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Reaction of Bis(pentafluorophenyl)borane with Methylidyne Complexes: Synthesis and Characterization of a Cationic Tungsten(VI) Borylalkylidyne Hydride

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Summary: Reaction of the tungsten methylidyne complexes (dmpe)$_2$W(X)$\equiv$CH (X = Cl, OTf) with HB(C$_6$F$_5$)$_2$ yields zwitterionic compounds upon electrophilic attack of the methylidyne ligand, in which the methylidyne hydrogen is strongly α-agostic (X = Cl) or is transferred to the tungsten center (X = OTf). Removal of hydride from the coordinated HB(C$_6$F$_5$)$_2$ with [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ gives a cationic borylalkylidyne hydride species.

The fundamental reactivity of boranes with transition-metal organometallic compounds is germane to important catalytic reactions such as olefin polymerization,[2] hydroboration,[3] and hydrocarbon borylation.[4] Perfluoroarylboranes are a critical subclass of boranes, due to their high stability and Lewis acidity.[5]

Some years ago, we first synthesized bis(pentafluorophenyl)borane, HB(C$_6$F$_5$)$_2$,[6] a highly active hydroboration reagent and synthon for the incorporation of Lewis acidic −B(C$_6$F$_5$)$_2$ groups into molecular frameworks.[7] A large part of the reason for this high activity, apart from the strongly Lewis acidic nature of this borane, is the relative ease with which it dissociates into the reactive monomer from the dimeric form it assumes as a solid. Thus, in solution, significant concentrations of monomeric HB(C$_6$F$_5$)$_2$ are present at room temperature.

In addition to exploring the hydroboration chemistry of this borane,[6,8] we have been systematically investigating its reactivity with a variety of organometallic compounds, including compounds with M−C single bonds (Cp$_2$MR$_2$, M = Zr,[9] Ti[10]), coordinated olefins, and M=C double bonds (Cp$_2$Ta(CH$_3$)=CH$_2$).[11] A hallmark of several of these reactions is the production of organometallic compounds with unprecedented boron-containing ligands. To extend these studies, we have investigated the reactions of HB(C$_6$F$_5$)$_2$ with the M$\equiv$C triple bond in the tungsten methylidyne complex (dmpe)$_2$W(Cl)$\equiv$CH,[12] first reported by Schrock in 1981.[13] This chemistry has led to the formation of a novel cationic borylalkylidyne complex, reported herein.

The dmpe-stabilized methylidyne complex (dmpe)$_2$W(Cl)$\equiv$CH was prepared as described by Schrock et al. from the closely related PMe$_3$ ligated species (PMe$_3$)$_4$W(Cl)$\equiv$CH by simple substitution chemistry.[12b] To aid in the acquisition of NMR and IR spectroscopic data, the ^{13}C- and ^{2}H-labeled isotopomers were similarly generated from labeled (PMe$_3$)$_4$W(Cl)$\equiv$^{13}CH and (PMe$_3$)$_4$W(Cl)$\equiv$CD, prepared from (PMe$_3$)$_4$WCl$_2$ and Al(^{13}CH$_3$)$_3$ or Al(CD$_3$)$_3$. The chloride ligand in these compounds can be exchanged for triflate by treatment with Me$_3$SiOTf. The use of the chelating phosphine precluded side reactions leading to formation of the PMe$_3$ adduct of HB(C$_6$F$_5$)$_2$, which became problematic in the reactions of (PMe$_3$)$_4$W(Cl)$\equiv$CH with the borane.

As expected on the basis of the earlier Schrock studies,[12] reaction of the bulky electrophile HB(C$_6$F$_5$)$_2$ with (dmpe)$_2$W(X)$\equiv$CH (X = Cl, OTf) leads to formation of zwitterionic adducts, **1a** (X = Cl) and **1b** (X = OTf), in which the borane attacks the methylidyne carbon (Scheme 1). In **1a**, the spectroscopic data indicate that the methylidyne hydrogen remains associated with the methylidyne carbon, although it engages in a strong α-agostic interaction with the tungsten center. Its resonance appears in the region typical of such d^2

