Tantalum-Mediated Oxidative Coupling of $C_2B_9H_{11}^{2-}$ Ligands. Synthesis and Characterization of $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$

Yue-Xin Su, Cathrine E. Reck, Ilia A. Guzei, and Richard F. Jordan*

Department of Chemistry, The University of Chicago, 5735 S. Ellis Avenue, Chicago, Illinois 60637, and Molecular Structure Laboratory, Iowa State University of Science and Technology, Ames, Iowa 50011

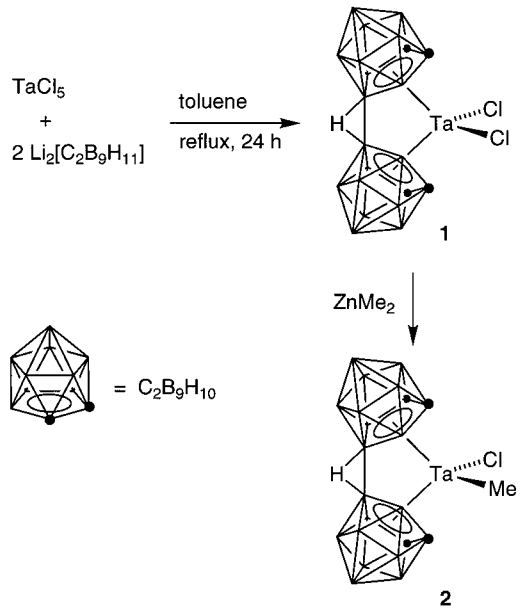
Received July 3, 2000

The reaction of $TaCl_5$ with 2 equiv of $Li_2[C_2B_9H_{11}]$ in refluxing toluene yields $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$ (**1**), which contains the unusual linked bis(carboranyl) ligand $[(\mu\text{-H})(C_2B_9H_{10})_2]^{3-}$, which is formed by formal oxidative coupling of two $C_2B_9H_{11}^{2-}$ ligands. Alkylation of **1** with $ZnMe_2$ yields $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaMeCl$ (**2**), which retains the linked bis(carboranyl) ligand.

Introduction

Group 5 metal bis(dicarbollide) bent metallocene compounds, $(\eta^5\text{-}C_2B_9H_{11})_2MR$, are interesting synthetic targets because they are isolobal and isoelectronic with the $(C_5R_5)_2ZrR^+$ cations which are the active catalysts in metallocene-catalyzed olefin polymerization.[1] In previous studies directed toward the synthesis of electrophilic group 5 metal carborane complexes, we prepared mono-dicarbollide $(\eta^5\text{-}C_2B_9H_{11})TaX_3$ (X = Cl, Me) piano stool complexes, mixed cyclopentadienyl dicarbollide bent metallocenes $(C_5H_4R)(C_2B_9H_{11})TaCl_2$ (R = H, Me), and anionic bis(dicarbollide) bent metallocenes $(\eta^5\text{-}C_2B_9H_{11})_2MX_2^-$ (X = Cl, Me, F).[2−5] Here we describe unusual Ta carborane species that contain the new linked bis(carboranyl) ligand $[(\mu\text{-H})(C_2B_9H_{10})_2]^{3-}$, which have been isolated during attempts to prepare $(\eta^5\text{-}C_2B_9H_{11})_2TaX$ compounds.[6,7]

Scheme 1



Results and Discussion

Synthesis of $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$ (1). The reaction of $TaCl_5$ with $Li_2[C_2B_9H_{11}]$ was investigated in an attempt to prepare $(\eta^5\text{-}C_2B_9H_{11})_2TaCl$.[8] The reaction of $TaCl_5$ with 2 equiv of $Li_2[C_2B_9H_{11}]$ in toluene (110 °C, 24 h), followed by removal of the volatiles under vacuum and sublimation of the residue, afforded a bright yellow solid, **1** (19%, Scheme 1). Crystals of **1** were isolated by sublimation of the isolated product at 160−170 °C onto a 25 °C probe. The synthesis of **1** was monitored by ^1H NMR (toluene-d_8, 110 °C, 24 h) in the presence of an internal standard (C_6Me_6). These experiments showed

(1) Leading references: (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (c) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255.

