Reactions of Bis(pentafluorophenyl)borane with Cp₂Ta(=CH₂)CH₃

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Summary: Reactions of Schrock's methyl methylene complex Cp₂Ta(=CH₂)CH₃ with HB(C₆F₅)₂ are described. Products arising from attack of the borane at the methylene ligand are isolated; the course of the reaction is dependent on the conditions employed and the equivalency of borane used.

Early transition metal organometallic compounds, in combination with strong Lewis acids, form highly reactive species which are commercially important as catalysts for various processes involving olefins.[1−3] Crucial to the understanding of existing catalyst systems and the development of new catalytic reactions are the intimate details of how these Lewis acids interact with various hydrocarbyl ligands.[4] Our studies involving the reactions of the borane HB(C₆F₅)₂,[5] **1**, with dialkyl zirconocenes[6] and olefin complexes of zirconium[7] have shown that electrophilic attack on these particular hydrocarbyl ligands occurs at the sterically more accessible portions of the HOMO.

To extend these studies to include alkylidene ligands, we have initiated a study involving the reactivity of borane **1** with Schrock's methyl methylene tantalocene complex, Cp₂Ta(=CH₂)CH₃.[8] In Cp₂Ta(=CH₂)CH₃, the HOMO is comprised mainly of the tantalum methylene

π bond,[9] and so one would expect electrophiles to attack via trajectories **a** or **b** (**I**); path **c** could be possible for

I
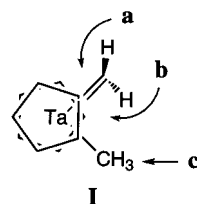
more bulky alkylidene ligands or electrophiles, since the SHOMO is relatively close in energy and associated with the Ta−CH₃ σ bond. For Cp₂Ta(=CH₂)CH₃, however, electrophiles such as MeI or "AlMe₃" react exclusively at the methylene ligand.[8] Few studies involving the reactivity of organotantalum compounds with organoboranes have appeared;[10] in addition to providing fundamental information and interesting structural chemistry, the possibility of discovering new catalytic chemistry is a goal of this research.

As in the reactions of HB(C₆F₅)₂ with group 4 metallocenes,[6] reactions with Cp₂Ta(=CH₂)CH₃ are strongly dependent on the conditions employed and the equivalency of borane used; Scheme 1 outlines the chemistry described herein. Direct reaction of 2 equiv of HB(C₆F₅)₂ with Cp₂Ta(=CH₂)CH₃ in toluene at room temperature gives the fully characterized dihydride compound **2** in 79% yield, along with 1 equiv of CH₃B(C₆F₅)₂.[6c] Spectral and analytical data are consistent with the structure shown in Scheme 1, particularly upfield shifted signals at 0.80 and 6.9 ($^1J_{CH}$ = 147 Hz) ppm in the ^{1}H and the ^{13}C NMR spectra, respectively, for the methylene moiety, broad (−3.27 ppm) and sharp (0.15 ppm) resonances for the bridging and terminal hydrides, respectively, and a ^{11}B chemical shift of −35.5 ppm, characteristic of anionic, four-coordinate boron.[11]

In addition to full spectroscopic characterization, the solid-state structure of product **2** has been determined crystallographically;[12] an ORTEP diagram is given in Figure 1 along with selected metrical parameters. Complex **2** is related to the zirconium derivative **II** (Scheme 1) except that the bridging methylene occupies an *exo* position in the metallocene wedge, implying (but

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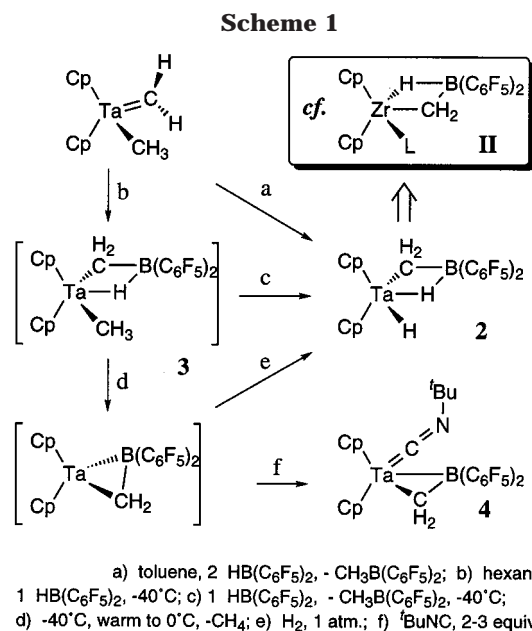(7) (a) Sun, Y.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1997**, *16*, 2509. (b) Piers, W. E.; Y. Sun, Y.; Lee, L. W. M. *Topics in Catalysis*, in press.
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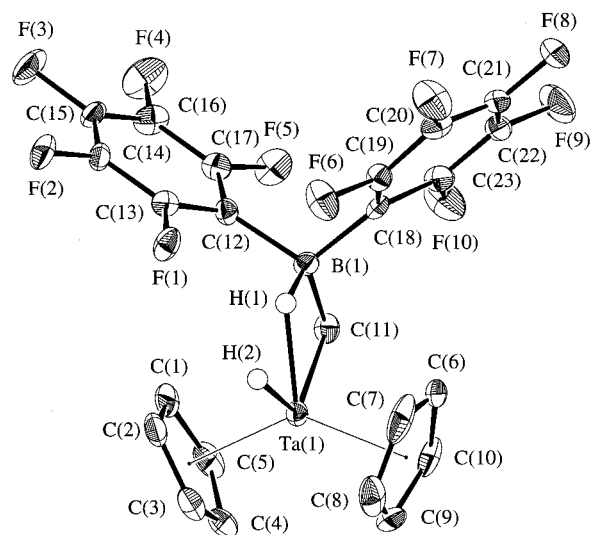(11) Kidd, R. G. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2.

