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# Transition Metal Promoted Reactions of Boron Hydrides. 15.[11] Titanium-Catalyzed Decaborane−Olefin Hydroborations: One-Step, High-Yield Syntheses of Monoalkyldecaboranes

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We have previously shown that a variety of late transition metal complexes can be used to catalyze the reactions of polyboranes with olefins and acetylenes to yield alkyl or alkenyl-substituted products.[1] Recently, however, early transition metal complexes have also been found to catalyze olefin and acetylene hydroborations with monoboranes such as catecholborane (HBcat) or pinacolborane.[2] For example, Hartwig has recently reported[2a] that $Cp_2Ti(CO)_2$ catalyzes the hydroboration reactions of HBcat with acetylenes, while $Cp_2TiMe_2$ is an effective catalyst in reactions of HBcat with olefins. These reports suggested that early metal metallocene catalysts might also be useful for reactions involving polyboranes with the possibility of new types of activities and selectivities. We report in this communication our discovery of a titanium-catalyzed reaction that has allowed the systematic, high-yield syntheses of monoalkyldecaboranes.

We previously reported[3] that either chloroplatinic acid or platinum dibromide catalyze decaborane−olefin hydroboration to give dialkyldecaboranes, $6,9\text{-}(RC_2H_4)_2B_{10}H_{12}$, in high yields. In contrast, we have now found that decaborane−olefin hydroboration reactions employing catalytic amounts of $Cp_2Ti(CO)_2$ yield exclusively *monoalkyl*decaboranes, $6\text{-}(RC_2H_4)B_{10}H_{13}$. Analysis of reaction mixtures with GC/MS revealed that, even with more forcing conditions and longer reaction times, no dialkyl products are formed.

$$B_{10}H_{14} + 2RHC{=}CH_2 \xrightarrow{PtBr_2} 6,9\text{-}(RC_2H_4)_2\text{-}B_{10}H_{12} \tag{1}$$

$$B_{10}H_{14} + RHC{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} 6\text{-}(RC_2H_4)\text{-}B_{10}H_{13} \tag{2}$$

Gaines[4] has recently reported multistep synthetic routes to monoalkyldecaboranes, but the titanium-catalyzed reactions are a significant improvement, since they provide simple, high-yield, one-step routes to such compounds directly from decaborane. Reactions are typically carried out without solvent at 80−90 °C, in an excess of olefin and ~5 mol % catalyst, and give greater than 90% isolated yields. The catalyst is also active for long periods. For example, $^{11}B$ NMR analysis of an experiment where ~10 mmol samples of decaborane were added ca. every 2 days (total decaborane added, 7.11 g, 58.2 mmol) to a reaction mixture containing 0.24 mmol of $Cp_2Ti(CO)_2$ (0.41 mol %) and an excess of 1-octene (39.0 mL, 249 mmol) showed no decrease in the rate of formation of alkyl product over 12 days. Workup of this reaction at completion required only flash filtering the solution through a silica gel column and vacuum evaporization of the volatiles to give a 90.5% isolated yield (12.4 g, 52.7 mmol) of 6-octyldecaborane.

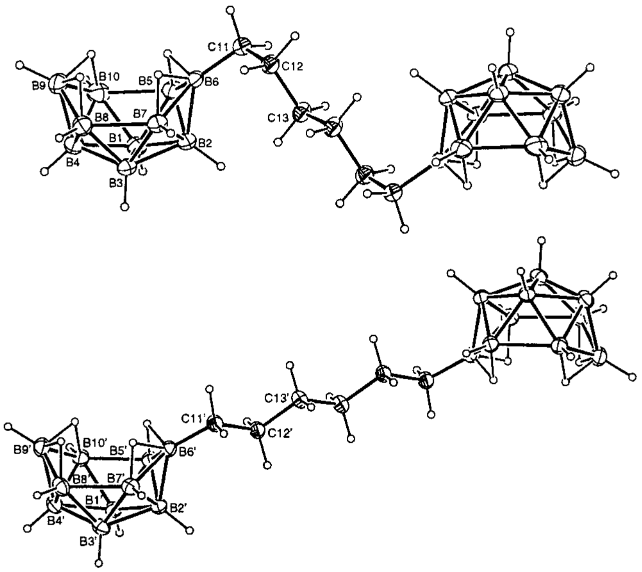

**Figure 1.** ORTEP representation of the structure of $6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2$. The two independent molecules in the unit cell are shown. Selected bond lengths (Å), top structure: B5−B6, 1.802 (4); B6−B7, 1.794 (4); B7−B8, 1.992 (4); B8−B9, 1.778 (5); B9−B10, 1.781 (5); B6−C11, 1.570 (3); C11−C12, 1.535 (3); C12−C13, 1.520 (3); C13−C13, 1.514 (5).

Perhaps of most interest, it was found that the titanium-catalyzed reactions of decaborane with nonconjugated diolefins, such as 1,5-hexadiene, give, depending upon reaction conditions and stoichiometries, high yields of either alkenyl-substituted (88%) or linked-cage products (92%).

$$B_{10}H_{14} + \text{xs } CH_2{=}CH(CH_2)_2CH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} 6\text{-}(CH_2{=}CH(CH_2)_4)B_{10}H_{13} \tag{3}$$

$$B_{10}H_{14} + CH_2{=}CH(CH_2)_2CH{=}CH_2 \xrightarrow{Cp_2Ti(CO)_2} 6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2 \tag{4}$$

A single-crystal X-ray study[5] of $6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2$ has confirmed the linked-cage structure shown in the ORTEP representation in Figure 1 in which the two decaborane cages are joined by the 6-carbon chain that is attached to the 6-boron vertex on each cage. As can be seen in Figure 1, the two independent molecules in the unit cell differ only in the conformation of the linking chain.

