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An Efficient Route to Group 6 and 8 Metallaborane Compounds: Synthesis of *arachno*-[Cp*Fe(CO)B_3H_8] and *closo*-[(Cp*M)$_2B_5H_9$] (M = Mo, W)

K. Geetharani,[a] Shubhankar Kumar Bose,[a] Goutam Pramanik,[a] Tanmoy Kumar Saha,[a] V. Ramkumar,[a] and Sundargopal Ghosh*[a]

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Reaction of [Cp*Fe(CO)$_2$I] (Cp* = η^5-C_5Me_5) with an excess amount of BH_3·thf in toluene at 75 °C or with $LiBH_4$ at –78 °C leads to the isolation of hydrogen-rich ferraborane *arachno*-[Cp*Fe(CO)B_3H_8] in good yield. In a similar fashion, reaction of [Cp*M(CO)$_3$Cl] (M = Mo and W) with an excess amount of BH_3·thf at 80 °C or at –78 °C with $LiBH_4$ yielded metallaboranes [(Cp*M)$_2B_5H_9$] (M = Mo, W). Isolated yields of *closo*-[(Cp*M)$_2B_5H_9$], (M = Mo and W), both from $LiBH_4$ and BH_3·thf, are good. All compounds were characterized in solution by IR, ^{1}H, ^{11}B, and ^{13}C NMR spectroscopy and mass spectrometry and the structural types were unequivocally established by crystallographic analysis of *arachno*-[Cp*Fe(CO)B_3H_8].

Introduction

Metallaborane chemistry is an interesting and diverse area of cluster chemistry that is closely allied to both polyhedral metal compounds and boron hydrides.[1–6] Although it continues to be an area of intense research, development in this area has been much slower partly due to the lack of high-yielding, convenient synthetic methods and suitable precursors.[4,7] Synthetic methods for the generation of transition-metal cluster compounds have historically been based around conditions that favor more stable products.[8] 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 transition-metal halides.[9] Fehlner et al. showed that the addition of monoboranes ($LiBH_4$·thf, BH_3·thf, or $BHCl_2$·SMe_2) to monocyclopentadienylmetal chlorides, [Cp*MCl]$_n$, is an excellent method for the preparation of metallaboranes containing transition metals ranging from groups 5 to 9.[10] Despite having well-developed routes to metallaboranes of second to third row transition metals of group 5 to 9, there are not many suitable synthetic routes are available for first row transition metals. The synthetic route depends on the selective conversion of metal polyborohydrides to metallaboranes by hydrogen elimination. The method fails when competing pathways have lower overall barriers than that leading to metallaboranes. Thus, the three first-row transition metals (Mn, Fe, Ni) fail to yield metallaboranes through the route discussed above and the only metal-containing products observed were metallocenes (Mn, Fe)[11,12] or metal (Ni).[12]

As the metallaboranes derived from first-row transition metals have properties distinctively different from those of their heavier congeners, for examples, V vs. Nb and Ta;[13] Cr vs. Mo and W;[14,15] Mn vs. Re;[16] Fe vs. Ru and Os;[17–19] or Co vs. Rh and Ir,[20,21] an alternative synthetic route has been employed to access first-row metallaboranes. Using this method, that is, the reaction of metal hydrides with boranes, a good number of metallaborane compounds were synthesized.[17,22–26] One of our main objectives was to explore suitable metal precursors for metallaboranes containing metals from groups 5–9. Thus, in our continuing search for alternative metal precursors, containing the Cp*M fragment, we found that mono(halo)(cyclopentadienyl)metal carbonyl, [Cp*M(CO)$_n$X] (M = Fe, X = I, n = 2; M = Mo or W, X = Cl, n = 3) are very useful to group 6 and 8 metallaboranes. In the following we describe the results of the reactions between these new metal carbonyl precursors and monoborane reagents, for example, BH_3·thf or $LiBH_4$ to afford *arachno*-2-[Cp*Fe(CO)B_3H_8] and *closo*-[(Cp*M)$_2B_5H_9$] (M = Mo, W).

