# Small Carborane Ligands as Tailorable Cp Surrogates. Halogenation, Alkylation, and Arylation at Metal and Cage Positions on $CpX_2M(Et_2C_2B_4H_4)$ Complexes (M = Ta, Nb)[1]

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Synthetic methods for the derivitization of sandwich complexes of the type $CpCl_2M(2,3\text{-}Et_2C_2B_4H_4)$ (M = Ta, Nb) have been further developed via regiospecific halogenation and alkylation at boron vertexes and at the metal center. Treatment of the parent complexes with elemental halogens or *N*-halosuccinimides generated B(5)-monohalo, B(4,5)-dihalo, and in some cases B(4,5,6)-trihalo complexes; these compounds, in turn, reacted with Grignard reagents to give the corresponding B-alkyl and B-aryl derivatives. Similarly, the heterodinuclear bent triple-decker complex $Cp^*Co(Et_2C_2B_3H_3)Cl_2Ta(Et_2C_2B_4H_4)$ was treated with an excess of *N*-bromosuccinimide to afford the B-tribromo derivative **7a**. The new compounds were characterized via $^{11}B$, $^1H$, and $^{13}C$ NMR, IR, and mass spectroscopy and elemental analysis, augmented by an X-ray diffraction study on **7a** and by UV−visible and electrochemical data on some of the complexes.



## Introduction

The ability to achieve facile substitution on carborane ligands while bound to a transition metal is central to the development of metallacarborane chemistry in useful directions such as catalysis, materials synthesis, and drug design. A signal advantage that is afforded by *nido*-$R_2C_2B_4H_4^{2-}$ and cyclic planar $R_2C_2B_3H_5^{2-}$ ligands (six-electron donors analogous to $C_5H_5^-$) in transition metal complexes is the relative facility with which they can be modified via introduction of substituents *while they are bound to the metal*,[2] a property that is somewhat more limited in metallocenes and other metal−hydrocarbon systems.[3] This in turn allows one to tune the electronic environment at the metal center, and hence its reactivity, via the attachment of electron-withdrawing or electron-releasing groups to the carborane cage. We have reported elsewhere on the insertion of alkenes, alkynes, and other organic substrates at the metal centers of early transition metal $CpR_2M(Et_2C_2B_4H_4)$ complexes where R is methyl or phenyl.[4] In this chemistry, the carborane ligand usually functions in a spectator role, although there are instances in which substitution at BH vertices, cage fusion, and cage expansion have been observed.[2,4]

A different situation arises in the case of halogenation. Studies involving late transition metal−carborane complexes such as $Cp'Co(Et_2C_2B_4H_4)$ [Cp′ = Cp or Cp* ($C_5Me_5$)] have shown that Cl, Br, or I substituents can be introduced onto the carborane ligand in a controlled manner,[5] and the resulting B-halo derivatives have been used to prepare novel linked-cage and B-organo species.[6] However, the participation of *early* transition metal carborane complexes, which are generally more reactive, in reactions with halogenating agents had not been broadly explored.[7] The site of halogenation—at the metal, on the cage, or both—and the potential conversion of B-halo derivatives to B-organosubstituted species were our major concerns. The present study was initiated to explore these issues, with the broader purpose of extending the range of application of these early transition metal−carborane complexes to organic synthesis.

## Results and Discussion

**Halogenation on the Carborane Ligand.** Earlier work in our group[5] demonstrated that halosuccinimides

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(1) Organotransition-Metal Metallacarboranes. 54. Part 53: Parker, K. G.; Russell, J. M.; Sabat, M.; Grimes, R. N. *Collect. Czech. Chem. Commun.* **1999**, *64*, 819.

(2) (a) Grimes, R. N., *J. Organometallic Chem.* **1999**, *581*, 1. (b) Grimes, R. N. *Appl. Organomet. Chem.* **1996**, *10*, 209, and references therein.

(3) In general, metal−cyclopentadienyl complexes other than ferrocene do not survive conditions required for aromatic substitution. Ferrocene has a well-developed derivative chemistry but cannot be directly halogenated or nitrated because of oxidation to ferricinium ion and does not undergo Diels−Alder and similar reactions of conjugated dienes (see: Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; p 1287). Outstanding examples of ligand modification have been described for $[CpFe(arene)]^+$ complexes: (a) Astruc, D. *Tetrahedron* **1983**, *39*, 4027−4095. (b) Moulines, F.; Djakovitch, L.; Delville-Desbois, M.-H.; Robert, F.; Gouzerh, P.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1995**, 463−464. (c) Buchholz, D.; Gloaguen, B.; Fillaut, J.-L.; Cotrait, M.; Astruc, D. *Chem. Eur. J.* **1995**, *1*, 374−381.

(4) (a) Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014. (b) Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1997**, *16*, 3993. (c) Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1998**, *17*, 3865.

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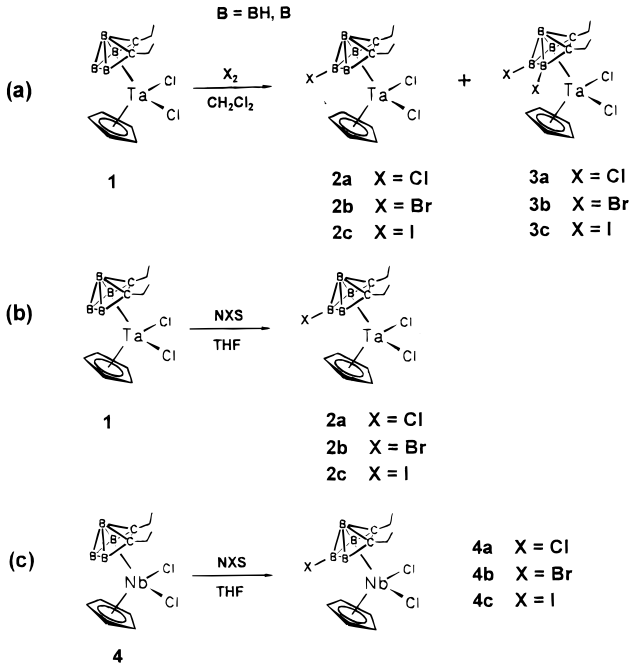
**Scheme 1**




and elemental halogens can be employed to effect halogen substitution at one or more BH locations on closo-$C_2B_4M$ clusters where M is Co, Fe, or Ru. In the present study, treatment of the dichlorotantalacarborane $CpCl_2Ta(Et_2C_2B_4H_4)$ (**1**) with elemental chlorine, bromine, or iodine at room temperature in dichloromethane gave B(5)-monohalo derivatives (**2a**−**c**) and, depending on the reaction conditions, higher halogenated complexes (**3a**−**c**), as shown in Scheme 1(a). The reaction of **1** with $Cl_2$ over a 2 h period gave a 90:10 **2a**/**3a** mixture ($^1$H NMR assay), and after 24 h the ratio was 10:90. No other products were detected and the complexes were recovered quantitatively. However, when conducted under ultraviolet light (450 W mercury arc), the reaction proceeded much further, with mass spectra of the products indicating the addition of up to six chlorines and implying that chlorination occurs on the Cp ring as well as the carborane cage. Bromination and iodination proceeded more slowly: treatment of **1** with $Br_2$ gave the monobromo species **2b** essentially quantitatively, but further reaction led to a mixture of **2b** and the dibromo complex **3b** with the former predominating. In the case of iodine, the monoiodo product **2c** was isolated in pure form after 24 h; longer reaction times gave diiodo complexes **3c**.

