Organometallics **1998,** *17,* 3865−3874

Alkene and Alkyne Insertion Reactions with Tantalum Metallacarborane Complexes: the $Et_2C_2B_4H_4^{2-}$ Carborane Ligand as a Spectator and Participant[1]

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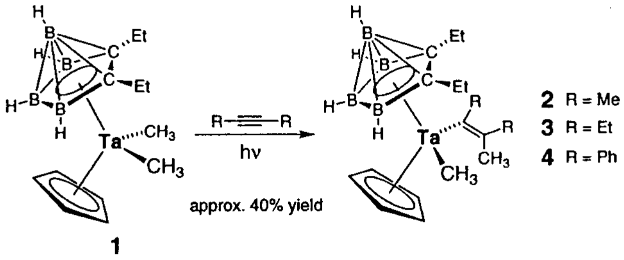
The tantalum carborane complex $(Et_2C_2B_4H_4)CpTaMe_2$ (**1**) is thermally stable but undergoes clean photochemical insertion with alkynes to give vinyltantalum species, in contrast to the thermal reactivity of isoelectronic group 4 metallocenes which give methylidene intermediates. Certain tantalum vinyltitanium products display NMR resonances indicative of γ-agostic Ta−H_3C interactions sufficiently strong to stabilize two different regioisomers. Decomposition of these species occurs by apparent alkyne deinsertion and ejection of the tantalum fragment to give $R_2Et_2C_4B_4H_4$ (R = Me, Et, Ph) carborane clusters. The analogous diphenyl complex $(Et_2C_2B_4H_4)CpTaPh_2$ (**8**) is thermally reactive, eliminating benzene and undergoing trapping reactions of the derived benzyne intermediate with alkynes. The structures of the resulting metallaindene complexes are supported by X-ray crystallography, protonolysis, and spectroscopy. Insertions occur with good regioselectivity, controlled by steric and stereoelectronic factors that differ somewhat from those observed for zirconocene and titanocene analogues. Reaction of complex **8** with excess styrene results in a novel triple-insertion process in which styrene units are added to both ortho positions of an aryl ligand and to the central boron atom of the C_2B_3 ring. The proposed mechanism (supported by the use of styrene-d_8 and alkylated metallacarborane starting materials) features two benzyne intermediates, derived from activation of both *ortho*-CH bonds, and one insertion into a putative Ta−B bond. An important hypothesis is that a Ta−C fragment can undergo intramolecular insertion into a carborane B−H bond, a step unknown for cyclopentadienyl C−H bonds and one that is potentially relevant to the use of metallacarborane complexes as catalysts for olefin polymerization and related processes.

Introduction

We have recently reported on our efforts to map the organometallic reactivity of early transition metal metallacarborane complexes with unsaturated small molecules.[2−5] Photochemical and thermal insertion reactions of isocyanides and alkynes have led to different products, indicative of both insertion and rearrangement processes.[4,5] Here we report the reactions of alkynes and alkenes with Ta(V) metallacarborane compounds demonstrating sequential C−H and B−H bond activation processes, the former through benzyne intermediates and the latter by an unknown mechanism.

Scheme 1



Results and Discussion

The tantalum(V) dimethyl complex **1** was found to be inert when heated (90 °C, 24 h) with an excess of either diphenylacetylene or dimethylacetylene dicarboxylate. However, photolysis in the presence of excess amounts of 2-butyne, 3-hexyne, or diphenylacetylene gave vinyltantalum species **2**, **3**, and **4**, respectively (Scheme 1), analogous to the facile *thermal* insertion chemistry of Cp_2TiMe_2.[6] Unlike the titanocene system,[6,7] however, the formation of metallacyclobutenes is not observed upon subsequent heating (90 °C) or photolysis. We see no other signs of the formation of tantalum methylidene intermediates[8] by elimination of methane from **1**, in contrast to the strong evidence for such intermediates

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[1] (a) Organotransition-Metal Metallacarboranes. 52. For part 51, see: Curtis, M. A.; Houser, E. J.; Sabat, M.; Grimes, R. N. *Inorg. Chem.* **1998**, *37*, 102−111. (b) Based in part on the Ph.D. Thesis of E. Boring, University of Virginia, 1998.

[2] Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014−3029.

[3] Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163−1164.

[4] Boring, E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1997**, *16*, 3993−4000.

[5] Curtis, M. A.; Finn, M. G.; Grimes, R. N. *J. Organomet. Chem.* **1998**, *550*, 469−472.

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[8] Complex **1** shows no ROMP activity with norbornene or a furan−maleimide cycloadduct upon heating or photolysis nor do we observe metallacyclobutane formation in the presence of these and other olefins.

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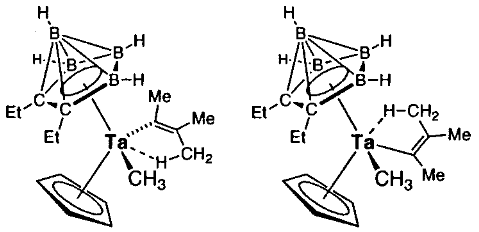
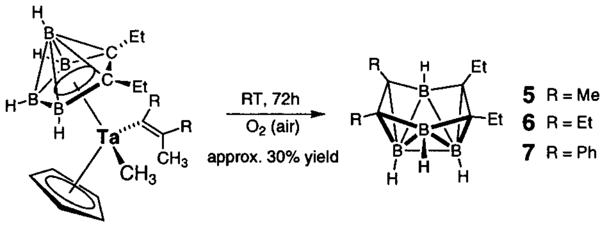
Scheme 2



2a **2b**

Scheme 3



2 (R=Me), **3** (R=Et), **4** (R=Ph)

observed in higher-temperature thermolysis of Cp_2TiMe_2[7,9,10] and other systems.[11] Photolysis of Cp_2TiMe_2 in the presence of diphenylacetylene has been shown to produce mostly a titanacyclopentadiene (presumably from Cp_2Ti^{II})[12,13] and an unstable vinyltitanocene species analogous to **4**.[14,15] Thus, as we have found previously for other processes,[2–5] dimethyl complex **1** displays reactivity analogous to its isoelectronic group 4 metallocene congeners but with enhanced ground-state stability. In this case, it is stimulated by irradiation not to undergo ethane elimination to a Ta(III) intermediate, but rather to react as Cp_2TiMe_2 does under gentle heating.[16]

Complex **2** is isolated as a 2:1 mixture of isomers (**2a** and **2b**), clearly resolved in the NMR spectra. Each isomer displays one methyl ^1H (0.09 and 0.03 ppm) and ^{13}C resonance that is significantly upfield from the others, in addition to the expected high-field resonances of the methyl groups bound directly to the metal. Similar upfield CH_3 signals are observed for complexes **3** and **4**, but only one isomer is resolved in each case. Use of $(Et_2C_2B_4H_4)CpTa(CD_3)_2$ with 2-butyne and diphenylacetylene provides the deuterium-substituted analogues of **2** and **4** in similar yields, for which the upfield NMR signals are missing. These data suggest that an agostic interaction[17–19] may inhibit rotation about the Ta–vinyl bond, giving rise to "H-in" vs "H-out" isomers (analogous to N-in vs N-out of iminoacyl complexes)[4] as shown in Scheme 2.[20] Complexes **3** and **4** exist as single isomers, presumably because of a steric preference. Agostic interactions are somewhat unexpected in these complexes, which are relatively electron-rich despite their formal 16-electron configuration. A definitive identification of agostic Ta–H bonding in **2**–**4** must await additional structural and/or spectroscopic data.

Complexes **2**–**4** proved to be mildly air sensitive, decomposing to the carboranes $Et_2R_2C_4B_4H_4$, for which structures **5**–**7** are proposed (Scheme 3). A compound corresponding to **5** was obtained by Sneddon and coworkers from the reaction of $NiCl_2$ and $(Et_2C_2B_4H_4)Li_2$ in the presence of terminal alkynes[21] and from the neutral $Et_2C_2B_4H_6$ and 2-butyne in the presence of ruthenium carbonyl phosphine catalysts.[22] Other $R_2R'_2C_4B_4H_4$ carboranes have also been reported,[23,24] and the nido cage structure shown in Scheme 3 has recently been observed by X-ray crystallography for $H_4C_4B_4Et_4$.[25] Remarkably, the formation of these products in our case requires that the C–C bond formed in the alkyne insertion process be broken, such that only the original R_2C_2 alkyne fragment, rather than the vinyl moiety, is incorporated into the new carborane cage. It is tempting to speculate that the agostic interaction discussed above assists in reversing the alkyne insertion event. Exposure of **2**–**4** to moisture alone without O_2 does not cause decomposition. The cage-expansion process and the sensitivity of the formally Ta(V) complexes to oxygen, both unusual in metallocene chemistry, highlight some of the ways in which early transition metal group *n* complexes of the C_2B_4 system differ from cyclopentadienyl complexes of group $n - 1$. Note that a cage expansion event involving an isonitrile substrate in which the CpTa center is retained has also been reported by us,[4] and a related boratabenzene ring fusion has been observed by Ashe and co-workers.[26]

In contrast to the thermal stability of **1**, the tantalum diphenyl complex **8** is reactive upon heating, being converted to a stable benzyne adduct in the presence of trimethylphosphine.[3] In the absence of phosphine and the presence of alkynes, five-membered metallacycles **9**–**13** are produced in generally excellent yields, presumably resulting from the addition of alkyne to a reactive benzyne intermediate (Scheme 4). The analogous zirconocene compounds are well-known;[27–29] the

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(15) Rausch, M. D.; Boon, W. H.; Alt, H. *J. Organomet. Chem.* **1977**, *141*, 299–312.

(16) Interestingly, the analogous complex $(Et_2C_2B_4Br_3H)(Cp)TaMe_2$, in which the three "ring" borons bear bromine substituents instead of hydrogen, does not undergo the same chemistry. Photolysis in the presence of 3-hexyne produces a product tentatively identified as the metallacyclopentadiene expected from the combination of two alkynes and a (carborane)(Cp)Ta^{III} fragment. This and other reactions of metallacarborane complexes of varying electronic and steric properties will be reported in due course.

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(19) Grubbs, R. H.; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85–93.

