ORGANIC LETTERS

2000
Vol. 2, No. 5
695−698

Mechanistic Studies on Selectivity in the $B(C_6F_5)_3$-Catalyzed Allylstannation of Aldehydes: Is Hypercoordination at Boron Responsible?

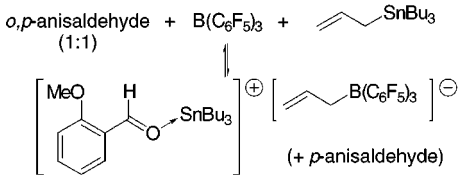
James M. Blackwell, Warren E. Piers,*,† and Masood Parvez

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

wpiers@ucalgary.ca.

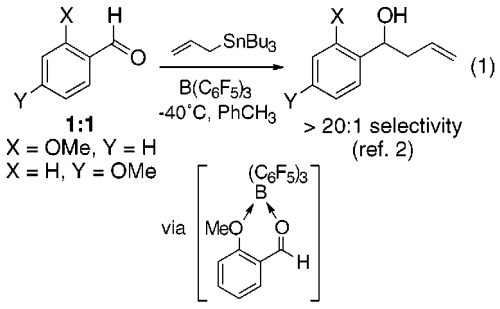
Received January 14, 2000

ABSTRACT



The selective, $B(C_6F_5)_3$-catalyzed allylstannation of aldehydes with proximal donor groups is shown to proceed via borane abstraction of the allyl group from the tin reagent and activation of the substrate by "Bu_3Sn^+". This is supported by a number of ^{19}F NMR experiments. The selectivity of the reaction is not attributable to hypercoordinate boron as proposed by the discoverers of this highly selective reaction but likely involves chelation at tin.

The Lewis acid-catalyzed allylstannation reaction is a well-established method for the stereoselective formation of C−C bonds.[1] Recently, Maruoka and co-workers reported[2] some remarkably selective allylstannation reactions catalyzed by Lewis acids, including $B(C_6F_5)_3$.[3] The chemoselectivity manifests itself in the preferential reduction of a carbonyl function with a proximal donor group; for instance, as shown in eq 1, allylation of the formyl group in *o*-anisaldehyde is favored by a >20:1 margin over that in *p*-anisaldehyde, in a competitive situation. The explanation proffered invoked selective binding of the *o*-anisaldehyde to $B(C_6F_5)_3$, aided by chelation of the Lewis acid such that the boron atom assumes a hypercoordinate geometry.[4]



While chelation by bifunctional substrates to Lewis acids is an important strategy to effect selectivity in organic reactions,[5] including allylstannation,[6] historically, boron-based Lewis acids have been viewed as nonchelating Lewis acids.[7] This, combined with the rarity of bona fide examples

† Phone: 403-220-5746. FAX: 403-289-9488.

10.1021/ol0000105 CCC: $19.00
Published on Web 02/11/2000

(1) Santelli, M.; Pons, J.-M. *Lewis Acids and Selectivity in Organic Synthesis;* CRC Press: Boca Raton, 1995; p 91.

(2) (a) Ooi, T.; Uraguchi, D.; Kagushima, N.; Maruoka, K. *J. Am. Chem. Soc.* **1998**, *120*, 5327. (b) Maruoka, K.; Ooi, T. *Chem. Eur. J.* **1999**, *5*, 829. (c) Ooi, T.; Uraguchi, D.; Maruoka, K. *Tetrahedron Lett.* **1998**, *39*, 8105.

(3) (a) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, 345. (b) Ishihara, K.; Yamamoto, H. *Eur. J. Org. Chem.* **1999**, 527.

(4) Akiba, K. *The Chemistry of Hypervalent Compounds*; John Wiley & Sons: Chichester, 1999.

(5) (a) Reetz, M. T. *Acc. Chem. Res.* **1993**, *26*, 462. (b) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

(6) (a) Keck, G. E.; Boden, E. P. *Tetrahedron Lett.* **1984**, *25*, 265. (b) Suzuki, I.; Yamamoto, Y. *J. Org. Chem.* **1993**, *58*, 4783. (c) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.

(7) See ref 1, pp 134−146 and references therein.

of hypercoordinate boron[8] and the relatively bulky C_6F_5 groups present in this particular borane, makes chelation at boron a controversial suggestion for the origin of selectivity in these reactions.[9] Thus, although the synthetic utility of the chemistry is clear, the ascribed origin of the selectivity warrants further scrutiny. On the basis of extensive mechanistic studies, we have demonstrated that the $B(C_6F_5)_3$-catalyzed *hydrosilation* of carbonyl functions occurs via an unusual mechanism involving borane activation of the Si−H bond.[10] It occurred to us that a similar phenomenon may be operative in these allylstannation reactions.

