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Reactions of a Borataalkene Ligand at Tantalocene Centers: Isonitrile Insertion into the B−C Bond of the $[CH_2B(C_6F_5)_2]$ Ligand via the η^1 Bonding Mode

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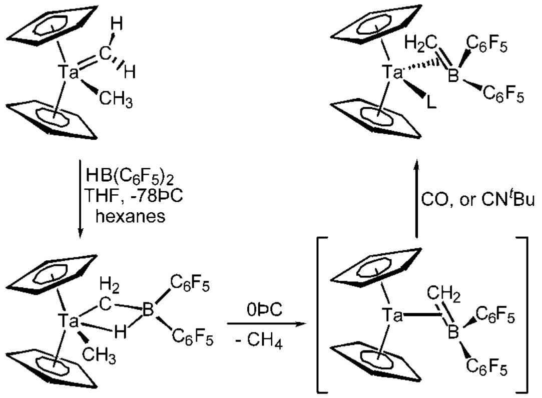
Trapping of the tantalocene borataalkene complex $Cp_2Ta[CH_2B(C_6F_5)_2]$ with 2 equiv of cyclohexyl or benzyl isocyanide gives Ta(III) products where the metallocene fragment is ligated by an η^3-1-azaallyl ligand incorporating an iminoacyl boryl fragment on the central carbon atom. This unique ligand assembly arises via reaction of the isocyanide reagent with the η^1 form of the borataalkene ligand, demonstrating a new reactivity mode for this relatively unexplored class of boratahydrocarbon ligands.

Introduction

Recently, we reported the generation and trapping of the borataalkene complex $Cp_2Ta[CH_2B(C_6F_5)_2]$ via reaction of Schrock's methylidene methyl complex $Cp_2Ta{=}CH_2(CH_3)$[2] and the highly reactive borane $HB(C_6F_5)_2$[3] (Scheme 1).[4] The borane here serves as a synthon for "$B(C_6F_5)_2$", while the methylidene unit of the borataalkene is incorporated via B−C bond formation upon electrophilic attack of $Cp_2Ta{=}CH_2(CH_3)$ by the borane;[2,5] loss of methane via reductive elimination provides part of the driving force for the reaction. Thus, the boratalkene ligand $[CH_2B(C_6F_5)_2]^-$ is assembled in the metal's coordination sphere, providing an opportunity to explore the characteristics and reactivity of this family of boratahydrocarbon ligands at a transition metal center for the first time.[6] While the potential ligating properties of this family of ligands have been recognized for some time,[6e] the lack of suitable "$[R_2C{=}BR_2]^-$" sources has hampered the development of their transition metal chemistry.

Scheme 1



The naked borataalkene complex $Cp_2Ta[CH_2B(C_6F_5)_2]$ could not be isolated or physically characterized; computational evidence suggests that the singlet and triplet states of this d^2 species are close in energy, resulting in kinetic instability. However, it could be trapped with π-acids such as carbon monoxide and *tert*-butyl isocyanide (*t*-BuNC) as shown in Scheme 1. Computational and physical evidence strongly supports an η^2 bonding mode for the $[CH_2B(C_6F_5)_2]$ ligand in these complexes. Furthermore, we have recently demonstrated that the borataalkene ligand exhibits "olefin-like" reaction chemistry when the putative intermediate $Cp_2Ta[CH_2B(C_6F_5)_2]$ is trapped with alkynes in that reductive coupling to form tantala-3-boratacyclopentenes is observed,[7] in analogy with chemistry found in the isoelectronic $Cp_2Zr(\eta^2$-olefin) reagents.[8] However, in these studies we also point out the η^2 bonding mode for this ligand is tenuous and susceptible to slippage into an η^1 bonding mode. This notion is supported by some other recent computational results on the parent borataethylene species $[CH_2BH_2]^-$, where resonance contributions for an olefin-like covalent formulation (η^2) versus an ionic resonance contributor more consistent with η^1