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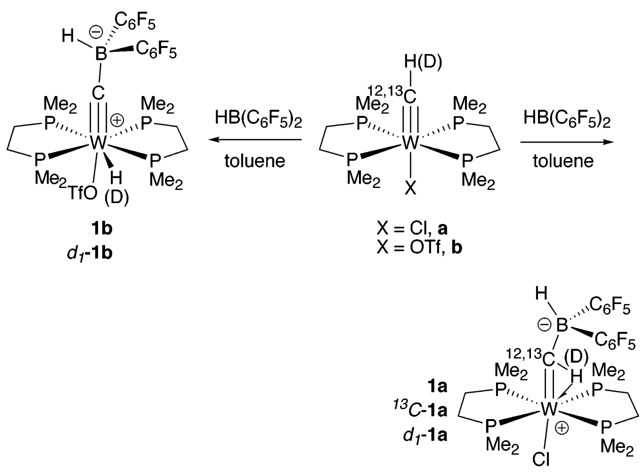
Scheme 1



agostic alkylidenes[14] at −7.58 ppm as a quintet ($^{3}J_{PH}$ = 9.9(2) Hz, $^{2}J_{WH}$ = 41(1) Hz), indicating that the position of agostic coordination is dynamic on the NMR time scale; the room-temperature ^{31}P NMR spectrum exhibits a single resonance at 20.7 ppm with tungsten satellites ($^{1}J_{PW}$ = 253 Hz). Low-temperature NMR studies failed to freeze out a slow exchange regime, indicating a low barrier for migration of the agostic hydrogen between CP_2 faces. A very low $^{1}J_{CH}$ value of 50(1) Hz, obtained from the ^{1}H NMR spectrum of *^{13}C-***1a**, is consistent with the agostic nature of this bond. The hydridoborate moiety is indicated by an ^{11}B NMR chemical shift of −18.1 ppm and a broad quartet resonance in the ^{1}H NMR spectrum at 3.23 ppm ($^{1}J_{BH}$ = 88(2) Hz). Zwitterionic complex **1a** is isoelectronic with the tantalum alkylidene complex $(dmpe)_2Ta(Cl){=}C(H)^{t}Bu$,[15] which also exhibits a strong α-agostic interaction with NMR properties similar to those described for **1a**.[16]

The triflate product **1b** exhibits NMR properties distinctly different from those observed for **1a**. While the parameters associated with the hydridoborate moiety are similar, those pertaining to the methylidyne C−H unit indicate that the hydrogen has transferred completely to the metal. No resonance in the upfield region around −7.5 ppm associated with α-agostic protons, as seen for **1a**, was observed. Rather, a quintet for the W−D moiety in *d*-**1b** was detected at 1.90 ppm ($^{2}J_{PD}$ = 6.1 Hz) in the $^{2}H\{^{1}H\}$ NMR spectrum, which is obscured by dmpe proton resonances in the ^{1}H NMR spectrum. Furthermore, the two compounds differ in their color; the formally d^2 **1a** is orange, while the d^0 configuration of **1b** arrived at upon oxidative addition of the methylidyne C−H bond is consistent with its observed lack of color. In the isoelectronic Ta manifold, replacement of Cl for OTf yields an equilibrium mixture of $(dmpe)_2Ta(OTf){=}C(H)^{t}Bu$ and $(dmpe)_2Ta(H)(OTf){\equiv}C^{t}Bu$.[15]

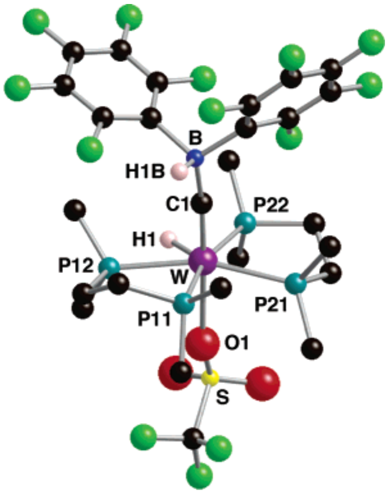


Figure 1. Crystalmaker diagram of the molecular structure of **1b**. Selected bond distances (Å): W−P(11), 2.506(2); W−P(12), 2.4833(16); W−P(21), 2.5351(18); W−P(22), 2.4763); W−O(1), 2.400(5); W−C(1), 1.792(6); C(1)−B, 1.613(9); C(31)−B, 1.651(9); C(41)−B, 1.628(9). Selected bond angles (deg): P(11)−W−P(21), 87.00(8); P(12)−W−P(22), 117.83(6); W−C(1)−B, 168.5(5); C(31)−B−C(41), 109.5(5).

