

Structural Characterization of Manganese(II) Compounds with Methylalumoxane (MAO) and AlMe₂ Units

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Summary: Manganese complexes with AlMe₃ have been synthesized with the aim of investigating Mn(II) active centers in catalytic ethylene polymerization. Reactions of [Mn₄(μ-Cl)Cl₃(μ-OCH₂CH₂OCH₃)₄(HOCH₂CH₂OCH₃)₃]₂ (**1**) with an excess of AlMe₃ at room temperature in toluene give the heterometallic cage [Mn₃Al(μ₃-OCH₂CH₂OCH₃)(μ-Cl)₃(μ-OCH₂CH₂OCH₃)₂(thf)₂(Me)₂Cl] (**2**; 30%). A similar reaction carried out under reflux led to the formation of the methylalumoxane species [MnAl₃(μ₃-O)(μ-OCH₂CH₂OCH₃)₃(Me)₆] (**3**; 51%). X-ray diffraction studies have shown complexes **2** and **3** to contain AlMe₂⁺ and [Al₃(μ₃-O)(Me)₆]⁺ moieties capped by [Mn₃(μ₃-OCH₂CH₂OCH₃)(μ-Cl)₃(μ-OCH₂CH₂OCH₃)₂(thf)₂Cl]⁻ and [Mn-(μ-OCH₂CH₂OCH₃)₃]⁻ macrounits, respectively. The tendency of a manganese center to exchange aluminum methyl groups in **2** and **3** is strongly reduced by alkoxide ligands.

Introduction

In the past 10 years, efforts to develop alternatives to group IV metallocene single-site olefin polymerization catalysts have resulted in major breakthroughs.^{1,2} An important result was the discovery that pentacoordinated iron(II) or cobalt(II) derivatives containing bis(arylimino)pyridine ligands efficiently polymerize ethylene in the presence of methylalumoxane (MAO).³

Comprehensive contributions to this topic have been provided by Hlatky,^{3a} Gibson,^{3b} and Marks.^{3c} Gambarotta and co-workers⁴ recently reported an approach to Mn(II) complexes and compared their performance in olefin polymerization with that of Fe(II) and Ni(II) catalysts. In this approach, they showed that the compound [MnCl₂L₂] (L = [2,6-(i-Pr)PhN=C(Me)]₂-(C₅H₃N)), in contrast to its iron and cobalt analogues, does not exhibit ethylene polymerization activity upon activation with methylalumoxane (MAO). Also, the complexes Mn(acac)₃, Cp₂Mn, and Mn(salen)Cl in combination with MAO yielded only trace amounts of polymers.⁵ Generally, several orders of magnitude lower activities are observed for Mn(II) species bearing ligands which give highly active catalysts with other late transition metals.

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Recently we described the synthesis and structural characterization of the compound [Mn₄(μ-Cl)Cl₃(OCH₂CH₂OCH₃)₄(HOCH₂CH₂OCH₃)₃]₂ (**1**), composed of two Mn₄ cubane units linked together by two μ-Cl ions (Scheme 1).⁶ We have been exploring the use of **1** for the preparation of the new manganese compounds [Mn₃Al(μ₃-OCH₂CH₂OCH₃)(μ-Cl)₃(μ-OCH₂CH₂OCH₃)₂(thf)₂(Me)₂Cl] (**2**) and [MnAl₃(μ₃-O)(μ-OCH₂CH₂OCH₃)₃(Me)₆] (**3**), and here we report the details of their crystal structures.

Results and Discussion

When **1** was reacted at room temperature with an excess of AlMe₃ in toluene, **2** was obtained in 30% yield. A similar reaction carried out under reflux led to the formation of **3** in 51% yield. However, direct treatment of MnCl₂ with AlMe₃ in toluene gave an oily product, purification of which was demanding and gave a problematic result. **2** and **3** are sensitive toward moisture but can be stored as solids at room temperature under dinitrogen for weeks. They are insoluble in aliphatic and aromatic hydrocarbons but are soluble in thf and CH₂Cl₂. Preliminary tests of the catalytic properties of **2** and **3** for ethylene polymerization have shown no activity. This result agrees with the absence of a Mn–CH₃ bond in **2** and **3**.

