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Synthesis and Chemistry of Zwitterionic Tantala-3-boratacyclopentenes: Olefin-like Reactivity of a Borataalkene Ligand

Kevin S. Cook,[†] Warren E. Piers,*[,†,1] and Robert McDonald[‡]

*Contribution from the Department of Chemistry, University of Calgary, 2500 University Drive
N. W., Calgary, Alberta, T2N 1N4, Canada, and X-ray Structure Laboratory,
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada*

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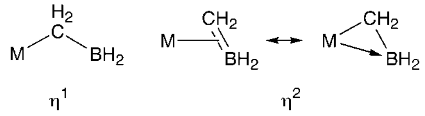
Abstract: The compounds $Cp'_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$, where $Cp' = C_5H_5$, **a** series, and C_5H_4Me, **b** series, are generated via treatment of $Cp'_2Ta(=CH_2)CH_3$ with $HB(C_6F_5)_2$. When allowed to undergo irreversible methane loss in the presence of an excess of the sterically modest alkynes 2-butyne or phenylacetylene, the putative intermediates $Cp'_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2]$ **1a** and **1b** are trapped as the tantala-3-boratacyclopentene compounds **2** and **3**, respectively. In these complexes, the alkyne and borataalkene ligands have reductively coupled at the d^2 tantalum center. For the unsymmetrical alkyne, a kinetic product resulting from coupling in the opposite regiochemical sense is observed; the thermodynamic products **3-t** incorporate the phenyl group in the α position of the tantalaboratacyclic ring. Two of these compounds (**2b** and **3b-t**) were characterized crystallographically. For bulkier alkynes (diphenylacetylene, 1-phenyl-1-propyne, and 3-hexyne), intermediates with similar spectroscopic properties to the tantala-3-boratacyclopentenes were observed, but the ultimate products were the vinylalkylidene compounds **5-(R,R′)**. Compound **5-(Ph,Me)** was characterized crystallographically, and it was found that the vinylalkylidene binds to the metal in an η^1-bonding mode, with the tantalum center receiving further ligation through a hydridoborate moiety. Mechanistic studies suggest that these products arise via retrocyclization of the tantala-3-boratacyclopentenes formed kinetically. These studies represent the first studies concerning the reactivity of a borataalkene ligand at a transition metal center and show that it can behave in an “olefin-like” manner, despite having a more flexible array of bonding modes available to it than an olefin.

Introduction

Borataalkenes are uninegative analogues of the ubiquitous olefin family of ligands.[2] Whereas alkenes invariably bind to one metal in an η^2 fashion via the textbook Dewar−Chatt−Duncanson (D−C−D) description of σ-donation and π-back-donation,[3] little is known about the coordination chemistry or reactivity of the borataalkenes. In principle, such ligands may bind in an η^1 mode through the carbon atom (Chart 1), particularly in d^0 complexes,[4] or via an η^2 linkage. Fundamentally, the bonding description for this latter mode may mirror the Dewar−Chatt−Duncanson model for olefins,[5] or be comprised of a covalent metal−C σ bond and a metal to boron dative bond. A priori, a fair degree of flexibility in the bonding of these ligands may thus be expected.

Chart 1



The lack of concrete information concerning the chemistry of borataalkene ligands contrasts with the coordination chemistry of other families of “boratahydrocarbon” ligands (e.g., the boratabenzenes[6]), which is well developed; indeed, transposition of carbon for boron in cyclic π ligands has been a fruitful strategy for new ligand development.[7] The paucity of borataalkene chemistry may stem in part from the fact that, unlike boratabenzenes, borataalkenes are not easily generated, and convenient reagents for borataalkene installation are not widely available. Furthermore, they exhibit a tendency to dimerize. Those that have been prepared[8] are thus characterized by large substituents on boron and/or carbon to provide the steric

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* To whom correspondence should be addressed.

[†] University of Calgary.

[‡] University of Alberta.

(1) Phone: 403-220-5746. Fax: 403-289-9488. E-mail: wpiers@ucalgary.ca. S. Robert Blair Professor of Chemistry 2000−2005, E. W. R. Steacie Fellow 2001−2003.

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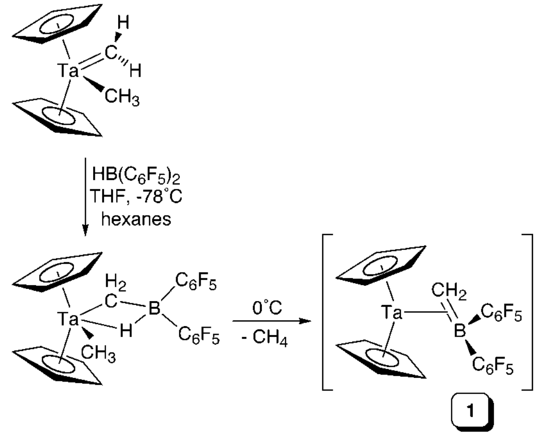
10.1021/ja025547n CCC: $22.00

Scheme 1



saturation necessary for stability. This presumably dampens the ability of the borataalkene to coordinate to metals in η^2-bonding modes which mimic the neutral olefinic ligand.

The lack of suitable borataalkene synthons for coordination to transition metals via traditional means suggests a synthetic route in which the borataalkene fragment is assembled within the transition metal's coordination sphere as an alternative. Recently, we showed that the elements of the borataalkene ligand $[CH_2B(C_6F_5)_2]^-$ can be conjoined via hydroboration of the Ta═C double bond in Schrock's methylidene methyl complex $Cp_2Ta({=}CH_2)CH_3$ with 1 equiv of the highly reactive borane $HB(C_6F_5)_2$ (Scheme 1).[9] Loss of methane from $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ occurs rapidly at 0 °C via reductive elimination, producing the borataalkene complex **1** in situ. Although **1** is isoelectronic to the well-known ethylene complex of decamethyltitanocene,[10] it is not isolable or stable in solution for very long. DFT computations showed that it's instability likely stems from a thermal equilibrium between a singlet state, where the borataalkene ligand is essentially η^2 bound with D−C−D bonding character, and an η^1-bound triplet state. However, by carrying out the methane reductive elimination in the presence of a π-acidic trapping agent, such as CO or CN^{t}Bu, **1** was trapped as the adducts $Cp_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2]L$. Spectroscopic, crystallographic, and computational evidence all supported a description of the borataalkene ligand consistent with unsymmetrical η^2-binding in the ground state. However, some evidence was garnered to suggest that the borataalkene ligand can slip to an η^1-bonding configuration, which may influence its reactivity and is one distinct difference from classical olefin/transition metal chemistry.[11]

The study summarized above convincingly showed that the borataalkene ligand *binds* like an olefin to the $Cp_2Ta(L)$ fragment. The question arises, does it *react* like an olefin? The reaction chemistry of bound olefins is extraordinarily rich and largely dependent on the metal fragment in question. Because the "$Cp_2Ta[CH_2B(C_6F_5)_2]$" fragment is a d^2 metallocene isoelectronic to the group 4 olefin complexes (exemplified by "$Cp_2Zr[CH_2CH(R)]$" moiety, Negishi's reagent[12]), we wondered if the borataalkene ligand would reductively couple with an alkyne function to give metallacyclopentene stuctures in analogy to the well-documented (and synthetically useful) coupling of alkynes and olefins at a zirconium center.[13] Herein we describe the trapping of **1** with various alkynes and the ensuing organometallic chemistry of the resulting tantala-3-boratacyclopentenes.