This assignment for **1b** was supported by X-ray crystallographic analysis of colorless needles of the compound; a Crystalmaker diagram of the molecular structure is shown in Figure 1 along with selected metrical parameters. While the hydride bonded to tungsten was not located and refined, its presence in the P_4W plane between P(12) and P(22) is clearly indicated by the very different interligand P−W−P angles: P(11)−W−P(21) = 87.00(8)° and P(12)−W−P(22) = 117.83(6)°. The W−C(1) bond distance of 1.792(6) Å is at the low end of those found for W≡C,[17] and the W−C(1)−B angle deviates from linearity (168.5(5)°) probably to alleviate adverse steric interactions. The C(1)−B distance of 1.613(9) Å is typical of a boron−carbon single bond.

Removal of H_2 from compounds **1** would lead to complexes with a novel boron-containing ligand. Heating samples of **1a** leads to ill-defined decomposition processes in which no definitive evidence for H_2 loss was observed. We thus sought to remove the elements of H_2 via a hydride abstraction/deprotonation protocol. While we have been unsuccessful in completing the protocol, the distorted alkylidene **1a** reacts with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in benzene to yield Ph_3CH and an orange oil, **2**, which precipitates out of this medium. The oil can be solubilized with bromobenzene, but to acquire NMR data, the resulting solid that crystallizes from C_6D_6/C_6D_5Br must be redissolved in CD_2Cl_2/C_6D_5Br mixtures, in which it is sparingly soluble. NMR data are consistent with formation of a compound in which the B−H hydride has been removed,[18] and the agostic alkylidene hydrogen has transferred to the W center (Scheme 2).

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(16) IR spectroscopy gave inconclusive data concerning the α-agostic interaction for **1a**. A very low stretch of 2200 cm^{-1} was reported for the agostic C−H moiety of $(dmpe)_2Ta(Cl){=}C(H)^{t}Bu$,[14] but we do not observe a band in this region of the spectrum. Rather, a weak band in the spectrum of **1a** at 2801 cm^{-1} is observed, and this band disappears in the spectrum of *d*-**1a**. While this falls within the range of 2250−2800 cm^{-1} generally observed for agostic C−H functions,[13] the expected ν_{C-D} band at ~2000 cm^{-1} was not observed, so we cannot with complete confidence assign this to the agostic C−H stretch.

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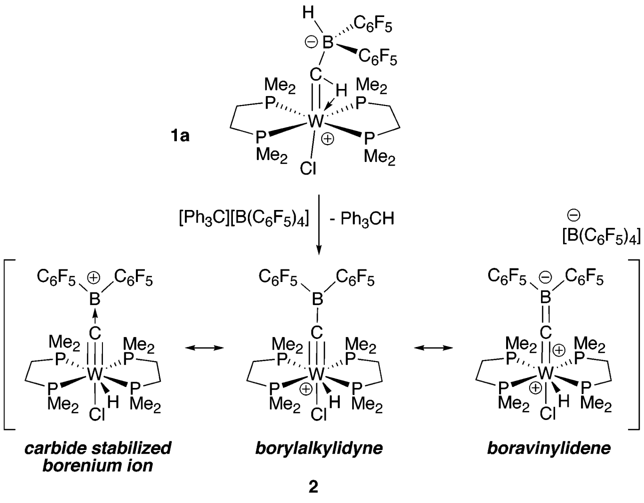
Scheme 2



The ^{19}F NMR spectrum of **2** exhibits two sets of three resonances in a 2:1 ratio. The more intense set is attributed to the $[B(C_6F_5)_4]^-$ anion by virtue of the small separation (3.4 ppm) between the resonances for the para and meta fluorines.[19] The smaller set, however, has a more substantial $\Delta\delta_{m,p}$ gap of 10.4 ppm, which is suggestive of the three-coordinate boron center expected upon H^- abstraction. The ^{11}B NMR spectrum shows two signals: one at −17 ppm for the borate boron and one at 40 ppm for the neutral boron atom. In the ^{1}H NMR spectrum, no signal for the hydridoborate is present, nor is there a resonance in the region associated with an α-agostic C−H. Rather, a symmetrical pentet appears at 4.5 ppm, with a large $^2J_{PH}$ value of 39(1) Hz (cf. the value of 9.9(2) Hz seen in **1a**). Upon cooling to 220 K, this resonance transforms into a triplet of triplets with $^2J_{PH}$ values of 70(1) Hz and ~8(2) Hz (the small coupling was barely resolvable in the low-temperature limit). These values compare well to the couplings of 90 and 10 Hz observed in $(dmpe)_2Ta(H)(ClAlMe_3){\equiv}C^tBu$ between the Ta−H and the trans and cis dmpe phosphines, respectively.[15] Finally, the ^{13}C resonance for the alkylidyne carbon was located (using ^{13}C-labeled **2**) as a broad signal at 265.0 ppm, and the $^2J_{CH}$ value of 5.5(2) Hz unequivocally establishes that cleavage of the C−H bond has occurred to produce compound **2**.

