The Synthetic Utility of the Hypercoordination of Boron and Aluminum

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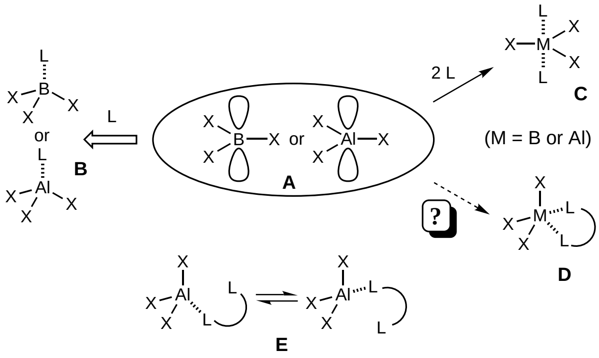
Abstract: A new concept is disclosed for the hypercoordination of boron and aluminum as typical main group elements, and their synthetic utility is demonstrated by means of several synthetic examples. B and Al Lewis acid reagents were successfully utilized in several chelation-controlled nucleophilic and electrophilic reactions of various substrates (fluoroepoxides, fluorocarbonyl compounds, and alkoxycarbonyl compounds) through unprecedented pentacoordinate chelate-type complex formation. The reactions take advantage of the exceedingly high affinity of B and Al to fluorine and oxygen, and hence, contrary to previous observations, can be classified as chelating Lewis acid reagents rather than non-chelating Lewis acids. In addition to the experimental demonstration of the pentacoordinate chelate-type B and Al complexation, such pentacoordinate complex formation of B and Al Lewis acids with various bidentate substrates is also proven by low-temperature NMR spectroscopy.

Keywords: aluminum · boron · chelation · coordination modes · synthetic methods

Introduction

Boron and aluminum reagents 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 which makes these compounds electrophilic or Lewis acidic.[2] Accordingly, trivalent B and Al compounds **A** (Scheme 1) 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] Although pentacoordination of type **C** (M = Al; X = Et; L = phosphine) in 1:1 Et_3Al/diphosphine complexes has been previously claimed with $Ph_2PCH_2PPh_2$, $MeN(PPh_2)_2$, and $EtN(PPh_2)_2$,[5] recent evidence obtained for the $Me_3Al/Ph_2PCH_2PPh_2$ complex points only to a highly fluxional molecule in solution with tetracoordinate aluminum species of type **E** even at − 80 °C.[6] Accordingly, most chemists still believe that only tricoordination/tetracoordination chemistry of B and Al exists, and hence trivalent B and Al compounds **A** have long been regarded as non-chelating Lewis acids.[2, 7] Little attention has been paid to the existence of another pentacoordinate, chelate-type complex **D**, and its nature remains elusive despite its potential importance from mechanistic as well as synthetic points of view. We have found that such a pentacoordinate complex **D** is indeed easily observable in simple reaction systems, and should find considerable utility in organic synthesis (Scheme 1).



Scheme 1. Coordination pattern of boron and aluminum compounds.

Discussion

Selective alkylation of fluoroepoxides via pentacoordinate Al: Since aluminum, in addition to its well-known high oxygenophilicity (Al–O = 511 ± 3 kJ mol^{-1}), has an exceedingly high affinity toward fluorine (as is evident from the bond strengths in several diatomic molecules of metal–fluorine: Al–F, 663.6 ± 6.3 kJ mol^{-1}; Li–F, 577 ± 21 kJ mol^{-1}; Ti–F, 569 ± 34 kJ mol^{-1}; Si–F, 552.7 ± 2.1 kJ mol^{-1}; Sn–F, 466.5 ± 13 kJ mol^{-1}; Mg–F, 461.9 ± 5.0 kJ mol^{-1}[8]), organoaluminum reagents seem quite suitable for fluorine-assisted selective transformation of oxygen-containing organofluorine sub-

