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Synthesis and structure of $[(\eta^5\text{-}C_5Me_5)WCl_2(\mu\text{-}H)]_2$. A dinuclear tungsten hydride with a double bond formed from the reaction of BH_3THF with $(\eta^5\text{-}C_5Me_5)WCl_4$

Melanie A. Peldo, Maoyu Shang, Thomas P. Fehlner *

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

## Abstract

The reaction of limited quantities of BH_3THF with $Cp*WCl_4$, $Cp* = \eta^5\text{-}C_5Me_5$, leads to the formation of $[Cp*WCl_2(\mu\text{-}H)]_2$ and BH_2Cl in good yield. Structural characterization by spectroscopic and crystallographic techniques reveals the presence of two $Cp*WCl_2$ fragments in a transoid arrangement connected by a formal W=W double bond ($d_{WW} = 2.5150(5)$ Å) bridged by two hydrogen atoms. Reaction of $[Cp*WCl_2(\mu\text{-}H)]_2$ with additional BH_3THF leads ultimately to $Cp^*_2W_2B_5H_9$, thereby providing information on the role of $[Cp*WCl_2(\mu\text{-}H)]_2$ as an intermediate in the formation of $Cp^*_2W_2B_5H_9$ from the reaction of $Cp*WCl_4$ with an excess of BH_3THF. © 2000 Elsevier Science S.A. All rights reserved.

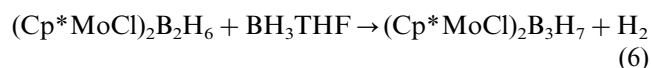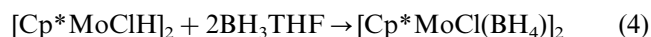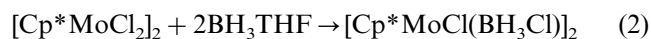*Keywords:* Metal hydride; Tungsten; Borane; Metallaboranes

1. Introduction

In a continuing series of publications we have described the evolution of a general route to mono- and dimetallaboranes via the reactions of monocyclopentadienyl metal chloride complexes with monoboranes [1–6]. The route utilizing $LiBH_4$ is easily understood in terms of rapid chloride metathesis by $[BH_4]^-$ followed by H_2 elimination and B–B and M–B bond formation. The Ta [7] and Mo [3] systems define reaction (1), $Cp* = \eta^5\text{-}C_5Me_5$, for the synthetic route in its simplest form.

$$[Cp*MX_2]_2 + 2LiBH_4 \rightarrow [Cp*MX(BH_4)]_2$$
$$\rightarrow (Cp*MX)_2B_2H_6 + H_2 \qquad (1)$$
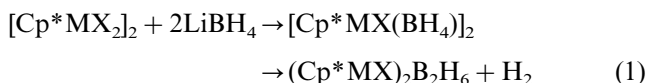
Less transparent is the pathway associated with the formation of metallaboranes from monocyclopentadienyl metal chloride complexes utilizing BH_3THF instead of $LiBH_4$ as the source of boron. Significantly, BH_2Cl is the coproduct and chlorine sink. In addition, more borane fragments are incorporated in the metal-

laborane product via this route compared with $LiBH_4$. Thus, for Mo [3] and W [4], $Cp^*_2M_2B_5H_9$ is the ultimate product.

Considering the fact that metal chloroborohydrides are known [8,9], we have suggested a reaction pathway [5] via a polyborohydride intermediate (reactions (2–4) illustrated for Mo [10]). In similar fashion to the $LiBH_4$ route, metallaboranes are formed (reaction (5)) but then undergo cluster expansion with additional BH_3THF (reaction 6). Hence, even though a polyborohydride is postulated as an intermediate in both cases, the two monoboranes access different metallaboranes. In this pathway, the borane serves three distinct roles — removal of Cl, formation of the borohydride, and growth of the borane fragment of the initial metallaborane.

