoselectivity (with respect to the phosphino group).[5b] With olefins bearing a chiral auxiliary, asymmetric inductions up to 87 % *de* were observed, although with low chemical yields.[5c] Here we report the synthesis of the first stable, optically active phosphino(silyl)carbenes, and subsequent highly selective cyclopropanation reactions.

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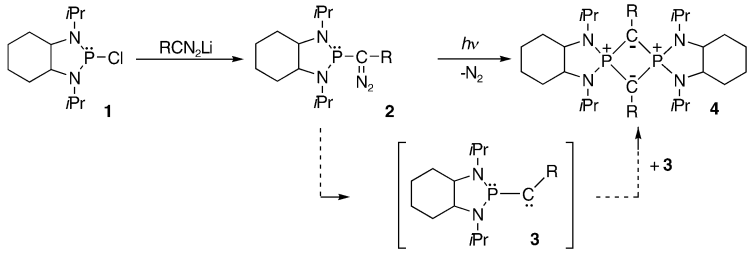
Results and Discussion

Phosphino(silyl)carbenes are best described as phosphorus vinyl ylides with a planar phosphorus atom,[6] and only those bearing amino substituents at phosphorus are stable.[4d] Therefore, the obvious way to introduce chirality was to use a cyclic diamino C_2-symmetric system at phosphorus. To evaluate the stability of this type of phosphino(silyl)carbene, racemic or achiral diamines were first used. With the (±)-*trans-N,N′*-diisopropylcyclohexane-1,2-diamine,[7a] the diazo compound **2** was obtained in near quantitative yield as a yellow oil (Scheme 1). Attempts to prepare the corresponding carbene **3** by photolysis of **2** at −40 °C gave the heterocycle **4**. This 1,3-diphosphete,[8] which is formally the head-to-tail [2+2] dimer of carbene **3**, has been fully characterized; the results of the X-ray diffraction study of **4** are given in Figure 1.

Since, the [bis(diisopropylamino)phosphino](trimethylsilyl)carbene is stable at ambient temperature and shows no tendency for dimerization, the instability of carbene **3** was rather surprising, and could be due to the strained bicyclic structure introduced by the diaminocyclohexane ligand. To check this hypothesis we prepared the phosphino(trimethylsilyl)diazomethane **6** derived from the achiral *N,N′*-diiso-

DOI: 10.1002/chem.200305722



Scheme 1. R = $SiMe_3$.

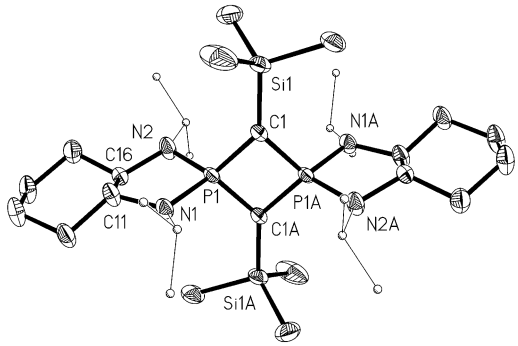


Figure 1. Structure of 1,3-diphosphete **4** (thermal ellipsoids drawn at 50% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

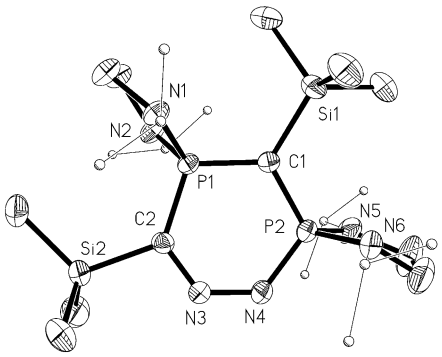
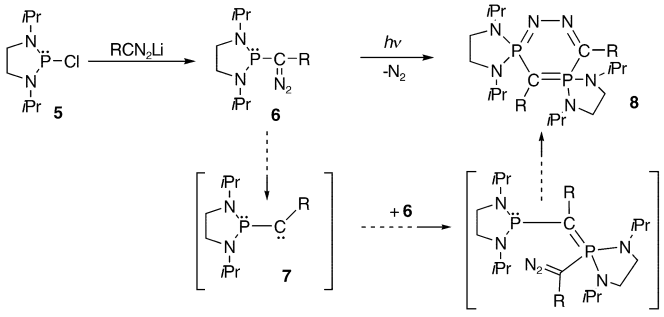