(2) Uhrhammer, R.; Crowther, D. J.; Olson, J. D.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1992**, *11*, 3098.

(3) Uhrhammer, R.; Su, Y.-S.; Swenson, D. C.; Jordan, R. F. *Inorg. Chem.* **1994**, *33*, 4398.

(4) For other group 5 metal carborane chemistry see: (a) Boring, E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1997**, *17*, 33993. (b) Stockman, K. E.; Houseknecht, K. L.; Boring, E. A.; Sabat, M.; Finn, M. G.; Grimes, R. N. *Organometallics* **1995**, *14*, 3014. (c) Houseknecht, K. L.; Stockman, K. E.; Sabat, M.; Finn, M. G.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 1163. (d) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1984**, *3*, 599. (e) Batsnov, A. S.; Churakov, A. V.; Howard, J. A. K.; Hughes, A. K.; Johnson, A. L.; Kingsley, A. J.; Neretin, I. S.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1999**, 3867.

(5) For related group 4 metal carborane chemistry see: (a) Bei, X.; Kreuder, C.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 1085. (b) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508. (c) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (d) Crowther, D. J.; Swenson, D. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1995**, *117*, 10403. (e) Kreuder, C.; Jordan, R. F.; Zhang, H. *Organometallics* **1995**, *14*, 2993. (f) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630. (g) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455.

(6) (a) Recent work on the develoment of group 5 metal olefin polymerization catalysts is summarized in: Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *3385*, 428.

(7) For studies of Ta borrolide complexes including application in olefin polymerization see: (a) Bazan, G. C.; Donnelly, S. J.; Rodroguez, G. *J. Am. Chem. Soc.* **1995**, *117*, 2671. (b) Sperry, C. K.; Cotter, W. D.; Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 7791. (c) Sperry, C. K.; Bazan, G. C.; Cotter, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 1, 1513.

(8) Su, Y.-X.; Ph.D. Thesis, The University of Iowa, 1998.

10.1021/om000566w CCC: $19.00
Publication on Web 10/12/2000

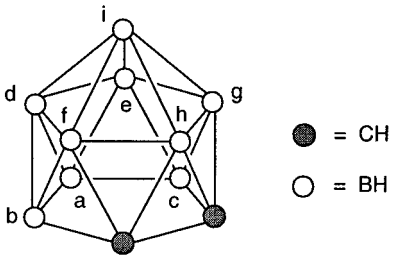


Figure 1. Labeling scheme used for ^{11}B NMR assignments.

that **1** was present in the final solution in ca. 20% yield and that no other toluene-soluble ^1H NMR-active species were formed in significant yield. Therefore, the amount of **1** that is isolated by sublimation is close to the total amount of **1** that is formed. No other reaction products could be identified. Compound **1** is air-stable in the solid state and in benzene solution for months and is thermally stable to 150 °C in the solid state. Compound **1** is soluble in benzene and toluene, reacts with CH_2Cl_2 to give $(C_2B_9H_{11})TaCl_3$, and does not form adducts with nitrogen or oxygen donors such as pyrazine or dioxane.

The characterization of **1** proved to be challenging. The $^{11}B\{^1H\}$ NMR spectrum of **1** contains five resonances in a 1:2:2:3:1 intensity ratio. The δ −6.8 (3B) resonance is broader than the remaining resonances. A C_{2v}-symmetric structure containing two equivalent $C_2B_9H_{11}^{2-}$ ligands (in which the sides of each dicarbollide are equivalent) would produce a six-line spectrum with an intensity ratio of 1:2:2:2:1:1. Therefore, the $^{11}B\{^1H\}$ NMR spectrum suggests that **1** has C_{2v} symmetry, but two resonances (intensity 1B and 2B) are coincident at δ −6.8. Consistent with a C_{2v} structure, singlets are observed in the ^1H (δ 4.4 in C_6D_6) and $^{13}C\{^1H\}$ (δ 71.6 in toluene-d_8) NMR spectra for the CH units of **1**. The NMR spectra of **1** are temperature independent down to −80 °C.