Results and Discussion

As described previously,[9] the methyl hydride derivative formed upon hydroboration of $Cp_2Ta({=}CH_2)CH_3$[14] with $HB(C_6F_5)_2$[15] (Scheme 1) can either be isolated as a reasonably well-behaved solid or generated in situ in THF solution at temperatures below −40 °C. Analogous chemistry is observed for the 1,1′-dimethyl substituted derivative, which was also employed in this study to impart crystallinity on the products. When generated and allowed to undergo first order loss of methane in the presence of an excess of an alkyne reagent, the course of the reaction was found to be quite dependent on the nature of the alkyne. For the sterically less bulky alkynes 2-butyne or phenylacetylene, the putative borataalkene intermediates **1a** (**a** series, $Cp = C_5H_5$) and **1b** (**b** series, $Cp = C_5H_4Me$) were trapped by alkyne to form the zwitterionic tantala-3-boratacyclopentene complexes shown in Scheme 2, in a reaction analogous to the reductive coupling of an olefin and an alkyne at a group 4 metallocene center.[16,17]

For the symmetrical 2-butyne, one product was observed, and no intermediates were detected when the reactions were monitored via NMR spectroscopy. Several lines of spectroscopic evidence are consistent with the formation of the zwitterionic tantala-3-boratacyclopentene **2**. For comparative purposes, selected solution NMR data for these and other new compounds are presented in Table 1. In **2a**, the chemical shift of 6.13 ppm observed for the Cp protons is indicative of a cationic Ta(V) center (cf. the shift of 6.61 ppm for $[Cp_2TaMe_2]^+[BF_4]^-$ in d_8-THF). The ^{11}B chemical shifts of −32.7 and −30.8 ppm for **2a** and **2b**, respectively, are as expected for an anionic, four-

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Scheme 2

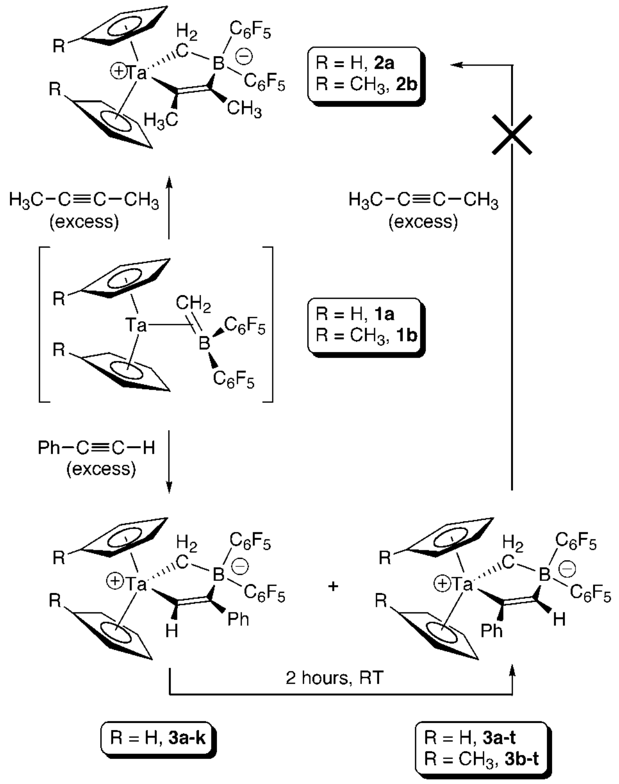

Table 1. Selected NMR Data for New Compounds

cmpd	Cp (^{1}H) (ppm)	CH$_2$ (^{1}H) (ppm)	^{11}B (ppm)	^{19}F $\Delta_{m,p}$ (ppm)
2a	6.13	4.02	−32.7	2.5
2b		3.90	−30.8	2.8
3a-k	6.30	4.53	−24	3.2
3a-t	6.03	2.99	−34.6	2.8
3b-t		2.85	−32.9	2.7
5-(Ph,Ph)	5.65, 5.57		−11.2	4.9, 3.8
5-(Ph,Me)	5.53, 5.47		−12.2	4.8, 4.1
5-(Et,Et)	5.60, 5.39		−13.1	4.4, 3.9
6-(Ph,Ph)	5.76	2.62	4.0	7.7
6-(Ph,Me)	6.13	4.12	−37.2	2.7
6-(Et,Et)	6.04	3.75	−38.2	2.9
II-CO[9]	5.03	1.06	7.2	5.4
II-CNR[9]	4.90	1.13	8.5	5.1

coordinate boron center,[18] while the separation between the meta and para fluorine resonances in the ^{19}F NMR spectrum ($\Delta_{m,p} = 2.5$ ppm, **2a**; 2.8 ppm, **2b**) is strong empirical evidence for a borate moiety.[19] These data demonstrate the zwitterionic nature of these products. The regiochemistry of metallacycle formation (i.e., with the B atom in a β position) is established by two resonances in the ^{13}C NMR spectrum for the methylene and vinyl carbons of the product, which are significantly broadened due to bonding with the quadrupolar boron nucleus. In fact, the latter quaternary carbon was not detected in these spectra. Thus, the alkyne undergoes cyclization with the borataalkene ligand exclusively via B−C bond formation.[20] Presumably, formation of an unfavored Ta−B bond, and the steric problems itinerant with placement of a bulky $-B(C_6F_5)_2$ group in the α position, are two factors in dictating the observed regiochemistry.

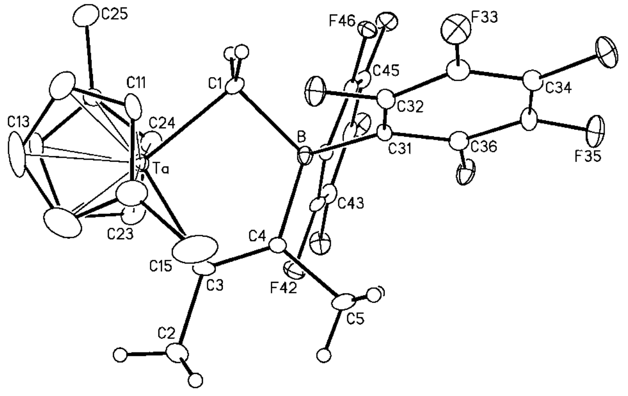

Figure 1. ORTEP diagram of **2b**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

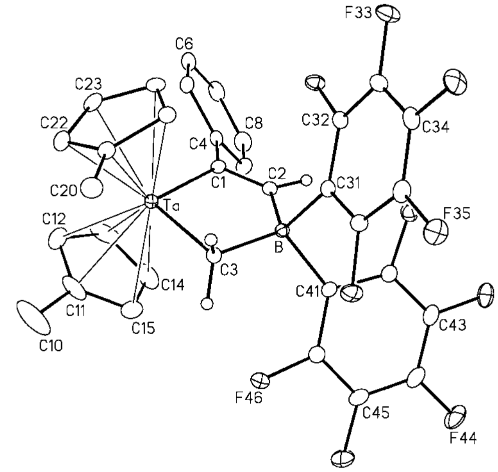

Figure 2. ORTEP diagram of **3b-t**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

In the case of phenylacetylene, another regiochemical possibility stemming from the sense of alkyne addition arises, and, indeed, when the reaction of **1a** and this alkyne is followed by NMR spectroscopy, a kinetic product **3a-k** is in evidence in the early stages of the reaction. Thermal rearrangement to the thermodynamic product **3a-t** occurs at room temperature over the course of a few hours. As can be seen in Table 1, all products **3** (including **3a-k**) share the spectroscopic characteristics of the tantala-3-boratacyclopentene compounds **2**. On the basis of a crystal structure of **3b-t** (see below), we assign the thermodynamic isomers as the coupled products where the phenyl moiety is attached to the α-carbon; consequently, the kinetic isomer **3a-k** is likely the β-phenyl isomer. This assignment was supported by the results of an ^{1}H/^{19}F NOESY experiment wherein irradiation of the ortho fluorines in **3a-t** yielded enhancement in the vinylic proton adjacent to the borate moiety.