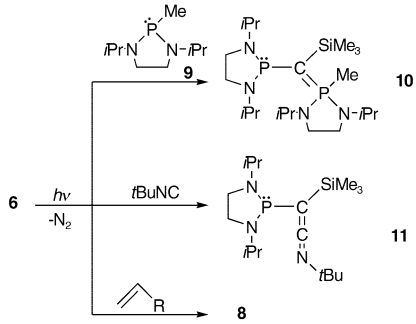
Figure 2. Strcture of six-membered heterocycle **8** (thermal ellipsoids drawn at 50% probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

propyl-1,2-ethanediamine.[7b] Photolysis of **6** in solution in pentane at −80 °C afforded the six-membered heterocycle **8** in near quantitative yield (Scheme 2). The presence of two nonequivalent phosphorus atoms was indicated by an AX system in the ^{31}P NMR spectrum [δ = 26.7 and 36.3 ppm, J(P,P) = 34 Hz]. The heterocyclic structure of **8** was unambiguously established by a single-crystal X-ray diffraction study (Figure 2). Interestingly, compound **8**, which presents an endocyclic phosphazine unit, is perfectly stable at room temperature. There was no evidence for the release of dinitrogen to afford the corresponding 1,3-diphosphete.



Scheme 2. R = $SiMe_3$.

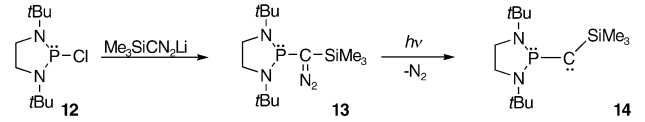
The formation of **8** probably results from the reaction of the transient carbene **7** with the starting diazo compound **6**. One can imagine the interaction of the carbene center of **7** with the phosphine center of **6**,[9] followed by an intramolecular Staudinger–Meyer reaction.[10] To validate this hypothesis, we conducted the photolysis of **6** in the presence of the phosphine **9**. In this case, the formation of **8** was avoided, and phosphorus ylide **10** was isolated (Scheme 3). The coupling of the phosphine with the carbene center was indicated by an AX system in the ^{31}P NMR spectrum [δ = 54.2 and 127.7 ppm, J(P,P) = 147 Hz]. Interestingly, transient carbene **7** can also be trapped by *tert*-butyl isocyanide, which affords the corresponding phosphinoketeneimine **11** in good yield [IR: $\tilde{\nu}$ = 1979 (ν(CCN)) cm^{-1}]. However, no cyclopropanation reactions occurred in the presence of either electron-poor or electron-rich olefins; only the formation of **8** was observed.



Scheme 3.

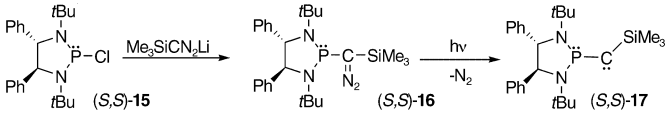
These results clearly demonstrate that the stability of phosphino(silyl)carbenes is dramatically related to the steric bulk of the amino substituents at phosphorus. To confirm this, the five-membered ring skeleton was kept unchanged,

while the isopropyl groups on nitrogen were replaced by *tert*-butyl substituents. In this case, the corresponding carbene **14** appeared to be perfectly stable at room temperature and could be isolated in near quantitative yield (Scheme 4).



