



## Pentacoordinate vs. Tetracoordinate Complexation for Alkoxy carbonyl Compounds with Dialkylboron Triflates and Trifluoroacetates ?

Takashi Ooi, Daisuke Uraguchi, and Keiji Maruoka\*

*Department of Chemistry, Graduate School of Science, Hokkaido University*

*Sapporo 060-0810, Japan*

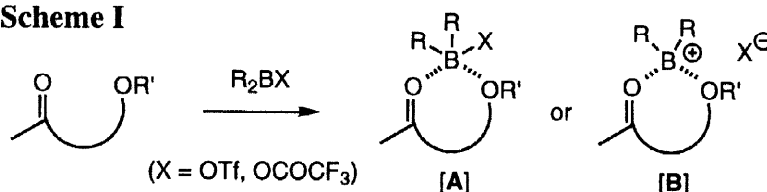
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**Abstract:** The implication of hitherto unknown pentacoordinate complex formation for alkoxy carbonyl compounds with  $\text{Et}_2\text{BX}$  ( $\text{X} = \text{OTf}$ ,  $\text{OCOCF}_3$ ) is presented by several reduction/allylation experiments and low-temperature  $^{13}\text{C}$ ,  $^{11}\text{B}$  NMR spectroscopy.

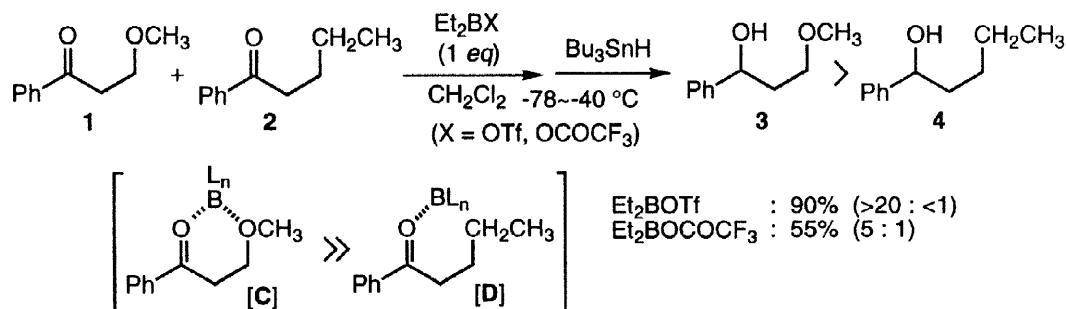
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Recently we disclosed the unprecedented pentacoordinate chelate-type complex formation of alkoxy carbonyl substrates with trialkylaluminum and trialkylboron Lewis acids.<sup>1</sup> The success on the new discovery of such pentacoordination is ascribed to the appropriate choice of aluminum and boron Lewis acids possessing poor leaving groups. In contrast to these trialkylmetal Lewis acids, reaction of alkoxy carbonyl substrates with dialkylboron species of type  $\text{R}_2\text{BX}$  possessing a good leaving group  $\text{X}$  may form either a pentacoordinate complex [A] or a charged tetracoordinate complex [B] with exclusion of the leaving group  $\text{X}$  (Scheme I).<sup>2,3</sup> The present study reports the implication of pentacoordinate complex formation on the reaction of alkoxy carbonyl compounds with  $\text{R}_2\text{BX}$  ( $\text{X} = \text{OTf}$ ,  $\text{OCOCF}_3$ ).