$$[Cp*MoCl_2]_2 + 2BH_3THF \rightarrow [Cp*MoCl(BH_3Cl)]_2 \qquad (2)$$

$$[Cp*MoCl(BH_3Cl)]_2 \rightarrow [Cp*MoClH]_2 + 2BH_2Cl \qquad (3)$$

$$[Cp*MoClH]_2 + 2BH_3THF \rightarrow [Cp*MoCl(BH_4)]_2 \qquad (4)$$

$$[Cp*MoCl(BH_4)]_2 \rightarrow (Cp*MoCl)_2B_2H_6 + H_2 \qquad (5)$$

$$(Cp*MoCl)_2B_2H_6 + BH_3THF \rightarrow (Cp*MoCl)_2B_3H_7 + H_2 \qquad (6)$$

* Corresponding author. Fax: + 1-219-6316652.
E-mail address: fehlner.1@nd.edu (T.P. Fehlner).

An interesting question raised by this pathway is the nature of the chloroborohydride to borohydride conversion step. Specifically, we wonder whether a metal hydride is an intermediate in the reaction, i.e. are reactions (3) and (4) distinct, or does BH_3THF add directly to $[Cp*MoCl(BH_3Cl)]_2$ to effect Cl/H exchange? In the Mo [3] system we have observed NMR evidence for the presence of a hydride which may, or may not, be an intermediate on the pathway leading to final products. Now metal borohydrides are known sources of metal hydrides [11], i.e. the reverse of reaction (4) is an established reaction. One example of addition of borane to a metal hydride exists for osmium showing reversibility is possible [12]. The characterization of hydrides as distinct intermediates in our system would have two, potentially useful, implications. First, metal hydrides become potential precursors to new metallaboranes via addition of borane. Second, the reaction of metal chlorides with BH_3THF becomes a potential route to metal hydrides possibly inaccessible via existing methods.

In this first study we address the question of hydride intermediates in the tungsten system [4]. This metal was chosen as we had already noted competition between reduction and metallaborane formation thereby suggesting that H_2 elimination from hydrides, i.e. reduction, was relatively slow. To summarize, on reaction with excess BH_3THF, both $Cp*WCl_4$ and $[Cp*WCl_2]_2$ produce $Cp_2^*W_2B_5H_9$ (**1**), ostensibly suggesting that reduction of the W^V complex to the W^{III} complex precedes metallaborane formation. On the other hand, with the better reducing agent $LiBH_4$ as the monoborane, formation of $Cp*W(BH_4)_4$ is facile allowing H_2 elimination to generate *arachno*-$Cp*WH_3B_4H_{10}$. The intermediate loses H_2 to yield *nido*-$Cp*WH_3B_4H_8$ as the final product. This counterintuitive result was rationalized by assuming efficient removal of chlorine by $LiBH_4$ permits H_2 elimination from the polyborohydride (and metallaborane formation) to dominate hydride formation by loss of BH_3. Hence, reduction by H_2 elimination from the tungsten hydride cannot occur. These observations led us to examine more closely the apparent reduction process taking place in the reaction of BH_3THF with $Cp*WCl_4$. As a consequence, we are able to report the formation of a new tungsten hydride and to provide information on its role in the overall reaction system.

2. Experimental

2.1. General experimental information

All operations were conducted under an argon atmosphere using standard Schlenk techniques. Before use, toluene was distilled under N_2 over sodium metal.