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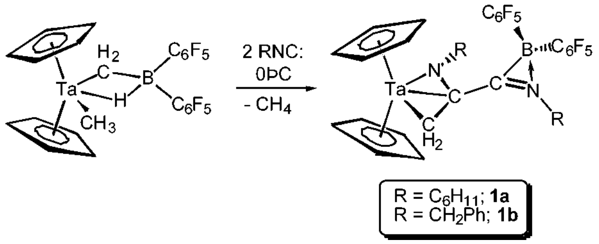
Scheme 2



bonding were found to be 36.7% and 63.3%, respectively.[9] This opens up the opportunity for borataalkene reactivity patterns that involve the η^1 bonded species. Indeed, we have found that when we attempted to trap $Cp_2Ta[CH_2B(C_6F_5)_2]$ with cyclohexyl isocyanide or benzyl isocyanide, products analagous to that found for *t*-BuNC were not isolated. Rather, products we believe arise from the trapping of $Cp_2Ta[\eta^1\text{-}CH_2B(C_6F_5)_2]$ were isolated and characterized, demonstrating a reactivity pattern arising from the ambihapto bonding properties of these ligands.

Results and Discussion

When the methyl hydride generated from $Cp_2Ta{=}CH_2(CH_3)$ and $HB(C_6F_5)_2$ as described previously[4b] is allowed to undergo methane loss in the presence of two or more equivalents of cyclohexyl or benzyl isocyanide, a dark purple solution develops over the course of 3 h. This contrasts with the observed color evolution of the analogous reactions involving *t*-BuNC or CO, which end up as orange solutions, and suggests a different reaction course for the less bulky isocyanide trapping agents. Removal of THF and introduction of hexanes allows for the isolation of crystalline, dark purple solids in moderate yields, which have been identified as the unusual η^3-1-azaallyl tantalum(III) compounds **1a** (cyclohexyl isocyanide) and **1b** (benzyl isocyanide) shown in Scheme 2.

The ^1H NMR and $^{19}F\{^1H\}$ NMR spectra for even recrystallized samples of compounds **1** are broadened, but indicate that 2 equiv of isocyanide reagent are used in the reaction. In the ^1H NMR spectrum (THF-d_8) of cyclohexylisocyanide derivative **1a**, for example, broad resonances are found at 5.27 and 4.24 ppm integrating in a 10:2 ratio, while the region between 2.2 and 0.9 ppm integrates for 22 hydrogens. The $^{19}F\{^1H\}$ NMR spectrum is also broadened, but signals for the *ortho* (−131.4 ppm), *meta* (−159.0 ppm), and *para* (−164.0 ppm) fluorines of the pentafluorophenyl ring are present. The ^1H and $^{19}F\{^1H\}$ NMR spectra for the benzylisocyanide derivative, **1b**, are also somewhat broadened, but the integrations in the ^1H NMR spectra again suggest that two benzyl isocyanide moieties have been incorporated into the product. Microanalytical data for the two complexes are also consistent with this conclusion.

