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Communications

Efficient Olefin Diboration by a Base-Free Platinum Catalyst

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Summary: $Pt(NBE)_3$ and $Pt(COD)_2$ (NBE = norbornene, COD = 1,5−cyclooctadiene) catalyze the addition of 2,2′-bis(1,3,2-benzodioxaborole) (CatB−BCat) to α-olefins. The reactions proceed smoothly under ambient conditions to give 1,2-diborylalkanes in high yield, and the catalyst is compatible with common functional groups.

Catalytic transfer of B−X bonds to unsaturated substrates has attracted considerable attention. Largely due to the synthetic versatility of the hydroboration reaction, most of these efforts have centered on metal-mediated additions of B−H bonds to olefins and alkynes.[1] Though less common when compared to hydroboration reactions, transition metal catalysts can effect additions of B−E bonds to unsaturated substrates.[2−5] Most of the reports in this regard involve B−E (E = B, Si, Sn) additions to C≡C bonds. For example, Miyaura and Suzuki reported that $Pt(PPh_3)_4$ catalyzes the *cis*-addition of B−B bonds to alkynes.[2] While clean chemistry is observed for alkynes, analogous additions to olefins are not realized in this system.[6] To date, B−B bond additions to olefins have met with limited success. In a recent report, Baker et al. found that Au−phosphine complexes catalyze olefin diboration by CatB−BCat.[7] Although these additions require prolonged reaction times at elevated temperatures, the complex distributions of borylated products observed in more active Rh systems are avoided. This communication describes the Pt-catalyzed addition of B−B bonds to olefins under mild conditions.

In recent work involving the reactivity of organoplatinum complexes with B−B bonds, we examined the details of the Pt-catalyzed addition of B−B bonds to alkynes mediated by *cis*-$(PPh_3)_2Pt(BCat)_2$.[8,9] Our findings were consistent with a phosphine dissociative mechanism where low-coordinate diboryl complexes mediate alkyne coordination and insertion steps. It seemed possible that catalytic activity could be enhanced to the extent that olefin diboration would be observed if the requirement for phosphine dissociation could be eliminated. The most obvious candidates for

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

[1] For a review, see: Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179−1191.

[2] Ishiyama, T.; Matsuda, N.; Miyaura, N.; Suzuki, A. *J. Am. Chem. Soc.* **1993**, *115*, 11018−11019.

[3] Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713−720.

[4] For catalytic additions of B−Sn bonds to alkynes, see: Onozawa, S.; Hatanaka, Y.; Sakakura, T.; Shimada, S.; Tanaka, M. *Organometallics* **1996**, *15*, 5450−5452.

[5] For catalytic additions of B−Si to alkynes, see: Suginome, M.; Nakamura, H.; Ito, Y. *J. Chem. Soc., Chem. Commun.* **1996**, 2777−2778.

[6] Pt(0)−catalyzed additions of B−B bonds to alka-1,3-dienes has been recently reported, see: Ishiyama, T.; Yamamoto, M.; Miyaura, N. *J. Chem. Soc., Chem. Commun.* **1996**, 2073−2074.

[7] Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336−1337.

[8] Iverson, C. N.; Smith, M. R., III. *Organometallics* **1996**, *15*, 5155−5165.

[9] Marder and co-workers have drawn similar conclusions regarding the mechanism of alkyne diboration, see: Lesley, G.; Nguyen, P.; Taylor, N. J.; Marder, T. B.; Scott, A. J.; Clegg, W.; Norman, N. C. *Organometallics* **1996**, *15*, 5127−5154.

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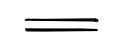
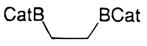
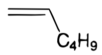
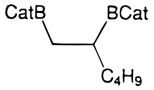
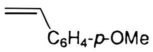
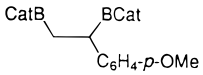
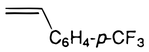
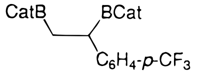
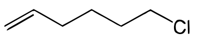
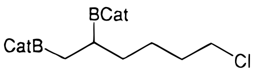
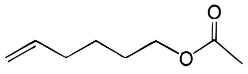
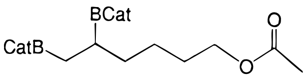
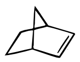
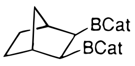
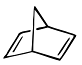
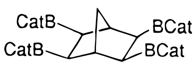
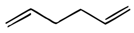
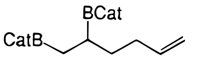
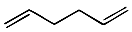
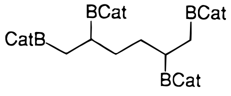
Table 1. Products and Yields for Diborations of Selected Olefins[a]