To investigate the possibility of B−H−B or B−H−Ta bridging in **1**, the ^1H-coupled ^{11}B NMR spectrum was obtained. In the ^{11}B NMR spectrum, the four high-field resonances split into doublets (J_{B-H} = 156−170 Hz) consistent with the presence of a terminal H at each boron, while the lowest field resonance (δ 13.2) broadens by 49 Hz but does not split. This result indicates that the boron giving rise to the δ 13.2 resonance either (i) is not bonded to a hydrogen, and the broadening is due to long range J_{B-H} coupling, or (ii) is bonded to a hydrogen that is involved in a bridging interaction that reduces the J_{B-H} value. The magnitude of the excess line width (49 Hz) is most consistent with the latter possibility.[9] The δ 13.2 resonance was assigned to the central boron in the C_2B_3 face (B_a, Figure 1) by a $^{11}B-^{11}B$ COSY experiment. This assignment is consistent with previous results for related compounds, including $[PPN][(C_2B_9H_{11})_2TaX_2]$ (X = Cl, F),[3] $(C_2B_9H_{11})TaCl_3$,[2] and the $(C_2B_9H_{11})_2Co^-$ anion.[10]

The mass spectrum of **1** contains a molecular ion envelope at *m/e* = 515 corresponding to the formula $(C_2B_9H_{10})_2(H)TaCl_2$ and a $[M - Cl]^+$ envelope at *m/e* = 480. Comparison of the simulated and observed molecular ion envelopes reveals that the latter is unsymmetrical and contains extra peaks extending down to *m/e* = 504 due to loss of up to six hydrogens from the molecular ion. This is a common phenomenon for carborane and metallocarborane compounds.[11] The mass spectral results establish that the Cl/Ta ratio for **1** is 2:1, but do not allow precise determination of the number of hydrogens that are present. It was not possible to obtain reproducible elemental analyses for spectroscopically pure crystalline samples of **1**. However, quantitative $^{11}B\{^1H\}$ NMR spectra of **1** in the presence of an internal standard (*o*-carborane) established that isolated **1** is ≥95% pure.

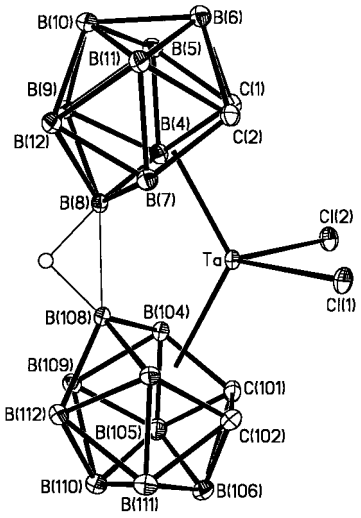


Figure 2. Molecular structure of $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$ (**1**). Terminal hydrogens are omitted. Thermal ellipsoids are drawn at the 30% probability level.

