mL) was added 1 mmol of the corresponding alcohol (ROH), and the reaction was stirred at room temperature for 1 h. A solution of H_2O (0.045 g, 2.5 mmol) in 2 mL of THF was added via syringe. The formation of a gel was observed rapidly; in the case of [K,18-crown-6][$Si(OMe)_5$], a white precipitate was observed (see Table I). The IR spectrum shows the SiOSi stretching frequency (1100 cm^{-1}) with shoulders at 970 and 1230 cm^{-1} characteristic of a SiOPh bond.

$HSi(OR)_3$ (R = Me, Et, *n*-Bu, *i*-Pr, Ph). H_2O (0.045 g, 2.5 mmol) was added neat via syringe to the solution of $HSi(OR)_3$ (1 mmol) in THF (10 mL). The solution was kept at room temperature without stirring under the conditions of Table III. The solvent was removed under vacuum to give a viscous liquid. IR spectra were recorded neat as a film with use of NaCl windows. (A KBr pellet was used in the case of the hydrolysis product of $HSi(OPh)_3$). See Table III.

$HSi(OR)_3$ + KOR (10%) (R = Me, Et, *n*-Bu, *i*-Pr, Ph). A 0.1-mmol portion of KOR was added to 5 mL of THF, and the mixture was stirred for 5 min. The solution was then added to the solution of the corresponding trialkoxysilane $HSi(OR)_3$ (1 mmol) and H_2O (0.045 g, 2.5 mmol) in THF (5 mL). The mixture was kept at room temperature under the conditions of Table III. IR spectra (KBr pellet) were recorded after evaporation of the solvent under vacuum.

K[$HSi(OR)_4$] (R = Me, Et, *n*-Bu, *i*-Pr, Ph). A solution of H_2O (0.045 g, 2.5 mmol) in THF (2 mL) was added to a solution of K[$HSi(OR)_4$] (1 mmol) in THF (8 mL), and the mixture was kept at room temperature without stirring under the conditions of Table III. IR spectra of the products were recorded after evaporation of the solvent under vacuum (KBr pellet). See Table III.

Alcoholysis Reaction of K[$HSi(OR)_4$] (R = Me, Et, *n*-Bu, Ph). To a solution of K[$HSi(OR)_4$] (8.0 mmol) and 18-crown-6 (8.0 mmol) in THF (20 mL) at 0 °C was added the corresponding alcohol ROH (8 mmol), neat, and the reaction mixture was stirred at room temperature for 1 h. Removal of the solvent under vacuum gave a white-yellow solid. ^{29}Si NMR spectral data are given in Table III. Data are identical with those for [K,18-crown-6][$Si(OR)_5$].[14]

Hydrogen Titration. After Hydrolysis of $HSi(OEt)_3$. The viscous liquid obtained after reaction of 1 mmol of $HSi(OEt)_3$ and evaporation of THF was dissolved in 5 mL of THF of a Schlenck tube, and 0.1 g of solid KOH was added. Gas evolution was measured with a gas buret over water. The reaction needs 20 min for 22 mL of gas while 98% (0.98 mmol) was obtained.

After Hydrolysis of $HSi(OMe)_3$. The same procedure as for the hydrolysis of $HSi(OEt)_3$ was used starting form 0.5 mmol of $HSi(OMe)_3$. Reaction time was 20 min. Ten milliliters of gas was obtained (0.045 mmol, 90%).

Reaction with HCl(g). To a solution of K[$H_2Si(O\text{-}i\text{-}Pr)_3$], K[$HSi(O\text{-}i\text{-}Pr)_4$], or $HSi(O\text{-}i\text{-}Pr)_3$ (1 mmol) in THF (10 mL) at −78 °C was bubbled HCl gas (dried through H_2SO_4) for 10 min. The excess HCl was pumped off immediately at low temperature, and the products were analyzed by gas chromatography. The results are given in Scheme V. The same procedure was used to follow the reactions of Scheme IV.

K[$H_2Si(O\text{-}i\text{-}Pr)_3$] + *i*-PrOH. A solution of *i*-PrOH (0.22 g, 3.7 mmol) in 5 mL of THF was added rapidly to a solution of K[$H_2Si(O\text{-}i\text{-}Pr)_3$] (0.90 g, 3.7 mmol) in THF (15 mL) at −78 °C. The mixture was stirred at −78 °C for 3 h and then treated with HCl gas at −78 °C. Gas chromatographic analysis gave 25% $Si(O\text{-}i\text{-}Pr)_4$ and 60% $HSi(O\text{-}i\text{-}Pr)_3$.

$HSi(O\text{-}i\text{-}Pr)_3$ + KO-*i*-Pr. A solution of $HSi(O\text{-}i\text{-}Pr)_3$ (0.32 g, 1.5 mmol) in THF (1 mL) was added rapidly to a solution of KO-*i*-Pr (0.15 g, 1.5 mmol) in THF (9 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and then treated with HCl gas at −78 °C. Gas chromatographic analysis gave 65% $Si(O\text{-}i\text{-}Pr)_4$ and 25% $HSi(O\text{-}i\text{-}Pr)_3$.

Synthesis of Stable Boryl-Substituted Diazomethane and Nitrilimines

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Addition of bis(diisopropylamino)chloroborane to the lithium salt of (triisopropylsilyl)-, [bis(diisopropylamino)phosphino]-, and [bis(diisopropylamino)thioxophosphoranyl]diazomethane led to the corresponding stable *N*-borylnitrilimines **6–8** in 80, 90, and 95% yield, respectively. Addition of sulfur to C-phosphinonitrilimine **7** gave the thioxophosphoranyl analogue **8**. The chloroborane reacted with the lithium salt of diazomethane, leading to a mixture of [bis(diisopropylamino)boryl]diazomethane (**11**) (54% yield) and bis[bis(diisopropylamino)boryl]nitrilimine (**9**) (20% yield). Compound **9** can be obtained in good yield by reacting the lithium salt of [bis(diisopropylamino)boryl]diazomethane with chloroborane. Photolysis of nitrilimines **6–9** afforded the corresponding carbodiimides **12–15**. The regioselectivity and stereoselectivity of the 2 + 3 cycloaddition reactions of **6–8** with olefins were studied.