The B-monohalo and B,B′-dihalo complexes were obtained as orange crystalline solids and characterized by $^{11}$B and $^{13}$C NMR and mass spectrometry. Proof that the bromo substituent in **2b** is located on the middle equatorial boron B(5) rather than the apex boron B(7) was obtained via X-ray crystallography; the data are of insufficient quality to permit full refinement, but do establish the position of the bromine.[8a] (NMR spectra alone cannot unequivocally distinguish between the B(5)−Br and B(7)−Br isomers, both of which have mirror symmetry; this situation has precedent in cobaltacarborane chemistry, as in the 5,5′- and 7,7′-$[Cp^*Co(Et_2C_2B_4H_3)]_2$ dimers, the structures of which required X-ray data for confirmation.[6,9]) Analogous B(5)-halo structures are assumed for the monochloro and monoiodo species **2a** and **2c**, whose NMR spectra closely resemble those of **2b**.

The effect of cage-halogenation on electron donation from the carborane ligand to the metal[4a] can be seen in the reduction potentials of **2a**−**c** in $CH_2Cl_2$, which are less negative by 0.28, 0.24, and 0.30 V, respectively, compared to the parent complex **1** ($E_{0.5}$(red) [0/−] vs ferrocene = −1.08 V for **1**, −0.80 V, for **2a**, −0.84 V for **2b**, and −0.78 V for **2c**). As expected, the introduction of halogens onto the cage reduces the transfer of electron density to the metal, rendering the metal center easier to reduce; the opposite is true when electron-releasing alkyl groups are placed on the metal, as in the Ta-dimethyl complex $CpMe_2Ta(Et_2C_2B_4H_4)$,[4a] whose reduction potential is −1.86 V in $CH_2Cl_2$.

The mixtures of di- and polyhalo complexes obtained in reactions with elemental halogens proved difficult to separate via the usual chromatographic methods, and we sought more controllable routes that would afford cleaner products. As depicted in Scheme 1b, **1** reacted with 1 equiv of *N*-chloro-, *N*-bromo-, or iodosuccinimide in THF to generate the B-monohalo products in high yield. Attempts at further cage-halogenation via treatment with excess halosuccinimide gave inconclusive results; while there was spectroscopic evidence of the formation of dibromo and diodo products in some experiments, these compounds were not isolated.

Analogous 1:1 reactions of the dichloroniobium complex **4** with *N*-halosuccinimides gave the B(5)-monohalo derivatives **4a**−**c**, again quantitatively, as orange-red air-stable solids (Scheme 1c). Characterization of these compounds from their multinuclear NMR spectra and mass spectra was supplemented by X-ray crystallographic data on **4b**, which established that bromo monosubstitution occurs at B(5) as expected.[8b]

Perhalogenation of the equatorial boron atoms was explored in two systems. As depicted in Scheme 2, treatment of **1** with a large excess of $Br_2$ at 60 °C gave $CpCl_2Ta(Et_2C_2B_4HBr_3)$ (**5**) in high yield as a red-orange solid exhibiting spectroscopic data consistent with mirror symmetry, thereby supporting the proposed structure. A similar procedure was employed to B-perbrominate, the bent triple-decker complex **6**,[4a] an analogue of **1** in which a Cp*Co unit replaces the isolobal apical BH group. The dark red product $Cp^*Co(Et_2C_2B_3Br_3)$-$TaCpCl_2$ (**7a**) was isolated in 91% yield and characterized via multinuclear NMR, mass spectroscopy, and an X-ray crystal structure determination. Treatment of **6** with *N*-iodosuccinimide afforded a product that was spectroscopically identified as a B-diiodo derivative, $Cp^*Co(Et_2C_2B_3HI_2)TaCpCl_2$ (**7b**).

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

(6) Wang, X.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 4668.

(7) In the only prior report of cage halogenation of an early transition metal−small carborane complex, mono- and di-B-iodo derivatives of $(\eta^8$-$C_8H_8)Ti(Et_2C_2B_4H_4)$ were prepared via reaction of the parent compound with MeI and $I_2$, respectively. See: Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1984**, *3*, 599.

(8) (a) For **2b**: $Z = 4$, monoclinic space group $P21/c$, $a = 13.664(4)$ Å, $b = 7.789(3)$ Å, $c = 16.296(7)$ Å, $\beta = 107.63(3)°$. (b) For **4b**: $Z = 4$, monoclinic space group $P21/c$, $a = 13.582(6)$ Å, $b = 8.060(4)$ Å, $c = 16.201(8)$ Å, $\beta = 107.15(3)°$.

(9) Curtis, M. A.; Müller, T.; Beez, V.; Pritzkow, H.; Siebert, W.; Grimes, R. N. *Inorg. Chem.* **1997**, *36*, 3602.

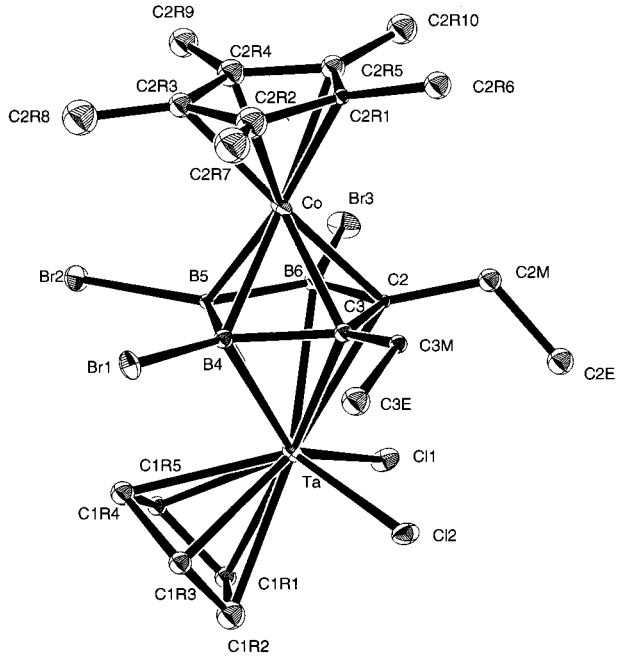
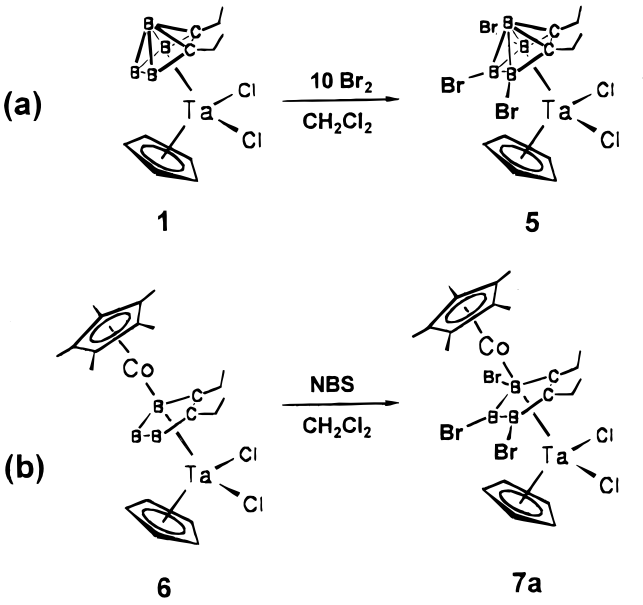



**Figure 1.** Molecular structure of $Cp^*Co(Et_2C_2B_3Br_3)$-$TaCpCl_2$ (**7a**) showing 30% ellipsoids.

**Scheme 2**




The molecular structure, crystal data, and selected bond distances and angles of **7a** are presented in Figure 1 and Tables 1 and 2, while additional crystallographic data are provided as Supporting Information. Although the structure is similar in its main features to that of the parent compound $Cp^*Co(Et_2C_2B_3H_3)TaCpCl_2$ reported earlier,[4a] some differences are notable. In **7a** the carborane cage C−C distance [C(2)−C(3)] is slightly shorter at 1.42(3) Å vs 1.48(1) in the parent species, while the Co and Ta atoms in **7a** are further from the $C_2B_3$ ring plane than their counterparts in the nonbrominated species (for Co, 1.559 vs 1.536 Å; for Ta, 2.062 vs 1.995 Å). These observations can be attributed to a combination of steric crowding (a consequence of the three bromine atoms pushing the Cp*Co and CpTa moieties further out from the carborane ring) and electron withdrawal by the bromines that presumably