Scheme 2 indicates that **2** may be viewed as being a borylalkylidyne, a boravinylidene, or even a tungsten carbide stabilized borenium ion. The ^{19}F and ^{11}B NMR data discussed above are consistent with a measure of π-donation from W≡C to the vacant p orbital on the boron, since the $\Delta\delta_{m,p}$ and ^{11}B chemical shift values fall between the normal values for purely three-coordinate neutral ($\Delta\delta_{m,p} \approx 15-18$ ppm, $^{11}B > 50$ ppm) and four-coordinate neutral adducts ($\Delta\delta_{m,p} \approx 7-8$ ppm, $^{11}B \approx 10-20$ ppm). To probe this issue further, the molecular structure of **2** (the cationic portion is shown in Figure 2) confirms the gross features of the structure of **2** as determined spectroscopically. The pattern of P−W−P angles indicates the presence of a W−H moiety. The boron center is clearly trigonal planar in geometry (the sum of the C−B−C angles is 359.6(4)°), and the W(1)−C(13)−B(1) angle is essentially linear at 176.0(4)°. The W(1)−C(13) distance of 1.821(2) Å is indicative of a tungsten−carbon triple bond, but the C(13)−B(1) length of 1.521(6) Å is ~0.1 Å shorter than a typical boron−carbon single bond. Together with the spectroscopic data, it appears that an apt description of the bonding in **2** falls somewhere between the “borylalkylidyne” and “boravinylidene” resonance structures shown in Scheme 2. The importance of the latter resonance structure is perhaps indicated by the fact that hydride abstraction from the hydridoborate moiety in **1a** triggers transfer of the agostic alkylidene hydrogen to the metal, allowing for π donation to the newly vacant Lewis acid orbital on boron.

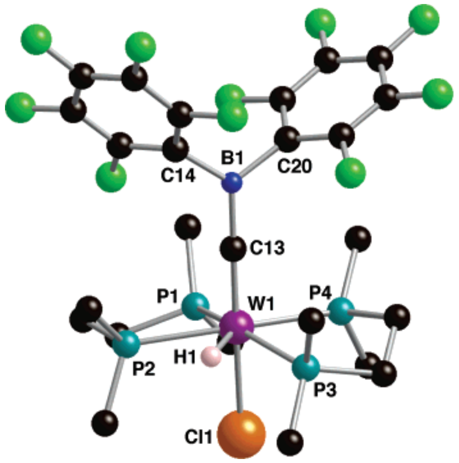


Figure 2. Crystalmaker diagram of the molecular structure of **2**. Selected bond distances (Å): W(1)−C(13), 1.821(5); W(1)−P(2), 2.4861(12); W(1)−P(3), 2.5041(12); W(1)−Cl(1), 2.5524(12); W(1)−P(4), 2.5545(12); W(1)−P(1), 2.5710(13); B(1)−C(13), 1.512(7); B(1)−C(14), 1.578(7); B(1)−C(20), 1.591(7). Selected bond angles (deg): P(2)−W(1)−P(3), 118.22(4); P(4)−W(1)−P(1), 85.51(4); C(13)−B(1)−C(14), 124.7(4); C(13)−B(1)−C(20), 120.9(4); C(14)−B(1)−C(20), 114.0(4); B(1)−C(13)−W(1), 176.0(4).

Attempts to deprotonate **2** have thus far met with failure, probably due to preferential nucleophilic attack by the base at the electrophilic boron center of the borylalkylidyne/boravinylidene ligand. Future research will continue in this vein using weakly nucleophilic bases, in addition to exploring the reactivity and bonding of these novel new boron-containing ligands.

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Supporting Information Available: Text giving experimental details and tables of atomic coordinates, anisotropic displacement parameters, and all bond distances, bond angles, and torsion angles for the structurally characterized molecules presented here; crystallographic data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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