B–H Agostic Interactions

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Reactivity of a Terminal Chromium Borylene Complex towards Olefins: Insertion of a Borylene into a C–H Bond**

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In the rapidly developing field of terminal transition metal borylene complexes, a fascinating reactivity profile has begun to emerge, which is heavily dominated by reactions involving the partial or total cleavage of the M=B bond.[1] Importantly, terminal Group 6 aminoborylene complexes have been found to transfer the borylene moiety to other transition metals, which has proven invaluable in widening the variety of borylene complexes.[2] Recently we reported the synthesis of aminoborirenes through a similar borylene transfer from Group 6 borylenes to alkynes.[3] In 2007, Aldridge et al. reported the spectacular insertion reaction of carbodiimide substrates into the M=B and the usually unreactive N=B bonds of cationic terminal aminoborylene complexes, completely reorganizing the ligation of the boron atom.[4] Furthermore, terminal borylene complexes have elicited comparisons to carbene complexes owing to their ability to undergo a metathesis reaction with Ph_3PS.[5] With benzophenone and dicyclohexylcarbodiimide (DCC), intermediate products containing a four-membered ring were obtained, which were formed regioselectively by addition of the more electronegative elements of C=N or C=O to the M=B bond, suggesting an "interrupted" metathesis by [2+2] cycloaddition.[6] As the transfer of a borylene fragment to an alkyne is facile with Group 6 borylene complexes, we were interested in their behavior with olefins, which we presumed would present a greater resistance towards functionalization. In addition to the lower reactivity of the C=C double bond, the simple transfer product (with a saturated three-membered BCC ring) would lack the 2π-electron aromatic stabilization of borirenes. We thus turned our attention to the reactivity of $[(OC)_5Cr{=}BN(SiMe_3)_2]$ (**1**)[7] towards unactivated olefins, and we present herein the first selective insertion of the borylene moiety into a C–H bond.

The irradiation of **1** in the presence of an excess of 3,3-dimethyl-1-butene in THF at room temperature led to two poorly resolved ^{11}B NMR resonances, having similar chemical shifts at $\delta = 46.7$ and 43.5 ppm, which are shifted significantly upfield relative to the signal of **1** ($\delta = 92.1$ ppm). After 40 h irradiation, nearly all of the starting material had been consumed. After workup a red oil was obtained. The ^1H NMR spectroscopic analysis of this crude oil also indicated the presence of two compounds, **2** and **3**, in a ratio of 1:3. In the ^1H NMR spectra of compound **2**, only two signals for two protons in the olefinic region were visible, a doublet at $\delta = 6.64$ ppm ($^3J_{H,H} = 17.1$ Hz), and a doublet of doublets at $\delta = 6.23$ ppm ($^3J_{H,H} = 17.1$ Hz, $^3J_{H,H} = 6.9$ Hz), which were shifted slightly downfield relative to the three olefinic protons of the starting material ($\delta = 5.83$ and 4.93 ppm). The coupling pattern of the α-olefinic proton at 6.23 ppm was unexpected, and is explained by a ^3J coupling to a proton attached to boron that leads to a doublet of doublets, which is in accordance with that of the known compound *trans*-styryl(diisopropyl)aminoborane ($^3J = 17.4$ Hz).[8] The boron-bound proton was not detected in the ^1H NMR spectrum at ambient temperature but by variable-temperature NMR experiments in $[D_8]$toluene at −50 °C, which showed a broad singlet at $\delta = 5.47$ ppm. In the $^{13}C\{^1H\}$ NMR spectrum the boron-bound carbon atom from compound **2** was found at $\delta = 128.5$ ppm as a broad singlet.

A coupling pattern similar to that of **2** was observed in the ^1H NMR spectrum of compound **3**, that is, a doublet at $\delta = 4.91$ ppm ($^3J_{H,H} = 15.4$ Hz) and a doublet of doublets at $\delta = 3.72$ ppm ($^3J_{H,H} = 15.4$ and $^3J_{H,H} = 4.5$ Hz), which are both shifted upfield relative to the signals of **2**. The latter signal showed a ^1H–^{13}C long-range correlation to a carbon signal belonging to CO ligands in an HMBC NMR experiment, suggesting coordination of the C=C bond to the chromium fragment. This led us to assign the set of signals to compound $[(OC)_4Cr\{(H_3C)_3CHC{=}CHBHN(SiMe_3)_2\}]$ (**3**; Scheme 1). Furthermore, a broad ^1H NMR singlet resonance (peak width at half height: 87.5 Hz) at $\delta = -10.62$ ppm suggested the presence of a hydride-like proton, and the $^1H\{^{11}B\}$ NMR spectra showed a sharper peak (width at half height: 17.5 Hz) for the same resonance, which is consistent with a Cr-H-B bridge existing in solution.[9] A COSY correlation between this signal and an olefinic proton served to reinforce the proposed connectivity of compound **3**.