Results and Discussions

Isolation and Characterization of *arachno*-[Cp*Fe(CO)-B_3H_8]

Reaction of [Cp*Fe(CO)$_2$I] (**1**) with BH_3·thf or $LiBH_4$ yields *arachno*-[Cp*Fe(CO)B_3H_8] (**2**) (Scheme 1). The Cp analogue of **2** was previously synthesized by Gaines in 1974

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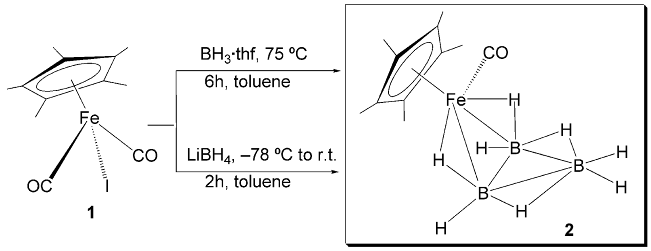
[a] Department of Chemistry, Indian Institute of Technology Madras
Chennai 600036, India
Fax: +91-44-2257-4202
E-mail: sghosh@iitm.ac.in

from the reaction of [CpFe(CO)$_2$I] with [B$_3$H$_8$]$^-$;[16b,27] however, no detailed structural studies were available. The isolated yield of **2** from the above route was considerably higher than that obtained with the polyborane anion and transition-metal halide route. Compound **2** was characterized spectroscopically – the data are in accord with the Cp analogue – as well as by a single-crystal X-ray diffraction study.



Scheme 1.

The parent ion in the mass spectrum fragments by the loss of a molecule of CO and the molecular mass corresponds to [Cp*Fe(CO)B$_3$H$_8$]. The IR spectrum of compound **2** also supports the presence of a terminal carbonyl ligand by the appearance of a band at 1967 cm^{-1}. The molecular formula combined with Wade's rules[28,29] suggests that **2** is a seven skeletal electron pair (*sep*) *arachno*-[Cp*Fe(CO)B$_3$H$_8$], a metal analogue of [B$_4$H$_{10}$]. The ^{11}B NMR of compound **2** shows two types of boron environments in a 1:2 ratio, the chemical shifts and multiplicities of two signals are more characteristic of those observed for a metal–B$_3$H$_8$ complex[30] rather than borallyl complexes.[13c,16b,31–35] Besides the Cp* protons, the ^{1}H{^{11}B} NMR spectrum of **2** reveals eight protons associated with the boron cage in an integral ratio of 1:1:2:2:2, where two equivalent BHB and FeHB protons appeared at –1.87 and –15.43 ppm, respectively. The room-temperature ^{1}H NMR spectrum of **2** for the [B$_3$H$_8$] fragment protons clearly reveals that the molecule is not fluxional.

The molecular structure of **2**, determined by single-crystal X-ray diffraction analysis, confirms the structural inferences made on the basis of spectroscopic results. The molecular structure of **2** (Figure 1) is similar to that of [B$_4$H$_{10}$] and best described as a butterfly *arachno*-cluster, where one of the wing-tips, that is, the BH$_2$ group, is replaced by a [Cp*Fe(CO)] fragment. The bond lengths in **2** compare well with molecules of similar geometry[3,4] as well as borallyl complexes[13c,16b,31–35] (Scheme 2). In molecule **2**, there is a noncrystallographic mirror plane through Fe1, B3, and C11, and the dihedral angle between the planes B2–B1–Fe1 and B1–B2–B3 is 122.7°, typical of all known *arachno*-2-metallatetraboranes. Relative to the differences in the covalent radii, the average Fe–B distance (2.24 Å) is shorter than those of the heavier metal analogues (Table 1). The crystal structure of *arachno*-2-[Cp*Fe(CO)B$_3$H$_8$] shows that the pentamethylcyclopentadienyl ligand is in the *exo* position and the CO ligand is in the *endo* position. The geometry of **2** is also similar to that observed in *arachno*-type 2-[Cp*ReH$_3$B$_3$H$_8$],[25] 2-[Cp*Ru(PMe$_3$)B$_3$H$_8$],[36] and 2-[Cp*Fe(PMe$_3$)B$_3$H$_8$],[37] in which the pentamethylcyclopentadienyl ligand is shown to be in the *exo* position. Although compound **2** is isoelectronic with [Cp*M(CO)B$_3$H$_7$] (M = Ir, Co)[31b,32] and [Cp*IrB$_3$H$_9$],[21a] the latter two types, that is, group 9 metals, prefer the borallyl structure.