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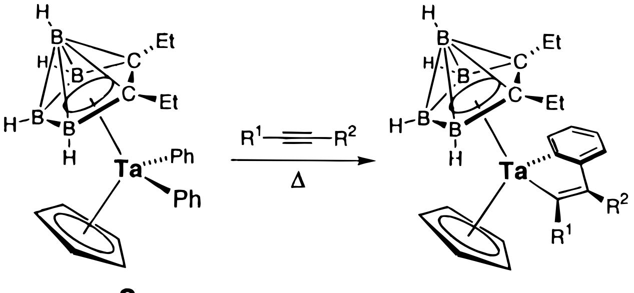
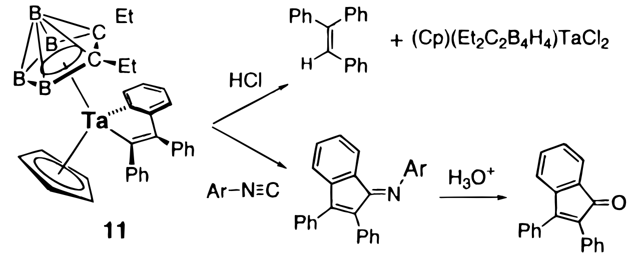
Scheme 4



8

Cpd.	R^1	R^2	Yield
9a	Ph	H	5%
9b	H	Ph	87%
10a	Ph	CH_3	11%
10b	CH_3	Ph	82%
11	Ph	Ph	92%
12	Et	Et	95%
13	$SiMe_3$	H	88%

Scheme 5



first example of related tantalum metallacycles was the $(C_5H_5)(CH_3)_2M(C_6H_4)CH_2CH_2$ system of Schrock and coworkers (M = Ta, Nb).[30] Befitting the enhanced stability afforded by the carborane fragment, the insertion reactions shown in Scheme 4 were all performed in air with unpurified reagent-grade solvents. No further reactions occur upon additional heating in the presence of excess alkyne. The metallaindene products are stable to the following conditions: room-temperature storage in air for weeks, ultraviolet irradiation (Hanovia lamp) in benzene solution for 12 h, and thermal or photochemical reaction with alkynes, alkenes, or nitriles.

The metallacycle carbon fragments can be released by treatment with acid. Thus, protonation of diphenylacetylene adduct **11** at room temperature gave triphenylethylene, and reaction with 2,6-dimethylphenyl isocyanide afforded 2,6-dimethylphenylimino-2,3-diphenylindenone (Scheme 5).[31] However, complexes **10b** and **11** are inert toward prolonged reaction with $PhPCl_2$ at 85 °C, which afforded phosphole derivatives from analogous titanocene metallacycles under much milder conditions.[32]

That terminal alkynes undergo insertion to give metallacyclopentadienes, rather than deprotonation to acetylide species of the type (carborane)CpTa(Ph)(C≡CR), is demonstrated by the absence of acetylenic ^{13}C NMR resonances, the appearance of a vinylic signal at 7.48 ppm for complex **13** (the corresponding peaks for **9a** and **9b** are obscured by aromatic resonances), and the isolation of the corresponding alkenes upon treatment with HCl. Unsymmetrical alkynes are incorporated with substantial regioselectivity, as shown by the isolated yields listed in Scheme 4. The molecular structure of the major isomer **10b** from 1-phenyl-1-propyne insertion was determined by X-ray crystallography and is shown in Figure 1 (Table 1). The structure shows the expected flat metallaindenyl moiety bisecting the carborane−Ta−Cp angle, with the pendant phenyl group found away from the tantalum center and oriented roughly perpendicular to the Ta−C4−C5−C6−C7 plane. The same regiochemical preference was demonstrated for phenylacetylene insertion by protonolysis of the major isomer **9b** to give exclusively 1,1-diphenylethylene.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex 10b

Ta−C4	2.20(1)	Ta−C1R3	2.43(1)
Ta−C7	2.18(1)	C4−C5	1.33(2)
Ta−C2	2.35(1)	C5−C6	1.50(2)
Ta−C3	2.47(1)	C6−C7	1.41(2)
Ta−B6	2.41(1)	C4−C12	1.51(2)
Ta−C1R1	2.40(1)	C5−C13	1.52(2)
Ta−C1R2	2.43(1)		
Ta−C4−C5	108.7(9)	Ta−C4−C12	125.9(8)
C4−C5−C6	122(1)	C5−C4−C12	125(1)
C5−C6−C7	118(1)	C4−C5−C13	121(1)
C6−C7−Ta	108.5(8)	C6−C5−C13	117(1)
C4−Ta−C7	82.0(4)		

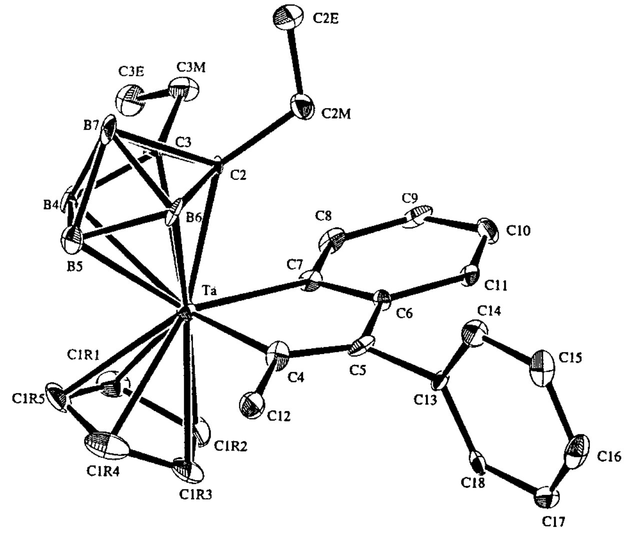


Figure 1. ORTEP drawing of the solid-state structure of **10b** showing 30% probability ellipsoids with atom-numbering scheme. H atoms are omitted for clarity.

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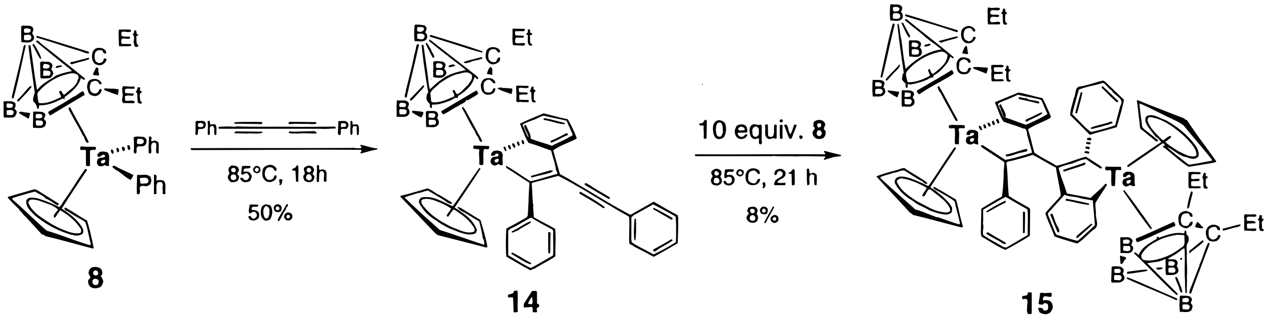
(30) Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 263−264.

(31) Exposure of metallacycle **11** to $PhPCl_2$ in refluxing THF afforded predominantly the vinyl complex $(Et_2C_2B_4H_4)(Cp)Ta(C_2Ph_3)$Cl but also 15% of the monophenyl chloride complex $(Et_2C_2B_4H_4)(Cp)$TaPhCl (products characterized by NMR, mass spectrometry, elemental analysis, and reaction with HCl to liberate triphenylethylene in the first case). While the first product may arise from reaction of **11** with trace HCl contaminating the chlorophosphine reagent, the formation of the monophenyl adduct suggests a novel reaction of the P−Ph bond. No phosphole formation was observed, in contrast to the reported reactivities of titanocene and zirconocene metallacycles with $PhPCl_2$.

(32) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310−2312.

Scheme 6



These results contrast somewhat with the chemistry of zirconocene and titanocene benzyne and alkyne complexes, which insert unsymmetrical alkynes with little selectivity or with preference for the isomer having the larger substituent adjacent to the metal center.[33−35] Thus, the (carborane)CpTa center appears to be more congested than Cp_2Zr or Cp_2Ti, giving rise to the observed regioselectivity by virtue of a steric effect. The structure of the {trimethylsilyl}acetylene insertion product **13**, isolated as a single isomer, is assigned on the basis of NOE enhancements in the vinylic (10.4%) and Cp (4.1%) resonances observed upon irradiation of the $SiMe_3$ signal, with no enhancement found for any aromatic resonance. This regiochemical outcome, with the $SiMe_3$ group next to the metal, is consistent with the strong electronic stabilization provided by the silyl group to the incipient negative charge at the α-carbon, as is consistently observed in insertion reactions of metallocene−alkyne complexes.[33−35]

Reaction of 2 equiv of **8** with 1,4-diphenylbutadiyne under standard conditions gave **14** in approximately 50% yield plus approximately 4% of a bis-insertion product tentatively identified as structure **15** (Scheme 6). Treatment of **14** with 10 equiv of **8** in a separate step results in the conversion of only 8% of **14** to **15** before all of the diphenyl complex is consumed (monitored by NMR), consistent with the steric crowding expected for the highly substituted bridging diene unit of **15**.

The alkyne insertion products are chiral, with the metal atom as the stereogenic center, in contrast to the axial chirality that characterizes the highly useful *ansa*-metallocene complexes first developed by Brintzinger and co-workers. The expected configurational stability of our structures was demonstrated by the complete resolution of **9b** by high-performance liquid chromatography using a Chiralcel OD-H column. The enantiomers isolated on a small scale in this manner are characterized by $[\alpha]^{20}_D = -565 \pm 20°$ ($c = 0.50$ g/100 mL of cyclohexane) for the faster-eluting isomer and $[\alpha]^{20}_D = +555 \pm 20°$ ($c = 0.60$ g/100 mL of cyclohexane) for the slower-eluting isomer.[36] The mirror-image circular dichroism spectra of the two enantiomers along with their UV−vis spectrum are shown in Figure 2. The sinusoidal quality of the CD spectra allows some of the component bands of the electronic spectrum to be clearly identified.

