DOI: 10.1002/ejic.200600799

A Facile Synthesis of Carbamoylsilanes, -boranes and -phosphane Oxides – Isolation of the First Uncomplexed Carbamoylborane

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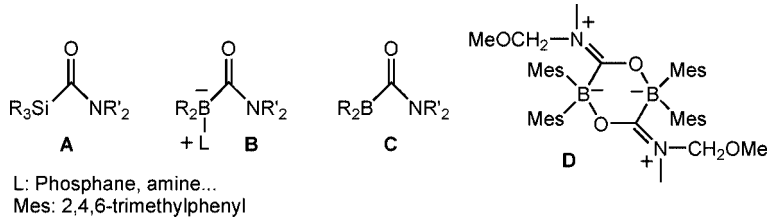
Keywords: Carbenes / Rearrangement / Boron / Silicon

C-(Trimethylsilyloxy)-, *C*-(triisopropylsilyloxy)-, *C*-(diphenylboryloxy), *C*-[bis(diisopropylamino)boryloxy]- and *C*-(di-*tert*-butylphosphoryloxy)-*N*,*N*-diisopropylaldiminium salts are readily prepared in good to excellent yields from either diisopropylformamide or (chloromethylene)diisopropylammonium chloride. Deprotonation of these aldiminium salts leads to transient (amino)(oxy)carbenes, which cleanly rearrange to carbamoyl derivatives. This synthetic methodology gives access to sterically hindered carbamoylsilanes, -boranes and phosphane oxides that are hardly accessible by other routes. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2006)

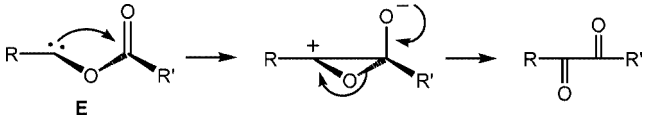
Although first described over 30 years ago,[1] the carbamoylsilanes **A** remain difficult to prepare. Most of the known synthetic routes[2] have a rather limited scope of application and/or proceed in low to medium yields. The most powerful preparative methods are the low-temperature metalation/silylation of the corresponding *N*,*N*-dialkylformamide,[3] and the *trans*-silylation of carbamoylsilanes with the desired silyl chloride.[4] These synthetic routes, however, are inefficient when bulky substrates are involved. Despite the difficulties associated with their synthesis, carbamoylsilanes have found various synthetic applications.[4,5] In the boron series, the *B*-complexed carbamoylboranes **B**[6] have been known for a long time, and have even been described as potent cytotoxic agents in different cancer cells,[7] but so far no examples of free carbamoylboranes **C** have been reported. Even with bulky aryl groups at the boron atom, Cunico et al. have shown that carbamoylboranes spontaneously dimerize to give the six-membered heterocycles **D**[8] (Scheme 1).



Scheme 1.

Here we describe a general route for the high-yield synthesis of carbamoyl derivatives, which include sterically relatively hindered carbamoylsilanes, as well as the first example of a noncomplexed carbamoylborane. The latter has been characterized by a single-crystal X-ray diffraction study. To further demonstrate the broad scope of application of our synthetic methodology, the preparation of a carbamoylphosphane oxide[9] is also described.

Moss et al.[10] have shown that the (phenylcarbonyloxy)-carbenes **E** quickly rearrange to 1,2-diketones, due to the carbanion-like attack of the carbene lone pair at the electrophilic carbonyl group (Scheme 2). Accordingly, any nucleophilic carbenes,[11] featuring an electrophilic center in β-position should rearrange as well. In contrast with most carbenes,[12] highly nucleophilic transient and even stable aminocarbenes[13] are readily accessible, and therefore our synthetic strategy towards carbamoyl derivatives is based on



Scheme 2.