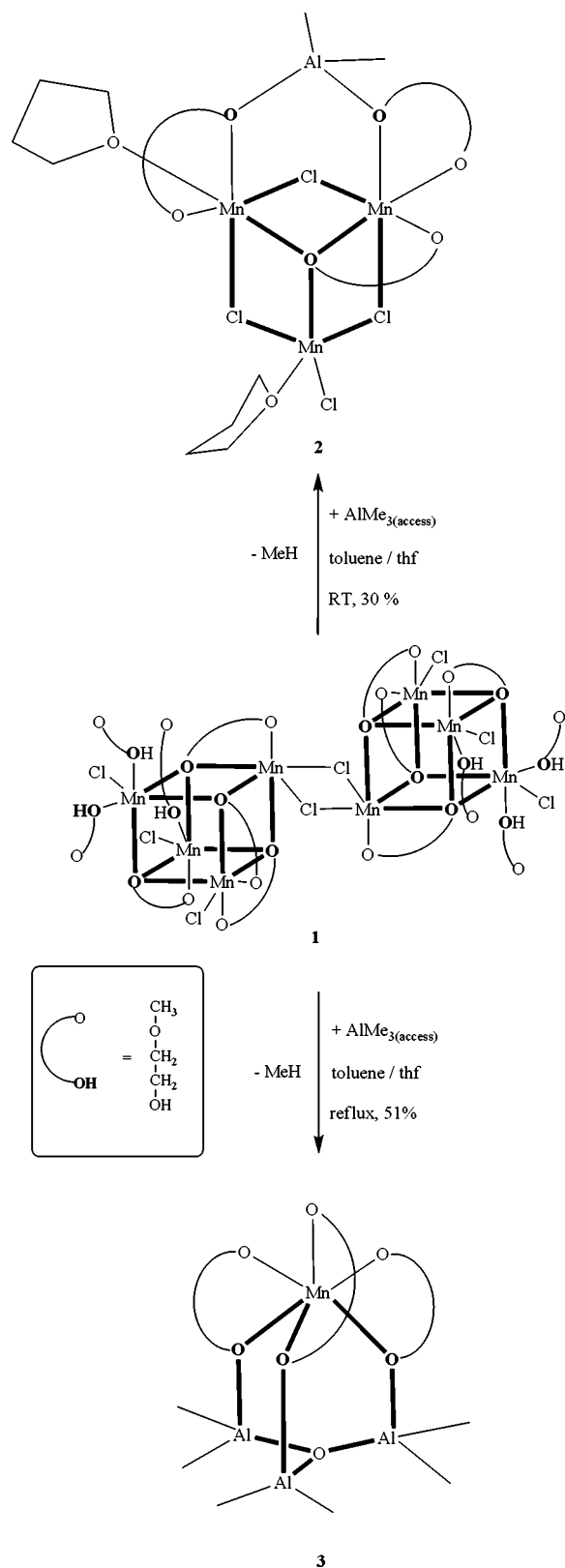
Complex **2** (Figure 1) contains two types of manganese(II) centers, five-coordinate (Mn1) and six-coordinate (Mn2, Mn3), and one four-coordinate aluminum atom (Al1). Each of the six-coordinate Mn atoms is surrounded by one μ₃-O alkoxo, one μ₂-O alkoxo, two μ₂-Cl atoms, and two ether O atoms of the coordinated ligand molecule. The coordination sphere of the five-coordinated Mn atom is composed of two μ₂-Cl, one terminal Cl, one μ₃-O alkoxo, and one O atom of the coordinated thf molecule. The three Mn(II) moieties are held together by μ₃-OCH₂CH₂OCH₃ alkoxo oxygen atom to form a triangular Mn₃(μ₃-O) core. The bond lengths of Mn–O alkoxo range from 2.138(2) Å at the octahedral Mn2 atom to 2.186(2) Å at the five-coordinated (trigonal-bipyramidal) Mn1 atom. The Mn···Mn distances in **2** are in the range 3.274(2)–3.388(2) Å and compare well with relevant distances (3.154(1)–3.372(1) Å) reported for other divalent Mn complexes.⁷