The tantala-3-boratacyclic nature of these compounds was confirmed via crystal structure determinations on **2b** and **3b-t**; ORTEP diagrams are presented in Figures 1 (**2b**) and 2 (**3b-t**), while comparative selected metrical data are given in Table 2. The coupling of the alkynes with $[CH_2{=}B(C_6F_5)_2]^-$ is indicated by: (1) a lengthening of the CH_2-B bonds to values consonant with B−C single bonds as compared to the values found in the

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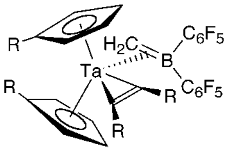
Table 2. Selected Metrical Data for Tantala-3-boratacyclopentene Compounds **2b** and **3b-t**

2b		**3b-t**	
	Bond Lengths (Å)		
Cp(1)[a]−Ta	2.128(3)	Cp(1)[b]−Ta	2.1152(15)
Cp(2)[c]−Ta	2.120(3)	Cp(2)[d]−Ta	2.1135(13)
Ta−C(1)	2.116(6)	Ta−C(3)	2.158(3)
Ta−C(3)	2.124(5)	Ta−C(1)	2.128(3)
C(1)−B	1.734(9)	C(3)−B	1.672(4)
C(3)−C(4)	1.337(9)	C(1)−C(2)	1.327(4)
C(4)−B	1.677(10)	C(2)−B	1.675(4)
C(3)−C(2)	1.520(9)	C(1)−C(4)	1.485(4)
C(4)−C(5)	1.508(8)		
B−C(31)	1.672(10)	B−C(31)	1.658(4)
B−C(41)	1.664(10)	B−C(41)	1.667(4)
	Bond Angles (deg)		
Cp(1)[a]−Ta−Cp(2)[c]	127.4(3)	Cp(1)[b]−Ta−Cp(2)[d]	128.53(15)
C(1)−Ta−C(3)	98.6(3)	C(1)−Ta−C(3)	101.72(10)
Ta−C(1)−B	96.5(4)	Ta−C(3)−B(1)	93.81(16)
Ta−C(3)−C(4)	103.5(5)	Ta−C(1)−C(2)	96.91(19)
C(2)−C(3)−C(4)	125.3(6)	C(4)−C(1)−C(2)	124.9(2)
C(3)−C(4)−C(5)	121.6(6)		
C(3)−C(4)−B	124.4(6)	C(1)−C(2)−B	131.1(2)
C(4)−B−C(1)	114.2(5)	C(2)−B−C(3)	116.1(2)
C(41)−B−C(31)	108.9(5)	C(41)−B−C(31)	106.0(2)
C(4)−B−C(41)	110.1(5)	C(2)−B−C(41)	101.9(2)
C(1)−B−C(31)	109.4(5)	C(3)−B−C(31)	115.3(2)

[a] C(10)−C(14). [b] C(11)−C(15). [c] C(20)−C(24). [d] C(21)−C(25).

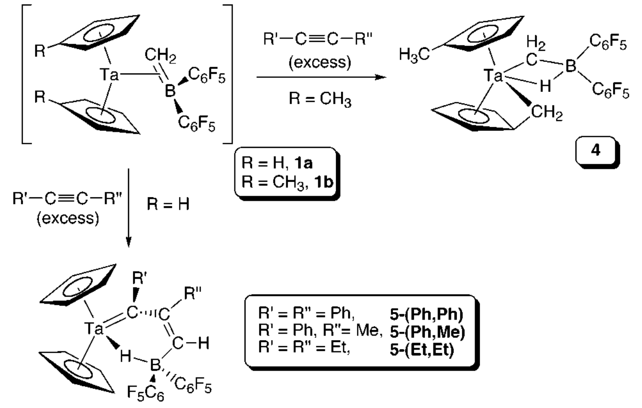
η^2-borataalkene complexes $Cp_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2]L$ of 1.525(7) Å (L = ^{t}BuNC) and 1.508(8) Å (L = CO);[9] (2) $B-C_{vinyl}$ bond lengths of 1.667(10) Å (**2b**) and 1.675(4) Å (**3b-t**), which are as expected for $B_{sp^3}-C_{sp^2}$ single bonds; and (3) a C(3)−C(4) bond length of 1.337(9) Å for **2b** and a C(1)−C(2) distance of 1.327(4) Å for **3b-t**, indicative of carbon−carbon double bonds. The rings in these compounds are close to being planar, with only slight puckering observed about the methylene carbon. The boron centers are tetrahedral, and while the angles about the vinylic carbon centers sum to ~360°, the α carbon is somewhat more distorted from the ideal than the β center.



I

These reactions show that the borataalkene ligand in **1** behaves in an “olefin-like” manner and the reductive coupling with an alkyne mimics the chemistry observed in group 4 chemistry with normal olefin ligands.[13] The resulting tantala-3-boratacyclopentenes are, to our knowledge, unique heterocycles which have not been observed to date. The conversion of **3a-k** to **3a-t** indicates that the coupling of the alkyne with the borataalkene ligand is reversible, another feature this reaction shares with the olefin/alkyne[13] and alkyne/alkyne[21] coupling at a zirconium center. However, the intimate details of the mechanisms of the formation of these compounds and of the conversion of **3a-k** to **3a-t** are to this point open to speculation. Likely, **1** is trapped by the alkyne to form an alkyne/borataalkene complex, **I**,[22] which then undergoes reversible coupling to form the heterometallacyclic products. Once ligated, it is unlikely that the alkyne is labile, ruling out a dissociative mechanism for the conversion of **3a-k** to **3a-t**. In support of this, treatment of **3a-t** with an excess of 2-butyne does not result in formation of **2a** (Scheme 2). Furthermore, when compounds **2a** and **3b-t** are mixed and heated gently, no crossover products (i.e., **2b** or **3a-t**) are observed. On the other hand, a mechanism involving rotation of coordinated alkyne also seems unlikely given the generally large barrier to rotation of alkyne and olefin[23] ligands in d^2 tantalocenes; we could find no evidence for the exchange of the vinylic methyl groups in **2a** on the NMR time scale. In the absence of firm experimental evidence, we speculate that the strong Lewis acidic boron center available in an η^1-bonded borataalkene ligand may play a role in the isomerization of **3a-k** to **3a-t**.

Scheme 3



Use of more sterically encumbered alkynes in this reaction provides some evidence to support the viability of intermediates akin to **I**, and shows that the reversibility of cyclization allows for the isomerization of tantala-3-boratacyclopentenes to other types of organometallic products. The chemistry is outlined in Scheme 3. The alkynes diphenylacetylene, 1-phenyl-1-propyne, and 3-hexyne are apparently too bulky to trap 1,1′-dimethyl borataalkene complex **1b**; in these reactions, the only product observed is the self-trapped “tuck-in” complex **4**, which is the product observed when **1b** is allowed to form in the absence of an external trapping agent. Compound **4** was fully characterized via NMR spectroscopy and microanalysis; details are found in the Experimental Section. In the C_5H_5 **a** series, however, alkyne coordination with these bulkier substrates does occur, but the ultimate products have been characterized as the vinylalkylidene complexes **5-(R,R′)**.

Compounds **5-(Ph,Ph)** and **5-(Ph,Me)** were isolated in 70−80% yield, while **5-(Et,Et)** was generated only in solution. In the ^{1}H NMR spectra of compounds **5**, the most obvious difference in comparison to the products **2a** and **3a** discussed above is that the two Cp ligands are now diastereotopic, indicating that the plane of symmetry bisecting the Cp donors

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(22) Several complexes of general formula $Cp_2Ta(\eta^2\text{-}RCCR')X$ are known: (a) Labinger, J. A.; Schwartz, J.; Townsend, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 4009. (b) Green, M. L. H.; Jousseaume, B. *J. Organomet. Chem.* **1980**, *193*, 339. (c) Herberich, G. E.; Englert, U.; Heoveler, M.; Savvopoulous, I. *J. Organomet. Chem.* **1990**, *399*, 35. (d) Deutch, P. P.; Maguire, J. A.; Jones, W. D.; Eisenberg, R. *Inorg. Chem.* **1990**, *29*, 686. (e) Yasuda, H.; Yamamoto, H.; Arai, T.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1991**, *10*, 4058.

