COMMUNICATION

Methylmethacrylate complexes of sterically hindered aluminum aryloxides: activation of methacrylic esters

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Abstract—The interaction of $AlR_2(BHT)(OEt_2)$ and $AlMe(BHT)_2$ with methylmethacrylate (MMA) leads to the formation of the Lewis acid–base complexes $AlR_2(BHT)(MMA)$ [R = Me (**1**), Et (**2**)] and $AlMe(BHT)_2(MMA)$ (**3**), respectively. The molecular structure of **1** has been determined by X-ray crystallography. The decrease in the C=O and C=C stretching frequencies in the IR spectrum, and downfield shift in the ^{13}C NMR spectrum of the α- and γ-carbons of the MMA, when compared to free MMA, is presented with respect to the activator ability of sterically crowded aryloxide compounds of aluminum to the aluminum–porphyrin catalyzed (Inoue) polymerization of MMA. © 1997 Elsevier Science Ltd

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Aluminum porphyrin compounds have been shown to initiate the living polymerization of methacrylic esters (e.g., methylmethacrylate, MMA, **I**) [1]. The resulting polymethacrylate polymers (i.e., poly-methylmethacrylate, PMMA, **II**) having well controlled molecular weights and narrow molecular weight distributions.

(I)   (II)
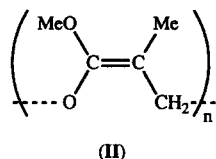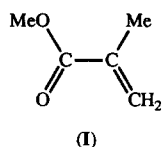
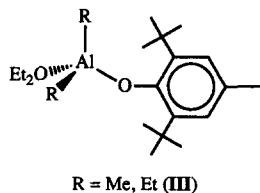The reaction is greatly accelerated in the presence of sterically hindered aluminum Lewis acids, in par-

ticular $AlMe(BHT)_2$ [2,3]. The generally accepted role of the Lewis acidic sterically crowded phenoxide compound in the 'Inoue polymerization' reaction is to activate (via coordination) the monomer towards nucleophilic attack of the anionic living polymer [1].

We have previously shown that the complexation of organic carbonyls to sterically crowded aryloxide compounds of aluminum results in making the α-carbon susceptible to nucleophilic attack [4]. For conjugated ketones, such as cyclohexenone, nucleophilic attack is specific to the γ- rather than α-carbon [5,6]. It is expected that a similar effect occurs for methacrylic esters, such that their complexation to a sterically crowded aluminum aryloxide will result in the activation of the γ-carbon towards nucleophilic attack.

The interaction of $AlR_2(BHT)(OEt_2)$ (**III**) [7] and $AlMe(BHT)_2$ [8] with methylmethacrylate (MMA) in

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pentane solution leads to the formation of the Lewis acid–base complexes $AlR_2(BHT)(MMA)$ [R = Me (1), Et (2)] and $AlMe(BHT)_2(MMA)$ (3), respectively. Compounds 1–3 have been characterized by ^1H and ^{13}C NMR, and IR spectroscopy.† In addition, the molecular structure of 1 has been confirmed by X-ray crystallography‡ and is shown in Fig. 1.

R = Me, Et (III)

The geometry around aluminum in compound 1 is essentially the same as observed for $AlMe_2$ (BHT)(O═CPh_2) [9], and the aryloxide Al—O distance [1.738(8) Å] is within the range previously observed for other 4-coordinate aluminum aryloxides [10]. While the Al—O bond distance to methylmethacrylate [1.867(8) Å] is within the range expected for a normal Al—O σ bond (1.8–2.0 Å) [11], it is worth noting that like other aluminum–ester interactions [1.887(6), 1.851(7) Å] [8,12], it is shorter than observed for aluminum–ketone or aluminum–aldehyde interactions [1.903(6)–1.96(1) Å] [4,9,13]. This difference is in line with the electron-donor ability of the ester's MeO substituent. Unfortunately, the relatively large e.s.d's for the bond lengths and angles within the MMA ligand preclude any meaningful comparison with crystallographically characterized examples of non-coordinated methacrylic esters. However, all bond lengths and angles are within the values reported for similar species [14].

We have previously demonstrated that the complexation of ketones to sterically crowded aryloxide compounds of aluminum results in the lowering of the ketone's LUMO energy level, which is O═C π^* in character and centered on the α-carbon (IV), making electron transfer from either Li metal or an alkyl lithium reagent favorable [6]. An alternative explanation of the effect of the aluminum Lewis acid upon the ketone assumes that the contribution of resonance form V is increased over VI, resulting in a decrease in the C═O bond order and placing a positive charge on the α-carbon, consequently activating it to nucleophilic attack. The reduction of the C═O bond strength may be seen from the shift in the IR of a ketone upon complexation (Δv = 50–130 cm^{-1}) [9].