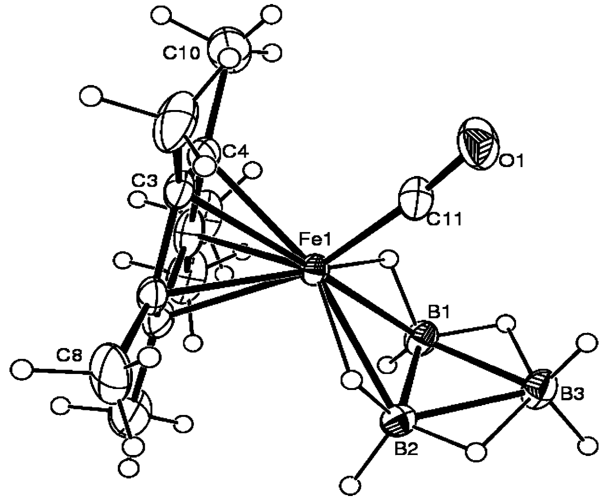
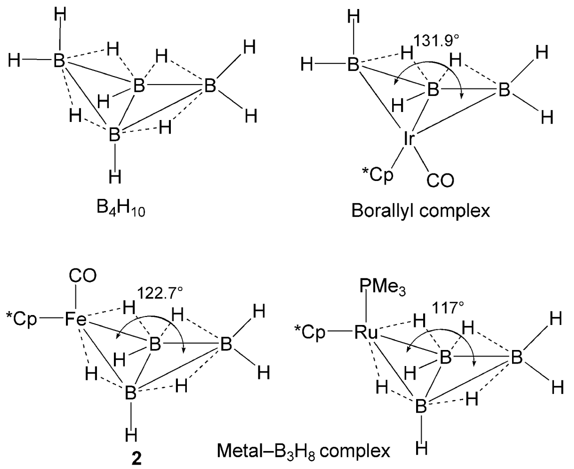


Figure 1. Molecular structure and labeling diagram for [Cp*Fe(CO)B$_3$H$_8$] (**2**). Relevant bond lengths [Å] and angles [°]: Fe1–B1 2.248(4), Fe1–B2 2.251(4), B1–B2 1.725(5), B1–B3 1.793(5), B2–B3 1.805(5), B2–B1–Fe1 67.55(18), B3–B1–Fe1 105.0(2), B3–B2–Fe1 104.5(2), B1–B3–B2 57.3(2).



Scheme 2. Structural comparison of metalborallyl and metal–B$_3$H$_8$ complexes.

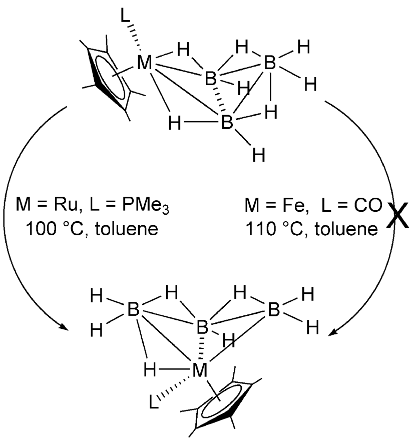
The reaction of open metal clusters with boranes or metalcarbonyl fragments constitutes a useful way of generating derivatives that are more stable than the original cluster.[38] Thus, in order to evaluate the reactivity of this new ferraborane, pyrolysis of **2** was performed with BH$_3$·thf at 90 °C, which afforded no products, even under very drastic reaction conditions. This is in distinct contrast to the situation with [Cp*IrB$_3$H$_9$], which yielded *arachno*-[Cp*IrB$_4$H$_{10}$] and *nido*-type [(Cp*Ir)B$_5$H$_9$], [(Cp*Ir)B$_9$H$_{13}$], and [(Cp*Ir)$_2$B$_8$H$_{12}$] clusters with BH$_3$·thf under the same reaction conditions. Further, a facile wing-to-hinge isomerization of *arachno*-[Cp*Ru(PMe$_3$)B$_3$H$_8$] occurs at 100 °C; however,

Table 1. Comparison of the structural parameters of *arachno*-[Cp*Fe(CO)B_3H_8] (**2**) with metal–B_3H_8 and borallyl complexes.

	Metallaboranes	$d_{avg.}$ [M–B] [Å]	$d_{avg.}$ [B–B] [Å]	Dihedral angle [°]	^{1}H NMR [ppm] [B–H–B], [M–H–B]	^{11} BNMR [ppm]
B_3H_8 Complexes	[Cp*Fe(CO)B_3H_8] **2**	2.24	1.77	122.7[a]	–1.87, –15.4	–0.5 and –41.3
	[Cp*Ru(PMe$_3$)B_3H_8]	2.34	1.84	117[a]	–0.34, –12.01	–1.9 and –34.6
	[Cp*Re(H_3)B_3H_8]	2.43	1.76	124.7[a]	0.1, –10.3	6.2 and –39.9
Borallyl Complexes	[Cp*Co(CO)B_3H_7]	2.06	1.82	126.4[b]	–4.0[c]	6.1 and –0.8
	[Cp*Ir(CO)B_3H_7]	2.18	1.84	131.9[b]	–4.68[c]	–4.9 and –11.6

[a] Angle between the planes M2–B1–B3 and B1–B3–B4 (M = Fe, Ru, Re). [b] Angle between the planes B2–M1–B3 and B4–B3–M1 (M = Ir, Co). [c] No [M – H–B] proton in borallyl complex.

