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Hypercoordination of Aluminum: Evidence for the Implication of Pentacoordinate Complexes in the R_2AlCl-Promoted Reduction of Alkoxycarbonyl Substrates

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Abstract

R_2AlCl-promoted reductions of alkoxycarbonyl substrates with Bu_3SnH were found to proceed diastereoselectively through the formation of pentacoordinate chelate-type complexes which have been characterized by ^{13}C NMR spectroscopy.

Keywords: Aluminum and compounds; Carbonyl compounds; Complexes; Reduction.

Dialkylaluminum halides (R_2AlX), especially chlorides, are recognized as one of the most familiar Lewis acids and routinely employed for a number of Lewis acid-promoted synthetic transformations such as Diels-Alder reactions, conjugate additions, amide formations, and carbonyl alkylations [1-4]. Among those, electrophilic carbonyl alkylation with R_2AlX proceeds through the formation of tetracoordinate aluminum-carbonyl complex [5]. When the substrates possessing certain heteroatom functionalities are used, chelation-controlled reaction often takes place, which is believed to proceed *via* tetracoordinate complex [**A**] resulting from the coordination of carbonyl to the cationic aluminum center. However, there is another possibility which has emerged based on our recent observation of the hypercoordination of boron and aluminum: R_2AlX could form chelate-type pentacoordinate aluminum complexes [**B**] with heteroatom-substituted carbonyl compounds without releasing the halogen atom (X) [6-8]. Here we wish to highlight the new aspect of R_2AlCl by showing the synthetic and spectroscopic evidence for the implication of such unfamiliar chelate formation in the R_2AlCl-promoted reduction of alkoxycarbonyl substrates.

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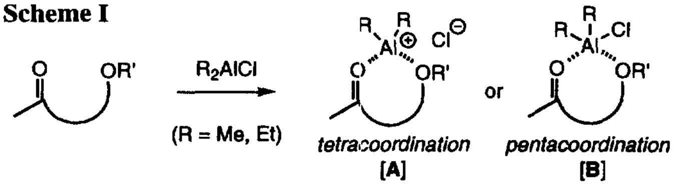
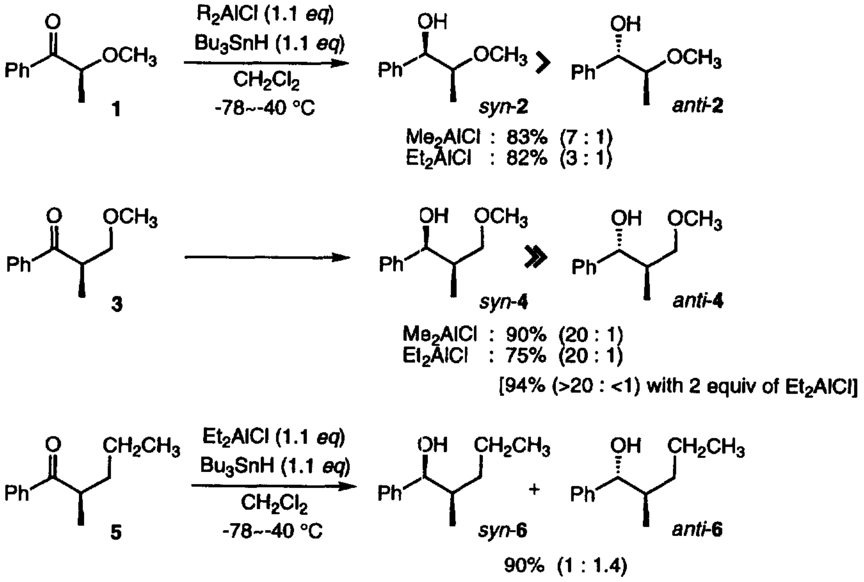
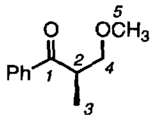
Scheme I