Multiple crystallizations of the crude material in hexane at −60 °C and removal of the residual precursor **1** led to the isolation of red crystals of **3** which were suitable for single-crystal X-ray structural analysis.[10] The thin monoclinic plate of **3** showed a very good diffraction pattern up to $2\theta = 62°$, thus allowing refinement of the structure with unconstrained positions of boron-bound and olefinic hydrogen atoms. Hence, the structural changes imposed by coordination of

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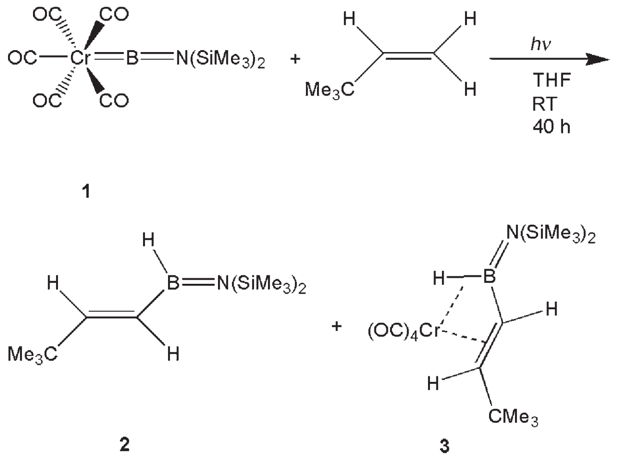


Scheme 1. Synthesis of vinylaminoboranes **2** and **3** by photochemically induced borylene insertion.

the vinylaminoborane moiety to the chromiumcarbonyl fragment could be studied in some detail.

The molecular structure of **3** confirms the assignment of the complex as a formally chromium(0) olefin complex with a weak coordination to a B−H bond (Figure 1). The N=B−C=C chain is strongly distorted from planarity and has a dihedral angle of 134.6°. As a result, the C=C bond is in position to share its electron density with the metal, and at the same time the boron-bound hydrogen H1 is aligned *trans* to the C1-O1 carbonyl group. The C5−C6 bond length (1.3723(17) Å) in **3** is comparable to that reported by Aldridge et al. for the cationic olefin complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(H_2C{=}CH\mathit{t}Bu)]^+$, which has a C−C distance of 1.393(9) Å.[11] The C5−B1 distance is in the expected range of C−B single bonds (1.5482(18) Å) but is surprisingly unperturbed by the close Cr-H-B association, the distance agreeing well with the vinylborane complex $[(OC)_4Fe\{H_2C{=}CHBCH_3N(CH_3)_2\}]$ (**4**) of Schmid et al., in which the boron atom is distant from the metal center.[12] The B1−N1 bond of **3** (1.4034(16) Å) is also within the range of B=N bonds (for example **4**, 1.416(14) Å). The close Cr1−B1 (2.2996(13) Å) and Cr1-H1 (1.764(15) Å) distances, in addition to the ^{1}H NMR data, support the idea of B−H σ bonding to the metal center, and the overall structure of the H−B−C=C moiety is reminiscent of a distorted *cis*-butadiene-type ligand, although the B−C bond does not appear to be involved in the bonding.

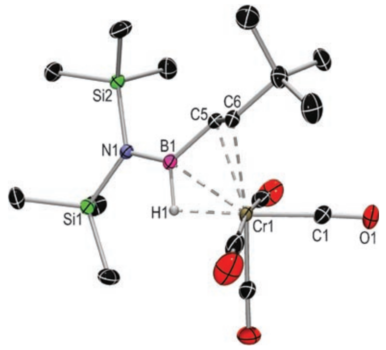
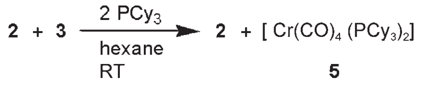


Figure 1. Molecular structure of **3**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: N1–B1 1.4034(16), B1–H1 1.197(15), H1–Cr1 1.764(15), B1–Cr1 2.2995(13), B1–C5 1.5482(18), C5–C6 1.3723(17); N1-B1-C5 131.54(11).

