

Note

## Reaction of *nido*-1,2-(Cp\**RuH*)<sub>2</sub>B<sub>3</sub>H<sub>7</sub> with ethynylferrocene to yield new metallacarboranes

Hong Yan <sup>a,\*</sup>, Bruce C. Noll <sup>b</sup>, Thomas P. Fehlner <sup>b</sup>

<sup>a</sup> State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, No. 22 Hankou Road, Nanjing, Jiangsu 210093, China

<sup>b</sup> Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556, USA

Received 13 July 2006; received in revised form 4 August 2006; accepted 4 August 2006

Available online 12 August 2006

### Abstract

Addition of ethynylferrocene to *nido*-1,2-(Cp\**RuH*)<sub>2</sub>B<sub>3</sub>H<sub>7</sub> (**1**) at ambient temperature leads to *nido*-1,2-(Cp\**Ru*)<sub>2</sub>(1,5- $\mu$ -C{Fc}Me)B<sub>3</sub>H<sub>7</sub> (**2**, **3**) and *closo*-4-Fc-1,2-(Cp\**RuH*)<sub>2</sub>-4,6-C<sub>2</sub>B<sub>2</sub>H<sub>3</sub> (**4**). Compounds **2** and **3** represent a pair of geometric isomers, *nido*-species in which the regiochemistry of the alkyne reduction conforms to the Markovnikoff rule. Compound **4** is an octahedral structure in which the inserted alkyne is on an open face of the *closo* cluster.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Boron; Metallaboranes; Metallacarboranes; Alkynes; Cluster

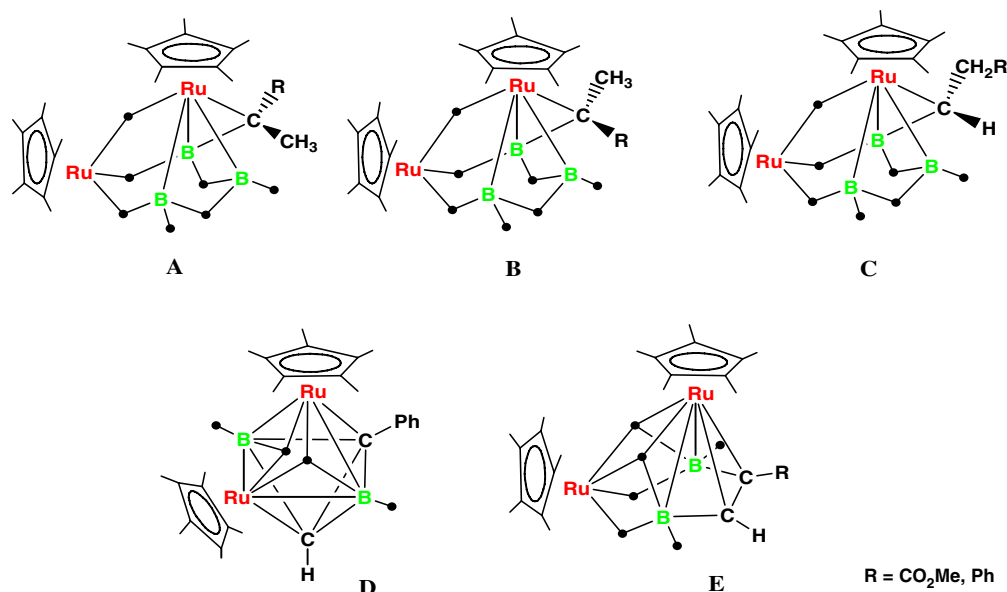
### 1. Introduction

A convenient and high-yield route to metallaboranes from the reactions of monocyclopentadienylmetal halides (groups 5–9) with monoboranes has been developed [1,2]. This provides the possibility to investigate the systematic reaction chemistries for such a type of hybrid metal-boron complexes. Traditionally, metallacarboranes were synthesized via a sequence of steps from boranes to carboranes to metallacarboranes [3–6]. In fact, examples of insertion of alkynes into metallaboranes to generate metallacarboranes also had been reported [7–9], but further investigations were blocked by limited sources of the metallaboranes. Now the situation has changed with quantities of varieties of metallaboranes available. Thus, routes to prepare metallacarboranes from metallaboranes and alkynes can be explored in greater detail than before. It was observed that a metal plays a critical role. For exam-

ple, the dirhodaborane leads predominantly to catalytic cyclotrimerization of alkynes [10,11]; the diiridaborane needs a molybdenum center to promote alkyne insertion [12]; and the diruthenaborane, *nido*-1,2-(Cp\**RuH*)<sub>2</sub>B<sub>3</sub>H<sub>7</sub> (**1**) leads to diverse, unprecedented products even at ambient temperature.

