

Double Coordination and Activation Ability of Methylalumoxane (MAO) for Hetero Functionality: Pivotal Role as Polymerization Cocatalyst

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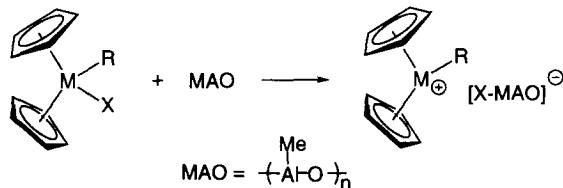
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Abstract: A new insight in the crucial role of methylalumoxane (MAO) as polymerization cocatalyst has been demonstrated by using typical carbonyl reduction and electrophilic alkylation by comparison with various MAO analogues, $(\text{Me}_2\text{Al})_2\text{O}$, $\text{MeAl}(\text{OPr}^i)_2$, and $\text{Me}_2\text{AlOPr}^i$. Furthermore, the high ligand-abstraction ability of MAO for a zirconocene complex is evaluated by the allylzirconation of internal alkyne, where MAO was found to be more satisfactory as cocatalyst than $(\text{Me}_2\text{Al})_2\text{O}$ and Me_3Al in terms of reactivity.

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Since the pioneering work of olefin polymerizations with homogeneous metallocene catalysts (*i.e.*, Kaminsky catalysts) in selective polymer synthesis by Kaminsky *et. al.*,^{1,2} a variety of metallocene complexes have been elaborated for this purpose.³ In all of these, methylalumoxane (MAO) has been extensively utilized as cocatalyst to generate highly active, cationic olefin polymerization catalysts.⁴ This cocatalyst is now indispensable and recognized to play a pivotal role as a highly efficient ligand abstractor from metallocene complexes. The corresponding higher alkyl analogues such as ethylalumoxane are reported to be less effective. Why is MAO so effective as cocatalyst for various olefin polymerizations compared to other organoaluminum compounds? This question has long been cloaked in darkness. We here wish to report new insight to this long-standing problem utilizing our recently developed bidentate Lewis acid chemistry.⁵



First, we examined the reactivity of MAO for typical carbonyl reduction and electrophilic alkylation by comparison with $\text{MeAl}(\text{OPr}^i)_2$ as monomeric MAO analogue, and the selected results are shown in Table I. Complexation of acetophenone with MAO (1 equiv in Al-unit)⁶ in toluene/CH₂Cl₂ and subsequent treatment of Bu₃SnH (1.1 equiv) at -78 °C for 3 h afforded α -phenethyl alcohol in 35% yield (entry 1). Use of 2 equiv (in Al-unit) of MAO further enhanced the yield (70%) of α -phenethyl alcohol (entry 2). In marked contrast, however, treatment of this ketone with $\text{MeAl}(\text{OPr}^i)_2$ (1~2 equiv) under

otherwise similar reduction conditions gave none of the reduction product (entry 3). These results imply the importance of the Al-O-Al unit for activation of the ketone carbonyl. More interesting results were obtained in the reduction of acetophenone with a series of other methylaluminum reagents. Thus, $(\text{Me}_2\text{Al})_2\text{O}$ exhibited higher reactivity than MAO (entry 5).⁷ Notably, the activation mode of $(\text{Me}_2\text{Al})_2\text{O}$ is superior to that of the parent Me_3Al (entry 5 vs. 4). The ethyl analogue, $(\text{Et}_2\text{Al})_2\text{O}$ somewhat reduced the reactivity (entry 7). We also carried out the electrophilic alkylation of isobutyrophenone trimethylsilyl enol ether (**1**) with benzhydryl chloride producing α -alkylated ketone **2** (entries 8-14).⁸ In the case of dialkylaluminum derivatives, simple alkylation of benzhydryl chloride giving Ph_2CHR **3** ($\text{R} = \text{Me, Et}$) was found to be a serious side-reaction (entries 11, 12, and 14). Hence, MAO seems to be an appropriate catalyst for such electrophilic alkylation in terms of both its electrophilic and nucleophilic character.