$Cp*WCl_4$ was prepared as described in the literature [13]. BH_3THF (1.0 M) and $LiBH_4$ (2.0 M) (both in THF) were used as received from Aldrich. NMR spectra were recorded on a 300 MHz Varian FT-NMR spectrometer. Residual protons of solvent were used as reference (δ, 7.15 ppm, benzene) while a sealed tube containing $[(Me_4N)(B_3H_8)]$ in acetone-d_6 (δ_B, -29.7 ppm) was used as the external reference for the ^{11}B-NMR. Mass spectra (m/z) were obtained on a Jeol JMS-AX505HA spectrometer using the EI mode with perfluorokersene as the standard. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

2.2. Synthesis of $[Cp*WCl_2(\mu\text{-}H)]_2$ (**3**)

In a typical reaction, 190 mg (0.243 mmol) $Cp*WCl_4$ was dissolved in 20 ml toluene at room temperature (r.t.) to produce an orange solution. Addition by syringe of 0.62 ml (0.619 mmol, three molar equivalents) BH_3THF produces an immediate change in color to a kelly green solution with gas evolution. Stirring is continued for an additional hour although a reaction appears to take place within 5 min. After filtering the reaction solution through Celite, green crystals of **3** were obtained at $-20°C$ (152 mg, 0.21 mmol, 80%). Compound **3** is modestly air-sensitive in solution but much less so in the solid state. EIMS: $P^+_{max} = 780$; isotopic distribution characteristic of an ion containing the W_2Cl_4 fragment; Exact mass: $C_{30}H_{32}Cl_4W_2$, calc. for weighted average of isotopomers lying within instrument resolution 780.0277, obs. 780.0238. ^{1}H-NMR: (C_6D_6, 22°C), 2.04 (s, 15H, C_5Me_5), 1.94 (s, 1H, $J_{WH} = 121.9$ Hz, μ-H). Anal. Calc. for $C_{20}H_{32}Cl_4W_2$: C, 30.72; H, 4.12. Found: C, 30.16; H, 4.66%.

2.3. Molecular structure of **3**

Crystallographic information is listed in Table 1. A black plate-like crystal of **3** having dimensions of $0.35 \times 0.12 \times 0.06$ mm^3, formula $C_{20}H_{32}Cl_4W_2$, was measured on an Enraf–Nonius CAD4 computer controlled k-axis diffractometer equipped with a graphite crystal, incident beam monochromator with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) at r.t. Structure solution and refinement (based on F^2) were performed on a PC by using the SHELXTL V5 package. All reflections, including those with negative intensities, were included in the refinement. Non-hydrogen atoms were found by direct methods, and the remaining non-hydrogen atoms were found in succeeding difference Fourier synthesis. Difference Fourier synthesis located all hydrogen atoms, with cyclopentadienyl hydrogens refined with idealized riding models, which restrained the C–H distances 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 atom. The hydride atom was refined isotropically without any restraint.

Table 1
Crystal data and structure refinement for [Cp*WCl$_2$(μ-H)]$_2$ (3)

Empirical formula	C$_{20}$H$_{32}$Cl$_4$W$_2$
Formula weight	781.96
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	8.0980(8)
b (Å)	13.0034(14)
c (Å)	11.2518(12)
β (°)	100.978(9)
Volume (Å^3)	1163.1(2)
Z	2
D_{calc} (Mg m^{-3})	2.233
$F(000)$	736
Wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	10.345
Crystal size (mm)	$0.35 \times 0.12 \times 0.06$
Temperature (K)	293(2)
Diffractometer	Enraf–Nonius CAD4
θ range for data collection (°)	2.42–25.00
Index ranges	$0 \leq h \leq 9$, $0 \leq k \leq 15$, $-13 \leq l \leq 13$
Scan method	ω–2θ
Scan rate (° min^{-1})	1.37–8.24 (in ω)
Scan width (°)	$0.70 + 0.35 \tan \theta$ (in ω)
Total data collected	2207
Unique data	2059 [$R_{int} = 0.0475$]
Unique observed data [$I > 2\sigma(I)$]	1550
Absorption correction	Empirical based ψ-scan data
Max/min transmission	0.5757 and 0.1225
Refinement method	Full-matrix on F^2 (SHELXL-93)
Weighting scheme	σ weight
Data/restraints/parameters	2059/0/123
Goodness-of-fit on F^2	0.026
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0260$, $wR_2 = 0.0689$
R indices (all data)	$R_1 = 0.0350$, $wR_2 = 0.0728$
Extinction coefficient	0.0027(2)
Largest difference peak and hole (e Å^{-3})	1.216 and -1.674
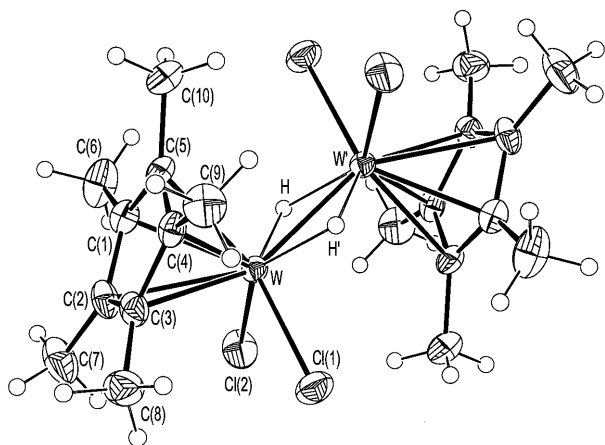
Fig. 1. Molecular structure of [Cp*WCl$_2$(μ-H)]$_2$ (3).

