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Synthesis of Mono- and Ditungstaboranes from Reaction of Cp^*WCl_4 and $[Cp^*WCl_2]_2$ with $BH_3\cdot thf$ or $LiBH_4$ ($Cp^* = \eta^5$-C_5Me_5). Control of Reaction Pathway by Choice of Monoboron Reagent and Oxidation State of Metal Center

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Reaction between Cp^*WCl_4 or $[Cp^*WCl_2]_2$ ($Cp^* = \eta^5$-C_5Me_5) and $BH_3\cdot thf$ affords the new tungstaborane $(Cp^*WCl)_2B_2H_6$, **2**, which reacts with further $BH_3\cdot thf$ to give $(Cp^*W)_2B_5H_9$, **1**. The structure of **1** has been determined by a single-crystal X-ray diffraction study and is best described as a bicapped trigonal bipyramidal, the same as previously found for Cr and Mo analogues. The first step of this reaction is reduction of Cp^*WCl_4 to $[Cp^*WCl_2]_2$ by $BH_3\cdot thf$, paralleling that of the Cp^*MoCl_4 system. In contrast with its lighter congener, reaction between $LiBH_4$ and Cp^*WCl_4 or $[Cp^*WCl_2]_2$ gives different metallaboranes depending on the oxidation state of the starting material and rate of addition of borane. With Cp^*WCl_4 and fast addition of $LiBH_4$ the monometallic, crystallographically characterized, metallaborane *nido*-2-$(Cp^*WH_3)B_4H_8$, **3**, is formed in good yield along with the coproduct $(Cp^*WH_3)_2B_2H_6$, **4**. We have observed the time-dependent behavior of the formation of **3**, allowing the elucidation of intermediates on the reaction pathway. Reaction between $[Cp^*WCl_2]_2$ and 6 equiv of $LiBH_4$ affords only $(Cp^*W)_2(B_2H_6)_2$, **5**, demonstrating that in the formation of **3** and **4** $LiBH_4$ does not prereduce Cp^*WCl_4 to $[Cp^*WCl_2]_2$. Slow addition of $LiBH_4$ to Cp^*WCl_4 results in the reduced, dimeric complex $(Cp^*W)_2HCl(B_2H_6)$, **6**, which is formulated as having a W≡W triple bond.

Introduction

Synthetic methods for the generation of transition metal cluster species have historically been based around conditions that favor more stable products,[1] such as elevated temperatures or pressures, although there are notable exceptions to this.[2] The development of metallaborane chemistry has followed a similar pathway, with new species often afforded from conditions that favor the thermodynamic product, either through thermolysis or by simple metathesis reactions between a preformed polyborane anion and a transition metal halide.[3−5]

We have recently been investigating the reactivity between cyclopentadienyl transition metal halides and the monoboron reagents $BH_3\cdot thf$ and $LiBH_4$, which often afford metallaboranes in high yield under mild (room temperature or slightly above) conditions. Using this methodology new metallaboranes have been synthesized by reaction between $[Cp^*MCl_n]_m$ and $BH_3\cdot thf$ or $LiBH_4$, M = Cr,[6] Mo,[7] Re,[8] Ru,[9] Co,[10] and Rh.[11] The mild conditions often mean that products that occupy relatively shallow potential energy wells on the reaction pathway may be accessed. For example, reaction between Cp^*MoCl_4 and $BH_3\cdot thf$ ultimately results in the isolation of $(Cp^*Mo)_2B_5H_9$, but by judicious choice of reaction conditions, the novel metallaborane $(Cp^*MoCl)_2B_3H_7$ may be isolated as an intermediate on this reaction pathway.[7]

One of the driving forces behind this investigation is the possibility of rational high-yield syntheses of metallaboranes from a wide range of transition metals. This would allow a systematic examination of how subtle variations of metal center influence the nature of the resulting cluster. For group 6 metals, we have previously presented full accounts of the chemistry of Cr and Mo, and we now describe a similar study of the related chemistry of the heaviest member of the group 6 triad. Indeed the chemistry of {Cp*Cr}and {Cp*Mo} fragments with monoboron reagents displays variations between the metals,[6,7] and we considered whether the

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chemistry associated with a {Cp*W} fragment would mimic {Cp*Mo} or display other interesting variations.

Green et al. have reported a number of interesting tungstaboranes using the same approach; that is, the reaction between $LiBH_4$ and (η^5-C_5H_4R)WCl_4 (R = Me, ^iPr) provides several spectroscopically characterized tungstaboranes in modest yield.[12] As tungstaboranes are rare[13] and structurally characterized examples even more so,[14–16] we have reexamined this system using our own approach, which includes BH_3·thf as well as $[BH_4]^-$ as the boron source. We now report here results of reactions between Cp^*WCl_4 and BH_3·thf and $LiBH_4$ to afford mono- and bis(tungstaborane)s in good yield, two of which have also been characterized by X-ray crystallography. We also demonstrate the ability to influence final product distributions by kinetic control of the reaction.

Experimental Section

General Methods. All manipulations were carried out under a dinitrogen or argon atmosphere using standard Schlenk line or drybox techniques. Tetrahydrofuran (THF), toluene, and hexanes were all distilled from sodium benzophenone ketal. Starting materials Cp^*WCl_4 and $[Cp^*WCl_2]_2$ were prepared by the methods of Schrock[17] and Green.[18] BH_3·thf (1 M) and $LiBH_4$ (2 M) solutions (Aldrich) were used as received without further purification. $LiBD_4$ was prepared by a modification of the method described by Brown.[19]

NMR spectra were measured on a Varian-300 or Varian-500 FT-NMR at room temperature in C_6D_6 solutions unless otherwise noted. Residual protons of the solvent were used for reference in ^1H NMR experiments (δ, ppm: benzene, 7.15; toluene, 2.09). A sealed tube containing $[(NMe_4)(B_3H_8)]$ (δ, ppm −29.7) was used as the external reference to ^{11}B NMR experiments. Coupling constants are given in hertz. ^1H-{selective ^{11}B} experiments were used to assign resonances where possible. Spin−lattice relaxation time (T_1) measurements were carried out at 500 MHz by the inversion−recovery method using 180°−τ−90° pulse sequences with calibration of the 90° pulse at all reported temperatures, with T_1 values reported using software provided with the NMR spectrometer. Infrared spectra were measured on a Nicolet 205 FT-IR spectrometer. Mass spectra were measured on a JEOL JMS-AX 505HA mass spectrometer using EI or FAB (NBA matrix) mode. Perfluorokerosene and poly(ethylene glycol) were used as the standard for EI and FAB high-resolution mass spectra, respectively. Elemental analysis was performed by M-H-W Laboratories, Phoenix, AZ.

$(Cp^*W)_2B_5H_9$ (1). In a flame-dried Young's tube equipped with a Teflon tap, Cp^*WCl_4 (0.240 g, 0.522 mmol) was suspended in toluene (5 cm^3). BH_3·thf (3.2 cm^3, 3.2 mmol) was added via syringe, the tube was closed, and the contents were heated at 55 °C for 72 h. Volatiles were removed in vacuo, and the resulting orange residue was extracted into hexanes. Filtration, concentration, and cooling to −40 °C of this extract afford yellow *microcrystals* of $(Cp^*W)_2B_5H_9$ (**1**) (0.100 g, 0.143 mmol, 55% yield). Crystals suitable for a X-ray diffraction study were grown by slow evaporation of a concentrated hexanes solution of (**1**). ^1H NMR δ, ppm: 6.42 (4 H, 2 + 2 coincidence, pcq, H(1,5) and H(2,4)), 3.94 (1 H, pcq, H(3)), 2.08 (s, 30 H, Cp*), −8.20 [br pcq 4 H, B−*H*−W]. ^{11}B δ, ppm: 49.2 [1 B, B(3), *J*(HB) 174], 46.9 [2 B, B(2,4), *J*(HB) 170], 26.8 [br, 2 B, B(1,5), *J*(HB) 153]. IR (KBr, cm^{-1}): 2494 sh, 2462 m (B−H). MS (FAB) 20 C 5 B 2 W: 701.2584 (calcd), 701.2565 (obs). Anal. Calcd for $C_{20}H_{39}B_5W_2$: C, 34.25, H, 7.71. Found: C, 34.63, H, 7.35

$(Cp^*WCl)_2(B_2H_6)$ (2). In a flame-dried Young's tube equipped with a Teflon tap $[Cp^*WCl_2]_2$ (0.098 g, 0.126 mmol) was suspended in toluene (ca. 10 cm^3). BH_3·thf (1.4 cm^3, 1.4 mmol) was added via syringe. The solution was then heated for ca. 8 h at 55 °C. Removal of the toluene in vacuo, extraction of the dark brown residue into hexanes, and filtration through flame-dried Celite afforded a dark brown solution. Concentration in vacuo and cooling to −40 °C for 2 days afforded a brown solid of very air-sensitive $(Cp^*WCl)_2(B_2H_6)$ **(2)** (0.039 g, 0.053 mmol, 42% yield). ^1H NMR δ, ppm: 2.04 (30 H, Cp*), −13.80 (4 H, B−*H*−W). ^{11}B δ, ppm: −47.8 (br, fwhm 365). MS (EI) 20 C 2 B 2 W 2 Cl: 736.1401 (calcd), 736.1378 (obs). Due to the sensitivity of the sample, satisfactory microanalysis was not obtained.