Since aromatic aldehydes form isolable adducts with $B(C_6F_5)_3$,[11] the issue of chelation at boron in the absence of a tin nucleophile was probed initially. Multinuclear NMR spectral analysis of the adduct, **1**, formed from $B(C_6F_5)_3$ and *o*-anisaldehyde, suggests a structure typical of other aldehyde adducts of $B(C_6F_5)_3$,[11] with no unusual coordination environments at boron. Indeed, an X-ray structure determination of **1** shows a tetrahedral boron center bound only to the carbonyl oxygen (Figure 1). This particular conformation appears to

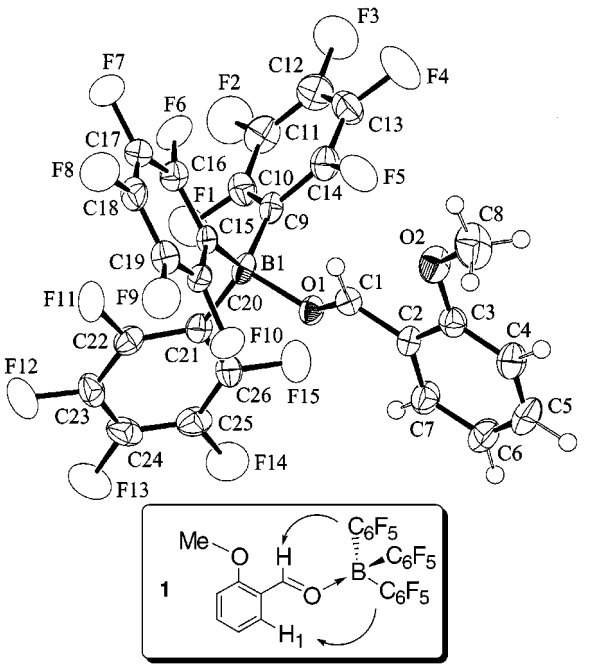
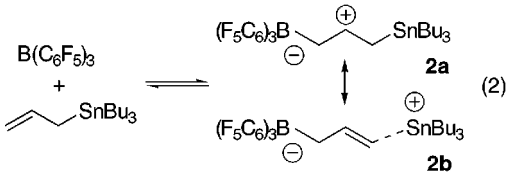


Figure 1. Molecular structure of $B(C_6F_5)_3$/*o*-anisaldehyde **1**. Selected bond distances (Å): B(1)−O(1), 1.589(5); C(1)−O(1), 1.262(4); C(1)−C(2), 1.418(5). Selected bond angles (deg): C(1)−O(1)-B(1), 127.0(3); C(2)−C(1)-O(1), 121.6(4); O(1)−B(1)-C(9), 104.5(3); O(1)−B(1)-C(15), 108.9(3); O(1)−B(1)-C(21), 101.6(3).

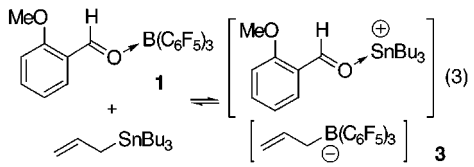
be maintained in solution as demonstrated by a $^{19}F/^{1}H$ NOE experiment. Irradiation of the *ortho* fluorines leads to enhancement in the aldehyde proton resonance as well as that of the aromatic proton H_1 (Figure 1, inset);[12] no enhancement in the signal for the methoxy protons is observed, as might be expected if this group were coordinated to boron. Thus, in the ground state, this adduct assumes a normal, four-coordinate geometry at boron both in solution and in the solid state.

In the absence of aldehyde, $B(C_6F_5)_3$ reacts reversibly with allyltributylstannane, eq 2.[13] ^{19}F and ^{11}B NMR spectra of a



1:1 mixture of $B(C_6F_5)_3$ and allyltributylstannane (−60 °C, C_7D_8) are consistent with formation of tetracoordinate, anionic borate, i.e., **2**. A resonance appears at −12.2 ppm in the ^{11}B NMR spectrum,[14] while a chemical shift difference of 4.5 ppm between the *para* and *meta* fluorine resonances,[15] $\Delta_{m,p}$, is indicative of borate formation with the stannylium ion still partially associated with the allyl fragment. This latter point is also supported by ^{1}H and ^{13}C NMR data, which suggest that resonance structure **2a** makes a significant contribution since both the proton and the carbon of the central methine in the allyl group are shifted downfield to 8.0 and 190 ppm, respectively, relative to allyltributylstannane. However, a resonance at 186 ppm in the $^{119}Sn\{^{1}H\}$ NMR spectrum implies that the tin also possesses considerable cationic character.[16]

Since the formation of both **1** and **2** are reversible, the equilibrium depicted in eq 3 may be studied under conditions



where allylation is slow. ^{19}F and ^{1}H NMR spectra of a 5:1

(8) Lee, D. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 5745.

