Facile, Metal-Mediated Dehydrogenative Borylation of Ethylene: Selective Conversion of a Titanium-Bound Olefin to a Vinylboronate Ester[†]

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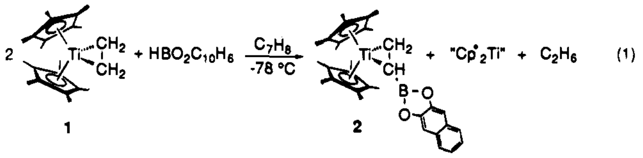
In metal-mediated hydroboration chemistry, metal complexes can play important roles in rate acceleration of the hydroboration reaction, stereoselective addition of boranes to prochiral olefins, and formation of products which are generally not accessible in the realm of traditional hydroboration chemistry.[1-4] Key steps that are common to most catalytic systems can be summarized by borane oxidative addition to an electronically unsaturated metal center, insertion of an olefin to yield an alkyl intermediate, and formation of the alkylborane product by reductive elimination of the alkyl and boryl ligands.[5] We have been exploring reactivity of transition metal olefin complexes with borane reagents with two main objectives in mind. First, olefin complexes can behave as latent sources of electron-rich, low-valent metal centers that can potentially serve as convenient precursors for synthesizing metal boryl complexes.[6-8] Second, reactions of simple metal olefin complexes with hydroboranes have been largely overlooked, and it seemed that with judicious choice of the metal system, chemistry that is mechanistically distinct from more common metal-mediated hydroboration chemistry might be observed. Our first results that bear on this latter point form the basis for this Communication.

$Cp^*{}_2Ti(\eta^2\text{-}CH_2{=}CH_2)$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_5$) is a 16-electron olefin complex with a rich reaction chemistry.[9,10] The metal–olefin linkage exhibits reactivity consistent with formulation as a Ti^{IV} metallacyclopropane species (*viz.*, **1** + 2HCl → C_2H_6 + $Cp^*{}_2TiCl_2$) or a π-complex of Ti^{II} (oxidative atom transfer reagents react to form Ti^{IV} complexes with liberation of ethylene).[11] Based on these precedents, we envisioned two potential modes of reactivity for **1** with hydroboranes: formation of ring-opened products, such as $Cp^*{}_2Ti(H)(CH_2CH_2BR_2)$, or oxidative addition to yield a boryl hydride species that would likely undergo insertion chemistry with the liberated olefin. In light of these expectations, the chemistry we observed was surprising.

Toluene solutions of $Cp^*{}_2Ti(\eta^2\text{-}CH_2{=}CH_2)$ reacted immediately with catecholborane at −78 °C, accompanied by a color change of the lime green solution to amber. Following solvent removal at room temperature, the ^1H NMR spectrum of the crude reaction mixture indicated clean formation of a diamagnetic product with inequivalent Cp* environments, three high-field vinyl multiplets (characteristic for an unsymmetrical olefin coordinated to a decamethylmetallocene fragment),[12] and two aryl multiplets due to one catecholate group. ^{11}B NMR revealed a single boron resonance at 36 ppm which, in conjunction with the ^1H NMR data, convincingly suggested that the diamagnetic product was best formulated as $Cp^*{}_2Ti(\eta^2\text{-}CH_2{=}C(H)(BO_2C_6H_4))$. Significantly, borylation of an unactivated olefin has proceeded without bond reduction, and the overall transformation is consistent with a B—H/C—H metathesis accompanied by B—C bond formation and formal loss of dihydrogen.[13-16] $Cp^*{}_2Ti(\eta^2\text{-}CH_2{=}C(H)(BO_2C_{10}H_6))$ (**2**), the analogous product, prepared from **1** and the borane derived from 2,3-dihydroxynaphthalene and BH$_3$·thf ($HBO_2C_{10}H_6$, **3**), was isolated as a lemon yellow microcrystalline powder in 44% yield.[17]



Attempts to follow the reaction of **1** and **3** by ^1H NMR (toluene-d_8, −80 °C) indicated rapid formation of **2** with concomitant production of ethane, attributed to hydrogenation of the starting material, **1**. The balanced reaction in eq 1 is consistent with our observations that **2** is best prepared by reacting **1** and **3** in a 2:1 ratio, maximum yields of **2** never exceed 50%, and pentane-soluble, paramagnetic $Cp^*{}_2Ti$[18] is generated in the course of the reaction. This latter point was confirmed by performing the reaction in eq 1 in the presence of ethylene (0.5 mol equiv). In this case, ethylene traps $Cp^*{}_2Ti$ to produce **1** and **2** in a 3:2 ratio.