Examination was focused on the stereoselective reduction of alkoxycarbonyl compounds. Initial reaction of α-methoxypropiophenone (**1**) and Me_2AlCl (1.1 equiv) and subsequent treatment with Bu_3SnH (1.1 equiv) in CH_2Cl_2 at -78~-40 °C for 1.5 h gave rise to the corresponding *sec*-alcohol **2** in 83% yield with *syn*/*anti* ratio of 7:1. Use of Et_2AlCl as a promotor also afforded *syn*-**2** preferentially in 82% yield. β-Methoxy ketone **3** can be reduced in a similar manner, which exhibited excellent diastereoselectivities. It is noteworthy that the reaction of **3** proceeded with the comparable reactivity and selectivity using 2 equiv of Et_2AlCl and the total lack of diastereoselectivity was observed in the reduction of a carbon analogue of **3**, 2-methyl-1-phenylpentan-1-one (**5**) by Et_2AlCl (1.1 equiv)/Bu_3SnH system.



Although these results indicate that the stereochemical outcome of the reduction was governed by the chelate formation, it was still not clear whether a conventional tetracoordinate complex of type [**A**] or pentacoordinate [**B**] was operative. Therefore, we set out to take low temperature ^{13}C NMR spectroscopy of several Et_2AlCl complexes. The original signal of carbonyl carbon C-1 in β-methoxy ketone **3** occurred at δ 202.84, and the signals of ethereal carbons C-4 and C-5 appeared at δ 74.63 and 58.78, respectively. When **3** was complexed with Et_2AlCl in a 1:1 molar ratio in CD_2Cl_2 at -50 °C, a single set of peaks for each carbon of **3** was detected by ^{13}C NMR analysis at -50 °C and a downfield shift of carbonyl carbon C-1 as well as ethereal carbons C-4 and C-5 was observed at δ 209.16, 75.18 and 59.86, respectively. It should be added that the carbonyl peak of the 1:1 2-methyl-1-phenylpentan-1-one (**7**)/Et_2AlCl complex [**E**] appeared at δ 214.19 (δ 204.55 for free **7**) and the ethereal carbon peaks of the methyl 3-phenypropyl ether (**8**)/Et_2AlCl complex [**F**] occurred at δ 75.14 and 59.36 (δ 71.70 and 58.39 for free **8**) under similar analytical conditions. However, addition of β-methoxy ketone **3** to 2 *equiv* of Et_2AlCl in CD_2Cl_2 at -50 °C showed the signal of carbonyl carbon C-1 at δ 217.63, and the signals of ethereal carbons C-4 and C-5 at δ 76.39 and 63.76, respectively. The observed significant downfield shift can be accounted for by the formation of a six-membered tetracoordinate complex of type [**D**] with cationic aluminum species which could be more Lewis acidic than Et_2AlCl itself. Consequently, the ^{13}C NMR analysis suggests the intervention of pentacoordinate chelate complex [**C**] in the present R_2AlCl-promoted reduction of alkoxycarbonyl compounds as long as 1 equiv of R_2AlCl is used, while employment of 2 equiv of R_2AlCl results in the *in situ* production of a cationic aluminum center to be chelated as discussed by Evans *et al.* [9] in their studies of asymmetric Diels-Alder cycloaddition reactions utilizing chiral 2-oxazolidones [10].



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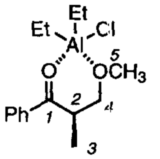
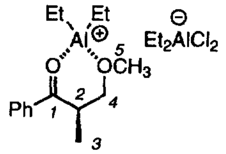
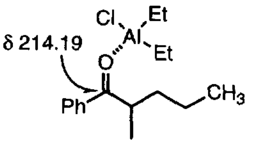


complex [**C**]

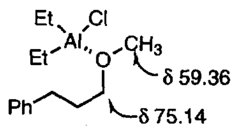


complex [**D**]

CMR Data	C-1	C-2	C-3	C-4	C-5
free **3**	δ 202.84	δ 40.58	δ 14.48	δ 74.63	δ 58.78
3 + Et_2AlCl	δ 209.16	δ 40.99	δ 14.72	δ 75.18	δ 59.86
3 + $2Et_2AlCl$	δ 217.63	δ 40.42	δ 16.89	δ 76.39	δ 63.76



7/Et_2AlCl complex [**E**]



8/Et_2AlCl complex [**F**]

Acknowledgments

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