$(Cp^*WH_3)B_4H_8$ (3) and $(Cp^*WH_3)_2B_2H_6$ (4). In a flame-dried Schlenk tube, Cp^*WCl_4 (0.52 g, 1.11 mmol) was suspended in toluene (40 cm^3) and cooled to −78 °C. $LiBH_4$ (3.2 cm^3, 6.40 mmol) was added via syringe and the reaction warmed slowly to room temperature with stirring. At ca. −60 °C the solution was homogeneous and dark green. Further warming to ca. 0 °C resulted in a color change to pale green and gas evolution. The solution was then stirred at room temperature for 1 h. Removal of volatiles in vacuo, extraction of the residue into hexanes, and filtration afforded a pale green solution, concentration and cooling of which to −40 °C afforded a mixture (ca. 10:1) of $(Cp^*WH_3)B_4H_8$ (**3**) and $(Cp^*WH_3)_2B_2H_6$ (**4**). Concentration and cooling of the resulting supernatant afforded a further small batch of **3** and **4** (total mass 0.255 g, 0.685 mmol, 62% based on W). Pure **3** may be isolated in essentially quantitative yield by gentle heating of a toluene solution of the mixture to 50 °C for 20 min and subsequent recrystallization from cold hexanes. Crystals of **3** suitable for an X-ray diffraction study were grown by slow evaporation of a concentrated hexanes solution under an argon atmosphere.

Spectroscopic Data for 3. ^1H NMR δ, ppm (−10 °C, toluene-d_8, 500 MHz): 5.89 (1 H, pcq, H(4)), 3.00 (2 H, pcq, H(3,5)), 1.84 (s, 15 H, Cp*), 1.10 (1 H, pcq, H(1)), −1.77 (s br, 2 H, W−*H*), −2.08 (br, 2 H, B−*H*−B), −2.72 [s br, 1 H, W−*H*, *J*(WH) 64], −8.15 (b, 2 H, B−*H*−W). ^1H NMR δ, ppm (−90 °C, toluene-d_8, 500 MHz): 6.17 (br, 1 H, H(4)), 3.71 (br, 1 H, H(3 or 5)), 2.36 (br, 1 H, H(3 or 5)), 1.74 (s, 15 H, Cp*), 1.00 (br, 1 H, H(1)), −0.21 (br, W−*H*), −1.90 (br, 2 H, B−*H*−B), −3.32 (br, 1 H, W−*H*), −7.11 (br, 1 H, W−*H*−B), −8.98 (br, 1 H, W−*H*−B). ^{11}B δ, ppm: 4.7 [1 B, B(4) *J*(HB) 146], −12.2 [2 B, B(3, 5) *J*(HB) 143], −31.2 [1 B, B(1) *J*(HB) 157]. IR (KBr, cm^{-1}): 2556, 2521 m (B−H). MS (FAB) 10 C 4 B 1 W: 372.1930 (calcd), 372.1932 (obs). Anal. Calcd for $C_{10}H_{26}B_4W$: C, 32.2; H, 7.02. Found: C, 32.1; H, 6.94.

Spectroscopic Data for 4. ^1H NMR δ, ppm (−10 °C, toluene-d_8, 500 MHz): 4.87 (2 H, pcq, BH_t), 1.70 (s, 30 H, Cp*), −0.06 (br, 4 H, B−*H*−W), −0.88 (s br, 2 H, W−*H*), −1.07 (br, 4 H, W−*H*). ^{11}B δ, ppm: −42.4 [2 B, *J*(HB) 146]. MS (EI) 20 C 2 B 2 W: 672.2514 (calcd), 672.2529 (obs).

$(Cp^*WD_3)B_4D_8$ (3b). In a procedure similar to that employed for the synthesis of **3**, $LiBD_4$ (0.5 M solution in thf) was reacted with Cp^*WCl_4, from −78 °C to room temperature, for

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a total time of 4 h. Characterization by ^{1}H, ^{11}B, and ^{2}H NMR confirmed a formulation and structure for **3b** identical to that found for **3**. MS (FAB) 10 C 11 D 4 B 1 W: 383.2450 (calcd), 383.2426 (obs).

$(Cp^*W)_2(B_2H_6)_2$ (5). In a flame-dried Schlenk tube, $[Cp^*WCl_2]_2$ (0.090 g, 0.116 mmol) was dissolved in toluene (10 cm^3) and cooled to −78 °C. $LiBH_4$ (0.35 cm^3, 0.694 mmol) was added via syringe. The solution was warmed to room temperature and stirred overnight. Removal of the solvent in vacuo, extraction of the residue into hexanes, followed by filtration, concentration, and cooling to −40 °C afforded brown $(Cp^*W)_2(B_2H_6)_2$ (**5**) (0.050 g, 0.072 mmol, 62% yield).

Spectroscopic Data for 5. ^{1}H NMR δ, ppm: 1.65 (s, 30 H, Cp*), 0.3 (4 H, BH_t), −10.24 (br, 8 H, B−*H*−W). ^{11}B δ, ppm: −53.9 [2 B, fwhm 220]. MS (FAB) 20 C 4 B 2 W: 695.2756 (calcd), 695.2748 (obs). Due to the sensitivity of the sample, satisfactory microanalysis was not obtained.

$(Cp^*W)_2HCl(B_2H_6)_2$ (6). In a flame-dried Schlenk tube, equipped with a pressure-equalizing dropping funnel, Cp^*WCl_4 (0.121 g, 0.261 mmol) was suspended in 20 cm^3 of toluene (or thf) and cooled to 0 °C. Dropwise addition of $LiBH_4$ (0.52 cm^3, 1.04 mmol in 10 cm^3 toluene (or thf)) over 1 h to the rapidly stirred solution resulted in gas evolution and a dark green homogeneous solution. The solution was warmed to room temperature and stirred for a further 1 h. Volatiles were removed in vacuo, and the residue was extracted into hexanes. Repeated recrystallization from hexanes at −20 °C afforded pure, brown, $(Cp^*W)_2HCl(B_2H_6)_2$ (**6**) (0.015 g, 0.021 mmol, 16% yield).

Spectroscopic Data for 6. ^{1}H NMR δ, ppm: 9.98 (2 H, pcq, BH_t), 2.00 (s, 15 H, Cp*), 1.84 (s, 15 H, Cp*), −1.95 (2 H, br, B−*H*−W), −4.20 [s, 1 H, W−H, *J*(WH) 112], −5.00 (2 H, br, B−*H*−W). ^{11}B δ, ppm: 101.5 [2 B, *J*(HB) 110]. MS (FAB) 20 C 2 B 2 W 1 Cl, 702.1789 (calcd), 702.1823 (obs).

X-ray Structure Determinations on 1 and 3. Diffraction data were collected at a temperature of 20 °C with an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromatic Mo Kα X-radiation source using the $\omega/2\theta$ scan technique. SDP software was used to process the intensity data.[20] Lorentz and polarization corrections and a linear decay correction were applied to the data. An empirical absorption correction based on ψ scans was also applied to the data. Structure solution and refinement were performed on a PC by using the SHELXTL package.[21] Least-squares refinement was carried out on F^2 for all reflections. After all non-hydrogen atoms were refined anisotropically, difference Fourier synthesis located all hydrogen atoms. In the final refinement cyclopentadienyl hydrogen atoms were refined with an idealized riding model that restrained the C−H distance to 0.96 Å and the isotropic thermal parameter of a hydrogen atom to 1.5 times the equivalent isotropic thermal parameter of its bonded carbon atom. The B−H hydrogen atoms were refined isotropically with bond length restraints, which used free variables in the refinement to confine bond distances around their mean values. The three hydride atom—H(1), H(2), and H(3)—were found by difference Fourier synthesis after all non-hydrogen atoms were refined anisotropically to convergence. In the final least-squares refinement, these hydride atoms were treated isotropically with bond length restraint for these W−H bonds by the use of a free variable which converged to 1.70(5) Å. Detailed crystallographic data are given in Table 1.

Table 1. Crystal Data and Structure Refinement for 2 and 3

	2	3
empirical formula	$C_{20}H_{39}B_5W_2$	$C_{10}H_{26}B_4W$
fw	701.26	373.40
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.130(2)	14.5152(14)
b (Å)	11.734(3)	7.8302(8)
c (Å)	11.955(3)	14.297(2)
α (deg)	108.93(2)	
β (deg)	92.16(2)	116.296(9)
γ (deg)	91.00(2)	
volume (Å)	1210.0(5)	1456.7(3)
Z	2	4
D_c (Mg/m^3)	1.925	1.703
F(000)	664	720
wavelength (Å)	0.71073	0.71073
abs coeff (mm^{-1})	9.502	7.896
cryst size (mm)	0.23 × 0.18 × 0.07	0.18 × 0.09 × 0.05
temp (K)	293	293
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
θ range, deg	2.11 → 25.00	2.85 → 25.01
no. of data collected	4242	2718
no. of unique data	4242	2560
no. of unique obsd data [$I > 2\sigma(I)$]	3850	1994
abs corr	ψ scans	ψ scans
max. and min. transmission	0.9990, 0.5933	1.0000, 0.6511
refinement method	SHELXL-93	SHELXL-93
weighting scheme	σ weight	σ weight
no. of data/restraints/ parameters	4242/19/284	2560/15/186
goodness-of-fit on F^2	1.227	1.022
final *R* indices [$I > 2\sigma(I)$]^a (wR^2)^b	0.0492 (0.1372)	0.0361 (0.0834)
R indices (all data)	0.0534 (0.1409)	0.0537 (0.0926)
max./min. residual e density	2.769/−1.792	1.465/−0.881

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR^2 = [\sum w(F_o^2 - F_c^2)^2/(w|F_o|^2)^2]^{1/2}$.