(23) (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *157*, 413. (b) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *194*, 309.

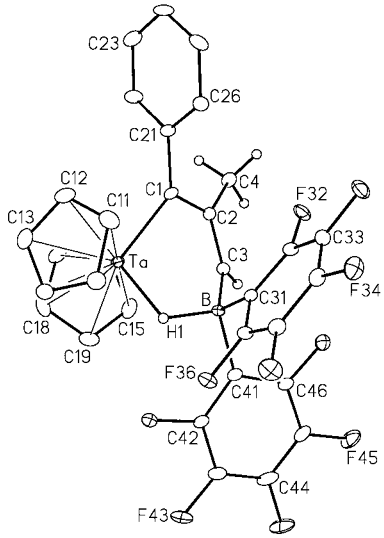

Figure 3. ORTEP diagram of **5-(Ph,Ph)**. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level.

is absent in these products. The Cp resonances appear slightly upfield of those found in the zwitterionic tantala-3-boratacyclopentenes in the region 5.5−5.7 ppm, reflecting less charge separation between tantalum and boron. In addition to signals derived from the alkyne moiety, resonances integrating to *one* proton each are found at around 4.5 ppm and upfield near −4.0 ppm in the spectra of compounds **5**. The latter signal is characteristic of a Ta−H−B(C_6F_5)$_2$ hydridoborate moiety, while the former is attributable to an olefinic hydrogen. When the synthesis of **5-(Ph,Ph)** is performed starting from Cp$_2$Ta(=CD$_2$)CD$_3$ and DB(C_6F_5)$_2$, both of the one proton resonances disappear in the ^{1}H NMR spectrum, showing that these protons arise from the methylidene unit since the CD$_3$ and DB deuterons are lost as CD$_4$ upon decomposition of *d*$_4$-**1a**.[9] The anionic, four-coordinate nature of the boron center is supported by both the ^{11}B and the ^{19}F NMR data (Table 1), and the C_6F_5 groups are also diastereotopic as would be expected. Finally, the ^{13}C NMR spectral data are consistent with the presence of a vinylalkylidene unit. Upfield resonances ranging from 213 to 245 ppm are observed for the alkylidene carbons, while signals at 154−156 ppm are assigned to the vinyl carbon attached to the alkylidene moiety. Resonances broadened by the quadrupolar boron nucleus in the region spanning 98−114 ppm were detected using the HMQC pulse sequence and correlate to the proton resonances at around 4.5 ppm. $^1J_{CH}$ coupling constants of about 137 Hz were measured for these CH groups.

This assignment was confirmed by crystallographic analysis of **5-(Ph,Me)**, which also confirmed the regiochemistry of alkyne incorporation in this particular instance. Figure 3 shows an ORTEP diagram, while Table 3 gives selected metrical data for **5-(Ph,Me)**.[24] The vinylalkylidene moiety is bonded in an η^1 fashion[25] to the tantalum center on the basis of the long distances from Ta to C(2) (2.695(5) Å) and C(3) (2.707(5) Å). The Ta−C(1), C(1)−C(2), and C(2)−C(3) distances of 2.062(5), 1.408(6), and 1.379(6) Å are in line with values found in other vinylalkylidene structures which have been described as “localized”.[25a] However, the Ta−C(1)−C(2)−C(3) torsion angle of −38.8(5)° allows for some conjugation between the Ta=C and C=C bonds, partially delocalizing the electron density across these atoms. In addition to the alkylidene unit, the tantalum center is satiated by the borohydride moiety, which binds quite strongly to the tantalum atom; the Ta−H distance of 1.80(4) Å is close to values found for terminal Ta−H bonds.[26] This supports the notion that charge separation is low in these compounds.

Table 3. Selected Metrical Data for Vinylalkylidene Compound **5-(Ph,Me)**

Bond Lengths (Å)			
Cp(1)^a−Ta	2.095(2)	Cp(2)^b−Ta	2.174(2)
Ta−C(1)	2.062(5)	Ta−H(1)	1.80(4)
Ta−C(2)	2.695(5)^c	Ta−C(3)^c	2.707(5)
C(1)−C(2)	1.408(6)	C(2)−C(3)	1.379(6)
C(3)−B	1.570(7)	B−H(1)	1.34(4)
C(1)−C(21)	1.503(6)	C(2)−C(4)	1.503(6)
B−C(31)	1.633(7)	B−C(41)	1.643(6)
Bond Angles (deg)			
Cp(1)^a−Ta−Cp(2)^b	125.8(2)	C(1)−Ta−H(1)	102.7(13)
Ta−C(1)−C(2)	100.2(3)	Ta−H(1)−B(1)	115.5
C(1)−C(2)−C(3)	115.5(4)	C(1)−C(2)−C(4)	112.2(4)
C(2)−C(3)−B	129.4(4)	C(3)−B−H(1)	109.2(17)
C(3)−B−C(31)	119.3(4)	C(3)−B−C(41)	111.5(4)
C(41)−B−C(31)	109.6(4)		

^{a} C(10)−C(14). ^{b} C(15)−C(19). ^{c} Nonbonded distance.

To probe the route by which these vinylalkylidene products are formed, the reactions with the bulkier alkynes were followed by NMR spectroscopy at low temperature. In each case, an intermediate was observed, and selected data for these species are given above in Table 1. For the alkynes 1-phenyl-1-propyne and 3-hexyne, the intermediates **6-(Ph,Me)** and **6-(Et,Et)** have similar spectral characteristics to those found for the zwitterionic tantala-3-boratacyclopentenes **2a** and **3a-k**/**3a-t**, and on this basis we assign them these structures. In the case of diphenylacetylene, however, the NMR data are markedly different, particularly the ^{11}B and ^{19}F parameters. As can be seen in Table 1, the data for **6-(Ph,Ph)** are closer to that found for the CO and CN^{t}Bu trapped products Cp$_2$Ta[η^2-CH$_2$B(C_6F_5)$_2$]L, which contain an intact dihapto borataalkene ligand.[27] Thus, diphenylacetylene does not appear to couple with the borataalkene ligand, and this intermediate has a structure akin to the proposed alkyne intermediate **I**. The reasons for this may stem from the steric bulk of the alkyne, but the greater π-acidity of this alkyne in comparison to the others employed in this study[28] may also stabilize the alkyne complex relative to the tantala-3-boratacyclopentene structure. The observation of this species strongly suggests that η^2-alkyne/η^2-borataalkene intermediates such as **I** are viable ones in the formation of the tantala-3-boratacyclopentene products **2** and **3**.

As these reactions are monitored further, the intermediates **6** are observed to convert smoothly and cleanly to the vinylalkylidene products **5**; no other intermediates are detected. Interest-

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(24) To our knowledge, only one other tantalum vinylalkylidene has been structurally characterized, see ref 16b.