The formation of the AlMe₂ moiety seems to be a result of the interaction of AlMe₃ with protons of coordinated alcohol ligands to manganese atoms in **1**. The interaction proceeds with liberation of methane and structural reorganization of **1** followed by substitution of one Mn(II) atom in each cubane unit by an AlMe₂ moiety (Scheme 1).

The four-coordinated aluminum atom in **3** (Figure 2) is surrounded by two methyl groups and one μ₃-O oxo and one

(6) For the synthetic details of **1**, see the Supporting Information.

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Scheme 1. Possible Mechanism for the Formation of **2** and **3**

μ -O alkoxy oxygen atom of the $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$ unit. Three AlMe_2 moieties are held together by $\mu_3\text{-O}$ oxo oxygen atom to form the methylalumoxane cation $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$. In this unit the Al–O and Al–C bond distances are in accordance with those found in $[\text{MgAl}_3(\mu_3\text{-O})(\text{thffo})_3(\text{Me})_6]$ (thffo = 2-tetrahydrofurfuroxide) species.⁸ The six-coordinate sphere of the manganese Mn(II) atom in the $[\text{Mn}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_3]^-$ moiety of **3** is formed by three ether and three alkoxy oxygen atoms of

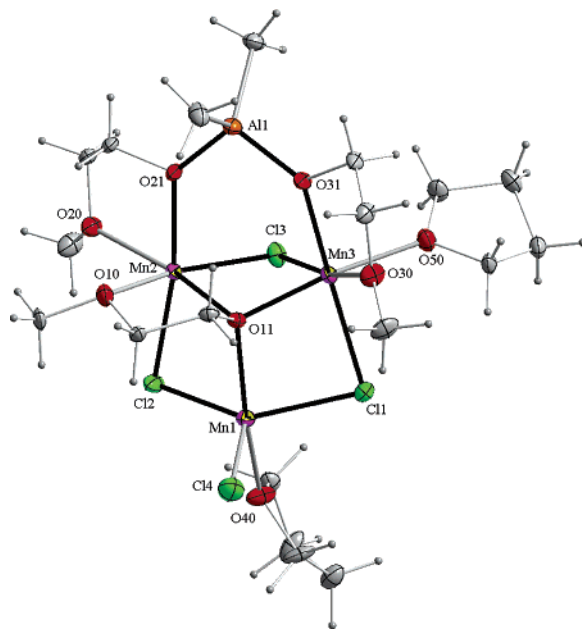


Figure 1. Molecular structure of **2** (ORTEP plot, thermal ellipsoids set at the 50% probability level). Selected bond distances (Å): Mn1–Cl1 = 2.474(2), Mn1–Cl2 = 2.498(2), Mn1–Cl4 = 2.334(2), Mn2–Cl2 = 2.490(2), Mn2–Cl3 = 2.503(2), Mn3–Cl3 = 2.493(1), Mn3–Cl1 = 2.532(2), Mn1–O11 = 2.186(2), Mn2–O11 = 2.160(2), Mn2–O21 = 2.138(2), Mn3–O31 = 2.151(2), Mn3–O11 = 2.167(2), Mn1–O40 = 2.202(2), Mn2–O20 = 2.218(2), Mn3–O50 = 2.187(2), Mn3–O30 = 2.255(2), Al1–O21 = 1.801(2), Al1–O31 = 1.806(2), Al1–Cl1 = 1.972(3), Al1–Cl2 = 1.972(3), Mn1···Mn2 = 3.374(2), Mn1···Mn3 = 3.388(2), Mn2···Mn3 = 3.274(2), Mn2···Mn1 = 3.374(2), Mn2···Al1 = 3.602(2), Mn3···Al1 = 3.689(2).