**Table 1. Crystallographic Data for $Cp^*Co(Et_2C_2B_3Br_3)Cl_2TaCp$ (7a)**

| | |
|---|---|
| empirical formula | $CoTaBr_3Cl_2B_3C_{21}H_{30}\cdot 0.5CH_2Cl_2$ |
| fw | 907.86 |
| cryst color and habit | dark red block |
| cryst dimens | 0.36 × 0.26 × 0.48 mm |
| cryst syst | monoclinic |
| lattice params | $a$ = 9.881(4) Å |
| | $b$ = 19.240 (7) Å |
| | $c$ = 15.301(5) Å |
| | $V$ = 2903(1) Å$^3$ |
| space group | $P2_1/n$ |
| $Z$ | 4 |
| $D_{calc}$ | 2.09 g·cm$^{-3}$ |
| radiation | Mo Kα ($\lambda$ = 0.71069 Å) |
| $\mu$(Mo Kα) | 87.59 cm$^{-1}$ |
| abs corr | $\psi$ scans (transm factors 0.25−1.00) |
| temperature | −120 °C |
| $2\theta_{max}$ | 46° |
| no. of reflns measd | total: 4478 |
| | unique: 4195 ($R_{int}$ = 0.045) |
| no. of reflns $I > 3\sigma(I)$ | 2710 |
| no. of variables | 171 |
| residuals $R$; $R_w$ | 0.087; 0.114 |
| goodness of fit | 2.48 |
| max peak in final diff map | 3.41 e/Å$^3$ |

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7a**

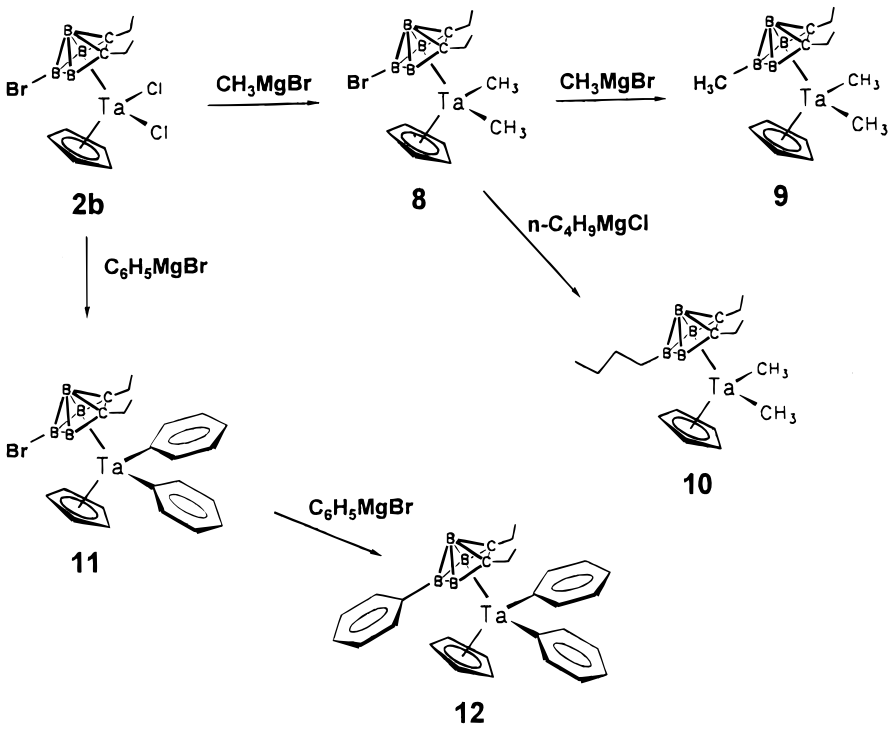
| | | | |
|---|---|---|---|
| Ta−Cl(1) | 2.345(5) | B(4)−B(5) | 1.78(3) |
| Ta−Cl(2) | 2.373(5) | B(5)−B(6) | 1.66(3) |
| Ta−C(2) | 2.51(2) | Br(1)−B(4) | 1.86(2) |
| Ta−C(3) | 2.47(2) | Br(2)−B(5) | 2.02(2) |
| Ta−B(4) | 2.49(2) | Br(3)−B(6) | 1.93(2) |
| Ta−B(5) | 2.42(2) | Co−C(2) | 2.06(2) |
| Ta−B(6) | 2.51(2) | Co−C(3) | 2.06(2) |
| C(2)−C(3) | 1.42(3) | Co−B(4) | 2.10(2) |
| C(2)−B(6) | 1.51(3) | Co−B(5) | 2.04(2) |
| C(3)−B(4) | 1.68(3) | Co−B(6) | 2.13(2) |
| Cl(1)−Ta−Cl(2) | 95.1(2) | B(4)−B(5)−B(6) | 108(2) |
| C(2M)−C(2)−C(3) | 119(2) | C(2)−B(6)−B(5) | 105(2) |
| C(2M)−C(2)−B(6) | 124(2) | Br(1)−B(4)−C(3) | 135(2) |
| C(3)−C(2)−B(6) | 117(2) | Br(1)−B(4)−B(5) | 128(1) |
| C(2)−C(3)−C(3M) | 125(2) | Br(2)−B(5)−B(4) | 124(1) |
| C(3M)−C(3)−B(4) | 120(2) | Br(2)−B(5)−B(6) | 128(2) |
| C(2)−C(3)−B(4) | 114(2) | Br(3)−B(6)−C(2) | 127(1) |
| C(3)−B(4)−B(5) | 97(1) | Br(3)−B(6)−B(5) | 128(2) |

weakens the metal−$C_2B_3$ ring interaction. This latter effect is also probably responsible for the apparent increase in carborane C−C bond order relative to the unsubstituted compound, which is consistent with reduced delocalization (hence a more localized electronic structure in the cage C−C region) in the $CoC_2B_3Ta$ polyhedral cluster.

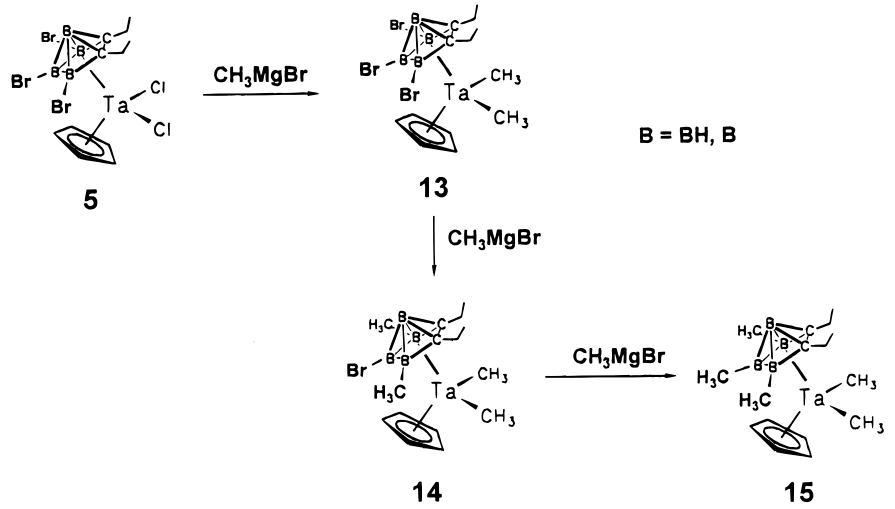
Cyclic voltammetry measurements on **4c** and **5**, as in the cases of **2a**−**c** above, show a substantial lowering of the electron-donating ability of the carborane ligands when they are halogenated; thus, in $CH_2Cl_2$ solution $E_{0.5}$(red) (0/−) vs ferrocene was found to be −0.43 for the monoiodo complex **4c** compared to −0.60 V for the parent species **4**, while the value for the tribromo complex **5** is −0.51 vs −1.08 V for **1**, a very large effect demonstrating that the $Et_2C_2B_4HBr_3^{2-}$ ligand is a much poorer donor than its nonhalogenated counterpart.

