

Synthesis and Evolution of Phosphanylcarbene–Borane Adducts

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Photolysis of [bis(dicyclohexylamino)phosphanyl](trimethylsilyl)diazomethane leads to the corresponding stable carbene **1b**, which reacts with triethylborane affording a borane–carbene adduct **2b**, characterized by spectroscopy in solution before rearrangement and fragmentation into *P*-dicyclohexylamino-*C*-(ethyl)(trimethylsilyl)phosphaalkene **3b**; trimethylsilyltrifluoromethanesulfonate adds to **1b** giving the methylenephosphonium **4b**.

The formation of transient adducts of electrophilic carbenes with Lewis bases is well documented,¹ but there are only two reports of main group 3 adducts of carbene,² including a stable alane–carbene complex.^{2a} We have shown that the stable [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene **1a**³ presents both carbene and phosphorus–carbon multiple bond reactivity, while calculations⁴ concluded that **1a** was best formulated as a phosphorus vinyl ylide. Since classical phosphorus ylides are known to react at carbon with Lewis acids giving stable adducts,⁵ it was tempting to try to prepare a phosphanylcarbene–borane complex.

Monitoring the reaction of triethylborane with [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene **1a** in toluene solution at -80°C by ³¹P NMR spectroscopy, two new signals were observed at $\delta +116.0$ (**2a**) and 249.4 (**3a**). After a few minutes, the high-field signal disappeared, and after work-up, phosphaalkene **3a**[†] and (diethyl)(diisopropyl-

amino)-borane were isolated. To increase the stability of the primary formed product, tricyclohexylborane and (dimesityl)(methyl)borane were used, but no reaction occurred, likely because of the excessive steric hindrance of the Lewis acid. However, by exchanging the diisopropylamino substituents for dicyclohexylamino groups, a new stable (phosphanyl) (silyl)carbene **1b**[‡] was obtained, which quantitatively reacts with triethylborane giving **2b**[†] ($\delta^{31}\text{P} + 121.3$). Compound **2b** is stable in solution for several weeks at -20°C or 24 h at room temp. As previously, slow decomposition of **2b** leads to phosphaalkene **3b**[†] and (diethyl)(dicyclohexylamino)borane, which were isolated in near quantitative yield (Scheme 1).

The expected borane–carbene adducts **2** can be regarded as methylenephosphonium type compounds **4**.⁶ Thus, in order to

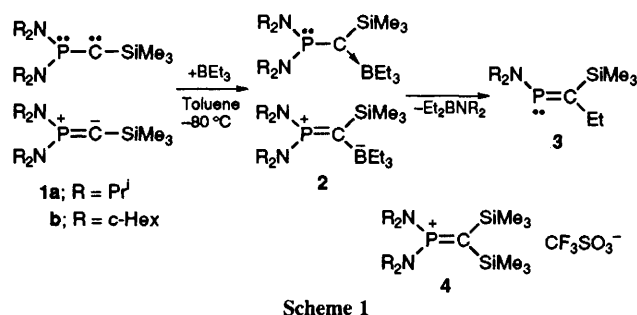
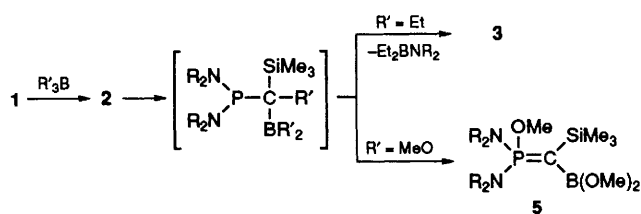


Table 1

	$\delta^{31}\text{P}$ NMR	$\delta^{13}\text{C}$ NMR ($^1J_{\text{PC}}/\text{Hz}$)
1a	-40.7	142.7 (159.3)
1b	-31.4	139.3 (160.2)
2a	116.0	—
2b	121.3	54.2 (63.5)
4a	130.8	76.5 (87.6)
4b	134.2	73.4 (87.2)