Scheme 1 illustrates some of the ruthenacarborane products. If pushed, some undergo further conversions [13–17]. Relative to internal alkynes, terminal ones create novel compounds, e.g., the first M–B alkylidene complexes generated from cooperative reactivities of metal hydrides and boron hydrides of **1**. Moreover, an alkyne functionalized with CO<sub>2</sub>Me, is involved in an unexpected chemical transformation, e.g., C=O coordination, C–O bond cleavage, and the O atom inserted into a B–H bond [16]. The large role of the alkyne substituents in the number and type of the ruthenacarboranes observed was not previously appreciated. To further explore this feather of the chemistry we now describe the reactivity of ethynylferrocene with **1**. The results provide the additional insight into the nature of the metallaborane/alkyne reactive interaction.

\* Corresponding author. Tel.: +86 25 83686724; fax: +86 25 83314502.  
E-mail address: hyan1965@nju.edu.cn (H. Yan).



Scheme 1.

## 2. Results and discussion

*nido*-1,2-(Cp\**Ru*)<sub>2</sub>(1,5- $\mu$ -C{Fc}Me)B<sub>3</sub>H<sub>7</sub> (**2**) and (**3**) were isolated together in a combined yield of 16%. Attempts to separate the two compounds were not successful due to similar polarities as well as low stabilities on a silica gel column. However, both solid-state structures were successfully determined by selection of the crystals with different unit cells. They are shown in Figs. 1, 2 and Table 1. Both structures display a  $\mu$ -alkylidene bridge over one Ru–

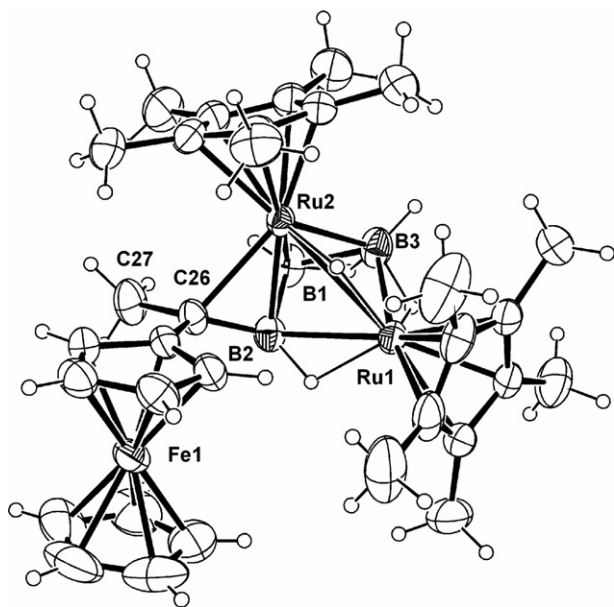


Fig. 1. Molecular structure of **2**. Selected bond length (Å). Ru(1)–B(3) 2.3000(19), Ru(1)–B(2) 2.4022(17), Ru(1)–Ru(2) 2.8889(2), Ru(2)–B(2) 2.1273(18), Ru(2)–B(1) 2.131(2), Ru(2)–B(3) 2.1694(18), Ru(2)–C(26) 2.3145(14), B(1)–B(3) 1.807(3), B(1)–B(2) 1.869(3), B(2)–C(26) 1.506(2), C(26)–C(27) 1.523(2).