the $\text{OCH}_2\text{CH}_2\text{OCH}_3$ ligands. The formation of the manganese complex **3** containing an $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$ unit is unusual. We suppose that the $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$ unit is formed by the addition of an AlMe_2 moiety to the oxygen atom in $\text{Me}_2\text{-AlOAlMe}_2$.⁹ This is reminiscent of the hydrolysis of AlMe_3 , which forms the methylalumoxane (MAO) polymerization cocatalyst.¹⁰

The tendency of the alkylaluminum AlMe_2 moiety in **2** to exchange methyl groups with a manganese chloride is strongly reduced by alkoxy ligands. Further investigation showed that, even with an excess of AlMe_3 , the manganese chloride atoms remained untouched. Similarly, in **3** the methylalumoxane moiety $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$ does not provide an alkyl function to the manganese atom. This is in contrast to our earlier observations. During the reaction of the methylalumoxane moiety with Cp_2ZrCl_2 the methyl group of $[\text{Al}_3(\mu_3\text{-O})(\text{Me})_6]^+$ is replaced by a ligand alkoxy oxygen atom, providing alkyl functions in return.¹¹ The described structures of compounds **2**

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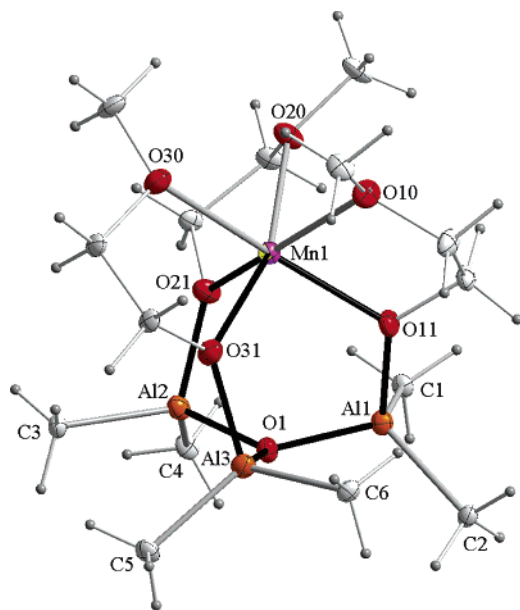


Figure 2. Molecular structure of **3** (ORTEP plot, thermal ellipsoids set at the 50% probability level). Selected bond distances (Å): Mn1–O11 = 2.117(2), Mn1–O21 = 2.119(2), Mn1–O31 = 2.111(2), Mn1–O20 = 2.242(2), Mn1–O30 = 2.257(2), Mn1–O10 = 2.258(2), Al1–O11 = 1.811(2), Al2–O21 = 1.815(2), Al3–O31 = 1.815(2), Al1–O1 = 1.828(2), Al2–O1 = 1.830(2), Al3–O1 = 1.829(2), Al1–C1 = 1.974(2), Al1–C2 = 1.982(2), Al2–C4 = 1.976(2), Al2–C3 = 1.978(2), Al3–C5 = 1.972(2), Al3–C6 = 1.978(2), Mn1···Al3 = 3.3471(11), Mn1···Al1 = 3.3536(9), Mn1···Al2 = 3.3604(11), Al1···Al3 = 3.1163(10), Al1···Al2 = 3.1323(10), Al1···Mn1 = 3.3536(9), Al2···Al1 = 3.1323(10), Al2···Al3 = 3.1425(10), Al2···Mn1 = 3.3604(11), Al3···Al1 = 3.1163(10), Al3···Al2 = 3.1425(10), Al3···Mn1 = 3.3471(11).

and **3** are important to understand the poor manganese catalyst performance. Further studies are necessary to find preferred geometries and specific ligands able to create an active manganese site.