Scheme 1

a) toluene, 2 HB(C$_6$F$_5$)$_2$, - CH$_3$B(C$_6$F$_5$)$_2$; b) hexanes,
1 HB(C$_6$F$_5$)$_2$, -40°C; c) 1 HB(C$_6$F$_5$)$_2$, - CH$_3$B(C$_6$F$_5$)$_2$, -40°C;
d) -40°C, warm to 0°C, -CH$_4$; e) H$_2$, 1 atm.; f) ^{t}BuNC, 2-3 equiv.

not conclusively proving) that the borane approaches the *endo* face of the methylene ligand in Cp$_2$Ta(=CH$_2$)-CH$_3$, i.e., via trajectory **b**.

When Cp$_2$Ta(=CH$_2$)CH$_3$ is treated with 1 equiv of borane **1** in toluene, rapid methane evolution is observed as the reaction solution's color deepens to a dark green. Since no signals are observed in the ^{1}H NMR spectra of these solutions, likely paramagnetic species are produced in this reaction. In contrast, methane evolution is not observed when this reaction is carried out in hexanes; instead, a moderately stable, diamagnetic tan solid precipitates. This product slowly decomposes as a solid even at −40 °C and is persistent in solution only at temperatures below −10 °C in THF-d_8. NMR spectral data are consistent with the structure **3** shown in Scheme 1, in which the μ-H ligand occupies the *endo* position of the metallocene wedge. The resonance for this proton (−1.54 ppm) exhibits cross-peaks with both the methyl and methylene protons in the low-temperature ROESY map, while an NOE between CH$_3$ and CH$_2$ is absent. Treatment of **3** with a second equivalent of borane **1** leads to formation of **2** and CH$_3$B(C$_6$F$_5$)$_2$. However, when samples of **3** are warmed above −10 °C, methane evolution ensues and green solutions are again formed. For d_1-**3** (generated from Cp$_2$Ta(=CH$_2$)CH$_3$ and d_1-**1**) only CH$_3$D is produced, as determined by ^{1}H NMR. These observations strongly suggest that the first equivalent of borane **1** attacks the *endo* face of the Ta=CH$_2$ unit, while the second engages in an alkyl/hydride exchange with the Ta−CH$_3$ group. This latter step must be rapid since it competes effectively with the facile reductive elimination of methane, which occurs from **3** in the absence of a second equivalent of borane.

The precise nature of the paramagnetic compound(s) resulting from decomposition of **3** is not yet known, but the direct product clearly has the empirical formula