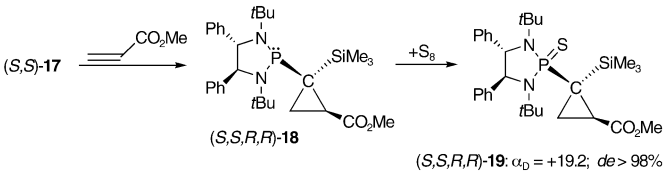
Scheme 4.

Taking these results into account, the (*S,S*)-, and (*R,R*)-*N,N'*-di-*tert*-butyl-1,2-diphenyl-1,2-ethanediamines[7c] were used to prepare the corresponding enantiomerically pure phosphino(silyl)diazo compounds (*S,S*)-**16** and (*R,R*)-**16**, respectively. Both enantiomers have been isolated in good yields as yellow oils [δ(P) = 116.3 ppm; IR: $\tilde{\nu}$ = 2018 ($\nu(CN_2)$) cm^{-1}]. The photolysis of solutions of (*S,S*)-**16** and (*R,R*)-**16** in toluene at −40 °C gave, after evolution of dinitrogen, the corresponding stable optically pure carbene (*S,S*)-**17** and (*R,R*)-**17**, respectively. The reactions were monitored by ^{31}P NMR spectroscopy (δ = −32.7 ppm) and were complete after 18 h (Scheme 5).



Scheme 5.

Addition of two equivalents of methyl acrylate to a solution of each enantiomer of carbene **17** in toluene cleanly yields the corresponding cyclopropanes **18**. According to ^{31}P and ^{1}H NMR spectrocospy, prior to any purification, only one diastereomer could be detected in each experiment (*de* > 98 %). After addition of elemental sulfur the corresponding thioxo derivatives (*S,S,R,R*)-**19** (α_D = +19.2) and (*R,R,S,S*)-**19** (α_D = −19.2) were isolated as colorless crystalline solids in 85 and 80 % yield, respectively (Scheme 6).



Scheme 6.

The absolute configuration of the two newly formed chiral centers and the total *syn* diastereoselectivity (with respect to the phosphino group) were confirmed by two X-ray diffraction studies (Figure 3 and Figure 4).

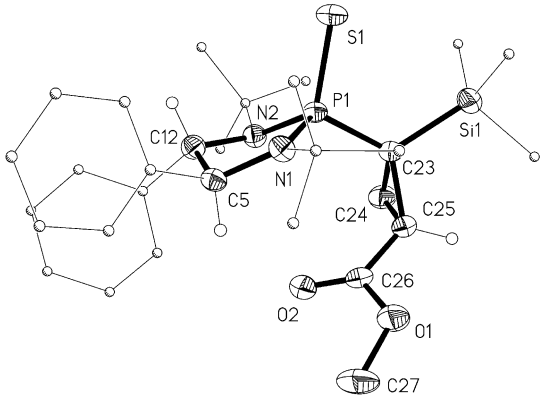


Figure 3. Strcture of (*SSRR*)-**19** (thermal ellipsoids drawn at 50 % probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

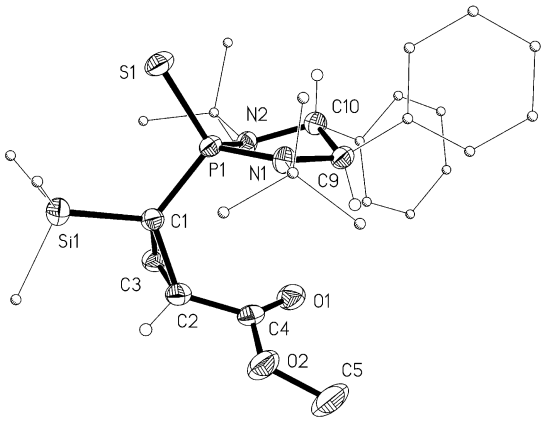
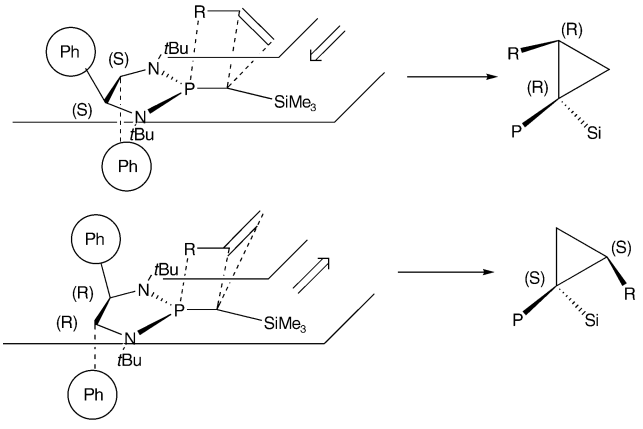