(9) For the Lewis acids with larger central atoms in Maruoka's studies, the hypercoordinate explanation is more reasonable.

(10) (a) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* Submitted for publication. (c) See also: Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.

(11) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369.

(12) A similar enhancement of the *ortho* hydrogen resonances in the benzaldehyde adduct of $B(C_6F_5)_3$ was observed; in fact, molecular models show that these protons come into reasonably close contact with the C_6F_4 groups, attesting to the steric impact of this Lewis acid.

(13) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001.

(14) Kidd, R. G. In *NMR of Newly Accessible Nuclei, Volume 2*; Laszlo, P., Ed.; Academic Press: New York, 1983.

(15) Typically, neutral, three-coordinate pentafluorophenyl borane compounds exhibit a peak separation between the *para* and *meta* fluorine resonances of >15 ppm. As the environment about boron proceeds through neutral, four-coordinate (as in adduct **1**) to anionic, four-coordinate geometries, this parameter gets smaller as the resonance for the *para* fluorine shifts upfield due to shielding provided by the delocalization of the growing negative charge on boron. This was used by Horton and de With[15a] to assess the extent of ion pairing between organometallic cations and $[MeB(C_6F_5)_3]^-$. It is a sensitive tool for assessing the coordination environment around boron in C_6F_5-substituted boranes. (a) Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.

(16) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729.

solution of *o*-anisaldehyde and $B(C_6F_5)_3$ (−60 °C, C_7D_8) were acquired to establish the shifts for the borane adduct **1** (Figure 2a, $\Delta_{m,p} = 8.4$[11]). One equivalent of allyltributylstannane

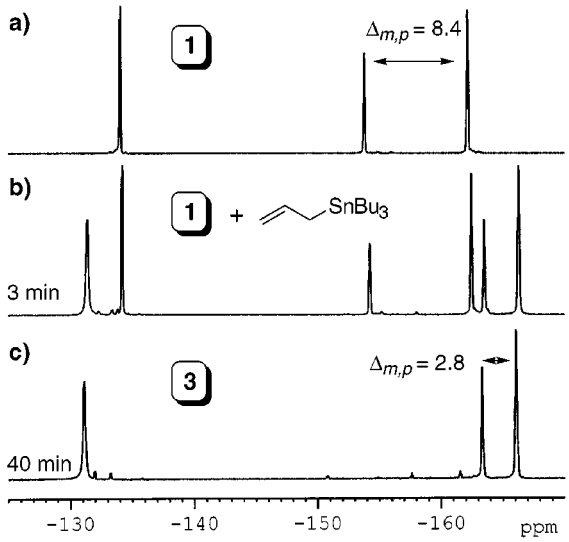


Figure 2. 282 MHz ^{19}F NMR spectra (−60 °C) of (a) **1** (formed from *o*-anisaldehyde and 20% $B(C_6F_5)_3$); (b) sample 3 min after addition of 1 equiv (relative to aldehyde) of allyltributyltin; (c) sample 40 min after addition, containing exclusively ion-pair **3**.

relative to *o*-anisaldehyde was added without allowing the sample to warm appreciably. A second set of signals appears in the ^{19}F NMR spectrum (Figure 2b), and the value of 2.8 ppm for $\Delta_{m,p}$ is diagnostic of formation of ion-pair **3**, in which *o*-anisaldehyde is coordinated to Bu_3Sn^+ and the allylborate anion (i.e., $[(C_3H_5)B(C_6F_5)_3]^-$) is completely dissociated. Over time at −60 °C, the allylborate signals completely supplant those for aldehyde adduct **1**, Figure 2c.