Introduction

Main-group element-substituted diazo compounds have been widely studied[1] except in the boron series. Indeed, only two examples of α-boryldiazomethane, characterized by IR in solution, have been reported.[2] The lack of examples in this class of compounds is probably due to the ability of Lewis acids to catalyze the decomposition of diazo derivatives.[1] Moreover, very little is known among the possible structural isomers of α-boryldiazo derivatives. To the best of our knowledge, a few borylcarbodiimides

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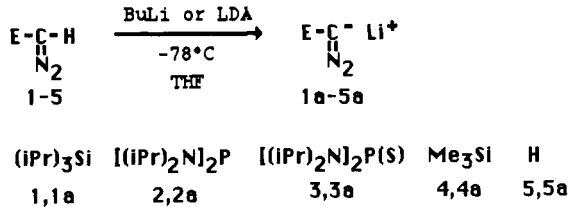
Scheme I



have been characterized,[3] but no boron-substituted diazirines, isodiazirines, cyanamides, isocyanamides, or nitrilimines have been prepared.

We have recently shown that the reaction of various electrophiles with the lithium salt of heterosubstituted diazomethanes led to the corresponding diazo compounds or nitrilimines, depending on the nature of both reagents.[4] Here we report the syntheses of the first isolable α-diazo borane and borylnitrilimines, and of some new borylcarbodiimides. The dipolarophilic activities and the photochemical behavior of the nitrilimines are presented.

Results

Bis(diisopropylamino)chloroborane[5] was chosen as the boron starting material, since the presence of bulky amino groups should decrease the Lewis acid character of boron and prevent intermolecular reactions. Five different diazo lithium salts **1a–5a** were chosen for this study. They were prepared by addition, at −78 °C, of a stoichiometric amount of BuLi or lithium diisopropylamide (LDA) to a THF solution of (triisopropylsilyl)diazomethane (**1**),[4a] [bis(diisopropylamino)phosphino]diazomethane (**2**),[4c] [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**3**),[4c] (trimethylsilyl)diazomethane (**4**),[6] and diazomethane **5**[7,8] (Scheme I).

Since we have already shown[4] that the use of hindered diazo lithium salts allows the synthesis of stable nitrilimines, and, since there was no obvious reasons why borylnitrilimines should be less stable than the heterosubstituted ones that have already been prepared, we first studied the reaction of the chloroborane with **1a**, **2a**, and **3a**. We obtained the corresponding *N*-borylnitrilimines **6–8** in 80, 90, and 95% yield, respectively. The *C*-silylnitrilimine **6** was isolated, after recrystallization from cold acetonitrile, as white crystals (mp <20 °C), and the *C*-phosphinonitrilimine **7** is a yellow oil, which was purified by distillation [110–115 °C (0.2 mmHg)], while the *C*-(thioxophosphoranyl)nitrilimine **8** cannot be distilled and was obtained as a yellow oil. Interestingly, addition of elemental sulfur to **7** afforded the thioxophosphoranyl analogue **8** (Scheme II).

Since the lithium salt of (trimethylsilyl)diazomethane (**4a**) gave stable diazo compounds with hindered chlorophosphanes,[9] we then studied the reaction of **4a** with chloroborane. The reaction carried out in THF, at −78 °C, gave rise to two main products. The minor one (10% yield), with a boiling point of 40–45 °C (10^{-2} mmHg), presented a strong infrared absorption at 2043 cm^{-1} and appeared to be bis(trimethylsilyl)diazomethane (**10**).[10] The major one (70% yield) featured a broad and strong absorption at 2160 cm^{-1} and was identified as bis[bis(diisopropylamino)boryl]nitrilimine (**9**). This *C*- and *N*-borylnitrilimine **9** is thermally stable and was obtained as a yellow oil after distillation at 110–120 °C (10^{-3} mmHg) (Scheme II).

Taking into account this unexpected result, we tried the reaction of the simplest diazo lithium salt **5a** with the chloroborane. Once more, according to IR spectroscopy, two products were obtained and were purified by distillation. The lighter product [bp 70–74 °C (0.1 mmHg)] was isolated as a yellow oil (54% yield) and was unambiguously characterized as the C-unsubstituted α-boryldiazomethane **11**. The heavier product appeared to be the *C*- and *N*-borylnitrilimine **9** (20% yield) (Scheme II).

Photolysis of boryldiazomethane **11** led to a complicated mixture of products. In contrast, irradiation of nitrilimines **6–9** cleanly led to the corresponding carbodiimides **12–15**. Once more, addition of sulfur to phosphinocarbodiimide **13** afforded the thioxophosphoranyl analogue **14** (Scheme III).

The three nitrilimines **6–8** only reacted with electron-poor dipolarophiles, while no cycloaddition was observed with the fully borylated nitrilimine **9**. Three olefins, methyl acrylate, dimethyl fumarate, and dimethyl maleate, were chosen in order to study the regioselectivity and the stereoselectivity of the 2 + 3 cycloaddition reactions. The *C*-silylnitrilimine **6** reacted with methyl acrylate, leading to a mixture of 5- and 4-substituted pyrazolines **16** and **17** in a 6/4 ratio, in 85% total yield. In contrast, nitrilimines **7** and **8** added onto methyl acrylate in one direction only, affording the 5-substituted pyrazolines **18** and **19** in 75 and 90% yield, respectively. On column chromatography, *N*-boryl pyrazoline **19** was partly (50%) transformed into the *N*-hydropyrazoline **19′**. The reaction of **6**, **7**, and **8** with dimethyl fumarate led only to the trans isomers **20**, **21**, and **22** in 75, 95, and 95% yield, respectively. Dimethyl maleate did not react with C-silylated nitrilimine **6**, while with **7** and **8** a slow reaction occurred, leading to a mixture of trans and cis adducts **21**/**23** and **22**/**24** in 50/50 and 70/30 ratios, respectively. The cycloadducts **18**, **21**, and **23**, originating from the *C*-phosphinonitrilimine **7**, can be converted by treatment with elemental sulfur into the corresponding thioxophosphoranyl pyrazolines **19**, **22**, and **24** (Scheme IV).

Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^{1}H, ^{31}P, ^{29}Si, ^{11}B, and ^{13}C NMR spectra were recorded on Bruker AC80, WM250, or AM300 spectrometers. ^{1}H, ^{29}Si, and ^{13}C chemical shifts are reported in parts per million relative to Me_4Si as external standard. ^{31}P NMR and ^{11}B NMR downfield shifts are expressed with a positive sign, in parts per million, relative to external 85% H_3PO_4 and $BF_3{\cdot}OEt_2$, respectively. Infrared spectra were recorded on a Beckman IR10 or a Perkin-Elmer lattice spectrometer (Model 598), using a polystyrene film for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet pho-

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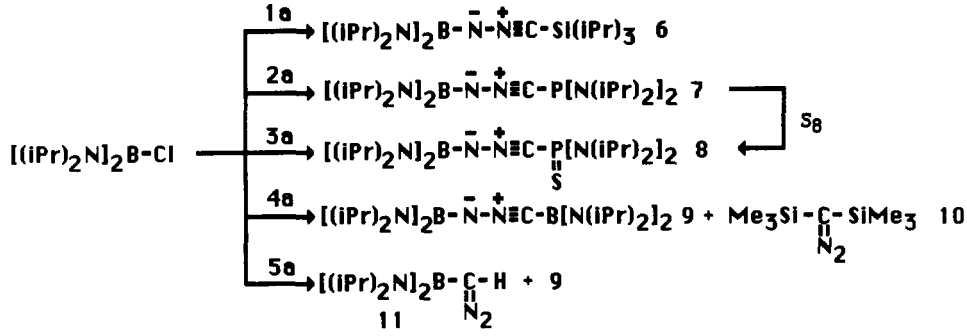
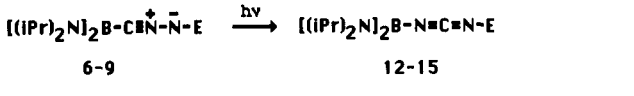
Scheme II



Scheme III



tochemical reactor. Conventional glassware was used. Liquid chromatography was performed on silica gel.

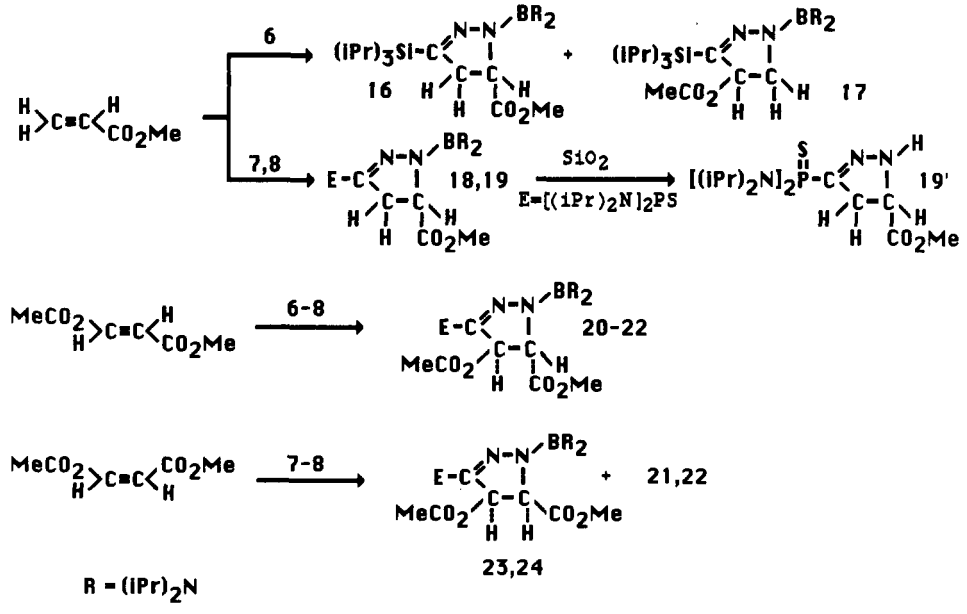
Caution: Diazomethane is toxic and potentially explosive.

Synthesis of *C*-(Triisopropylsilyl)-*N*-[bis(diisopropylamino)boryl]nitrilimine (6). To a THF solution (30 mL) of (triisopropylsilyl)diazomethane (0.6 g, 3 mmol) and dibenzo-18-crown-6 ether (1.2 g, 3 mmol), at −95 °C, was added dropwise the stoichiometric amount of BuLi in hexane (3 mmol). The solution was stirred at −95 °C, for 30 min; then a THF solution (50 mL) of bis(diisopropylamino)chloroborane (0.74 g, 3 mmol) was added dropwise. The reaction mixture was allowed to return slowly to ambient temperature, over a period of 2 h. The solvent was removed in vacuo, and the residue was treated with pentane and filtered. After evaporation of the pentane, the residue was recrystallized from cold acetonitrile affording **6** as a white solid (0.98 g, 80% yield): mp <20 °C; ^{29}Si NMR ($CDCl_3$) +8.35; ^{11}B NMR ($CDCl_3$) +22; ^{1}H NMR ($CDCl_3$) 1.06 (br s, 21 H, CH_3CHSi), 1.14 (d, J(HH) = 6.7 Hz, 24 H, CH_3CHB), 3.35 (sept, J(HH) = 6.7 Hz, 4 H, CH_3CHB); ^{13}C NMR ($CDCl_3$) 12.6 (s, CHSi), 18.2 (s, CH_3CHSi), 24.0 (s, CH_3CHB), 45.1 (s, CNN), 46.6 (s, CH_3CHB); IR ($CDCl_3$) 2164 cm^{-1} (CNN). Anal. Calcd for $C_{22}H_{49}N_4BSi$: C, 64.68; H, 12.09; N, 13.71. Found: C, 64.58; H, 12.18; N, 13.84.

Synthesis of *C*-[Bis(diisopropylamino)phosphino]-*N*-[bis(diisopropylamino)boryl]nitrilimine (7). To a THF solution (30 mL) of [bis(diisopropylamino)phosphino]diazomethane (0.54 g, 2 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexane (2 mmol). After the mixture had been stirred for 30 min, at −78 °C, a stoichiometric amount of bis(diisopropylamino)chloroborane (0.49 g, 2 mmol) was added dropwise. The solution was allowed to warm to room temperature, over a period of 2 h, and the solvent was removed in vacuo. The residue was treated with pentane and filtered. After evaporation of the pentane and distillation, **7** was obtained as a yellow oil (0.87 g, 90% yield): bp 110–115 °C (0.2 mmHg); ^{31}P NMR ($CDCl_3$) +45.1; ^{11}B NMR ($CDCl_3$) +29; ^{1}H NMR ($CDCl_3$) 1.05 (d, J(HH) = 6.7 Hz, 12 H, CH_3CHP), 1.18 (d, J(HH) = 6.7 Hz, 12 H, CH_3CHP), 1.33 (d, J(HH) = 6.6 Hz, 24 H, CH_3CHB), 3.33 (sept d, J(HH) = 6.7 Hz, J(PH) = 13.4 Hz, 4 H, CH_3CHP), 3.65 (sept, J(HH) = 6.6 Hz, 4 H, CH_3CHB); ^{13}C NMR ($CDCl_3$) 23.50, 23.56 (s, CH_3CHP), 23.71 (s, CH_3CHB), 24.00, 24.08 (s, CH_3CHP), 46.49 (s, CH_3CHB), 49.25 (d, J(PC) = 11.8 Hz, CH_3CHP), 61.87 (d, J(PC) = 48.3 Hz, CNN); IR ($CDCl_3$) 2113 cm^{-1} (CNN). Anal. Calcd for $C_{25}H_{56}N_6PB$: C, 62.22; H, 11.70; N, 17.42. Found: C, 62.00; H, 11.75; N, 17.48.