Styrene was used as a probe for olefin reactivity with the putative benzyne intermediate derived from **8**. Reaction with 10 equiv of styrene in refluxing benzene for 16 h afforded the product of a single insertion **16**, isolated in 63% yield and characterized by ^1H NMR, ^{13}C NMR, and mass spectrometry (Scheme 7). Complex **16** was purified by column chromatography in air but decomposed to a complex mixture of materials upon extended exposure to the atmosphere at room temperature. When **16** and excess styrene were heated for 60 h, a new complex **17** was formed in high yield and was found to contain the elements of three styrene units (Scheme 7). The X-ray crystal structure of **17** is shown in Figure 3 (Table 2), revealing styrene fragments on *both* sides of the Ta−aryl bond (one as a phenethyl group and one incorporated into a metallacycle) as well as a phenethyl unit on the central ring boron, B(5). NMR and crystallographic parameters show that each contains a saturated ethyl unit; thus, three insertion reactions have occurred using two aryl−H bonds and one B−H bond. Direct insertion of styrene into the B(5)−H bond is unlikely because no such insertion occurs with (carborane)(Cp)$TaCl_2$ or (carborane)(Cp)-$TaMe_2$ complexes.

Use of styrene-d_8 gives **16**-d_8 with *no* proton resonances visible in the sp^3 region other than those of the carborane ethyl groups, as expected for the trapping of the putative intermediate benzyne with alkene (verified by mass spectrometry). Further reaction with styrene-d_8 gave **17**-d_{24} by mass spectrometry, displaying a new broad singlet at 1.61 ppm (2H) as the only non-carborane aliphatic resonance. This signal is assigned to H^1 and H^2 shown in Scheme 7, which derive from the B−H and C−H bonds that are apparently conserved in the second and third insertion steps.

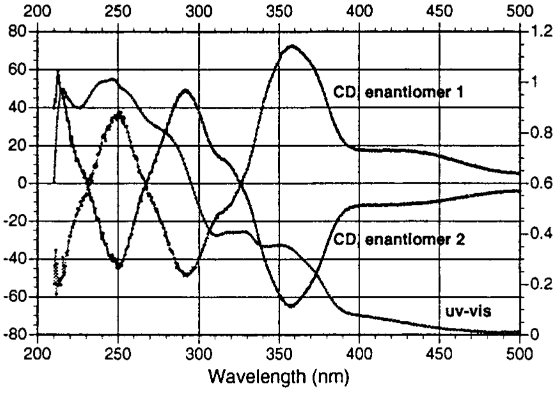


Figure 2. Electronic spectrum of racemic **9b** (0.088 mM), and circular dichroism of the resolved enantiomers (2.7 mM), both in cyclohexane.

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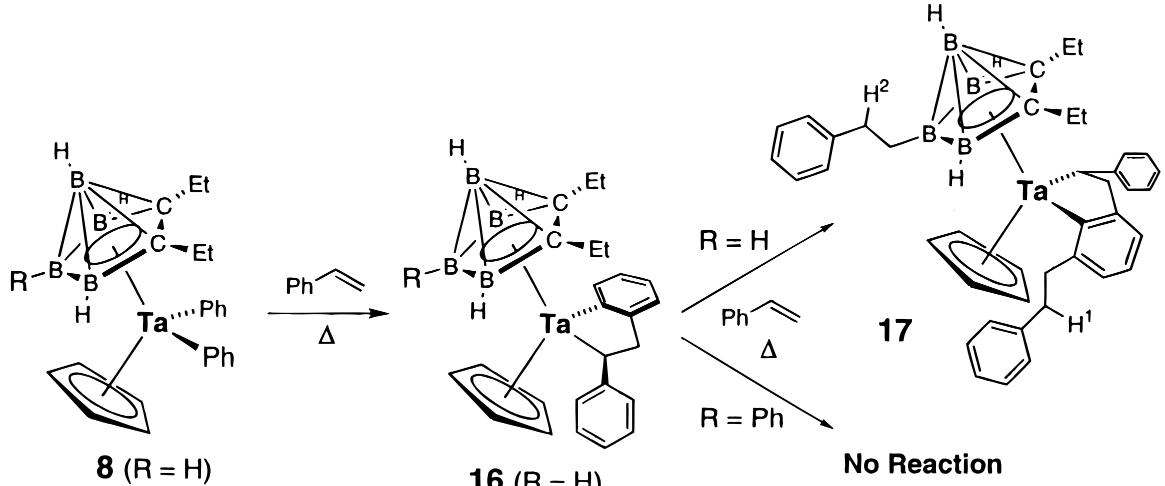
[33] Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047−1058 and references therein.

[34] Cámpora, J.; Buchwald, S. L. *Organometallics* **1993**, *12*, 4182−4187.

[35] Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1989**, *111*, 2870−2874.

Scheme 7



8 (R = H)
18 (R = Ph)

16 (R = H)
19 (R = Ph)

17

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 17

Ta−C4	2.24(1)	Ta−C1R1	2.37(1)
Ta−C17	2.176(7)	B5−C26	1.63(1)
Ta−C2	2.47(1)	C4−C11	1.54(1)
Ta−C3	2.472(9)	C11−C12	1.54(1)
Ta−B4	2.45(1)	C18−C19	1.53(1)
Ta−C1R4	2.427(9)	C26−C27	1.48(1)
Ta−C1R5	2.41(1)		
Ta−C4−C11	99.4(5)	Ta−B5−C26	133.8(7)
Ta−C4−C5	122.2(6)	B5−C26−C27	112.4(8)
C4−C11−C12	115.8(8)	C26−C27−C28	119.1(9)
C11−C12−C17	120.1(7)	C16−C18−C19	111.5(9)
Ta−C17−C12	105.3(5)	C18−C19−C20	113.6(9)

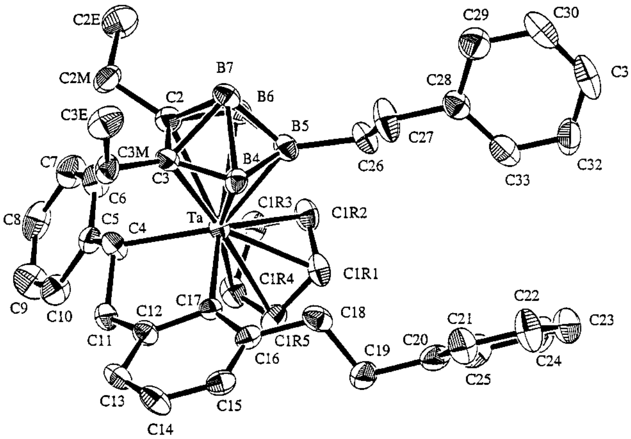
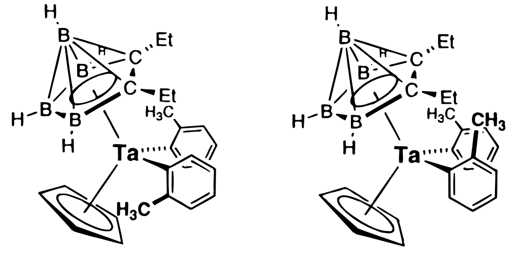


Figure 3. ORTEP drawing of the solid-state structure of **17** showing 30% probability ellipsoids with atom-numbering scheme. H atoms are omitted for clarity.

To further probe the sequence of events, these active hydrogen atoms were replaced by carbon fragments. Thus, the triphenyl complex **18**, prepared from a B(5)-brominated[37] tantalum dichloride precursor, reacts with styrene to give only the monoinserted complex **19**; no further reaction is observed, even upon extended heating (Scheme 7). In addition, we attempted to prepare the bis(*o*-tolyl) complex **20** from $(Et_2C_2B_4H_4)CpTaCl_2$ and (*o*-tolyl)MgBr, employing forcing conditions to overcome the steric hindrance of the system. Two compounds of the desired composition were isolated, which are tentatively assigned as the syn and anti *o*-tolyl isomers shown in Scheme 8. These isomers were separated by column chromatography and do not interconvert at room temperature.[38] Exposure of each isomer to an excess of styrene in refluxing benzene leads to consumption of the starting diaryl species, but no identifiable organometallic products could be isolated from the resulting complex mixture. The reaction of *trans*-stilbene with **8** was similarly unrewarded with identifiable products.

Scheme 8



***anti*-20** ***syn*-20**

The sequence of steps shown in Scheme 9 is consistent with the above observations. Metallacycle intermediate **16** results from trapping of benzyne complex **21**. Note that the regioselectivity of insertion is opposite to that observed for alkynes: the bulkier alkene substituent is found adjacent to the metal center. It is not clear whether this difference is the result of stereoelectronic

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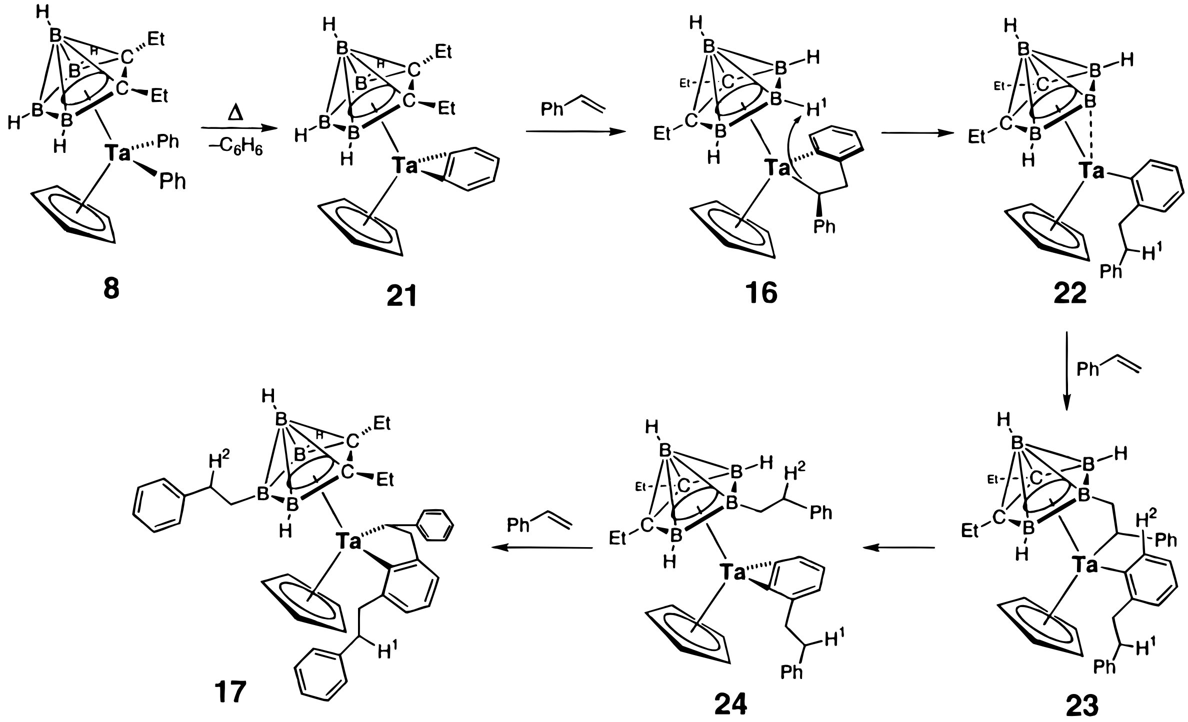
(36) For comparison, the optical rotation of (*S*,*S*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)titanium dichloride is $[\alpha]_{435}^{25} = -3300°$ (Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, *232*, 233−247).