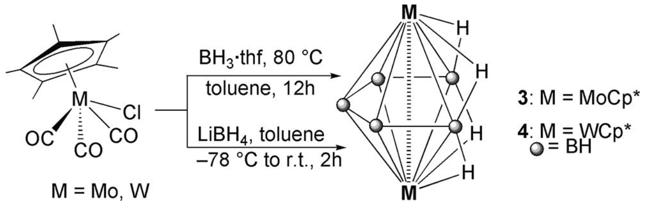
compound **2** being the congener of *arachno*-[Cp*Ru(PMe$_3$)-B_3H_8] does not undergo the same thermal rearrangement (Scheme 3). Thus, it seems to us that **2** should in fact be highly stable under thermal conditions.



Scheme 3. Wing-to-hinge isomerization of *arachno*-[Cp*Ru(PMe$_3$)-B_3H_8].

Reaction of [Cp*M(CO)$_3$Cl] with BH_3·thf and $LiBH_4$ (M = Mo, W)

Reaction of [Cp*M(CO)$_3$Cl] (M = Mo, W) with both BH_3·thf and $LiBH_4$ yielded metallaboranes [(Cp*M)$_2B_5H_9$] (**3**: M = Mo, **4**: M = W) (Scheme 4). Monitoring these reactions by ^{11}B NMR spectroscopy showed that compounds **3** and **4** are produced as a sole product. Reaction of [Cp*M(CO)$_3$Cl] with $LiBH_4$ takes place at low temperature, whereas with BH_3·thf heating is required. Hence, in the latter reaction the largest barrier is encountered. Compounds **3** and **4** were characterized spectroscopically in comparison with the reported data.[15b,15c]



Scheme 4. Preparation of [(Cp*M)$_2B_5H_9$] from [Cp*M(CO)$_3$Cl].

A comparison of these observations with the metal polychloride precursor [Cp*MCl$_4$] is informative. The reaction of [Cp*MoCl$_4$] with borohydride yields [(Cp*MoCl)$_2B_2H_6$], [(Cp*MoCl)$_2B_4H_{10}$], [(Cp*Mo)$_2$(B_2H_6)$_2$], and [(Cp*MoCl)$_2$-B_3H_7] in approximately equal abundances.[15b] Similarly, the W analogue, that is, [Cp*WCl$_4$], upon reaction with borohydrides yields [(Cp*WCl)$_2B_2H_6$], [(Cp*WH$_3$)$_2B_2H_6$], [(Cp*WH$_3$)B_4H_8], and [(Cp* W)$_2$HCl(B_2H_6)].[15c] In contrast, [Cp*M(CO)$_3$Cl] (M = Mo and W) yield only [(Cp*M)$_2$-B_5H_9]. In the case of metal polychlorides, a metalpolyborohydride intermediate is produced through a fast metathesis reaction with borohydrides, and the fate of this complex is determined by competition between elimination of BH_3 and H_2. The former yields hydrides and is enhanced by factors that stabilize the Lewis acid, namely, basic solvents or donor substituents. In contrast, elimination of H_2 from metalpolyborohydrides leads to B–B and M–B bond formation. Thus, a drawback of the polychloride route is the formation of several intermediate species, which in turn may undergo cluster growth with metal hydrides or borane, and interesting compound or not, this reduces the selectivity of the preparation. Consequently, the isolated yields are considerably higher in [Cp*M(CO)$_3$Cl] (M = Mo and W).

The fact that [Cp*M(CO)$_3$Cl] is a well-defined compound in solution leads to a more selective reaction than the polychloride/borohydride route. That is, as discussed above, the polychloride route generates many byproducts and requires a chromatographic step or fractional crystallization, a procedure that inevitably reduces the isolated yield. Thus, the new route described in this report will find the most use for metals for which chromatography is not possible; for example, Cr, or Nb.[39] In contrast, the preparation and handling of the polychlorides are less attractive, as the net yield from purchased compounds is lower and the overall time required is considerably higher.