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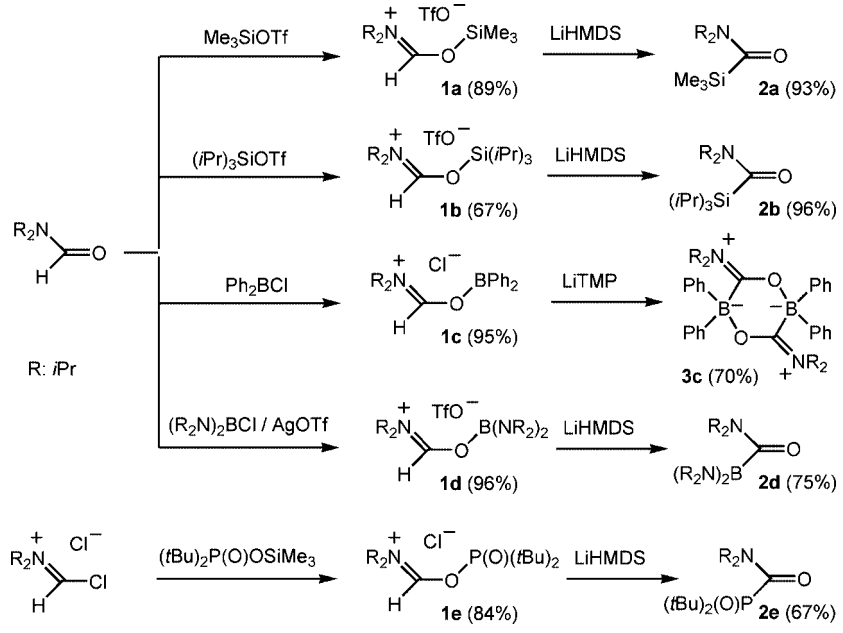
the rearrangement of the appropriately substituted aminocarbenes.

The classical precursors for aminocarbenes are the corresponding aldiminium salts. The desired silyloxy derivative **1a** was readily obtained in 89% yield by treatment of diisopropylformamide with 1 equiv. of trimethylsilyl trifluoromethanesulfonate at –78 °C. Subsequent deprotonation of **1a** with lithium bis(trimethylsilyl)amide (LiHMDS) in THF quickly occurred at –78 °C, and after work up the carbamoylsilane **2a** was isolated in 93% yield (Scheme 3). The overall yield for this two-step process (83%) is comparable to that obtained using the metalation/silylation route (81%).[3b] To demonstrate the potential synthetic utility of this new route, we extended our approach to the triisopropylsilyl analogue **2b**, which was reported to be not accessible by the other routes due to steric hindrance.[4] Using triisopropylsilyl trifluoromethanesulfonate, the aldiminium salt **1b** was obtained in 67% yield, and after subsequent deprotonation with LiHMDS, **2b** was isolated in 96% yield. All attempts to spectroscopically characterize the initially formed aminocarbene (iPr$_2$N–C–OSiiPr$_3$) failed; unsurprisingly the rearrangement to the carbamoyl isomer is not sensitive to the steric bulk.

We then turned our attention to the group 13 carbamoyl derivatives. Treatment of diisopropylformamide with 1 equiv. of chlorodiphenylborane in diethyl ether at room temperature led, after workup, to the iminium salt **1c** in 95% yield. Deprotonation of **1c** with the lithium salt of 2,2,6,6-tetramethylpiperidine occurred at –78 °C in THF. After purification by chromatography on silica gel and recrystallization in hexane at –20 °C, the derivative **3c** was isolated as white crystals (70% yield, m.p. 261–263 °C). Compound **3c** displayed a broad signal at δ = 1.8 ppm in the ^{11}B NMR spectrum, consistent with a tetracoordinate boron atom possessing anionic character. Despite the poor quality of the crystals, a single-crystal X-ray diffraction study showed that **3c** has a structure similar to the previously reported compound **D**.[8] Taking advantage of the possibility of using sterically hindered substrates, we investigated the possibility of preparing an isolable uncomplexed carbamoylborane. We chose diisopropylamino substituents at the boron atom, their π-donating properties also imparting electronic protection to the molecule. The iminium salt **1d** was prepared in 96% yield by the reaction of diisopropylformamide with 1 equiv. of chlorobis(diisopropylamino)borane in the presence of a stoichiometric amount of silver trifluoromethanesulfonate. As expected, deprotonation of **1d** with LiHMDS in THF afforded the carbamoylborane **2d**, which after recrystallization was obtained as thermally highly stable colorless crystals in 75% yield (m.p. 228–230 °C). The ^{11}B NMR spectrum of **2d** exhibits a signal at δ = 29.2 ppm, which is in agreement with a tricoordinate boron atom possessing two amino groups. The ^{13}C NMR spectrum shows the presence of a signal at rather low field (δ =190.0 ppm) consistent with an amide-type carbon atom substituted by an electron-withdrawing group. The single-crystal X-ray diffraction study confirms the monomeric nature of the carbamoyl borane **2d** (Figure 1). As expected, N1, C1, B1, N2 and N3 are in a perfectly planar environment, which demonstrates the interaction of N1 with the carbonyl group, and N2 and N3 with the boron center. It is noteworthy that all attempts to characterize the putative carbene intermediate here also failed, even when the deprotonation reaction was monitored by NMR spectroscopy at –78 °C.

