

Significance of Borane Tuning in Titanium-Catalyzed Borylation Chemistry[†]

Douglas H. Motry, Aimee G. Brazil, and Milton R. Smith, III*

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

Received April 4, 1996

The potential for transition metal promoted boron–carbon bond formation is reflected by recent design of catalysts that accelerate hydroboration reactions¹ and mediate transformations that are prohibitively disfavored on kinetic grounds.^{2,3} Although considerable effort has been focused on late metal systems,⁴ we⁵ and others⁶ have been interested in borylation chemistry effected by lanthanide and early transition element complexes. In this vein, we recently reported that Cp*₂Ti(η²-CH₂=CH₂) (**1**)⁷ and catecholborane (HBCat) afford the vinylboronate ester complex, Cp*₂Ti(η²-CH₂=C(H)BCat) (**2**).⁵ A mechanism was proposed where C–B bond formation proceeds by ring-opening σ-bond metathesis, and β-hydrogen elimination accounts for retention of the C=C bond.^{8–10} A catalytic circuit could be closed by a series of stoichiometric reactions; however, at-

[†] A portion of this work was presented at the 210th ACS National Meeting, Chicago, 1995, INOR 091.

(1) For a review of transition-metal catalyzed hydroboration, see: Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991**, *91*, 1179–1191.

(2) For catalytic diborylation of olefins, see: Baker, R. T.; Nguyen, P.; Marder, T. B.; Westcott, S. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1336–1337.

(3) For catalytic addition of B–B bonds to alkynes, see: Ishiyama, T.; Matsuda, N.; Murata, M.; Ozawa, F.; Suzuki, A.; Miyaura, N. *Organometallics* **1996**, *15*, 713–720.

(4) (a) Hewes, J. D.; Kreimendahl, C. W.; Marder, T. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1984**, *106*, 5757–5759. (b) Manning, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878–879. (c) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1989**, *111*, 592–597. (d) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 6917–6918. (e) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1988**, *53*, 5178–5179. (f) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426–3428. (g) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671–6679. (h) Evans, D. A.; Fu, G. C.; Anderson, B. A. *J. Am. Chem. Soc.* **1992**, *114*, 6679–6685. (i) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863–8869. (j) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350–9359. (k) Westcott, S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975–979. (l) Brown, J. M.; Hulmes, D. I.; Layzell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673–1674. (m) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866–878.

(5) Motry, D. H.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995**, *117*, 6615–6616.

(6) (a) Harrison, K. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220–9221. (b) Erker, G.; Noe, R.; Wingbermhle, D.; Petersen, J. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1213–1215. (c) Burgess, K.; Jaspars, M. *Tetrahedron Lett.* **1993**, *34*, 6813–6826. (d) Evans, D. A.; Muci, A. R. *J. Org. Chem.* **1993**, *58*, 5307–5309. (e) Burgess, K.; van der Donk, W. A. *Organometallics* **1994**, *13*, 3616–3620. (f) Burgess, K.; van der Donk, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 6561–6569. (g) Bijpost, E. A.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal., A: Chem.* **1995**, *95*, 121–128. (h) Pereira, S.; Srebnik, M. *Organometallics* **1995**, *14*, 3127–3128. (i) Pereira, S.; Srebnik, M. *J. Am. Chem. Soc.* **1996**, *118*, 909–910. (j) He, X.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 1696–1702. (k) Sun, Y.; Piers, W. E.; Rettig, S. J. *Organometallics* **1996**, *15*, 4110–4112.

(7) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136–1143.

(8) A similar mechanism was proposed by Erker to account for reactivity between zirconocene and hafnocene butadiene complexes and 9-BBN.^{6b} More recent reports invoke similar mechanisms for reactions of boranes with olefin complexes.^{6i,k}

(9) Rhodium systems mediate related dehydrogenative borylation for aryl substituted olefins, and reasonable yields of vinylboranes have been produced when oxazaborolidine derivatives from ephedrine are used as the borane source.^{4m} However, dehydrogenative borylations for unactivated olefins are rare^{4k,6b,10} and mixtures of vinylboranes and normal hydroboration products are usually observed in these cases.