**Alkylation and Arylation of Bromo−Tantalacarborane Complexes.** In a previous study[4a] it was shown that $Cp'Cl_2Ta(R_2C_2B_4H_4)$ complexes (R = Et or $SiMe_3$) undergo alkylation at the metal by treatment with Grignard reagents such as $CH_3MgBr$. In the present work, we found that reaction of the B-bromo, tantalum−dichloro complex **2b** occurs first at tantalum;

**Scheme 3**




**Scheme 4**




thus, treatment with 2 molar equiv of $CH_3MgBr$ affords the tantalum−dimethyl complex **8**, while excess Grignard reagent produces the B(5)-methyl complex **9** (Scheme 3). As shown, the B(5)-butyl derivative **10** was similarly prepared by treating **8** with *n*-$C_4H_9MgCl$. Characterization of these compounds via multinuclear NMR, mass spectroscopy, and elemental analysis was straightforward.

Alkylation of carboranes at boron vertices via Grignard reagents is unusual, with very few reports prior to this work, all of them to our knowledge involving catalytic cross-coupling on icosahedral $C_2B_{10}H_{12}$ derivatives.[10] To further explore the scope of reactivity of magnesium reagents toward the tantalum−small carborane complexes, we treated **2b** with phenylmagnesium bromide, obtaining the $TaPh_2$ complex **11** and the $TaPh_2$−BPh species **12**, as shown in Scheme 3, isolated as yellow-brown oils or solids and characterized spectroscopically. This approach was also employed to prepare B-polyalkyl derivatives, as demonstrated by the synthesis of **13**, **14**, and the pentamethyl complex **15** in 64−86% isolated yields, illustrated in Scheme 4.

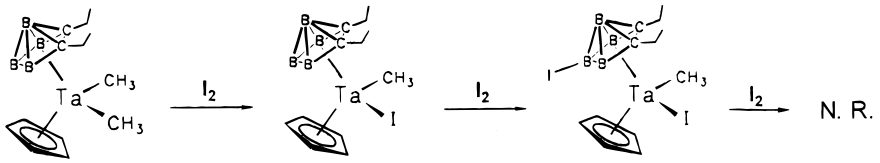
The dimethyl tantalacarborane[4a] **16** reacted with iodine only slowly, apparently generating the monoiodo complex **17** and proceeding to the Ta,B(5)-diiodo derivative **18** (Scheme 5); however, these compounds could not be obtained in pure form and were tentatively identified from NMR and mass spectra only. Prolonged exposure of **18** to iodine gave no evidence of further iodination.

## Conclusion

It is well established that small carborane ligands can stabilize a wide range of transition metal and main group metal sandwich complexes,[2,11] but proper devel-

(10) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095, and references therein.

**Scheme 5**




**16** **17** **18**

opment of this area requires systematic methods for introducing desired substituents on the carborane cage and at the metal centers. In combination with our earlier published work,[4] the approaches reported in this paper allow the preparation of a wide variety of early transition metal−$C_2B_4$ and −$C_2B_3$ complexes that are suitably derivatized for specific purposes. In our laboratory, current applications of this chemistry include the synthesis of multinuclear systems constructed from metallacarborane cages and organic linkers,[2b] the development of new catalyst systems for olefin polymerization,[12] and the preparation of small carborane-based antitumor complexes.[13]

## Experimental Section

**Instrumentation.** $^1$H NMR (300 MHz) and $^{13}$C NMR (75.5 MHz) spectra were recorded on a GE QE-300 spectrometer, while $^{11}$B NMR (115.8 MHz) spectra were obtained on a Nicolet NT-360 instrument. All spectra were recorded in $CDCl_3$ solution. Unit resolution mass spectra were obtained on a Finnegan MAT 4600 spectrometer using perfluorotributylamine (FC43) as a calibration standard. Each compound exhibited a strong parent envelope whose intensity pattern was consistent with the calculated spectrum based on natural isotopic abundances. Elemental analyses were conducted on a Perkin-Elmer 2400 CHN analyzer using 2,4-dinitrophenylhydrazone as a standard. Owing to incomplete combustion (not uncommon in polyhedral boron clusters), the carbon analyses for **2a** and **9** were slightly outside normal limits, and a satisfactory analysis for **7a** was not obtained; however, the spectra for all compounds were clean, and **7a** was characterized by X-ray diffraction and multinuclear NMR spectroscopy. Visible−ultraviolet spectra were obtained on a Hewlett-Packard 8452A diode array with a HP Vectra computer interface, and infrared spectra were recorded in $CH_2Cl_2$ solution on a Mattson Cygnus FTIR spectrometer.

**Materials and Procedures.** All reactions were conducted under an inert atmosphere unless otherwise indicated. Workup of products was generally carried out in air using benchtop procedures. Column chromatography was performed on silica gel 60 (Merck) and on silica gel 60 plates (ICN). Solvents were distilled from appropriate drying agents under an inert atmosphere. The parent metallacarboranes $CpCl_2Ta(Et_2C_2B_4H_4)$ (**1**), $CpCl_2Nb(Et_2C_2B_4H_4)$ (**4**), $Cp^*Co(Et_2C_2B_3H_3)Cl_2Ta(Et_2C_2B_4H_4)$ (**6**), and $CpMe_2Ta(Et_2C_2B_4H_4)$ (**16**) were obtained as described elsewhere.[4a]

**Reactions of $CpCl_2Ta(Et_2C_2B_4H_4)$ (1) and Derivatives with Elemental Halogens. (a) With $Cl_2$.** A 0.200 g (0.45 mmol) sample of **1** was dissolved in 10 mL of dry THF in a scintillation vial, which was capped with a septum, and the solution was saturated with chlorine gas. The solution was allowed to stand for 2 h, the solvent was removed by rotary evaporation, and the solid residue was flash-chromatographed through 3 cm of silica gel in $CH_2Cl_2$, yielding one orange-yellow band, which was column-chromatographed in 4:1 petroleum ether/$CH_2Cl_2$ to afford 0.188 g (0.39 mmol, 89%) of orange crystalline $CpCl_2Ta(Et_2C_2B_4H_3$-5-Cl) (**2a**) plus a small amount (ca. 0.04 mmol) of $CpCl_2Ta(Et_2C_2B_4H_3$-4,5-$Cl_2$) (**3a**). When the reaction was conducted with 0.159 g (0.35 mmol) of **1** and allowed to proceed for 24 h, workup as before gave 14 mg (0.03 mmol, 8%) of **2a** and 0.162 g (0.31 mmol, 90%) of **3a**. For **2a**: $^1$H NMR ($\delta$, $CDCl_3$): 6.47 ($C_5H_5$, s), 3.07 ($CH_2$, dq), 2.64 ($CH_2$, dq), 1.20 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 124.7 (carborane cage carbon, br s), 116.8 ($C_5H_5$), 23.1 ($CH_2$), 14.6 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 40.4 (1B, s), 25.5 (2B, d, $J_{BH}$ = 135 Hz), 6.5 (1B, d, $J$ = 157 Hz). MS: $m/z$ 481 (molecular ion envelope), 446 (−Cl). Anal. Calcd for $C_{11}H_{18}B_4Cl_3Ta$: C, 27.48; H, 3.77. Found: C, 28.15; H, 3.80. For **3a**: $^1$H NMR ($\delta$, $CDCl_3$): 6.47 ($C_5H_5$, s), 3.17 ($CH_2$, dq), 2.83 ($CH_2$, dq), 2.64 ($CH_2$, dq), 1.29 ($CH_3$, t), 1.07 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 124.0 (carborane cage carbon, br s), 118.2 ($C_5H_5$), 23.1 ($CH_2$), 21.6 ($CH_2$), 14.6 ($CH_3$), 13.0 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 12.6 (3B, unresolved coupling), −0.8 (1B, d, $J_{BH}$ = 129 Hz). MS $m/z$ 515 (molecular ion envelope), 481 (−Cl). Anal. Calcd for $C_{11}H_{17}B_4Cl_4Ta$: C, 25.64; H, 3.33. Found: C, 25.35; H, 3.44.

