

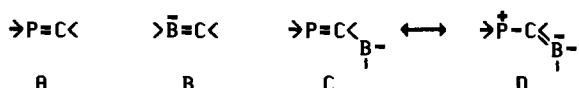
New Synthesis and First X-ray Crystal Study of a C-Borylated Phosphorus Ylide

Klaus Horchler von Locquenghien,^{t,‡} Antoine Baceiredo,[†]
Roland Boese,^{*,§} and Guy Bertrand^{*,†}

Laboratoire de Chimie de Coordination du CNRS
205, route de Narbonne, 31077 Toulouse Cedex, France
Institut für Anorganische Chemie, Universität-GH Essen
Universitätsstrasse 3-5, 4300 Essen, FRG

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Phosphorus ylides A have been widely used in organic and organometallic synthesis.¹ More recently, the synthetic potential of boron methylenide ions B has been demonstrated.² Theoreticians have been attracted by the unusual phosphorus–carbon³ and boron–carbon bonding⁴ in such compounds. Numerous so-called stabilized phosphorus ylides have been studied in which the negative charge is delocalized into an organic,⁵ organometallic,⁶ or heteroatomic⁷ framework. Only little attention has been devoted to C-borylated phosphorus ylides C⁸ although they are of special interest: they can also be considered as C-phosphonio-substituted borataalkenes D.



We have recently reported that the stable [bis(diisopropylamino)phosphanyl](trimethylsilyl)carbene **1** underwent formal 1,2-additions with a variety of electrophiles.⁹ Thus a novel entry to the intriguing species of type CD was obvious. Indeed, when a toluene solution of **1** is treated with a stoichiometric amount of dimesitylfluoroborane (**2a**)¹⁰ and trimethoxyborane (**2b**), at

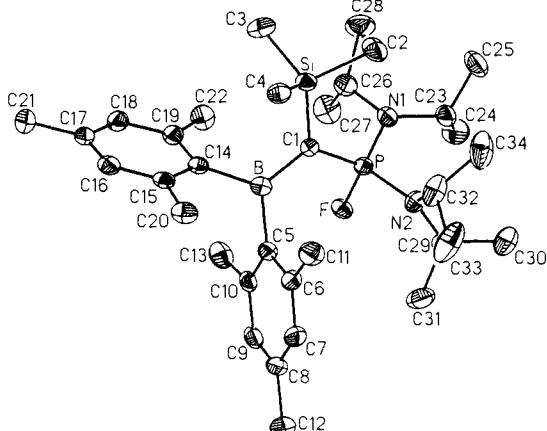
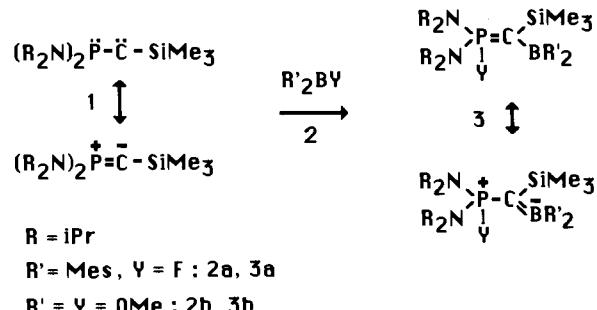


Figure 1. Molecular structure of **3a** showing the atom-numbering scheme. Pertinent bond lengths (pm), bond angles (deg), and dihedral angles (deg) are as follows: B–C1 152.5 (4), P–C1 169.6 (2), Si–C1 187.2 (3), B–C14 162.9 (3), B–C5 161.5 (4), P–F 158.5 (1), P–N1 166.3 (2), P–N2 165.5 (2); P–C1–Si 123.3 (1), P–C1–B 117.9 (2), Si–C1–B 118.8 (2), C1–B–C5 123.4 (2), C5–B–C14 114.6 (2), C1–B–C14 122.0 (2); C14–B–C1–P –147.9, C14–B–C1–Si 32.3, C5–B–C1–P 30.6, C5–B–C1–Si –149.1, C1–B–C5–C6 72.4, C1–B–C5–C10 –110.0, C1–B–C14–C19 63.7, C1–B–C14–C15 –122.8.

room temperature, a quantitative reaction occurs leading to the desired compounds **3a** and **3b**, respectively.¹¹