As the temperature is raised to −40 °C, allylation begins to occur and signals for both **1** and **3** are again observable. The reappearance of **1** is likely due to the regeneration of $B(C_6F_5)_3$ after allylation occurs, which competitively coordinates aldehyde over allyltributyltin. This is supported by a separate experiment in which *o*-anisaldehyde is added to a solution of **2** at −78 °C and analyzed immediately by low-temperature ^{19}F NMR spectroscopy. A mixture of **1** and **3** is initially observed, even though the $B(C_6F_5)_3$ is presumably interacting to a large extent with allyltributylstannane prior to aldehyde addition (eq 2). Over time **1** is converted to **3**, indicating that ion-pair **3** is thermodynamically favored whereas adduct **1** is kinetically preferred. This is entirely consistent with the relative basicities of an aldehyde versus allyltributylstannane toward $B(C_6F_5)_3$.

The equilibrium of eq 3 was also examined using ^1H NMR spectroscopy. Although complicated by the fact that only 20% catalyst is used,[17] signals corresponding to **1** are easily distinguishable from those of free aldehyde prior to allylstannane addition due to slow exchange in this temperature regime.[11] Upon addition of allyltin reagent, signals for **1** disappear and are replaced by one set of aldehyde resonances which are the average of those for **3** and free *o*-anisaldehyde. Apparently, even at −80 °C, exchange between free and bound aldehyde when "Bu_3Sn^+" is the Lewis acid is rapid on the NMR time scale.[18] Because of this fast exchange process, the precise structure of the cationic portion of ion pair **3** is unclear, i.e., we have been unable to obtain direct evidence for a chelated structure, though such a species is entirely reasonable for a tin-based Lewis acid.[19,20] Circumstantial support for this notion lies in the results of similar spectroscopic investigations using *p*-anisaldehyde instead of the *ortho* isomer.

Under conditions in which ion-pair **3** is formed, none of the corresponding *p*-anisaldehyde species can be detected (by monitoring for allylborate using ^{19}F NMR spectroscopy) upon addition of allyltributylstannane to a mixture of *p*-anisaldehyde and 20% $B(C_6F_5)_3$.[21a] Warming to −60 °C, conditions that accelerate conversion of **1** to **3**, still gives no evidence for ion-pair formation. At −20 °C, where allylation ensues, allylborate signals are detectable, but the resonances are minor compared to those of the $B(C_6F_5)_3$/*p*-anisaldehyde adduct, **4**. For some reason then, *o*-anisaldehyde is more effective at liberating "Bu_3Sn^+" from species **2** than is *p*-anisaldehyde.

This observation is intriguing in light of the fact that toward $B(C_6F_5)_3$ *p*-anisaldehyde is more basic than *o*-anisaldehyde. This was established in an experiment where equimolar amounts of the aldehydes compete for 20% $B(C_6F_5)_3$.[21b] Cooling to a regime where exchange is slow (−60 °C) reveals that the *p*-anisaldehyde/$B(C_6F_5)_3$ adduct **4** is favored over **1** by a 2.4:1 ratio. However, when allyltributylstannane is added to a 1:1 mixture of *o*- and *p*-anisaldehyde at −60 °C in the presence of 20% $B(C_6F_5)_3$, the resonances for **1** disappear first with concomitant appearance of allylborate signals, followed by a gradual but complete conversion of **4** to allylborate. Presumably, this is due to the presence of a surplus of *o*-anisaldehyde in this experiment since without *o*-anisaldehyde present no allylborate is formed from **4** under similar conditions (see above). This experiment shows that $B(C_6F_5)_3$ is kinetically accessible

(17) Even with as little as 20% $B(C_6F_5)_3$, ion-pair **3** is sparingly soluble in toluene, leading to formation of a liquid clathrate oil at the bottom of the NMR tube. This behavior was observed by Lambert[13] in the study of related ion pairs such as $[Bu_3Sn]^+[B(C_6F_5)_4]^-$. Attempts to use a higher mol % of $B(C_6F_5)_3$ leads to partial allylation which also complicates analysis.

(18) Although we have not yet probed the exchange process in detail, the larger size of the tin atom should allow for rapid associative exchange. Notably, the observed *o*-anisaldehyde resonances in this sample are shifted analogously to the stoichiometric complexing of $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ [13] to *o*-anisaldehyde. Furthermore, when $[Bu_3Sn]^+[B(C_6F_5)_4]^-$ is treated with an excess of *o*-anisaldehyde, free and coordinated aldehydes are not distinguishable by ^1H NMR at low temperature.

(19) (a) Davies, A. G.; Goddard, J. P.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Dalton Trans.* **1986**, 1873. (b) Edlund, U.; Arshadi, M.; Johnels, D. *J. Organomet. Chem.* **1993**, *456*, 57. (c) Blaschette, A.; Wieland, E.; Jones, P. G.; Hippel, I. *J. Organomet. Chem.* **1993**, *445*, 55. (d) Nugent, W. A.; McKinney, R. J.; Harlow, R. L. *Organometallics* **1984**, *3*, 1315.