**(b) With $Br_2$.** Treatment of **1** with 1 equiv of $Br_2$ in $CH_2Cl_2$ over 8 h gave the monobromo derivative **2b** almost exclusively, but a faster and more efficient route to the latter compound is via *N*-bromosuccinimide (vide infra). In turn, **2b** was readily converted to the dibromo species **3b**: A 0.150 g sample (0.34 mmol) of **2b** in 10 mL of $CCl_4$ or benzene was treated with 0.1 mL of $Br_2$ and stirred for 3 h, the volatiles were removed, and the oily residue was dissolved in $CH_2Cl_2$ and filtered through 2 cm of silica. After removal of the solvent, NMR and mass spectroscopy revealed a mixture of $CpCl_2Ta(Et_2C_2B_4H_3$-5-Br (**2b**), $CpCl_2Ta(Et_2C_2B_4H_2Br_2)$ (**3b**), and higher brominated derivatives, with **3b** as the main product. Recrystallization from hexane at −20 °C gave 0.138 g (0.26 mmol, 77%) of orange crystalline **3b** (characterization data for **2b** are given below). For **3b**: $^1$H NMR ($\delta$, $CDCl_3$): 6.53 ($C_5H_5$, s), 3.10 ($CH_2$, m), 3.00 ($CH_2$, m), 2.93 ($CH_2$, m), 2.73 ($CH_2$, m), 1.33 ($CH_3$, s), 1.10 ($CH_3$, s). $^{11}$B NMR ($\delta$, $CDCl_3$): 30.3 (1B, s), 24.7 (1B, br s), 21.8 (1B, s), 5.8 (1B, d, $J$ = 126 Hz). MS (CI in $CH_4$): $m/z$ 602, frag. 566 (−Cl).

A reaction conducted with 0.150 g (0.34 mmol) of **2b** and an excess of bromine (1 mL of liquid $Br_2$) in 10 mL of $CCl_4$ with heating for 24 h, followed by removal of the volatiles and filtration of the residue through 2 cm of Celite in hexane and removal of solvent, gave 0.160 g (0.23 mmol, 82%) of ($CpCl_2$-$Ta(Et_2C_2B_4H$-4,5,6-$Br_3$) (**5**) as a red-orange powder. $^1$H NMR ($\delta$, $CDCl_3$): 6.50 ($C_5H_5$, s), 3.08 ($CH_2$, dq), 2.86 ($CH_2$, dq), 1.21 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 120.1 ($C_5H_5$), 23.4 ($CH_2$), 13.6 ($CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 31.1 (1B, s), 22.2 (2B, s), 2.5 (1B, d, $J$ = 173 Hz). IR ($CH_2Cl_2$, cm$^{-1}$): 3087 s, 2974 s, 2917 s, 2848 s, 2628 s, 1470 w, 1451 s, 1394 m, 1300 m, 1048 s, 866 s. UV−vis ($\lambda_{max}$, nm; $CH_2Cl_2$): 232 (100%), 386 (14%). MS: $m/z$ 683 (molecular ion envelope), 648 (−Cl), 569 (−Br, −Cl). Anal. Calcd for $C_{11}H_{16}B_4Br_3Cl_2Ta$: C, 19.34; H, 2.37. Found: C, 19.67; H, 2.52.

**(c) With $I_2$.** Treatment of **1** with iodine under conditions similar to those used in the synthesis of **2a** and **2b** proceeded very slowly, affording only the B(5)-monoiodo complex $CpCl_2$-$Ta(Et_2C_2B_4H_3$-5-I) (**2c**) in 24 h; over longer periods (days), small amounts of the diiodo derivative **3c** could be detected by NMR and mass spectroscopy.

**Reactions of $CpCl_2Ta(Et_2C_2B_4H_4)$ (1) with *N*-Halosuccinimides. (a) With *N*-Chlorosuccinimide.** A 0.100 g (0.22 mmol) sample of **1** was dissolved in 3 mL of $CH_2Cl_2$. Five

equivalents of *N*-chlorosuccinimide (NCS) was added, and the solution was stirred for 1 h. The volatiles were removed by rotary evaporation, and the solid residue was redissolved in hexane, filtered to remove the excess NCS, and column-chromatographed to afford 0.100 g (0.21 mmol, 99%) of orange crystalline $CpCl_2Ta(Et_2C_2B_4H_3$-5-Cl) (**2a**), characterized as above.

**(b) With *N*-Bromosuccinimide.** A 0.200 g (0.44 mmol) sample of **1** was dissolved in 10 mL of dry THF in a scintillation vial, 78 mg (0.44 mmol) of *N*-bromosuccinimide was added, and the vial was capped. Over a 1 h period the yellow solution changed to deep brown. After 2 h the solvent was removed and the residue was flash-chromatographed through 3 cm of silica gel in $CH_2Cl_2$, yielding 0.226 g (0.43 mmol, 97%) of orange crystalline $CpCl_2Ta(Et_2C_2B_4H_3$-5-Br) (**2b**). $^1$H NMR ($\delta$, $CDCl_3$): 6.49 ($C_5H_5$, s), 3.08 ($CH_2$, dq), 2.64 ($CH_2$, dq), 1.21 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 123.7 (carborane cage carbon, br s), 116.7 ($C_5H_5$), 22.7 ($CH_2$), 14.1 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 35.4 (1B, s), 24.4 (2B, d, $J_{BH} = 154$ Hz), 1.8 (1B, d, $J = 168$ Hz). MS: *m*/*z* 525 (molecular ion envelope), 490 (−Cl). Anal. Calcd for $C_{11}H_{18}B_4Cl_2TaBr$: C, 25.15; H, 3.45. Found: C, 25.59; H, 3.05.

**(b) With *N*-Iodosuccinimide.** The procedure described in the preceding paragraph was followed using 0.200 g (0.44 mmol) of **1** and 0.100 g (0.44 mmol) of *N*-iodosuccinimide. Over a 1 h period the yellow solution changed to deep red-orange. After 2 h the solvent was removed and the residue was worked up as above, affording 0.252 g (0.44 mmol, 99%) of orange crystalline $CpCl_2Ta(Et_2C_2B_4H_3$-5-I) (**2c**). $^1$H NMR ($\delta$, $CDCl_3$): 6.49 ($C_5H_5$, s), 3.08 ($CH_2$, dq), 2.64 ($CH_2$, dq), 1.23 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 124.7 (carborane cage carbon, br s), 117.2 ($C_5H_5$), 23.1 ($CH_2$), 14.6 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 26.8 (1B, d, $J = 144$ Hz), 20.5 (2B, s), 1.8 (1B, d, $J = 159$ Hz). MS: *m*/*z* 574 (molecular ion envelope), 490 (−Cl). Anal. Calcd for $C_{11}H_{18}B_4Cl_2TaI$: C, 23.09; H, 3.17. Found: C, 23.58; H, 3.32.