Results

Reaction of Cp^*WCl_4 with $BH_3\cdot thf$: $(Cp^*W)_2B_5H_9$ (1). Treatment of a toluene suspension of orange Cp^*WCl_4 with 6 equiv of $BH_3\cdot thf$ results in an immediate change to a dark green, homogeneous, solution ($[Cp^*WCl_2]_2$, vide infra) with concomitant gas formation (presumably dihydrogen), while the ^{11}B NMR spectrum shows that BH_2Cl has also been formed. Heating this mixture for 72 h at 55 °C results in an orange solution, from which the new compound $(Cp^*W)_2B_5H_9$, **1**, may be isolated in moderate yield, as the sole product of the reaction, as an orange solid, characterized initially by ^{11}B and ^{1}H NMR spectroscopy. The NMR data for **1** are similar to those reported for the both the Mo and Cr analogues.[12,22] The ^{11}B{^{1}H} NMR spectrum displays three resonances, which are all doublets in the coupled spectrum, at δ 49.2 (1 B), 46.9 (2 B), and 26.8 (2 B) ppm. The ^{1}H NMR spectrum shows a single Cp* resonance, signals due to BH_t groups, and an integral 4 H signal at δ −8.20 ppm assigned to B−*H*−W groups. Selective ^{1}H{^{11}B} experiments have assigned the individual resonances in the ^{11}B and ^{1}H NMR spectra.

The molecular structure of **1**, as determined by a single-crystal X-ray diffraction study, is shown in Figure 1, while salient bond lengths and angles given in Table 2. The solid-state structure is consistent with the solution NMR data, **1** having approximate C_{2v} symmetry, being isostructural with both the Cr [22] and Mo

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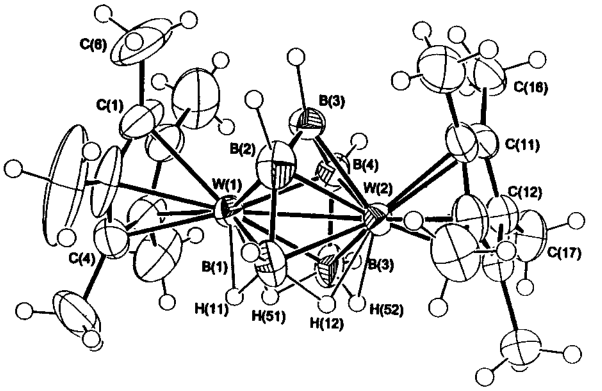

Figure 1. Molecular structure of $(Cp^*W)_2B_5H_9$, **2**, with thermal ellipsoids at 40% probability.

analogues,[12] and is best described as a bicapped *closo* trigonal bipyramid, B(5) and B(1) capping the W(1)−B(4)−W(2) and W(1)−B(2)−W(2) triangular faces, respectively. The observed skeletal electron pair (sep) count of six is consistent with this description. Such a geometry requires a W−W bonding interaction; the W−W distance at 2.8170(8) Å is consistent with this description.[23] Moreover, Fenske Hall approximate molecular orbital calculations on **1** show that the HOMO is based upon a $d_{z^2}-d_{z^2}$ orbital, with its antibonding and unfilled partner residing ca. 15 eV to higher energy.[24] Bond distances and angles are similar in **1** and $\{(\eta\text{-}C_5H_4Me)Mo\}_2B_5H_9$,[12] in accord with the similar sizes of Mo and W metal centers.[25] Consistent with the view of **1** as a bicapped trigonal bipyramid and not a triple decker complex, the Cp* rings are not coplanar, tilted some 13.3° (average of two planes) from the mean plane of the five boron atoms. Reaction between **1** and excess BH_3·thf or excess $LiBH_4$ at 55 °C for up to 1 week did not result in any new metallaboranes (by ^{11}B NMR).

Reaction between $[Cp^*WCl_2]_2$ and BH_3·thf: $(Cp^*WCl)_2B_2H_6$ (2). Reaction between a toluene solution of $[Cp^*WCl_2]_2$ and 6 equiv of BH_3·thf for 8 h at 55 °C affords a brown, very air-sensitive, solution that shows one major boron-containing species in solution characterized by a broad peak at δ −47.8 ppm in the $^{11}B\{^1H\}$ NMR spectrum, which becomes significantly broader on coupling to ^1H, as well as peaks due to BH_2Cl and unreacted BH_3·thf. Workup by removal of volatiles and extraction into hexanes afforded a brown solid, the ^{11}B NMR spectrum of which showed only the δ −47.8 ppm resonance, while the ^1H NMR spectrum shows a single peak at δ 2.04 ppm, assigned to 2 Cp* ligands, and a broad peak at δ −13.8 ppm of relative integral 4 H in the region associated with $B-H-M$ groups. The NMR data are similar to those found for $(Cp^*MoCl)_2(B_2H_6)$: [7] δ − 44.1 ppm in the ^{11}B NMR and δ −13.4 ppm for the $B-H-Mo$ groups in the high-field region of the ^1H NMR spectrum. Accurate mass measurements are in agreement with the formulation of this new compound as $(Cp^*WCl)_2(B_2H_6)$, **2**. As formulated, **2** is also similar to $(Cp^*TaBr)_2(B_2H_6)$,[26] which is present in two forms in solution, with symmetric and asymmetric $\{B_2H_6\}^{2-}$ ligands, and $\{(CO)_3Fe\}_2(B_2H_6)$,[27] for which the $\{B_2H_6\}^{2-}$ ligand is fluxional in solution. The ^1H NMR spectrum of **2** is invariant down to − 80 °C, showing that the $\{B_2H_6\}$ ligand in **2** is not fluxional.

Previously it has been noted that group 6 compounds of the type $[(\eta\text{-}C_5R_5)MCl_2]_2$ can have two, four, or no bridging chloride ligands, for Cr, Mo, and W, respectively.[17] The solid-state structure of $[Cp^*WCl_2]_2$ shows four bridging chloride ligands,[28] demonstrating that changes in ancillary ligands on the metal can affect the coordination mode of the chloride ligands. As $(Cp^*MoCl)_2B_2H_6$ adopts bridging chloride ligands in the solid state,[7] it is tempting to suggest that the chlorides also adopt a similar bonding mode in **2**. Thus, viewing **2** as a metallaborane, it has an electron count of six sep or 40 cluster valence electrons (cve) consistent with a M_2B_2 tetrahedron. Alternatively, if treated as a coordination complex between two W(III) centers and a $\{B_2H_6\}^{2-}$ ligand, both metal centers attain an 18-electron configuration by invoking a metal−metal bond. Compound **2** may also be generated by direct reaction between Cp^*WCl_4 and 6 equiv of BH_3·thf at 55 °C overnight. Heating a toluene solution of **2** with 6 equiv of BH_3·thf for 48 h at 55 °C results in the formation of **1** as the major boron-containing product.

Reaction of Cp^*WCl_4 with 6 equiv of $LiBH_4$: $(Cp^*WH_3)B_4H_8$ (3) and $(Cp^*WH_3)_2B_2H_6$ (4). Reaction between a toluene suspension of Cp^*WCl_4 and 6 equiv of $LiBH_4$ at low temperature affords an initially dark green, homogeneous, solution. On warming to ca. 0 °C, vigorous gas evolution is observed with a concomitant change in color of the solution to pale green. Low-temperature ^{11}B and ^1H NMR studies have identified the intermediates in this reaction (vide infra). The pale green solid that is isolated was identified by multinuclear and variable-temperature NMR spectroscopy as a mixture of two products. The major one of these (ca. 90%), which can be separated free of the minor product and has also been characterized by X-ray crystallography, is *nido*-2-$(Cp^*WH_3)B_4H_8$, **3**. The minor product has been formulated from spectroscopic data as $(Cp^*WH_3)_2B_2H_6$, **4**, and could not be isolated free of **3**.

The solid-state structure of **3** is shown in Figure 2, with selected bond lengths and angles given in Table 3. It is evident that the molecular structure is based upon *nido*-B_5H_9, a basal {BH} fragment substituted with $\{Cp^*WH_3\}$, supporting the earlier proposed structure for $\{(\eta\text{-}C_5H_4\text{-}{}^iPr)WH_3\}B_4H_8$, isolated from reaction between $LiBH_4$ and $(\eta\text{-}C_5H_4\text{-}{}^iPr)WCl_4$.[12] As the $\{Cp^*WH_3\}$ fragment may be considered to be a two-electron three-orbital donor fragment to cluster bonding,[29] **3** has 7 sep, consistent with the observed *nido* structure. All three hydride ligands were located and refined and adopt an approximate planar arrangement, reminiscent of that found in $Cp^*_2MH_3$ (M = Nb,[30] Ta[31]) or the proposed solution structure of $[Cp^*_2WH_3]^+$.[32] Bond lengths and angles in the metallaborane core are similar to those

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $(Cp^*W)_2B_5H_9$ (2)

W(1)−B(1)	2.29(2)	W(1)−B(2)	2.22(2)	W(1)−B(3)	2.17(2)
W(1)−B(4)	2.23(2)	W(1)−B(5)	2.317(14)	W(2)−B(1)	2.27(2)
W(2)−B(2)	2.22(2)	W(2)−B(3)	2.17(2)	W(2)−B(4)	2.20(2)
W(2)−B(5)	2.30(2)	B(1)−B(2)	1.70(3)	B(2)−B(3)	1.73(2)
B(3)−B(4)	1.68(2)	B(4)−B(5)	1.73(2)	W(1)−W(2)	2.8170(8)
W(1)−H(11)	1.84(7)	W(2)−H(12)	1.83(7)	W(1)−H(51)	1.84(7)
W(2)−H(52)	1.84(7)				
B(1)−B(2)−(3)	120.6(12)	B(2)−B(3)−B(4)	122.5(12)	B(3)−B(4)−B(5)	122.5(13)
W(1)−B(1)−W(2)	76.4(5)	W(1)−B(2)−W(2)	78.9(5)	W(1)−B(3)−W(2)	80.9(5)

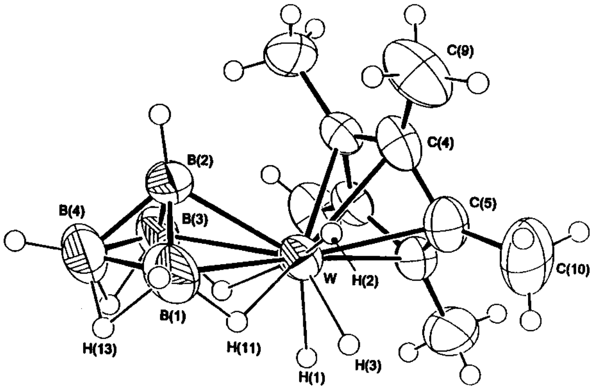

Figure 2. Molecular structure of $(Cp^*WH_3)B_4H_8$, **3**, with thermal ellipsoids at 40% probability.