(37) Stockman, K. E.; Garrett, D. L.; Grimes, R. N. *Organometallics* **1995**, *14*, 4661−4667.

(38) An attempted synthesis of the analogous zirconocene complex, $Cp_2Zr(o\text{-}C_6H_4Me)_2$, was reported to give a thermally unstable mixture lacking a substantial amount of the desired compound (Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189−202), although a successful synthesis was later claimed (Chen, S.-S.; Wang, C.-T. *K'o Hsueh T'ung Pao* ***1980***, *25*, 270−271; *Chem. Abstr.* 94: 208952). Zirconocene and titanocene bis(*o*-tolyl) complexes are assumed to undergo rapid elimination to the analogous benzyne (Rausch, M. D.; Mintz, E. A. *J. Organomet. Chem.* **1980**, *190*, 65−72 and references therein). Since neither isomer of **20** provides insertion products analogous to those of the diphenyl complex **8**, as one would expect for a *meta*-substituted aryl complex, we do not believe that *m*-tolyl groups are formed here. However, the characterization data presently in hand do not rule out this possibility.

Scheme 9



factors or the differing steric demand in the approach of alkyne vs alkene to the benzyne intermediate. The first novel step in the reaction mechanism is the proposed cleavage of the newly formed Ta−C bond. We envision an addition of B(5)−H across this bond, giving an intermediate **22** that is stabilized by enhanced interaction of B(5) with the metal center; it is this step that is blocked by the placement of a phenyl group on B(5). Insertion of styrene gives a new proposed metallacycle (**23**), which undergoes a second benzyne-generating C−H activation to give **24**. Note of course that the organic fragment that accepts the H atom is not released but rather remains attached to B(5) as a phenethyl group. Blocking this step with the *o*-tolyl complex **20** would leave the system at the point of intermediate **23**, which can be expected to undergo other types of decomposition reactions. Capture of benzyne **24** with a third equivalent of styrene completes the suggested sequence, giving **17**.

The proposed step of the greatest mechanistic significance in Scheme 9 is the suggested intramolecular insertion of a Ta−C bond into the B(5)−H bond in going from **16** to **22**. Thus, while the carborane fragment usually gives rise to extra stability, it may also provide for additional reactivity by making available alternative reaction pathways. These contrasting themes have emerged in our studies of the olefin polymerization activity of related group 4 metallacarborane systems, as will be reported in due course.

Experimental Section

^{1}H (300 MHz), ^{11}B (115.8 MHz), and ^{13}C (75.5 and 125.3 MHz) NMR spectra were acquired on Nicolet NT-360 and GE QE−300 instruments. Unless otherwise noted, the ^{1}H NMR spectra of all new carborane complexes display ethyl CH_2 signals as doublets of quartets with coupling constants of 15 and 7.5 Hz, and ethyl CH_3 as triplets with $J = 7.5$ Hz. UV-vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Unit resolution mass spectra were obtained on a Finnegan MAT 4600 spectrometer using perfluorotributylamine (FC43) as the calibration standard and chemical ionization using CH_4; both positive- and negative-ion spectra were recorded. The values reported are for the technique that provides the molecular ion as the base peak. In all cases, strong parent ion envelopes were observed. Elemental analyses were obtained in this department on a Perkin-Elmer 2400 CHN analyzer using 2,4-dinitrophenylhydrazone as the calibration standard. Infrared spectra were recorded as thin films on a Nicolet Impact-400 spectrometer. Photolyses were performed in Pyrex flasks using a water-cooled 450-W Hanovia mercury arc lamp at a distance of approximately 15 cm. All solvents were distilled under a dry nitrogen atmosphere from Na/benzophenone. $(Et_2C_2B_4H_4)(C_5H_5)Ta(CH_3)_2$ (**1**) and $(Et_2C_2B_4H_4)(C_5H_5)Ta(C_6H_5)_2$ (**8**) were prepared as previously described.[2] $(Et_2C_2B_4H_4)(Cp)Ta(CD_3)_2$ was prepared by an analogous procedure, starting from 150 mg of $(Et_2C_2B_4H_4)(Cp)TaCl_2$ and 3 equiv of CD_3MgBr in 5 mL of THF for 2 h at room temperature. The complex was purified by filtration through silica gel (CH_2Cl_2 eluant) and isolated in 98% yield. ^{1}H NMR (δ, $CDCl_3$): 6.03 (s, 5H), 2.81 (m, 4H), 1.30 (t, 6H). MS: *m/z* 412. All other reagents were purchased and used as received. Unless otherwise indicated, reactions and purifications were performed in air.

Reactions of Alkynes with 1. $(Et_2C_2B_4H_4)(Cp)Ta(CH_3)[(CH_3)C{=}C(CH_3)_2]$ (2). Under an argon atmosphere, a solution of complex **1** (100 mg, 0.247 mmol) in 5 mL of benzene was treated with dry, degassed 2-butyne (133 mg, 2.5 mmol) via syringe. With constant stirring, the reaction flask was irradiated for 6 h, causing a color change to dark red-brown. The volatiles were removed in vacuo, and the solid residue was dissolved in hexane (in air atmosphere) and immediately filtered through a Celite plug. Evaporation of the solvent gave **2** as a reddish oil (43 mg, 38% yield). A dark yellow solid remaining on the frit could not be characterized. NMR analysis of **2** revealed the presence of two stereoisomers. For the major isomer: ^{1}H NMR (δ, C_6D_6) 5.11 (s, C_5H_5), 2.53, 2.26 (m, m, 2H, 2H, carborane ethyl CH_2), 1.82 (s, 3H, vinylic C−*Me*), 1.74 (s, 3H, vinylic C−*Me*), 1.18 and 0.90 (t, t, 3H, 3H, carborane ethyl CH_3), 0.03 (s, 3H, vinylic C−*Me* (agostic)),

−0.22 (s, 3H, Ta−*Me*); ^{13}C NMR (δ, C_6D_6) 129.3 (vinyl), 125.6 (vinyl), 106.1 (Cp), 29.4 (vinylic C−*Me*), 25.5 (vinylic C−*Me*), 24.8, 24.1 (carborane ethyl C*H*$_2$), 19.7 (vinylic C−*Me* (agostic)), 17.0, 15.9 (carborane ethyl C*H*$_3$), 10.4 ($^1J_{CH}$ = 146 Hz, Ta−*Me*). For the minor isomer: ^{1}H NMR (δ, $CDCl_3$) 5.11 (s, 5H, C_5H_5), 2.47, 2.01 (m, m, 2H, 2H, carborane ethyl C*H*$_2$), 2.22 (s, 3H, vinylic C−*Me*), 1.97 (s, 3H, vinylic C−*Me*), 1.004 and 0.997 (t, t, 3H, 3H, carborane ethyl C*H*$_3$), 0.09 (s, 3H, vinylic C−*Me* (agostic)), −0.24 (s, 3H, Ta−*Me*); ^{13}C NMR (δ, $CDCl_3$) 129.0 (vinyl), 127.3 (vinyl), 108.7 (Cp), 30.3 (vinylic C−*Me*), 27.5 (vinylic C−*Me*), 25.4, 23.6 (carborane ethyl C*H*$_2$), 20.3 (vinylic C−*Me* (agostic)), 19.2, 16.8 (carborane ethyl C*H*$_3$), 10.9 (Ta−*Me*). For the mixture of isomers: ^{11}B NMR (δ, $CDCl_3$) 3.5 (1B, d, *J* = 146 Hz), −1.1 (1B, d, *J* = 146 Hz), −13.5 (1B, d, *J* = 132 Hz), −16.8 (1B, d, *J* = 161 Hz); IR (CH_2Cl_2, cm^{-1}): 2961 (w), 2917 (w), 2875 (w), 2525 (w, B(H)), 2324 (w), 1517 (w), 1362 (w), 817 (w); UV−vis (CH_2Cl_2, nm) 406 (25%), 348 (44%), 300 (100%); MS (negative ion), *m*/*z* 458. Anal. Calcd for $TaC_{17}B_4H_{31}$: C, 44.42; H, 6.80. Found: C, 44.13; H, 6.92.

$(Et_2C_2B_4H_4)(Cp)Ta(CD_3)[(CH_3)C{=}C(CD_3)(CH_3)]$ (2-*d*$_6$). Reaction of $(Et_2C_2B_4H_4)(Cp)Ta(CD_3)_2$ (100 mg) and 5 equiv of 2-butyne by the above procedure provided **2**-*d*$_6$ in 37% yield. For the major isomer: ^{1}H NMR (δ, C_6D_6) 5.11 (s, 5H), 2.53, 2.26 (m, m, 2H, 2H), 1.82 (s, 3H), 1.74 (s, 3H), 1.18 and 0.90 (t, t, 3H, 3H). For the minor isomer: ^{1}H NMR (δ, C_6D_6) 5.11 (s, 5H), 2.47, 2.01 (m, m, 2H, 2H), 2.22 (s, 3H), 1.97 (s, 3H), 1.004 and 0.997 (t, t, 3H, 3H). For the mixture of isomers: MS (negative ion), *m*/*z* 464.