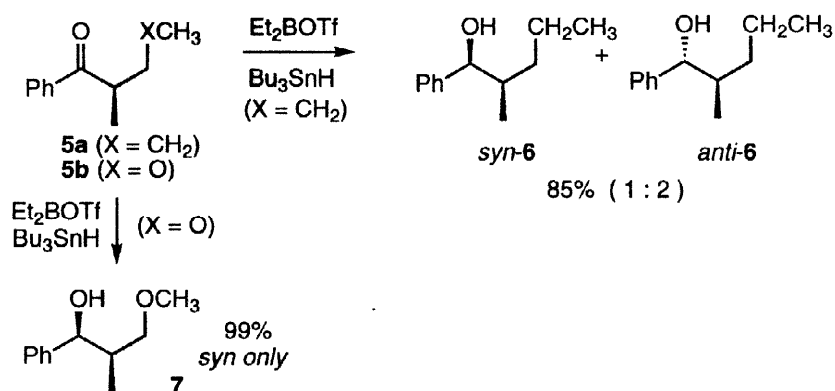
**Scheme I**



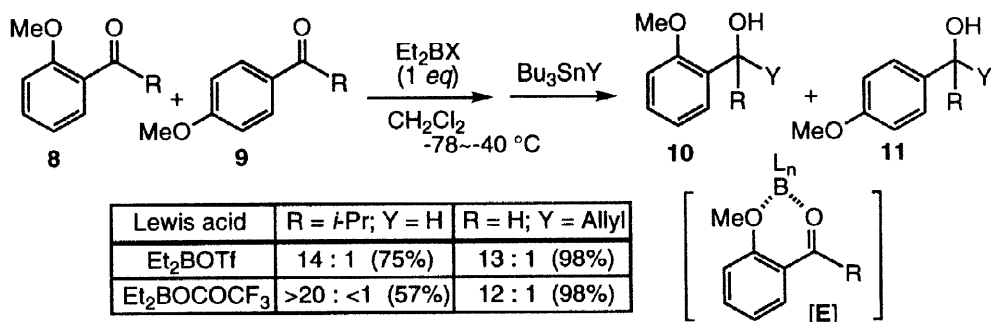
Initial treatment of an equimolar mixture of  $\beta$ -methoxy ketone **1** and its deoxy analogue **2** with  $\text{Et}_2\text{BOTf}$  ( $\text{Tf} = \text{OSO}_2\text{CF}_3$ , 1 equiv)<sup>4,5</sup> in toluene at  $-78^\circ\text{C}$  for 10 min and subsequent chelation-induced reduction with  $\text{Bu}_3\text{SnH}$  (1.1 equiv) gave rise to  $\beta$ -methoxy alcohol **3** predominantly accompanied by **4** in a ratio of  $>20: <1$ . Here, a chelation intermediate [C] seems to be more reactive than a simple coordination complex [D] judging from the observed high chemoselectivity.<sup>6</sup> A similar tendency in selective reduction between **1** and **2** was also observed with  $\text{Et}_2\text{BOCOCF}_3$ .<sup>4</sup>



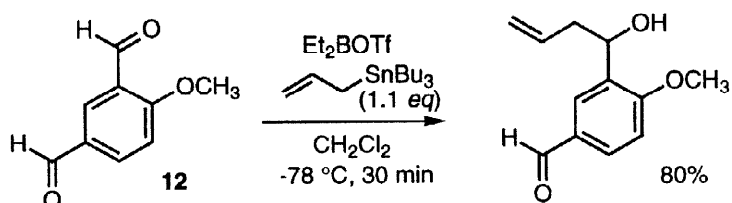
Moreover, Et<sub>2</sub>BOTf-promoted reduction of simple  $\alpha$ -substituted ketone **5a** (X = CH<sub>2</sub>) with Bu<sub>3</sub>SnH gave a mixture of diastereomeric alcohols **6**, whereas chelation-controlled reduction of  $\beta$ -methoxy- $\alpha$ -methyl ketone **5b** (X = O) with Et<sub>2</sub>BOTf/Bu<sub>3</sub>SnH afforded single diastereomer **7** exclusively.<sup>6</sup>