reported for the quasi isostructural compounds *nido*-2-$(Cp^*TaCl_2)B_4H_8$[33] and *nido*-2-$(CpCo)B_4H_8$.[34] For example the tungsten−boron bond lengths, W−B(1) 2.433(11) Å, W−B(2) 2.229(9) Å, and W−B(3) 2.441(10) Å, compare well with the equivalent distances in $(Cp^*TaCl_2)B_4H_8$ at 2.495(11), 2.249(12), and 2.495(14) Å, respectively, the slightly shorter lengths in **3** consistent with the difference in covalent radii between W and Ta. The structural similarity between these two compounds is further reinforced by the lack of mirror symmetry present in each of these molecules, the metal−ligand fragment being canted by ca. 60° away from the W−B(2)−B(4) axis, as found in $(Cp^*TaCl_2)B_4H_8$. The underlying electronic factors that govern the twist of the $\{Cp^*WH_3\}$ and $\{Cp^*TaCl_2\}$ fragments in these molecules have been discussed elsewhere.[29] Briefly, the observed structure is one in which orbital overlap between the metal fragment based HOMO is maximized with the borane fragment's LUMO.

Compound **3** is routinely isolated in yields of ca. 60%, in contrast to the yields reported for $\{(\eta\text{-}C_5H_4{}^iPr)WH_3\}B_4H_8$ of ≈1%. The dramatic difference in the isolated yields is baffling as, in our hands, when prepared under comparable conditions, **3** passes down a column under anaerobic conditions and does not show sensitivity to change in solvent from toluene to thf to ether. It is also interesting to note that **3** and **4** are the only significant products of reaction, and coproducts analogous to those reported previously[12] were not observed. It is unlikely that the change in ligand from $\{C_5H_4{}^iPr\}$ to $\{C_5Me_5\}$ is significant, as the reaction between $(\eta^5\text{-}C_5R_5)MoCl_4$ (R = H, Me) and $LiBH_4$ showed no significant differences in final product distributions or yield on change of the ancillary ligand.[7]

Compound **3** displays three resonances in the room-temperature $^{11}B\{^1H\}$ NMR spectrum, all doublets in the coupled spectrum, at δ 4.7, −12.2, and −31.2 ppm, in the ratio 1:2:1, respectively. The room-temperature ^1H NMR spectrum shows a single Cp* resonance and relatively broad signals in the high-field region, integrating to 11 H overall. As expected, the positioning and pattern of the resonances are very similar to those found in $\{(\eta\text{-}C_5H_4{}^iPr)WH_3\}B_4H_8$.[12]

Variable-Temperature ^1H NMR Studies on 3. Cooling a sample of **3** to ca. −5 °C results in a sharpening of the high-field signals in the ^1H NMR spectrum (Figure 3) so that four distinct environments are now observed. Relatively sharp peaks at δ −1.77 (2 H) and −2.72 (1 H) ppm are assigned to two equivalent W−*H* groups [H(1,2)] and a unique W−H group [H(3)], respectively. The latter signal shows coupling to ^{183}W of ca. 64 Hz. Broad, integral 2 H, peaks at δ −2.08 and −8.15 ppm are assigned to B−*H*−B and B−*H*−W groups, respectively. These assignments have been confirmed by $^1H\{\text{selective } ^{11}B\}$ NMR experiments. Warming a sample of **3** to +70 °C results in the onset of coalescence of the W−*H* peaks, but due to significant decomposition[35] above these temperatures, the high-temperature limiting spectrum was not recorded. Progressive cooling of the sample to −90 °C resulted in the unique W−*H* resonance remaining essentially unchanged, while that due to the equivalent W−*H* groups becomes broad, disappears into the baseline, and reappears as two broad signals at δ − 0.2 and δ − 3.3 ppm. In a similar fashion the B−*H*−W signal broadens and splits into broad integral signals at δ −7.1 and −9.0 ppm. This spectrum is fully consistent with the solid-state structure as determined by X-ray diffraction. The ^{11}B NMR spectrum recorded at this lowest temperature showed only very broad, featureless signals.

Overall, these data are consistent with the presence of at least two fluxional processes occurring for the $\{Cp^*WH_3\}$ fragment at or below room temperature. At a temperature of ca. −5 °C the molecule displays a plane of mirror symmetry in solution, with two of the W−*H* ligands equivalent and both the B−*H*−W being equivalent. At temperatures above this, the three W−*H* groups begin to become equivalent, with no significant change in the position of B−*H*−B or B−*H*−W resonances. Below this temperature two of the W−*H* ligands gradually become inequivalent, so that at −90 °C they are observed as two separate signals, with the molecule lacking an overall plane of symmetry, confirmed by two

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $(Cp^*WH_3)B_4H_8$ (3)

W−B(1)	2.433(11)	W−B(2)	2.299(9)	W−B(3)	2.441(10)
W−H(1)	1.70(5)	W−H(2)	1.70(5)	W−H(3)	1.70(5)
W−H(11)	1.64(6)	W−H(31)	1.62(6)	B(1)−B(2)	1.69(2)
B(1)−B(4)	1.77(2)	B(2)−B(3)	1.693(14)	B(2)−B(4)	1.667(14)
B(3)−B(4)	1.75(2)				
B(1)−W−B(3)	64.5(5)	H(1)−W−H(2)	124(4)	H(1)−W−H(3)	58(4)
H(2)−W−H(3)	66(3)	B(1)−B(2)−B(3)	100.5(8)	B(4)−B(2)−W	109.0(6)
B(4)−B(3)−W	100.3(7)				

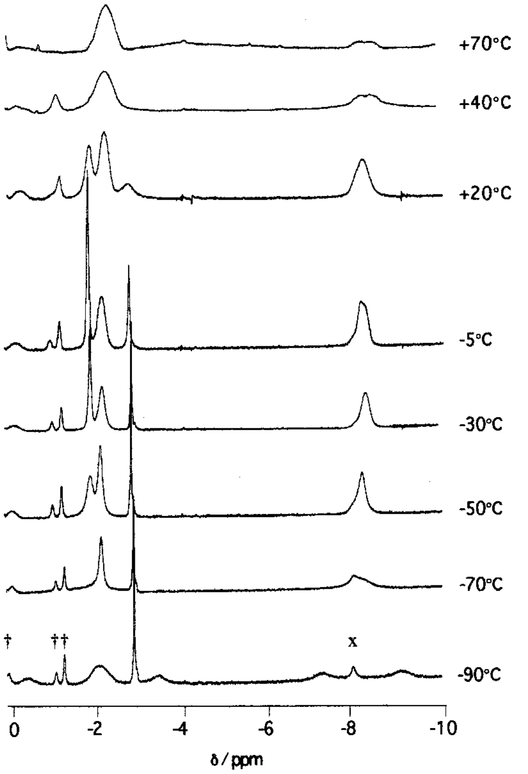


Figure 3. Variable-temperature ^1H NMR spectra for $(Cp^*WH_3)B_4H_8$, **3**, showing the high-field region. Spectra measured at +70 and +50 °C in toluene-d_8 at 300 MHz. All other spectra were recorded at 500 MHz, in toluene-d_8 solutions. “x” marks a minor decomposition product of $(Cp^*W)_2B_5H_9$, **2**. † denotes signals due to $(Cp^*WH_3)_2B_2H_6$, **4**.

resonances also being observed for B−*H*−W groups at this lowest temperature. $\{(\eta\text{-}C_5H_4{}^iPr)WH_3\}B_4H_8$ has also been studied by variable-temperature ^1H NMR spectroscopy and spin-saturation transfer experiments, and our results for **3** complement those reported earlier, in that for $\{(\eta\text{-}C_5H_4{}^iPr)WH_3\}B_4H_8$ the low-temperature limit for the fluxional processes was not reached.[12]

A plausible explanation for the fluxional behavior involves two complementary mechanisms. At higher temperatures, pairwise exchange[36] of H(1)/H(3) or H(2)/H(3), etc., would equilize all three sets of W−*H* ligands. This exchange is frozen out at lower temperatures, leaving a mechanism that makes H(1) and H(2) equivalent, such as a simple libration of the $\{Cp^*WH_3\}$ fragment around the W−B(4) axis (Scheme 1). This libration is frozen out at low temperature to reveal a structure that lacks a mirror plane of symmetry, fully consistent with the solid-state structure. That the single W−*H* resonance at $\delta \approx -3.0$ ppm [H(3)] remains virtually unchanged throughout the low-temperature regime suggests that its environment and bonding mode do not change significantly, consistent with a simple low-energy libration of the $\{Cp^*WH_3\}$ fragment. $\Delta G^\ddagger$ for this lower energy process is estimated to be ≈12 kcal/mol.

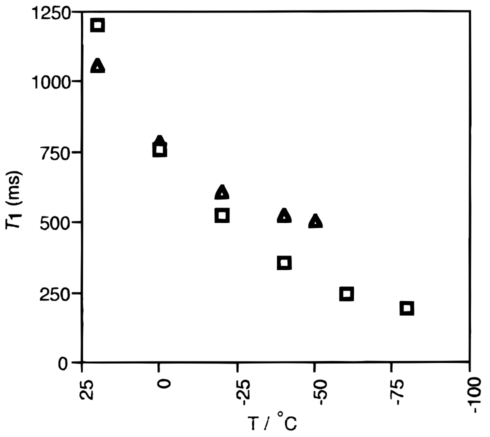
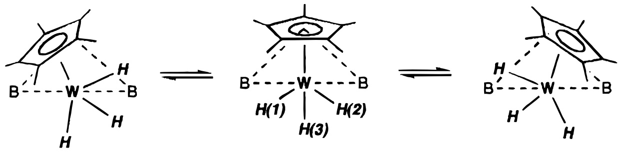


Figure 4. Plot of T_1 vs temperature for $(Cp^*WH_3)B_4H_8$, **3**, in toluene-d_8 (500 MHz). △ denotes the T_1 values for the two hydride ligands that are equivalent at −5 °C (see text), while □ refers to the unique hydride at this temperature.