$(Et_2C_2B_4H_4)(Cp)Ta(CH_3)[(Et)C{=}C(Et)(CH_3)]$ (3). The above procedure with 10 equiv of 3-hexyne (202 mg) provided **3** as a red oil in 43% yield (52 mg). Filtration of a hexane solution of this material through a 1 cm alumina plug and removal of the solvent gave 50 mg of a dark orange solid. ^{1}H NMR (δ, $CDCl_3$): 5.49 (s, 5H, C_5H_5), 2.46 (m, 2H), 2.32 (q, *J* = 6.6 Hz, 4H), 2.16 (m, 2H), 1.22, 1.14, 1.04, 0.99 (each t, *J* = 7.8 Hz, each 3H), −0.23 (s, 3H, Ta−C═C*Me*), −0.53 (s, 3H, Ta−Me). ^{13}C NMR (δ, $CDCl_3$): 127.0, 126.9, 105.9 (Cp), 27.6, 25.9, 25.6, 25.0, 24.3, 17.0, 16.8, 16.0, 15.9, 10.8. ^{11}B NMR (δ, $CDCl_3$): 2.9 (1B, d, *J* = 147 Hz), −0.8 (1B, d, *J* = 147 Hz), −13.7 (1B, d, *J* = 132 Hz), −18.1 (1B, d, *J* = 160 Hz). IR (CH_2Cl_2, cm^{-1}): 2959 (s), 2930 (s), 2875 (s), 2576 (s, B(H)), 2344 (w), 1497 (w), 1378 (w), 821 (w). UV−vis (CH_2Cl_2, nm): 404 (100%), 346 (33%), 302 (83%). MS: *m*/*z* 487. Anal. Calcd for $TaC_{19}H_{35}B_4$: C, 46.80; H, 7.23. Found: C, 46.25; H, 7.48.

$(Et_2C_2B_4H_4)(Cp)Ta(CH_3)[(Ph)C{=}C(Ph)(CH_3)]$ (4). The above procedure with 5 equiv of diphenylacetylene (220 mg) provided **4** as a dark red oil in 34% yield (40 mg), following elution through a 25-cm column of neutral alumina using 4:1 pentane:CH_2Cl_2. The reaction was also conducted with 1 equiv of diphenylacetylene in a minimum volume of benzene solution (approximately 1 mL). Photolysis for 10 h was followed by removal of the volatiles in vacuo and purification of the residue by passage through a short alumina plug in hexane solution to give a 41% yield (49 mg) of **4**. ^{1}H NMR (δ, C_6D_6): 7.33 (d, *J* = 3.9 Hz, 2H), 7.22 (t, *J* = 2.1 Hz, 1H), 7.13 (t, *J* = 3.9 Hz, 2H), 7.10 (t, *J* = 3.9 Hz, 2H), 6.95 (d, *J* = 3.9 Hz, 2H), 6.85 (t, *J* = 2.1 Hz, 1H), 5.47 (s, 5H), 2.55 (m, 2H), 2.32 (m, 2H), 1.22 (t, 3H), 0.96 (t, 3H), 0.14 (s, 3H, Ta−C═C*Me*), −0.10 (s, 3H, Ta−*Me*). ^{13}C NMR (δ, C_6D_6): 143.2, 141.5, 132.2, 128.8, 126.6, 126.3, 108.0 (Cp), 30.2 (Ta−*Me*), 24.7, 24.4, 16.9, 15.9, 14.0 (Ta−C═C*Me*). ^{11}B NMR (δ, $CDCl_3$): 4.2 (1B, d, *J* = 146 Hz), −1.3 (1B, d, *J* = 146 Hz), −11.4 (1B, d, *J* = 131 Hz), −15.1 (1B, d, *J* = 160 Hz). IR (cm^{-1}, CH_2Cl_2): 3075 (s), 2943 (s), 2800 (m), 2543 (B(H), s), 2312 (w), 1610 (w), 1436 (w), 875 (w). UV−vis (nm, CH_2Cl_2): 425 (100%), 330 (45%), 290 (11%). MS (negative ion), *m*/*z* 583. Anal. Calcd for $TaC_{27}H_{35}B_4$: C, 55.55; H 6.04. Found: C, 54.33; H, 6.23.

$(Et_2C_2B_4H_4)(Cp)Ta(CD_3)[(Ph)C{=}C(Ph)(CD_3)]$ (4-*d*$_6$). The standard procedure, using $(Et_2C_2B_4H_4)(Cp)Ta(CD_3)_2$ (100 mg) and 5 equiv of diphenylacetylene, afforded **4**-*d*$_6$ in 41% yield (59 mg) as a red oil. ^{1}H NMR (δ, C_6D_6): 7.33 (d, *J* = 3.9 Hz, 2H), 7.22 (t, *J* = 2.1 Hz, 1H), 7.13 (t, *J* = 3.9 Hz, 2H), 7.10 (t, *J* = 3.9 Hz, 2H), 6.95 (d, *J* = 3.9 Hz, 2H), 6.85 (t, *J* = 2.1 Hz, 1H), 5.47 (s, Cp), 2.55 (m, 2H), 2.32 (m, 2H), 1.22 (t, 3H), 0.96 (t, 3H). MS (negative ion) *m*/*z* 590.

Decomposition of Alkyne Adducts 2−4. $Et_2Me_2C_4B_4H_4$ (5). Complex **2** (100 mg, 0.22 mmol) was dissolved in 5 mL of methylene chloride and allowed to stir in air for 72 h. The solution was filtered through a 3-cm plug of silica, and the volatiles were removed in vacuo to give **5** as a clear oil (12 mg, 30% yield), showing NMR data that match the reported values[21] and an appropriate mass spectrum. ^{1}H NMR (δ, C_6D_6): 2.30 (m, 4H), 1.88 (s, 6H), 1.02 (t, 6H). ^{11}B NMR (δ, C_6D_6): −11.1 (d, 2B), −12.5 (d, 1B), −12.9 (d, 1B). MS: *m*/*z* 184.

$Et_4C_4B_4H_4$ (6). The above procedure was applied to 100 mg of complex **3**, (36 h reaction time), providing **6** as a clear oil (14 mg, 32%), with the expected[21] NMR spectrum. ^{1}H NMR (δ, $CDCl_3$): 2.52, 2.35 (m, 8H), 1.10 (t, 12H). MS: *m*/*z* 212.

$Et_2Ph_2C_4B_4H_4$ (7). The above procedure was applied to 100 mg of complex **4**, (24 h reaction time). The reaction mixture was filtered through a 3-cm plug of Celite and then purified by preparative TLC (silica; 4:1 hexane:CH_2Cl_2). The second (major) band proved to be **7**, isolated as a clear oil in 36% yield (19 mg). ^{1}H NMR (δ, $CDCl_3$): 7.20 (m, 4H), 7.08 (m, 2H), 7.05 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 1H), 2.63 (m, 2H), 2.52 (m, 2H), 1.19 (t, 6H). ^{13}C NMR (δ, $CDCl_3$): 139.1, 131.5, 128.3, 128.2, 128.1, 128.0, 127.7, 127.1, 25.2, 13.6. MS: *m*/*z* 307.

Reactions of Alkynes with 8 (See Scheme 4 for Yields of Isolated Products). $(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(HCC(C_6H_5))$ (9a and 9b). A mixture of **8** (100 mg, 0.189 mmol) and phenylacetylene (96 mg, 0.94 mmol, 5 equiv) was heated at reflux in 2 mL of benzene for 12 h, causing a slow color change to dark brown. After removal of the solvent, the residue was freed of phenylacetylene by hexane elution through a 3-cm plug of silica. When all the phenylacetylene was eluted (TLC), the plug was washed with CH_2Cl_2 until free of colored material. Removal of the solvent affords a clean mixture of **9a** and **9b**. The two isomers can be separated on a 25-cm silica column eluting with 8:1 hexane:CH_2Cl_2. For **9a**: ^{1}H NMR (δ, $CDCl_3$) 7.38 (m, 6H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 2H), 6.19 (s, 5H), 3.18 (m, 1H), 2.86 (m, 2H), 2.62 (m, 1H), 1.24 (t, 3H), 1.13 (t, 3H); ^{13}C NMR (δ, $CDCl_3$) 144.5, 136.2, 133.4, 132.3, 131.2, 129.3, 129.1, 128.8, 128.7, 124.7, 122.7, 111.6, 109.8 (Cp), 24.8, 24.2, 14.8, 14.3; ^{11}B NMR (δ, $CDCl_3$) 40.2 (1B, d, *J* = 122 Hz), 28.7 (1B, d, *J* = 104 Hz), 25.5 (1B, d, *J* = 133 Hz), 0.4 (1B, d, *J* = 118 Hz); IR (CH_2Cl_2, cm^{-1}) 3087 (w), 2968 (m), 2924 (m), 2885 (w), 2563 (B(H), s), 1565 (w), 1472 (m), 1380 (w), 1257 (w), 1033 (m), 834 (s), 750 (s), 721 (s); UV−vis (CH_2Cl_2, nm) 240 (100%), 272 (77%), 333 (43%), 414 (5%); MS *m*/*z* 554. Anal. Calcd for $TaC_{25}H_{29}B_4$: C, 54.23; H, 5.28. Found: C, 54.62; H, 5.76. For **9b**: ^{1}H NMR (δ, $CDCl_3$) 7.37 (m, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.28 (m, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.84 (t, *J* = 7.8 Hz, 2H), 6.13 (s, 5H), 2.47 (m, 1H), 2.34 (m, 1H), 2.02 (m, 1H), 1.85 (m, 1H), 1.22 (t, 3H), 1.06 (t, 3H); ^{13}C NMR (δ, $CDCl_3$) 145.3, 136.5, 128.1, 127.9, 127.6, 127.5, 127.2, 126.9, 126.8, 126.5, 124.6, 115.6, 109.3 (Cp), 24.3, 24.1, 14.6, 14.1; ^{11}B NMR (δ, $CDCl_3$) 39.6 (1B, d, *J* = 124 Hz), 29.8 (1B, d, *J* = 100 Hz), 23.4 (1B, d, *J* = 124 Hz), −0.2 (1B, d, *J* = 124 Hz); IR (CH_2Cl_2, cm^{-1}) 3043 (w), 2968 (m), 2924 (m), 2874 (w), 2571 (B(H), s), 1596 (w), 1489 (m), 1445 (m), 1382 (w), 1262 (w), 1011 (w), 834 (s), 765 (s), 721 (s), 696 (m); UV−vis (CH_2Cl_2, nm) 242 (100%), 276 (82%), 328 (42%), 348 (36%), 404 (7%); MS *m*/*z* 554. Anal. Calcd for $TaC_{25}H_{29}B_4$: C, 54.23; H, 5.28. Found: C, 54.21; H, 5.70.

Enantiomeric resolution of **9b** was accomplished in 0.5−1.0 mg aliquots on a Chiralcel OD-H analytical HPLC column (Chiral Technologies, Inc.), elution with 2% 2-propanol in hexane at 1.0 mL/min (retention times, isomer 1 = 7.0 min; isomer 2 = 8.6 min). Approximately 6 mg of each pure enantiomer was isolated; the enantiomeric purity of each was verified by HPLC analysis on the same column. Circular dichroism measurements (Figure 2; Jasco J-720 spectropolarimeter) were performed on 2.7 mM solutions of each enantiomer in cyclohexane at 24 °C, in a cell of 1 mm path length.