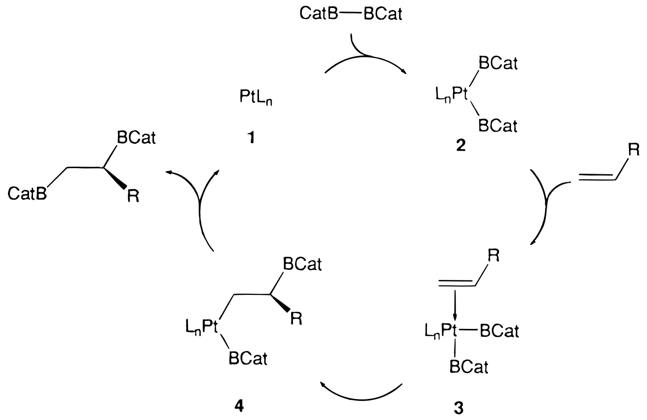
Entry	olefin	product	% yield[b]
1			84
2			95
3			90
4			95
5			85
6			88
7[d]			93
8[d]			89
9			82
10[c]			87

[a] [CatB−BCat]:[olefin] = 1:1, except for entries 8 and 10 where [CatB−BCat]:[olefin] = 2:1. Unless otherwise indicated, the catalyst used is Pt(COD)$_2$. [b] Yields reported are based on the crude material obtained by solvent evaporation. [c] The tetraborylated product is presumably a mixture of diastereomers. [d] Pt(NBE)$_3$ was used as the catalyst.

testing this hypothesis are the base-free Pt compounds reported by Stone and co-workers.[10]

In our initial report, we found that Pt(NBE)$_3$ (**1**) reacts readily with 2,2′-bis(1,3,2-benzodioxaborole) (CatB−BCat) to generate *cis,exo*-bis(catecholboryl)norbornane and unidentified Pt species.[11] When **1** or Pt(COD)$_2$ (**2**) is used as the catalyst precursor, diboration chemistry is observed for the substrates in Table 1.[12] Reactions are typically complete after 10 min under ambient conditions. Upon introduction of the diboron reagent, the solution turns deep red and appears to remain homogeneous. Addition of mercury to the reaction mixture had no effect on the catalytic activity; however, we have not been able to identify the catalytically active species. Conversion is clean, as judged by NMR (^{1}H, ^{11}B), product yields are high, and B$_2$Cat$_3$, the decomposition product that is often observed when catecholate-substituted borane reagents are employed, does not form in significant quantities.[13−15]

Scheme 1



If the mechanism for diboration is similar to that observed in the Pt-catalyzed addition of CatB−BCat to alkynes, alkene borylation proceeds via insertion into a Pt−B bond of Pt−diboryl species and the diborylated alkane is released by B−C reductive elimination from the boryl−alkyl intermediate, as depicted in Scheme 1. It is assumed that α-olefin insertion into the Pt−B bond gives a primary alkyl intermediate as related insertions into metal−carbon and metal−hydrogen bonds usually give primary metal−alkyl complexes.

For α-olefins, 1,2-diboration products are observed exclusively. The diboration reaction tolerates various functional groups as long as the functionality does not reside at allylic positions. For internal olefins, clean diboration is observed for norbornene and norbornadiene. For these substrates, only one stereoisomer is formed as the B−B bond adds preferentially to the *exo* olefin face. Clean reactivity is not observed for other internal olefins. For example, the reaction between CatB−BCat and *trans*-3-hexene gave a complex mixture of products. ^{11}B NMR spectra indicated significant quantities of HBCat and B$_2$Cat$_3$, in addition to a broad resonance in the region typical for alkylborane products. Similar complications were observed when diborations of other internal olefins were attempted.

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(10) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271−277.

(11) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 4403−4404.