Scheme 1



Relaxation Rate Measurements on 3. Longitudinal relaxation times (T_1) have been measured for the three W−*H* groups in **3** over the temperature range +25 to −90 °C. Such measurements on metal polyhydrides have been shown to be indicative of the nature of the bonding in such species, whether “classical” or “nonclassical” metal hydrides.[37,38] In fact the observed fluxionality could also be explained if a $\{Cp^*WH(\eta^2\text{-}H_2)\}$ fragment was invoked. Figure 4 shows a plot of T_1 vs temperature. The value of T_1 for the unique hydride ligand H(3) at −5 °C appears to reach a minimum of 190 ms at −80 °C. As this signal clearly cannot be due to a coordinated dihydrogen ligand, it serves as a useful internal reference. T_1 values for the two equivalent W−H groups were not measured below −50 °C due to the signal broadening into the B−*H*−B signal. However, the lowest value recorded, of 510 ms, clearly puts these two W−H groups in the region associated with classical dihydride ligands.[37b]

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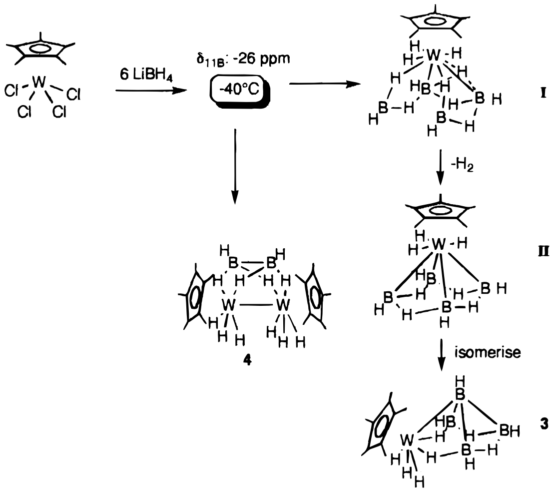
$(Cp^*WH_3)_2B_2H_6$ (4). The minor product formed alongside **3** has been identified by multinuclear NMR and accurate mass spectroscopy and is formulated as $(Cp^*WH_3)_2B_2H_6$, **4**. Compound **4** is always formed in ca. 10% yield relative to **3**, irrespective of reaction conditions, and changing solvent from toluene to THF affords no difference in overall product yields or the ratio of **3** to **4**. Compound **4** could not be isolated free of **3**, and thus spectroscopic data for **4** are reported on a mixture of these two compounds. **4** displays a single resonance in the $^{11}B\{^1H\}$ NMR spectrum, at δ −42.4 ppm, which splits into a broad doublet on coupling to ^1H, demonstrating equivalence of the two boron atoms in solution. The ^1H NMR spectrum displays a single Cp* resonance at δ 1.70 ppm (relative integral 30 H) and an integral 2 H partially collapsed quartet at δ 4.87 ppm. In the high-field region a broad, integral 4 H, peak at −0.06 ppm is assigned to B−*H*−W groups, which sharpens on selective irradiation of the δ −42.4 ppm peak in the ^{11}B NMR spectrum. Two sharper signals are observed at δ −0.88 and −1.07 ppm, in the ratio 2:4, with respect to the Cp* resonance, and are assigned to W−*H* groups.

Compound **4** is thus formulated as having a bis-$\{Cp^*WH_3\}^{2+}$ unit, symmetrically bridged by a $\{B_2H_6\}^{2-}$ fragment, similar to **2**. Unlike **2**, however, the formal oxidation state of each W center in **4** is W(V), and not W(III). This is perhaps reflected in the low-field shift for the B−*H*−W groups, cf. δ −0.06 ppm in **4** vs δ −13.8 ppm in **2**, although this shift may also be affected by the six high trans-influence hydride ligands in **4** compared with only two chloride ligands in **2**. As such, **4** possess 6 sep or 40 cve, consistent with a M_2B_2 tetrahedron. As a coordination complex, each W center attains an 18-electron configuration by forming a metal−metal bond, consistent with the observed diamagnetism. Compound **4** is thermally unstable, decomposing rapidly at 50 °C in toluene to form unidentified, insoluble, products. This instability is exploited to afford pure **3** by simply heating a mixture of **3** and **4** and subsequent recrystallization from hexanes. A variable-temperature ^1H NMR study on **4** shows that the W−*H* resonances are unchanged in position and line shape from ca. −5 to −90 °C (Figure 3). Above this temperature, the two signals coalesce to a single peak at ca. +20 °C, while above +50 °C rapid decomposition occurs. These data suggest that at ambient temperatures rapid exchange of all three hydride ligands takes place, presumably by a pairwise mechanism as seen for **3**. At lower temperatures a static structure appears to persist, which also lends the molecule an asymmetric structure in solution.

Identification of Intermediates on the Pathway of Formation of 3 and 4 by Low-Temperature ^{11}B and ^1H NMR Spectroscopies. We have followed the reaction between Cp^*WCl_4 and $LiBH_4$ at low temperature by ^1H and ^{11}B NMR. This has allowed the time-dependent behavior of the system to be investigated and, through this, the spectroscopic identification of intermediates on the pathway to **3**, namely, *arachno*-1-$(Cp^*WH_3)B_4H_{10}$, **I**, and *nido*-1-$(Cp^*WH_3)B_4H_8$, **II**.

Six equivalents of $LiBH_4$ in thf-d_8 was added to Cp^*WCl_4 in toluene-d_8 at −80 °C, and the ^{11}B and ^1H NMR spectra of the resulting dark green solution were measured at increasing 20 °C intervals. Over the temperature range −80 to −60 °C a signal at δ −25.8 ppm is observed in the $^{11}B\{^1H\}$ NMR spectrum, which broadens on coupling to ^1H, while a signal at δ ca. 0 ppm is assigned to BH_3. In the high-field region of the ^1H NMR spectrum at these temperatures, a broad, partially collapsed, quartet [*J*(HB) ca. 150 Hz] is observed at δ −3.3 ppm. Between −40 and −20 °C the δ −25.8 ppm peak starts to diminish in intensity and two new signals at δ −5.1 and δ −7.0 ppm grow in, accompanied by a small peak at δ −42.4 ppm, identified as compound **4**. The two major peaks at δ −5.1 and δ −7.0 ppm are of equal area, although the higher field signal is significantly broader. On decoupling, the low-field peak at δ −5.1 ppm becomes a broad doublet [*J*(HB) 155 Hz], while the high-field signal broadens, but no fine structure is observed. The ^1H NMR spectrum recorded at this temperature shows one major Cp*-containing species by a peak at δ 1.37 ppm. In the high-field region six resonances are observed. Two broad, overlapping, resonances in the region associated with B−*H*−B groups in the ratio 1 H:2 H are seen at δ −2.08 and −2.20 ppm. Two sharper resonances observed at δ −4.16 and −4.54 ppm, in the ratio 2 H:1 H, respectively, are assigned to W−*H* groups. An integral 2 H resonance at δ −7.01 ppm and an integral 1 H signal at δ −8.83 ppm are assigned to W−*H*−B and μ_3-H groups, respectively.

Scheme 2



Overall, these data fit the proposed formulation: $(Cp^*WH_3)B_4H_{10}$, **I** (Scheme 2). As formulated, **I** would have 8 sep, giving it an *arachno*-MB_4 structural motif. The isoelectronic compound *arachno*-1-$(Cp^*Co)B_4H_{10}$[10] displays two peaks in the ^{11}B NMR spectrum at δ 5.1 and −5.7 ppm. 1-$(Cp^*Co)B_4H_{10}$ has been shown to reductively eliminate H_2, on heating to 70 °C, to afford *nido*-1-$(Cp^*Co)B_4H_8$. In a similar fashion, **I** loses H_2 on warming from −20 °C to room temperature to afford **3** over a period of 30 min. During this period, a new peak is observed in the $^{11}B\{^1H\}$ NMR spectrum at δ −8.0 ppm, which grows in intensity and then falls away, in a fashion characteristic of an intermediate species. A plot of relative concentration of ^{11}B-containing species in solution against time is shown in Figure 5.