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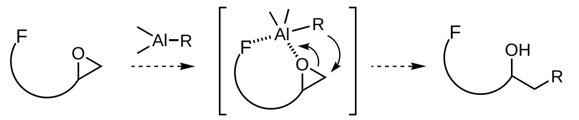
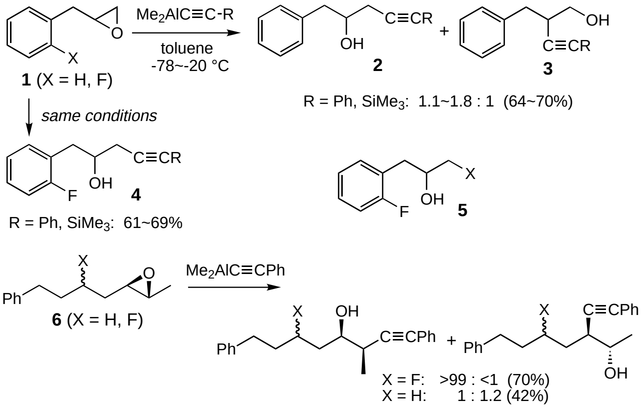
strates.[9] Accordingly, we first studied the selective alkylation of fluoroepoxides as model substrates for our case study, which represents the first experimental demonstration of the intervention of pentacoordinate chelate complexes of trialkylaluminums as plausible intermediates (Scheme 2).[10]



Scheme 2. Selective alkylation of fluoroepoxides via pentacoordinate chelate intermediates.

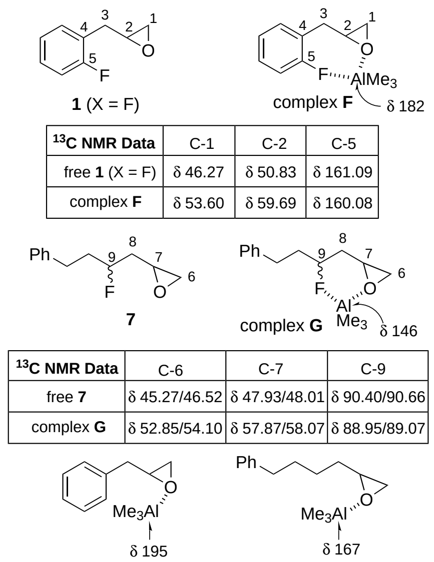
Alkylation of terminal or 1,2-disubstituted epoxides normally provides a regioisomeric mixture of corresponding ring-opening alcohols. For instance, treatment of 3-phenyl-1,2-epoxypropane **1** (X = H) with $\mathrm{Me_2AlC{\equiv}CPh}$ in toluene at −78 to −20 °C gave rise to a mixture of 1,5-diphenyl-4-pentyn-2-ol **2** (R = Ph) and 2-benzyl-4-phenyl-3-butyn-1-ol **3** (R = Ph) (64 % combined yield) in a ratio of 1.1:1 (Scheme 3).



Scheme 3. Selective alkynylation of fluoroepoxides.

In marked contrast, however, reaction of its fluoro analogue, 3-(2-fluorophenyl)-1,2-epoxypropane **1** (X = F) with $\mathrm{Me_2Al\text{-}C{\equiv}CPh}$ under similar reaction conditions afforded 1-(2-fluorophenyl)-5-phenyl-4-pentyn-2-ol **4** (R = Ph) exclusively in 61 % yield (Scheme 3). The metal effect on the regioselectivity for the present alkynylation was also examined. Attempted reaction of fluoroepoxide **1** (X = F) with $\mathrm{PhC{\equiv}CMgBr}$ or $\mathrm{PhC{\equiv}CTiCl(O\mathit{i}Pr)_2}$ gave rise to halohydrin **5** (X = Cl or Br) as sole isolable product.[11] Use of $\mathrm{PhC{\equiv}CLi}$ for the substrates **1** and **6** significantly retarded the epoxide cleavage irrespective of the presence or absence of a fluoro group. In the case of 1,2-*trans*-disubstituted fluoroepoxide **6** (X = F), a high level of regioselectivity was observed as well. Even a δ-fluoro epoxide showed moderate selectivity.[10]