A mechanism that accounts for the formation of **2**, $Cp^*{}_2Ti$, and ethane is outlined in Scheme 1. The reaction is initiated by borane-induced ring opening of the metallacyclopropane to generate $Cp^*{}_2Ti(H)(CH_2CH_2BO_2C_{10}H_6)$ (**4**),[19,20] which under-

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[†] A portion of this work was presented at the 207th ACS National Meeting in San Diego, CA, Spring 1994 (Abstract INOR 038).

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

(2) Evans, D. A.; Fu, G. C.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1992**, *114*, 6671.

(3) 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.

(4) Harrison, K. M.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220.

(5) Lanthanide-based systems operate in analogous fashion, where oxidative addition/reductive elimination steps are replaced by appropriate σ-bond metatheses.[4]

(6) This approach has recently proven effective for preparing iridium trisboryl complexes, where various hydrogenated and boronated organic products account for the fate of the olefinic ligand: Nguyen, P.; Blom, H. P.; Westcott, S. A.; Taylor, N. J.; Marder, T. B. *J. Am. Chem. Soc.* **1993**, *115*, 9329–30.

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

(8) Lantero, D. R.; Smith, M. R., III, manuscript in preparation.

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

(10) Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006.

(11) Smith, M. R., III.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 7049.

(12) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

(13) Zirconocene and hafnocene butadiene complexes react thermally with 9-borabicyclo[3.3.1]nonane (9-BBN) to yield allylborane complexes which can be converted to a vinylborane complex by sequential heating and photolysis: Erker, G.; Noe, R.; Wingbermuhle, D.; Petersen, J. L. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1213.

(14) Palladium-catalyzed, pentaborane(9)-olefin coupling reactions, where alkane products are observed as byproducts, have been reported; however, the mechanistic details of these transformations are not known: Davan, T.; Corcoran, E. W.; Sneddon, L. G. *Organometallics* **1983**, 2, 1693.

(15) Westcott, S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975–9.

(16) In this paper, catalytic conversion of vinylarenes to vinylboronate esters and vinylalkanes is described. The operative mechanism in this (and related systems) likely involves B—H oxidative addition, followed by olefin insertion/β-H elimination sequences. This conversion is sensitive to the nature of the borane reagent and limited to arene-substituted olefins for reasons outlined in ref 15: Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866.

(17) While reacting **1** and **3** in a 2:1 ratio cleanly generates **2**, we see a moderate increase in yield (5%) for **1**:**3** ≈ 1:1. Spectral data for **2**: ^1H NMR (C_6D_6) δ 7.52 (m, 2H, $O_2C_{10}\mathit{H}_6$), 7.33 (s, 2H, $O_2C_{10}\mathit{H}_6$), 7.18 (m, 2H, $O_2C_{10}\mathit{H}_6$), 3.58 (dd, 1H, $H_2C{=}C\mathit{H}B$), 2.89 (dd, 1H, $\mathit{H}_2C{=}CHB$), 2.64 (dd, 1H, $\mathit{H}_2C{=}CHB$), 1.73 (s, 15H, $C_5(C\mathit{H}_3)_5$), 1.72 (s, 15H, $C_5(C\mathit{H}_3)_5$); ^{11}B NMR(C_6D_6) δ 36; ^{13}C NMR(C_6D_6) δ 108.86 (t, $^1J_{CH}$ = 146 Hz, $H_2\mathit{C}{=}CHB$), 88.12 (br, $H_2C{=}\mathit{C}HB$); MS *m/e* 318 (47, $Cp^*{}_2Ti$), 196 (100, $H_2C{=}C(H)(BO_2C_{10}H_6)$).