In order to broaden the scope of this synthetic methodology, we also prepared the phosphane oxide substituted iminium salt **1e** (84% yield) by treatment of (chloromethylene)diisopropylammonium chloride with 1 equiv. of tBu$_2$P(O)OSiMe$_3$. Deprotonation of **1e** with LiHMDS in



Scheme 3.

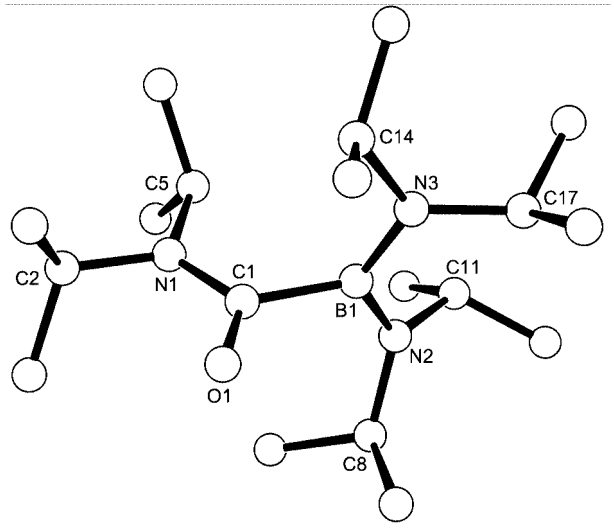


Figure 1. Molecular view of the crystal structure of **2d** (H atoms omitted). Selected bond lengths [Å] and angles [°]: B1–N2 1.4394(17), B1–N3 1.4223(17), B1–C1 1.6185(18), C1–O1 1.2449(14), C1–N1 1.3644(15); N3–B1–N2 124.35(11), N3–B1–C1 116.22(11), N2–B1–C1 119.31(11), O1–C1–N1 121.04(11), O1–C1–B1 118.54(10), N1–C1–B1 120.43(10), C1–N1–C5 120.89(10), C1–N1–C2 121.91(10), C5–N1–C2 117.07(10), B1–N2–C11 122.20(10), B1–N2–C8 122.68(10), C11–N2–C8 114.98(10), B1–N3–C17 120.08(10), B1–N3–C14 118.84(10), C17–N3–C14 120.33(10).

THF afforded the carbamoylphosphane oxide **2e**, which was isolated in 67% yield (Scheme 3).

This work is a new demonstration of the usefulness of the readily available aminocarbenes in organic synthesis. Moreover, the ready availability of these carbamoyl derivatives should favour their use for various synthetic applications.

Experimental Section

General: All manipulations were performed under argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{31}P and ^{11}B NMR spectra were recorded with Varian Inova 300, 500 and Bruker Avance 300 spectrometers. The high purity of all isolated products have been confirmed by multinuclear NMR spectroscopy.