Although the hypothetical existence of pentacoordinate trialkylaluminum complexes with fluoroepoxides is strongly implied by the above alkynylation experiments, more direct evidence was obtained by low-temperature ^{13}C NMR study of these aluminum complexes (Scheme 4). When **1** (X = F) was complexed with $\mathrm{Me_3Al}$ in a 1:1.1 molar ratio in $\mathrm{CD_2Cl_2}$ at −78 °C, the significant downfield shift of epoxide carbons C-1 and C-2 in structure **F** was observed with a concomitant upfield shift of C–F carbon C-5 at −78 °C; this supported the expected chelate formation of aluminum with fluoroepoxide **1** (X = F). It should be added that the upfield shift of the fluorine-bearing carbon was also observed in the ^{13}C NMR measurement of fluorobenzene with $\mathrm{Me_3Al}$ (1.1 equiv) in $\mathrm{CD_2Cl_2}$ at −78 °C.[12] A similar tendency is observed in the epoxide **7**/$\mathrm{Me_3Al}$ chelate complex **G** in $\mathrm{CD_2Cl_2}$ at −78 °C. Although these ^{13}C NMR data may not rigorously rule out the possibility of the involvement of a fluxional complex of type **E**, the low-temperature ^{27}Al NMR analysis of several trialkylaluminum complexes further supports the existence of pentacoordinate complexes **F** and **G**.[13]

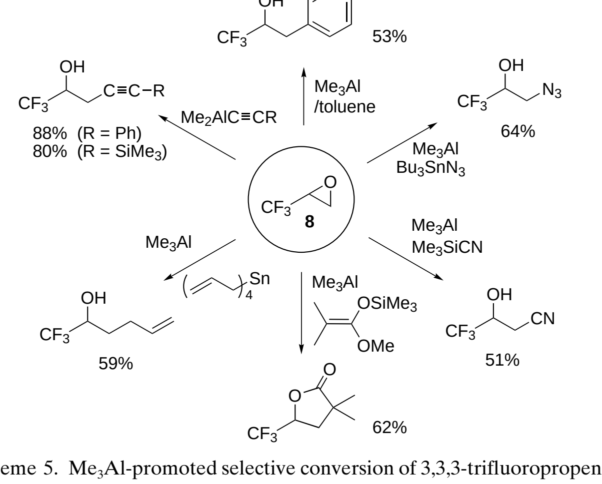


^{13}C NMR Data	C-1	C-2	C-5
free **1** (X = F)	δ 46.27	δ 50.83	δ 161.09
complex **F**	δ 53.60	δ 59.69	δ 160.08

^{13}C NMR Data	C-6	C-7	C-9
free **7**	δ 45.27/46.52	δ 47.93/48.01	δ 90.40/90.66
complex **G**	δ 52.85/54.10	δ 57.87/58.07	δ 88.95/89.07

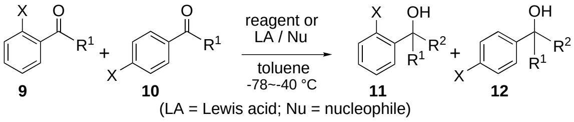
Scheme 4. NMR data for fluoroepoxides and their coordination complexes with $\mathrm{Me_3Al}$.

The new finding disclosed above permitted a new organoaluminum-promoted selective alkylation of 3,3,3-trifluoropropene oxide (TFPO, **8**) with several nucleophiles, which involves chelation-activated addition to fluoroepoxides via pentacoordinate $\mathrm{Me_3Al}$ complexes (Scheme 5).[14]



Scheme 5. $\mathrm{Me_3Al}$-promoted selective conversion of 3,3,3-trifluoropropene oxide (TFPO).

Table 1. Chemoselective functionalization of *o*- and *p*-substituted carbonyl derivatives.