New signals at δ −3.4 (4 H) and 1.58 ppm (15 H) are also observed in the ^1H NMR spectrum and follow time-dependent behavior similar to that seen in the ^{11}B NMR spectrum. A reasonable formulation of this intermediate species is *nido*-1-$(Cp^*WH_3)B_4H_8$, **II**, the positional iso-

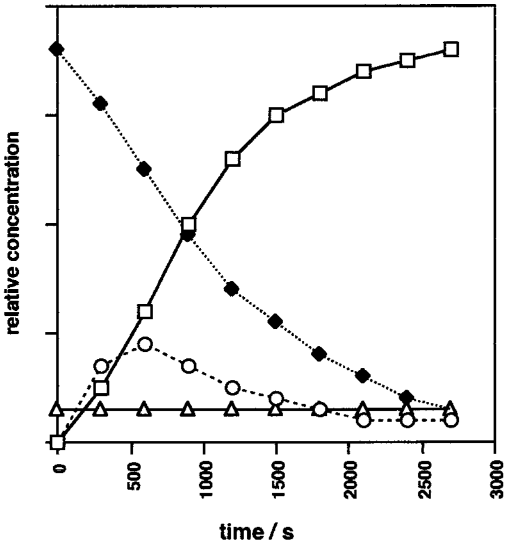


Figure 5. Plot of relative concentrations of ^{11}B vs time for the reaction Cp^*WCl_4 + 6 equiv of $LiBH_4$, on warming to room temperature. △ $(Cp^*WH_3)_2B_2H_6$, **4**; ○ *nido*-2-$(Cp^*WH_3)B_4H_8$, **3**; □ *nido*-1-$(Cp^*WH_3)B_4H_8$; ◆ *arachno*-1-$(Cp^*WH_3)B_4H_{10}$.

mer of **3**. Chemical shifts may be compared with that of *nido*-1-$(Cp^*Co)B_4H_8$,[39] which displays a single peak in the ^{11}B NMR spectrum at δ −2.9 ppm, while B−*H*−B signals are observed at δ −4.0 ppm in the ^1H NMR spectrum. Intermediate **II** isomerizes at ambient temperatures over a period of ca. 30 min to afford **3** (Scheme 2). There are few reported examples of isomerizations in *nido*-MB_4 metallaboranes. For example *nido*-2-$(Cp^*Co)B_4H_8$ rearranges to *nido*-1-$(Cp^*Co)B_4H_8$ on pyrolysis in a vacuum at 225 °C.[40] The differences between the isomerization processes observed for **II** and *nido*-2-$(Cp^*Co)B_4H_8$ are striking. In the tungsten system not only is the most stable isomer *nido*-2-WB_4, in contrast with the cobalt system, but the isomerization temperature is at least 225 °C lower for **II**, occurring below room temperature. Low-temperature isomerizations are rare in metallaborane chemistry.[41] This further highlights that, although $\{Cp^*WH_3\}$ and $\{CpCo\}$ are isolobal with respect to cluster bonding, the change in metal can make a dramatic difference in the resulting properties of the metallaborane.

The concentration of **4** is invariant throughout the experiment after it is first observed. The good mass balance of the system (by ^{11}B NMR) and the time correlation between the NMR signals establish the clean conversion of **I** to **II** to **3**. The half-life for loss of H_2 from **I**, to give **II**, is ca. 15 min. When the same reaction is repeated using $LiBD_4$, to ultimately afford $(Cp^*WD_3)B_4D_8$ (**3b**), the measured half-life for the transformation **I**-d_{13} to **II**-d_{11} is ca. 20 min, consistent with a normal kinetic isotope effect ($k_{H/D} \approx 1.33$) for loss of H_2 from **I**.

Reaction between $[Cp^*WCl_2]_2$ and Excess $LiBH_4$: $(Cp^*W)_2(B_2H_6)$ (5). Reaction between a toluene solution of $[Cp^*WCl_2]_2$ and 6 equiv of $LiBH_4$ affords a dark green solution, from which brown $(Cp^*W)_2(B_2H_6)_2$, **5**, may be isolated. Compound **5** displays a single resonance in the $^{11}B\{^1H\}$ NMR spectrum, at δ −53.9 ppm, which broadens on coupling to ^1H. This may be compared with the analogous compound $(Cp^*Mo)_2(B_2H_6)_2$, for which a peak at δ −58.6 ppm is observed for the four equivalent boron atoms.[7] In the ^1H NMR spectrum a broad, integral 8 H signal is observed at δ −10.2 ppm {cf. $(Cp^*Mo)_2(B_2H_6)_2$: δ −12.4 ppm}, with a single integral 30 H peak at δ 1.92, due to two Cp* groups, demonstrating that the molecule is highly symmetric in solution. Accurate mass spectra agree well with this formulation. **5** may be regarded as a metallaborane built from two edged-fused W_2B_2 tetrahedra (66 cve)[42] or as a bis-$\{B_2H_6\}^{2-}$ complex of $\{Cp^*W\}_2^{4+}$, giving each W center a formal oxidation state of +3. Compound **5** may also be generated by addition of 2 equiv of $LiBH_4$ to **2** in toluene.

Reaction between Cp^*WCl_4 and $LiBH_4$, Slow Addition of $LiBH_4$: $(Cp^*W)_2HCl(B_2H_6)$, (6). Reaction between a thf or toluene suspension of Cp^*WCl_4 and 4 equiv of $LiBH_4$, added dropwise over 1 h at 0 °C, results in a dark green solution, in contrast to fast addition of $LiBH_4$, which ultimately affords a pale green solution of **3**. A $^{11}B\{^1H\}$ NMR spectrum shows peaks due to **2**, **3**, **4**, **5**, and BH_3 in solution with an additional new product represented by a single peak at δ 101.5 ppm. In thf solution, this peak is by far the most major, while in toluene compound **3** is of approximate equal concentration. Repeated recrystallizations from hexanes at −20 °C gives a modest isolated yield of a dark brown solid, formulated by ^1H, ^{11}B, and mass spectrometries as $(Cp^*W)_2HClB_2H_6$, **6**.

Compound **6** shows a single peak in the $^{11}B\{^1H\}$ NMR spectrum at δ 101.5 ppm, which becomes a broad doublet on coupling to ^1H. The ^1H NMR spectrum of **6** shows two inequivalent Cp* environments, and an integral 2 H, partially collapsed, quartet assigned to two BH_t groups. In the high-field region is observed two broad, integral 2 H, peaks at δ −1.95 and δ −5.0 ppm and a sharp, integral 1 H, peak displaying tungsten satellites [*J*(WH) 112 Hz] at δ −4.20 ppm. Mass spectral data combined with the NMR data suggest an empirical formulation of $Cp^*_2W_2ClB_2H_7$; accurate mass measurements are in accord with this: calcd 702.1789, obs 703.1823. On the basis of the symmetry observed in the ^{11}B and ^1H NMR spectra, two chemically sensible structures may be proposed for **6**, as shown in Chart 2.

The relative intensity of the ^{183}W satellites in the ^1H NMR spectra shows that the hydride is terminally bound (observed 15%, calculated 16%), while the mirror plane of symmetry present in solution suggests that the chloride must also be terminal, and not bridging. The ^1H NMR spectrum is essentially unchanged over the temperature range +80 to −80 °C. At higher temperatures the signal due to BH_t groups is a clearly resolved quartet [*J*(BH) 136 Hz], while the two broad signals in the high-field region are resolved as partially collapsed quartets, demonstrating a direct connection to boron. As formulated, with both a terminal chloride and

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Chart 1

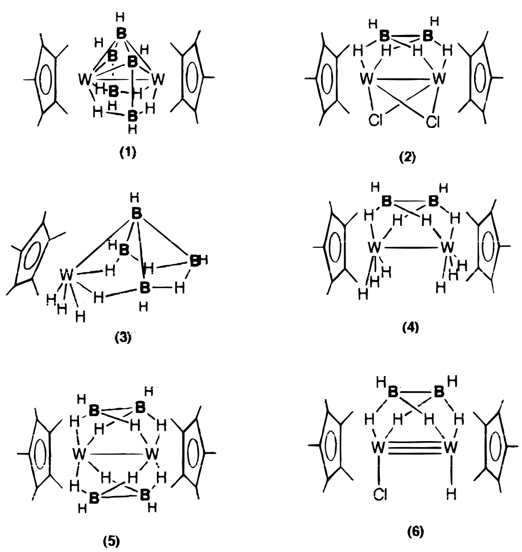
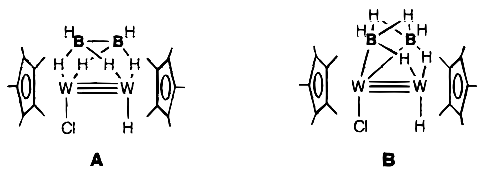


Chart 2



hydride ligand, to achieve an 18-electron configuration, a tungsten−tungsten triple bond has to be invoked. There are numerous examples of W≡W bonded species,[43] notably the compound $[(\eta^5\text{-}C_5H_4{}^iPr)WCl_2]_2$,[18] which bears four terminal chloride ligands and has a formal, $\sigma^2\pi^4$ metal−metal, triple bond. As formulated, **6** is also very similar to **2**, one hydride replacing a chloride ligand. However, the chemical shift in the ^{11}B-{^{1}H} NMR spectrum of δ 101.5 ppm is almost 150 ppm to lower field than found for **2**. Structure **B** has two direct W−B bonds, which can result in large downfield shifts for attached boron atoms,[44] and consequently also has two hydrogen atoms bridging the B−B vector. Although compounds have been reported that show such a feature, e.g., $R_4B_2H_2$,[45,46] and metallaboranes are known in which a single H bridges a B−B bond,[25,26] no metallaborane has been reported with two B−B hydrogen bridges. For this reason we favor structure **A**, which has a $\{B_2H_6\}^{2-}$ ligand, as seen in compounds **2**, **4**, and **5** and also has precedence in tantala-,[26] molybda-,[7] rhoda-,[47] and ferraborane[27] systems. The large downfield chemical shift in **6** can be ascribed to magnetic anisotropy effects commonly associated with metal−metal multiple bonds.[43] Although such effects are generally small (2−3 ppm) when ^{1}H nuclei are involved, with a quadrupolar nucleus such as ^{11}B this effect would be expected to be much larger, accounting for the large downfield shift. In support we note that dimetallaboranes with formal double bonds; for example, $(Cp^*Ta)_2(B_2H_6)_2$[25] [$\delta(^{11}B)$ −4 ppm] have ^{11}B resonances at significantly lower field than those with formal single bonds, e.g. $(Cp^*Mo_2)(B_2H_6)_2$[7] [$\delta(^{11}B)$ −59 ppm].

Compound **6** does not react significantly with $LiBH_4$ (by ^{11}B NMR, 55 °C for 3 days). On heating to +80 °C, in the absence of $LiBH_4$, new, as yet unidentified, decomposition peaks appear in the ^{1}H NMR spectrum.