**Reactions of $CpCl_2Nb(Et_2C_2B_4H_4)$ (4) with *N*-Halosuccinimides. (a) With *N*-Chlorosuccinimide.** A 0.100 g (0.28 mmol) sample of **4** was dissolved in 3 mL of $CH_2Cl_2$. One equivalent of *N*-chlorosuccinimide was added, and the mixture was stirred for 3 h. The volatiles were removed, and the mixture was redissolved in hexane and filtered to give $CpCl_2Nb(Et_2C_2B_4H_3Cl)$ (**4a**), identified mass spectroscopically from its molecular ion envelope (*m*/*z* 399), but not otherwise characterized.

**(b) With *N*-Bromosuccinimide.** A 0.054 g (0.15 mmol) sample of **4** was dissolved in 0.5 mL of dry THF in a 5 mm NMR tube, 1 equiv of *N*-bromosuccinimide was added, and the mixture was capped and shaken. The solution immediately turned from orange-red to deep red, and after shaking for 5 min the solution was homogeneous; after 10 min, the $^{11}$B NMR spectrum indicated that the reaction had proceeded cleanly to afford a single product. The solvent was removed by rotary evaporation, and the residue was dissolved in $CH_2Cl_2$ and flash-chromatographed through 3 cm of silica to give a single orange band. Removal of solvent afforded 0.065 g (0.15 mmol, 100%) of orange crystalline $CpCl_2Nb(Et_2C_2B_4H_3$-5-Br) (**4b**). $^1$H NMR ($\delta$, $CDCl_3$): 6.49 ($C_5H_5$, s), 3.09 ($CH_2$, dq), 2.64 ($CH_2$, dq), 1.23 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 124.7 (carborane cage carbon, br s), 119.3 ($C_5H_5$), 23.8 ($CH_2$), 14.3 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 40.1 (1B), 25.7 (2B, d, $J = 151$ Hz), 6.4 (1B, d, $J = 159$ Hz). MS: *m*/*z* 437 (molecular ion envelope), 490 (−Cl). Anal. Calcd for $C_{11}H_{18}B_4Cl_2NbBr$: C, 30.22; H, 4.15. Found: C, 30.51; H, 4.53.

**(c) With *N*-Iodosuccinimide.** The same procedure used in the preceding synthesis was followed using 0.050 g (0.14 mmol) of **4** in 0.5 mL of dry THF and 1 equiv of *N*-iodosuccinimide. The solution immediately turned from orange-red to deep red, and after shaking for 5 min the solution was homogeneous; after 10 min, the $^{11}$B NMR spectrum indicated that the reaction had proceeded cleanly to afford a single product. The solvent was removed by rotary evaporation, and the residue was dissolved in $CH_2Cl_2$ and flash-chromatographed through 3 cm of silica to give a single orange band. Removal of solvent afforded 0.073 g (0.15 mmol, 100%) of orange crystalline $CpCl_2Nb(Et_2C_2B_4H_3$-5-I) (**4c**). $^1$H NMR ($\delta$, $CDCl_3$): 6.54 ($C_5H_5$, s), 3.09 ($CH_2$, dq), 2.55 ($CH_2$, dq), 1.24 ($CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 124.7 (carborane cage carbon, br s), 119.6 ($C_5H_5$), 24.0 ($CH_2$), 14.1 ($CH_3$). $^{11}$B NMR ($\delta$, $CH_2Cl_2$): 28.2 (1B, d, $J = 147$ Hz), 25.7 (1B, s), 6.7 (1B, d, $J = 142$ Hz). MS: *m*/*z* 484 (molecular ion envelope), 490 (−Cl). Anal. Calcd for $C_{11}H_{18}B_4Cl_2NbI$: C, 27.29; H, 3.75. Found: C, 26.97; H, 4.19.

**$Cp^*Co(Et_2C_2B_3Br_3)TaCl_2Cp$ (7a).** A 0.100 g (0.160 mmol) sample of $Cp^*Co(Et_2C_2B_3H_3)TaCl_2Cp$ (6)[4a] was dissolved in 5 mL of dry THF, and 10 equiv of *N*-bromo succinimide was slowly added. The solution was stirred for 3 h, the volatiles were removed, and the mixture was dissolved in dichloromethane and flash-chromatographed through 2 cm of silica to give, following solvent removal, 0.128 g (0.146 mmol, 91%) of **7a**. $^1$H NMR ($\delta$, $CDCl_3$): 6.20 ($C_5H_5$, s), 3.22, 3.13 (ethyl $CH_2$, m), 1.70 ($C_5Me_5$, s), 1.54 (ethyl $CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 119.8 ($C_5H_5$), 94.5 ($C_5Me_5$), 26.2 (ethyl $CH_2$), 15.0 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 43.1 (2B, s), 22.8 (1B, s). MS (CI in $CH_4$): *m*/*z* 869. Anal. Calcd for $C_{21}H_{30}B_3Br_3Cl_2CoTa$: C, 29.14; H, 3.50. Found: C, 27.88, H, 3.83.

**$Cp^*Co(Et_2C_2B_3HI_2)TaCpCl_2$ (7b).** A 0.100 g (0.16 mmol) sample of $Cp^*Co(EtC_2B_3H_3)TaCl_2Cp$ (**6**) was dissolved in 10 mL of THF, 5 equiv of *N*-iodosuccinimide was added, and the solution was stirred for 8 h. Workup as in the preparation of **7** yielded 0.114 g (0.13 mmol, 82%) of **7b**. $^1$H NMR ($CDCl_3$): 6.23 ($C_5H_5$, s), 3.27 (ethyl $CH_2$, m), 2.94 (ethyl $CH_2$, m), 2.89 (ethyl $CH_2$, m), 1.66 ($C_5Me_5$, s, 15H), 1.45 (ethyl $CH_3$, t), 1.39 (ethyl $CH_3$, t). $^{11}$B NMR ($CDCl_3$): 36.5 (1B, s), 23.7 (1B, s), 0.4 (1B, br s). MS (CI in $CH_4$): *m*/*z* 880.

**$CpMe_2Ta(Et_2C_2B_4H_3$-5-Br) (8).** A 0.150 g (0.285 mmol) sample of **2b** was dissolved under argon in 5 mL of toluene, and 2 equiv of 3.0 M $CH_3MgBr$ in diethyl ether was slowly added, causing the solution to turn dark brown. After stirring the solution for 3 h, the volatiles were removed and the mixture was dissolved in $CH_2Cl_2$. The solution was filtered through 2 cm of silica, and the volatiles were removed to yield 0.128 g (0.26 mmol, 93%) of **8**. $^1$H NMR ($\delta$, $CDCl_3$): 6.12 ($C_5H_5$, s), 2.68 (ethyl $CH_2$, m), 1.28 (ethyl $CH_3$, t, $J = 7.8$ Hz), 0.00 (Ta−$CH_3$, s). $^{13}$C NMR ($\delta$, $CDCl_3$): 110.9 ($C_5H_5$), 50.7 (Ta−$CH_3$), 22.6 (ethyl $CH_2$), 14.4 (ethyl $CH_3$). $^{11}$B NMR ($CDCl_3$): 34.6 (1B, s), 21.7 (2B, d, $J = 151$ Hz), 0.2 (1B, d, $J = 164$ Hz). IR ($CH_2Cl_2$, $cm^{-1}$): 3132 w, 3107 w, 2981 s, 2937 s, 2849 w, 2603 (B(H), m), 1445 m, 1382 m, 1306 w, 1268 w, 1086 s, 1042 s, 865 9 s), 746 m. UV−vis ($CH_2Cl_2$, nm): 232 (100%), 354 (41%). MS (CI in $CH_4$): *m*/*z* 484. Anal. Calcd for $C_{13}H_{24}B_4BrTa$: C, 32.23; H, 5.00. Found: C, 32.62; H, 4.87.