Experimental Section

General Procedures. All experiments were performed under a dry dinitrogen atmosphere using Schlenk-type glassware. Solvents were dried over sodium wire and then distilled from the appropriate drying reagent (sodium benzophenone ketyl for thf, calcium hydride for CH_2Cl_2 , sodium for *n*-hexane and toluene) under dinitrogen prior to use. Starting materials were obtained from commercial suppliers and used as received, except as specifically noted. Microanalyses were conducted by an ASA-1 (GDR, Karl-Zeiss-Jena) instrument (in house).

[Mn₃Al(μ_3 -OCH₂CH₂OCH₃)(OCH₂CH₂OCH₃)₂(thf)₂(Me)₂-Cl₄] (2**).** A Schlenk flask was charged with **1** (3.00 g, 1.68 mmol), toluene (60 mL), and thf (20 mL). The clear solution was stirred vigorously at -20°C , and 25.8 mL of AlMe₃ (2.0 M solution in toluene, 51.6 mmol) was added dropwise. The mixture was warmed to room temperature and concentrated to 40 mL. The resultant precipitate was filtered off, and the filtrate was concentrated again to 10 mL. Next, a mixture of CH_2Cl_2 and thf (1:1) was added

Table 1. Crystallographic Data for **2 and **3****

	2	3
CCDC no.	299461	299462
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
<i>a</i> (Å)	14.271(4)	8.995(3)
<i>b</i> (Å)	15.302(5)	9.550(3)
<i>c</i> (Å)	14.920(5)	15.102(5)
α (deg)	90	90.09(2)
β (deg)	91.69(2)	90.27(2)
γ (deg)	90	111.26(2)
<i>V</i> (Å ³)	3256.7(18)	1100.6(7)
<i>Z</i>	4	2
density (g cm ⁻³)	1.495	1.292
μ (Mo K α) (mm ⁻¹)	1.536	0.688
<i>T</i> (K)	100(2)	100(2)
no. of rflns (measd)	21 678	14 091
no. of rflns (indep)	7023	4952
no. of rflns (obsd)	5119	4545
no. of params	321	244
R1 (<i>I</i> > 2 σ (<i>I</i>))	0.0442	0.0326
wR2 (all data)	0.0968	0.0741

dropwise until the solid dissolved. The clear solution was then layered with hexanes (10 mL). After 2 weeks crystals of **2** (1.94 g, 30%) were taken directly from the solution. Anal. Calcd for C₁₅H₃₉Al₃MnO₇: H, 8.41; C, 38.55; Mn, 11.76. Found: H, 8.17; C, 38.83; Mn, 11.94.

[MnAl₃(μ_3 -O)(OCH₂CH₂OCH₃)₃(Me)₆] (3**).** A Schlenk flask was charged with **1** (1.54 g, 0.86 mmol), toluene (30 mL), and thf (50 mL). The clear solution was stirred vigorously at 16°C , and 5 mL of AlMe₃ (2.0 M solution in toluene, 10.0 mmol) was added dropwise. The mixture was warmed and refluxed for 0.5 h. The resulting solution was layered with hexanes (20 mL) and left for crystallization. After 2 weeks pink crystals of **3** (0.86 g, 1.17 mmol, 51%) formed. Anal. Calcd for C₁₉H₄₃AlCl₄Mn₃O₈: H, 5.91; C, 31.13; Cl, 19.34; Mn, 22.48. Found: H, 5.81; C, 31.01; Cl, 19.86; Mn, 22.73.

Crystal Structure Analysis. Preliminary examination and intensity data collections were carried out on a KUMA KM4 κ -axis diffractometer with graphite-monochromated Mo K α radiation and with a CCD camera. All data were corrected for Lorentz, polarization, and absorption effects. The structures were solved by direct methods and refined by full-matrix least-squares methods on all F^2 data using the SHELXTL (version 5.10) program. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode. Experimental details are given in Table 1, and full data tables are included in the Supporting Information. Crystallographic data for **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are given in Table 1. Copies of the data can be obtained free of charge on application to the CCDC, 11 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.), +44(1123)336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Text, figures, and tables giving experimental and crystallographic details and CIF files giving crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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