Discussion

It is now well established that in reactions between cyclopentadienyl transition metal halides and BH_3·thf or $[BH_4]^-$ the mono boron reagent can perform more than one role.[48] BH_3·thf may act as a halide abstraction agent (forming BH_2Cl) and in doing so activate the metal center, as a cluster buildup reagent or as a reducing agent. Borohydride can be metathesized with halide, after which reduction can take place through successive loss of BH_3 and $^1/_2$ H_2, metallaboranes being formed by loss of H_2 alone or metal hydrides by loss of BH_3 alone. Now that the reactivity between {Cp*MCl} fragments and the two monoboron reagents has been examined for all the members of the group 6 triad, a comparison between the metallaborane chemistry of individual members can be used to show how the interplay between these various possible roles generates different chemistry.

Reaction with BH_3·thf. Reaction between BH_3·thf and $[Cp^*CrCl]_2$ affords one product, $(Cp^*Cr)_2B_4H_8$,[6] with no intermediate species observed. The isostructural and isoelectronic analogue of **1**, $(Cp^*Cr)_2B_5H_9$, is afforded only by reaction between $(Cp^*Cr)_2B_4H_8$ and BH_3·thf over extended time periods (ca. 3 weeks) at elevated temperatures.[22] With Cp^*MoCl_4 the reaction is more complex. Initially, Cp^*MoCl_4 is reduced by BH_3·thf to give $[Cp^*MoCl_2]_2$. This bimetallic Mo(III) complex then reacts with more BH_3·thf to give $(Cp^*MoCl)_2B_2H_6$. Further reaction with BH_3·thf results in a bifurcation of the reaction pathway. On one side, $(Cp^*MoCl)_2B_4H_{10}$ is formed, which bears the novel $\{B_4H_{10}\}^{2-}$ ligand, while on the other, stepwise cluster buildup ultimately results in the isolation of $(Cp^*Mo)_2B_5H_9$ via the reactive intermediate $(Cp^*MoCl)_2B_3H_7$.[7]

The reaction between BH_3·thf and Cp^*WCl_4 bears a close resemblance to the {Mo} system, the first step being facile reduction to the W(III) dimer, $[Cp^*WCl_2]_2$, shown by both **2** then **1** being formed when either Cp^*WCl_4 or $[Cp^*WCl_2]_2$ is used. Cluster buildup then results in the formation of $(Cp^*WCl)_2B_2H_6$ and then on to $(Cp^*W)_2B_5H_9$ as the final product. Although no analogues of $(Cp^*MoCl)_2B_4H_{10}$ or $(Cp^*MoCl)_2B_3H_7$ are observed, the two systems clearly follow a very similar pathway, as shown in Scheme 3.

Reaction with $LiBH_4$. Reaction between $[Cp^*CrCl]_2$ and $LiBH_4$ affords one product, the dimeric paramagnetic complex $[Cp^*Cr(BH_4)]_2$, the simple metathesis product of $[Cl]^-$ for $[BH_4]^-$. This complex is converted to $(Cp^*Cr)_2B_4H_8$ plus other products on heating.[6] Reaction between Cp^*MoCl_4 and $LiBH_4$ results in initial reduction to $[Cp^*MoCl_2]_2$ (as with reaction with BH_3·thf). Further reaction with $LiBH_4$ affords $(Cp^*MoCl)_2B_2H_6$ and then $(Cp^*Mo)_2(B_2H_6)_2$, both of which are derived from the simple metathesis products.[7]

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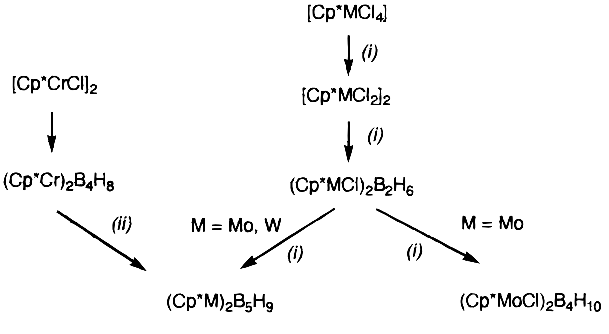
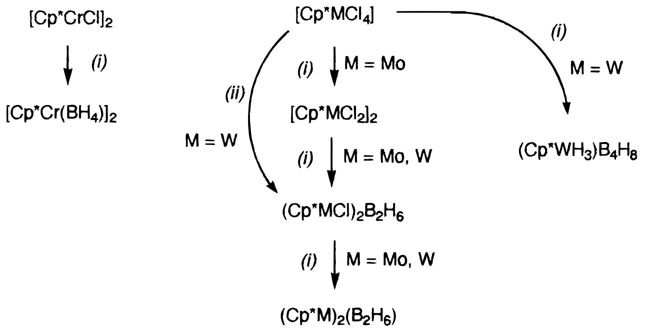
Scheme 3



(i) BH_3.thf, -BH_2Cl. *(ii)* BH_3.thf or BH_2Cl

Scheme 4



(i) excess $LiBH_4$, *(ii)* 2 + 2 equivalents $LiBH_4$

In contrast, reaction between 6 equiv of $LiBH_4$ and Cp^*WCl_4 does not result in reduction to $[Cp^*WCl_2]_2$. Instead the monometallic product $(Cp^*WH_3)B_4H_8$, **3**, is formed as the major product in good yield, along with the minor coproduct of $(Cp^*WH_3)_2B_2H_6$, **4**. Corroboration comes from the reaction of $[Cp^*WCl_2]_2$ and $LiBH_4$, which results in the isolation of $(Cp^*W)_2(B_2H_6)_2$, **5**, analogous to the {Mo} system. Clearly, $LiBH_4$ and Cp^*WCl_4 do not produce $[Cp^*WCl_2]_2$. As discussed, compound **5** may be considered as having two W(III) centers, while the oxidation state in **3** is clearly higher. Although formal oxidation states in metallaboranes are of limited value, the metal center is complexed with three hydrides, a $[Cp^*]^-$ ligand, and *arachno*-$\{B_4H_8\}^{2-}$, and a formal oxidation state of W(VI) is not unreasonable. Similarly, compound **4** may be considered as having two W(V) metal centers.

Following the reaction of Cp^*WCl_4 with $LiBH_4$ over a range of temperatures has allowed the observation of intermediate species formed at low temperature. The green color of the solution after addition of excess $LiBH_4$ at −78 °C, coupled with a peak in the ^{11}B NMR spectrum at δ −25.8 ppm, suggests a dimeric species in solution (color, diamagnetism). One possible formulation of this species is $[Cp^*W(BH_4)_nCl_{4-n}]_2$, the simple metathesis product of Cp^*WCl_4 with $LiBH_4$. The chemical shifts in the ^{11}B and ^1H NMR spectra of this species are consistent with this description, the broad signal in the ^{11}B NMR spectrum at δ −26 ppm possibly indicative of an η^1-BH_4 unit, while the signal at δ −3.3 ppm in the ^1H NMR is in the region associated with a fluxional η^1-BH_4 ligand,[49] although the mode of bonding of borohydride ligands in solution must be treated with caution.[50] Whatever the structure of this intermediate, at −20 °C it converts to *arachno*-1-$(Cp^*WH_3)B_4H_{10}$, **I**, along with **4**. That **3** and **4** are always formed in approximately equal proportions and that **4** is observed at low temperatures at the same time that **I** is seen, with its concentration remaining constant throughout, suggest that **I** and **4** arise from a common intermediate. Compound **4** may be generated from an intermediate $[Cp^*W(BH_4)_4]_2$ complex by loss of 6 equiv of BH_3[50] to give $[Cp^*WH_3(BH_4)]_2$, which loses H_2 to give the observed product, similar to the reaction of $[Cp^*WCl_2]_2$ with $LiBH_4$ to give **5**. Consistent with this, the observed ratio of BH_3 to **4** in the final reaction mixture is 6:1. Compound **3** may also be generated from such an intermediate. Loss of H_2 and resolution into two monometallic units could afford **I** and then **3**. An important observation is that yields of **3** are routinely greater than 60%, indicating that loss of a simple {Cp*W} fragment does not take place.

Although reaction between Cp^*WCl_4 and excess $LiBH_4$ does not show solvent dependence, we were interested in examining the effect of rate of addition of $LiBH_4$ to Cp^*WCl_4. If 2 equiv of $LiBH_4$ is added to a toluene suspension of Cp^*WCl_4, a dark green solution persists on warming to room temperature. The $^{11}B\{^1H\}$ NMR spectrum of this solution shows signals due to **3**, **4**, and BH_3·thf, in addition to a new peak at δ +3 ppm, which splits into a broad triplet on coupling to ^1H. Addition of excess $LiBH_4$ to this solution results in a ^{11}B NMR that now shows signals due to the major product compound **5** as well as **3** and **4** (in unchanged concentration), showing that this new intermediate species rapidly reacts with $LiBH_4$ to afford $(Cp^*W)_2(B_2H_6)_2$. That **3** and **4** are seen in the initial reaction mixture, even though a nonstoichiometric amount of $LiBH_4$ has been used, is readily explained by the insolubility of Cp^*WCl_4, meaning that the concentration of $LiBH_4$ in solution is always relatively high. Although the precise nature of this intermediate has not been elucidated, the triplet observed in the ^{11}B NMR spectrum suggests a $\{BH_2\}$ unit, while the intense green color and diamagnetism suggest a metal−metal dimer in solution, possibly a reduced W(III) species. The chemical shift is similar to that seen in $(Cp^*Ir)_2H_3(BH_4)$,[51] δ +5.5 ppm, which contains a (μ_2-BH_4) ligand that straddles the Ir−Ir bond. The rapid reaction of this intermediate with $LiBH_4$ to give **5** also suggests that only facile replacement of Cl^- with $[BH_4]^-$ is occurring, further evidence that reduction from W(V) to a W(III) intermediate has already happened.