***N*,*N*-Diisopropyl-*C*-(trimethylsilyloxy)aldiminium Salt 1a:** Me_3Si-OTf (0.69 mL, 3.9 mmol) was added dropwise to a solution of diisopropylformamide (0.56 mL, 3.9 mmol) in CH_2Cl_2 (10 mL) at –78 °C. The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent, the solid residue was washed with Et_2O (15 mL) to afford aldiminium salt **1a** as a white solid (1.21 g, 89%). ^{1}H NMR (CD_3CN, 25 °C): δ = 0.47 [s, 9 H, Si(CH_3)$_3$], 1.37 (d, ^{3}J = 6.9 Hz, 12 H, CHCH_3), 4.14 (m, 2 H, CHCH$_3$), 8.11 (s, 1 H, CH) ppm. ^{13}C NMR (CD_3CN, 25 °C): δ = –0.3 [Si(*C*H$_3$)$_3$], 20.0 (CH*C*H$_3$), 21.2 (CH*C*H$_3$), 51.5 (*C*HCH$_3$), 56.9 (*C*HCH$_3$), 120.9 (q, ^{1}J = 319.5 Hz, *C*F$_3$SO$_3$), 164.6 (*C*H) ppm.

(Diisopropylcarbamoyl)trimethylsilane (2a): A 1:1 mixture of LiHMDS/aldiminium salt **1a** (7.4 mmol) was cooled to –78 °C and THF (20 mL) was added. The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent, the solid residue was washed with hexane (30 mL). Extraction with CH_2Cl_2 (15 mL) gave, after concentration, a white solid (1.39 g, 93%). The physical and spectroscopic data are identical to those reported previously.[3b]

***N*,*N*-Diisopropyl-*C*-(triisopropylsilyloxy)aldiminium Salt 1b:** iPr$_3$Si-OTf (2.0 mL, 7.7 mmol) was added dropwise at –78 °C to a solution of diisopropylformamide (1.12 mL, 7.7 mmol) in CH_2Cl_2 (20 mL). The suspension was warmed to room temperature and stirred for 2 h. After evaporation of the solvent, the solid residue was washed with Et_2O (20 mL) to afford aldiminium salt **1b** as a white solid (2.25 g, 67%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.11 [d, ^{3}J = 7.2 Hz, 18 H, Si(CHCH_3)$_3$], 1.39 (d, ^{3}J = 7.2 Hz, 6 H, CHCH_3), 1.42 (d, ^{3}J = 7.2 Hz, 6 H, CHCH_3), 1.48 [sept, ^{3}J = 7.2 Hz, 3 H, Si(CHCH$_3$)$_3$], 4.09 (sept, ^{3}J = 7.2 Hz, 1 H, CHCH$_3$), 4.52 (m, 1 H, CHCH$_3$), 8.70 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 11.6 [Si(*C*HCH$_3$)$_3$], 17.2 [Si(CH*C*H$_3$)$_3$], 19.7 (CH*C*H$_3$), 20.9 (CH*C*H$_3$), 50.0 (*C*HCH$_3$), 56.4 (*C*HCH$_3$), 120.9 (q, $^{1}J_{CF}$ = 319.0 Hz, *C*F$_3$SO$_3$), 163.5 (*C*H) ppm.

(Diisopropylcarbamoyl)triisopropylsilane (2b): A 1:1 mixture of LiHMDS/aldiminium salt **1b** (1.1 mmol) was cooled to –78 °C and THF (10 mL) was added. The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent and extraction with CH_2Cl_2 (10 mL), a white solid was isolated (0.31 g, 96%). ^{1}H NMR ([D$_8$]THF, 25 °C): δ = 1.11 [d, ^{3}J = 6.8 Hz, 18 H, Si(CHCH_3)$_3$], 1.19 (d, ^{3}J = 6.6 Hz, 6 H, CHCH_3), 1.25 [m, 3 H, Si(CHCH$_3$)$_3$], 1.40 (d, ^{3}J = 6.8 Hz, 6 H, CHCH_3), 3.35 (sept, ^{3}J = 6.8 Hz, 1 H, CHCH$_3$), 3.92 (sept, ^{3}J = 6.6 Hz, 1 H, CHCH$_3$) ppm. ^{13}C NMR ([D$_8$]THF, 25 °C): δ = 13.9 [Si(*C*HCH$_3$)$_3$], 19.7 [Si(CH*C*H$_3$)$_3$], 21.3 (CH*C*H$_3$), 22.1 (CH*C*H$_3$), 46.9 (*C*HCH$_3$), 49.5 (*C*HCH$_3$), 186.0 (*C*) ppm.