**$CpMe_2Ta(Et_2C_2B_4H_3$-5-Me) (9).** A 0.100 g (0.19 mmol) sample of **2b** was dissolved in THF under argon, and 3 equiv of 3.0 M $CH_3MgBr$ was added, after which the mixture was stirred for 2 h. The volatiles were removed, leaving a brown oil, which was dissolved in $CH_2Cl_2$ and filtered through 2 cm of silica. Removal of solvent afforded 0.074 g (0.18 mmol, 93%) of yellow solid **9**. $^1$H NMR ($\delta$, $CDCl_3$): 5.95 ($C_5H_5$, s), 2.73 (ethyl $CH_2$, m), 1.27 (ethyl $CH_3$, t, $J = 7.8$ Hz), 0.67 (B[5]-$CH_3$, s), −0.13 (Ta−$CH_3$). $^{13}$C NMR ($\delta$, $CDCl_3$): 109.1 ($C_5H_5$, s), 48.5 (Ta−$CH_3$, s), 23.6 (ethyl $CH_2$, s), 15.2 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 39.4 (1B, s), 23.5 (2B, d, $J = 150$ Hz), 0.9 (1B, d, $J = 207$ Hz). MS (CI in $CH_4$) *m*/*z* 419, frag. 404. Anal. Calcd for $C_{14}H_{27}B_4Ta$: C, 39.98; H, 6.48. Found: C, 40.65; H, 6.72.

**$CpMe_2Ta(Et_2C_2B_4H_3$-5-$^n$Bu) (10).** A 0.050 g (0.103 mmol) sample of **8** was dissolved in 2 mL of toluene under argon, and 1 equiv of 2.0M *n*-BuMgCl in THF was syringed into the solution. After stirring for 3 h the volatiles were removed and the oily mixture was dissolved in $CH_2Cl_2$ and filtered through 2 cm of silica. The solvent was removed via rotoevaporation to yield 0.042 g (0.091 mmol, 88%) of **10** as a yellow-brown oil. $^1$H NMR ($\delta$, $CDCl_3$): 5.95 ($C_5H_5$, s), 2.72 (ethyl $CH_2$, m),

1.27 (ethyl $CH_3$, m), 1.26 (*n*-Bu, m), 0.87 (*n*-Bu, m), −0.13 (Ta−$CH_3$, s). $^{13}$C NMR ($\delta$, $CDCl_3$): 109.1 ($C_5H_5$), 40.5 ($CH_2$−$CH_3$), 27.2 ($CH_2$−$CH_2$), 23.6 (ethyl $CH_2$), 15.2 (ethyl $CH_3$), 11.6 (Ta−$CH_2$). $^{11}$B NMR ($\delta$, $CDCl_3$): 39.2 (s, 1B), 23.5 (d, 2B, $J$ = 156 Hz), 0.90 (d, 1B, $J$ = 206 Hz). MS (CI in $CH_4$): *m*/*z* 462, frag. 447.

**CpPh$_2$Ta (Et$_2$C$_2$B$_4$H$_3$-5-Br) (11).** A 0.100 g (0.190 mmol) sample of **2b** was dissolved in 10 mL of toluene under argon, 15 equiv of 3.0 M PhMgBr was added, and the solution immediately turned dark red. The solution was stirred for 2 h, the volatiles were removed, and the residue was stirred in $CH_2Cl_2$ for several minutes to quench the excess magnesium reagent. The solution was filtered through 2 cm of silica, and the volatiles were removed to afford **11** as a yellow oil together with biphenyl. The latter compound was removed by dissolving the mixture in hexane and flashing through a silica plug, which allowed the biphenyl to pass while retaining **11**. Pure **11** was then eluted from the silica by washing with $CH_2Cl_2$, affording 0.110 g (0.180 mmol, 95%) of yellow crystalline **11**. On some occasions small amounts of the B-phenyl derivative **12** (see following synthesis) were also obtained under this procedure and were separated from **11** by eluting in 4:1 hexane/$CH_2Cl_2$ on a silica TLC plate. $^1$H NMR ($\delta$, $CDCl_3$): 7.29 (t, $J$ = 7.9 Hz), 7.19 (d, $J$ = 7.9 Hz), 7.07 (t, $J$ = 7.3 Hz), 6.07 ($C_5H_5$, s), 1.99, 1.88 (ethyl $CH_2$), 1.03 (ethyl $CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 193.6, 136.1, 127.9, 125.7 (aryl carbons), 112.7 ($C_5H_5$), 23.9 (ethyl $CH_2$), 14.0 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 38.0 (1B, s), 24.4 (2B, d, $J$ = 80 Hz), 3.8 (1B, d, $J$ = 144 Hz).

**CpPh$_2$Ta (Et$_2$C$_2$B$_4$H$_3$-5-Ph) (12).** The above procedure was followed using 0.100 g (0.190 mmol) of **2b** and 15 equiv of 3.0 M PhMgBr, except that in this case the solution was stirred for several hours, during which its color turned dark green. The volatiles were removed by rotoevaporation, and the excess Grignard reagent was quenched by stirring in dichloromethane for several minutes. Workup as in the preceding synthesis, which allowed removal of biphenyl and separation from minor amounts of **11**, gave 0.109 g (0.180 mmol, 95%) of yellow solid **12** (in some runs, the silica flashing procedure had to be repeated in order to remove all of the biphenyl). $^1$H NMR ($\delta$, $CDCl_3$): 7.75 (d, $J$ = 6.8 Hz), 7.41 (t, $J$ = 6.8 Hz), 7.29 m 7.28 m, 7.08 m, 5.83 ($C_5H_5$, s), 2.07, 2.01 (ethyl $CH_2$, m), 1.07 (ethyl $CH_3$, t). $^{13}$C NMR ($\delta$, $CDCl_3$): 202.2, 195.0 (quat. carbon atoms in $C_6H_5$), 136.3, 133.7, 127.7, 127.6, 126.5, 125.2 (aryl carbons), 111.1 ($C_5H_5$), 24.1 (ethyl $CH_2$), 14.3 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 41.8 (s, 1B), 25.3 (d, 2B, $J$ = 105 Hz), 4.8 (d, $J$ = 83 Hz). MS (CI in $CH_4$): *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.

**CpMe$_2$Ta(Et$_2$C$_2$B$_4$HBr$_3$) (13).** A 0.300 g (0.44 mmol) sample of **5** was dissolved in 10 mL of toluene, 2.0 equiv of 3.0 M $CH_3MgBr$ was added, and the mixture was stirred for 2 h under argon. The volatiles were removed on a Schlenk line, and the mixture was dissolved to the point of saturation in hexane and recrystallized overnight at −20 °C to give 0.203 g (0.32 mmol, 73%) of yellow solid **13**. $^1$H NMR ($\delta$, $CDCl_3$): 6.14 ($C_5H_5$, s), 2.88, 2.75 (ethyl $CH_2$, m), 1.34 (ethyl $CH_3$, t, $J$ = 7.8 Hz), 0.18 (Ta−$CH_3$, s). $^{13}$C NMR ($\delta$, $C_6D_6$): 113.7 ($C_5H_5$, s), 57.4 (Ta−$CH_3$, s), 22.7 (ethyl $CH_2$, s) 13.9 (ethyl $CH_3$, s). $^{11}$B NMR ($\delta$, $CDCl_3$): 29.8 (1B, s), 21.1 (2B, s), 1.2 (1B, d, $J$ = 173 Hz). IR ($CH_2Cl_2$, cm$^{-1}$): 3132 w, 2981 s, 2937 s, 2849 m, 2603 (m, B(H)), 1445 s, 1381 m, 1306 w, 1268 w, 1086 s, 1042 s, 865 s, 746 w. UV−vis ($CH_2Cl_2$, nm) 232 (100%), 354 (41%). MS (CI in $CH_4$): *m*/*z* 640. Anal. Calcd for $C_{13}H_{22}B_4Br_3Ta$: C, 24.38; H, 3.46. Found: C, 23.86; H, 4.04.