DFT calculations on compound **3** reproduced its experimentally observed features very well.[13] The calculated NMR chemical shifts for the B−H moiety are almost identical to the experimental data ($\delta(^{11}B) = 43.4$ ppm; $\delta(^1H) = -10.6$ ppm). The conformation and bond lengths in particular of the vinylborane chain were depicted with high accuracy. Comparison of the computed geometry of borane **2** with that of complex **3** shows marginal shortening of N=B and B−C bonds and more pronounced elongation of B−H and C=C bonds (**2**: 1.199 Å and 1.347 Å; **3**: 1.257 Å and 1.373 Å, respectively). The most striking feature is the perturbation of the dihedral angle N=B−C=C from 180° in the free borane to 134.6° in **3**, which allows the H−B−C=C chain to align with the empty coordination site of the $\{Cr(CO)_4\}$ moiety. The coordination of the vinylborane by a C=C and a B−H bond is reflected in relatively high values of the Wiberg bond index (WBI, Cr···B: 0.23, Cr···H: 0.15, Cr···C5: 0.19, Cr···C6, 0.19). In contrast to the significant interaction of the boron-bound hydrogen atom with the chromium atom, the interaction of both olefinic hydrogen atoms with the metal center can be neglected (WBI = 0.0).

Complex **3** is very sensitive towards air and moisture, but could be stored in the solid state for several months under argon at −35 °C without decomposition.

The noncoordinated vinylborane **2** could be obtained as an analytically pure compound from the crude mixture of **2** and **3** upon reaction with two equivalents of PCy_3, which led to liberation of the borane and formation of $[Cr(CO)_4(PCy_3)_2]$ **5**, as indicated by a characteristic ^{31}P NMR resonance at $\delta = 69.4$ ppm (Scheme 2).[14] Vinylborane **2** was obtained as a colorless liquid, which is sensitive towards air and moisture but could be stored under argon at room temperature for several weeks without decomposition.



$$\mathbf{2} + \mathbf{3} \xrightarrow[\text{hexane, RT}]{2\ PCy_3} \mathbf{2} + \underset{\mathbf{5}}{[Cr(CO)_4(PCy_3)_2]}$$

Scheme 2. Addition of 2 equivalents of PCy_3 to the mixture of **2** and **3**.

It should be noted that a previous insertion of a borylene ligand into a C−H bond of dichloromethane was suggested by Aldridge in the reaction of the cationic borylene complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BMes)][BAr^F{}_4]$ with neutral ligands, providing the proposed compound $[\{Mes(Cl_2CH)B(\mu\text{-}H)\}_2]$; however, its formulation could not be conclusively determined (Mes = 2,4,6-$Me_3C_6H_2$; Ar^F = 3,5-bis(trifluoromethyl)-phenyl).[11] Selective, mild activations of olefinic C−H bonds are highly sought after in organic chemistry, as they can allow the construction of valuable molecules from simple, low-functionality feedstocks. The reaction reported herein yields a single regioisomer of an α-olefinic borane from a simple, unactivated olefin. The Suzuki–Miyaura coupling reaction, originally the palladium-mediated coupling of arylboranes and organic halides, has recently been extended with some success to include alkyl- and alkenylboranes, boronic acids, and borates.[15,16] Although the difficulty in synthesizing precursor **1** makes the reaction presented herein unfeasable at present as a practical route to α-olefinic boranes for use in the Suzuki–Miyaura coupling, the C−H activation by a borylene complex is itself unprecedented and could lay the foundation for an alternative procedure for the synthesis of borylated organic species.

Experimental Section

All manipulations were conducted under an argon atmosphere, either employing standard Schlenk or glovebox techniques. The complex **1** was prepared as described previously.[7] Irradiation experiments were performed in a 150 mL Schlenk flask equipped with a quartz cooling jacket in which a mercury lamp (125 W) was inserted vertically.

3: A pale yellow solution of **1** (580 mg, 1.60 mmol) and 3,3-dimethyl-1-butene (560 mg, 6.65 mmol) in THF (10 mL) was irradiated for 40 h at room temperature. The volatile components were then removed under vacuum, and the resulting brown residue was extracted with hexane (2 × 5 mL). The flask containing the dark suspension was placed in a centrifuge and the hexane solution separated from the black solid. The hexane solution was stored at −60 °C overnight and 105 mg of **1** was removed by crystallization. The hexane solution was stored over 3 days at −60 °C and 126 mg of **3** (20 % yield) was isolated as red crystals. ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 4.91$ (d, $^3J_{H,H} = 15.4$ Hz (*trans*), 1 H), 3.72 (dd, $^3J_{H,H} = 15.4$ Hz, $^3J = 4.5$ Hz, 1 H), 0.97 (s, 9 H), 0.18 ppm (s, 18 H); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 222.3$ (s, *C*O), 219.5 (s, *C*O),121.2 (s, =*C*H*t*Bu), 30.2 (s, -*C*(CH$_3$)$_3$), 29.4 (s, -C(*C*H$_3$)$_3$), 3.6 ppm (s, -N(Si(*C*H$_3$)$_3$)$_2$); ^{11}B{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): $\delta = 43.5$ ppm (s).

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[17] The Supporting Information includes the syntheses, full characterization, and spectroscopic data of compound **2**.