Figure 4. Structure of (*RRSS*)-**19** (thermal ellipsoids drawn at 50 % probability for non-hydrogen atoms; hydrogen atoms omitted for clarity).

The *syn*-selectivity has already been rationalized by invoking a second-order orbital interaction between the phosphorus center and the olefin substituent.[5b] The very high enantioselectivity observed is a consequence of the obstruction of one side of the phosphino(silyl)carbene by one of the phenyl groups, directing the approach of the olefin as indicated in Scheme 7.



Scheme 7.

Conclusion

In conclusion, we have presented the synthesis of the first stable optically pure phosphino(silyl)carbenes. They undergo highly stereoselective cyclopropanation reactions: total *syn* diastereoselectivity (with respect to the phosphino group), and *de* > 98%. The possible cleavage of the chiral auxiliary, as well as the enantioselective synthesis of oxiranes[11] are under investigations.

Experimental Section

General remarks: All manipulations were performed under an inert atmosphere of argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker 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 NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external standards of 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer FT-IR Spectrometer 1600.

General procedure for the synthesis of chlorophosphines 1, 5, 12, and 15: One equivalent of PCl_3 (18 mmol) was added dropwise at 0°C to a solution of diamine (18 mmol) and Et_3N (55 mmol) in toluene (30 mL). The reaction mixture was warmed to room temperature, and stirred for 2 h. After removal of ammonium salts by filtration, the solvent was removed under vacuum, and the chlorophosphines were obtained in near quantitative yields as colorless oils. Spectroscopic data for **1**,[12a] **5**,[12b] and **12**[12c] are in agreement with those previously described.

15: (*S,S*)-**15**, $[\alpha]_D^{20} = -25.4$; (*R,R*)-**15**, $[\alpha]_D^{20} = +25.4$ ($c = 0.05$ in CH_2Cl_2); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 176.0$ ppm; ^{1}H NMR (C_6D_6): $\delta = 1.25$ (s, 18H; CH_3C), 4.52 (d, $^3J_{(P,H)} = 6.1$ Hz, 2H; CHNP), 7.32 ppm (m, 10H; H_{aro}); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 30.5$ (d, $^3J_{(P,C)} = 11.9$ Hz, CCH_3), 55.1 (d, $^2J_{(P,C)} = 12.0$ Hz; PNC), 75.0 (d, $^2J_{(P,C)} = 11.1$ Hz; NCH), 127.4, 127.8, 128.7, 143.6 ppm (s; C_{aro}).

General procedure for the synthesis of phosphino(diazomethane) 2, 6, 13, and 16: One equivalent of the lithium salt of trimethylsilyldiazomethane [Me_3SiCN_2H (5 mmol) + BuLi (5 mmol) in THF (10 mL) at −78°C for 30 min] was added dropwise at −78°C to a solution of chlorophosphine (5 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature, and stirred for 1 h. The solvent was removed under vacuum, and the red residue was extracted with pentane (2×5 mL). After evaporation of pentane, the diazo compounds were obtained as yellow oils in good yields.