Conclusions

An efficient and high-yielding synthesis of *arachno*-[Cp*Fe(CO)B_3H_8] and *closo*-[(Cp*M)$_2B_5H_9$] (M = Mo, W) was discovered by reaction of [Cp*M(CO)$_n$X], (M = Fe, X = I, n = 2; M = Mo, W, X = Cl, n = 3) with monoborane reagents, BH_3·thf or $LiBH_4$. The direct generation of molybda- and tungstaborane illustrates that polyborane can be built up on the [Cp*M(CO)$_3$Cl] fragment, and the limitation of the monocyclopentadienylmetal halide route to metallaboranes can be circumvented by using them as alternative metal fragment sources. Furthermore, this new synthetic route represents an exciting development in metallaborane chemistry, as it would allow metallaboranes that are otherwise unavailable from air- and moisture-sensitive precursors to be synthesized; for example, [Cp*MCl$_x$], (M = V, x = 2; Hf, x = 3 or Nb, x = 4). Efforts to assess the scope, limitations, and synthetic applications of this metal precursor, as well a detailed mechanistic study, are now in process.

Experimental Section

General Procedures and Instrumentation: All the operations were conducted under an Ar/N$_2$ atmosphere by using standard Schlenk techniques and a glove box. Solvents were distilled prior to use under an atmosphere of argon. Cp*H, [Fe(CO)$_5$], [Mo(CO)$_6$], [W(CO)$_6$], LiBH$_4$, and BH$_3$·thf (Aldrich) were used as received. The external reference for the ^{11}B NMR, [Bu$_4$N(B$_3$H$_8$)], was synthesized by a literature method.[40] [Cp*Fe(CO)$_2$I][41] and [Cp*M(CO)$_3$Cl] (M = Mo, W)[42,43] were prepared as described in the literature. Thin-layer chromatography was carried on 250 mm *dia* aluminum-supported silica gel TLC plates (Merck TLC Plates). NMR spectra were recorded with a 400 or 500 MHz Bruker FTNMR spectrometer. Residual solvent protons were used as reference (CDCl$_3$, δ = 7.26 ppm), whereas a sealed tube containing [Bu$_4$N(B$_3$H$_8$)] in C$_6$D$_6$ (δ_B = –30.07 ppm) was used as an external reference for ^{11}B NMR spectroscopy. Infrared spectra were obtained with a Nicolet 6700 FTIR spectrometer. Mass spectra were obtained with a Jeol SX 102/Da-600 mass spectrometer/data system by using argon/xenon (6 kV, 10 mÅ) as the FAB gas.

Synthesis of *arachno*-[Cp*Fe(CO)B$_3$H$_8$] (2)

By using BH$_3$·THF as Monoborane Reagent: In a typical reaction, to a 100-mL Schlenk tube containing [Cp*Fe(CO)$_2$I] (0.06 g, 0.16 mmol) was added freshly distilled toluene (10 mL) to generate a brown solution. A sixfold excess of BH$_3$·thf (1.0 M in THF, 1 mL, 0.96 mmol) was added at room temperature. The solution was stirred for 6 h at 75 °C. The solvent was dried, and the residue was extracted into hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic workup by using silica gel TLC plates. Elution (hexane/CH$_2$Cl$_2$, 95:05) yielded reddish brown **2** (0.03 g, 72 %).

By using LiBH$_4$ as Monoborane Reagent: [Cp*Fe(CO)$_2$I] (0.08 g, 0.21 mmol) was dissolved in toluene (8 mL), and the mixture was cooled to –78 °C. LiBH$_4$ (0.62 mL, 1.26 mmol) was added dropwise with stirring. The dark-brown solution was stirred at room temperature for 2 h. Volatiles were removed in vacuo to give a dark-brown residue. This residue was extracted into hexane, and the solution was filtered through Celite. After removal of the solvent, the residue was subjected to chromatographic workup by using silica gel TLC plates. Elution (hexane/CH$_2$Cl$_2$, 95:05) yielded reddish brown **2** (0.02 g, 43 %). ^{11}B NMR (400 MHz, CDCl$_3$, 22 °C): δ = –0.5 (br. s, 1B), –41.3 (br. s, 2B) ppm. ^{1}H{^{11}B} NMR (400 MHz, CDCl$_3$, 22 °C): δ = 5.33 [partially collapsed quartet (pcq), 1 BH$_t$], 4.26 (pcq, 1 BH$_t$), 2.80 (pcq, 2 BH$_t$), 1.78 (s, 15 H, Cp*), –1.87 (s, 2B–H–B), –15.43 (s, 2Fe–H–B) ppm. ^{13}C NMR (400 MHz, CDCl$_3$, 22 °C): δ = 217.0 (s, Fe–CO), 89.7 (s, C$_5$Me$_5$), 8.8 (s, CH$_3$ in C$_5$Me$_5$) ppm. MS (FAB+): m/z (%) = 259 [M]$^+$, 231 [M – CO]$^+$. IR (hexane): $\tilde{\nu}$ = 2496 (w, B–H$_t$), 2437 (w, B–H$_t$), 1967 (s, Fe–CO) cm^{-1}. C$_{11}$H$_{23}$B$_3$FeO (259.58): calcd. C 50.90, H 8.93; found C 49.17, H 8.56.