Synthesis of *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)boryl]nitrilimine (8). To a THF solution (30 mL) of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (0.6 g, 2 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexane (2 mmol). The solution was stirred at −78 °C, for 30 min, and a THF solution (10 mL) of bis(diisopropylamino)chloroborane (0.49 g, 2 mmol) was added dropwise. The temperature was maintained at −78 °C until the addition was complete (10 min), and then the solution was allowed to return slowly to ambient temperature, over a period of 2 h. The solvent was removed in vacuo and the residue was treated with pentane and filtered. The residue was

Scheme IV



washed several times with pentane and, after evaporation, **8** was obtained as a yellow oil (0.98 g, 95% yield). ^{31}P NMR ($CDCl_3$) +31.8; ^{11}B NMR ($CDCl_3$) +27; ^1H NMR ($CDCl_3$) 1.12 (d, J(HH) = 6.6 Hz, 24 H, CH_3CHB), 1.32 (d, J(HH) = 6.8 Hz, 12 H, CH_3CHP), 1.37 (d, J(HH) = 6.8 Hz, 12 H, CH_3CHP), 3.47 (sept d, J(HH) = 6.6 Hz, 4 H, CH_3C*H*B), 3.70 (sept d, J(HH) = 6.8 Hz, J(PH) = 19.7 Hz, 4 H, CH_3C*H*P); ^{13}C NMR ($CDCl_3$) 22.25, 22.30, 22.68, 22.73 (s, *C*H_3CHP), 23.28 (s, *C*H_3CHB), 45.98 (s, CH_3CHB), 46.25 (d, J(PC) = 5.8 Hz, CH_3CHP), 55.67 (d, J(PC) = 132.2 Hz, CNN); IR ($CDCl_3$) 2095 cm^{-1} (CNN). Anal. Calcd for $C_{25}H_{56}N_6PBS$: C, 58.34; H, 10.97; N, 16.33. Found: C, 58.67; H, 11.16; N, 16.12.

Reaction of Nitrilimine 7 with Sulfur. To a toluene solution (10 mL) of **7** (0.49 g, 1 mmol) was added at room temperature an excess of elemental sulfur. After stirring for 2 h, at room temperature, the mixture was filtered and, after evaporation of the solvent, **8** was obtained as a yellow oil (0.50 g, 98% yield).

Reaction of the Lithium Salt of (Trimethylsilyl)diazomethane (4a) with Chloroborane. To a THF solution (100 mL) of (trimethylsilyl)diazomethane (1.94 g, 0.017 mol), at −78 °C, was added dropwise a hexane solution of BuLi (0.018 mol). The solution was stirred at −78 °C for 30 min. Then a THF solution (40 mL) of bis(diisopropylamino)chloroborane (4.2 g, 0.017 mol) was added dropwise. After stirring for 2 h at room temperature, evaporation of the solvent, treatment with pentane, filtration, and evaporation of the pentane, the residue was distilled. Bis(trimethylsilyl)diazomethane (**10**) (0.32 g, 10% yield) was first isolated [bp 40–45 °C (0.01 mmHg)], and its spectroscopic data were compared with those of an authentic sample.[10] Nitrilimine **9** was then obtained as a yellow oil (2.75 g, 70% yield; chloroborane): bp 110–120 °C (10^{-3} mmHg); ^{11}B NMR (C_7D_8, 348 K) +23, +28; ^1H NMR (C_7D_8) 1.16 (d, J(HH) = 6.8 Hz, 24 H, CH_3), 1.26 (d, J(HH) = 6.6 Hz, 24 H, CH_3), 3.30 (sept, J(HH) = 6.8 Hz, 4 H, CH), 3.53 (sept, J(HH) = 6.6 Hz, 4 H, CH); ^{13}C NMR (C_7D_8, 223 K) 23.05 and 23.30 (s, CH_3), 45.80 and 46.57 (s, CH), 65.80 (br s, CNN); IR (THF) 2160 cm^{-1} (CNN); mass spectrum, m/e 462 (M^+). Anal. Calcd for $C_{25}H_{56}N_6B_2$: C, 64.93; H, 12.21; N, 18.18. Found: C, 65.00; H, 12.26; N, 18.12.

Synthesis of [Bis(diisopropylamino)boryl]diazomethane (11). To an ethereal solution (100 mL) of diazomethane (1.68 g, 0.04 mol), at −78 °C, was added dropwise an ethereal solution (30 mL) of LDA (0.033 mol). The solution was stirred at room temperature for 1 h. After the solution was cooled to −78 °C, an ethereal solution of bis(diisopropylamino)chloroborane (8.0 g, 0.032 mol) was added dropwise. After the mixture was stirred for 2 h at room temperature and filtered and the solvent was evaporated, the residue was distilled. First, diazo compound **11** [bp 70–74 °C (0.1 mmHg)] was obtained as a yellow oil (4.35 g, 54% yield); then nitrilimine **9** distilled at 110–120 °C (10^{-3} mmHg) as a yellow oil (1.48 g, 20% yield; chloroborane) and its spectroscopic data were compared with an authentic sample prepared as mentioned above. **11**: ^{11}B NMR ($CDCl_3$) +34; ^1H NMR ($CDCl_3$, 273 K), 1.05 (d, J(HH) = 6.6 Hz, 24 H, CHCH_3), 3.17 (s, 1 H, CN_2H), 3.47 (sept, J(HH) = 6.6 Hz, 4 H, CH_3C*H*); ^{13}C NMR (C_7D_8, 223 K) 22.9 (s, *C*H_3CH), 36.51 (s, CN_2), 45.89 (s, CH_3*C*H); IR ($CDCl_3$) 2071 cm^{-1} (CN_2); mass spectrum, m/e 252 (M^+). Anal. Calcd for $C_{13}H_{29}BN_4$: C, 61.91; H, 11.59; N, 22.21. Found: C, 61.98; H, 11.52; N, 22.20.