$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(C_6H_5)CC(CH_3))$ (10a and 10b). The above procedure was performed with **8** (100 mg) and 1-phenyl-1-propyne (109 mg, 0.95 mmol, 5 equiv). Direct column chromatography of the crude product residue (25-cm silica; 4:1 hexane:CH_2Cl_2) provided **10b** (the major product) as a brown-red solid and **10a** (the minor product) as a dark green solid. X-ray quality crystals of **10b** were obtained by slow diffusion of hexane into a diethyl ether solution at −20 °C. For **10a**: ^1H NMR (*δ*, $CDCl_3$) 7.36 (m, 1H), 7.33 (m, 1H), 7.28 (d, *J* = 6.8 Hz, 2H), 7.21 (t, *J* = 6.8 Hz, 2H), 7.06 (m, 2H), 6.51 (m, 1H), 6.05 (s, 5H), 2.30 (m, 2H), 1.97 (m, 2H), 1.99 (s, 3H), 1.19 (t, 3H), 1.13 (t, 3H); ^{13}C NMR (*δ*, $CDCl_3$) 146.1, 135.3, 134.7, 130.4, 129.4, 128.1, 127.5, 126.2, 126.1, 125.2, 121.0, 110.6 (Cp), 24.5, 23.9, 18.9, 14.5, 14.1; ^{11}B NMR (*δ*, $CDCl_3$) 41.2 (1B, d, 130 Hz), 31.9 (1B, d, 133 Hz), 23.6 (1B, d, 165 Hz), 1.9 (1B, d, 104 Hz); IR (CH_2Cl_2, cm^{-1}) 3238 (s), 2968 (s), 2930 (s), 2880 (w), 2565 (B(H), s), 2263 (w), 1678 (s), 1602 (m), 1464 (s), 1268 (s), 1199 (w), 1092 (s), 1023 (s), 841 (s), 740 (s); UV−vis (CH_2Cl_2, nm) 234 (100%), 250 (88%), 316 (25%), 410 (5%); MS *m*/*z* 568. Anal. Calcd for $TaC_{26}H_{31}B_4$: C, 55.00; H, 5.59. Found: C, 54.57; H, 5.78. For **10b**: ^1H NMR (*δ*, $CDCl_3$) 7.44 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 10.7 Hz, 1H), 6.94 (t, *J* = 6.8 Hz, 2H), 6.81 (t, *J* = 6.8 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.52 (d, *J* = 6.8 Hz, 2H), 6.27 (s, 5H), 2.41 (m, 1H), 2.36 (m, 2H), 2.01 (m, 1H), 1.81 (s, 3H), 1.22 (t, 3H), 1.20 (t, 3H); ^{13}C NMR (*δ*, $CDCl_3$) 141.1, 135.4, 130.0, 129.4, 128.4, 128.1, 128.0, 127.5, 126.3, 125.9, 125.1, 122.3, 109.9 (Cp), 24.8, 24.2, 24.0, 14.5, 14.4; ^{11}B NMR (*δ*, $CDCl_3$) 39.9 (1B, d, *J* = 122 Hz), 31.8 (1B, d, *J* = 100 Hz), 24.1 (1B, d, *J* = 111 Hz), −1.3 (1B, d, *J* = 151 Hz); UV−vis (CH_2Cl_2, nm) 234 (100%), 250 (95%), 312 (24%), 394 (7%); IR (CH_2Cl_2, cm^{-1}) 3232 (m), 2968 (m), 2930 (m), 2880 (w), 2559 (B(H), s), 1376 (s), 1073 (w), 1017 (w), 841 (s), 734 (s), 702 (s); MS *m*/*z* 568. Anal. Calcd for $TaC_{26}H_{31}B_4$: C, 55.00; H, 5.59. Found: C, 54.65; H, 5.27.

$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(C_6H_5)CC(C_6H_5)$ (11). The above procedure was performed with **8** (100 mg) and diphenylacetylene (168 mg, 0.95 mmol, 5 equiv), the color of the reaction mixture changing from deep yellow to dark green. Workup as for **9a**/**b** provided **11** as a dark green oil. ^1H NMR (*δ*, $CDCl_3$): 7.20 (m, 1H), 7.14 (m, 1H), 7.10 (t, *J* = 6.8 Hz, 1H), 7.06 (t, *J* = 5.8 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.86 (t, *J* = 7.8 Hz, 2H), 6.83 (t, *J* = 6.8 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.13 (s, 5H), 2.41 (m, 1H), 2.36 (m, 1H), 2.02 (M, 1H), 1.91 (M, 1H), 1.23 (t, 3H), 1.18 (t, 3H). ^{13}C NMR (*δ*, $CDCl_3$): 145.8, 141.2, 135.7, 135.0, 134.99, 131.4, 131.2, 131.1, 129.9, 128.3, 127.6, 127.0, 126.2, 125.9, 124.8, 123.6, 110.7 (Cp), 24.3, 24.0, 14.6, 14.3. ^{11}B NMR (*δ*, $CDCl_3$): 42.6 (1B, d, *J* = 95 Hz), 32.6 (1B, d, *J* = 107 Hz), 24.3 (1B, d, *J* = 132 Hz), −0.6 Hz (1B, d, *J* = 112 Hz). IR (CH_2Cl_2, cm^{-1}): 3062 (w), 2968 (m), 2924 (m), 2867 (w), 2565 (s, B(H)), 1596 (w), 1439 (m), 1375 (w), 1262 (w), 734 (s), 834 (s), 708 (s). UV−vis (CH_2Cl_2, nm): 234 (100%), 252 (91%), 324 (38%). MS: *m*/*z* 629. Anal. Calcd for $TaC_{31}H_{33}B_4$: C, 59.11; H, 5.28. Found: C, 59.03; H, 5.44.

$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(C_2H_5)CC(C_2H_5))$ (12). The above procedure was performed with 50 mg of **8** and 10 equiv of 3-hexyne, heating for 24 h. The reaction solution changed to a dark green color after several hours. The green-brown oily residue remaining after removal of the solvent was purfied by column chromatography (silica, 25 cm, CH_2Cl_2 eluent) to give **12** as a brown-green oil. ^1H NMR (*δ*, $CDCl_3$): 7.22 (d, *J* = 7.8 Hz, 1H), 6.94 (m, *J* = 7.8 Hz, 2H), 6.44 (d, *J* = 7.8 Hz, 1H), 6.24 (s, 5H), 2.92 (m, 1H), 2.28 (m, 1H), 2.14 (m, 1H), 1.84 (m, 1H), 2.39 (q, *J* = 7.8 Hz, 4H), 1.17 (t, 3H), 1.16 (t, 3H), 1.12 (m, 3H), 1.08 (m, 3H). ^{13}C NMR (*δ*, $CDCl_3$): 143.7, 137.8, 137.3, 128.1, 127.9, 124.5, 122.7, 108.7 (Cp), 24.1, 23.7, 23.5, 23.1, 14.9, 14.3, 15.3, 15.1. ^{11}B NMR (*δ*, $CDCl_3$): 42.4 (1B, d, *J* = 118 Hz), 27.6 (1B, d, *J* = 108 Hz). UV−vis ($CDCl_3$, nm): 234 (96%), 254 (100%), 314 (24%). MS: *m*/*z* 535. Anal. Calcd for $TaC_{23}H_{33}B_4$: C, 51.76; H, 6.23. Found: C, 52.54; H, 6.01. Although the microanalytical data is not satisfactory, as occasionally happens for oils of this type, the identity of the compound is not in doubt and the NMR spectra show no impurities.

$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4(HC{=}CSi(CH_3)_3))$ (13). The above procedure was performed with 30 mg **8** and 8 equiv of (trimethylsilyl)acetylene, heating for 16 h. A color change to red-orange occurred over the first several hours. Purification of the crude product by filtration through a 3-cm plug of alumina provided **13** as an orange-yellow solid. ^1H NMR (*δ*, C_6D_6): 7.48 (s, 1H, C═C*H*), 6.98 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 5.70 (s, 5H), 2.28 (m, 2H), 2.14 (m, 2H), 1.23 (t, 3H), 1.12 (t, 3H), 0.28 (s, 9H). ^1H NMR (*δ*, $CDCl_3$): 7.36 (s, 1H, C═C*H*), 7.03 (t, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.14 (s, 5H), 2.36 (m, 1H), 2.24 (m, 1H), 2.21 (m, 1H), 1.88 (m, 1H), 1.184 (t, 3H), 1.176 (t, 3H), 0.18 (s, 9H). ^{13}C NMR (*δ*, $CDCl_3$): 136.6, 128.1, 127.7, 127.6, 126.7, 126.5, 126.4, 126.0, 109.1 (Cp), 24.2, 24.0, 14.5, 13.9, 1.51. IR (cm^{-1}, CH_2Cl_2): 3128 (w), 3052 (w), 2962 (m), 2933 (m), 2895 (m), 2871 (w), 25557 (B(H), s), 1494 (w), 1456 (w), 1437 (w), 1243 (m), 1017 (w), 891 (s), 822 (s), 752 (m), 721 (m). UV−vis (nm, CH_2Cl_2): 247 (100%), 272 (79%), 322 (51%), 350 (33%), 406 (6%). MS: *m*/*z* 549. Anal. Calcd for $TaC_{22}H_{33}B_4Si$: C, 48.06; H, 6.05. Found: C, 47.68; H, 6.12.