(18) When the reaction of $Cp^*{}_2Ti(CH_2{=}CH_2)$ with $HBO_2C_6H_4$ is performed under a nitrogen atmosphere, the solution immediately turns intensely blue, which is the characteristic color of the dinitrogen complexes $(Cp^*{}_2Ti)_2(N_2)_x$.[16] The amber color of the solution is restored on evacuation of the flask and readmission of argon.

(19) Ring-opening of a titanium metallacyclopropene by $(Et_2BH)_2$ has been recently reported: Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J.; Goddard, R.; Erker, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 197.

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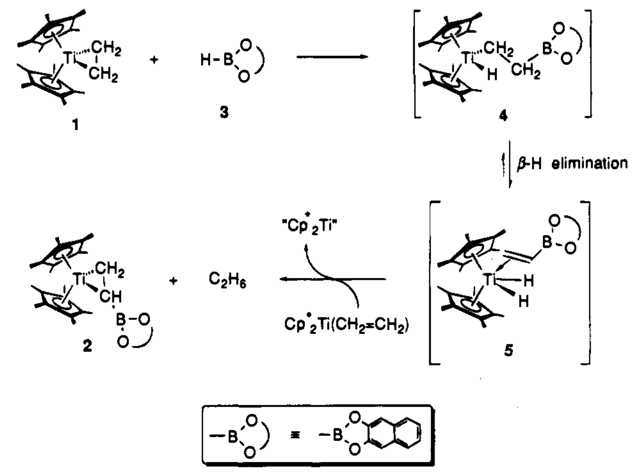
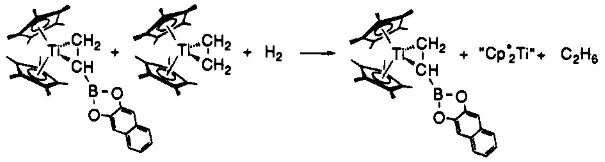
Scheme 1



goes β-H elimination to intermediate **5**.[21,22] Reaction of H_2 (lost from **5**) with the starting olefin complex accounts for ethane generation and formation of Cp*$_2$Ti. Based on the mass balance in eq 1, this mechanism requires selective hydrogenation of the ethylene complex in the presence of the substituted olefin product. It was not obvious that this should be the case; however, the ability to independently prepare the two compounds and expose them to hydrogen offered a direct test of this supposition. In fact, when a 1:1 mixture of **1** and **2** is exposed to H_2 (0.5 mol equiv), only the ethylene complex is hydrogenated (eq 2).

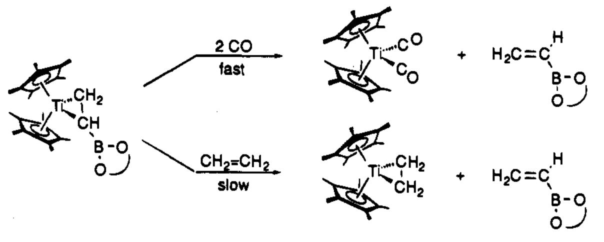


(2)

Since we were unable to observe intermediates by ^{1}H NMR, and any attempts to gain insight as to the mechanism of the transformation in eq 1 using kinetic measurements were thwarted by rapid reaction rates, we chose to address the fate of the borane hydride by isotopic labeling. In the mechanism outlined in Scheme 1, reversible β-H elimination from **4** could scramble deuterium into the β-position of the vinylborane ligand in **3**. Furthermore, the documented exchange between the hydride positions and methyl sites of the pentamethylcyclopentadienyl ligand in these systems[23] raises the possibility of deuterium scrambling into the ligand's methyl groups. Thus, the results from this experiment are potentially complicated since the *only* sites where deuterium incorporation is unlikely are the vinylic protons on the unsubstituted carbon of the vinylboronate ester fragment.

