Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 3095–3097 **3095**
DOI: 10.1021/ic100323e

Metal-Catalyzed Decaborane−Alkyne Hydroboration Reactions: Efficient Routes to Alkenyldecaboranes

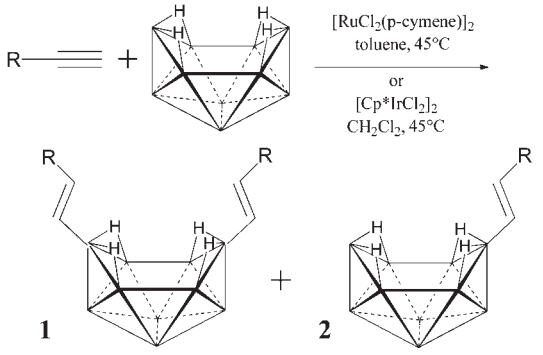
Shahana Chatterjee, Patrick J. Carroll, and Larry G. Sneddon*

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323

Received February 17, 2010

Transition-metal-catalyzed decaborane−alkyne hydroboration reactions have been developed that provide high-yield routes to the previously unknown di- and monoalkenyldecaboranes. These alkenyl derivatives should be easily modified starting materials for many biomedical and/or materials applications. Unusual catalyst product selectivity was observed that suggests quite different mechanistic steps, with the reactions catalyzed by the $[RuCl_2(p\text{-cymene})]_2$ and $[Cp^*IrCl_2]_2$ complexes giving the β−E alkenyldecaboranes and the corresponding reactions with the $[RuI_2(p\text{-cymene})]_2$ complex giving the α-alkenyldecaborane isomers.

We have shown that a variety of transition-metal complexes can be used to catalyze hydroboration reactions of polyboranes with olefins and acetylenes to yield alkyl- or alkenyl-substituted products.[1−4] For decaborane, we have reported that decaborane−olefin hydroborations were catalyzed by platinum catalysts, such as H_2PtCl_6 and $PtBr_2$, to produce dialkyldecaboranes[3] and by early-transition-metal $Cp_2Ti(CO)_2$ catalysts to selectively form monoalkyldecaboranes.[4] Corresponding metal-catalyzed decaborane−alkyne hydroboration reactions are of particular importance because they could provide high-yield routes to synthetically versatile alkenyldecaborane derivatives. However, we have previously been unsuccessful in achieving alkyne hydroboration reactions with decaborane.[5] One of the problems in using catalysts such as $IrCl(CO)(PPh_3)_2$ and $RhH(CO)(PPh_3)_3$, which were found[1] to be active for alkyne hydroborations with other polyboranes and borazines, is that the dissociated phosphine ligands from these complexes can react with decaborane to produce adducts such as 6,9-$(Ph_3P)_2B_{10}H_{12}$.[7] Thus, a limiting criterion for the selection of a transition-metal catalyst for decaborane−alkyne hydroborations is that the complex must not contain dissociable, strongly basic ligands. Two such complexes that appeared to meet this requirement were the arene complex $[RuCl_2(p\text{-cymene})]_2$, which Na and Chang reported[8] will catalyze the hydrosilylation of terminal alkynes to give good yields of vinylsilanes, and $[Cp^*IrCl_2]_2$,[9] which we had previously shown[10] to catalyze alkyne hydroborations with smaller polyboranes and the *o*- and *m*-$C_2B_{10}H_{12}$ carboranes. We report here that both $[RuCl_2(p\text{-cymene})]_2$ and $[Cp^*IrCl_2]_2$ also catalyze decaborane hydroboration of terminal alkynes[11] to give, depending upon catalyst loadings and reaction times, di- and monoalkenyldecaboranes (eq 1).



(1)

For example, a 3 h reaction of decaborane (0.242 g, 1.98 mmol) with excess 1-octyne (5.97 mmol) and $[RuCl_2(p\text{-cymene})]_2$

*To whom correspondence should be addressed. E-mail: lsneddon@sas.upenn.edu.