[†] Selected spectroscopic data for: **1b**, **2b**, **3a**, **3b** and **4b**. **1b**: ³¹P NMR (C_6D_6) $\delta -31.4$; ²⁹Si NMR (C_6D_6) $\delta -19.7$ (d, J_{PSi} 59.3 Hz); ¹³C NMR (C_6D_6) $\delta 3.9$ (d, J_{PC} 10.5 Hz, SiCH₃), 26.0 (s, NCCCC), 27.0 (s, NCCC), 36.6 (d, J_{PC} 2.2 Hz, NCC), 58.2 (d, J_{PC} 2.5 Hz, NC), 139.3 (d, J_{PC} 160.2 Hz, PC). **2b**: ³¹P NMR (C_7D_8) $\delta 121.3$; ¹³C NMR (C_7D_8) $\delta 4.3$ (d, J_{PC} 12.8 Hz, SiCH₃), 10.8 (d, J_{BC} 17.9 Hz, BCH₂CH₃), 19.5 (broad s, BCH₂), 27.0 (s, NCCCC), 28.2 and 28.54 (d, J_{PC} 4.9 and 9.0 Hz, NCCC), 37.4 and 36.9 (d, J_{PC} 13.0 and 15.9 Hz, NCC), 54.2 (d, J_{PC} 63.5 Hz, PC), 60.8 and 61.7 (d, J_{PC} 5.9 and 4.5 Hz, NC). **3a**: colourless oil; ³¹P NMR (C_6D_6) $\delta 249.4$; ²⁹Si NMR (C_6D_6) $\delta -2.36$ (d, J_{PSi} 59.1 Hz); ¹H NMR (C_6D_6) $\delta 0.26$ (d, J_{PH} 1.9 Hz, 9H, CH₃Si), 1.10 [d, J_{HH} 6.7 Hz, 12H, NC(CH₃)₂], 1.12 (t, J_{HH} 7.4 Hz, 3H, CH₂CH₃), 2.60 (qd, J_{HH} 7.4 Hz, J_{PH} 7.3 Hz, 2H, CH₂CH₃), 3.60 (sept d, J_{HH} 6.7 Hz, J_{PH} 13.5 Hz, 2H, NCH); ¹³C NMR (C_6D_6) $\delta 1.4$ (d, J_{PC} 12.9 Hz, SiCH₃), 17.8 (d, J_{PC} 7.6 Hz, CH₂-CH₃), 24.4 (d, J_{PC} 7.2 Hz, NCC), 26.1 (d, J_{PC} 12.9 Hz, CH₂-CH₃), 49.5 (d, J_{PC} 4.0 Hz, NC), 143.1 (d, J_{PC} 70.6 Hz, PC). **3b**: colourless oil; ³¹P NMR (C_6D_6) $\delta 252.0$; ¹H NMR (C_6D_6) $\delta 0.31$ (d, J_{PH} 1.8 Hz, 9H, CH₃Si), 0.80 to 2.25 (m, 20H, NCCCH₂), 1.19 (t, J_{PH} 8.3 Hz, 3H, CH₂CH₃), 2.63 (m, 2H, CH₂CH₃), 3.24 (m, 2H, NCH); ¹³C NMR (C_6D_6) $\delta 1.5$ (d, J_{PC} 12.9 Hz, SiCH₃), 18.0 (d, J_{PC} 7.6 Hz, CH₂-CH₃), 25.8 (m, NCCCC), 26.1 (d, J_{PC} 12.8 Hz, CH₂-CH₃), 35.7 (d, J_{PC} 6.9 Hz, NCC), 58.1 (d, J_{PC} 10.3 Hz, NC), 141.8 (d, J_{PC} 74.1 Hz, PC). **4b**: ³¹P NMR (C_6D_6) $\delta 134.2$; ²⁹Si NMR (C_6D_6) $\delta 0.4$; ¹³C NMR (C_6D_6) $\delta 3.2$ (d, J_{PC} 6.8 Hz, SiCH₃), 24.5 (s, NCCCC), 26.2 (s, NCCC), 35.2 and 36.6 (s, NCC), 62.6 and 64.0 (s, NC), 73.4 (d, J_{PC} 87.16 Hz, PC), 120.8 (q, J_{FC} 321.1 Hz, CF₃).

[‡] A pentane solution (10 ml) of [bis(dicyclohexylamino)phosphanyl](trimethylsilyl)diazomethane¹⁰ (0.5 g, 1 mmol) was irradiated at 254 nm. The reaction was monitored by ³¹P NMR spectroscopy and was complete after 36 h. The solvent was then removed under vacuum affording **1b** as a moisture-sensitive orange oil (90%).[†]



Scheme 2

compare the spectroscopic features of **2b**, methylenephosphonium **4b⁺** was prepared by addition of trimethylsilyltrifluoromethanesulfonate to phosphanylcarbene **1b**. Selected spectroscopic data are shown in Table 1. The ^{31}P NMR chemical shifts of compounds **2** are quite similar to those of the tricoordinated phosphorus cation **4**, and shifted toward low field by more than 150 ppm compared with the starting material **1**. The ^{13}C NMR signal for the quaternary carbon⁷ is substantially upfield from the free phosphanylcarbene ($\Delta\delta = 88.5$ ppm), even more than in the case of the carbene–alane adduct ($\Delta\delta = 44.4$ ppm), reported by Arduengo *et al.*^{2a} These data suggest that the electronic structure of **2** is much closer to the methylenephosphonium form than to the carbene–borane Lewis acid–Lewis base form.

Evolution of adducts **2** into phosphalkenes **3** can be easily understood as a classical 1,2-migration of an ethyl group from the four-coordinated boron atom to the electron deficient α -carbon⁸ followed by a 1,2-elimination of (diethyl)(diisopropylamino)borane. Note, that these results do not contradict the formal 1,2-addition of trimethoxyborane and dimesitylfluoroborane to **1a**, leading to the corresponding C-borylated phosphorus ylides **5**.^{3c} Indeed, in all cases, the borane–carbene adducts **2** rearrange to the β -boryl phosphanes, then depending on the nature of the substituents either a 1-2 elimination leads to **3**, or alternatively a classical methylenephosphane–phosphorus ylide conversion gives rise to **5** (Scheme 2).⁹

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