Synthesis of Carbodiimides 12–15. Deuterated benzene solutions (3 mL) of nitrilimines **6–9** (0.5 mmol) were irradiated, at 300 mm. The reactions were monitored by ^{31}P NMR and by IR and were complete and quantitative after 18 h. Compounds **12–15** were characterized in solution. Carbodiimide **13** can be transformed into **14** by stirring the benzene solution at room temperature, during 24 h, in the presence of an excess of elemental sulfur. **12**: ^{11}B NMR (C_6D_6) +22; ^1H NMR (C_6D_6) 1.13 (s, 21 H, CH_3CHSi), 1.18 (d, J(HH) = 7 Hz, 24 H, CH_3CHB), 3.46 (sept, J(HH) = 7 Hz, 4 H, CHB); ^{13}C NMR (C_6D_6) 11.00 (s, CHSi), 14.50 (s, *C*H_3CHSi), 20.50 (s, *C*H_3CHB), 48.25 (s, CH_3CHB); IR (C_6D_6) 2200 cm^{-1} (NCN). **13**: ^{31}P NMR (C_6D_6) +82.6; ^{11}B NMR (C_6D_6) +23; ^1H NMR (C_6D_6) 1.20 (d, J(HH) = 6.7 Hz, 12 H, CH_3CHP), 1.24 (d, J(HH) = 6.7 Hz, 24 H, CH_3CHB), 1.35 (d, J(HH) = 6.7 Hz, 12 H, CH_3CHP), 3.39 (sept, J(HH) = 6.7 H, 4 H, CH_3C*H*B), 3.61 (m, J(HH) = 6.7 Hz, 4 H, CH_3C*H*P); ^{13}C NMR (C_6D_6) 23.44, 23.72, 23.92, 24.05 (s, CH_3), 45.30 (d, J(PC) = 12.6 Hz, CH_3CHP), 47.96 (s, CH_3CHB); IR (C_6D_6) 2210 cm^{-1} (NCN). **14**: ^{31}P NMR (C_6D_6) +54.5; ^{11}B NMR (C_6D_6) +22; ^1H NMR (C_6D_6) 1.02 (d, J(HH) = 6.3 Hz, 12 H, CH_3CHP), 1.13 (d, J(HH) = 6.7 Hz, 24 H, CH_3CHB), 1.18 (d, J(HH) = 6.3 Hz, 12 H, CH_3CHP), 3.32 (sept, J(HH) = 6.7 Hz, 4 H, CH_3C*H*B), 3.53 (sept d, J(HH) = 6.3 Hz, J(PH) = 19.4 Hz, 4 H, CH_3C*H*P); ^{13}C NMR (C_6D_6) 22.27, 22.54, 23.39 (s, *C*H_3CHP), 23.73 (s, *C*H_3CHB), 46.16 (s, CH_3CHB), 46.24 (d, J(PC) = 6.1 Hz, CH_3CHP); IR (C_6D_6) 2200 cm^{-1} (NCN). **15**: ^{11}B NMR ($CDCl_3$) +23; ^1H NMR ($CDCl_3$) 1.13 (d, J(HH) = 6.7 Hz, 48 H, CH_3), 3.35 (sept, J(HH) = 6.7 Hz, 8 H, CH); ^{13}C NMR ($CDCl_3$) 23.43 (s, CH_3), 45.62 (s, CH), 128.11 (s, NCN); IR ($CDCl_3$) 2252 cm^{-1} (NCN).

Reaction of Nitrilimines 6–8 with Dipolarophiles. To a toluene solution (10 mL) of nitrilimines **6–8** (1 mmol) was added dropwise at room temperature a stoichiometric amount of methyl acrylate, dimethyl fumarate, or dimethyl maleate. The reactions were monitored by IR and/or ^{31}P NMR. The pyrazolines **16–24** were purified as indicated.

Pyrazolines 16 and 17. A mixture of the 5- and 4-substituted isomers was obtained in a 60/40 ratio (85% yield) as a pale yellow oil after evaporation of the solvent and several washings with pentane: ^{29}Si NMR ($CDCl_3$) +6.44 (**16**) and +7.11 (**17**); ^{11}B NMR ($CDCl_3$) +33; ^1H NMR ($CDCl_3$) 0.98–1.10 (m, CH_3CH), 2.90 (sept, J(HH) = 6.2 Hz, CH_3C*H*, **17**), 3.43 (sept, J(HH) = 7.0 Hz, CH_3C*H*, **16**), 3.58 (s, CH_3O, **17**), 3.59 (s, CH_3O, **16**), 3.70–4.27 (m, CH and CH_2 ring); ^{13}C NMR ($CDCl_3$) **16**, 11.97 (s, CHSi), 18.05 (s, *C*H_3CHSi), 23.91 (s, *C*H_3CHB), 46.54 (s, CH_2 ring), 47.36 (s, CH_3CHB), 51.21 (s, CH_3O), 57.41 (s, CH ring), 148.90 (s, C=N), 172.08 (s, C=O); **17**, 12.22 (s, CHSi), 18.15 (s, *C*H_3CHSi), 24.95 (s, *C*H_3CHB), 44.99 (s, CH_2 ring), 46.84 (s, CH_3*C*HB), 51.22 (s, CH_3O), 59.39 (s, CH ring), 152.5 (s, C=N), 175.34 (s, C=O); IR ($CDCl_3$) 1725 cm^{-1}.