Derivative **3b** is obtained as a viscous, colorless oil, but **3a** is an air-stable solid that can be recrystallized from an acetonitrile/THF (1/1) solution, affording colorless crystals (mp 168 °C) suitable for an X-ray diffraction study.¹³ The molecular structure of **3a** is illustrated in Figure 1 along with the atom-numbering scheme and the pertinent metric parameters. The B–C1 bond length (152.5 (4) pm) is shorter than a usual boron–carbon single bond (158–162 pm), longer than a boron–carbon double bond of, e.g., $Mes_2B=C=CH_2$ (144.4 (7) pm, mean value)^{2c} or of $'BuB=C(SiMe_3)_2$ (136.1 (5) pm)^{2c} and similar to that observed for **4** (152.2 (10) pm).^{2d} Consequently, the P–C1 bond length (169.6 pm) is longer than expected for a nonstabilized phosphorus ylide with three electronegative substituents at phosphorus. No structural data are available for phosphorus ylides of the type $(R_2N)_2FP=C(R')_2$, but a P–C_{ylide} bond length of 163–164 pm can be estimated from the known structure of the corresponding carbodiphosphorane.¹⁴ The angular sum at both

(11) This reaction formally resembles the well-known haloboration of alkynes.¹² However, preliminary mechanistic studies are more in favor of a carbene-type behavior of **1**.

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(13) X-ray structure analysis of **3a** at 160 K: monoclinic, $P2_1/n$, $a = 10.887$ (2) Å, $b = 13.865$ (2) Å, $c = 23.604$ (4) Å, $\beta = 98.13$ (1)°, $V = 3526.9$ (9) Å³, $Z = 4$, $\rho_{calcd} = 1.110$ g cm⁻³, $\mu = 1.4$ cm⁻¹; Mo Kα irradiation (graphite monochromator); 6362 independent intensities, of which 4891 have $F_o > 4\sigma(F)$; $3^\circ < 2\theta < 53^\circ$, 388 parameters, $R = 0.0471$, $R_w = 0.0544$.

^tLaboratoire de Chimie de Coordination du CNRS.

^{*}New address: BASF AG, Ammonia Laboratory, 6700 Ludwigshafen, FRG.

[†]Institut für Anorganische Chemie, Universität-GH Essen.

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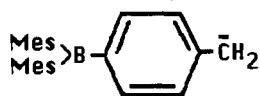
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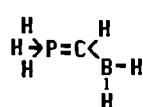
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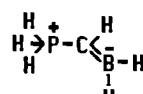
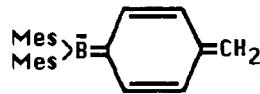
C1 and boron atom is 360° . Despite the bulky substituents at the B-C1 bond, the dihedral angle between the BC5C14 and the C1SiP planes is only 31.5° , which is much smaller than that found for Mes₂B (50°)¹⁵ but comparable to the value observed for **4** (25.8°).^{2d} These results as a whole suggest that, in the solid state, compound **3a** has partial boron–carbon double bond character.



4



5



In solution, a similar picture emerges from NMR spectroscopy.¹⁶ The ¹¹B chemical shift for **3a** of $+63.5$ lies between the shifts observed for MeBMes₂ ($+82.0$)¹⁷ and H₂C=BMes₂⁻ ($+35.0$).^{2c} Compared to the ¹¹B NMR data of previously reported C-borylated phosphorus ylides,^{8a} the ¹¹B nucleus in **3a** is slightly deshielded, probably due to the presence of bulky substituents at the PCB skeleton. The ¹³C NMR signal for the C1 atom is observed at $+54.4$, showing a strongly deshielded ylidic carbon atom compared to those in nonstabilized phosphorus ylides (e.g., $+7.3$ in (iPr₂N)₂PF=C(SiMe₃)₂¹⁸). In the ¹H and ¹³C NMR spectra of **3a**, separate signals are observed for the two mesityl groups. Even at 110°C , rotation about the B-C1 bond is slow relative to the NMR time scale, giving a rotation barrier $\Delta G^* > 90 \text{ kJ mol}^{-1}$.^{19,20} For the parent system **5**, the planar conformation has been calculated to be 120 kJ mol^{-1} more stable than the perpendicular one.^{21,22}

On the other hand, for **3b**, the two methoxy groups at the boron atom are equivalent even at -80°C , and therefore, no rotational

barrier could be determined. At low temperature, the molecule probably adopts a conformation with a perpendicular orientation of the bonding planes of the boron and carbon atoms, meaning that B–C π -interactions are negligible. In addition, the ¹¹B chemical shift of $+30.6$ is almost identical with that of MeB(OMe)₂.²³ Obviously, the dimethoxyboron group cannot compete with the σ^* orbital of the phosphorus moiety for the electron density at the ylidic carbon atom.