2: Yield 95%; IR (toluene): $\tilde{\nu} = 2019$ cm^{-1} (CN_2); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 93.4$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 0.19$ (s, 9H; CH_3Si), 1.16 (d, $^3J_{(H,H)} = 6.9$ Hz, 3H; CH_3), 1.18 (d, $^3J_{(H,H)} = 6.9$ Hz, 3H; CH_3), 1.21 (d, $^3J_{(H,H)} = 6.9$ Hz, 3H; CH_3), 1.32 (d, $^3J_{(H,H)} = 6.9$ Hz, 3H; CH_3), 1.73–2.51 (m, 8H; CH_2), 2.98 (m, 2H; CHN), 3.43 ppm (sept d, $^3J_{(H,H)} = 6.9$ Hz, $^3J_{(P,H)} = 13.8$ Hz, 2H; CHN).

6: Yield 92%; IR (toluene): $\tilde{\nu} = 2026$ cm^{-1} (CN_2); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 106.0$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 0.28$ (s, 9H; CH_3Si), 1.32 (d, $^3J_{(H,H)} = 6.3$ Hz, 12H; CH_3C), 3.11 (m, 2H; CH), 3.40 ppm (m, 4H; CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -0.6$ (s; CH_3Si), 21.9 (d, $^3J_{(P,C)} = 8.3$ Hz; CH_3C), 46.8 (d, $^2J_{(P,C)} = 8.3$ Hz; CH_2), 48.4 ppm (d, $^2J_{(P,C)} = 17.5$ Hz; CH).

13: Yield 90%; IR (pentane): $\tilde{\nu} = 2020$ cm^{-1} (CN_2); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 97.0$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 0.00$ (s, 9H; CH_3Si), 1.10 (s, 18H; CH_3C), 2.79 (m, 2H; CH_2), 3.21 ppm (m, 2H; CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 0.7$ (d, $^3J_{(P,C)} = 3.0$ Hz; CH_3Si), 29.1 (d, $^3J_{(P,C)} = 10.0$ Hz; CH_3C), 39.2 (d, $^1J_{(P,C)} = 15.0$ Hz; CN_2), 41.1 (d, $^2J_{(P,C)} = 7.5$ Hz; CH_3C), 45.3 ppm (d, $^2J_{(P,C)} = 7.5$ Hz; CH_2).

16: Yield 89%; (*S,S*)-**16** $[\alpha]_D^{20} = -18.8$, (*R,R*)-**16** $[\alpha]_D^{20} = +18.7$ ($c = 0.06$ in toluene); IR (toluene): $\tilde{\nu} = 2018$ cm^{-1} (CN_2); ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 116.3$ ppm; ^{1}H NMR (C_6D_6): $\delta = 0.29$ (s, 9H; CH_3Si), 1.20, 1.24 (s, 18H; CH_3C), 4.57 (d, $^3J_{(H,H)} = 8.0$ Hz, 1H; CHNP), 4.91 (dd, $^3J_{(H,H)} = 8.0$ Hz, $^3J_{(P,H)} = 3.0$ Hz, 1H; CHNP), 7.21 ppm (m, 10H; H_{aro}); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 1.4$ (s; CH_3Si), 30.3 (d, $^3J_{(P,C)} = 11.9$ Hz; CCH_3), 31.0 (d, $^3J_{(P,C)} = 11.8$ Hz; CCH_3), 30.3 (d, $^3J_{(P,C)} = 11.9$ Hz; CCH_3), 32.8 (d, $^1J_{(P,C)} = 56.1$ Hz; PC), 54.8 (s; PNC), 56.1 (d, $^2J_{(P,C)} = 24.8$ Hz; PNC), 73.6 (d, $^2J_{(P,C)} = 10.1$ Hz; NCH), 74.4 (d, $^2J_{(P,C)} = 7.3$ Hz; NCH), 127.7, 128.0, 128.5, 144.6 ppm (s; C_{aro}).

General procedure for the photolysis of diazophosphines 2, 6, 13, and 16: A solution of diazophosphine (0.3 mmol) in toluene or pentane (2 mL) was irradiated ($\lambda_{max} = 312$ nm) at −40°C. The evolution of the reaction was monitored by ^{31}P NMR spectroscopy.