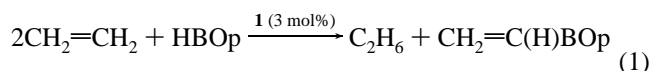
(10) Davan, T.; Corcoran, E. W.; Sneddon, L. G. *Organometallics* **1983**, *2*, 1693–1694.

tempted catalytic synthesis of CH₂=C(H)BCat from ethylene and HBCat gave CH₃CH₂BCat instead of CH₂=C(H)BCat. Hence, the selectivity for the stoichiometric reaction is lost under catalytic conditions. This paper reports the effects of a simple modification in the borane reagent that proves to be critical for catalytic control in this system.

In the reaction between ethylene and HBCat, catalyzed by **1**, a complex mixture of Ti species results from indiscriminate attack of HBCat. Reaction of the catecholate oxygen atoms in HBCat with the Lewis acidic Ti center could account for catalyst decomposition in this system.¹¹ Alternatively, subsequent borylations of compound **2** could generate other active species that account for the normal hydroboration product, CH₃CH₂BCat. Clearly, catalyst integrity must be maintained if the stoichiometric selectivities are to be preserved, and rates for catalyst degradation must be significantly slower than that for regeneration of the ethylene compound, **1**. The desired balance can be achieved by suppressing side reactions between the borane reagent and Ti species and/or by accelerating the displacement of the vinylborane by ethylene.

We chose to examine the reactivity of benzo-1,3,2-diazaborolane (HBOP),¹² the borane derived from BH₃ and *o*-phenylenediamine, for the following reasons. First, there is literature precedence for B–N linkages being more robust than B–O frameworks in isoelectronic compounds.¹³ Hence, HBOP should be less susceptible to metal-mediated disproportionation. Second, borylation of the coordinated vinylborane ligand could be suppressed to the extent that regeneration of the catalyst **1** competes in the catalytic cycle.^{14–18} Last, solutions to catalyst degradation could prove useful for harnessing reactivity of other Cp*₂Ti derivatives.

Solutions of **1** catalyze the reaction between ethylene and HBOP, and CH₂=C(H)BOP can be isolated in reasonable yield (58% isolated yield based on HBOP) at low catalyst loading (eq 1).



When the reaction is monitored by NMR, spectra indicate clean conversion of ethylene and HBOP to CH₂=C(H)BOP and ethane. Under these conditions, **1** is the major Ti-containing compound in solution, and the vinylboronate amide complex, Cp*₂Ti(η²-CH₂=C(H)BOP) (**3**), is not observed. The equilibrium between **1** and ethylene generates small quantities of the

(11) In early metal systems, Burgess and co-workers have observed rapid redistribution for the catecholate ligands of HBCat. They suggest that interactions between the catecholate oxygen and the acidic metal center are responsible for the exchange.^{6c,e} Similar promiscuity for catecholate ligands in HBCat has also been suggested as a mechanistic possibility in lanthanide-catalyzed hydroborations.^{6d}

(12) (a) Morales, H. R.; Tlahuex, H.; Santiesteban, F.; Contreras, R. *Spectrochim. Acta* **1984**, *40A*, 855–862. (b) Camacho, C.; Paz-Sandoval, M. A.; Contreras, R. *Polyhedron* **1986**, *5*, 1723–1732.

(13) Compared to borazine, boroxine (H₃BO₃) is kinetically unstable and readily disproportionates to B₂O₃ and B₂H₆ at room temperature: Porter, R. J.; Gupta, S. K. *J. Phys. Chem.* **1964**, *68*, 280–289.

(14) Pelter, A.; Smart, K.; Brown, H. C. *Borane Reagents*; Academic Press: London, 1988.