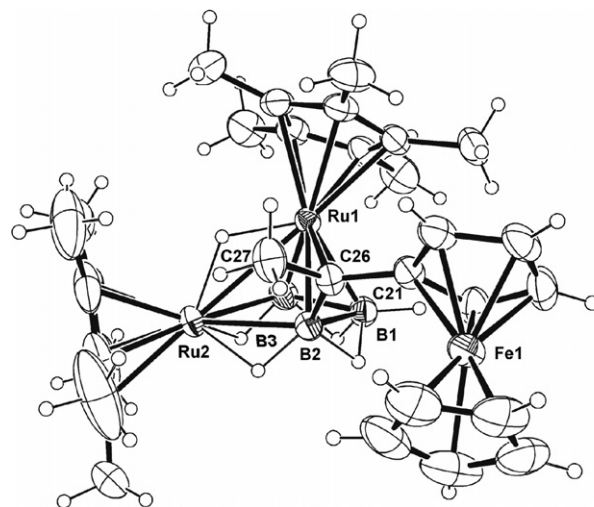


Fig. 2. Molecular structure of **3**. Selected bond length (Å). Ru(1)–B(3) 2.1714(18), Ru(1)–B(2) 2.1278(17), Ru(1)–B(1) 2.1159(18), Ru(1)–Ru(2) 2.8770(2), Ru(2)–B(2) 2.3852(17), Ru(2)–B(3) 2.3073(19), Ru(1)–C(26) 2.3304(15), B(1)–B(3) 1.820(3), B(1)–B(2) 1.845(3), B(2)–C(26) 1.503(2), C(26)–C(27) 1.522(2).

B edge that arises from Markovnikoff addition of the two framework hydrogen atoms to the alkyne. Clusters **2** and **3** are geometrical isomers relative to the orientation of the methyl and ferrocenyl groups with respect to the Ru–Ru edge of the cluster. Both contain a chiral carbon center.

The correspondence of structures with spectroscopic data were established by measuring the solid state structure and the solution proton NMR data with the same single crystal. Notably, the two geometrical isomers show remarkable differences in chemical shifts in their <sup>1</sup>H NMR spectra. Thus, they can be readily recognized in a mixture by NMR. For example, the two methyl groups generated from the alkyne reduction are located at 1.46 ppm in **2** and

1.77 ppm in **3**, respectively. Variable temperature (–90 to 25 °C)  $^1\text{H}$  NMR experiments show little change in the ratio of the two compounds. Heating up to 80 °C leads to decomposition rather than conversion from one to the other confirming the existence of a substantial barrier to interconversion. The two isomers are analogous to the clusters **A** and **B** generated from the methyl propiolate reaction [15] and shown in Scheme 1 as **C** is the analog of the anti-Markovnikoff addition of the alkyne. Based on our interpretation of the conversion of **A** and **B** to C–O inserted products, the barrier to isomer conversion in this system is lower than that for **2** and **3**.

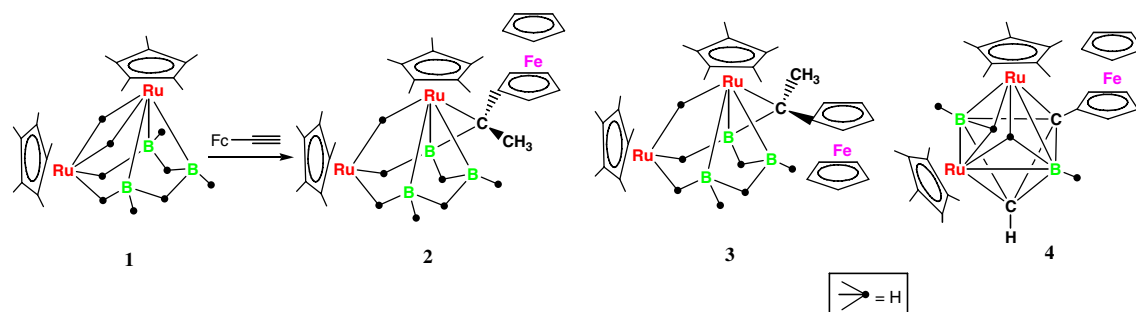
Table 1  
Crystallographic data and structure refinement information for **2** and **3**