***C*-(Diphenylboryloxy)-*N*,*N*-diisopropylaldiminium Salt 1c:** A Et_2O solution (10 mL) of diisopropylformamide (0.58 mL, 4.0 mmol) was added at –78 °C to a Et_2O solution (10 mL) of chlorodiphenylborane (0.70 mL, 4.0 mmol), and the suspension was stirred at room temperature for 12 h. After filtration, the solid residue was washed with Et_2O (20 mL) to afford aldiminium salt **1c** as a white solid (1.25 g, 95%). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 1.46 (d, ^{3}J = 6.9 Hz, 6 H, CHCH_3), 1.57 (d, ^{3}J = 6.6 Hz, 6 H, CHCH_3), 3.93 (sept, ^{3}J = 6.6 Hz, 1 H, CHCH$_3$), 4.41 (sept, ^{3}J = 6.9 Hz, 1 H, CHCH$_3$), 7.30–7.42 and 7.63–7.67 (m, 10 H, H_{ar}), 8.48 (s, 1 H, CH) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 20.1 (CH*C*H$_3$), 22.7 (CH*C*H$_3$), 48.6 (*C*HCH$_3$), 52.7 (*C*HCH$_3$), 126.5 (C_{ar}), 127.5 (C_{ar}), 128.5 (C_{ar}), 132.3 (C_{ar}), 165.6 (*C*H) ppm. ^{11}B NMR ($CDCl_3$, 25 °C): δ = 11.6 ppm.

Carbamoylborane Dimer 3c: A 1:1 mixture of TMPLi/aldiminium salt **1c** (1.0 mmol) was cooled to –78 °C and THF (10 mL) was added. The suspension was warmed to room temperature and stirred for 30 min. After evaporation of the solvent under vacuum, purification by chromatography on silica gel (hexane/ethyl acetate) gave a solid residue, which was recrystallized at –20 °C from hexane (0.20 g, 70%, m.p. 261–263 °C). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 0.45 (d, ^{3}J = 6.3 Hz, 12 H, CHCH_3), 1.16 (d, ^{3}J = 6.3 Hz, 12 H, CHCH_3), 3.20 (sept, ^{3}J = 6.6 Hz, 2 H, CHCH$_3$), 4.05 (sept, ^{3}J = 6.9 Hz, 2 H, CHCH$_3$), 7.15–7.27 and 7.41–7.45 (m, 20 H, H_{ar}) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 19.3 (CH*C*H$_3$), 21.1 (CH*C*H$_3$), 48.3 (*C*HCH$_3$), 53.4 (*C*HCH$_3$), 126.7 (C_{ar}), 127.2 (C_{ar}), 127.3 (C_{ar}), 127.9 (C_{ar}), 132.2 (C_{ar}), 134.3 (C_{ar}), 144.9 (C_{ar}), 147.4 (C_{ar}), 198.8 (*C*) ppm. ^{11}B NMR ($CDCl_3$, 25 °C): δ = 1.8 ppm.

***C*-[Bis(diisopropylamino)boryloxy]-*N*,*N*-diisopropylaldiminium Salt 1d:** A CH_2Cl_2 solution (10 mL) of AgOTf (2.03 g, 7.9 mmol) was added at –78 °C to a CH_2Cl_2 solution (10 mL) of diisopropylformamide (1.15 mL, 7.9 mmol) and chlorobis(diisopropylamino)borane (2.03 mL, 7.9 mmol). The suspension was then stirred at room temperature for 12 h. After filtration and evaporation of the sol-