2.4. General procedure for reactions of 3 with BH$_3$THF

BH$_3$THF (2.6 ml, ca. nine molar equivalents) is added to a toluene solution containing 200 mg (0.289 mmol) of **3** and heated to 80°C in an oil bath. After 7–8 h stirring product **1** is the sole boron-containing product observed. NMR-scale reactions of **3** with BH$_3$THF are monitored using toluene-d_8 for ^{1}H-NMR and toluene for ^{11}B-NMR. The reactions are carried out in the sealed tubes and spectra are taken periodically during the reaction.

2.5. Reaction of 3 with LiBH$_4$

A 152 mg (0.194 mmol) sample of **3** was dissolved in 10 ml toluene and allowed to stir at -77°C. LiBH$_4$ (0.39 ml, 0.776 mmol, four molar equivalents) was added via syringe. The kelly green solution was stirred for 45 min and allowed to warm to r.t. producing a yellow solution.

2.6. Pyrolysis of 3

A 50 mg (0.0695 mmol) sample of **3** was dissolved in an NMR tube with toluene-d_8 producing a kelly green solution. The sealed tube was allowed to heat in an oil bath set at 50°C for one week resulting in a loss of color and the formation of a yellow precipitate.

3. Results and discussion

3.1. Synthesis and characterization of [Cp*WCl$_2$(μ-H)]$_2$ (3)

The reaction of Cp*WCl$_4$ with 3 mol of BH$_3$THF leads to formation of BH$_2$Cl and the isolation of dark-green crystals of a new compound rather than orange Cp*$_2$W$_2$B$_5$H$_9$ (**1**), which is the product observed with an excess of borane. The ^{11}B-NMR is silent. The isotopic envelope of the parent ion in the mass spectrum matched that expected for two tungsten and two chlorine atoms with a minimum molecular weight corresponding to [Cp*WCl$_2$]$_2$. Exact mass measurements revealed the presence of hydride and gave a composition [Cp*WCl$_2$H]$_2$. The ^{1}H-NMR showed a Cp* resonance ($\delta = 2.05$) different from that of [Cp*WCl$_2$]$_2$ ($\delta = 2.40$), which is also green. An accompanying resonance at δ 1.94 has the proper intensity and tungsten satellites ($J_{WH} = 121.9$ Hz) consistent with two bridging hydrides (relative intensity 29% observed; 33% calculated for the ^{183}W–H–W isotopomer). The T_1 of the hydride resonance is 0.65 s at 25°C. Hence, the compound is formulated as [Cp*WCl$_2$(μ-H)]$_2$ (**3**).