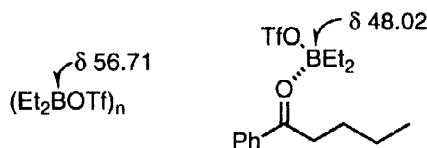
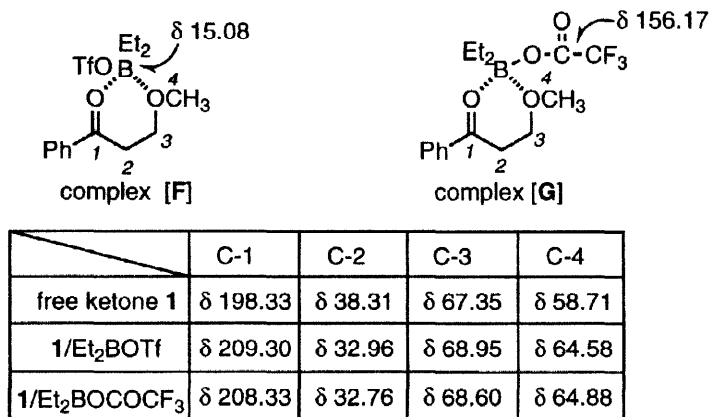
A discrimination experiment between *o*- and *p*-methoxyphenylcarbonyl compounds, **8** and **9** was carried out in a manner similar to that described above. Again, chelation-induced selective reduction of *o*-methoxyisobutyrophenone **8** (R = *i*-Pr) was observed to furnish *o*-methoxyphenyl carbinol **10** (R = *i*-Pr; Y = H) preferentially with Et<sub>2</sub>BX (X = OTf, OCOCF<sub>3</sub>) via a chelation complex [E]. The Et<sub>2</sub>BX-promoted (X = OTf, OCOCF<sub>3</sub>) discriminative allylation of an equimolar mixture of *o*- and *p*-anisaldehyde, **8** (R = H) and **9** (R = H) with allyltributyltin afforded *o*-methoxy homoallylic alcohol **10** (R = H; Y = CH<sub>2</sub>CH=CH<sub>2</sub>) predominantly.



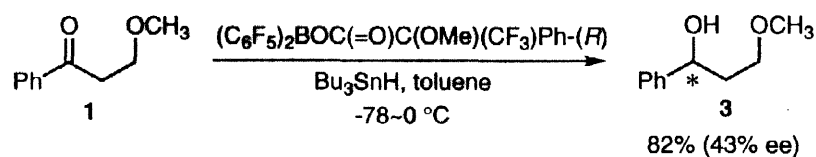
The chemoselective allylation of 2-methoxyphenyl-1,5-dicarboxaldehyde (**12**) appears feasible in the presence of organoboron Lewis acid as illustrated below.



The high chemo- and diastereoselectivity observed herein is ascribed to the effective chelate formation of  $\text{Et}_2\text{BX}$  ( $\text{X} = \text{OTf}, \text{OCOCF}_3$ ) with alkoxy-substituted carbonyl compounds via pentacoordinate or tetracoordinate complexes, [A] or [B]. Which is a plausible intermediate? Useful information on this point was obtained by carrying out low temperature  $^{13}\text{C}$  NMR study of the organoboron complex [C]. The original signal of carbonyl carbon C-1 in  $\beta$ -methoxy ketone **1** occurred at  $\delta$  198.33, and the signals of ethereal carbons C-3 and C-4 appeared at  $\delta$  67.35 and 58.71, respectively. When **1** was complexed with  $\text{Et}_2\text{BOTf}$  in a 1:1 molar ratio in  $\text{CD}_2\text{Cl}_2$  at  $-50^\circ\text{C}$ , a significant downfield shift of carbonyl carbon C-1 as well as ethereal carbons C-3 and C-4 was observed at  $\delta$  209.30, 68.95 and 64.58, respectively, with concomitant upfield shift of carbon C-2 at  $\delta$  32.96 ( $\delta$  38.31 for C-2 of free **1**) by  $^{13}\text{C}$  NMR analysis at  $-50^\circ\text{C}$ ; this could confirm the expected chelate formation of boron with  $\beta$ -methoxy ketone **1** illustrated as complex [F]. Similarly, the  $^{13}\text{C}$  NMR data of organoboron complex [G] showed the chelate formation. Here the trifluoroacetoxy moiety lies on boron atom as judged from the signal ( $\delta$  156.17) of trifluoroacetoxy carbonyl carbon, which is close to that of  $\text{CF}_3\text{CO}_2\text{Me}$ .<sup>7</sup> We also carried out the low temperature  $^{11}\text{B}$  NMR analysis of the organoboron complex [F].<sup>8,9</sup> The original signal of  $\text{Et}_2\text{BOTf}$  appeared at  $\delta$  56.71 in  $\text{CD}_2\text{Cl}_2$  at  $-50^\circ\text{C}$ .<sup>10</sup> Addition of valerophenone to  $\text{Et}_2\text{BOTf}$  in  $\text{CD}_2\text{Cl}_2$  showed the B signal at  $\delta$  48.02. However, when  $\text{Et}_2\text{BOTf}$  was complexed with  $\beta$ -methoxy ketone **1**, the upfield shift of the B signal was observed at  $\delta$  15.08, implying the formation of pentacoordinate complex [F].