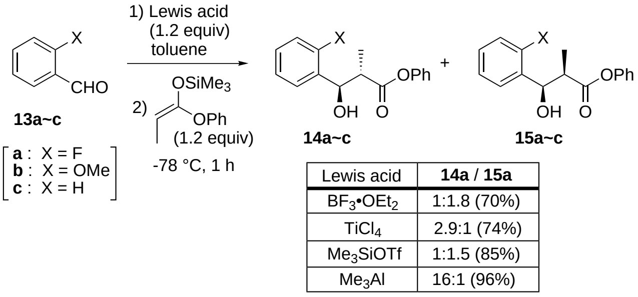


Run	Substrate (**9**&**10**)	Reagent Lewis acid / nucleophile	Product (**11**&**12**)	Ratio (**11**:**12**)
1	$X = F$; $R^1 = H$	$PhC{\equiv}CAlMe_2$	$R^2 = C{\equiv}CPh$	9.2:1
2		$PhC{\equiv}CMgBr$		3.7:1
3		$PhC{\equiv}CTiCl(OiPr)_2$		2.7:1
4		$PhC{\equiv}CLi$		1.8:1
5		$BuC{\equiv}CAlMe_2$	$R^2 = C{\equiv}CBu$	7.1:1
6		$PhC{\equiv}CLi$		1.1:1
7	$X = Cl$; $R^1 = H$	$PhC{\equiv}CAlMe_2$	$R^2 = C{\equiv}CPh$	2.4:1
8	$X = F$; $R^1 = H$	Me_3Al / $CH_2{=}CHCH_2SnBu_3$	$R^2 = CH_2CH{=}CH_2$	31:1
9		$TiCl_2(OiPr)_2$ / $CH_2{=}CHCH_2SnBu_3$		9.8:1
10		$MgBr_2$ / $CH_2{=}CHCH_2SnBu_3$		7.1:1
11		$LiClO_4$ / $CH_2{=}CHCH_2SnBu_3$		4.1:1
12		$SiCl_4$ / $CH_2{=}CHCH_2SnBu_3$		3.8:1
13	$X = F$; $R^1 = i$Pr	Me_3Al / Bu_3SnH	$R^2 = H$	34:1
14		Et_3Al / Bu_3SnH		26:1
15		Me_2AlCl / Bu_3SnH		7.3:1
16		$SiCl_4$ / Bu_3SnH		2.3:1
17		$TiCl_2(OiPr)_2$ / Bu_3SnH		1.9:1
18		$MgBr_2$ / Bu_3SnH		1.9:1
19	$X = OMe$; $R^1 = i$Pr	$(C_6F_5)_3B$ / Bu_3SnH	$R^2 = H$	$>20:1$
20		Me_3Al / Bu_3SnH		11:1
21	$X = OMe$; $R^1 = H$	$(C_6F_5)_3B$ / $CH_2{=}CHCH_2SnBu_3$	$R^2 = CH_2CH{=}CH_2$	$>20:1$
22		Me_3Al / $CH_2{=}CHCH_2SnBu_3$		$>20:1$

Selective alkylation of fluorocarbonyl compounds via pentacoordinate Al: Our concept is also applicable to the selective alkylation of fluorocarbonyl compounds with organoaluminum reagents as shown in Table 1.[15] The chelate formation of fluorocarbonyl substrates with Lewis acids is assumed to be generally a favorable process, and therefore accelerates the rate of reduction by the effective activation of carbonyl moiety compared to the non-chelation case.[7] Indeed, treatment of an equimolar mixture of 2-fluorobenzaldehyde **9** ($X = F$; $R^1 = H$) and 4-fluorobenzaldehyde **10** ($X = F$; $R^1 = H$) in toluene at −78 °C with $Me_2AlC{\equiv}CPh$ resulted in formation of two different propargyl alcohols **11** and **12** ($X = F$; $R^1 = H$, $R^2 = C{\equiv}CPh$) in a ratio of 9.2:1 (entry 1 of Table 1). The selectivity is lowered by switching the metal of $PhC{\equiv}C{-}M$ from Al to Mg, Ti, or Li (entries 2–4). A similar metal effect is observed with $BuC{\equiv}C{-}M$ ($M = AlMe_2$ or Li) (entries 5 and 6). The high affinity of aluminum to fluorine compared to other halogens is evident from the discrimination experiment between chloro analogues with $Me_2AlC{\equiv}CPh$, which shows only moderate selectivity (entry 7).