Synthesis of four-membered ring 4: After irradiation overnight, heterocycle **4** slowly crystallized in the toluene solution at −40°C as white crystals (75%). m.p. 250°C (decomp); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 48.8$ ppm; ^{1}H NMR ($CDCl_3$): $\delta = 0.28$ (s, 9H; CH_3Si), 0.32 (s, 9H; CH_3Si), 1.30 (d, $^3J_{(H,H)} = 6.9$ Hz, 12H; CH_3), 1.34 (d, $^3J_{(H,H)} = 6.9$ Hz, 12H; CH_3), 1.00–1.47 (m, 8H; CH_2), 2.10 (m, 8H; CH_2), 2.79 (m, 4H; CH), 4.14 ppm (sept, $^3J_{(H,H)} = 6.9$ Hz, 4H; CHN); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 1.3$ (s; CH_3Si), 4.0 (s; CH_3Si), 19.3 and 25.7 (s; CH_3), 24.4 and 32.8 (s; CH_2), 43.9 (d, $^2J_{(P,C)} = 21.6$ Hz; CHN), 60.1 ppm (d, $^2J_{(P,C)} = 20.4$ Hz; CHN).

Synthesis of six-membered heterocycle 8: After irradiation overnight, heterocycle **8** slowly crystallized in the toluene solution at −40°C as white crystals (80%). m.p. 162–163°C; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 26.7$ and 36.3 ppm (d, $J_{(P,P)} = 33.6$ Hz); ^{1}H NMR ($CDCl_3$): $\delta = 0.12$ (s, 9H; CH_3Si), 0.16 (s, 9H; CH_3Si), 1.14 (m, 24H; CH_3C), 3.13 (m, 8H; CH_2), 3.40 ppm (m, 4H; CH); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 0.8$ (s; CH_3Si), 3.0 (s; CH_3Si), 20.2–21.9 (m; CH_3C), 37.1 (d, $^2J_{(P,C)} = 9.2$ Hz; CH_2), 38.0 (d, $^2J_{(P,C)} = 8.3$ Hz; CH_2), 43.4 (d, $^2J_{(P,C)} = 9.2$ Hz; CH), 43.9 ppm (d, $^2J_{(P,C)} = 6.4$ Hz, CH); elemental analysis calcd (%) for $C_{24}H_{54}N_6Si_2P_2$: C 52.91, H 9.99, N 15.42; found: C 52.95, H 10.05, N 15.36.

Synthesis of phosphine 9: Methyllithium (3.5 mL, 5.0 mmol; 1.3 equiv) was added dropwise at −78°C to a solution of chlorophosphine **5** (0.82 g, 4.0 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature, and stirred for 1 h. The solvent was removed under vacuum, and the residue was extracted with pentane (2×5 mL). Phosphine **9** was obtained as a colorless oil, after evaporation of pentane (0.76 g, 88%). ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 95.3$ ppm.

Synthesis of phosphorus ylide 10: After irradiation of **6** overnight in the presence of 1.3 equivalents of phosphine **9**, ^{31}P NMR spectroscopy indicated the quantitative formation of ylide **10**, which was obtained as a yellow oil, after evaporation of pentane. ^{31}P{^{1}H} NMR (C_6D_6): $\delta = 54.2$ and 127.7 ppm (d, $J_{(P,P)} = 146.5$ Hz); ^{1}H NMR (C_6D_6): $\delta = 0.49$ (s, 9H; CH_3Si), 0.89 (d, $^3J_{(H,H)} = 6.6$ Hz, 6H; CH_3C), 1.05 (d, $^3J_{(H,H)} = 6.7$ Hz, 6H; CH_3C), 1.28 (d, $^3J_{(H,H)} = 7.6$ Hz, 6H; CH_3C), 1.32 (d, $^3J_{(H,H)} = 6.9$ Hz, 6H; CH_3C), 1.67 (dd, $J_{(P,H)} = 12.5$ and 8.4 Hz, 3H; CH_3P), 2.46–3.16 (m, 8H; CH_2), 3.52 ppm (m, 4H; CH); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 4.8$ (s; CH_3Si), 16.3 (dd, $J_{(P,C)} = 69.8$ and 28.5 Hz; CH_3P), 20.3 (d, $^3J_{(P,C)} = 6.4$ Hz; CH_3C), 20.9 (d, $^3J_{(P,C)} = 2.8$ Hz; CH_3C), 21.0 (d, $^3J_{(P,C)} = 5.5$ Hz; CH_3C), 22.9 (d, $^3J_{(P,C)} = 7.4$ Hz; CH_3C), 36.6 (d, $^2J_{(P,C)} = 8.3$ Hz; CH_2), 42.4 (d, $^2J_{(P,C)} = 9.2$ Hz; CH), 44.4 (s; CH_2), 47.9 ppm (d, $^2J_{(P,C)} = 28.5$ Hz; CH).