$(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4)((C_6H_5)CCCC(C_6H_5))$ (14) and $[(Et_2C_2B_4H_4)(Cp)Ta(C_6H_4)]_2((C_6H_5)CCCC(C_6H_5))$ (15). The standard procedure with 100 mg of **8** and 18 mg of 1,4-diphenylbutadiyne (0.5 equiv) was performed under a nitrogen atmosphere in degassed benzene. Evaporation of volatiles and chromatography as for **10** provided **14** as the major product (46% yield; 52% based on recovered starting material) and 6 mg of **15**. Complex **14** (20 mg, 0.018 mmol) was treated with 10 equiv of complex **8** in C_6D_6 solution and heated to 80 °C for 22 h, until all of **8** was consumed. NMR analysis showed the appearance of approximately 8% of **15** relative to the amount of **14** used, measured against the residual benzene signal as an internal standard. For **14**: ^1H NMR (*δ*, $CDCl_3$) 7.92 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 6.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.13 (m, 4H), 6.13 (s, 5H), 2.39 (m, 2H), 2.04 (m, 1H), 1.92 (m, 1H), 1.18 (t, 3H), 1.14 (t, 3H); ^{13}C NMR (*δ*, $CDCl_3$) 144.5, 139.8, 132.9, 131.8, 130.7, 128.8, 128.6, 128.2, 124.2, 122.3, 24.8, 24.2, 14.8, 14.3. For **15**: ^1H NMR (*δ*, $CDCl_3$) 8.02 (d, *J* = 7.8 Hz, 4H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.73 (d, *J* = 6.8 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 2H), 7.50 (t, *J* = 6.8 Hz, 4H), 7.42 (t, *J* = 6.8 Hz, 4H), 7.24 (t, *J* = 5.8 Hz, 2H), 5.41 (s, 10H), 1.58 (m, 4H), 1.39 (m, 4H), 0.78 (t, 6H), 0.69 (t, 6H); ^{13}C NMR (*δ*, $CDCl_3$) 146.4, 1141.8, 139.9, 138.3, 133.6, 129.1, 128.7, 128.6, 128.5, 126.0, 125.8, 123.7, 102.8 (Cp), 24.3, 21.0, 15.2, 14.4. Anal. Calcd for $Ta_2C_{50}H_{56}B_8$: C, 54.32; H, 5.11. Found: C, 54.43; H, 5.49.

Reactions of Alkyne Insertion Products with Electrophiles. Protonolysis of 11. Complex **11** (100 mg, 0.16 mmol) in diethyl ether was treated under a nitrogen atmosphere with HBF_4 (85% solution in ether, 64 mg, 2.1 equiv) by syringe with stirring at room temperature. After 12 h, the volatiles were removed and the oily residue was dissolved in CH_2Cl_2 and allowed to stir for 15 min before being flushed through a 3-cm plug of silica gel. The resulting material was purified by preparative TLC (4:1 hexane: CH_2Cl_2); the least polar band gave triphenylethylene as a white solid in 73% yield, with ^1H and ^{13}C NMR data matching the published spectra (Aldrich). ^1H NMR (*δ*, $CDCl_3$): 7.32 (m, 8H), 7.21 (m, 2H), 7.12 (m, 3H), 7.04 (m, 2H), 6.97 (s, 1H). ^{13}C NMR (*δ*, $CDCl_3$): 143.3, 142.5, 140.2, 137.3, 130.3, 129.5, 128.11, 127.9, 127.5, 127.4, 127.3, 126.6. MS: *m/z* 256. Analogous treatment of a THF solution of **11** in air with concentrated HCl (5 equiv) caused a color change from dark green to orange over several hours. Basic workup and ether extraction afforded several organometallic species, the dominant one identified as $(Et_2C_2B_4H_4)(Cp)TaCl_2$ by comparison with an authentic sample. Chromatography provided triphenylethylene in 63% yield.

Protonolysis of 9b. Complex **9b** (75 mg, 0.135 mmol) in 5 mL of diethyl ether was treated with 5 equiv of concentrated HCl dropwise with stirring, causing an immediate color change to yellow-orange. Basic workup (5% $NaHCO_3$), ether extraction, drying ($MgSO_4$), and evaporation provided a clear oil. The oil was purified by vacuum transfer at ambient temperature (10^{-5} Torr) into a trap at −30 °C, giving 16 mg (64%) of 1,1-diphenylethylene, identified by comparison to an authentic sample (Aldrich). ^1H NMR (δ, $CDCl_3$): 7.30 (m, 10H), 5.44 (s, 2H). ^{13}C NMR (δ, $CDCl_3$): 150.1, 141.7, 128.0, 127.9, 127.6, 114.3. The remaining nonvolatile residue was flushed through a silica plug with methylene chloride to give $(Et_2C_2B_4H_4)(C_5H_5)TaCl_2$ in a 38% yield.

Reaction of 11 with 2,6-Dimethylphenyl Isocyanide. Complex **11** (100 mg, 0.16 mmol) in 2 mL of toluene was treated with 2,6-dimethylphenylisocyanide (21 mg, 0.16 mmol) in air. Over the course of 12 h at room temperature, the color changed from dark green to dark brown. The volatiles were removed in vacuo and the resulting residue was purified by preparative TLC (alumina, 3:1 hexane:CH_2Cl_2). The dominant fraction was the third one, which provided 2,6-dimethylphenlimino-2,3-diphenylindenone as an orange crystalline powder in 72% yield, identified by the following data and by reaction with aqueous HCl (below). A similar yield and faster reaction time (3 h) was observed when 10 equiv of isocyanide was used. ^1H NMR (δ, $CDCl_3$): 7.36 (m, 1H), 7.28 (m, 1H), 7.22 (m, 1H), 7.20 (t, $J = 7.8$ Hz, 1H), 7.09 (d, $J = 6.8$ Hz, 2H), 7.02 (d, $J = 6.8$ Hz, 2H), 7.01 (t, $J = 6.8$ Hz, 2H), 6.92 (t, $J = 6.8$ Hz, 2H), 6.42 (d, $J = 7.8$ Hz, 1H), 2.07 (s, 6H). ^{13}C NMR (δ, $CDCl_3$): 166.3 (C═N), 149.5, 148.2, 144.6, 136.3, 133.5, 132.7, 130.9, 130.8, 129.1, 128.9, 128.4, 128.2, 128.0, 127.8, 127.7, 127.5, 127.2, 124.3, 123.3, 120.6, 18.4. IR (CH_2Cl_2, cm^{-1}): 3064 (m), 2921 (s), 2652 (m), 2561 (w), 1637 (s), 1591 (s), 1457 (s), 1359 (s), 1208 (s), 1091 (s), 755 (s), 699 (s). MS: *m/z* 385. Mp: 198−199 °C. Anal. Calcd for $C_{29}H_{23}N$: C, 90.35; H, 6.02; N, 3.64. Found: C, 90.62; H, 6.00; N, 4.42. A solution of the imino−indenone (50 mg) in 1 mL of methanol was treated with 5 equiv of concentrated HCl with stirring, causing an immediate color change from yellow-orange to dark red-orange. The residue remaining after evaporation of the solvent was extracted with ether and dried ($MgSO_4$) to yield a dark red solid identified as 2,3-diphenyl-1-indenone (93% yield) by the observation of identical ^1H NMR, mass spectrometry, and melting point data to reported values (Aldrich).

Reaction of 8 with Styrene. $(Et_2C_2B_4H_4)(Cp)Ta(C(C_6H_5)HCH_2C_6H_4)$ (16). A mixture of **8** (100 mg, 0.19 mmol) and styrene (197 mg, 1.9 mmol) in 5 mL of benzene was heated to reflux for 16 h in air. Evaporation of solvent and chromatography of the resulting residue (silica, 4:1 hexane:CH_2Cl_2) provides **16** as a dark red solid in 68% yield. **16** is somewhat air-sensitive in the solid form and decomposes into many products upon standing for 12 h; in solution, the material is somewhat more stable. ^1H NMR (δ, $CDCl_3$): 7.28 (m, 2H), 7.08 (t, $J = 7.8$ Hz, 2H), 6.99 (m, 3H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 5.87 (s, 5H), 5.38 (m, 1H), 4.05 (m, 1H), 3.14 (m, 1H), 2.35 (m, 2H), 1.36 (t, 3H), 1.17 (t, 3H). ^{13}C NMR (δ, $CDCl_3$): 150.3, 145.9, 136.8, 130.1, 130.0, 127.9, 127.6, 126.5, 126.2, 123.8, 110.6 (Cp), 67.2, 32.7, 24.4, 23.9, 14.4. MS: *m/z* = 555.

$(Et_2C_2B_4H_3CH_2CH_2Ph)(Cp)Ta[C(Ph)(H)CH_2C_6H_3(CH_2CH_2Ph)]$ (17). A solution of **16** (100 mg, 0.18 mmol) in 2 mL of benzene was heated at 85 °C for 62 h, causing a slow color change to dark red-brown. Purification by preparative TLC (silica, 8:1 hexane:CH_2Cl_2) provided **17** as the main product (91 mg, 0.119 mmol, 66%) as a red-orange solid. X-ray quality crystals were obtained by slow evaporation of a saturated toluene solution at room temperature. ^1H NMR (δ, $CDCl_3$): 7.23 (m, 5H), 7.13 (m, 3H), 7.03 (m, 3H), 6.72 (m, 4H), 5.72 (s, 5H), 3.95 (m, 2H), 3.56 (m, 2H), 2.93 (m, 2H), 2.86 (m, 1H), 2.60 (m, 2H), 2.33 (m, 1H), 2.08 (m, 2H), 1.64 (m, 4H), 1.30 (t, 3H), 0.95 (t, 3H). MS: *m/z* 764. Anal. Calcd for $C_{41}H_{47}B_4Ta$: C, 64.46; H, 6.20. Found: C, 64.12; H, 6.71.

$(Et_2C_2B_4H_4)(Cp)Ta(C(C_6D_5)DCD_2C_6H_4)$ (16-d_8) and $(Et_2C_2B_4H_3CD_2CHDC_6D_5)(Cp)Ta[C(C_6D_5)(D)CD_2C_6H_3(CD_2CHDPh)]$ (17-d_{24}). Complex **8** (50 mg, 0.95 mmol) and 8 equiv of styrene-d_8 were sealed in a C_6D_6 solution in an NMR tube. After 16 h of heating at 85 °C, NMR analysis revealed almost total conversion of **8** to **16**-d_8. ^1H NMR (δ, C_6D_6): 7.02 (t, $J = 7.3$ Hz, 1H), 6.91 (t, $J = 7.3$ Hz, 1H), 6.71 (d, $J = 7.4$ Hz, 1H), 6.54 (d, $J = 7.3$ Hz, 1H), 5.43 (s, 5H), 2.31 (m, 2H), 2.18 (m, 2H), 1.33 (t, 3H), 1.11 (t, 3H). ^1H NMR (δ, $CDCl_3$): 7.08 (t, $J = 7.3$ Hz, 1H), 6.96 (t, $J = 7.3$ Hz, 1H), 6.82 (d, $J = 7.4$ Hz, 1H), 6.66 (d, $J = 7.3$ Hz, 1H), 5.86 (s, 5H), 2.42 (m, 2H), 2.30 (m, 2H), 1.34 (t, 3H), 1.16 (t, 3H). ^{11}B NMR (δ, C_6D_6): 39.4 (1B, s), 31.7 (1B, bs), 25.3 (1B, bs), 3.4 (1B, bs). MS: *m/z* 563. Additional heating results in partial conversion in 16 h and complete conversion in 36 h to **17**-d_{24}. After 48 h, the latter compound was purified by preparative TLC (4:1 hexane:CH_2Cl_2). ^1H NMR (δ, $CDCl_3$): 7.26 (d, $J = 7.2$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 7.3$ Hz, 1H), 5.72 (s, 5H), 2.86 (m, 1H), 2.60 (m, 2H), 2.33 (m, 1H), 1.64 (bs, 2H, CDH−CH_2), 1.30 (t, 3H), 0.95 (t, 3H). ^{11}B NMR (δ, C_6D_6): 47.6 (1B, s), 24.5 (1B, bs), 2.4 (1B, bs), −3.4 (1B, bs). MS: *m/z* 788.