Molecular Structure of $\{(\mu\text{-H})(C_2B_9H_{10})_2\}TaCl_2$ (1). The foregoing results establish that **1** contains two Cl atoms per Ta, adopts a C_{2v}-symmetric structure, and contains an unusual structural feature at the central borons (B_a) of the C_2B_3 rings. The molecular structure of **1** was ultimately determined by X-ray diffraction and is shown in Figure 2. Crystallographic data and metrical parameters are summarized in Tables 1 and 2. Compound **1** adopts a bent-metallocene structure in which two eclipsed η^5-$C_2B_9H_{10}$ units are linked by a three-center, two-electron B−H−B bond involving the central borons of the C_2B_3 faces. The $B_{bridge}-B_{bridge}$ distance (1.870(4) Å) is 0.07 Å longer than the average B−B bond distance (1.80(2) Å), and the $B-H_{bridge}$ distance (1.29(3) Å) is ca. 0.2 Å longer than the average $B-H_{terminal}$ distance (1.07(4) Å). The B−H−B bridge angle is 93(2)°. The B−H−B bridge in **1** is similar to those in μ-$B_{20}H_{17}OH^{2-}$ ($B_{bridge}-B_{bridge}$ 1.907(9) Å; $B-H_{bridge}$ 1.17(6), 1.25(6) Å; B−H−B 104(8)°) and a^2-$B_{20}H_{10}^{3-}$ ($B_{bridge}-B_{bridge}$ 1.936(6) Å; $B-H_{bridge}$ 1.36(5) Å; B−H−B 91(3)°).[12] Thus, the bis(carboranyl) ligand in **1** is best represented as $[(\mu\text{-H})(C_2B_9H_{10})_2]^{3-}$, a formal 3−, 12-electron donor. The Ta−dicarbollide bonding in **1** is unsymmetrical due to the presence of the B−H−B bridge. The Ta−B_{bridge} distances (av 2.33 Å) are ca. 0.13

(9) Normal ranges for J_{B-H} values in carboranes and metallocarboranes are as follows: terminal B−H: J_{B-H} = 100−190 Hz; bridged B−H−M: J_{B-H} < 80 Hz; long-range B−H interactions (≥2 bonds): J_{B-H} usually unobservable. See: Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: New York, 1978; p 92.

(10) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413.

(11) (a) Spencer, J. T.; Pourian, M. R.; Butcher, R. J.; Sinn, E.; Grimes, R. N. *Organometallics* **1987**, *6*, 335. (b) Ditter, J. F.; Gerhart, F. J.; Williams, R. E. *Adv. Chem. Ser.* **1968**, *72*, 191.

Å shorter than the Ta−$B_{lateral}$ distances (av 2.45 Å) and 0.22 Å shorter than the Ta−C distances (av 2.56 Å). For comparison, the Ta−B and Ta−C distances in (η^5-$C_2B_9H_{11}$)$TaCl_3$ are all in the range 2.37−2.43 Å, and those in (C_5H_4Me)($C_2B_9H_{11}$)$TaCl_2$ are in the range 2.45 to 2.50 Å.[2] The bis(dicarbollide) complex (η^5-$C_2B_9H_{11}$)$_2$-$TaMe_2^-$ contains one symmetrically bonded (Ta−C,B: 2.51−2.57 Å) and one unsymmetrically bonded dicarbollide (Ta−C,B: 2.43−2.58 Å) ligand.[3] The centroid−Ta−centroid angle (123.7°) in **1** is ca. 14° smaller than that in ($C_2B_9H_{11}$)$_2TaMe_2^-$ (137.2°) due to the B−H−B link. The Cl−Ta−Cl angle (90.7°) in **1** is correspondingly larger than the C−Ta−C angle in ($C_2B_9H_{11}$)$_2TaMe_2^-$ (82.5°).[3] The solution NMR data for **1** are fully consistent with the solid-state structure.

Synthesis of {(μ-H)($C_2B_9H_{10}$)$_2$}TaClMe (2). The reaction of **1** with excess $ZnMe_2$ (4 equiv) in toluene (23 °C, 1.5 h) afforded {(μ-H)($C_2B_9H_{10}$)$_2$}TaClMe (**2**), which was isolated as yellow crystals (70%) by sublimation of the reaction residue at 105 °C. Alternatively, **2** can be recrystallized from toluene at −35 °C. Compound **2** is soluble and stable in benzene and toluene and does not react with Lewis bases such as dioxane or pyrazine.