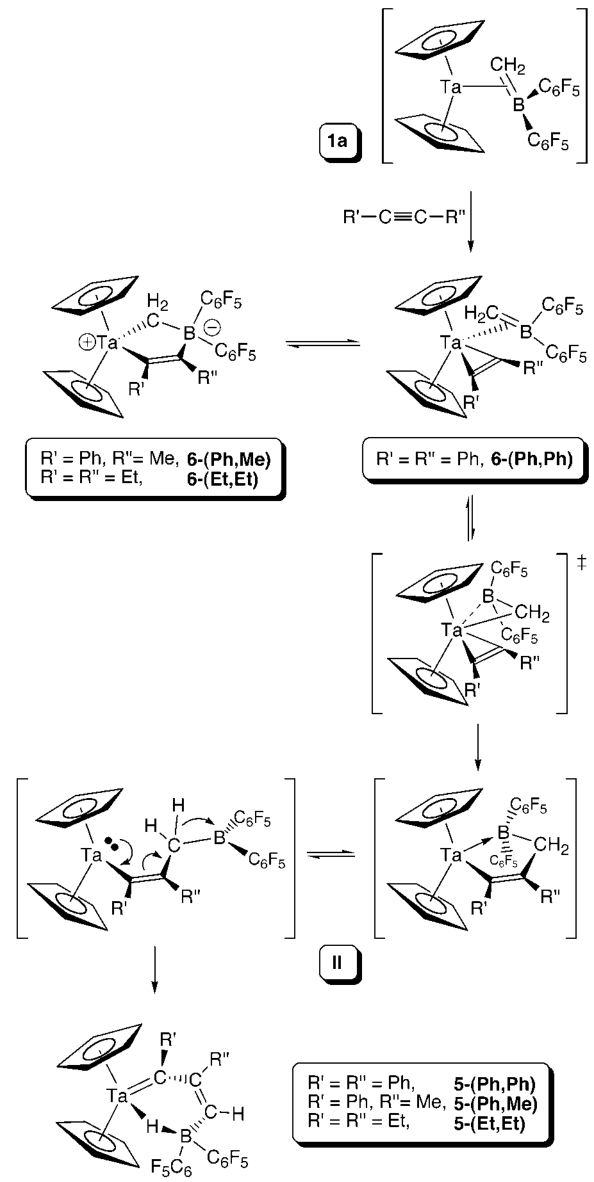
(25) The most common modes of bonding for the vinylalkylidene moiety are η^1 and η^3. See, for example: (a) Hoffmann, P.; Hämmerle, M.; Unfried, G. *New J. Chem.* **1991**, *15*, 769. (b) Mayr, A.; Asaro, M. F.; Glines, T. J.; van Engen, D.; Tripp, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 8187.

(26) The terminal Ta−H bond in Cp$_2$TaCH$_2$B(C_6F_5)$_2$(μ-H)(H) is 1.84(4) Å,[9] while the average distance in Cp$_2$TaH$_3$ is 1.774(3) Å: Wilson, R. D.; Koetzle, T. F.; Hart, D. W.; Kvick, A.; Tipton, D. L.; Bau, R. *J. Am. Chem. Soc.* **1977**, *99*, 1775.

(27) Note that the ^{11}B chemical shifts for purely η^1 [CH$_2$B(C_6F_5)$_2$] ligands are >50 ppm.[4]

(28) Baker, P. K.; Drew, M. G. B.; Meehan, M. M. *J. Chem. Soc., Dalton Trans.* **1999**, 765.

Scheme 4



ingly, the compounds **2a** and **3a** do not cleanly convert to vinylalkylidene products when heated; instead a variety of products arise. These observations suggest that the vinylalkylidenes form cleanly only when tantala-3-boratacyclopentene formation is readily reversible in the more sterically encumbered metallacycles. A plausible route to these compounds, which accounts also for the labeling experiment result, is given in Scheme 4.[29] Although tantala-3-boratacyclopentene formation occurs, for bulkier alkynes the equilibrium is shifted more toward the alkyne/borataalkene intermediates **I**; indeed, for diphenylacetylene, this species is dominant and identified as **6-(Ph,Ph)**. If the η^2-borataalkene is allowed to slip to the η^1-bonding mode, the alkyne can insert into the Ta−C bond of this ligand to form an intermediate **II**. Although insertions of olefins and presumably alkynes into tantalocene(III) alkyl bonds have high barriers,[30] the alkyl ligand here is not an ordinary hydrocarbyl ligand. The boryl group may lower the barrier to insertion by assuming an η^2-bonding mode in the transition state of the reaction. Another way to view this would be to look at this "insertion" step as a coupling of the alkyne with the borataalkene ligand with the opposite regiochemistry as that observed for the formation of compounds **2** and **3** and intermediates **6-(Ph,Me)** and **6-(Et,Et)**. The intermediate **II** can collapse to the vinylalkylidene products **5** via nucleophile-induced α-hydride migration to the strongly Lewis acidic boron center as shown. This type of migration has been implicated in the chemistry of other $RCH_2B(C_6F_5)_2$ compounds.[31] Vinylalkylidenes **5** are relatively stable materials in the solid state, but undergo further thermal conversions over the course of several hours at room temperature in solution.

Summary and Conclusions

This study offers the first glimpses of the chemistry which might be associated with borataalkene ligands. The reductive coupling of an alkyne with the borataalkene ligand $[CH_2B(C_6F_5)_2]^-$ has been conclusively demonstrated, and the fact that this ligand can exhibit "olefin-like" behavior despite the flexibility in bonding mode available is striking, especially in light of the bulky substitution on boron in this particular ligand. While the electron-withdrawing nature of the $-C_6F_5$ substitutents undoubtedly contributes to the favorability of the η^2-bonding mode for this ligand, our previous DFT computations did show these groups to have considerable steric impact on the stability of the dihapto binding.[9] It would, therefore, be of interest to find systems in which borataalkenes with less steric baggage could be generated. Complexes of the parent ligand $[H_2C{=}BH_2]^-$ represent particularly attractive targets in this regard, but present a significant challenge for synthetic chemists. Finally, these results open up the chemistry of the unique tantala-3-boratacyclopentene ring, which represent an unprecedented class of metallaheterocycle.

Experimental Section

General. General procedures have been described in detail elsewhere.[9a] $Cp_2Ta({=}CH_2)CH_3$,[14] $(\eta^5\text{-}C_5H_4Me)_2Ta({=}CH_2)CH_3$,[14] and $HB(C_6F_5)_2$[15] were prepared via literature procedures. Alkynes were purchased from Sigma−Aldrich and purified by distillation or used as received. Microanalyses were performed at least twice; some compounds consistently analyzed low in carbon by about 0.5−1.5%.

Synthesis of $Cp_2Ta[\kappa^2\text{-}\underline{C}H_2B(C_6F_5)_2(Me)C{=}\underline{C}(Me)]$, 2a. $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (344 mg, 0.501 mmol) was weighed into a 50 mL glass bomb, and toluene (15 mL) was condensed in at −78 °C. Under a flow of argon, 2-butyne (0.50 mL, 6.39 mmol) was syringed into the vessel which was sealed with a Kontes valve and allowed to warm to room temperature. The reaction was stirred for 1.5 h at 25 °C to give a dark orange solution. The toluene was removed under reduced pressure, and hexane (20 mL) was condensed onto the red oil at −78 °C; the system was sonicated to produce a light orange precipitate. The precipitate was isolated by filtration and dried under reduced pressure. Yield of **2a**: 279 mg, 77%. Anal. Calcd for $C_{27}H_{18}BF_{10}Ta$: C, 44.78; H, 2.57. Found: C, 44.31; H, 2.42. ^1H NMR (d_8-THF): 6.13 (s, 10H, C_5H_5), 4.02 (br s, 2H, CH_2), 2.35 (s, 3H, $TaCCH_3$), 1.36 (br

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(29) An alternative mechanism leading to a tantalacyclobutene derivative (which can rearrange to a vinylalkylidene via cycloreversion[16b]) involves loss of alkyne from intermediates **6** to give free **1**, which undergoes (reversible) α-elimination to yield an alkylidene hydride that is then trapped by alkyne to give the metallacyclobutene complex. This possibility was considered less likely since we have no evidence that loss of alkyne from species such as **I** or **6-(Ph,Ph)** is kinetically or thermodynamically significant. Furthermore, free **1** is known to decompose readily at room temperature, and the reactions to produce compounds **5** are clean and high yielding.