Figure 1. Molecular structure of **2** (thermal ellipsoids to 50% probability). Selected bond distances (Å): Ta(1)−Cp(1), 2.086; Ta(1)−Cp(2), 2.085; Ta(1)−C(11), 2.278(4); Ta(1)−H(1), 1.92(3); Ta(1)−H(2), 1.84(4); B(1)−C(11), 1.571(5). Selected bond angles (deg): Cp(1)−Ta(1)−Cp(2), 135.0; C(11)−Ta(1)−H(1), 65.6(10); C(11)−Ta(1)−H(2), 122.7(13); H(1)−Ta(1)−H(2), 57.3(15); Ta(1)−C(11)−B(1); 83.0(2); Ta(1)−H(1)−B(1), 106.3(18); C(11)−B(1)−H(1), 105.1(13); C(12)−B(1)−C(18), 118.1(3).
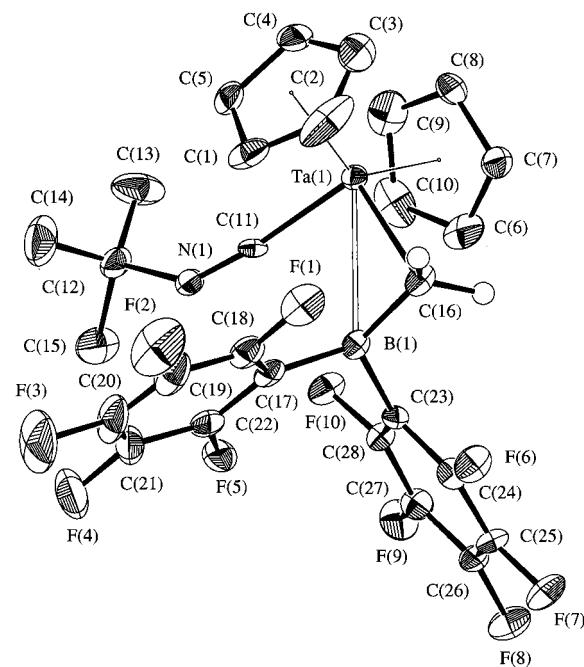
Figure 2. Molecular structure of **4** (thermal ellipsoids to 50% probability). Selected bond distances (Å): Ta(1)−Cp(1), 2.086; Ta(1)−Cp(2), 2.084; Ta(1)−B(1), 2.738(6); Ta(1)−C(16), 2.348(5); Ta(1)−C(11), 2.075(5); C(11)−N(1), 1.164(6); C(16)−B(1), 1.525(7). Selected bond angles (deg): Cp(1)−Ta(1)−Cp(2), 133.3; Ta(1)−C(16)−B(1), 87.3(3); Ta(1)−C(11)−N(1), 171.2(4); C(11)−N(1)−C(12), 136.0(5); Ta(1)−B(1)−C(16), 58.9(3); Ta(1)−B(1)−C(17), 113.2(3); Ta(1)−B(1)−C(23), 119.7(4); C(16)−B(1)−C(17), 124.7(5); C(16)−B(1)−C(23), 115.7(5); C(17)−B(1)−C(23), 113.7(4).

"Cp$_2$TaCH$_2$B(C$_6$F$_5$)$_2$".[13] Attempts to isolate or crystallize the material were stymied by its tendency to undergo decomposition both in solution and the solid. However, it may be trapped by dihydrogen to form **2** in 75%

isolated yield, or by ^{t}BuNC if **3** is allowed to decompose in the presence of this Lewis base (Scheme 1). The ^{11}B NMR spectrum of **4** (8.5 ppm) indicates that the boron center is four-coordinate, while the IR spectrum (ν_{CN} = 1882 cm^{-1}) suggests that the isocyanide ligand is bent at the nitrogen.[14] Indeed, these features are found in the solid-state structure of this compound,[15] Figure 2, where the boron center is rendered four-coordinate by a weak Ta–B interaction (Ta–B = 2.738(6) Å) and the C–N–C^{t}Bu angle is 136.0(5)°. The boron center is thus somewhat pyramidalized, lying 0.22 Å out of the plane defined by C(16), C(17), and C(23).

Compound **4** is intriguing in that the CH$_2$B(C$_6$F$_5$)$_2$ unit bonds to tantalum similar to how an olefin would bind, i.e., as an isoelectronic [H$_2$C=B(C$_6$F$_5$)$_2$]$^-$ fragment rather than a strongly σ-donating −CH$_2$B(C$_6$F$_5$)$_2$ ligand as in related titanium complexes L$_n$Ti(C$_6$F$_5$)CH$_2$B-(C$_6$F$_5$)$_2$,[16] where no metal–boron interaction is found.

This picture is consistent with the observation that the Ta(1)–C(16) distance of 2.348(5) Å is slightly longer than Ta–C bond lengths of ≈2.29 Å in related Cp$_2$Ta-(L)R complexes.[17] In addition, the $\nu_{C=N}$ stretch of 1882 cm^{-1} for the isocyanide ligand in **4** is substantially higher than those found in related complexes Cp$_2$Ta-(CNR)R[14] (which range from 1765 to 1807 cm^{-1}), indicating that the [H$_2$C=B(C$_6$F$_5$)$_2$]$^-$ ligand shares in accepting some of the π electron density from the tantalum center. This type of bonding may also account for the observed paramagnetism of the isocyanide free species "Cp$_2$TaCH$_2$B(C$_6$F$_5$)$_2$".[13] The trapping of this species with other agents will perhaps shed more light on the bonding character of this ligand.

Supporting Information Available: Experimental details and full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances and angles for **2** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

(13) It is not clear why "Cp$_2$TaCH$_2$B(C$_6$F$_5$)$_2$" should be paramagnetic. It is possible that decomposition products of this putative species account for the observed paramagnetism of the samples obtained from **3**, or perhaps a high-spin electron configuration is induced by η^2-bonding of the [CH$_2$=B(C$_6$F$_5$)$_2$]$^-$ ligand. Computational studies to address this latter question are under way.

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