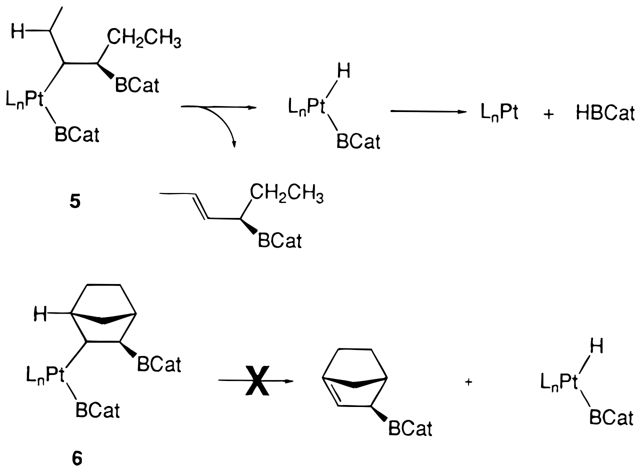
(12) The diboration products were characterized by ^{1}H, ^{11}B, ^{13}C NMR and mass spectrometry. See the Supporting Information for details.

(13) Typical conditions for catalytic reactions involving a gaseous olefin are given for diboration of ethylene: CatB−BCat (224 mg, 0.94 mmol) and 3 mol % of Pt(COD)$_2$ were weighed into an air-free flask and dissolved in 3 mL of toluene. The mixture was frozen and placed under vacuum, and ethylene (1 atm) was introduced. The mixture was warmed to room temperature and allowed to stir for several hours. The solvent was removed in vacuo, and the crude product was collected. Typical conditions for catalytic reactions involving a solid or liquid olefin are given for diboration of 4-vinylanisole: CatB−BCat (262 mg, 1.10 mmol) and 3 mol % of Pt(COD)$_2$ were weighed into a Schlenk flask. 4-Vinylanisole (148 mg, 1.10 mmol), dissolved in 3 mL of toluene, was then added to the solids in the flask. After the reaction mixture was stirred for 30 min at room temperature, the solvent was removed in vacuo and the crude product collected.

(14) While Pt(NBE)$_3$ or Pt(COD)$_2$ can be used to catalyze these additions, Pt(COD)$_2$ gave cleaner products, except in diborations of norbornene and norbornadiene.

(15) Diboration can be catalyzed in related Pt systems, see: Miyaura, N. Hokkaido University, personal communication, 1997.

Scheme 2



The generation of HBCat in attempted diborations of internal olefins most likely arises from β-H elimination pathways that compete with the reductive elimination of the diborylated alkane from intermediate **5** (Scheme 2). Subsequent addition of CatB−BCat to the vinylborane that results from β−H elimination would account for the complex mixture of borylated products. Apparently, β−H elimination pathways are not problematic in the diboration of α-olefins. The reasons behind the discrepancy between terminal and internal olefins are not obvious at this juncture. Perhaps β−H elimination is disfavored for hydrogens attached to a boron-substituted β-carbon center. If this is the case, the clean reactivity of norbornene and norbornadiene can be readily explained since β-hydrogen elimination from the bridgehead position in intermediate **6** would be disfavored as it requires formation of a highly strained olefin.

Compound **1** also catalyzes the addition of CatB−BCat to α,ω-dienes. For 1,5-hexadiene, equimolar quantities of diene and CatB−BCat give the B_2 product exclusively (entry 9). This result is moderately surprising since the diborylated olefin could compete with 1,5-hexadiene as the reaction proceeds giving rise to B_4 products. If olefin exchange at the platinum center is rapid relative to the insertion steps, the observed selectivity could be attributed to preferential olefin binding by 1,5-hexadiene, which can form chelate intermediates. Reactivity of conjugated dienes is less clean as 1,3-butadiene gave a mixture of products that included $CatBCH_2CH{=}CHCH_2BCat$.[6]

In summary, base-free platinum complexes serve as highly efficient catalysts for diboration of alkenes. Since these compounds are conveniently prepared in high yield, their chemistry can be conveniently explored. Given the synthetic utility of B−C bonds, these compounds may be useful synthons in coupling reactions[16] and related conversions to other functional groups.[17]

Note Added in Proof: A related report of Pt-catalyzed additions of B−B bonds to olefins has recently appeared: Ishiyama, T.; Yamamoto, M.; Miyaura, N. *J. Chem. Soc., Chem. Commun.* **1997**, 689−690.

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Supporting Information Available: Text giving the synthetic details, as well as spectroscopic and analytical data and NMR spectra, for the compounds in this paper (26 pages). Ordering information is given on any current masthead page.

OM970199X

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(16) An excellent review of Pd-catalyzed cross-couplings of boronic acids has recently appeared, see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(17) The crude diboryl product in entry 2 can be converted to 1,2-hexanediol (46% yield based on starting olefin) when subjected to a basic oxidative workup.