The advantage of aluminum reagents over other metal reagents was also seen in the Lewis acid promoted reactions of fluorocarbonyl compounds with other alkylating agents (entries 8–18 of Table 1). Thus, Me_3Al-promoted selective allylation of an equimolar mixture of 2- and 4-fluorobenzaldehydes with allyltributyltin afforded the homoallylic alcohol **11** ($X = F$; $R^1 = H$, $R^2 = CH_2CH{=}CH_2$) almost exclusively (entry 8).[15] A similar tendency is also observable in the selective reduction of *o*-fluorophenyl ketone **9** ($X = F$; $R^1 = i$Pr) over the *p*-fluoro analogue with Me_3Al/Bu_3SnH (entry 13). Again, unsatisfactory results were obtained with Ti, Mg, Li, and Si reagents in terms of chemical yield and selectivity (entries 9–12 and 16–18).

With this information on the metal effect at hand, we focused our attention on diastereoselective aldol reactions of fluoro aldehydes with ketene silyl acetals in the presence of Me_3Al. Despite the numerous reports of *syn*-selective aldol reactions with ordinary aldehydes, the corresponding *anti* selectivity has not been easily attainable.[16, 17] We have found that high *anti* selectivity is achieved in the aldol reactions of fluoro aldehydes with ketene silyl acetals in the presence of Me_3Al (Scheme 6). For example, Me_3Al-induced reaction of *o*-fluorobenzaldehyde (**13a**) with a substituted ketene silyl acetal gave rise to a mixture of fluoro *β*-hydroxy esters **14a** and **15a** with high diastereoselectivity (16:1), probably owing to the effective complexation of the carbonyl moiety, while the selectivity was dramatically lowered when other common Lewis acids such as $BF_3\cdot OEt_2$, $TiCl_4$, and Me_3SiOTf were

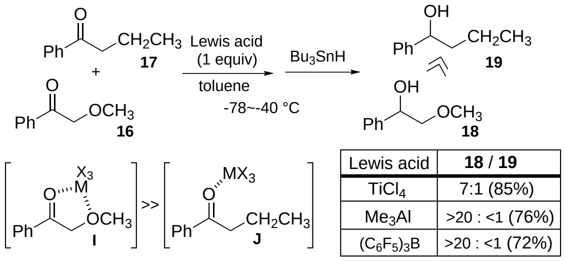


Lewis acid	14a / 15a
$BF_3{\bullet}OEt_2$	1:1.8 (70%)
$TiCl_4$	2.9:1 (74%)
Me_3SiOTf	1:1.5 (85%)
Me_3Al	16:1 (96%)

Scheme 6. Chelation-controlled diastereoselective aldol reactions.

used.[18] In contrast, however, *o*-anisaldehyde (**13b**) and benzaldehyde (**13c**) exhibited moderate selectivity (5.3:1). The importance of chelate formation for obtaining high *anti* selectivity was also demonstrated in comparison with the low diastereoselectivity (ratio, 3.5:1) in the aldol reaction with *p*-fluorobenzaldehyde.