(1) (a) Wilczynski, R.; Sneddon, L. G. *J. Am. Chem. Soc.* **1980**, *102*, 2857–2858. (b) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1981**, *20*, 3955–3962. (c) Wilczynski, R.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 506–514. (d) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1987**, *109*, 5867–5868. (e) Lynch, A. T.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 6201–6209.

(2) (a) Davan, T.; Corcoran, E. W., Jr.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693–1694. (b) Corcoran, E. W., Jr.; Sneddon, L. G. In *Advances in Boron and the Boranes*; Liebman, J. F., , Greenberg, A., Williams, R. E., Eds.; VCR: New York, 1988; pp 71−89.(c) Kadlecek, D.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2000**, *122*, 10868–10877.

(3) Mazighi, K.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1993**, *32*, 1963–1969.

(4) (a) Pender, M. J.; Wideman, T.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1998**, *120*, 9108–9109. (b) Pender, M. J.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **2001**, *123*, 12222–12231.

(5) Decaborane, unlike the isoelectronic SB_9H_{11} cluster,[6] is unreactive toward alkynes in the absence of a catalyst. See the Supporting Information for this paper.

(6) (a) Meneghelli, B. J.; Bower, M.; Canter, N.; Rudolph, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4355–4360. (b) Canter, N.; Overberger, C. G.; Rudolph, R. W. *Organometallics* **1983**, *2*, 569–570.

(7) Hawthorne, M. F.; Pitocelli, A. R. *J. Am. Chem. Soc.* **1958**, *80*, 6685.

(8) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887–1889.

(9) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301–307.

(10) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449–453.

(11) Neither catalyst showed activity for decaborane hydroboration of internal alkynes.

Published on Web 03/11/2010

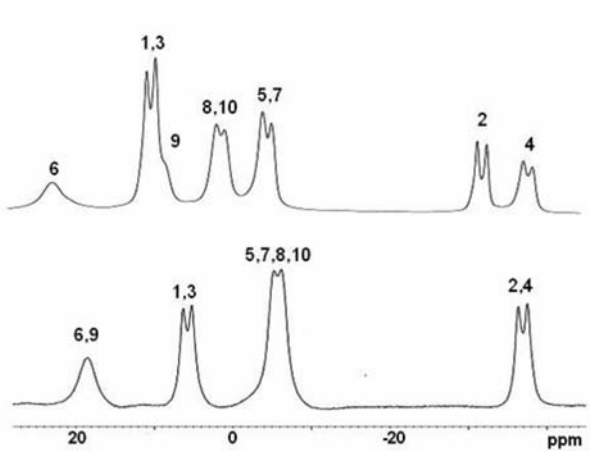


Figure 1. ^{11}B NMR spectra (128.4 MHz, C_6D_6) for **1** (bottom) and **2** (top). Comparisons (exptl/calcd assignments, ppm) of experimental and DFT/GIAO-calculated[12] shifts: (**1**) 19.9(2)/17.7, B6,9; 7.1(2)/7.9, B1,3; −4.4(4)/−5.9, B5,7,8,10; −35.7(2)/−37.2, B2,4. (**2**) 21.9/19.3, B6; 9.3(2)/10.5, B1,3; 8.0/4.3, B9; 0.4(2)/0.8, B8,10; −5.5(2)/−7.3, B5,7; −32.9/−34.4, B2; −38.7/−41.1, B4.

(0.21 mmol) at 45 °C gave, after column chromatography on silica gel using a hexanes eluent, a 42% yield (0.166 g, 0.71 mmol) of 6,9-(E−$CH_3(CH_2)_5CH$=$CH)_2B_{10}H_{12}$ (**1**) along with an 8% yield (0.047 g, 0.14 mmol) of 6-(E−$CH_3(CH_2)_5CH$=$CH)B_{10}H_{13}$ (**2**). The iridium catalyst proved to be even more active, giving an 83% isolated yield (0.277 g, 0.81 mmol) of **1** following the reaction of decaborane (0.120 g, 0.98 mmol) with excess 1-octyne (2.98 mmol) and $[Cp^*IrCl_2]_2$ (0.17 mmol) in ∼2 mL of toluene for 3 h at 45 °C.