Furthermore, asymmetric reduction of  $\beta$ -methoxyketone **1** with  $(\text{C}_6\text{F}_5)_2\text{BOC}(=\text{O})\text{C}(\text{OMe})(\text{CF}_3)\text{Ph}$ -(*R*) [prepared by mixing  $(\text{C}_6\text{F}_5)_3\text{B}$  and (*R*)- $\text{Ph}(\text{CF}_3)(\text{MeO})\text{CC}(=\text{O})\text{OH}$  at room temperature in toluene]<sup>11</sup> and  $\text{Bu}_3\text{SnH}$  at  $-78\sim 0^\circ\text{C}$  afforded **3** in 82% yield with moderate asymmetric induction (43% ee), suggesting a significant level of participation of the chiral acyloxy moiety.



Based on the experimental and spectroscopic data so far obtained, it is implicated that boron Lewis acids of type  $R_2BX$  ( $X = \text{OTf}, \text{OCOCF}_3$ ) form pentacoordinate chelate-type complexes [A] with alkoxy carbonyl substrates rather than the charged tetracoordinate chelate complexes [B]. Further studies are continued to characterize a real intermediate on the reaction of bidentate substrates with other boron Lewis acids possessing good leaving group.

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### References and Notes

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- (4)  $\text{Et}_2\text{BY}$  ( $\text{Y} = \text{OTf}$  or  $\text{OCOCF}_3$ ) were prepared by treatment of  $\text{Et}_3\text{B}$  with  $\text{TfOH}$  or  $\text{CF}_3\text{CO}_2\text{H}$  at  $25^\circ\text{C}$  for several hours.
- (5) Utility of  $R_2\text{BOTf}$  ( $\text{R} = \text{Et}, \text{Bu}$ ) as Lewis acids: Tanigucgi, N.; Kinoshita, H.; Inomata, K.; Kotake, H. *Chem. Lett.* **1984**, 1347. See also: Mukaiyama, T.; Inoue, T. *Chem. Lett.* **1976**, 559.
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- (7) The carbonyl carbon signal of  $\text{Et}_2\text{BOCOCF}_3$  ( $\delta$  156.28) is close to that of  $\text{CF}_3\text{CO}_2\text{Me}$  ( $\delta$  158.14) and not those of ionic species,  $\text{CF}_3\text{CO}_2\text{H}$  and  $\text{CF}_3\text{CO}_2^-\text{NHEt}_3^+$  ( $\delta$  162.23 and  $\delta$  161.94, respectively).
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- (9) Benn, R.; Rufinska, A. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 861. The  $^{11}\text{B}$  NMR chemical shifts are highly dependent on the ligands and structural types of organoboron compounds, and on the coordination number of the B atom. However, as the general tendency, the higher coordination number of the B atom in organoboron compounds causes the more upfield shift. See also ref 8.
- (10)  $\text{Et}_2\text{BOTf}$  may form a tetracoordinate structure due to self-association.
- (11) We utilized  $(\text{C}_6\text{F}_5)_2\text{BOC(=O)C(OMe)(CF}_3\text{)Ph-(R)}$  as a chiral Lewis acid, since attempted reduction of  $\beta$ -methoxyketone **1** with  $\text{Bu}_3\text{SnH}$  in the presence of  $\text{Et}_2\text{BOC(=O)C(OMe)(CF}_3\text{)Ph-(R)}$  or  $B\text{-(R)-Ph(CF}_3\text{)(MeO)CC(=O)O-9-BBN}$  gave only a trace of alcohol **3** due to their feeble Lewis acidity.