Selective reduction and alkylation of alkoxy carbonyl compounds via pentacoordinate B and Al: Since B and Al also have a high affinity for oxygen, as evident from the bond strengths in several diatomic molecules (B–O = 808.8, Al–O = 511 kJ mol^{-1}),[8] we chose α-methoxy ketone **16** and its deoxy analogue **17** as other model substrates for chelation-induced selective reduction with Bu_3SnH in the presence of several Lewis acids, particularly B Lewis acids (Scheme 7).[19]



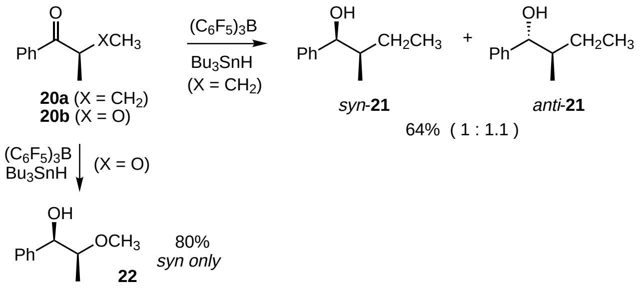
Lewis acid	18 / 19
$TiCl_4$	7:1 (85%)
Me_3Al	>20 : <1 (76%)
$(C_6F_5)_3B$	>20 : <1 (72%)

Scheme 7. Lewis acid-promoted chemoselective reduction of α-alkoxyketones with Bu_3SnH via chelate intermediate **I**.

Initial treatment of an equimolar mixture of α-methoxy ketone **16** and its deoxy analogue **17** with a commonly used chelating Lewis acid, $TiCl_4$, and Bu_3SnH in toluene at −78 °C for 10 min gave rise to a mixture of α-methoxy alcohol **18** accompanied by **19**. Under similar reaction conditions, reduction of **16** and **17** (1:1 ratio) with Me_3Al afforded α-methoxy alcohol **18** as sole isolable product via a favorable chelate intermediate **I** ($MX_3 = AlMe_3$).

Our attention has now been focused on the possibility of forming hypercoordinated chelation complexes with certain B Lewis acids. For this purpose, dialkylboron triflates are normally utilized in organic synthesis. However, there is a danger in using such dialkylboron triflates and trifluoroacetates as pentacoordinate chelating Lewis acids, because these reagents might give rise to conventional tetracoordinate chelates with loss of their triflate and trifluoroacetate moieties as good leaving groups. Accordingly, we utilized commercially available $(C_6F_5)_3B$, which possesses stable alkyl ligands, like Me_3Al as a reliable Lewis acid. This B Lewis acid seems to be satisfactory for the present chelation-controlled reactions.[19] Fortunately, reduction of **16** and **17** (1:1 ratio) in the presence of $(C_6F_5)_3B$ produced α-methoxy alcohol **18** almost exclusively (Scheme 7). The result implies the preferential formation of chelating pentacoordinate **I** ($MX_3 = (C_6F_5)_3B$) rather than a tetracoordinate **J**.

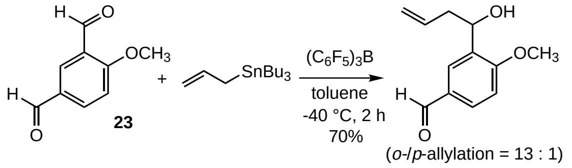
Moreover, $(C_6F_5)_3B$-promoted reduction of simple α-substituted ketone **20a** with Bu_3SnH gave a mixture of diastereomeric alcohols **21**, whereas chelation-controlled reduction of α-methoxy-α-methyl ketone **20b** with $(C_6F_5)_3B/Bu_3SnH$ afforded single diastereomer **22** exclusively (Scheme 8).[7]



Scheme 8. $(C_6F_5)_3B$-promoted stereoselective reduction of α-alkoxyketone with Bu_3SnH.

A discrimination experiment between *o*- and *p*-methoxyphenylcarbonyl compounds **9** and **10** (X = OMe; R^1 = *i*Pr or H) was carried out in a manner similar to that described above (entries 19–22 of Table 1). Again, chelation-induced selective reduction of *o*-methoxyisobutyrophenone **9** (X = OMe; R^1 = *i*Pr) was found to furnish *o*-methoxyphenyl carbinol **11** (X = OMe; R^1 = *i*Pr; R^2 = 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, **9** and **10** (X = OMe; R^1 = H) with allyltributyltin afforded *o*-methoxy homoallylic alcohol **11** (X = OMe; R^1 = H; R^2 = $CH_2CH{=}CH_2$) almost exclusively.