Table 2
Selected bond distances (Å) and angles (°) for [Cp*WCl$_2$(μ-H)]$_2$ (3)

Bond distances

W–Cl(1)	2.3720(14)	W–C(1)	2.317(5)
W–Cl(2)	2.3891(13)	W–C(2)	2.474(5)
W–W # 1	2.5150(5)	W–C(3)	2.480(5)
W–H	1.84(7)	W–C(4)	2.335(5)
		W–C(5)	2.304(5)

Bond angles

Cl(1)–W–Cl(2)	87.99(6)	Cl(2)–W–C(2)	81.16(12)
Cl(1)–W–C(2)	101.88(14)	Cl(1)–W–C(3)	80.63(13)
Cl(2)–W–C(2)	81.16(12)	Cl(2)–W–C(3)	105.13(12)
Cl(1)–W–C(3)	80.63(13)	C(5)–W–W # 1	93.40(13)
Cl(2)–W–C(3)	105.13(12)	C(1)–W–W # 1	112.47(13)
Cl(1)–W–H	137.2(17)	C(4)–W–W # 1	109.81(13)
Cl(2)–W–H	75(2)	Cl(1)–W–W # 1	109.28(4)
W # 1–W–H	46(2)	Cl(2)–W–W # 1	109.40(4)
C(5)–W–Cl(1)	129.61(13)	C(2)–W–W # 1	147.20(13)
C(1)–W–Cl(1)	135.95(13)	C(3)–W–W # 1	144.23(12)
C(4)–W–Cl(1)	94.13(14)	C(5)–W–H	90.7(18)
C(5)–W–Cl(2)	126.71(13)	C(1)–W–H	84.2(18)
C(1)–W–Cl(2)	91.05(13)	C(4)–W–H	125.0(18)
C(4)–W–Cl(2)	137.48(13)	Cl(1)–W–H	137.2(17)
Cl(1)–W–Cl(2)	87.99(6)	Cl(2)–W–H	75(2)
Cl(1)–W–C(2)	101.88(14)	C(2)–W–H	113.4(19)
		C(3)–W–H	141.4(18)

The molecular structure in the solid state is defined by a single-crystal X-ray diffraction study (Fig. 1, Tables 1 and 2) and it is completely consistent with the spectroscopic data. The bridging hydrides were located and refined isotropically without restraint. In addition, the structural study shows the chlorides to be terminal ligands and the Cp*WCl$_2$ fragments to be oriented in a transoid configuration. A plane bisecting the Cl–W–Cl angle containing the centroid of the Cp* ring is approximately perpendicular to the plane containing the W$_2$H$_2$ fragment. The W–H distance (1.84(7) Å) and W–H–W angle (88(2)°) are similar to those in diamagnetic W$_2$(μ-H)$_2$Cl$_4$(μ-dppm)$_2$, dppm = Bis(diphenylphosphino)methane, with an edge-sharing bioctahedral structure (1.79(8) Å and 84(2)°) [14].

Cp*WCl$_2$H is a d^2 fragment and, hence, the W–W interaction in 3 constitutes a formal double bond. Consistent with this, the W–W distance in 3 (2.5150(5) Å) is considerably shorter than those in the range associated with a single bond [15] while longer than those of [Cp'WCl$_2$]$_2$ (2.3678(6) Å), Cp' = η^5-C$_5$H$_4^i$Pr, and W$_2$(μ-H)$_2$Cl$_4$(μ-dppm) (2.3918(7) Å) both of which contain formal triple bonds between the d^3 tungsten fragments [14,16]. We conclude that 3 possesses a W=W double bond.