**CpMe$_2$Ta(Et$_2$C$_2$B$_4$H-4,6-Me$_2$-5-Br) (14).** A 0.100 g (0.15 mmol) sample of **5** was dissolved in 10 mL of THF under argon, and 5 equiv of 1.4 M MeLi (in diethyl ether) was syringed into the solution. After stirring for several hours, 10 mL of $CH_2Cl_2$ was added to quench any remaining MeLi. The volatiles were removed, and the mixture was dissolved in $CH_2Cl_2$, flashed through a silica plug, and column-chromatographed on a 10 in. basic alumina column in 4:1 hexane/$CH_2Cl_2$. The second band, which was the main fraction, was collected and the solvent removed to afford 0.049 g (0.095 mmol, 64%) of **14**. $^1$H NMR ($\delta$, $CDCl_3$): 5.95 ($C_5H_5$, s), 2.74 (ethyl $CH_2$, m), 1.20 (ethyl $CH_3$, m). $^{13}$C NMR ($\delta$, $CDCl_3$): 111.6 ($C_5H_5$), 51.2 (Ta−$CH_3$), 29.8 (B−$CH_3$), 21.4 (ethyl $CH_2$), 13.9 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 36.3 (s, 1B), 26.7 (s, 2B), 2.0 (d, $J$ = 166 Hz). MS (CI in $CH_4$): *m*/*z* 511, frag. 496 (−$CH_3$). Anal. Calcd for $C_{15}H_{28}B_4$-BrTa: C, 35.15; H, 5.51. Found: C, 35.41; H, 5.82.

**CpMe$_2$Ta(Et$_2$C$_2$B$_4$HMe$_3$) (15).** A 0.100 g (0.146 mmol) sample of **5** was dissolved in 5 mL of dry THF, and 20 equiv of 3.0 M $CH_3MgBr$ in diethyl ether was syringed into the swirling solution. On addition of the Grignard reagent, the solution became reddish-brown. The solution was stirred for 3 h, the volatiles were removed, and the residue was dissolved in $CH_2Cl_2$ and flashed through a 2 cm plug of silica. The solvent was removed, affording 0.056 g (0.125 mmol, 86%) of yellow solid **15**. $^1$H NMR ($\delta$, $CDCl_3$): 5.79 ($C_5H_5$, s), 2.74 (ethyl $CH_2$, m), 1.19 (ethyl $CH_3$, t, $J$ = 7.8 Hz), 0.56 (B[4,6]-$CH_3$, s), 0.49 (B[5]-$CH_3$, s), −0.34 (Ta−$CH_3$, s). $^{13}$C NMR ($\delta$, $CDCl_3$): 109.8 ($C_5H_5$), 48.6 (Ta−$CH_3$), 29.8 (B(4), B(6)−$CH_3$), 21.1 (ethyl $CH_3$), 13.9 (ethyl $CH_3$). $^{11}$B NMR ($\delta$, $CDCl_3$): 40.4 (1B, s), 28.7 (2B, s), 2.8 (1B, d, $J$ = 161 Hz). IR ($CH_2Cl_2$, cm$^{-1}$): 3119 w, 2936 s, 2829 w, 2540 (s, BH), 1438 s, 1313 s, 1174 m, 1017 m, 841 s. UV−vis ($CH_2Cl_2$, nm): 230 (100%), 390 (39%). MS (CI in $CH_4$): *m*/*z* 447. Anal. Calcd for $TaC_{16}H_{31}B_4$: C, 42.93; H, 6.98. Found: C, 42.65; H, 6.69.

**Reaction of CpMe$_2$Ta(Et$_2$C$_2$B$_4$H$_4$) (16) with I$_2$.** A 0.100 g (0.25 mmol) sample of **16** was dissolved in 5 mL of dry deoxygenated tetrahydrofuran, and a solution of 0.175 g of $I_2$ in THF was added via syringe. After the solution was stirred for 2 h the volatiles were removed, affording a dark yellow solid that has been tentatively characterized as CpMeITa-($Et_2C_2B_4H_4$) (**17**) (0.060 g, 0.116 mmol, 46%). $^1$H NMR ($CDCl_3$): 6.15 ($C_5H_5$, s), 2.63 (ethyl $CH_2$, m), 2.46 (ethyl $CH_2$, m), 2.36 (ethyl $CH_2$, m), 1.10 (ethyl $CH_3$, t), 1.03 (ethyl $CH_3$, t), 0.85 (Ta−$CH_3$, s). $^{13}$C NMR ($CDCl_3$): 113.5 ($C_5H_5$), 38.8 (Ta−$CH_3$), 22.0, 21.2 (ethyl $CH_2$), 15.4, 14.7 (ethyl $CH_3$). MS (CI in $CH_4$): *m*/*z* 517. When an additional equivalent of $I_2$ is employed, the predominant product formed is tentatively identified as CpMeITa($Et_2C_2B_4H_3$-5-I) (**18**). $^1$H NMR ($CDCl_3$): 6.33 ($C_5H_5$, s), 3.18 (ethyl $CH_2$, m), 3.08 (ethyl $CH_2$, m), 2.85 (ethyl $CH_2$, m), 1.37 (ethyl $CH_3$, t), 1.20 (ethyl $CH_3$, t), −0.251 (Ta−$CH_3$, s). $^{11}$B NMR ($CDCl_3$): 27.1 (1B, br s),[14] 22.8 (1B, br s),[14] 8.7 (1B, s), −5.2 (1B, br s).[14] MS (CI in $CH_4$): *m*/*z* 643. Full characterization of these compounds was not achieved because all purification attempts were unsuccessful.

**Electrochemistry.** Cyclic voltammetry was conducted in a one-compartment cell with a Pt disk (3 mm diameter) working electrode, a saturated Ag/AgCl reference electrode, and a platinum wire as the auxiliary electrode, using a Bioanalytical Systems CV27 voltammograph. Scan rates from 20 mV to 1 V s$^{-1}$ were employed; values reported were obtained at 200 mV s$^{-1}$. The solvent was $CH_2Cl_2$, purified via double distillation from $CaH_2$; the supporting electrolyte was 0.5 M $Bu_4NPF_6$, used as received. Potentials were measured against internal $Cp_2Fe/Cp_2Fe+$ (+0.55 V vs NHE).

**X-ray Crystallography.** A red, irregularly shaped crystal of approximate dimensions 0.36 × 0.26 × 0.49 mm was used for all X-ray measurements. The data collection was carried out on a Rigaku AFC6S diffractometer at −120 °C using Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). Unit cell dimensions were determined by applying the setting angles of 25 high-angles reflections. Intensities of three standard reflections were monitored during the data collection, showing no significant variance. The intensities were corrected for absorption by using $\psi$ scans of several reflections. The transmission factors ranged from 0.25 to 1.00. The structure was solved by direct methods (SIR92).[15] Calculations were performed on a Silicon Graphics Indigo 2 Extreme computer by applying the teXsan 1.7 software.[16] Full-matrix refinement with anisotropic ther-

mal displacement parameters for the Ta, Br, Co, and Cl atoms gave the final $R$ of 0.087 ($R_w = 0.114$). Difference Fourier maps indicated the presence of three peaks attributed to a partially occupied dichloromethane molecule. The non-hydrogen atoms of this solvent molecule were refined isotropically with the population parameter of 0.5. The final difference map showed a peak of 3.48 e/Å$^3$ in the vicinity of the dichloromethane solvent molecule.

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**Supporting Information Available:** Tables of atomic coordinates, thermal displacement parameters, and calculated mean planes for **7a**, and electrochemical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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