The ^{11}B NMR spectra of **1** and **2** (Figure 1) exhibit the C_{2v}- and C_s-symmetric patterns expected for 6,9- and 6-substituted decaboranes, with shifts of the singlet resonances of the alkenyl-substituted B6 and B9 (**1**) and B6 (**2**) borons at somewhat higher field than those of their corresponding alkyl analogues.[3,4] Their ^{11}B NMR spectra also agree with the density functional theory/gage-invariant atomic orbital (DFT/GIAO)-calculated chemical shift values given in the figure caption. The olefinic resonances in the ^{1}H NMR spectra of **1** and **2** show ABX_2 patterns characteristic of trans β-E substitution.

While **1** and **2** were liquids, the $[Cp^*IrCl_2]_2$-catalyzed reaction of decaborane with excess trimethylsilylacetylene produced a solid 6,9-(E−Me_3SiCH=$CH)_2B_{10}H_{12}$ (**3**) (90% isolated yield) product. A crystallographic determination of **3** (Figure 2) confirmed alkyne hydroboration at both of the B6 and B9 borons, with the resulting olefins having the predicted β-E structures.

The $[RuI_2(p\text{-cymene})]_2$ complex proved to be an even more effective catalyst than $[RuCl_2(p\text{-cymene})]_2$. For example, the 45 °C reaction of decaborane (0.241 g, 1.97 mmol) with excess 1-octyne (5.97 mmol) in the presence of 0.10 mmol of $[RuI_2(p\text{-cymene})]_2$ produced a 95% isolated yield (0.639 g, 1.87 mmol) of 6,9-$(H_2C$=$C\{(CH_2)_5CH_3)\}]_2B_{10}H_{12}$ (**4**). Most surprisingly, the reactions with the $[RuI_2(p\text{-cymene})]_2$ catalyst produced α isomers of the mono- and dialkenyldecaboranes (eq 2) instead of the β-E isomers found with the $[RuCl_2(p\text{-cymene})]_2$ catalyst. Thus, while the ^{11}B NMR spectra of **4** and **5** were essentially

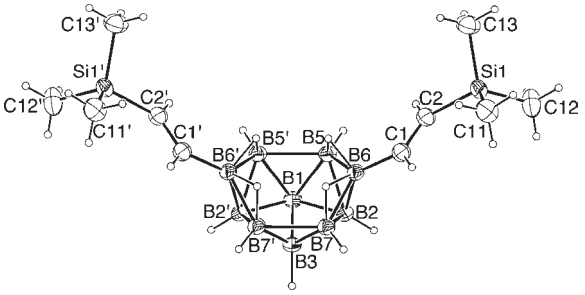


Figure 2. ORTEP drawing of the crystallographically determined structure of **3**. Selected bond lengths (Å) and angles (deg): C1−C2, 1.307(3); B6−C1, 1.557(3); C2−Si1, 1.867(2), B5−B6, 1.803(3); B6−B7, 1.799(3); B6−B2, 1.738(3); B6−C1−C2, 125.6(2); C1−C2−Si1, 127.71(19).