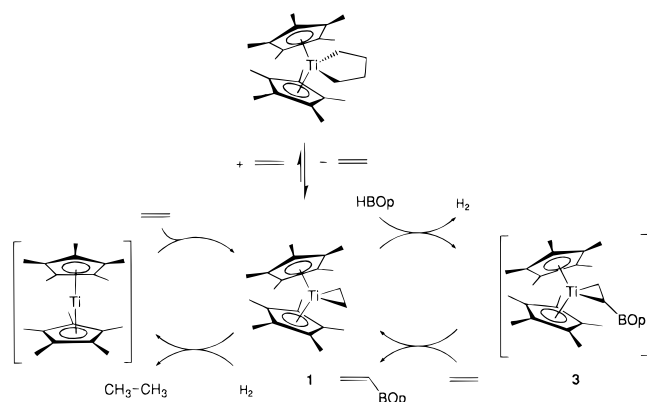
(15) For substituted boranes, ab initio calculations predict the follow ordering of activation energies for hydroboration of ethylene: BH₃ < BH₂-CH₃ < BHFC₃. This agrees with experimentally observed trends: Wang, X.; Li, Y.; Wu, Y.-D.; Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Org. Chem.* **1990**, *55*, 2601–2609.

(16) The decrease in rate for hydroboration relative to dialkylboranes has been attributed to O–B π-donation. The exceedingly slow rate for uncatalyzed hydroboration by HBOP¹⁷ is consistent with this notion: Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1983**, *48*, 5080–5082.

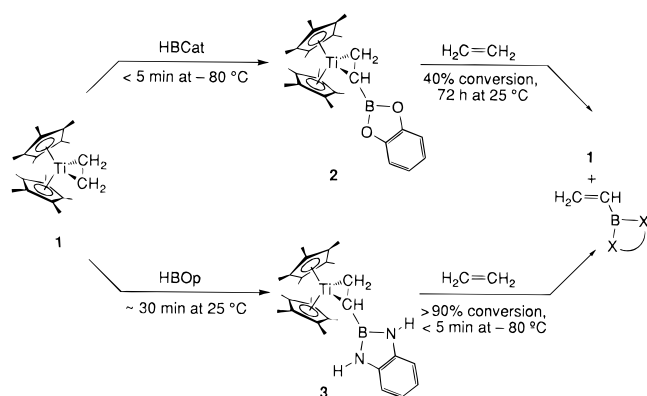
(17) In uncatalyzed reactions, no hydroboration products are evident after heating HBOP with 1-hexene for 1 week at 110 °C.

(18) If borylation of the vinylborane complex triggers catalyst decomposition, a nitrogen-substituted borane should better preserve catalyst integrity, assuming that heteroatom substitution at boron has similar effects on borylation and hydroboration rates.

Scheme 1



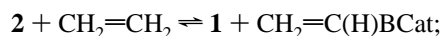
Scheme 2



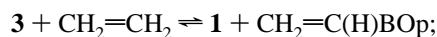
metallacyclopentane complex, $\text{Cp}^*_2\text{Ti}(\text{CH}_2)_4$; however, there is no evidence for participation of this species in borylation processes since C4 borylation products are not observed. The catalytic cycle for this dehydrogenative borylation is depicted in Scheme 1.

The catalytic process in Scheme 1 was dissected to assess the effects of borane modification on the discrete steps that comprise the catalytic pathway. As was observed for HBCat, the stoichiometric reaction between HBOp and **1** gives ethane and **3**, the nitrogen analog of compound **2**. However, borylation of **1** by HBOp proceeds at a substantially diminished rate relative to HBCat, as shown in Scheme 2. Hence, boron substituent effects on rates for borylation of the coordinated ethylene ligand in **1** parallel those observed for olefin hydroboration reactions. Significantly, selectivity for ethylene borylation is maintained, since diborylation products resulting from borane attack on **3** are not detected.