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Supplementary Material Available: Tables of bond distances, angles, dihedral angles with estimated standard deviations, atomic coordinates and equivalent isotropic displacement factors, and anisotropic atomic displacement factors and H atom coordinates (5 pages). Ordering information is given on any current masthead page.

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Oxidative Addition of SiH₄ to Pt(PH₃)₂. An ab Initio MO/MP4 Study

Shigeyoshi Sakaki*¹ and Masami Ieki

Department of Applied Chemistry
Faculty of Engineering
Kumamoto University, Kurokami, Kumamoto 860, Japan
Institute for Molecular Science
Okazaki 444, Japan

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The C–H oxidative addition is one of the important processes in catalytic reactions of transition-metal complexes.^{2,3} The Si–H oxidative addition is also expected to be important in reactions of various Si compounds with transition-metal complexes.^{4,5} In this regard, knowledge of the factors determining the Si–H oxidative addition is fundamental to understanding reactions of Si compounds with transition-metal complexes. However, a theoretical study of Si–H oxidative addition to transition metals has not been reported, to our knowledge, while coordination of SiH₄ and HSiCl₃ with CpMn(CO)₂⁶ and α -H abstraction in Cp₂Ti-

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(16) NMR data in CD₆ at 25 °C, with chemical shifts δ relative to external TMS [¹H, ¹³C, ²⁹Si], BF₃·OEt₂ (¹¹B), 85% phosphorus acid (³¹P), $J(^{31}\text{P}X)$ in parentheses and $J(^{19}\text{F}X)$ in braces, in hertz, are as follows. **3a**: ¹H NMR (200 MHz) 6.76 (s), 6.70 (s) (each 2 H, aryl H), 4.04 (9.4) (d sept) (4 H, NCH), 2.50 (s), 2.47 (s) (each 6 H, o-CH₃), 2.17 (s) (6 H, p-CH₃), 1.16 (d), 1.00 (d) (each 12 H, NC(CH₃)₂), 0.23 (s) (9 H, Si(CH₃)₃); ¹¹B NMR (96.3 MHz, CD₆, 75 °C) 63.5 ($\nu_{1/2} = 410 \text{ Hz}$); ¹³C NMR (50.3 MHz) 147.3 (<4) (br), 146.1 (27.1) (br) (ipso C), 141.0, 139.8, (<1) (o-C), 136.0, 135.4 (p-C), 128.7, 128.3 (m-C), 54.4 (127.7) (<3) (br) (PC), 48.4 (5.5) [1.8] (NC), 25.0, 24.7 (o-CH₃), 24.7 (4.0) [1.4], 24.5 (4.8) [1.1] (NCC), 21.2, 21.1 (p-CH₃), 4.8 (3.6) [1.8] (SiCH₃); ²⁹Si NMR (39.7 MHz) -10.9 (20.0) [0.7]; ³¹P NMR (32.4 MHz) 72.9 [100.6, 9]. **3b**: ¹H NMR (200 MHz) 4.03 (12.3) (d sept) (4 H, NCH), 3.63 (s) (6 H, B(OCH₃)₂), 3.53 (11.9) (d) (3 H, POCH₃), 1.20 (d), 1.18 (d) (each 12 H, NC(CH₃)₂), 0.31 (0.3) (9 H, Si(CH₃)₃); ¹¹B NMR (25.7 MHz) 30.6 ($\nu_{1/2} = 290 \text{ Hz}$); ¹³C NMR (50.3 MHz) 52.4 (4.8) (POC), 52.0 (BOC), 47.5 (6.8) (NC), 24.9 (2.1), 24.2 (4.1) (NCC), 4.3 (4.7) (SiCH₃), BC not observed; ²⁹Si NMR (15.9 MHz) -12.4 (6.6); ³¹P NMR (32.4 MHz) 69.2.

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