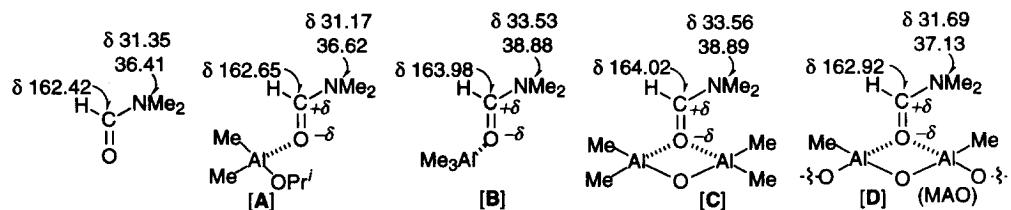
Table I. Evaluation of Various Organoaluminum Reagents for Carbonyl Reduction and Electrophilic Alkylation^a

entry	Al reagent (equiv)	reaction condition (°C, h)	% yield ^b
	$\text{Ph}-\overset{\text{H}}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$	1) Al reagent CH_2Cl_2	$\text{Ph}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{CH}_3$
		2) Bu_3SnH	
1	MAO (1 in Al-unit)	-78, 3	35 ^c [30] ^e
2	MAO (2 in Al-unit)	-78, 3	70 ^c [61] ^e
3	$\text{MeAl}(\text{OPr})_2$ (1~2)	-78, 3	~0
4	Me_3Al (1)	-78, 3	42
5	$(\text{Me}_2\text{Al})_2\text{O}$ (1)	-78, 3	82
6	$\text{Me}_2\text{AlOPr}^i$ (2)	-78, 3	~0
7	$(\text{Et}_2\text{Al})_2\text{O}$ (1)	-78, 3	39
8	MAO (1 in Al-unit)	-45, 0.5	43 ^c (11) ^d [40 (2) ^d] ^e
9	MAO (2 in Al-unit)	-45, 0.5	73 ^c (18) ^d [69 (4) ^d] ^e
10	$\text{MeAl}(\text{OPr})_2$ (1~2)	-45, 0.5	~0
11	Me_3Al (1)	-45, 0.5	40 (33) ^d
12	$(\text{Me}_2\text{Al})_2\text{O}$ (1)	-45, 0.5	59 (30) ^d
13	$\text{Me}_2\text{AlOPr}^i$ (2)	-45, 0.5	~0
14	$(\text{Et}_2\text{Al})_2\text{O}$ (1)	-45, 0.5	7 (70) ^d

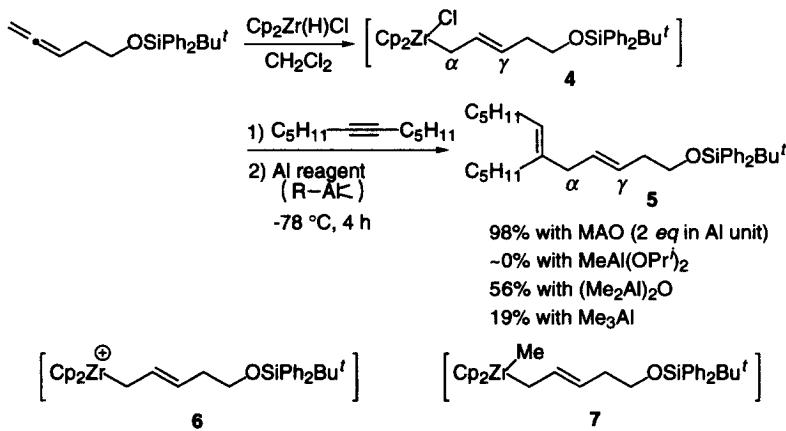
^a Carbonyl reduction and electrophilic alkylation were carried out with various Al reagents under the given reaction conditions ^b Isolated yield. ^c Use of MAO with the 24% Me_3Al content (available from Tosoh Akzo Corporation). See note 6. ^d Yields of simple alkylation products **3**. ^e Use of MAO (<1% of the Me_3Al content), which was prepared by vigorous treatment of Me_3Al in toluene with H_2O (1 equiv).