The kinetics and thermodynamics governing the displacement of the coordinated vinylborane ligands in compounds **2** and **3** differ markedly. For compound **2**, vinylborane displacement is slow, and an approximately thermoneutral equilibrium is reached after 72 h at ambient temperature. In contrast, vinylborane displacement from compound **3** is rapid, and the equilibrium strongly favors the ethylene complex (**1**) and $\text{CH}_2=\text{C}(\text{H})\text{BOP}$. Competitive binding experiments afforded the relative energies shown in eqs 2 and 3.¹⁹ Activation parameters for the displacement reaction could not be extracted because the reaction rates for **3** and ethylene ($-80\text{ }^\circ\text{C}$) were too fast for reliable analysis. The effects of borane modification on



$$\Delta G^\circ_{\text{rxn}} = 0.09(1) \text{ kcal/mol} \quad (2)$$



$$\Delta G^\circ_{\text{rxn}} < -4.5 \text{ kcal/mol} \quad (3)$$

reactivity were consistent with observations from the catalytic reaction as the kinetic and thermodynamic parameters governing the reactivity of **3** preclude its detection when excess ethylene is present. Although the differences in reactivity between O- and N-substituted vinylborane complexes are pronounced, the factors responsible for this disparity are not obvious.²⁰

The enhanced rate for displacement of the coordinated vinylborane ligand and the suppression of borane-promoted catalyst degradation both favor catalytic viability when HBOp is used as the borane reagent. The influence of the borane substituent on rates for vinylborane displacement was unexpected. The observed rate acceleration may be significant for dehydrogenative pathways, but the catalyst compatibility engendered by HBOp has more general applications in other titanocene systems. While Hartwig and co-workers recently reported that Cp_2TiMe_2 can serve as a precatalyst for addition of HBCat to olefins,^{6j,21} preliminary results suggest that the utility of HBCat, and other oxygen-substituted borane reagents, may be limited to the parent titanocene system.²² For titanocene derivatives with alkyl-substituted cyclopentadienyl rings, we observe rapid catalyst decomposition when hydroborations are attempted with HBCat. Although the parent titanocene system failed to catalyze additions of HBOp to olefins,²³ catalytic olefin hydroboration by HBOp proceeds smoothly for other $\text{Cp}'_2\text{Ti}$ derivatives and Ti^{III} species are not observed. The results from these investigations will be published in due course.

Acknowledgment. The NMR equipment was provided by the National Science Foundation (CHE-8800770) and the National Institutes of Health (1-S10-RR04750-01). We thank the administrators of the ACS Petroleum Research Fund, the Center for Fundamental Materials Research at Michigan State University, the Exxon Educational Foundation, the NSF REU program (A.G.B.), and the National Science Foundation (CHE-9520176) for support of this work.

Supporting Information Available: Synthetic details, as well as spectroscopic and analytical data, for the compounds in this paper (3 pages). See any current masthead page for ordering and Internet access instructions.

JA961111U

(19) The greatest error in this measurement is integration of the ethylene resonance which approaches the threshold for detection by NMR. A lower limit for the equilibrium constant was estimated by assuming that the ethylene resonance could have an integrated intensity as large as 2% of that of the most intense resonance.

(20) Given that the Cp^*_2Ti fragment generally will not accommodate substituted olefins,⁷ it can be argued that the stability of the borylated olefin complexes likely results from overriding electronic effects. The differences in reactivity between **3** and **2** could result from ground state destabilization of **3** relative to **2** or stabilization of $\text{CH}_2=\text{C}(\text{H})\text{BOp}$ relative to $\text{CH}_2=\text{C}(\text{H})\text{BCat}$. Although a lower activation energy for displacement of $\text{CH}_2=\text{C}(\text{H})\text{BOp}$ from **3** would be consistent with significant ground-state destabilization for **3**, this observation is not sufficient proof.

(21) Catalysis in this system is efficient; however, the catalytic activity for the Ti^{III} compound, $\text{Cp}_2\text{TiBCat}_2$, that forms during the course of the reaction is diminished relative to $\text{Ti}^{\text{IV}}/\text{Ti}^{\text{II}}$ species.

(22) Stoudt, S. J.; Motry, D. H.; Brazil, A. G.; Smith, M. R., III. Manuscripts in preparation.

(23) Compared to the thermal decomposition rate for Cp_2TiMe_2 , the $\text{B}-\text{H}/\text{Ti}-\text{Me}$ metathesis that initiates catalysis for HBCat^{6j} is prohibitively slow for HBOp.