NMR and mass spectral data establish that **2** is structurally analogous to **1**.[13] The ^{1}H NMR spectrum of **2** contains two dicarbollide C−H resonances (δ 4.14 (2H), 3.93 (2H)) and a single Ta−Me resonance (δ 1.25 (3H)), consistent with a C_s-symmetric structure and the presence of a single Ta−Me group. For a structure analogous to that of **1**, nine resonances of equal intensity are expected in the ^{11}B{^{1}H} NMR spectrum. The observed spectrum contains six resonances in a 1:1:3:1:2:1 intensity ratio, at chemical shifts similar to those observed for **1**. Evidently, several resonances are coincident. As for **1**, a low-field 1B resonance is observed at δ 10.9, which broadens by 31 Hz but does not split in the ^{1}H-coupled ^{11}B NMR spectrum. The remaining resonances all split into doublets (J_{B-H} = 141−176 Hz) due to B−H coupling. The ^{11}B−^{11}B COSY spectrum of **2** establishes that the δ 10.9 resonance is due to B_a (Figure 1), through which the two C_2B_3 units are linked. The mass spectrum of **2** contains a prominent envelope of peaks for the $[M - Me]^+$ ion at m/e = 480 with the expected series of $[M - Me - nH]^+$ peaks extending down to m/e = 461. The mass spectrum establishes that the Cl/Ta ratio of **2** is 1:1.

Possible Mechanism for the Formation of {(μ-H)($C_2B_9H_{10}$)$_2$}$TaCl_2$ (1). The low yield of **1** and lack of information concerning the other reaction product(s) make it difficult to study the mechanism of formation of this unusual compound. However, studies of related reactions provide some hints about how **1** might form. The following observations are relevant: (i) The reaction of $TaCl_5$ with 1 equiv of $Li_2[C_2B_9H_{11}]$ in toluene at 23 °C produces (η^5-$C_2B_9H_{11}$)$TaCl_3$ in 78% NMR yield (56% isolated). This result indicates that the initial step in the reaction of $C_2B_9H_{11}^{2-}$ and $TaCl_5$ is nucleophilic substitution of two chlorides.[2] (ii) The reaction of (η^5-$C_2B_9H_{11}$)$TaCl_3$ with [PPN][Tl($C_2B_9H_{11}$)] or Cs[Tl($C_2B_9H_{11}$)] in toluene at 23 °C produces [M][(η^5-$C_2B_9H_{11}$)$_2$-$TaCl_2$] (M^+ = PPN^+, Cs^+) in quantitative yield. Also, the reaction of (η^5-$C_2B_9H_{11}$)$TaCl_3$ with $Li_2[C_2B_9H_{11}]$ in THF-d_8 at 23 °C generates [Li(THF-d_8)$_4$][(η^5-$C_2B_9H_{11}$)$_2$-$TaCl_2$]. These results indicate that the second $C_2B_9H_{11}^{2-}$ reacts with ($C_2B_9H_{11}$)$TaCl_3$ via Cl^- replacement. However, no coupling of the $C_2B_9H_{11}^{2-}$ ligands is observed under these mild conditions with the large cations PPN^+, Cs^+, or $Li(THF)_4^+$. (iii) Heating [PPN][(η^5-$C_2B_9H_{11}$)$_2TaCl_2$] under vacuum (<10^{-3} Torr) at 130 °C in the solid state for several hours results in the sublimation of **1** (9% isolated). Observations (i)−(iii) suggest that **1** is formed by initial generation of (η^5-$C_2B_9H_{11}$)$_2TaCl_2^-$ followed by net loss of H^- from one of the B_a−H units with formation of the B−H−B bridge. The mechanism of hydride abstraction and the fate of the hydride are unknown; however it is possible that ion pairing of Li^+ at these B−H sites may be important.[14] The B−B oxidative coupling may be promoted by steric crowding between the two dicarbollide ligands of (η^5-$C_2B_9H_{11}$)$_2TaCl_2^-$ (cf. the structure of [PPN][(η^5-$C_2B_9H_{11}$)$_2TaMe_2$]).[3]

Metal-mediated oxidative coupling and oxidative fusion reactions of boranes, carboranes, and metallocarboranes have been extensively studied.[15] For example, oxidation of $B_{10}H_{10}^{2-}$ by Fe(III) or Ce(IV) yields $B_{20}H_{18}^{2-}$ in which two B_{10} cages are linked by two three-center, two-electron bonds, and oxidation of $C_2B_9H_{12}^-$ by Cr(VI) yields $C_4H_{18}B_{22}$, which is proposed to have a similar structure.[16,17] The formal loss of hydride in the formation of **1** is also related to the synthesis of "charge-compensated" dicarbollide ligands, wherein Fe(III) oxidation of $C_2B_9H_{12}^-$ in the presence of a suitable donor ligand L yields $C_2B_9H_{11}L$ compounds.[18]