1 reacted cleanly with $DBO_2C_{10}H_6$ to generate **2** and ethane at −80 °C, with the majority (85%) of deuterium label appearing in the evolved ethane. The remaining label (15%) was incorporated at the boron-substituted, vinylic position of the coordinated vinylborane.[24] These results are consistent with the mechanism proposed in Scheme 1, where HD loss from **5** is substantially faster than scrambling between hydride and ligand methyl sites.[25]

Scheme 2



Formation of the vinylborane product, **2**, was surprising since the failure of synthetic routes to substituted olefin complexes analogous to **1** has been attributed to unfavorable steric interactions between ligand and olefin substituents in the crowded coordination sphere of the Cp*$_2$Ti fragment. Thus, we suspected that the substituted olefin was weakly ligated, as would be required for catalytic formation of vinylboranes[26] from olefins and boranes, and might be displaced by sterically less demanding ligands. Indeed, **2** reacts cleanly with carbon monoxide and ethylene with ejection of the vinylboronate ester moiety (Scheme 2). The carbon monoxide reaction is rapid and produces the known Ti^{II} dicarbonyl complex.[27] The reaction with ethylene is slow and is complicated by competitive decomposition of **2** (40% conversion after 18 h at 25 °C). Although the starting olefin complex (**1**) is regenerated in this case, conversion of olefins to vinylboranes under catalytic conditions has not been successful.[28]

In conclusion, early transition-metal olefin complexes show promise for selective dehydrogenative boronation of olefins to form vinyl boronate esters. Specifically, the decamethyltitanocene fragment mediates a transformation where 2 mol of an unactivated olefin and 1 mol of a hydroborane are converted to 1 mol of an alkane and 1 mol of a vinylborane ester. Thus, the olefin complex, in its conversion to alkane and Cp*$_2$Ti, serves as the "sink" for hydrogen produced in this reaction, and reduced alkylboronate esters are not observed. The mechanism for this transformation is distinct from those operant in late-metal systems.[29] We are currently pursuing reactivity in related olefin systems with various borane reagents.

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Supplementary Material Available: Synthetic details (including ^{1}H and ^{11}B NMR data) (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(20) Metal-bound olefins are known to coordinate to trimethylaluminum: McDade, C.; Gibson, V. C.; Santersiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1.

(21) A similar intermediate has been proposed in the formation of Cp*$_2$Ti(η^2-$CH_2{=}CH_2$) via methane elimination from Cp*$_2$Ti(CH_2CH_3)(CH_3): Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793.

(22) Alternatively, the formation of Cp*$_2$TiH_2 and free $CH_2{=}CH$($BO_2C_{10}H_6$) or direct elimination of H_2 from **4** are also consistent with the current data.

(23) Bercaw, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 5087.

(24) Deuterium incorporation was determined by careful integration of the vinyl protons in the ^{1}H NMR spectrum and confirmed by simulation of the mass spectra of the vinylborane fragment for labeled and unlabeled **2**. When the reaction in eq 2 is performed using D_2, we observe similar isotopic distribution between ethane and **2**.

(25) A referee has suggested the possibility that free H_2 might not be involved in the hydrogenation of **1** and that ethane formation could result from bimolecular reactions of **1** and Cp*$_2$TiH_2. It should be possible to address this by reacting Cp*$_2$TiD_2 with Cp*$_2$Ti(η^2-$CH_2{=}CH_2$) in the presence of H_2; however, exchange between Cp*$_2$TiD_2 and H_2 is rapid. We have not been able to conclusively rule for or against this possibility.

(26) Singleton, D. A.; Martinez, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7423.

(27) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(28) Ethylene displacement of the vinylboronate ester is substantially slower than the reaction of **2** with excess borane reagent. The details of this chemistry are being investigated.

(29) A related reaction between thexylborane and Ru(PMe_3)$_4$(η^2-$CH_2{=}CH_2$) has been observed: Baker, R. T.; Calabrese, J. C.; Westcott, S. A.; Marder, T. B. *J. Am. Chem. Soc.*, in press.