	<b>2</b>	<b>3</b>
Formula	$\text{C}_{32}\text{H}_{49}\text{B}_3\text{FeRu}_2$	$\text{C}_{32}\text{H}_{49}\text{B}_3\text{FeRu}_2$
Formula weight	724.13	724.13
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	11.1810(6)	10.4005(6)
$b$ (Å)	12.2630(7)	13.2361(7)
$c$ (Å)	12.5537(7)	13.2681(7)
$\alpha$ (°)	99.5850(10)	111.6290(10)
$\beta$ (°)	99.5370(10)	107.6010(10)
$\gamma$ (°)	108.2530(10)	94.9760(10)
$V$ (Å <sup>3</sup> )	1567.62(15)	1577.41(15)
$Z$	2	2
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.534	1.525
$F(000)$	740	740
$\mu$ (mm <sup>–1</sup> )	1.427	1.419
Crystal size (mm)	$0.33 \times 0.17 \times 0.15$	$0.35 \times 0.17 \times 0.16$
$\theta$ Range (°)	3.95–31.53	3.94–31.51
Minimum and maximum transmission	0.8144 and 0.6502	0.8048 and 0.6366
Number of reflections collected	21 604	21 944
Number of unique reflections ( $R_{\text{int}}$ )	10 093 (0.0162)	10 206 (0.0146)
Data/restraints/parameters	10 093/0/393	10 206/0/371
Goodness-of-fit	1.051	1.038
$R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0233$ $wR_2 = 0.0609$	$R_1 = 0.0246$ $wR_2 = 0.0664$
$R$ indices (all data)	$R_1 = 0.0259$ $wR_2 = 0.0628$	$R_1 = 0.0281$ $wR_2 = 0.0684$
Largest difference in peak and hole (e/Å <sup>3</sup> )	0.543 and –0.465	0.822 and –0.426

In **2** and **3**, the two electron  $\mu$ -alkylidene ligand replaces two one electron B–H terminal hydrogen atoms. The seven skeletal electron pair (sep) count of **1** is retained consistent with retention of the framework of **1**. In our previous work with terminal alkynes, structures containing a  $\mu$ -alkylidene Ru–B bridge with Markovnikoff and anti-Markovnikoff regiochemistry have been reported by our group [16,17]. The anti-Markovnikoff products were not isolated from the reaction with ethynylferrocene, but this negative evidence does not rule out their formation due to the modest yield of **2** and **3**. Note that M–M bridged  $\mu$ -alkylidene fragments are well known in organometallic chemistry [18], and these Ru–B bridged  $\mu$ -alkylidene species may be treated as analogs.

*closo*-4-Fc-1,2-(Cp\* $\text{RuH}$ )<sub>2</sub>-4,6-C<sub>2</sub>B<sub>2</sub>H<sub>3</sub> (**4**) was isolated in a yield of 6%. Unfortunately, attempts to grow crystals failed. However, the spectroscopic data are very similar to those of cluster **D** in Scheme 1 and its proposed structure is shown in Scheme 2. Thus, the precise mass proves a formula  $\text{C}_{32}\text{H}_{43}\text{B}_2\text{FeRu}_2$  one hydrogen atom less than the proposed molecule. The  $^1\text{H}$  NMR data show a broad signal at 5.19 ppm that is characteristic of a BC–H fragment proving that the alkyne has been inserted into the cluster. Two equivalent triply bridging hydrides of Ru–H(B)–Ru and two equivalent B–H terminals are revealed by the two types of triplets ( $J = 5.0$  Hz) observed, similar coupling patterns for triply bridging hydrogens were observed in analogous clusters [17]. The  $^{11}\text{B}$  NMR spectrum displays a single boron resonance with  $J_{\text{B–H}} = 120$  Hz indicative of a single type of B–H fragment, consistent with the  $^1\text{H}$  data. The NMR data support a symmetric Ru<sub>2</sub>C<sub>2</sub>B<sub>2</sub> *closo* core structure, rather than an asymmetric *nido* core structure like that of **E** in Scheme 1. Additionally, **4** has the same pink color exhibited by *closo*-**D** (Scheme 1) distinctly different from the yellow or orange colors of the other *nido*-complexes in Scheme 1. A significant difference in the chemistry is that **4** arises at ambient temperature, whereas **D** is only observed at elevated temperatures.

In comparison with the alkynes used earlier [13–17], the reaction of **1** with ethynylferrocene at ambient temperature is faster and few species can be isolated. This is partly due to the incompatibility of the ferrocene moiety with the ruthenaborane cluster. This was demonstrated by letting ferrocene itself instead of ethynylferrocene react with **1**.



Scheme 2.

One was ferrocenium product and it was accompanied by a lot of decomposition of the metallaborane. Hence, the observed instability of products of **2** and **3** generated from ethynylferrocene may attribute to the reducing iron center of the ferrocenyl group. Hence, the properties of **2** and **3** are not due solely to the fact that the ferrocenyl group is larger than Ph or CO<sub>2</sub>Me group in HC≡CR. Variation of the alkyne substituent not only strongly affects overall reactivity but also the properties of the resulting products.