Experimental Section

General Considerations. All manipulations were performed on a high-vacuum line or in a glovebox under N_2. Solvents were distilled from sodium/benzophenone ketyl. Commercial $TaCl_5$ (STREM, 99.9%) was sublimed before use. *o*-Carborane (KATCHEM) was used as received. $Li_2[C_2B_9H_{11}]$ was prepared as described previously.[2] NMR spectra were obtained using flame-sealed or Teflon-valved tubes at ambient probe temperature. ^{1}H and ^{13}C NMR chemical shifts are reported vs $SiMe_4$ and were determined by reference to the residual solvent resonances. ^{11}B NMR spectra were referenced to external $BF_3(Et_2O)$ (δ 0, C_6D_6). The labeling scheme used for the ^{11}B NMR assignments is given in Figure 1. All coupling constants are given in hertz. Electron impact mass spectra (EI-

(12) (a) Li, F.; Shelly, K.; Kane, R. R.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 6506. (b) Watson-Clark, R.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1996**, *35*, 2963. (c) Li, F.; Shelly, K.; Kane, R. R.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2646. See also: Watson-Clark, R. A.; Shelly, K.; Hawthorne, M. F. *Inorg. Chem.* **2000**, *39*, 1901.

(13) A single-crystal X-ray structural analysis confirmed that the structure of **2** is analogous to that of **1**. However, the precision of this study was limited due to crystal twinning.

(14) For examples of M−H−B and M−B ion pairing in early metal carborane complexes see: (a) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (b) Marsh, R. E.; Schaefer, W. P.; Bazan, G. C.; Bercaw, J. E. *Acta Crystallogr.* **1992**, *C48*, 1416. (c) Oki, A. R.; Zhang, H.; Hosmane, N. S. *Organometallics* **1991**, *10*, 3964. (d) Siriwardane, U.; Zhang, H.; Hosmane, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 9637. (f) Jia, L.; Zhang, H.; Hosmane, N. S. *Acta Crystallogr.* **1993**, *C49*, 453. (g) Hosmane, N. S. *J. Organomet. Chem.* **1999**, *581*, 13, and references therein.

(15) (a) Grimes, R. *Coord. Chem. Rev.* **1995**, *143*, 71. (b) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (c) Grimes, R. N. *Acc. Chem. Res.* **1987**, *11*, 420.

(16) Watson-Clark, R. A.; Hawthorne, M. F. *Inorg. Chem.* **1997**, *36*, 5419, and references therein.

(17) Janousek, Z.; Hermanek, S.; Plesek, J.; Stibr, B. *Collect. Czech. Chem. Commun.* **1974**, *39*, 2363.

(18) Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024, and references therein.

Table 1. 1. Summary of Crystallographic Data for 1

empirical formula	$C_4H_{21}B_{18}Cl_2Ta$
fw	515.64
temp (K)	173(2)
radiation, λ (Å)	Mo Kα, 0.71073
cryst syst	Triclinic
space group	P1(bar)
unit cell dimens	$a = 6.8021(4)$ Å, $\alpha = 80.876(1)°$ $b = 9.8283(5)$ Å, $\beta = 82.638(1)°$ $c = 14.3491(7)$ Å, $\gamma = 76.251(1)°$
volume (Å^3)	915.90(8)
Z	2
d(calcd, Mg/m^3)	1.870
μ (mm^{-1})	6.274
diffractometer	Bruker CCD-1000
cryst size (mm^3)	0.35 × 0.20 × 0.20
θ range (deg)	2.75−28.25
index ranges	$-8 \le h \le 8$, $-12 \le k \le 13$, $0 \le l \le 18$
no. of reflns total	8088
no. of ind reflns	4138 [R(int) = 0.0185]
absorption corr	empirical with SADABS
max. and min. transmn	0.3667 and 0.2174
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	4138/0/316
goodness-of-fit on F^2	1.078
R indices [$I > 2\sigma(I)$][a,b]	R1 = 0.0188, wR2 = 0.0471
R indices (all data)[a,b]	R1 = 0.0196, wR2 = 0.0475
max. resid density (e/Å^3)	0.762 and −1.986