Synthesis of keteneimine 11: After of irradiation of **6** overnight in the presence of three equivalents of *t*BuNC, ^{31}P NMR spectroscopy indicated the quantitative formation of keteneimine **11**, which was obtained as a yellow oil, after evaporation of pentane. IR ($CDCl_3$): $\tilde{\nu} = 1979$ cm^{-1} (>C=C=N-); ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 104.1$ ppm; ^{1}H NMR (C_6D_6): $\delta = 0.15$ (s, 9H; CH_3Si), 1.17 (d, $^3J_{(H,H)} = 6.4$ Hz, 12H; CH_3CN), 1.26 (s, 9H; CH_3C), 2.99–3.27 ppm (m, 6H; CH_2 and CH); ^{13}C{^{1}H} NMR (C_6D_6): $\delta = 0.5$ (s; CH_3Si), 22.4 (d, $^3J_{(P,C)} = 11.0$ Hz; CH_3CN), 23.1 (d, $^3J_{(P,C)} = 10.1$ Hz; CH_3CN), 30.5 (s; CH_3C), 47.6 (d, $^2J_{(P,C)} = 9.2$ Hz; CH_2), 49.2 (d, $^2J_{(P,C)} = 19.3$ Hz; CH), 44.4 (s; CH_2), 47.9 ppm (d, $^2J_{(P,C)} = 28.5$ Hz; CH).

Preparation of phosphino(silyl)carbenes 14 and 17: After irradiation of **13** or **16** overnight at −40°C, ^{31}P NMR spectroscopy indicated the quantitative formation of the corresponding carbenes **14** ($\delta = -36.0$ ppm) and **17** ($\delta = -32.7$ ppm), which are stable at room temperature, and were used without any further purification.

Synthesis of cyclopropanes 19: Methyl acrylate (0.6 mmol; 2 equiv) was added at room temperature to a solution of carbene **17** (0.3 mmol) in toluene (3 mL). The resulting mixture was stirred at room temperature for 30 min. ^{31}P NMR spectroscopy indicated the quantitative formation of cyclopropane **18** ($\delta = 126.0$ ppm). Treatment of this solution with an excess of elemental sulfur gave the corresponding thioxophosphoranyl derivative **19**, which was purified by column chromatography (heptane/toluene: 1/1) and recrystallized from a pentane/diethyl ether (50/50) solution as