Compared to a W–H–W bridging hydride in a cluster, e.g. Cp*$_3$W$_3$(μ-H)B$_8$H$_8$, $\delta = -15.3$, $J_{WH} = 67$ Hz [17], 3 exhibits a much lower chemical shift and a much higher coupling constant. However, both the chemical shift and coupling constant of 3 are similar to those of the hydride [Cp'WCl$_2$(μ-H)]$_2$ (δ 1.24, d 26.4%, $J_{WH} =$

112 Hz) reported earlier [16]. Although the latter compound was described as the *cis* isomer, albeit without crystallographic confirmation, it was also formulated with a W=W double bond by extrapolation from the structure of its precursor [Cp'WCl$_2$]$_2$. Consistent with the trend in chemical shifts, W$_2$(μ-H)$_2$Cl$_4$(μ-dppm)$_2$ (W≡W triple bond) exhibits a quintet at $\delta = 4.516$, $J_{WH} = 108$ Hz, in the ^{1}H-NMR spectrum [14]. On the other hand, the NMR parameters for the bridging hydrogens of 3 are considerably different from those observed for [CpW(CO)$_2$(μ-H)]$_2$, Cp = η^5-C$_5$H$_5$, ($\delta = -13.24$, $J_{WH} = 83.1$ Hz) which is formulated with a W=W double bond albeit without crystallographic characterization [18].

[Cp'WCl$_2$(μ-H)]$_2$ was prepared directly by the reaction of [Cp'WCl$_2$]$_2$ with H$_2$ under mild conditions [16]. Warming under reduced pressure regenerated [Cp'WCl$_2$]$_2$. In contrast heating 3 leads to the production of a precipitate and loss of the green color and ^{1}H-NMR resonances characteristic of 3. The resulting colorless solution contains no [Cp*WCl$_2$]$_2$ (color and ^{1}H-NMR); however, there is an unknown signal at δ 1.90 and evidence for dissolved H$_2$ ($\delta = 4.52$). Note that in contrast to [Cp'WCl$_2$]$_2$, which contains four terminal Cl ligands and a triple bond [16], [Cp*WCl$_2$]$_2$ possesses four bridging Cl ligands and a W–W distance of 2.626(1) Å attributed to a W–W single bond [19]. Clearly thermal dissociation of H$_2$ from 3 to form [Cp*WCl$_2$]$_2$ is not expected to play a role in its chemistry. These observations are summarized in Scheme 1.

3.2. The role of [Cp*WCl$_2$(μ-H)]$_2$ (3) in the formation of Cp$_2^*$W$_2$B$_5$H$_9$ (1)

A survey of the reactivity of 3 with nine equivalents of BH$_3$THF showed complete conversion to 1, 7–8 h at 80°C. BH$_2$Cl is observed as a coproduct. These observations are consistent with 3 being an intermediate formed before the rate-determining step in the overall conversion of Cp*WCl$_4$ to 1 by BH$_3$THF. Note that previously [4] we attributed the generation of a transient dark-green solution during the reaction of Cp*WCl$_4$ with BH$_3$THF to the presence of [Cp*WCl$_2$]$_2$ as an intermediate. However, as both 3 and [Cp*WCl$_2$]$_2$ have similar colors, the earlier observation is ambiguous.

A number of experiments were carried out in which the reaction of 3 with BH$_3$THF was monitored by ^{11}B- and ^{1}H-NMR to seek information on possible intermediates. Substantial consumption of 3 and production of BH$_2$Cl was evident after 30 min at 80°C. More importantly the formation Cp$_2^*$W$_2$Cl$_2$B$_2$H$_6$ (2) was observed in ca. 40% yield (^{11}B-NMR) using the formation of BH$_2$Cl as a measure of the extent of reaction in Eq. (7).

Scheme 1.