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(1) For previous papers in this series, see: Fazen, P. J.; Sneddon, L. G. *Organometallics* **1994**, *13*, 2867−2877 and references therein.

(2) For examples, see: (a) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696−1702. (b) Hartwig, J. F.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. *J. Am. Chem. Soc.* **1996**, *118*, 10936−10937. (c) Hartwig, J. F.; Waltz, K. M.; Muhoro, C. N.; He, X.; Eisenstein, O.; Bosque, R.; Maseras, F. In *Advances in Boron Chemistry*; Siebert, W., Ed.; Royal Society: London, 1997; pp 491−502. (d) Motry, D. H.; Brazil, A. G.; Smith, M. R., III *J. Am. Chem. Soc.* **1997**, *119*, 2743−2744. (e) Motry, D. H.; Smith, M. R., III *J. Am. Chem. Soc.* **1995**, *117*, 6615−6616. (f) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 4, 3127−3128. (g) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909−910. (h) Bijost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1995**, *95*, 121−128. (i) Erker, G.; Noe, R.; Wingbermuhle, D.; Petersen, J. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1213- 1214.

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

(4) (a) Gaines, D. F.; Bridges, A. N. *Organometallics* **1993**, *12*, 2015−2016. (b) Bridges, A. N.; Powell, D. R.; Dopke, J. A.; Desper, J. M.; Gaines, D. F. *Inorg. Chem.* **1998**, *37*, 503- 509.

(5) Crystal data: $C_6B_{20}H_{38}$; triclinic $P\bar{1}$; $a = 10.017$ (9) Å; $b = 14.2662$ (10) Å; $c = 8.14226$ (6) Å; $\alpha = 94.144$ (4)°; $\beta = 104.290$ (3)°; $\gamma = 82.144$ (6)°; $V = 1116.1$ (2) Å$^3$; $Z = 2$; $D_{cal} = 0.992$ g/cm$^3$; $T = -73$ °C; $R(Rw) = 0.078(0.159)$. X-ray intensity data were collected on a MSC/RAXIS IIc area detector employing graphite-monochromated Mo Kα radiation and the structure solved by direct methods (SIR92) and refined by standard procedures (teXsan package, Molecular Structures Corp.) as described in the Supporting Information.

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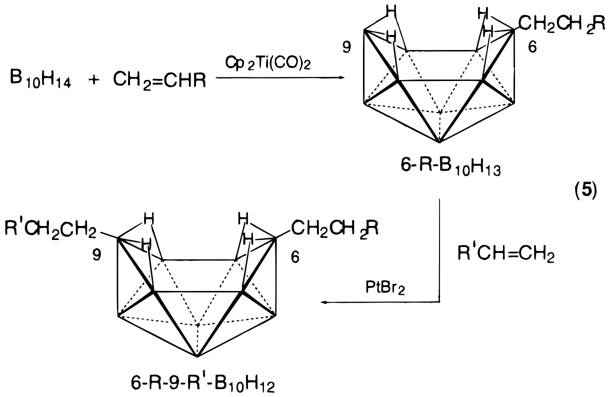
As illustrated by the reactions in eqs 3 and 4, the titanium-catalyzed reactions provide simple, efficient entries into two new important classes of polyborane clusters. The polymerization reactions of the olefin-substituted compounds, such as 6-($H_2C{=}CH(CH_2)_4$)$B_{10}H_{13}$, are now being investigated as a route to new types of decaborane−polyolefin polymers, while the linked-cage compounds, such as 6,6′-$(CH_2)_6(B_{10}H_{13})_2$, are being explored as the starting materials for the construction of new types of chelating polyborane ligands, including linked-cage carboranes and heteroatom boranes, that are needed for the construction of multicage metallaborane or metallacarborane arrays.

The titanium- and platinum-catalyzed reactions are complementary and now give systematic, high-yield, one-step routes to mono- and dialkyldecaboranes, respectively. As shown in eq 5, the sequential use of $Cp_2Ti(CO)_2$ and $PtBr_2$ catalysts provides the first general route to asymmetrical dialkyldecaboranes:



(5)

For example, the reaction of a sample of the 6-octyldecaborane, prepared with the titanium-catalyzed reaction described above, with excess allylbenzene and 3.5 mol % platinum dibromide for 4 h gave a 97% isolated yield of 6-($C_8H_{17}$)-9-($PhC_3H_6$)$B_{10}H_{12}$ product.

The mechanism of catalytic action, as well as why only monosubstituted products are obtained in the titanium-catalyzed reaction, while dialkyl products predominate in the platinum reactions, is yet to be determined. Hartwig's earlier studies of the titanium-catalyzed reactions of catecholborane showed that the formation of $Cp_2Ti{-}HBcat$ acid−base $\sigma$ adducts, where there is electron donation from the titanium fragment to the boron-centered LUMO orbital on the catecholborane borane, might be important.[2b,c] Similar types of $Cp_2Ti{-}B_{10}H_{14}$ adducts involving electron donation to the acidic 6-boron atom of decaborane may also be important in the decaborane−olefin reactions, and, indeed, the fact that monoalkyldecaboranes have reduced Lewis acidities compared to the parent $B_{10}H_{14}$[6] could explain why they are not converted to the dialkyl products in the titanium reactions. Further studies of both the mechanism and applications of titanium-catalyzed polyborane reactions are in progress.

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**Supporting Information Available:** Synthetic procedures and spectroscopic, analytical and crystallographic characterization data (18 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(6) For example, unlike the parent $B_{10}H_{14}$, the monoalkyldecaboranes do not form adducts with bases, such as diethyl sulfide or acetonitrile.