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = q/\sigma^2(F_o^2) + (aP)^2 + bP$.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 1

Ta−Cl(1)	2.3494 (7)	Ta−B(4)	2.428(3)
Ta−Cl(2)	2.3600(7)	Ta−B(104)	2.436(3)
Ta−C(1)	2.542(3)	Ta−B(7)	2.464(3)
Ta−C(101)	2.544(3)	Ta−B(107)	2.467(3)
Ta−C(2)	2.566(3)	Ta−B(8)	2.331(3)
Ta−C(102)	2.574(3)	Ta−B(108)	2.328(3)
Ta−CNT(1)[a]	2.006	C(1)−C(2)	1.572(4)
Ta−CNT(2)	2.010	C(101)−C(102)	1.576(4)
B(8)−B(108)	1.870(4)	av B−B	1.80(2)
av B−C	1.70(3)	av B−H(terminal)	1.07(4)
B(8)−H(8)	1.29(3)		

Cl(1)−Ta−Cl(2)	90.78(2)	CNT(1)−Ta−CNT(2)	124.2
CNT(1)−Ta−Cl(1)	108.4	CNT(1)−Ta−Cl(2)	109.4
CNT(2)−Ta−Cl(1)	109.1	CNT(2)−Ta−Cl(2)	109.8
B(8)−H(8)−B(108)	92.8		

[a] CNT = centroid of C_2B_3 donor rings of the η^5-$C_2B_9H_{10}$ units.

MS) were obtained with a VG TRIO-1 instrument operating at 70 eV with a direct inlet probe.

{(μ-H)($C_2B_9H_{10}$)$_2$}TaCl$_2$ (1). Solid $Li_2[C_2B_9H_{11}]$ (2.001 g, 13.68 mmol) was added in portions to an orange slurry of $TaCl_5$ (2.451 g, 6.842 mmol) in toluene (300 mL). The mixture was refluxed for 24 h. The volatiles were removed under vacuum to yield a brown, sticky residue. The residue was dried under vacuum at 60 °C for 2 h to yield a brown solid. The solid was ground into a fine powder and sublimed (<0.001 Torr) at 160−170 °C for 10 h onto a −78 °C coldfinger, yielding **1** as a bright yellow solid (0.670 g, 19%). Sublimation of **1** at 160−170 °C onto a glass surface at ambient temperature gave X-ray quality crystals. Alternate synthesis: Sublimation (<0.001 Torr) of $[PPN][(C_2B_9H_{11})_2TaCl_2]$[3] at 130 °C for 10 h produced **1** as a yellow solid (9%). Compound **1** can be recrystallized from toluene or benzene as yellow crystals. ^{1}H NMR (C_6D_6): δ 4.42 (s, 4H, CH), 5.0−1.0 (br, 18H, BH). ^{13}C{^{1}H} NMR (C_6D_6): δ 71.6. ^{11}B{^{1}H} NMR (C_6D_6): δ 13.2 (1B, $w_{1/2}$ =116 Hz, B_a), 0.74 (2B, B_d, B_e), −1.4 (2B, B_b, B_c), −6.8 (3B, B_f, B_g, B_h, or B_i), −11.3 (1B, B_h or B_i). ^{11}B NMR (C_6D_6): δ 13.2 (s, $w_{1/2}$ = 165 Hz, B_a), 0.74 (d, J_{B-H} = 160, B_d, B_e), −1.4 (d, J_{B-H} = 156, B_b, B_c), −6.8 (d, J_{B-H} = 170, B_f, B_g, B_h, or B_i), −11.3 (d, J_{B-H} = 164, B_h or B_i). ^{11}B−^{11}B COSY (C_6D_6) correlations: B_a−(B_b,B_c) strong; B_a−(B_d,B_e) medium; (B_d,B_e)−(B_b,B_c) weak; (B_d,B_e)−(B_f,B_g) medium. IR: 2596 cm^{-1} (terminal B−H). EI/MS: *m*/*e* 515 (M^+ and $M^+ - n$H), 480 (M^+ − Cl and M^+ − Cl − *n*H).