In conclusion, the reaction of *nido*-1,2-(Cp\**Ru*H)<sub>2</sub>B<sub>3</sub>H<sub>7</sub> with ethynylferrocene leads to isolation of a pair of isomers of new *nido*-ruthenacarboranes as well as a *closo*-ruthenacarborane. The redox activity of the external cluster iron center as well as its size is evident in the properties and stabilities of the new compounds.

### 3. Experimental

#### 3.1. General procedures

All operations were conducted under argon atmosphere using standard Schlenk techniques. Solvents were dried with appropriate reagents and distilled before use under N<sub>2</sub>. LiBH<sub>4</sub> (2 M in THF), [(Cp\**Ru*Cl<sub>2</sub>)*n*] (Strem) were used as received. HC≡CFc [19] *nido*-1,2-(Cp\**Ru*)<sub>2</sub>B<sub>3</sub>H<sub>9</sub> [20] were prepared according to the literature procedures. Silica gel (ICN 32–63, 60 Å) was purchased from ICN Biomedicals GmbH and predried at 180 °C before use. NMR spectra were recorded on a Bruker AMX 400 or a Varian 500 FT NMR spectrometers. Residual proton signals of solvents were used as reference: <sup>1</sup>H (δ, ppm, benzene-d<sub>6</sub>, 7.16). For <sup>11</sup>B an external reference was used: a sealed capillary containing [(Me<sub>4</sub>N)(B<sub>3</sub>H<sub>8</sub>)] in acetone-d<sub>6</sub> (δ, ppm, –29.7). Infrared spectra were measured on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. Mass spectra were obtained on a JEOL LMS-AX505 spectrometer using the EI or FAB ionization modes.

#### 3.2. Synthesis of **2**, **3** and **4**

To the orange solution of **1** (180 mg, 0.35 mmol) in hexanes (20 mL) was added FcC≡CH (250 mg, 1.19 mmol). The resulting mixture was stirred for 20 h at ambient temperature. After removal of solvent the residue was chromatographed on silica gel. Elution with hexanes gave FcCH=CH<sub>2</sub>; elution with hexanes/toluene (30:1) gave a red mixture of **2** and **3** (42 mg, 16%); elution with hexane/toluene (10:1) gave a pink compound of **4** (15 mg, 6%).

**2** <sup>1</sup>H{<sup>11</sup>B} (C<sub>6</sub>D<sub>6</sub>): δ 4.851 (m, 1H, CH–Fc), 4.222 (m, 1H, CH–Fc), 4.076 (s, 5H, Cp–Fc), 4.054 (m, 1H, CH–Fc), 3.975 (m, 1H, CH–Fc), 3.698 (br. 2H, B–Ht), 1.847 (s, 15H, Cp\*), 1.630 (s, 15H, Cp\*), 1.462 (s, 3H, Me), –2.694 (s, br. 1H, B–H–B), –2.961 (s, br. 1H, B–H–B), –11.166 (s, br. 1H, B–H–Ru), –11.203 (br. 1H, B–H–Ru), –15.334 (s, 1H, Ru–H–Ru). <sup>11</sup>B{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>): δ 19.83, 12.26, 9.70 (1:1:1). IR (KBr, cm<sup>–1</sup>): 2500, 2440 (ν<sub>B–H</sub>). Exact EI-MS (70 eV): *m/z* (%) [M<sup>+</sup>–5H] (100).

Anal. Calc., 722.1223 for C<sub>32</sub>H<sub>45</sub>B<sub>3</sub>FeRu<sub>2</sub>; found, 722.1237.

**3**. <sup>1</sup>H{<sup>11</sup>B} (C<sub>6</sub>D<sub>6</sub>): δ 4.219 (m, 1H, CH–Fc), 4.145 (m, 1H, CH–Fc), 4.028 (s, 5H, Cp–Fc), 4.020 (m, 1H, CH–Fc), 3.948 (m, 1H, CH–Fc), 3.698 (br. 1H, B–Ht), 3.571 (br. 1H, B–Ht), 1.837 (s, 15H, Cp\*), 1.773 (s, 3H, Me), 1.604 (s, 15H, Cp\*), –2.165 (s, br. 1H, B–H–B), 2.377 (s, br. 1H, B–H–B), –11.336 (s, br. 1H, B–H–Ru), –11.636 (br. 1H, B–H–Ru), –15.269 (s, 1H, Ru–H–Ru). <sup>11</sup>B{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>): δ 18.22, 13.74, 11.42 (1:1:1). IR (KBr, cm<sup>–1</sup>): 2500, 2440 (ν<sub>B–H</sub>). Exact EI-MS (70 eV): *m/z* (%) [M<sup>+</sup>–5H] (100). Anal. Calc., 722.1223 for C<sub>32</sub>H<sub>45</sub>B<sub>3</sub>FeRu<sub>2</sub>; found, 722.1237.