$$[Cp^*WCl_2(\mu\text{-}H)]_2 + 4BH_3THF$$

$$\rightarrow 2BH_2Cl + Cp_2^*W_2Cl_2B_2H_6 + 2H_2 \qquad (7)$$
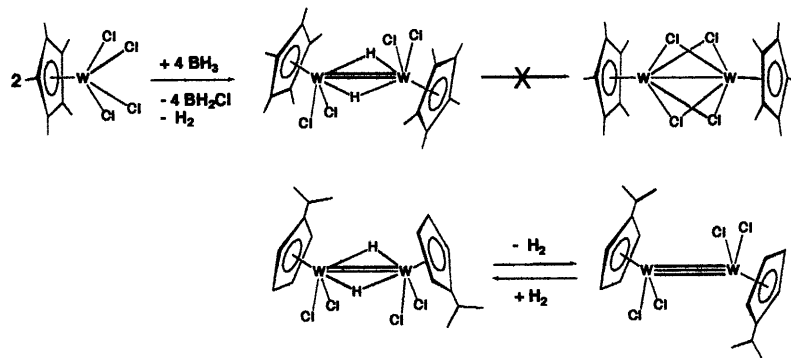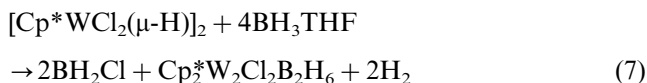
Although two unidentified ^{11}B multiplets were observed at similar intensities to **2**, only **2** exhibited the time behavior of an intermediate, i.e. after 1 h it had disappeared completely and signals corresponding to **1** had begun to grow in. We have already shown that the reaction of **2** with BH_3THF produces **1** [4].

The reaction of **3** with $LiBH_4$ was briefly investigated to see if tungstaboranes would result. Reaction occurred immediately on warming the green solution to r.t. as evidenced by a color change and disappearance of the ^1H-NMR signals of **3**. No new significant ^1H- or ^{11}B-NMR signals were observed under the conditions explored thus far.

Our present understanding of the system is summarized in Scheme 2. Although both Cp^*WCl_4 and $[Cp^*WCl_2]_2$ react with BH_3THF to produce **1**, the former is not simply reduced to $[Cp^*WCl_2]_2$ by borane. However, **3** formally contains W^{IV} and BH_3THF can be considered to reduce Cp^*WCl_4 to **3** in the first step. The evidence suggests that **3** must then add BH_3THF to form the first metallaborane product. As BH_2Cl is produced immediately, reaction with the W–Cl bond of **3** rather than the hydride is favored. Thus, rather than being formed directly from **3**, H_2 elimination ('reduction') takes place from a chloroborohydride or borohydride intermediate that precedes the formation of **2**.

The earlier study showed that the reaction of $[Cp^*WCl_2]_2$ with either limited BH_3THF or $LiBH_4$ leads to the formation of dinuclear $Cp_2^*W_2Cl_2B_2H_6$, **2**, which, in turn, can be converted into **1** by adding borane. In the reaction of **3** with borane, **2** exhibits the concentration/time behavior of an intermediate. Thus, the rate-determining step in the overall conversion of Cp^*WCl_4 to **1** is the reaction of BH_3THF with **3** thereby permitting **2** to be isolated in good yield. Although the most stable metallaborane in this preparative scheme for Cr [20], Mo and W exhibits structure **1**,

the contrasting reactivities of intermediate products in each system reflect the differing metal properties, e.g. presumably $[Cp^*MoCl_2H]_2$ is an intermediate in the formation of $Cp_2^*Mo_2B_5H_9$ from Cp^*MoCl_4 via $[Cp^*MoCl_2]_2$. It is the relative stability of W–H bonds towards H_2 elimination that permits **3** to be isolated. Although the hydride **3** is an intermediate in metallaborane formation, it is the chloride rather than the hydride ligands of **3** that probably account for its reactivity with borane.

