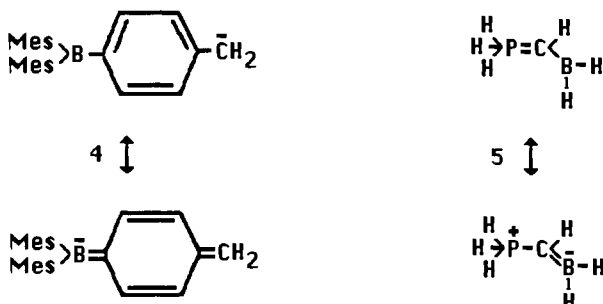


C1 and boron atom is 360° . Despite the bulky substituents at the B–C1 bond, the dihedral angle between the B C5 C14 and the C1 Si P planes is only 31.5° , which is much smaller than that found for Mes_2B (50°)¹⁵ but comparable to the value observed for **4** (25.8°).^{2d} These results as a whole suggest that, in the solid state, compound **3a** has partial boron–carbon double bond character.



In solution, a similar picture emerges from NMR spectroscopy.¹⁶ The ^{11}B chemical shift for **3a** of $+63.5$ lies between the shifts observed for MeBMe_2 ($+82.0$)¹⁷ and $\text{H}_2\text{C}=\text{BMe}_2^-$ (-35.0).^{2c} Compared to the ^{11}B NMR data of previously reported C-borylated phosphorus ylides,^{8a} the ^{11}B nucleus in **3a** is slightly deshielded, probably due to the presence of bulky substituents at the PCB skeleton. The ^{13}C 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 $(\text{iPr}_2\text{N})_2\text{PF}=\text{C}(\text{SiMe}_3)_2$).¹⁸ In the ^1H and ^{13}C 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 $\Delta G^\ddagger > 90\text{ kJ mol}^{-1}$.^{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 ^{11}B chemical shift of $+30.6$ is almost identical with that of $\text{MeB}(\text{OMe})_2$.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 SiH_4 to $\text{Pt}(\text{PH}_3)_2$. An ab Initio MO/MP4 Study

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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 SiH_4 and HSiCl_3 with $\text{CpMn}(\text{CO})_2$ ⁶ and α -H abstraction in Cp_2Ti

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(16) NMR data in C_6D_6 at 25°C , with chemical shifts δ relative to external TMS (^1H , ^{13}C , ^{29}Si), $\text{BF}_3\cdot\text{OEt}_2$ (^{11}B), 85% phosphoric acid (^{31}P), $^J(^{31}\text{P})\text{X}$ in parentheses and $^J(^{19}\text{F})\text{X}$ 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, α -CH₃), 2.17 (s) (6 H, p -CH₃), 1.16 (d), 1.00 (d) (each 12 H, $\text{NC}(\text{CH}_3)_2$), 0.23 (s) (9 H, $\text{Si}(\text{CH}_3)_3$); ^{11}B NMR (96.3 MHz, C_6D_6 , 75°C) 63.5 ($\nu_{1/2} = 410\text{ Hz}$); ^{13}C NMR (50.3 MHz) 147.3 (<4) (br), 146.1 (27.1) (br) (ipso C), 141.0, 139.8, (<1) (α -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 (α -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] (SiCH_3); ^{29}Si NMR (39.7 MHz) -10.9 (20.0) [0.7]; ^{31}P NMR (32.4 MHz) 72.9 [1006.9]. **3b**: ^1H NMR (200 MHz) 4.03 (12.3) (d sept) (4 H, NCH), 3.63 (s) (6 H, $\text{B}(\text{OCH}_3)_2$), 3.53 (11.9) (d) (3 H, POCH_3), 1.20 (d), 1.18 (d) (each 12 H, $\text{NC}(\text{CH}_3)_2$), 0.31 (0.3) (9 H, $\text{Si}(\text{CH}_3)_3$); ^{11}B NMR (25.7 MHz) 30.6 ($\nu_{1/2} = 290\text{ Hz}$); ^{13}C 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) (SiCH_3), BC not observed; ^{29}Si NMR (15.9 MHz) -12.4 (6.6); ^{31}P NMR (32.4 MHz) 69.2.

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