vent, the solid residue was washed with Et_2O (30 mL) to afford **1d** as a white solid (3.70 g, 96%). ^1H NMR ($CDCl_3$, 25 °C): δ = 1.16 (d, ^3J = 6.5 Hz, 24 H, CHCH_3), 1.48 (d, ^3J = 7.0 Hz, 6 H, CHCH_3), 1.53 (d, ^3J = 7.0 Hz, 6 H, CHCH_3), 3.44 (sept, ^3J = 6.5 Hz, 4 H, C*H*CH$_3$), 4.33 (sept, ^3J = 7.0 Hz, 1 H, C*H*CH$_3$), 4.63 (sept, ^3J = 7.0 Hz, 1 H, C*H*CH$_3$), 8.70 (s, 1 H, C*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 19.6 (CH*C*H$_3$), 22.9 (CH*C*H$_3$), 23.8 (CH*C*H$_3$), 46.4 (*C*HCH$_3$), 50.9 (*C*HCH$_3$), 53.0 (*C*HCH$_3$), 120.9 (q, ^1J = 319.5 Hz, *C*F$_3$SO$_3^-$), 164.6 (*C*H) ppm. ^{11}B NMR ($CDCl_3$, 25 °C): δ = 27.7 ppm.

Bis(diisopropylamino)(diisopropylcarbamoyl)borane (2d): A 1:1 mixture of LiHMDS/aldiminium salt **1d** (5.0 mmol) was cooled to –78 °C and THF (20 mL) was added. The suspension was then warmed to room temperature and stirred for 30 min. After evaporation of the solvent and extraction with Et_2O (40 mL), a solid residue was obtained. After washing with hexane (10 mL) and extraction with CH_2Cl_2 (30 mL), evaporation of the solvent gave a white solid that was recrystallized from Et_2O at –20 °C to give **2d** as colorless crystals (1.27 g, 75%, m.p. 228–230 °C). ^1H NMR ($CDCl_3$, 25 °C): δ = 1.20 (d, ^3J = 6.9 Hz, 18 H, CHCH_3), 1.23 (d, ^3J = 7.2 Hz, 12 H, CHCH_3), 1.45 (d, ^3J = 6.9 Hz, 6 H, CHCH_3), 3.28 (sept, ^3J = 6.9 Hz, 1 H, C*H*CH$_3$), 3.53 (sept, ^3J = 7.2 Hz, 4 H, C*H*CH$_3$), 3.86 (sept, ^3J = 6.9 Hz, 1 H, C*H*CH$_3$) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 20.3 (CH*C*H$_3$), 21.1 (CH*C*H$_3$), 24.6 (CH*C*H$_3$), 25.0 (CH*C*H$_3$), 45.0 (*C*HCH$_3$), 48.2 (*C*HCH$_3$), 49.7 (*C*HCH$_3$), 190.0 (*C*) ppm. ^{11}B NMR ($CDCl_3$, 25 °C): δ = 29.2 ppm.

***C*-(Di-*tert*-butylphosphoryloxy)-*N*,*N*-diisopropylaldiminium Salt 1e:** A CH_3CN solution (10 mL) of di-*tert*-butyl(trimethylsilyloxy)phosphane oxide (0.50 g, 2.0 mmol) was added at –78 °C to a CH_3CN solution (10 mL) of (chloromethylene)diisopropylammonium chloride (0.37 g, 2.0 mmol). The suspension was stirred at room temperature for 3 h. After evaporation of the solvent, the solid residue was washed with Et_2O (15 mL) to afford **1e** as a white solid (0.55 g, 84%). ^{31}P NMR ($CDCl_3$, 25 °C): δ = +87.8 ppm. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.35 [d, ^3J = 15.9 Hz, 18 H, C(CH_3)$_3$], 1.47 (d, ^3J = 6.6 Hz, 6 H, CHCH_3), 1.54 (d, ^3J = 6.3 Hz, 6 H, CHCH_3), 4.30 (sept, ^3J = 6.6 Hz, 1 H, C*H*CH$_3$), 5.18 (sept, ^3J = 6.3 Hz, 1 H, C*H*CH$_3$), 9.38 (d, ^3J = 6.6 Hz, 1 H, C*H*) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 20.4 (CH*C*H$_3$), 20.6 (CH*C*H$_3$), 26.1 [C(*C*H$_3$)], 37.5 [d, ^1J = 67.9 Hz, *C*(CH$_3$)], 51.4 (*C*HCH$_3$), 59.0 (*C*HCH$_3$), 162.0 (*C*H) ppm.