4. Conclusions

The electrophilic hydride, BH_3THF, provides a new route to a tungsten hydride in a reaction with a monocyclopentadienyl tungsten chloride when used in the correct stoichiometry. This dinuclear hydride, which
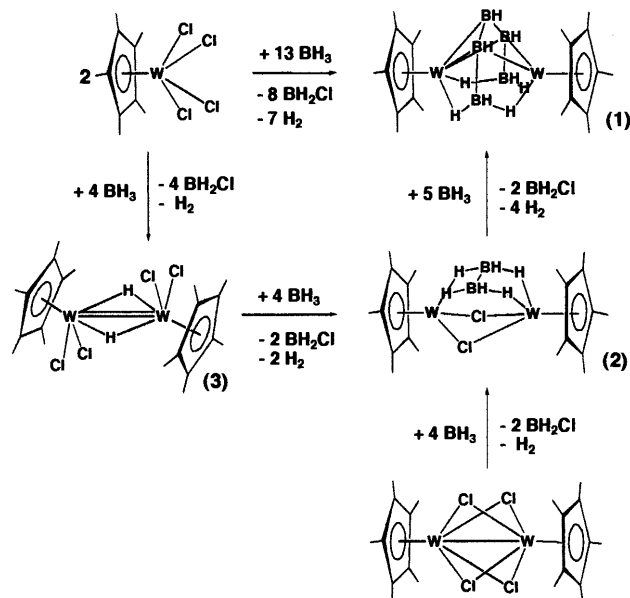
Scheme 2.

has been structurally characterized, can be used to generate tungstaboranes with BH_3THF; however, it appears that reaction takes place via the chlorides rather than the hydrides. Once again, variation in the identity of the transition metal logically modifies the reaction chemistry. Consequently, metallaborane chemistry is moving from a structure-dominated chemistry to a systematic-reaction chemistry that parallels, but does not duplicate, that of carbon–transition metal chemistry [21].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 137074 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: + 44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

References

[1] Y. Nishihara, K.J. Deck, M. Shang, T.P. Fehlner, B.S. Haggerty, A.L. Rheingold, Organometallics 13 (1994) 4510.
[2] J. Ho, K.J. Deck, Y. Nishihara, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 117 (1995) 10 292.
[3] S. Aldridge, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 120 (1998) 2586.
[4] A.S. Weller, M. Shang, T.P. Fehlner, Organometallics 18 (1999) 53.
[5] X. Lei, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 121 (1999) 1275.
[6] X. Lei, A.K. Bandyopadhyay, M. Shang, T.P. Fehlner, Organometallics 18 (1999) 2294.
[7] C. Ting, L. Messerle, J. Am. Chem. Soc. 111 (1989) 3449.
[8] Y. Kawano, M. Shimoi, Chem. Lett. (1998) 935.
[9] S.H. Lawrence, S.G. Shore, T.F. Koetzle, J.C. Huffman, C.-Y. Wei, R. Bau, Inorg. Chem. 24 (1985) 3171.
[10] S. Aldridge, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 119 (1997) 11 120.
[11] H.D. Empsall, E.M. Hyde, E. Mentzer, B.L. Shaw, M.F. Uttley, J. Chem. Soc. Dalton Trans. (1976) 2069.
[12] P.W. Frost, J.A.K. Howard, J.L. Spencer, J. Chem. Soc. Chem. Commun. (1984) 1362.
[13] R.C. Murray, L. Blum, A.H. Liu, R.R. Schrock, Organometallics 4 (1985) 953.
[14] T.E. Concolino, J.L. Eglin, E.J. Valente, J.D. Zubkowski, Polyhedron 16 (1997) 4137.
[15] A.L. Rheingold, J.R. Harper, Acta Crystallogr. Sect. C 47 (1991) 184.
[16] M.L.H. Green, P. Mountford, J. Chem. Soc. Chem. Commun. (1989) 732.
[17] A.S. Weller, M. Shang, T.P. Fehlner, J. Am. Chem. Soc. 120 (1998) 8283.
[18] K.A. Mahmoud, A.J. Rest, H.G. Alt, J. Chem. Soc. Dalton Trans. (1984) 187.
[19] C.J. Harlan, R.Q. Jones, S.U. Koshmieder, C.M. Nunn, Polyhedron 9 (1990) 669.
[20] S. Aldridge, T.P. Fehlner, M. Shang, J. Am. Chem. Soc. 119 (1997) 2339.
[21] T.P. Fehlner (Ed.), Inorganometallic Chemistry, Plenum, New York, 1992.