Finally, the chemoselective *o*-allylation of 2-methoxyphenyl-1,5-dicarboxaldehyde (**23**) appears feasible in the presence of organoboron Lewis acid (Scheme 9).



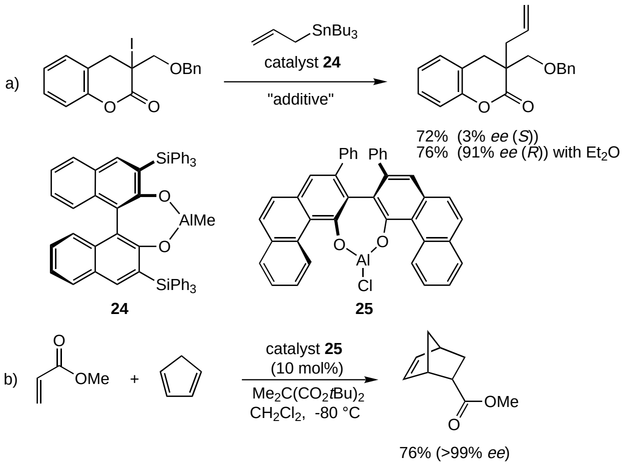
Scheme 9. Chemoselective allylation of 2-methoxyphenyl-1,5-dicarboxaldehyde.

Conclusion

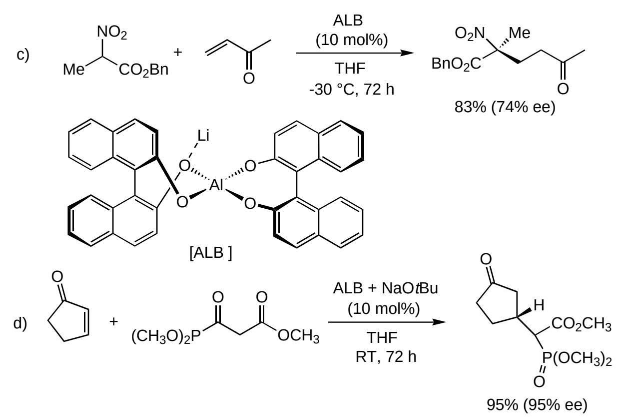
We have successfully demonstrated that boron and aluminum Lewis acids are capable of forming pentacoordinate chelate-type complexes in certain simple reaction systems, which opens new avenues of understandings and utilities of these elements in selective organic synthesis. Therefore, boron and aluminum Lewis acids can no longer be classified as non-chelating Lewis acids.

After our first paper appeared on the hypercoordination of aluminum Lewis acids,[10] Hoshino and Wulff reported independently the synthetic utility of hypercoordinated aluminum Lewis acids, though not of a chelate type, in asymmetric radical allylation and the asymmetric Diels–Alder reaction, respectively, by using Et_2O and $Me_2C(CO_2t\text{Bu})_2$ as additives (Scheme 10);[21, 22] Keller and Shibasaki detected the existence of hypercoordinated chiral aluminum catalysts in asymmetric Michael reactions (Scheme 11).[23, 24]

In contrast to these synthetic examples with hypercoordinated Al Lewis acids, none of the hypercoordinated B Lewis acids have been introduced besides our own examples (see



Scheme 10. Asymmetric synthesis using hypercoordinated Al Lewis acids (Hoshino et al., ref. [21]; Wulff et al., ref. [22]).



Scheme 11. Asymmetric Michael reactions with hypercoordinated Al catalysts (Keller et al., ref. [23]; Shibasaki et al., ref. [24]).

above). However, even the ordinary boron Lewis acids such as $BF_3 \cdot OEt_2$ and R_2BOTf might be able to form hypercoordinated structures with various bidentate ligands. Therefore, the hypercoordination of main-group elements may provide an exciting and growing area in coordination, mechanistic, and synthetic chemistry in the near future.

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