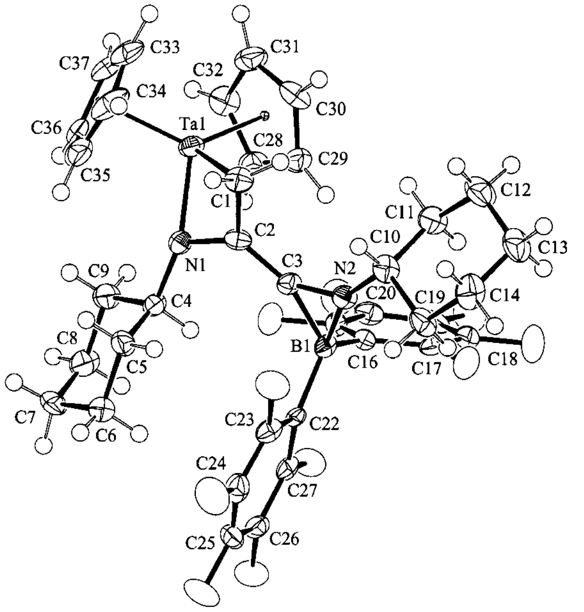


Figure 1. Molecular structure of **1a**. Selected bond distances (Å): Cp(1)−Ta(1), 2.095(7); Cp(2)−Ta(1), 2.109(7); Ta(1)−C(1), 2.231(7); Ta(1)−N(1), 1.995(5); Ta(1)−C(2), 2.373(6); C(1)−C(2), 1.468(8); C(2)−N(1), 1.403(7); C(2)−C(3), 1.401(8); C(3)−N(2), 1.292(7); C(3)−B(1), 1.579(9); N(2)−B(1), 1.542(8); B(1)−C(16), 1.594(9); B(1)−C(22), 1.622(9). Selected bond angles (deg): Cp(1)−Ta(1)−Cp(2), 128.9(3); C(1)−Ta(1)−N(1), 67.6(2); Ta(1)−C(1)−C(2), 76.8(4), C(1)−C(2)−N(1), 110.5(6); C(1)−C(2)−C(3), 127.5(6); N(1)−C(2)−C(3), 121.4(5); C(3)−N(2)−C(10), 136.9(6); C(2)−C(3)−N(2), 136.9(6); C(2)−C(3)−B(1), 158.2(6); C(3)−B(1)−N(2), 48.9(3); C(3)−B(1)−C(16), 118.0(6); C(16)−B(1)−C(22), 118.5(5).

Table 1. Summary of Data Collection and Refinement Details for 1a

formula	$C_{37}H_{34}BN_2F_{10}Ta$
fw	888.43
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.666(3)
b, Å	18.668(4)
c, Å	15.406(3)
β, °	98.36(2)
V, Å^3	3319.4(12)
Z	4
d_{calc}, mg m^{-3}	1.778
$F(000)$	1752.00
μ, cm^{-1}	33.94
T, °C	−103
cryst dimens, mm^3	0.45 × 0.30 × 0.12
rel transmn factors	0.5285−1.0000
scan type	$\omega-2\theta$
2θ (max), deg	50.1
no. of unique reflns	6070
no. of reflns with $I > 3\sigma I$	3831
no. of variables	460
R	0.030
R_w	0.029
gof	1.52
max Δ/σ (final cycle)	0.00
residual density, e/Å^3	−0.63−0.91

The solid-state structure determined for **1a** confirms that two cyclohexyl isocyanide units have been incorporated into the product via net insertion of two isocyanide molecules into the *carbon−boron* bond of the borataalkene bond in $Cp_2Ta[CH_2B(C_6F_5)_2]$. The product contains a bent metallocene tantalum(III) fragment ligated by an η^3-1-azaallyl ligand with an iminoacyl boryl fragment attached to the central carbon atom of the azaallyl moiety. Figure 1 shows the molecular structure along with selected metrical data, while crystallographic details are provided in Table 1. While there are azaallyl complexes of vanadium[10] and niobium[11] known, according to a recent review,[12] com-

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[9] Bachler, V.; Metzler-Nolte, N. *Eur. J. Inorg. Chem.* **1998**, 733.

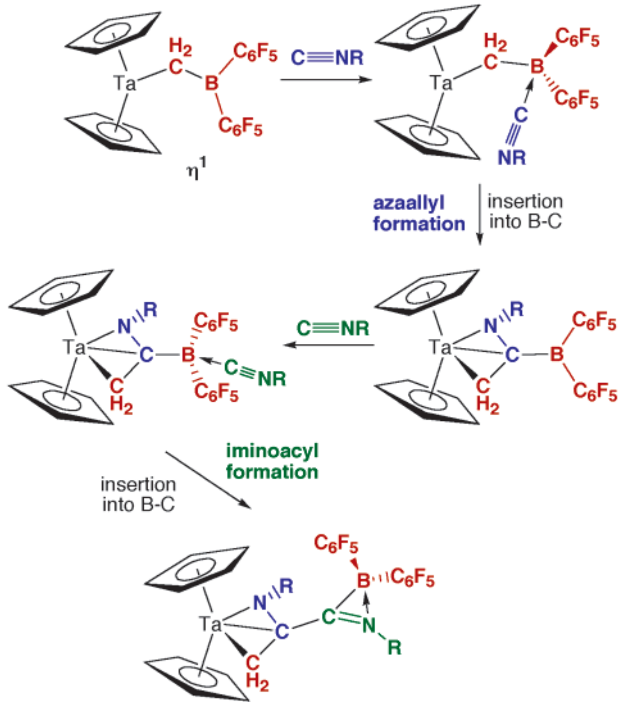
pounds **1** are the first examples of 1-azaallyl complexes of tantalum.