Slow addition of four equiv of $LiBH_4$ to Cp^*WCl_4 results in the isolation of a new dimeric complex, identified spectroscopically as $(Cp^*W)_2HClB_2H_6$, **6**. Both the metal centers in **6** may be considered as W(III), demonstrating that reduction by $LiBH_4$ has occurred. Presumably reduction from Cp^*WCl_4 to $[Cp^*WCl_2]_2$ is the first step, with subsequent metathesis of two chloride ligands with $[BH_4]^-$ to afford a $\{B_2H_6\}^{2-}$ complex. At the present time it is not clear why **6** is formed and not **2**, and why the remaining chloride is unreactive to further borohydride substitution, although the chloride

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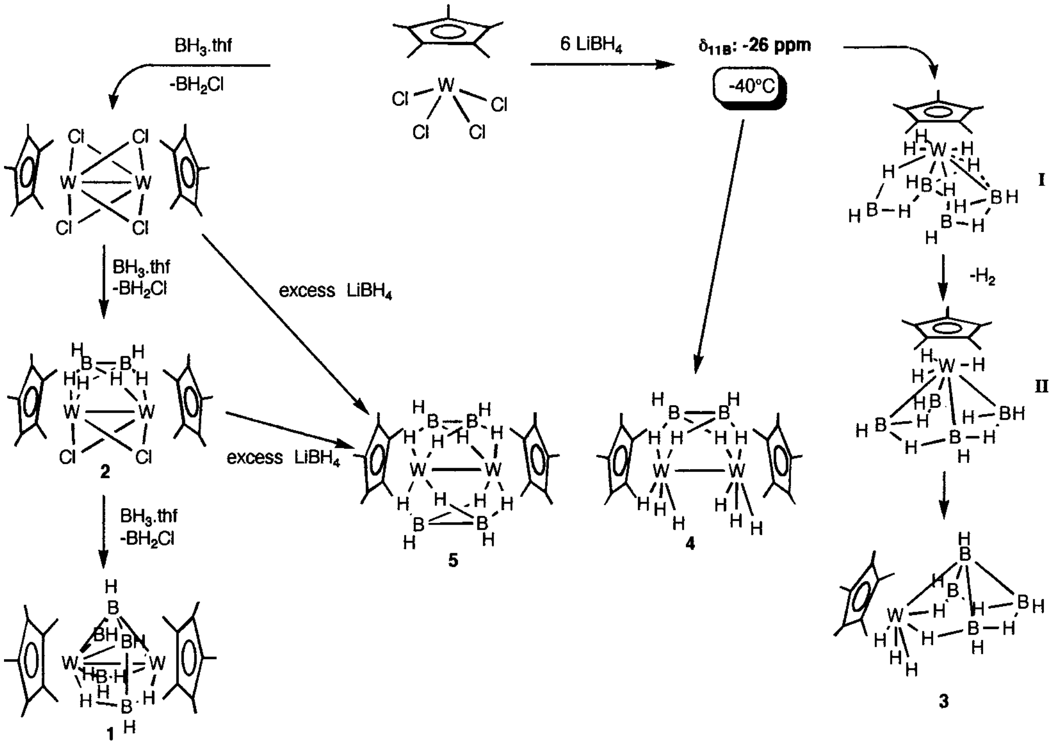
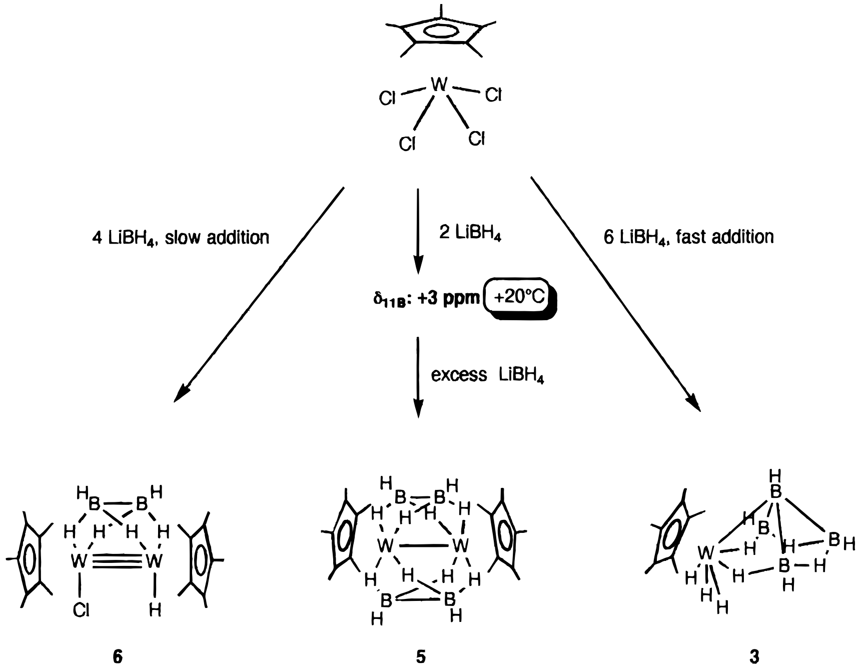
Scheme 5



Scheme 6



ligand being terminal and not bridging could well result in differing reactivity.

This order dependence of the addition of $LiBH_4$ allows two different reaction pathways to be accessed. For one pathway, in which an excess of $LiBH_4$ is used, rapid substitution of chlorides for $[BH_4]^-$ results, giving the low-temperature intermediate seen at δ −25.8 ppm in the ^{11}B NMR spectrum, which then affords **3** and **4** on warming. When only 2 equiv of $[BH_4]^-$ is used, complete replacement of the chloride ligands is not possible, and the (slower) reductive elimination of H_2[52] or HCl[53] is allowed to proceed (presumably by loss of BH_3 to afford a metal hydride) to give an intermediate that has two W(III) centers. That this intermediate species readily reacts with $LiBH_4$, to give **5**, also suggests that it bears reactive chloride groups, which are readily replaced by borohydride. Slow addition of four equiv of $LiBH_4$ also allows reduction of the metal center to occur, but now gives the dimeric, triple-bonded, species **6**. A full reactivity scheme, based on the observations reported

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here, for the reaction between Cp^*WCl_4 and BH_3·thf or $LiBH_4$ is given in Schemes 5 and 6.

The absence of a reductive pathway on the reaction of excess $LiBH_4$ with Cp^*WCl_4, compared with the facile reduction observed with Cp^*MoCl_4, is consistent with W−H bonds being significantly stronger than Mo−H bonds.[54] Green has demonstrated a similar pattern of behavior between dimetallic Mo and W hydride species. For example the complex $[\{(\eta\text{-}C_5H_4Me)MoCl_2\}_2(\mu\text{-Cl})(\mu\text{-H})]$ reductively eliminates HCl to afford $[(\eta\text{-}C_5H_4Me)MoCl_2]_2$, while the tungsten analogue does not.[53] Overall, the trend observed for group 6 triads on their reactivity with monoboron reagents is broadly similar to that found in the corresponding organometallic chemistry of the group. Chromium organometallic complexes tend to have relatively low oxidation states (+2 and +3), while for Mo and W complexes oxidation states across the entire possible range are common.[55] Likewise, the only reactive Cr species with BH_3·thf or $LiBH_4$ is the Cr(II) compound $[Cp^*CrCl]_2$, whereas for Mo and W, oxidation states ranging from +5 (Mo, W), to +3 (Mo, W), to +2 (Mo) are all reactive with monoboron reagents. An instructive correlation is that found between the reduction potentials[56] for the group 6 triad and these experimental observations. Reduction of Cr(III) to Cr(II) is by far the most difficult (−0.40 V), consistent with metallaboranes only being afforded when $[Cp^*CrCl]_2$ is used.[6] For Mo, reduction from Mo(V) to Mo(III) (+0.31 V) is significantly easier, resulting in facile reduction of Cp^*MoCl_4 by both BH_3·thf and $[BH_4]^-$. The W(V) to W(III) reduction potential (−0.2 V) suggests that such a process will be less favored than for Mo, consistent with the chemistry reported above.

Conclusion

The difference in reactivity between the two monoboron reagents may be traced to the higher activation barriers associated with activation of the metal center by BH_3·thf, meaning that the product distributions that arise are influenced primarily by thermodynamic factors (i.e., the most stable metallaborane is formed) in reactions between the neutral borane and transition metal cyclopentadienyl halide species. Halide metathesis with excess borohydride is extremely rapid (metal borohydride species being observed at −60 °C), resulting in product distributions that can be thought of as being controlled primarily by kinetic factors, that have metal centers in high formal oxidation states, viz., **3** and **4**. That $(Cp^*W)_2(B_2H_6)_2$ or $(Cp^*W)_2HCl(B_2H_6)$ are formed when the rate of addition of $LiBH_4$ to Cp^*WCl_4 is changed shows that there is a complex interplay between kinetic and thermodynamic pathways in this system, the full details of which remain to be elucidated. Reactions between transition metal halides and reducing agents such as $LiBH_4$ or $LiAlH_4$ are often worked up by quenching with water or alcohols to afford metal hydrides. The products we describe here, formed by reaction between Cp^*WCl_4 and $LiBH_4$, suggest that any intermediate species in hydride-based reductions, formed prior to quenching, could have interesting structures and properties in their own right and merit further study.

The ability to control reactions, through relatively subtle variations in oxidation state of starting material or rate of addition of boron reagent, allows for final product distributions to be controlled in a systematic manner, potentially allowing for a wide range of metallaborane species to be synthesized in good yield from readily accessible reagents. In this spirit, the isolation, in good yield, of **3**, which contains potentially reactive W−H groups, allows for the further development of its chemistry, and we are currently pursuing this.[35]

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

Supporting Information Available: Tables of crystal data, positional and equivalent isotropic thermal parameters, bond distances and angles, and general displacement expressions for compounds **1** and **3** are available (22 pages). Crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

OM980743H

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