Di-*tert*-butyl(diisopropylcarbamoyl)phosphane Oxide (2e): A 1:1 mixture of LiHMDS/salt **1e** (1.0 mmol) was cooled to –78 °C and THF (10 mL) was added. The suspension was warmed to room temperature and stirred for 20 min. After evaporation of the solvent and extraction with hexane (10 mL), a solid residue was obtained (0.19 g, 67%). ^{31}P NMR ($CDCl_3$, 25 °C): δ = +52.3 ppm. ^1H NMR ($CDCl_3$, 25 °C): δ = 1.17 (d, ^3J = 6.3 Hz, 6 H, CHCH_3), 1.32 [d, ^3J = 14.1 Hz, 18 H, C(CH_3)$_3$], 1.41 (d, ^3J = 6.3 Hz, 6 H, CHCH_3), 3.43 (sept, ^3J = 6.3 Hz, 1 H, C*H*CH$_3$), 5.80 (m, 1 H, C*H*CH$_3$) ppm. ^{13}C NMR ($CDCl_3$, 25 °C): δ = 19.9 (CH*C*H$_3$), 20.8 (CH*C*H$_3$), 26.9 [C(*C*H$_3$)], 36.5 [d, ^1J = 57.6 Hz, *C*(CH$_3$)], 46.6 (*C*HCH$_3$), 47.6 (*C*HCH$_3$), 169.2 (d, ^1J = 97.0 Hz, *C*) ppm.

Crystal Structure Determination of Carbamoylborane 2d: A Bruker X8-APEX X-ray diffraction instrument with Mo radiation was used for data collection. All data frames were collected at low temperatures (T = 100 K) using an ω/φ-scan mode (–0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program. A Sir92 software package was used for direct methods of phase determination and structure refinement. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full-matrix least-squares procedure on F^2. All hydrogen atoms were included in the refinement in calculated positions riding on the atoms to which they were attached. Drawings of molecules were performed using ORTEP 3. Crystal and structure parameters of **2d**: size 0.38 × 0.20 × 0.09 mm, triclinic, space group $P\bar{1}$, a = 9.7141(6) Å, b = 12.2962(7) Å, c = 18.7798(12) Å, α = 92.122(4)°, β = 101.343(4)°, γ = 93.291(4)°, V = 2193.1(2) Å^3, $\rho_{calcd.}$ = 1.028 g/cm^3, $2\theta_{max}$ = 55.76°, Mo radiation (λ = 0.71073 Å), temperature = 100(2)° K, reflections collected = 33410, independent reflections = 10433, R_{int} = 0.0301, absorption coefficient μ = 0.062 mm^{-1}; max/min transmission = 0.9945/0.9769, 457 parameters were refined and converged at R_1 = 0.0457, wR_2 = 0.1132, with intensity $I > 2\sigma(I)$, the final difference map was 0.986–0.337 e·Å^{-3}. CCDC-618399 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We are grateful to the NIH (R01 GM 68825) for financial support of this work.