A number of transition metal complexes containing the η^3-azaallyl fragment have been crystallographically characterized, and the geometric parameters of **1a** show good agreement with the previously determined structures.[12] In **1a**, the azaallyl fragment exhibits asymmetric η^3 coordination to the tantalum center with the Ta(1)−N(1) distance of 1.995(5) Å, significantly less than the Ta(1)−C(1) and Ta(1)−C(2) distances of 2.231(7) and 2.373(6) Å, respectively. This asymmetry is reminiscent of η^3-azaallyl bonding to Li^+ and other electrophilic metal centers, but contrasts with complexes of the less electrophilic transition metals, where similar M−C and M−N bond distances are observed. The Ta(1)−C(2) bond length is close to those of 2.33(2) and 2.32(1) Å observed for the Ta−olefin bonds in $Cp_2Ta(\eta^2\text{-}C_8H_8)(CH_2CH_3CH_3)$,[13] supporting an η^3-bonding description for the ligand in **1a**.

The second isocyanide fragment is bound to the η^3-azaallyl ligand through the central carbon atom and forms an iminoacyl moiety in which the imine nitrogen coordinates internally to the $B(C_6F_5)_2$ center, such that the boron atom is four coordinate. This is consistent with both the solution ^{11}B and ^{19}F NMR data. Such a bonding arrangement is unusual for this functional group, the few examples of which tend to be η^1 bound,[14] or undergo dimerization to a six-membered heterocycle.[15] The bonding of the iminoacyl nitrogen to boron is indicated in **1a** by the B(1)−N(2) bond distance of 1.542(8) Å and the angles about C(3) (B(1)−C(3)−N(2) = 48.9(3)°; C(2)−C(3)−B(1) = 158.2(6)°), which stray significantly from those expected for an sp^2 carbon center. The imino nitrogen N(2) is planar, as indicated by the sum of the angles about this nucleus (360.0°). Presumably, the high Lewis acidity of the perfluoroaryl-substituted boron center coupled with the steric barriers toward dimerization results in this unique iminoacyl boron moiety.

In light of this structural assignment, the broadening apparent in the NMR spectra of these compounds is likely due to a temperature-dependent fluxional process associated with the azaallyl moiety, since most reported $Cp_2Ta^{III}(\eta^3\text{-allyl})$[16] or $Cp_2Ta^{III}(\eta^3\text{-heteroallyl})$[17] complexes are diamagnetic. Variable-temperature ^1H and ^{19}F NMR spectroscopy support this notion. Heating samples of analytically pure **1a** to 60 °C results in sharpening of the resonances in both experiments, giving averaged signals for the Cp rings in the ^1H spectrum and the C_6F_5 rings in the ^{19}F spectrum. In the latter case, the peak separation between the *meta* and *para* fluorine resonance is 5.1 ppm, indicating that in this averaged structure the nitrogen remains coordinated to the boron and that exchange of the diastereotopic C_6F_5 rings occurs via flipping of the azaallyl ligand and rotation about the C(2)−C(3) bond. Upon cooling the sample, standard coalescence behavior is observed in both experiments, with the most severe broadening observed at room temperature. At about −20 °C, ^1H and ^{19}F spectra consistent with the solid state structure of **1a**, where groups of the same connectivity are diastereotopic, are observed.

Scheme 3



Detailed mechanistic studies have not been performed on this reaction, although monitoring the reaction at low temperature reveals a complex mixture of species. Likely, the products are formed via two isonitrile insertions into the B−C bond of the η^1 bonded borataalkene ligand, as depicted in Scheme 3. Insertion of isocyanides into B−C bonds is a well-precedented reaction for organoboranes; the above-mentioned six-membered heterocycles are prepared via an insertion reaction of boranes BR_3 with isocyanides and dimerization of the resulting boron-substituted iminoacyl compound.[15] Furthermore, double insertion of *t*-BuNC into an aluminum carbon bond of Cp_3Al has been reported.[18] Since the reaction is done in the presence of excess isocyanide, the situation is probably more complex than what is shown, and other valid possibilities are conceivable.[19]

In conclusion, we have demonstrated a reactivity mode for the borataalkene ligand $[CH_2B(C_6F_5)_2]$ that likely involves the η^1 form of the ligand. This observation complements our recent delineation of an "olefin-like" reactivity mode through the η^2 bonding mode of the ligand.[7] The reaction chemistry of this class of ligands is unexplored, and our studies have indicated

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that both olefin-like reactivity and behavior consistent with access to an η^1 bonding mode may be expected.

Experimental Section

General Considerations. General procedures have been reported in detail elsewhere.[4b] Isocyanides were purchased from Aldrich-Sigma and dried over activated 4 Å molecular sieves before use.