colorless crystals. m.p. 179–180 °C; (*S,S,R,R*)-**19** $[\alpha]_D^{20}=19.1$; 80% yield. (*R,R,S,S*)-**19** $[\alpha]_D^{20}=-19.2$ ($c=0.05$ in CH_2Cl_2); 85% yield. $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta=87.6$ ppm; ^1H NMR (C_6D_6): $\delta=0.30$ (s, 9H; CH_3Si), 1.24, 1.37 (s, 18H; CH_3C), 1.72 (ddd, $J=4.0$, 5.8 and 11.7 Hz, 1H; CH_{ring}), 2.29 (ddd, $J=5.8$, 6.4 and 13.7 Hz, 1H; CH_{ring}), 2.71 (ddd, $J=4.0$, 6.4 and 23.1 Hz, 1H; CH_{ring}), 4.23 (dd, $^3J_{(H,H)}=8.0$ Hz, $^3J_{(P,H)}=3.6$ Hz 1H; CHNP), 4.53 (d, $^3J_{(H,H)}=8.0$ Hz, 1H; CHNP), 6.63–7.99 ppm (m, 10H; H_{aro}); elemental analysis calcd (%) for $C_{30}H_{45}N_2O_2SiPS$: C 64.71, H 8.15, N 5.03; found: C 64.70, H 8.17, N 5.10 for (*S,S,R,R*)-**19**, and C 64.75, H 8.20, N 4.98 for (*R,R,S,S*)-**19**.

Crystallographic data for 4, 8, (*S,S,R,R*)-19 and (*R,R,S,S*)-19: Data for all structures were collected at low temperature ($T=173(2)$ K for **4** and $T=193(2)$ K for the other structures) using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å). The structures were solved by direct methods (SHELXS-97)[13] and all non-hydrogen atoms were refined anisotropically using the least-squares method on F^2.[14] Crystal data for **4**: $C_{16}H_{33}N_2PSi$, $M_r=312.50$, triclinic, space group $P\bar{1}$ with $a=10.366(2)$, $b=10.462(2)$, $c=10.968(2)$ Å, $\alpha=65.165(3)$, $\beta=65.088(3)$, $\gamma=67.073(3)°$, $V=945.7(3)$ Å^3, $Z=2$. A total of 5492 reflections (3779 independent, $R_{int}=0.0830$) were collected, largest residual electron density: 0.697 eÅ^{-3}, $R1=0.0519$ (for $I>2\sigma(I)$) and $wR2=0.1448$ (all data). Crystal data for **8**: $C_{24}H_{54}N_6P_2Si_2$, $M_r=544.85$, monoclinic, space group $P2_1/c$ with $a=18.318(2)$, $b=11.540(2)$, $c=16.753(2)$ Å, $\beta=116.009(2)°$, V=3182.7(7) Å^3, $Z=4$. A total of 15136 reflections (5189 independent, $R_{int}=0.0587$) were collected, largest residual electron density: 0.647 eÅ^{-3}, $R1=0.0528$ (for $I>2\sigma(I)$) and $wR2=0.1505$ (all data). Crystal data for (*S,S,R,R*)-**19**: $C_{30}H_{45}N_2O_2PSSi$, $M_r=556.80$, orthorhombic, space group $P2_12_12_1$ with $a=10.5171(6)$, $b=15.4110(8)$, $c=19.2820(10)$ Å, V=3125.2(3) Å^3, $Z=4$. A total of 18390 reflections (6398 independent, $R_{int}=0.0316$) were collected, largest residual electron density: 0.254 eÅ^{-3}, $R1=0.0305$ (for $I>2\sigma(I)$) and $wR2=0.0742$ (all data). Crystal data for (*R,R,S,S*)-**19**: $C_{30}H_{45}N_2O_2PSSi$, $M_r=556.80$, orthorhombic, space group $P2_12_12_1$ with $a=10.528(1)$, $b=15.439(2)$, $c=19.311(2)$ Å, $V=3138.8(6)$ Å^3, $Z=4$. A total of 23078 reflections (6391 independent, $R_{int}=0.0355$) were collected, largest residual electron density residue: 0.230 eÅ^{-3}, $R1=0.0332$ (for $I>2\sigma(I)$) and $wR2=0.0761$ (all data).

CCDC-224336 (**4**), CCDC-224337 (**8**), CCDC-224338 ((*S,S,R,R*)-**19**), and CCDC-224339 ((*R,R,S,S*)-**19**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at 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.ac.uk).

Acknowledgment

Thanks are due to the CNRS for financial support of this work, and to the French–Polish Associate European Laboratory for a grant to J. K.

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Received: November 14, 2003
Revised: January 7, 2004 [F5722]