[1] G. J. D. Peddle, R. W. Walsingham, *J. Chem. Soc. D* **1969**, 462.
[2] a) J. E. Baldwin, A. E. Derome, P. D. Riordan, *Tetrahedron* **1983**, *39*, 2989; b) A. Orita, K. Ohe, S. Murai, *Organometallics* **1994**, *13*, 1533; c) A. Orita, K. Ohe, S. Murai, *J. Organomet. Chem.* **1994**, *474*, 23.
[3] a) R. F. Cunico, *Tetrahedron Lett.* **2001**, *42*, 1423; b) R. F. Cunico, J. Chen, *Synth. Commun.* **2003**, *33*, 1963.
[4] R. F. Cunico, A. R. Motta, *J. Organomet. Chem.* **2006**, *691*, 3109.
[5] a) R. F. Cunico, R. K. Pandey, J. X. Chen, A. R. Motta, *Synlett* **2005**, 3157; b) R. F. Cunico, R. K. Pandey, *J. Org. Chem.* **2005**, *70*, 9048; c) R. F. Cunico, R. K. Pandey, *J. Org. Chem.* **2005**, *70*, 5344; d) J. X. Chen, R. K. Pandey, R. F. Cunico, *Tetrahedron Asymmetry* **2005**, *16*, 941; e) R. F. Cunico, A. R. Motta, *Org. Lett.* **2005**, *7*, 771; f) J. X. Chen, R. F. Cunico, *J. Org. Chem.* **2004**, *69*, 5509; g) R. F. Cunico, B. C. Maity, *Org. Lett.* **2003**, *5*, 4947; h) J. X. Chen, R. F. Cunico, *Tetrahedron Lett.* **2003**, *44*, 8025; i) R. F. Cunico, B. C. Maity, *Org. Lett.* **2002**, *4*, 4357; j) J. X. Chen, R. F. Cunico, *Tetrahedron Lett.* **2002**, *43*, 8595; k) R. F. Cunico, *Tetrahedron Lett.* **2002**, *43*, 355.
[6] a) B. F. Spielvogel, F. U. Ahmed, K. W. Morse, A. T. McPhail, *Inorg. Chem.* **1984**, *23*, 1776; b) C. K. Sood, A. Sood, B. F. Spielvogel, J. A. Yousef, B. Burnham, I. H. Hall, *J. Pharm. Sci.* **1991**, *80*, 1133; c) C. H. Sutton, M. W. Baize, L. J. Todd, *Inorg. Chem.* **1994**, *33*, 4221; d) G. Rana, K. Vyakaranam, B. F. Spielvogel, S. J. Li, C. Zheng, J. A. Maguire, N. S. Hosmane, *Inorg. Chim. Acta* **2003**, *342*, 255.
[7] a) I. H. Hall, C. J. Gilbert, A. T. McPhail, K. W. Morse, K. Hassett, B. F. Spielvogel, *J. Pharm. Sci.* **1985**, *74*, 755; b) I. H. Hall, C. O. Starnes, B. F. Spielvogel, P. Wisian-Neilson, M. K. Das, L. Wojnowich, *J. Pharm. Sci.* **1979**, *68*, 685; c) B. Burnham, S. Y. Chen, A. Sood, B. F. Spielvogel, I. H. Hall, *Pharmazie* **1995**, *50*, 779.
[8] R. F. Cunico, C. Zheng, *Inorg. Chem. Commun.* **2002**, *5*, 1066.
[9] a) P. Beudaert, V. Lamare, J. F. Dozol, L. Troxler, G. Wipff, *J. Chem. Soc., Perkin Trans. 2* **1999**, 2515; b) C. Boehme, G. Wipff, *Inorg. Chem.* **2002**, *41*, 727; c) R. N. Kapoor, P. Guillory, L. Schulte, F. Cervantes-Lee, I. Haiduc, L. Parkanyi, K. H. Pannell, *Appl. Organomet. Chem.* **2005**, *19*, 510.
[10] R. A. Moss, S. Xue, W. Liu, K. Krogh-Jespersen, *J. Am. Chem. Soc.* **1996**, *118*, 12588.

[11] For a recent discussion on carbenephilicity: R. A. Moss, *Acc. Chem. Res.* **2006**, *39*, 267.
[12] For general reviews on carbene chemistry: a) R. A. Moss, M. S. Platz, M. Jones Jr, (Eds.), *Reactive Intermediate Chemistry*, Wiley, New York, **2004**; b) U. H. Brinker (Ed.), *Advances in Carbene Chemistry*, JAI, Greenwich, CT, **2001**.
[13] For reviews on aminocarbenes: a) F. E. Hahn, *Angew. Chem.* **2006**, *118*, 1374; *Angew. Chem. Int. Ed.* **2006**, *45*, 1348; b) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815; c) E. Peris, R. H. Crabtree, *Coord. Chem. Rev.* **2004**, *248*, 2239; d) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247; e) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; f) D. Enders, T. Balensiefer, *Acc. Chem. Res.* **2004**, *37*, 534; g) W. Kirmse, *Angew. Chem.* **2004**, *116*, 1799; *Angew. Chem. Int. Ed.* **2004**, *43*, 1767; h) R. W. Alder, M. E. Blake, M. E. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020; *Angew. Chem. Int. Ed.* **2004**, *43*, 5896; i) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857; j) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

Received: August 29, 2006
Published Online: October 23, 2006