(30) Parkin, G.; Bunel, E.; Burger, B. J.; Trimmer, M. S.; Van Asselt, A.; Bercaw, J. E. *J. Mol. Catal.* **1987**, *41*, 21.

(31) Parks, D. J.; Piers, W. E. *Tetrahedron* **1998**, *54*, 15469.

s, 3H, BCCH_3). ^{13}C NMR (d_8-THF, −30 °C): 180.1 (TaC_αCH$_3$), 110.0 (C_5H$_5$), 78.6 (CH$_2$), 25.0 (TaCCH$_3$), 21.2 (BCCH$_3$). ^{11}B{^{1}H} NMR (d_8-THF): −32.7. ^{19}F{^{1}H} NMR (d_8-THF): −129.7 (4F, *o*-F), −162.5 (2F, *p*-F), −165.2 (4F, *m*-F).

Synthesis of (η^5-$C_5H_4Me)_2$Ta[κ^2-$\underline{C}H_2B(C_6F_5)_2$(Me)C═$\underline{C}$(Me)], 2b. The procedure used was identical to that for the synthesis and isolation of **2a**. Reagents used: (η^5-$C_5H_4Me)_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (250 mg, 0.35 mmol), 2-butyne (0.50 mL, 6.39 mmol). Yield of **2b**: 222 mg, 0.31 mmol, 87%. X-ray quality crystals were grown through layering a saturated solution of CH_2Cl_2 with hexanes and cooling to −35 °C. Anal. Calcd for $C_{29}H_{22}BF_{10}Ta$: C, 46.30; H, 2.95. Found: C, 45.35; H, 2.95. ^{1}H NMR (d_8-THF): 6.25 (m, 2H, C_5H_4Me), 5.86 (m, 4H, C_5H_4Me), 5.55 (s, 2H, C_5H_4Me), 3.90 (s, 2H, CH_2), 2.30 (s, 3H, TaCCH_3), 2.15 (s, 6H, $C_5H_4CH_3$), 1.35 (s, 3H, BCCH_3). ^{13}C NMR (d_8-THF, −30 °C): 183.2 (TaCCH$_3$), 122.9 (C-Me, C_5H_4Me), 115.7 (C_5H$_4$-Me), 115.3 (C_5H$_4$Me), 106.8 (C_5H$_4$Me), 103.9 (C_5H$_4$Me), 82.5 (CH$_2$), 25.0 (TaCCH$_3$), 21.8 (BCCH$_3$), 14.9 (C$_5$H$_4$$CH_3$). ^{11}B{^{1}H} NMR ($d_8$-THF): −30.8. ^{19}F{^{1}H} NMR (d_8-THF): −126.6 (4F, *o*-F), −162.5 (2F, *p*-F), −165.3 (4F, *m*-F).

Synthesis of $Cp_2Ta[\kappa^2$-$\underline{C}H_2B(C_6F_5)_2C(H)$═$\underline{C}(C_6H_5)]$, 3a-t. $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (300 mg, 0.437 mmol) was weighed into a 50 mL glass bomb, and THF (15 mL) was condensed in at −78 °C. Phenylacetylene (150 μL, 1.37 mmol) was added via syringe under a flow of argon, and the vessel was sealed with a Kontes valve. The solution was allowed to warm and was stirred at 25 °C for 5 h. The orange solution was then transferred to a 25 mL round-bottom flask, and the THF was removed under reduced pressure to give an orange oil. Hexane (20 mL) was condensed in at −78 °C, and the solution was sonicated to give a yellow powder. The hexane, residual THF, and alkyne were removed in vacuo, and a second portion of hexane (15 mL) was then condensed in, the yellow precipitate filtered, and dried under vacuum. Yield of **3a**: 285 mg, 84%. Anal. Calcd for $C_{31}H_{18}BF_{10}Ta$: C, 48.21; H, 2.35. Found: C, 47.70; H, 2.10. ^{1}H NMR (d_8-THF): 7.44 (m, 4H, C$_6H_5$), 7.26 (t, $^3J_{H-H}$ = 1H, C$_6H_5$), 6.38 (s, 1H, CH), 6.03 (s, 10H, C$_5H_5$), 2.98 (s, 2H, CH_2). ^{13}C NMR (d_8-THF): 179.8 (Ta-CC$_6$H$_5$), 142.1 (*ipso*-C, C_6H$_5$), 129.5 (C_6H$_5$), 128.5 (C_6H$_5$), 127.7 (C_6H$_5$), 108.2 (C_5H$_5$), 92.3 (CH), 42.8 (CH$_2$). ^{11}B{^{1}H} NMR (d_8-THF): −34.6. ^{19}F{^{1}H} NMR (d_8-THF): −135.2 (4F, *o*-F), −164.0 (2F, *p*-F), −166.5 (4F, *m*-F).

Generation of $Cp_2Ta[\kappa^2$-$\underline{C}H_2B(C_6F_5)_2C(H)$═$\underline{C}(C_6H_5)]$, 2a-k. $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (35 mg, 0.051 mmol) was loaded into a sealable NMR tube equipped with a sidearm isolated from the tube by a Kontes valve. A solution of PhCCH (15μL, 0.14 mmol) in d_8-THF was placed in the sidearm, and the whole apparatus was degassed. The phenylacetylene solution was then condensed into the tube at −78 °C, and the sample was assayed by NMR spectroscopy under temperature-controlled conditions. NMR data for **2a-k**, ^{1}H NMR (THF-d_8, 10 °C): 8.39 (s, 1H, CH), 6.31 (s, 10H, C$_5H_5$), 4.53 (s, 2H, CH_2). ^{11}B{^{1}H} NMR (THF-d_8, −78 °C): −24.3. ^{19}F{^{1}H} NMR (THF-d_8, 10 °C): −130.3 (4F, *o*-F), −163.6 (2F, *p*-F), −166.7 (4F, *m*-F).

Synthesis of (η^5-$C_5H_4Me)_2Ta[\kappa^2$-$\underline{C}H_2B(C_6F_5)_2C(H)$═$\underline{C}(C_6H_5)]$, 3b-t. The procedure used was identical to that for the synthesis and isolation of **3a-t**. Reagents used: (η^5-$C_5H_4Me)_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)-(CH$_3$) (250 mg, 0.364 mmol), phenylacetylene (125μL, 1.14 mmol). Yield of **3b-t**: 211 mg, 0.264 mmol, 72%. Anal. Calcd for $C_{33}H_{22}BF_{10}Ta$: C, 49.53; H, 2.77. Found: C, 49.87; H, 2.63. ^{1}H NMR (d_8-THF): 7.41 (m, 4H, C$_6H_5$), 7.24 (m, 1H, C$_6H_5$), 6.49 (s, 1H, CH), 6.05 (m, 2H, C$_5H_4$), 5.93 (m, 2H, C$_5H_4$), 5.60 (m, 2H, C$_5H_4$), 5.55 (m, 2H, C$_5H_4$), 2.85 (s, 2H, CH_2), 2.09 (s, 6H, C$_5$H$_4$CH_3). ^{13}C{^{1}H} NMR (d_8-THF): 187.0 (Ta-CC$_6$H$_5$), 145.7 (*ipso*-C, C_6H$_5$), 129.4 (C_6H$_5$), 128.3 (C_6H$_5$), 127.8 (C_6H$_5$), 124.4 (CMe, C$_5$H$_4$Me), 112.3 (C_5H$_4$), 110.9 (C_5H$_4$), 106.6 (C_5H$_4$), 101.5 (C_5H$_4$), 96.4 (CH), 46.4 (CH$_2$), 14.5 (CH$_3$). ^{11}B{^{1}H} NMR (d_8-THF): −32.9. ^{19}F{^{1}H} NMR (d_8-THF): −132.9 (4F, *o*-F), −162.1 (2F, *p*-F), −164.8 (4F, *m*-F).