Pyrazolines 18, 19, and 19′. Compound **18** derived from nitrilimine **7** was characterized in solution and transformed into **19**, by stirring the reaction mixture for 2 h at room temperature in the presence of elemental sulfur. After filtration, evaporation of the solvent, and several washings with pentane, **19** was obtained as a colorless oil (0.45 g, 75% yield). Compound **19** was also obtained in the reaction of nitrilimine **8** with methyl acrylate (0.54 g, 90% yield). On column chromatography, **19** was partly (50%) transformed into **19′**, which was obtained as a colorless oil. **18**: ^{31}P NMR (C_6D_6) +36.4 (J(PH) = 9.4 Hz); ^{11}B NMR (C_6D_6) +27. **19**: R_f = 0.6 (pentane/ether 90/10); ^{31}P NMR ($CDCl_3$) +57.2; ^{11}B NMR ($CDCl_3$) +28; ^1H NMR ($CDCl_3$) 1.25 (m, 48 H, CH_3CH), 3.36, 3.50, and 4.54 (ABMX system (X = P), J(AB) = 18.2 Hz, J(AM) = 5.6 Hz, J(BM) = 13.4 Hz, J(AX) = 0.8 Hz, J(BX) = 0.4 Hz, 3 H, CH and CH_2 ring), 3.63 (s, 3 H, CH_3O), 3.69 (sept, J(HH) = 7 Hz, 4 H, CH_3C*H*B), 3.85 (sept d, J(HH) = 7 Hz, J(PH) = 16.3 Hz, 4 H, CH_3C*H*P); ^{13}C NMR ($CDCl_3$) 23.20, 23.23, 23.51, 23.54, 23.62, 23.66, 23.71, 23.73, 24.40, 24.46 (s, *C*H_3CH), 41.70 (d, J(PC) = 26.4 Hz, CH_2 ring), 47.13 (d, J(PC) = 5.9 Hz, CH_3*C*HP), 47.35 (d, J(PC) = 5.0 Hz, CH_3*C*HP), 48.34 (s, CH_3*C*HB), 51.45 (s, CH_3O), 60.80 (d, J(PC) = 4.5 Hz, CH ring), 147.45 (d, J(PC) = 152.0 Hz, C=N), 174.04 (s, C=O); IR ($CDCl_3$) 1745 cm^{-1} (C=O). Anal. Calcd for $C_{29}H_{62}N_6O_2PBS$: C, 57.98; H, 10.40; N, 13.99. Found: C, 58.12; H, 10.42; N, 14.06. **19′**: R_f = 0.1 (pentane/ether 90/10); ^{31}P NMR ($CDCl_3$) +54.6; ^1H NMR ($CDCl_3$) 1.15, 1.23 (d, J(HH) = 6.8 Hz, 24 H, CH_3CH), 3.35, 3.43, and 4.16 (ABM system, J(AB) = 17.7 Hz, J(AM) = 11.6 Hz, J(BM) = 4.0 Hz, 3 H, CH_2 and CH ring), 3.62 (s, 3 H, CH_3O), 3.70 (sept d, J(HH) = 6.8 Hz, J(PH) = 17.2 Hz, 4 H, CH_3C*H*), 6.64 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 23.00, 23.04, 23.17, 23.22 (s, *C*H_3CH), 40.85 (d, J(PC) = 25.2 Hz, CH_2 ring), 46.38 (d, J(PC) = 5.5 Hz, CH_3*C*H), 46.80 d, (d, J(PC) = 5.7 Hz, CH_3*C*H), 52.40 (s, CH_3O), 59.48 (d, J(PC) = 4.4 Hz, CH ring), 152.30 (d, J(PC) = 144.0 Hz, C=N), 173.30 (s, C=O); IR ($CDCl_3$) 1740 cm^{-1} (C=O). Anal. Calcd for $C_{17}H_{35}N_4O_2PS$: C, 52.28; H, 9.03; N, 14.35. Found: C, 52.01; H, 8.89; N, 14.30.

Pyrazoline 20 was obtained in pure form by recrystallization from cold pentane (0.42 g, 75% yield): mp = 90 °C; ^{29}Si NMR ($CDCl_3$) +8.4; ^{11}B NMR ($CDCl_3$) +33; ^1H NMR ($CDCl_3$) 1.01 (d, J(HH) = 7.1 Hz, 9 H, CH_3CHSi), 1.07 (d, J(HH) = 7.1 Hz, 9 H, CH_3CHSi), the signal of CHSi is under that of CH_3, 1.10 (d, J(HH) = 6.9 Hz, 24 H, CH_3CHB), 3.47 (sept, J(HH) = 6.9 Hz, 4 H, CH_3C*H*B), 3.61 (s, 3 H, CH_3O), 3.63 (s, 3 H, CH_3O), 4.17 (d, J(HH) = 6.9 Hz, 1 H, CH ring), 4.79 (d, J(HH) = 6.9 Hz, 1 H, CH ring); ^{13}C NMR ($CDCl_3$) 12.24 (s, CHSi), 17.97 (s, *C*H_3CHSi), 23.82 (s,

CH_3CHB), 47.77 (s, CH_3CHB), 51.61 (s, CH_3O), 51.66 (s, CH_3O), 63.13 (s, CH ring), 63.18 (s, CH ring), 147.80 (s, C=N), 170.35 (s, C=O), 173.61 (s, C=O); IR ($CDCl_3$) 1720 cm^{-1} (C=O). Anal. Calcd for $C_{28}H_{57}N_4O_4BSi$: C, 60.85; H, 10.40; N, 10.14. Found: C, 60.98; H, 10.41; N, 10.16.