{(μ-H)($C_2B_9H_{10}$)$_2$}TaMeCl (2). A solution of $ZnMe_2$ in toluene (0.60 mL, 2.0 M, 1.2 mmol) was added dropwise to a solution of **1** (0.160 g, 0.311 mmol) in toluene (30 mL). The mixture was stirred for 1.5 h at ambient temperature. The volatiles were removed under vacuum. The crude product was sublimed (<0.001 Torr) at 105 °C onto a −78 °C coldfinger, yielding **2** as a yellow solid (0.108 g, 70%). Alternate synthesis: A solution of $ZnMe_2$ in toluene (0.60 mL, 2.0 M, 1.2 mmol) was added dropwise to a solution of **1** (0.160 g, 0.311 mmol) in toluene (30 mL). The mixture was stirred for 1.5 h at 23 °C. The volatiles were removed under vacuum. To ensure complete removal of the $ZnMe_2$, toluene (10 mL) was added to the residue and the volatiles were removed again under vacuum. This process was repeated twice, and the final residue was dried under vacuum for 18 h. Toluene (10 mL) was added, the slurry was filtered, and the precipitate was washed with toluene (3 × 5 mL). The filtrate and washes were combined, concentrated to 6 mL, and stored at −35 °C for several hours, yielding **2** (0.114 g, 75%) as yellow crystals. ^{1}H NMR (toluene-d_8): δ 4.14 (s, 2H, CH), 3.93 (s, 2H, CH), 1.25 (s, 3H, Me), 5.0−1.0 (br, BH). ^{13}C NMR (toluene-d_8): δ 67.5 (d, J_{C-H} = 174, CH), 65.7 (d, J_{C-H} = 165, CH), 64.0 (q, J_{C-H} = 127, Me). ^{11}B-{^{1}H} NMR (C_6D_6): δ 10.9 (1B $w_{1/2}$ =122 Hz, B_a), 1.3 (1B, B_d, or B_e), −2.0 (3B, B_d or B_e, B_b, B_c), −8.0 (1B, B_i), −9.5 (2B, B_f, B_g), −11.8 (1B, B_h). ^{11}B NMR (C_6D_6): δ 10.9 (s, $w_{1/2}$ = 153 Hz, B_a), 1.3 (d, J_{B-H} = 147, B_d or B_e), −2.0 (d, J_{B-H} = 141, B_d or B_e, B_b, B_c), −8.0 (d, J_{B-H} = 149, B_i), −9.5 (d, J_{B-H} = 176, B_f, B_g), −11.8 (d, J_{B-H} ca. 170, B_h). ^{11}B−^{11}B COSY (C_6D_6) correlations: B_a−(B_b,B_c) strong; B_a−(B_d,B_e) medium; (B_d,B_e)−(B_b,B_c) medium; (B_d or B_e)−(B_f,B_g) weak, (B_f,B_g)−(B_h) medium. EI MS: *m*/*e* 480 (M^+ − Me and M^+ − Me − *n*H).

Acknowledgment. This work was supported by NSF grant CHE-9413022. Several early experiments were performed by Dr. Donna J. Crowther.

Supporting Information Available: Summary of data collection and structure solution and refinement procedures used in the X-ray diffraction analysis of **1**; drawing showing molecular structure and atom labeling for **1**; tables of crystal and refinement data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for **1**; NMR and mass spectra for **1** and **2.** This material is available free of charge via the Internet at http://pubs.acs.org.

OM000566W