Preparation of Complexes 1a and 1b. $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (315 mg, 0.46 mmol) was weighed into a 50 mL glass bomb, and THF (20 mL) was condensed in at −78 °C. Cyclohexyl isocyanide (300 μL, 2.4 mmol) or benzyl isocyanide (112 uL, 0.92 mmol) was syringed into the vessel at −78 °C under a flow of argon. The vessel was sealed under 1 atm of argon and stirred at 25 °C for 4 h. The resulting deep purple solution was transferred via cannula into a 50 mL round-bottom flask with filtering frit and THF removed in vacuo to give a dark purple oil. Hexane (45 mL) was condensed into the vessel at −78 °C to give a purple solution with purple precipitate. The hexane was removed in vacuo to leave a sticky purple powder and a second portion of hexanes (15 mL) introduced. After stirring at RT for 20 min, the mixture was cooled to −78 °C to precipitate the product, which was isolated by cold filtration and drying under vacuum. The crude product was recrystallized from CH_2Cl_2/hexanes. Yield of **1a**: 278 mg, 0.31 mmol, 66%. Anal. Calcd for $C_{37}H_{34}N_2BF_{10}Ta$: C, 50.02; H, 3.86; N, 3.15. Found: C, 49.60; H, 4.00; N, 3.15. ^1H NMR (THF-d_8, RT): 5.27 (v br s, 10H, C_5H_5), 4.24 (br m, 2H, CH_2), 2.2−0.9 (br m, 22H, C_6H_{11}). ^1H NMR (THF-d_8, −30 °C): 5.63 (s, 5H, C_5H_5), 5.01 (s, 5H, C_5H_5), 4.25 (m, 1H, CHH), 4.13 (m, 1H, CHH), 2.2−0.5 (m, C_6H_{11}). $^{11}B\{^1H\}$ NMR (THF-d_8): −16.6. $^{19}F\{^1H\}$ NMR (THF-d_8, RT): −131.4 (4F, *o*-F), −159.0 (2F, *p*-F), −164.0 (4F, *m*-F). $^{19}F\{^1H\}$ NMR (THF-d_8, −30 °C): −131.8, −133.2 (2 × 2F, *o*-F), −158.3, −159.0 (t, 2 × 1F, *p*-F), −163.4, −164.1 (m, 2 × 2F, *m*-F). Yield of **1b**: 196 mg, 0.31 mmol, 65%. Anal. Calcd for $C_{39}H_{26}N_2BF_{10}Ta\cdot CH_2Cl_2$: C, 48.56; H, 2.85; N, 2.83. Found: C, 48.42; H, 3.12; N, 3.03. ^1H NMR (THF-d_8): 7.19 (m, 8H, C_6H_5), 6.99 (d, 2H, C_6H_5), 5.33 (s, 4H, CH_2-C_6H_5), 5.30 (br, 2H, Ta-CH_2), 5.14 (br s, 10H, C_5H_5). $^{11}B\{^1H\}$ NMR (THF-d_8): −15.5. $^{19}F\{^1H\}$ NMR (THF-d_8): −130.1 (4F, *o*-F), −156.1 (2F, *p*-F), −160.6 (4F, *m*-F).

X-ray Structure Determination of 1a. A summary of crystal data and refinement details for **1a** is given in Table 1. X-ray quality crystals of the purple compound **1a** were grown from a saturated solution in CH_2Cl_2 layered with hexanes at −35 °C, mounted on a glass fiber, and immediately placed in a liquid N_2 cold stream on the diffractometer. Measurements were made using a Rigaku AFC6S diffractometer with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) source at −103 °C with the $\omega - 2\theta$ scan technique to a maximum 2θ value of 50.1°. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions and were not refined. All calculations were performed using the TEXAN[20] crystallographic software package of Molecular Structure Corporation.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, and complete bond distances, angles, and torsion angles for **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) (a) A referee has proffered the intriguing suggestion that the η^1 boratalkene may be in equilibrium with a methylidene-boryl isomer, $Cp_2Ta{=}CH_2[B(C_6F_5)_2]$, which is trapped to eventually yield products **1**. The viability of this pathway awaits computational investigation, but α-migrations involving groups other than hydrogen typically have quite high barriers.[19b] Nonetheless, given the vacant p orbital associated with the boron center, such a process may be germane to the chemistry of η^1 borataalkene ligands. (b) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

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