**4**. <sup>1</sup>H{<sup>11</sup>B}(C<sub>6</sub>D<sub>6</sub>): δ 5.191 (s, br. 1H, B–CH), 4.359 (t, *J* = 1.8 Hz, 2H, CH–Fc), 4.206 (s, 5H, Cp–Fc), 3.974 (t, *J* = 1.8 Hz, 2H, CH–Fc), 2.001 (s, 15H, Cp\*), 1.828 (s, 15H, Cp\*), 1.558 (t, br. *J* = 5.0 Hz, 2H, B–Ht), –11.988 (s, br. 2H, Ru–H(B)–Ru). <sup>11</sup>B (C<sub>6</sub>D<sub>6</sub>): δ –19.32 (*J*<sub>B–H</sub> = 120 Hz). IR (KBr, cm<sup>–1</sup>): 2532 (ν<sub>B–H</sub>). Exact EI-MS (70 eV): *m/z* (%) [M<sup>+</sup>–H] (30). Anal. Calc., 709.0987 for C<sub>32</sub>H<sub>43</sub>B<sub>2</sub>FeRu<sub>2</sub>; found, 709.0964.

### Acknowledgements

This work was supported by the Chinese National Science Foundation No. 20471017 and the US National Science Foundation CHE 9986880.

### Appendix A. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited to the Cambridge crystallographic Data Centre as supplementary publication No. 614310 and 614311 for **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12, Union Road, Cambridge CB21EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.003.

### References

- [1] T.P. Fehlner, J. Chem. Soc. Dalton Trans. (1998) 1525.
- [2] T.P. Fehlner, Organometallics 19 (2000) 2643.
- [3] M.F. Hawthorne, D.C. Young, P.A. Wegner, J. Am. Chem. Soc. 87 (1965) 1818.
- [4] M.F. Hawthorne, G.B. Dunks, Science 178 (1972) 462.
- [5] R.N. Grimes, Pure Appl. Chem. 54 (1982) 43.
- [6] C.A. Plumb, L.G. Sneddon, Organometallics 11 (1992) 1681.
- [7] R.N. Grimes, Pure Appl. Chem. 39 (1974) 455.
- [8] E.J. Ditzel, X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, Z. Sisan, B. Stibr, M. Thornton-Pett, J. Chem. Soc. Chem. Commun. (1990) 1741.
- [9] J. Bould, N.P. Rath, L. Barton, J.D. Kennedy, Organometallics 17 (1998) 902.
- [10] H. Yan, A.M. Beatty, T.P. Fehlner, Angew. Chem. Int. Ed. 40 (2001) 4498.
- [11] H. Yan, A.M. Beatty, T.P. Fehlner, Organometallics 21 (2002) 5029.

- [12] F. Montigny, R. Macias, B.C. Noll, T.P. Fehlner, *Angew. Chem. Int. Ed.* 45 (2006) 119.
- [13] H. Yan, A.M. Beatty, T.P. Fehlner, *Angew. Chem. Int. Ed.* 41 (2002) 2578.
- [14] H. Yan, A.M. Beatty, T.P. Fehlner, *J. Organomet. Chem.* 680 (2003) 66.
- [15] H. Yan, A.M. Beatty, T.P. Fehlner, *J. Am. Chem. Soc.* 124 (2002) 10280.
- [16] H. Yan, A.M. Beatty, T.P. Fehlner, *J. Am. Chem. Soc.* 125 (2003) 16367.
- [17] H. Yan, B.C. Noll, T.P. Fehlner, *J. Am. Chem. Soc.* 127 (2005) 4831.
- [18] C. Elschenbroich, A. Salzer, *Organometallics*, VCH, New York, 1989.
- [19] S.J. Luo, Y.H. Liu, C.M. Liu, Y.M. Liang, Y.X. Ma, *Synth. Commun.* 30 (2000) 1569.
- [20] X. Lei, M. Shang, T.P. Fehlner, *J. Am. Chem. Soc.* 121 (1999) 1275.