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Hypercoordination of Boron and Aluminum: Synthetic Utility as Chelating Lewis Acids

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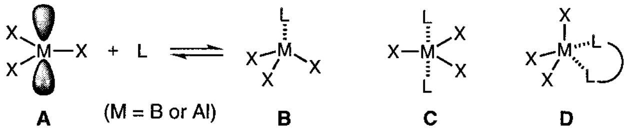
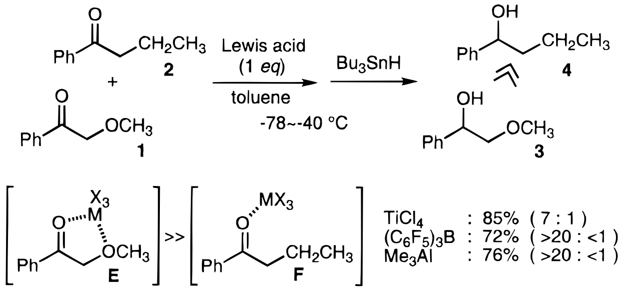
Boron and aluminum compounds have been widely utilized in both organic and inorganic syntheses.[1] Many of the reaction characteristics common to both these elements depend on the availability of the empty p orbital that makes these compounds electrophilic or Lewis acidic.[2] Accordingly, trivalent B and Al compounds **A** (BX_3 and AlX_3) readily react with a variety of neutral or negatively charged Lewis bases (L) to form the corresponding tetracoordinate complexes **B**. Several restricted examples of neutral pentacoordinate, trigonal-bipyramidal complexes of type **C** (M = B, Al), where ligands L occupy two axial positions, have recently been isolated and characterized.[3,4] However, the majority still involve the tricoordination/tetracoordination chemistry of boron and aluminum, and hence trivalent B and Al compounds **A** have long been regarded as nonchelating Lewis acids.[2,5] Little attention has been given to the existence of another pentacoordinate, chelate-type complex **D**,[6] and its nature remains elusive despite its potential importance from mechanistic as well as synthetic points of view. Here we wish to report such a pentacoordinate complex **D** is observable with commercially available $(C_6F_5)_3B$ and Me_3Al in simple reaction systems, and should find considerable utility in organic synthesis.

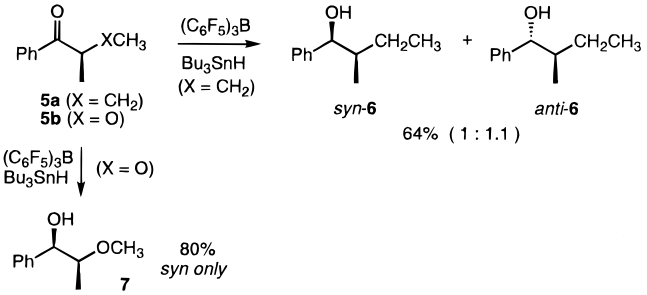


Since boron and aluminum have high affinity to oxygen, as evident from the bond strengths in several diatomic molecules of metal−oxygen (B−O = 808.8 kJ/mol, Al−O = 511 kJ/mol),[7] we chose α-methoxy ketone **1** and its deoxy analogue **2** as model substrates for chelation-induced selective reduction with Bu_3SnH in the presence of several Lewis acids. We assumed that the chelate formation of substrate **1** with Lewis acids is generally a favorable process, and therefore accelerates the rate of reduction by the effective activation of carbonyl moiety compared to the nonchelation case.[5] Indeed, initial treatment of an equimolar mixture of α-methoxy ketone **1** and its deoxy analogue **2** with a commonly used chelating Lewis acid, $TiCl_4$ (1 equiv) in toluene at −78 °C for 10 min, and subsequent chelation-induced reduction with Bu_3SnH (1.1 equiv) gave rise to α-methoxy alcohol **3** predominantly accompanied by **4** in a ratio of 7:1. Under similar reaction conditions, reduction of **1** and **2** (1:1 ratio) with $(C_6F_5)_3B$ (1 equiv),[8,9] which is originally identified as a nonchelating Lewis acid, afforded α-methoxy alcohol **3** as a major product (ratio of **3**/**4** = >20:<1). A similar tendency in selectivity between **1** and **2** was also observed with Me_3Al. These results imply the preferable formation of chelating pentacoordinate **E** (MX_3 = $(C_6F_5)_3B$ or Me_3Al) rather than a tetracoordinate **F** (MX_3 = $(C_6F_5)_3B$ or Me_3Al).[5,6]

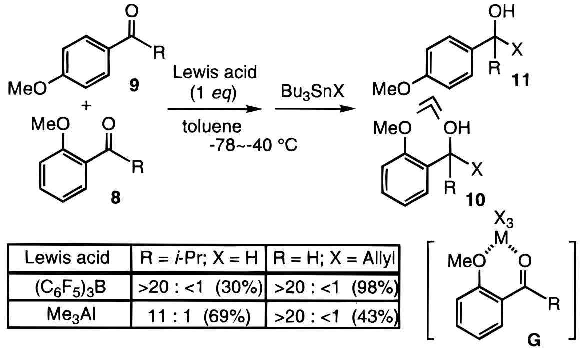


$TiCl_4$	: 85%	(7 : 1)
$(C_6F_5)_3B$	: 72%	(>20 : <1)
Me_3Al	: 76%	(>20 : <1)

Moreover, $(C_6F_5)_3B$-promoted reduction of simple α-substituted ketone **5a** (X = CH_2) with Bu_3SnH gave a mixture of diastereomeric alcohols **6**, whereas chelation-controlled reduction of α-methoxy-α-methyl ketone **5b** (X = O) with $(C_6F_5)_3B/Bu_3SnH$ afforded single diastereomer **7** exclusively.[5]



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; X = H) preferentially with $(C_6F_5)_3B$ and Me_3Al. The $(C_6F_5)_3B$- and Me_3Al-promoted 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; X = $CH_2CH{=}CH_2$) predominantly.



Lewis acid	R = *i*-Pr; X = H	R = H; X = Allyl
$(C_6F_5)_3B$	>20 : <1 (30%)	>20 : <1 (98%)
Me_3Al	11 : 1 (69%)	>20 : <1 (43%)

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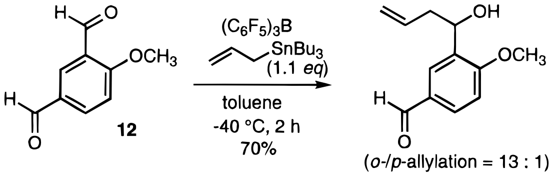
The chemoselective allylation of 2-methoxyphenyl-1,5-dicarboxaldehyde (**12**) appears feasible in the presence of organoboron Lewis acid as illustrated below.



The high chemo- and stereoselectivity observed herein is ascribed to the effective chelate formation of $(C_6F_5)_3B$ and Me_3Al with alkoxy-substituted carbonyl compounds. Hence, we successfully demonstrated that boron and aluminum Lewis acids are capable of forming pentacoordinate complexes of type **D** in certain simple reaction systems, which opens new avenues of understandings and utilities of these elements in selective organic synthesis.

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