$(Et_2C_2B_4H_3Ph)(Cp)TaPh_2$ (18). $(Et_2C_2B_4H_3Br)(Cp)TaCl_2$ was prepared by treatment of a CH_2Cl_2 solution of $(Et_2C_2B_4H_4)(Cp)TaCl_2$ with 3 equiv of *N*-bromosuccinimide at room temperature for 1 h.[37] Removal of volatiles and filtration of a hexane suspension of the residue provides the B(5)-brominated product in quantitative yield. A toluene solution of $(Et_2C_2B_4H_3Br)(Cp)TaCl_2$ (100 mg, 0.19 mmol) was treated under argon atmosphere with 15 equiv of 3.0 M PhMgBr, causing an immediate color change to dark red. Over the course of several hours at room temperature, the color changed to dark green. The volatiles were removed by evaporation, and the residue was stirred in CH_2Cl_2 for several minutes. The solution was filtered through a plug of silica gel, and the volatiles were removed to give a yellow oil. The crude product was freed of biphenyl by flash chromatography through a 5-cm column of silica gel, followed by elution of complex **18** with CH_2Cl_2. Evaporation of solvent yields **18** as a yellow solid in 95% yield. A repeat silica filtration to remove biphenyl was occasionally required for reactions performed on larger scale. ^1H NMR (δ, $CDCl_3$): 7.75 (d, $J = 6.8$ Hz, 1H), 7.41 (t, $J = 6.8$ Hz, 1H), 7.29 (m, 1H) 7.28 (m, 2H), 7.08 (m, 1H), 5.83 (s, 5H), 2.07 (m, 2H), 2.01 (m, 2H), 1.07 (t, 6H). ^{13}C NMR (δ, $CDCl_3$): 202.2, 195.0 (note that these *ipso* Ta−Ph resonances are not equivalent), 136.3, 133.7, 127.7, 127.6, 126.5, 125.2, 111.1, 24.1, 14.3. ^{11}B NMR (δ, $CDCl_3$): 41.8 (s, 1B), 25.3 (d, 2B, $J = 105$ Hz), 4.8 (d, $J = 83$ Hz). MS: *m/z* 606. Anal. Calcd For $C_{29}H_{33}B_4Ta$: C, 57.40; H, 5.49. Found: C, 57.55; H, 5.21.

Reaction of 18 with Styrene-d_8. For convenience in NMR monitoring, this reaction was performed with deuterated styrene. A solution of complex **18** (28 mg, 0.046 mmol) and 8 equiv of styrene-d_8 in 1 mL of degassed C_6D_6 was added, and the solution was heated at 85 °C for 36 h under nitrogen in a sealed NMR tube. The resulting metallacycle **19** was analyzed directly. ^1H NMR (δ, C_6D_6): 7.84 (d, $J = 7.8$ Hz, 2H), 7.40 (t, $J = 7.8$ Hz, 2H), 7.21 (t, $J = 7.8$ Hz, 1H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.92 (t, $J = 7.8$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 7.8$ Hz, 1H), 5.37 (s, 5H), 2.40 (m, 1H), 2.35 (m, 1H), 2.27 (m, 1H), 2.13 (m, 1H), 1.32 (t, 3H), 1.11 (t, 3H). ^1H NMR (δ, $CDCl_3$): 7.56 (d, $J = 7.8$ Hz, 2H), 7.34 (t, $J = 7.8$ Hz, 2H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.11 (t, $J = 7.8$ Hz, 1H), 6.98 (t, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H)

Table 3. Crystallographic Data for Complexes 10b and 17

	10b	17
empirical formula	$C_{26}H_{31}B_4Ta$	$C_{41}H_{46}B_4Ta$
fw	567.72	763.00
cryst color and habit	red plate	red needle
cryst dimens	0.34 × 0.18 × 0.42 mm	0.24 × 0.28 × 0.44 mm
cryst syst	monoclinic	orthorhombic
a, Å	9.940(4)	11.862(3)
b, Å	13.226(5)	20.961(5)
c, Å	17.865(6)	15.003(3)
β, deg	93.62(3)	105.50(3)
V, Å^3	2344(1)	3594(1)
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	16
D_{calc}, g cm^{-3}	1.61	1.41
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
μ (Mo Kα), cm^{-1}	46.94	30.81
temp	−100 °C	23 °C
$2\theta_{max}$	46°	46°
no. of reflns measd	total: 3211 unique: 2967 (R_{int} = 0.033)	total: 1934
no. of reflns measd	total: 3647 unique: 3422 (R_{int} = 0.032)	total: 5167 unique: 4382 (R_{int} = 0.042)
no. of reflns $I > 3\sigma(I)$	2348	3147
no. of variables	279	410
residuals *R*; R_w	0.045; 0.068	0.031; 0.038
goodness of fit	1.22	1.30
max peak in final diff map	1.50 e/Å^3	0.52 e/Å^3

5.83 (s, 5H), 2.41 (m, 3H), 2.31 (m, 1H), 1.38 (t, 3H), 1.20 (t, 3H). MS: *m/z* 639.

$Et_2C_2B_4H_4$)(Cp)Ta(*o*-$C_6H_4Me)_2$ (20). A solution of ($Et_2C_2B_4H_4$)(Cp)TaCl_2 (75 mg, 0.168 mmol) in 3 mL of degassed toluene was treated with *o*-tolylmagnesium bromide (1.68 mL of 2 M solution in ether, 20 equiv) and allowed to stir at room temperature for 12 h. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 and filtered through a 3-cm silica plug. The mixture containing several products was purified by preparative TLC (4:1 hexane:CH_2Cl_2) to give three fractions. The first was identified as ($Et_2C_2B_4H_4$)(Cp)Ta(*o*-C_6H_4Me)Cl. ^{1}H NMR (δ, $CDCl_3$): 7.15 (m, 2H), 7.01 (m, 2H), 6.22 (s, 5H), 3.06 (m, 1H), 2.76 (m, 2H), 2.51 (m, 1H), 2.17 (s, 3H), 1.18 (t, 3H), 1.02 (t, 3H). ^{13}C NMR (δ, $CDCl_3$): 148.3, 131.8, 131.7, 126.1, 125.9, 125.6, 111.0 (Cp), 25.8, 23.0, 22.9, 14.0, 13.8. The second and third fractions were found to be composed of different isomers of **20**. For fraction 2: ^{1}H NMR (δ, $CDCl_3$) 7.58 (m, 1H), 7.20 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 (m, 3H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 6.12 (s, 5H), 2.67 (m, 1H), 2.55 (m, 2H), 2.45 (m, 1H), 2.20 (s, 6H), 1.21 (t, 3H), 0.94 (t, 3H); ^{13}C NMR (δ, $CDCl_3$) 148.3, 135.8, 135.7, 131.6, 131.5, 126.8, 126.6, 125.5, 121.5, 121.3, 117.9, 117.7, 109.7 (Cp), 26.0, 23.2, 22.8, 18.5, 14.1, 14.0; ^{11}B NMR (δ, $CDCl_3$) 32.0 (d, 1B, 124 Hz), 22.7 (bs, 1B), 15.7 (bs, 1B), −3.2 (d, 1B, 116 Hz); MS *m/z* 557. For fraction 3: ^{1}H NMR (δ, $CDCl_3$) 7.22 (s, 1H), 7.14 (m, 3H), 7.07 (t, 1H), 6.92 (s, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 1H), 6.10 (s, 5H), 2.60 (m, 2H), 2.44 (m, 2H), 2.26 (s, 3H), 2.14 (s, 3H), 1.19 (t, 3H), 1.02 (t, 3H); ^{13}C NMR (δ, $CDCl_3$) 140.1, 137.0, 131.4, 128.1, 126.9, 125.3, 121.5, 117.1, 110.5 (Cp), 22.93, 22.86, 21.6, 18.1, 14.4, 14.1; ^{11}B NMR (δ, $CDCl_3$) 34.2 (d, 1B, 136 Hz), 22.7 (bs, 1B), 13.1 (bs, 1B), −3.5 (d, 1B, 116 Hz); MS *m/z* 557.

X-ray Crystallography. X-ray measurements were carried out on a Rigaku AFC6S diffractometer using Mo Kα radiation (λ = 0.710 69 Å) at −100 °C for complex **10b** and 23 °C for **17**. Calculations were performed on a VAXstation 3520 computer using the TEXSAN 5.0 software[39] and in the later stages on a Silicon Graphics Indigo 2 Extreme computer with the teXsan 1.7 package. Relevant crystallographic data are listed in Table 3. Unit cell dimensions were determined by applying the setting angles of 25 high-angle reflections. Three standard reflections were monitored during the data collection, showing no significant variance. The intensities were corrected for absorption by applying Ψ scans of several reflections with transmission factors in the range 0.10−1.00 for **10b** and 0.80−1.00 for **17**. Both structures were solved by direct methods in SIR88.[40] Full-matrix least-squares refinement was carried out with anisotropic thermal displacement parameters for all non-hydrogen atoms. The hydrogen atoms were found in difference Fourier maps and were subsequently included in the calculations without further refinement. The final difference map for **10b** showed a peak of 1.5 e/Å^3 close to the Ta atom; the final difference map for **17** was essentially featureless with the highest peak of 0.52 e/Å^3. The results of the refinements are presented in Table 3.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, complete bond distances and angles, and least-squares planes for all crystal structures (14 pages). Ordering information is given on any current masthead page.

OM980242W

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(39) *TEXSAN 5.0, Single-Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1989.

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