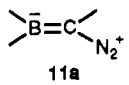
Pyrazolines 21 and 22. Derivative **21** was obtained after evaporation of the solvent and several washings with pentane as a pale yellow oil (0.59 g, 95% yield). Addition of a stoichiometric amount of elemental sulfur to a chloroform solution of **21** quantitatively gave the corresponding thioxophosphoranyl derivative **22**, which was isolated as a pale yellow oil. **22** (0.62 g, 95% yield) was also obtained from nitrilimine **8**. **21**: ^{31}P NMR ($CDCl_3$) +26.7; ^{11}B NMR ($CDCl_3$) +27; ^1H NMR ($CDCl_3$) 1.02 (d, J(HH) = 6.6 Hz, 6 H, CH_3CHP), 1.06 (d, J(HH) = 6.6 Hz, 6 H, CH_3CHP), 1.15 (d, J(HH) = 7.0 Hz, 24 H, CH_3CHB), 1.17 (d, J(HH) = 7.0 Hz, 6 H, CH_3CHP), 1.23 (d, J(HH) = 7.0 Hz, 6 H, CH_3CHP), 3.58 (m, 8 H, CH_3CH), 3.65 (s, 3 H, CH_3O), 3.73 (s, 3 H, CH_3O), 3.97 (dd, J(HH) = 1.4 Hz, J(PH) = 7 Hz, 1 H, CH ring), 4.74 (dd, J(HH) = 1.4 Hz, J(PH) = 7 Hz, 1 H, CH ring); ^{13}C NMR ($CDCl_3$) 23.41 (s, CH_3CHB), 23.57, 23.69, 23.79, 23.91, 24.00, 24.08 (s, CH_3CHP), 47.70 (d, J(PC) = 12.84 Hz, CH_3CHP), 47.80 (d, J(PC) = 11.13 Hz, CH_3CHP), 47.95 (s, CH_3CHB), 52.00 (s, CH_3O), 52.10 (s, CH_3O), 59.80 (d, J(PC) = 44.4 Hz, CH ring), 64.50 (d, J(PC) = 3.85 Hz, CH ring), 146.70 (d, J(PC) = 17.4 Hz, C=N), 171.71, 173.42 (s, C=O); IR ($CDCl_3$) 1740 cm^{-1} (C=O). **22**: ^{31}P NMR ($CDCl_3$) +57.0; ^{11}B NMR ($CDCl_3$) +27; ^1H NMR ($CDCl_3$) 1.15, 1.23, 1.25, 1.34, 1.35, 1.38 (d, J(HH) = 7 Hz, 48 H, CH_3CH), 3.68 (s, 3 H, OCH_3), 3.72 (s, 3 H, CH_3O), 3.83 (m, 4 H, CH_3CHP), 4.06 (sept, J(HH) = 7 Hz, 4 H, CH_3CHB), 4.22 (d, J(HH) = 4.5 Hz, 1 H, CH ring), 4.62 (d, J(HH) = 4.5 Hz, 1 H, CH ring); ^{13}C NMR ($CDCl_3$) 23.32, 23.79, 23.80, 24.18, 24.23, 24.28, 24.35 (s, CH_3CH), 46.97 (d, J(PC) = 6.7 Hz, CH_3CHP), 47.13 (d, J(PC) = 5.1 Hz, CH_3CHP), 48.13 (s, CH_3CHB), 53.35 (s, CH_3O), 56.95 (d, J(PC) = 18.7 Hz, CH ring) 66.05 (d, J(PC) = 3.6 Hz, CH ring), 143.27 (d, J(PC) = 158.2 Hz, C=N), 171.38, 172.19 (s, C=O); IR ($CDCl_3$) 1740, 1750 cm^{-1} (C=O). Anal. Calcd for $C_{31}H_{64}N_6O_4PBS$: C, 56.52; H, 9.80; N, 12.76. Found: C, 56.85; H, 9.97; N, 12.67.

Reaction of Nitrilimines 7 and 8 with Dimethyl Maleate. In both cases, the reaction is complete after 18 h. Starting from nitrilimine **7** and according to ^{31}P NMR, a mixture of trans adduct **21** and cis adduct **23** (^{31}P NMR +32.2) in a 50/50 ratio was obtained. To this toluene solution was added an excess of sulfur. After the solution was stirred for 2 h at room temperature, the remaining sulfur was filtered off and the solvent evaporated in vacuo. The cis adduct **24** was characterized from the mixture with the trans adduct **22**. A mixture of the two isomers **22** and **24** in a 70/30 ratio (according to ^{31}P NMR) was also obtained from nitrilimine **8**.

24: ^{31}P NMR ($CDCl_3$) +56.4; ^1H NMR ($CDCl_3$) 1.09–1.39 (m, 48 H, $CHCH_3$), 3.59, 3.66 (s, 6 H, CH_3O), 3.5–4.2 (m, 8 H, CH_3CH), 4.73 (AB system, J(AB) = 13.7 Hz, 2 H, CH ring); ^{13}C NMR ($CDCl_3$) 21.59–24.17 (m, $CHCH_3$), 46.59–48.88 (m, CH_3CH), 51.91, 51.99 (s, CH_3O), 58.60 (d, J(PC) = 24.9 Hz, CH ring), 65.00 (d, J(PC) = 3 Hz, CH ring), 143.51 (d, J(PC) = 159.03 Hz, C=N), 169.78, 171.11 (s, C=O).

Discussion

Spectroscopic Characterization of Nitrilimines 6–9 and Diazo Compound 11. We have already reported[4] that the differentiation by IR of nitrilimines versus diazo derivatives is sometimes tricky. Indeed, depending on the nature of the substituents, the stretching frequencies of diazo derivatives have been observed from 1950[11] to 2228 cm^{-1},[12] while those of nitrilimines appeared between 2010[4a,d] and 2170 cm^{-1}.[13] Both absorptions are strong but the nitrilimine one is broader. In the case of the derivatives reported here, nitrilimines **6–9** show an IR absorption between 2095 and 2164 cm^{-1}, while diazo compound **11** has a stretching frequency at 2071 cm^{-1}. The high frequency of the borylnitrilimine absorptions can be easily rationalized by the stabilization of the negative charge on the terminal nitrogen by boron, favoring a propargylic structure $C{\equiv}N^+{-}N^-$ versus a cumulenic structure $C^-{=}N^+{=}N$, which increases the CN bond order. The comparison of the IR frequencies of several nitrilimines (Table I) with the same C-substituent confirms this assumption. An increasing frequency is observed in the order $R_2P < R_3Si < R_2B < R_3P^+$. In contrast, the rather low frequency observed for diazo derivative **11** is rather surprising since one could think that the existence of a possible resonance form **11a**, involving a diazonium group, should shift the



11a

absorption toward higher frequency.[1a] NMR spectroscopy is certainly the most useful technique for the structural assignments. In the case of the C-phosphorus nitrilimines **7** and **8**, the ^{31}P NMR chemical shift (+45.1 and +31.8, respectively) is at high field, as we have already observed in other nitrilimines.[4] ^{11}B NMR is not very helpful since the signals are very broad and the range very narrow; however, the boron signals of nitrilimines **6–9** (+22 to +29) are at higher field than that for diazo compound **11** (+34). Note that the two signals of the boron atoms of **9** can only be differentiated at 348 K. The definitive structural assignments are based on ^{13}C NMR, although it should be mentioned that the observation of the signal due to the carbon of the CNN moiety is only possible at low temperature (223 K). For nitrilimines **6–9** the chemical shifts are in the range +45 to +66, while the diazo carbon of **11** is at +36, which is in good agreement with the values reported for other derivatives of the same type. It seems that there is no correlation between this chemical shift and the infrared frequencies. The presence of the hydrogen on the carbon atom of **11** (excluding the possible nitrilimine isomer) is proved by a ^{13}C–H coupling constant of 169.5 Hz.