Synthesis of (η^5,η^1-$C_5H_4CH_2$)(η^5-$C_5H_4Me)Ta[CH_2B(C_6F_5)_2](\mu$-H), 4. ($\eta^5$-$C_5H_4Me)_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (480 mg, 0.672 mmol) was weighed into a 50 mL glass bomb, and THF (20 mL) was condensed in at −78 °C. The vessel was backfilled with argon and closed. The solution was stirred at 10 °C for 1.5 h and then warmed to room temperature and stirred for an additional 30 min to give a green solution. The THF was removed until 2−3 mL remained, and hexane (40 mL) was condensed in at −78 °C. This solution was stirred for 45 min at −78 °C to precipitate a gray/green solid. The solid product was isolated by filtration and dried under vacuum. Yield of **4**: 382 mg, 0.547 mmol, 81%. The crude product can be recrystallized in low yield by layering a toluene solution with hexanes and placing at −35 °C for 24 h. Anal. Calcd for $C_{41}H_{25}NBF_{20}Ta$: C, 43.01; H, 2.31. Found: C, 42.48; H, 2.35. ^{1}H NMR (THF-d_8): 6.40 (s, 1H, C$_5H_4$), 5.87 (s, 1H, C$_5H_4$), 5.60 (s, 1H, C$_5H_4$), 5.31 (s, 1H, C$_5H_4$), 5.12 (s, 1H, C$_5H_4$), 5.07 (s, 1H, C$_5H_4$), 4.63 (s, 1H, C$_5H_4$), 3.88 (s, 1H, C$_5H_4$), 3.01 (s, 1H, C$_5$H$_4$CH_aH$_b$), 2.94 (s, 1H, C$_5$H$_4$CH$_a$$H_b$), 2.04 (s, 3H, C$H_3$), 1.49 (d, 1H, C$H_aH_b$), 0.58 (d, 1H, CH$_a$$H_b$), −3.85 (br s, 1H, BH). ^{13}C NMR (THF-d_8): 122.3 (C_5H$_4$), 115.7 (*ipso*-C, C_5H$_4$), 114.8 (*ipso*-C, C_5H$_4$), 104.2 (C_5H$_4$), 102.5 (C_5H$_4$), 100.3 (C_5H$_4$), 99.9 (C_5H$_4$), 99.2 (C_5H$_4$), 98.6 (C_5H$_4$), 92.8 (C_5H$_4$), 57.1 (C$_5$H$_4$$CH_aH_b$), 15.2 ($CH_3$), 11.1 ($CH_aH_b$). ^{11}B{^{1}H} NMR (THF-d_8): −33.5. ^{19}F{^{1}H} NMR (THF-d_8): −127.7 (2F, *o*-F), −129.0 (2F, *o*-F), −160.1 (1F, *p*-F), −160.8 (1F, *p*-F), −163.9 (4F, *m*-F).

Synthesis of $Cp_2Ta[\kappa^2$-$\underline{C}(C_6H_5)C(C_6H_5)$═$C(H)B(C_6F_5)_2\underline{H}]$, 5-(Ph,-Ph). $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (300 mg, 0.44 mmol) and diphenylacetylene (78 mg, 0.44 mmol) were weighed into a 25 mL round-bottom flask equipped with a filtering frit. THF (15 mL) was condensed into the flask at −78 °C; the reaction mixture was allowed to warm and was stirred at 25 °C for 3 h during which time the solution turned dark orange. Solvent was removed under reduced pressure, and hexane (20 mL) was added by vacuum transfer. The solvent was removed from the resulting orange suspension under reduced pressure to remove any remaining THF. Hexane (10 mL) was again condensed into the flask at −78 °C, and the orange precipitate was isolated by filtration and dried under vacuum. Yield of **5-(Ph,Ph)**: 293 mg, 0.35 mmol, 80%. Anal. Calcd for $C_{37}H_{22}BF_{10}Ta$: C, 52.39; H, 2.61. Found: C, 50.20; H, 3.12. ^{1}H NMR (d_8-THF): 7.54 (m, C$_6$H$_5$), 7.39 (m, C$_6$H$_5$), 7.26 (m, C$_6$H$_5$), 7.14 (m, C$_6$H$_5$), 6.89 (m, C$_6$H$_5$), 5.65 (s, 5H, C$_5$H$_5$), 5.57 (s, 5H, C$_5$H$_5$), 4.08 (br d, J = 3.4 Hz, 1H, CH), −3.96 (br s, 1H, BH). ^{13}C NMR (d_8-THF, −25 °C): 213.2 (Ta═C), 156.9 (C(C$_6$H$_5$)═CH), 154.3 (*ipso-C*, C$_6$H$_5$), 143.0 (*ipso-C*, C$_6$H$_5$), 131.0 (C_6H$_5$), 128.5 (C_6H$_5$), 128.1 (C_6H$_5$), 127.7 (C_6H$_5$), 125.1 (C_6H$_5$), 114.2 (C_6H$_5$), 102.5 (C_5H$_5$), 98.6 (CH, $^1J_{CH}$ = 136.5 Hz), 98.5 (C_5H$_5$). ^{11}B{^{1}H} NMR (d_8-THF): −11.2. ^{19}F{^{1}H} NMR (d_8-THF): −125.8 (2F, *o*-F), −128.0 (2F, *o*-F), −158.2 (1F, *p*-F), −159.2 (1F, *p*-F), −163.2 (4F, *m*-F).

Synthesis of $Cp_2Ta[\kappa^2$-$\underline{C}(C_6H_5)C(CH_3)$═$C(H)B(C_6F_5)_2\underline{H}]$, 5-(Ph,-Me). $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu$-H)(CH$_3$) (300 mg, 0.437 mmol) was weighed into a 50 mL glass bomb, and THF (15 mL) was condensed in at −78 °C. 1-Phenyl-1-propyne (150 μL, 1.20 mmol) was added via syringe into the reaction vessel at −78 °C under a flow of argon. The cold bath was removed, and the reaction was stirred at 25 °C for 3 h. The THF was removed under reduced pressure to leave a viscous orange oil. The oil was broken into an orange powder by sonication under hexane (20 mL). The precipitate was isolated by filtration and dried in vacuo. Yield of **5-(Ph,Me)**: 255 mg, 323 mmol, 74%. X-ray quality crystals were grown by layering a saturated solution in CH_2Cl_2 with hexane and cooling to −35 °C. Anal. Calcd for $C_{32}H_{20}BF_{10}Ta$: C, 48.88; H, 2.35. Found: C, 50.24; H, 2.68. ^{1}H NMR (d_8-THF): 7.25 (m, 2H, C$_6H_5$), 6.98 (m, 1H, C$_6H_5$), 6.63 (m, 2H, C$_6H_5$), 5.53 (s, 5H, C$_5H_5$), 5.47 (s, 5H, C$_5H_5$), 4.38 (d, 1H, CH), 1.70 (s, 3H, CH_3), −4.35 (br s, 1H, BH). ^{13}C NMR (d_8-THF, −25 °C): 225.9 (Ta═C), 155.4 (C(C$_6$H$_5$)═CH), 154.7 (*ipso-C*, C$_6$H$_5$), 128.5 (C$_6$H$_5$), 128.0 (C$_6$H$_5$), 125.4 (C$_6$H$_5$), 109.9 (CH, $^1J_{CH}$ = 137.0 Hz), 102.1 (C$_5$H$_5$), 98.3 (C$_5$H$_5$), 23.1 (CH$_3$). ^{11}B{^{1}H} NMR (d_8-THF): −12.2. ^{19}F{^{1}H} NMR (d_8-THF): −122.3 (br, 1F, *o*-F), −125.0 (br, 1 F, *o*-F), −125.7 (2F, *o*-F), −157.6 (1F, *p*-F), −159.0 (1F, *p*-F), −162.4 (br, 2F, *m*-F), −163.1 (2F, *m*-F).