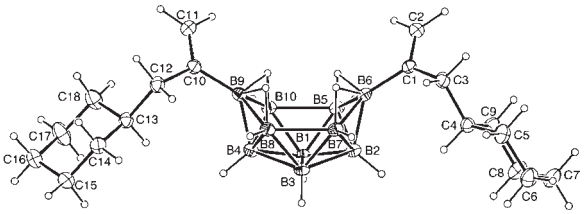
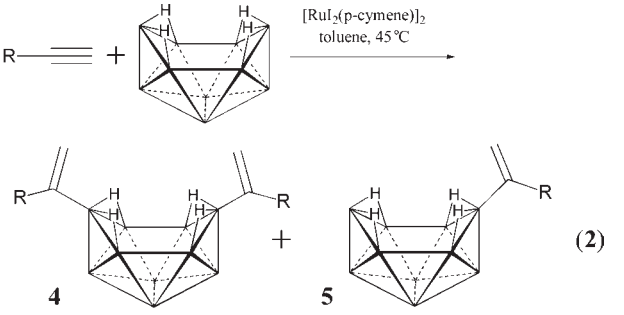


Figure 3. ORTEP drawing of the crystallographically determined structure of **6**. Selected bond lengths (Å) and angles (deg): C1−C2, 1.329(2); B6−C1, 1.563(2); C10−C11, 1.328(2); B9−C10, 1.568(2); B5−B6, 1.802(2); B6−B7, 1.806(2); B8−B9, 1.816(2); B9−B10; 1.803(2); C2−C1−C3, 120.91(13); C2−C1−B6, 119.65(13); C3−C1−B6, 119.42(11); C11−C10−C12, 121.28(13); C11−C10−B9, 120.09(13); C12−C10−B9, 118.62(12).

identical with those of **1** and **2**, their ^{1}H NMR spectra were quite different in the olefinic region, each exhibiting a characteristic AB α-olefin pattern.



(2)

As shown in Figure 3, α-olefin formation was confirmed by the crystallographic determination of 6,9-$(H_2C$=$C\{CH_2$-$(C_6H_{11})\}]_2B_{10}H_{12}$ (**6**), which was obtained in 55% isolated yield from the reaction of decaborane with excess 3-cyclohexylpropyne and $[RuI_2(p\text{-cymene})]_2$.

The scope and mechanism of catalytic action, as well as why different isomers are formed with the $[RuCl_2(p\text{-cymene})]_2$ and $[RuI_2(p\text{-cymene})]_2$ catalysts, are currently under investigation. Preliminary NMR studies have shown that $[RuCl_2(p\text{-cymene})]_2$ reacts with $B_{10}H_{14}$ to form a Ru−H complex, whereas no such Ru−H complex was observed in the NMR spectra of $[RuI_2(p\text{-cymene})]_2$-catalyzed reactions. This difference suggests that the $[RuCl_2(p\text{-cymene})]_2$ complex may react to form the β-E isomers by a process similar to that of the Chalk−Harrod mechanism of hydrosilylation[13]

(12) DFT/GIAO-calculated chemical shifts at the B3LYP/6-311G* level are for the model compounds 6,9-(E−CH_3CH=$CH)_2B_{10}H_{12}$ and 6-(E−CH_3CH=$CH)B_{10}H_{13}$.

(13) (a) Harrod, J. F.; Chalk, A. J. *J. Am. Chem. Soc.* **1965**, *87*, 1133. (b) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16–21.

involving the oxidative addition of decaborane to ruthenium, followed by alkyne coordination, decaborane insertion, and reductive elimination of the product. On the other hand, $[RuI_2(p\text{-cymene})]_2$ may be reacting by a mechanism involving a concerted B−H addition similar to the one proposed by Trost and Ball[14] to account for the formation of α-vinylsilane products from $[Cp^*Ru(MeCN)_3]^+$-catalyzed alkyne hydrosilylation reactions.

In conclusion, the metal-catalyzed decaborane−alkyne hydroboration reactions reported herein now provide the first routes to the previously unknown di- and monoalkenyldecaboranes. We are now undertaking systematic investigations of the transformations of these easily modified alkenyl derivatives to a wide range of functional decaborane derivatives of potential interest for either biomedical or materials applications.

Acknowledgment. We thank the National Science Foundation for support.

Supporting Information Available: Synthetic and computational details, spectral characterizations, and X-ray crystallographic data for **3** and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(14) (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644–17655. (b) Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578–11582.