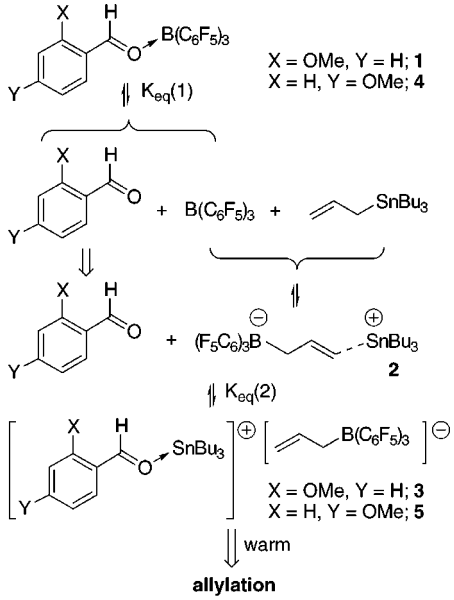
(20) Chelation of similar substrates to *neutral* tin Lewis acids is also precedented: (a) Keck, G. E.; Andrus, M. B.; Castellino, S. *J. Am. Chem. Soc.* **1989**, *111*, 8136. (b) Keck, G. E.; Castellino, S. *J. Am. Chem. Soc.* **1986**, *108*, 3847. (c) Reetz, M. T.; Harms, K.; Reif, W. *Tetrahedron Lett.* **1988**, *29*, 5881. (d) Wong, C. Y.; Woolins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175.

(21) See Supporting Information for ^{19}F NMR experiments pertaining to these experiments: (a) Figure S1. (b) Figures S2.

from **4** at low temperatures and that failure to observe formation of the "Bu_3Sn^+" adduct of *p*-anisaldehyde at low temperature is not due to an absence of free $B(C_6F_5)_3$ necessary to activate the allyltin reagent. We conclude that whereas *p*-anisaldehyde is the stronger base toward $B(C_6F_5)_3$, *o*-anisaldehyde is more basic toward "Bu_3Sn^+". It is possible that this is due to chelation at tin by *o*-anisaldehyde, but this remains to be firmly established.

In light of these experiments, we propose that the primary role of $B(C_6F_5)_3$ is to activate the allyltin reagent after dissociation from the aldehyde substrate (Scheme 1). Preliminary kinetic studies lend support for this notion in that excess substrate has an inhibitory effect on the rate of allylation. Under identical conditions, allylation of *o*-anisaldehyde is only 43% complete after 10 min when 4 equiv of aldehyde substrate is present, versus being 75% complete in the same time frame using only 1 equiv. A substrate inhibition effect in the $B(C_6F_5)_3$-catalyzed hydrosilation of carbonyl functions was also observed[10a] and suggests that lowering the amount of free borane present in the system impedes the reaction.

Scheme 1



In this picture, there is no need to invoke hypercoordination at boron to rationalize the observed selectivity toward *o*-anisaldehyde. The key selectivity determining factor appears to be the influence of each aldehyde on the formation of the allylborate ion pairs **3** or **5** ($K_{eq}(2)$, Scheme 1). This step is more facile for *o*-anisaldehyde, perhaps because the *o*-methoxy group is able to chelate to tin in the same way that Maruoka et al. proposed for the borane.[2] Alternatively, the donor group may accelerate allylation of **3** from another equivalent of allyltributyl tin in an acyclic, antiperiplanar transition state via chelating stabilization of the developing tributylstannyl cation as allylation occurs. This has been suggested by Yamataka and co-workers[22] to explain anomalously high rates for BF_3-catalyzed allylstannation of benzaldehydes with *ortho* halogens. We are addressing these questions further, but regardless, the experiments reported herein establish that catalysis by "Bu_3Sn^+" is a more plausible explanation for the observed selectivities in this particular (and by extension other[2]) $B(C_6F_5)_3$-catalyzed processes.

Acknowledgment. Funding for this work was provided by NSERC of Canada's Research Grants Program. J.M.B. thanks NSERC and the Izaak Walton Killam Foundation for fellowship support. W.E.P. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996−2000)

Supporting Information Available: Experimental details and characterization data for adduct **1**, along with tables of crystal data, atomic coordinates, isotropic thermal parameters, and bond lengths and angles, for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0000105

(22) Yamataka, H. Nishikawa, K.; Hanafusa, T. *Chem. Lett.* **1990**, 1711.