Synthesis of *closo*-[(Cp*M)$_2$B$_5$H$_9$] (M = Mo and W)

By using BH$_3$·THF as Monoborane Reagent: In a typical reaction, to a solution of [Cp*Mo(CO)$_3$Cl] (0.09 g, 0.28 mmol) in toluene was added a 10-fold excess of BH$_3$·thf (2.80 mL, 2.80 mmol) at room temperature, and the color of the mixture changed from red-orange to brown. After stirring at 80 °C for 12 h, the solvent was removed, and the residue was extracted into hexane and passed through Celite. After removal of the solvent, the residue was subjected to chromatographic workup by using silica gel TLC plates. Elution (hexane) yielded red orange [(Cp*Mo)$_2$B$_5$H$_9$] (0.07 g, 48 %). In the case of the reaction of [Cp*W(CO)$_3$Cl] with BH$_3$·thf, under the same conditions, no products were produced.

Note that the spectral and structural characterization of *closo*-[(Cp*M)$_2$B$_5$H$_9$] (M = Mo and W) was reported earlier by Fehlner.[15b,15c]

By using LiBH$_4$ as Monoborane Reagent: In a typical reaction, to a solution of [Cp*Mo(CO)$_3$Cl] (0.08 g, 0.23 mmol) dissolved in freshly distilled toluene (8 mL) was added a sevenfold excess of LiBH$_4$ (0.80 mL, 1.61 mmol) at –78 °C, and the reaction mixture was warmed slowly to room temperature and left to stir for an additional 2 h. Toluene was removed in vacuo, the dark-brown residue was extracted into hexanes, and the solution was passed through Celite to afford a red brown solution. After removal of the solvent, the residue was subjected to chromatographic work up by using silica gel TLC plates. Elution (hexane) yielded red orange [(Cp*Mo)$_2$B$_5$H$_9$] (0.05 g, 46 %). Isolated yield of W analogue from [Cp*W(CO)$_3$Cl] was 37 % (0.05 g). Note that in case of [(Cp*W)$_2$-B$_5$H$_9$] preparation, the experimental conditions were modified. After the addition of LiBH$_4$ at –78 °C, reaction mixture was warmed slowly to room temperature and thermolyzed at 60 °C for 12 h.

X-ray Structure Determination: CCDC-707826 (for **2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data were collected and integrated by using a Bruker Apex II CCD area detector system equipped with graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation at 173 K. The structure was solved by heavy atom methods by using SHELXS-97 and refined by using SHELXL-97 (G. M. Sheldrick, University of Göttingen). X-ray quality crystal of **2** was grown by cooling a concentrated hexane/CH$_2$Cl$_2$ (9.5:0.5) solution to –4 °C over a period of 2 d.

Crystal Data for [Cp*Fe(CO)B$_3$H$_8$] (2): C$_{11}$H$_{23}$B$_3$FeO; M = 259.57 g mol^{-1}; monoclinic, $P2_1/c$, a = 13.0325(6) Å, b = 8.1250(3) Å, c = 13.5871(6) Å, β = 93.667(2)°; Z = 4; $\rho_{\text{calcd.}}$ = 1.201 Mg m^{-3}, Final R indices [$I > 2\sigma(I)$] R_1 = 0.0443, wR_2 = 0.1197, Index ranges $-13 \leq h \leq 17$, $-10 \leq k \leq 7$, $-17 \leq l \leq 16$, Crystal size $0.35 \times 0.30 \times 0.15$ mm^3, 9286 Reflections collected, 3216 independent reflections, [R(int) = 0.0244], Goodness-of-fit on F^2 1.168.

Acknowledgments

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