Generation of $Cp_2Ta[\kappa^2\text{-}\underline{C}(CH_2CH_3)C(CH_2CH_3){=}C(H)B(C_6F_5)_2\underline{H}]$, 5-(Et,Et). The compound was not isolable but was generated in solution using the procedure described above for **2a-k**. Reagent amounts: $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (35 mg, 0.051 mmol), 2-hexyne (15 μL, 0.13 mmol). NMR yield of **5-(Et,Et)** > 95%. ^1H NMR (d_8-THF, −25 °C): 5.60 (s, 5H, C_5H_5), 5.39 (s, 5H, C_5H_5), 4.74 (br d, $J = 4.35$ Hz, 1H, CH), 3.26 (m, 1H, $TaCCH_aH_b$), 3.01 (m, 1H, $TaCCH_aH_b$), 2.35 (m, 1H, $BCCH_aH_b$), 2.20 (m, 1H, $BCCH_aH_b$), 1.34 (m, 3H, $TaCCH_2CH_3$), 0.85 (m, 3H, $BCCH_2CH_3$). ^{13}C NMR (d_8-THF, −25 °C): 245.4 ($Ta{=}C$), 157.8 (TaC−C), 115.6 (CH), 101.6 (C_5H_5), 98.2 (C_5H_5), 34.4 ($TaC{-}CH_2$), 27.1 ($BC{-}CH_2$), 19.0 ($BCCH_2{-}CH_3$), 13.9 ($TaCCH_2{-}CH_3$). $^{11}B\{^1H\}$ NMR (d_8-THF, −25 °C): −12.2. $^{19}F\{^1H\}$ NMR (d_8-THF): (br, 1F, *o*-F), (br, 1F, *o*-F), (2F, *o*-F), (1F, *p*-F), (1F, *p*-F), (br, 2F, *m*-F), (2F, *m*-F).

Generation of $Cp_2Ta[\eta^2\text{-}CH_2B(C_6F_5)_2](PhCCPh)$, 6-(Ph,Ph). $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (35 mg, 0.051 mmol) and PhCCPh (9 mg, 0.051 mmol) were loaded into a sealable NMR tube equipped with a sidearm isolated from the tube by a Kontes valve. d_8-THF was placed in the sidearm, and the whole apparatus was degassed. The THF was then condensed into the tube at −78 °C, and the sample was assayed by NMR spectroscopy under temperature-controlled conditions. ^1H NMR (THF-d_8, 10 °C): 5.76 (s, 10H, C_5H_5), 2.62 (s, 2H, CH_2). $^{11}B\{^1H\}$ NMR (THF-d_8, −78 °C): 4.0. $^{19}F\{^1H\}$ NMR (THF-d_8, 10 °C): −129.0 (4F, *o*-F), −154.5 (2F, *p*-F), −162.2 (4F, *m*-F).

Generation of $Cp_2Ta[\kappa^2\text{-}\underline{C}H_2B(C_6F_5)_2(CH_3)C{=}\underline{C}(C_6H_5)]$, 6-(Ph,Me). A procedure analogous to that described for **2a-k** was employed. Reagent amounts: $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (35 mg, 0.051 mmol), $PhCCCH_3$ (15 μL, 0.12 mmol). ^1H NMR (THF-d_8, 10 °C): 6.13 (s, 10H, C_5H_5), 4.12 (s, 2H, CH_2), 1.27 (s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (THF-d_8, −78 °C): −37.2. $^{19}F\{^1H\}$ NMR (THF-d_8, 10 °C): −131.4 (4F, *o*-F), −163.6 (2F, *p*-F), −166.3 (4F, *m*-F).

Generation of $Cp_2Ta[\kappa^2\text{-}\underline{C}H_2B(C_6F_5)_2(CH_3CH_2)C{=}\underline{C}(CH_2CH_3)]$, 6-(Et,Et). A procedure analogous to that described for **2a-k** was employed. Reagent amounts: $Cp_2Ta(CH_2B(C_6F_5)_2)(\mu\text{-}H)(CH_3)$ (35 mg, 0.051 mmol), 2-hexyne (15 μL, 0.13 mmol). ^1H NMR (THF-d_8, 10 °C): 6.04 (s, 10H, C_5H_5), 3.75 (s, 2H, $Ta{-}CH_2$), 3.05 (br s, 2H, $TaC{-}CH_2$), 1.23 (t, 3H, $TaCCH_2{-}CH_3$), 0.24 (t, 3H, $BCCH_2{-}CH_3$). $^{11}B\{^1H\}$ NMR (THF-d_8, −78 °C): −38.2. $^{19}F\{^1H\}$ NMR (THF-d_8, 10 °C): −128.9 (4F, *o*-F), −162.0 (2F, *p*-F), −164.9 (4F, *m*-F).

X-ray Crystallography. Colorless crystals of **2b**, **3b-t**, and **5-(Ph,Me)** were obtained by layering CH_2Cl_2 or $ClCH_2CH_2Cl$ solutions with hexanes. See Table 4 for crystallographic experimental data. Data were collected on a Bruker P4/RA/SMART 1000 CCD diffractometer[32] using Mo Kα radiation at −80 °C. Unit cell parameters were obtained from a least-squares refinement of the setting angles of the number of reflections from the data collection. An empirical absorption correction was applied to the data through use of the SADABS procedure. The structures were solved using the direct methods program SHELXS-86,[33] and full-matrix least-squares refinement on F^2 was completed using the program SHELXL-93.[34] Hydrogen atoms were assigned positions on the basis of the geometries of their attached carbon atoms and were given isotropic thermal parameters 20% greater than the equivalent isotropic displacement parameters of the attached carbons.

Table 4. Summary of Data Collection and Refinement Details for **2b**, **3b-t**, and **5-(Ph,Me)**

	2b	3b-t	5-(Ph,Me)
formula	$C_{29}H_{22}F_{10}BTa$	$C_{33}H_{22}F_{10}BTa\cdot 0.5C_2H_4Cl_2$	$C_{32}H_{20}F_{10}BTa$
fw	752.23	849.74	786.24
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a, Å	9.6947(6)	14.9651(7)	12.5920(6)
b, Å	12.0858(8)	12.6093	11.5277(6)
c, Å	21.2732(14)	16.1443	19.4942(9)
β, °	103.1000(10)	108.2173(11)	
V, Å^3	2492.5(3)	2967.1(2)	2687.9(2)
Z	4	4	4
d_{calc}, mg m^{-3}	2.005	1.902	1.943
μ, mm^{-1}	4.504	3.883	4.182
T, °C	−80	−80	−80
crystal dimensions, mm^3	0.24 × 0.08 × 0.03	0.42 × 0.34 × 0.12	0.16 × 0.15 × 0.06
rel. transmission factors	0.9010−0.6644	0.6529−0.2923	0.7875−0.5542
2θ (max), deg	52.80	52.78	52.76
total data	12 482	14 551	13 116
independent reflections	5098	6057	5501
no. of observations[a]	4022	5458	4404
no. of variables	374	426	402
restraints	0	0	0
R_1 $F_o^2 \geq 2\sigma(F_o^2)$	0.0367	0.0230	0.0329
wR_2 $F_o^2 \geq -3\sigma(F_o^2)$	0.0564	0.0623	0.0769
GOF	0.863	1.052	0.988
residual density, e/Å^3	−0.917−1.516	−1.149−1.206	−0.982−1.249

[a] $F_o^2 \geq 2\sigma(F_o^2)$).

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Supporting Information Available: Full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances and angles for **2b**, **3b-t**, and **5-(Ph,Me)** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker.

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