Formation of Nitrilimine 9. The formation of the bis[bis(diisopropylamino)boryl]nitrilimine (**9**) in the reaction of the lithium salts of diazomethane or (trimethylsilyl)diazomethane with chloroborane has to be explained. We have checked that diazoborane **11** does not react spontaneously with bis(diisopropylamino)chloroborane, but it appeared that, if this reaction is carried out in the presence of LDA, we observe the quantitative formation of **9**. Thus, it is quite likely that there is a competition between the reaction of LDA with diazomethane and with boryldiazomethane. In other words, the acidities of the protons of diazomethane and of **11** are quite comparable. It is more difficult to understand the reaction of

Table I. Comparison of the IR Stretching Frequencies of Several Nitrilimines

XCNNY			
X	Y	ν(CNN), cm^{-1}	ref
$[(iPr)_2N]_2P(S)$	$^+PMe[N(iPr)_2]_2$	2170	16
$[(iPr)_2N]_2P(S)$	$B[N(iPr)_2]_2$	2095	*a*
$[(iPr)_2N]_2P(S)$	$Si(iPr)_3$	2050	4a
$[(iPr)_2N]_2P(S)$	$P[N(iPr)_2]_2$	2040	4b
$[(iPr)_2N]_2P$	$B[N(iPr)_2]_2$	2113	*a*
$[(iPr)_2N]_2P$	$Si(iPr)_3$	2110	4a
$(iPr)_3Si$	$B[N(iPr)_2]_2$	2164	*a*
$(iPr)_3Si$	$Si(iPr)_3$	2120	4a
$[(iPr)_2N]_2B$	$B[N(iPr)_2]_2$	2160	*a*
$[(iPr)_2N]_2B$	$P[N(iPr)_2]_2$	2145	*b*

[a] This work. [b] Unpublished results.

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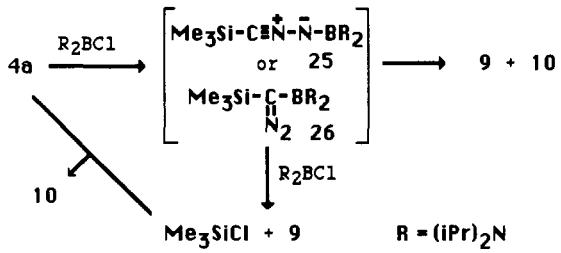
Scheme V



(trimethylsilyl)diazomethane with chloroborane. A possible explanation would be the formation of *C*-silylnitrilimine **25** or diazo compound **26**, which would undergo an exchange reaction with chloroborane leading to **9** and trimethylchlorosilane, which could subsequently react with **4a** to give bis(trimethylsilyl)diazomethane (**10**). Although the reactivities of trimethylsilyl and triisopropylsilyl groups are hardly comparable, it should be noted that no reaction occurred between *C*-silylnitrilimine **6** and chloroborane. Another possible hypothesis would be the disproportionation of the initially formed nitrilimine **25** or diazo derivative **26** into the observed products (Scheme V).

Thermal and Photochemical Behavior of 6–9 and 11. The thermal stability of the borylnitrilimines is really surprising, having in mind that until our first report in 1988 nitrilimines were considered only as transient intermediates. All attempts to thermally rearrange **6–9** into diazo derivatives or one of their structural isomers failed. The high thermal stability of diazo compound **11** is probably due to the fact that the boron, being substituted by two nitrogens, is a very weak Lewis acid.

The four nitrilimines **6–9** cleanly rearrange under irradiation into the corresponding carbodiimides **12–15**. The mechanism of this rearrangement has already been discussed.[14,15]

Reactivity of Nitrilimines. We have already shown that reactions at the nitrogen substituent of nitrilimines are possible, keeping the 1,3-dipole skeleton unchanged.[16] The formation of *C*-(thioxophosphoranyl)nitrilimine **8** by addition of sulfur to the *C*-phosphinonitrilimine **7** demonstrates that it is also possible to do chemistry at the C-substituent. These results considerably increase the scope of application of these nitrilium betaines.

Nitrilimines **6–8** only reacted with electron-poor dipolarophiles, which is surprising since we have shown that when a electron-withdrawing group (a phosphonio group) is attached to the nitrogen end, the nitrilimines become electrophilic.[17] The fully borylated nitrilimine **9** did not undergo any reaction with the usual electron-rich or -poor olefins. The steric hindrance is comparable to that of other nitrilimines previously reported, and thus the nonreactivity observed suggests electronic interactions of the boron at carbon and the 1,3-dipole.

The reaction of methyl acrylate with nitrilimines **6–8** leads us to discuss the question of regioselectivity of the 2 + 3 cycloadditions. According to Sustmann,[18] acceptor substituents on the nitrilimine increase the LUMO (dipole) control, leading to 5-substituted pyrazolines as observed for nitrilimines **7** and **8**. To rationalize the formation of the mixture of 5- and 4-substituted pyrazolines **16** and **17**, one can argue that the presence of an electron-donating group (the silyl group) raises the FMO energies and thus the reaction is LUMO and HOMO (dipole) controlled. In fact, analyzing our results as a whole, it seems that the nature of the C-substituent governs the regioselectivity of the cycloaddition reactions.

Previous studies of the addition of transient nitrilimines[19] onto geometrically isomeric alkenes concluded that cis addition predominated and that the trans isomer was more reactive. Nitrilimines **6–9** react with dimethyl fumarate, affording the corresponding trans adducts **20–22**. Dimethyl maleate did not react with the *C*-silylnitrilimine **6** and gave rise to a mixture of trans and cis adducts **21/23** and **22/24** with nitrilimines **7** and **8**, respectively. We have checked that no epimerization of the cis adducts **23** and **24** occurred under the experimental conditions used. This result corroborates our findings with the stable *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphino]nitrilimine, where we concluded that the nonstereoselectivity observed with dimethyl maleate was due to a "nonconcerted addition" process.[4b,20]

Conclusion

The results reported here show that, given the right substituents, α-diazo boranes and *N*- and/or *C*-borylnitrilimines can be thermally stable. The reactivity of the *N*-borylnitrilimines is quite usual but, surprisingly, the *C*-borylnitrilimine appeared to be quite unreactive. Further studies are under way in order to obtain a greater understanding of this phenomenom.

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