Based on these experimental data, the high reactivity of the Al-O-Al moiety is ascribed to the eminent simultaneous coordination to a carbonyl oxygen and alkyl chloride, thereby allowing the double

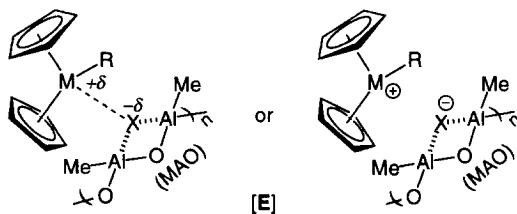
activation of such hetero functionality with the Al-O-Al unit. Convincing evidence was obtained by low-temperature ^{13}C NMR spectroscopy using DMF as a carbonyl substrate. Thus, the 75 MHz ^{13}C NMR measurement of the 1:1 $\text{Me}_2\text{AlOPr}^i$ -DMF complex (**A**) in CDCl_3 at -50 °C showed that the original signal of DMF carbonyl at δ 162.42 shifted only slightly to δ 162.65.⁹ This result suggests the feeble Lewis acidity of $\text{Me}_2\text{AlOPr}^i$. In contrast, Me_3Al showed higher Lewis acidity as observed by the downfield shift for the DMF carbonyl (δ 163.98) in the 1:1 Me_3Al -DMF complex (**B**). The 1:1 $(\text{Me}_2\text{Al})_2\text{O}$ -DMF chelation complex (**C**) under similar conditions undergoes a downfield shift for the DMF carbonyl (δ 164.02), implying the strong electrophilic activation of the DMF carbonyl by intervention of the double coordination complex (**C**).¹⁰ MAO, $(\text{MeAlO})_n$, showed moderate coordination ability (δ 162.92) in (**D**) compared to $(\text{Me}_2\text{Al})_2\text{O}$ and Me_3Al . A similar tendency is observed in the signals of DMF *N,N*-dimethyl groups among these methylaluminum reagents.



Recently, Suzuki and coworkers reported the regioselective allylzirconation of terminal alkynes in the presence of MAO in high yields.^{11,12} We have examined the ligand-abstraction ability of MAO and its analogues for zirconocene complex **4** by the following allylzirconation of internal alkyne, giving the allylation product **5**. Here again, MAO was found to be most satisfactory as cocatalyst in terms of reactivity.¹³ $(Me_2Al)_2O$ showed lower reactivity than MAO. With Me_3Al , the key zirconocene cation complex **6** is readily susceptible to the facile nucleophilic alkylation producing **7**, which, compared to **4**, is not a good precursor for regenerating this complex.¹⁴



A plausible structure of homogeneous metallocene catalysts would therefore be described as shown in (E), where the bidentate Al-O-Al unit of MAO is crucially important for activating a metallocene ligand X effectively. The new findings disclosed herein provide valuable information on the rational design of new and highly efficient polymer catalysts.¹⁵



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- (9) Attempted addition of one more equiv of $\text{Me}_2\text{AlOPr}^i$ to the complex (A) did not cause any noticeable shift for the DMF carbonyl.
- (10) The 1:2 or 2:1 $(\text{Me}_2\text{Al})_2\text{O}$ -DMF mixture exhibited the following ^{13}C NMR chemical shifts for DMF: δ 163.51 ($\text{C}=\text{O}$), 32.73 and 38.13 (Me_2N) in the 1:2 mixture; δ 164.03 ($\text{C}=\text{O}$), 33.54 and 38.87 (Me_2N) in the 2:1 mixture. Hence, two DMF carbonyls coordinate separately to two aluminum centers of $(\text{Me}_2\text{Al})_2\text{O}$ in the 1:2 mixture, while the double coordination complex (C) still predominates in the 2:1 mixture.
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- (13) A similar tendency is also observed with several MAO analogues by Suzuki *et al.* (Yamanoi, S.; Matsumoto, T.; Suzuki, K., private communication).
- (14) Compound 7 was prepared independently by treatment of 4 with MeLi in ether and subsequent removal of ether/ CH_2Cl_2 solvents by vacuum evaporation. Attempted reaction of the compound 7, thus prepared, with 6-dodecyne and MAO (2 equiv in Al unit) under similar conditions gave allylation product 5 in 47% yield.
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