(IV)   (V)   (VI)
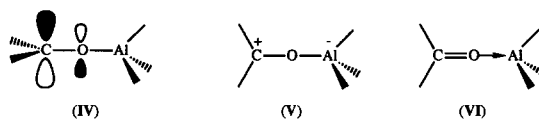
In the case of the complexation of MMA to aluminum Lewis acids (VII), there are four possible resonance forms (VII–X). Significant activation towards polymerization would be most favored in IX.
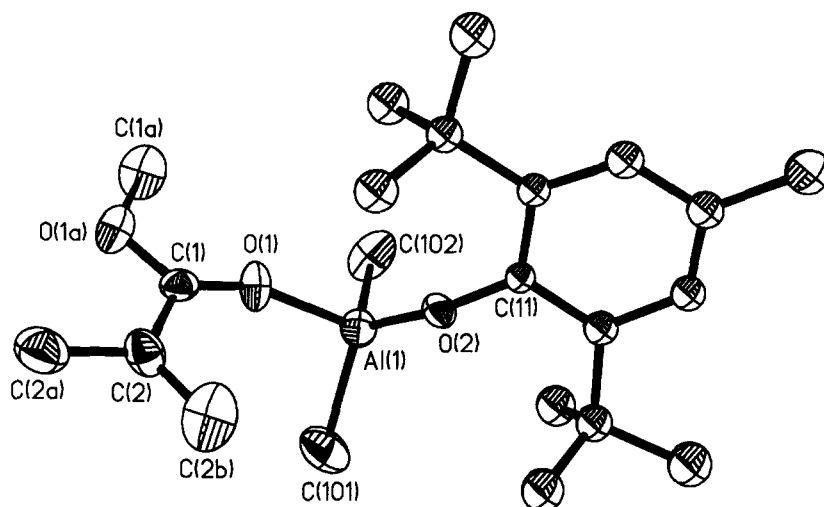
(VII)   (VIII)

(IX)   (X)
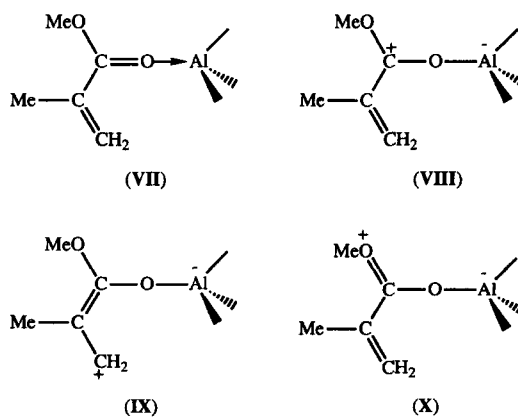
Fig. 1. Molecular structure of AlMe$_2$(BHT)(MMA). Thermal ellipsoids are shown at the 30% level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)—O(1) 1.867(8), Al(1)—O(2) 1.738(8), Al(1)—C(101) 1.98(2), Al(1)—C(102) 1.96(1), O(1)—C(1) 1.20(1), O(1a)—C(1) 1.30(1), O(1a)—C(1a) 1.45(1), C(1)—C(2) 1.52(2), C(2)—C(2a) 1.43(2), C(2)—C(2b) 1.33(2), O(1)—Al(1)—O(2) 99.9(4), O(1)—Al(1)—C(101) 100.7(5), O(1)—Al(1)—C(102) 105.5(5), O(2)—Al(1)—C(101) 118.1(5), O(2)—Al(1)—C(102) 114.0(6), C(101)—Al(1)—C(102) 115.3(7), Al(1)—O(1)—C(1) 160.7(9), Al(1)—O(2)—C(11) 150.5(7), O(1)—C(1)—O(1a) 123(1), O(1)—C(1)—C(2) 124(1), C(1)—O(1a)—C(1a) 116.2(9), C(1)—C(2)—C(2a) 118(1), C(1)—C(2)—C(2b) 118(1), C(2a)—C(2)—C(2b) 124(1).

Table 1 gives selected IR spectroscopic data for the MMA complexes 1–3. As was observed for ketones [9] the v(C=O) for MMA is shifted to lower wavenumber ($\Delta v = 63$–74 cm^{-1}) upon complexation to the aluminum. The v(C=C) stretch also shows a shift to lower wavenumber, $\Delta v = 19$–23 cm^{-1}. These shifts are consistent with both VIII and IX contributing to the overall resonance structure.

While IR spectroscopy is useful in probing changes in bond order it is insensitive to changes in formal charge, which is more closely related to the electrophilic nature of an atom center. We have previously shown that the effective increase in positive charge on the α-carbon of ketones, upon coordination to aluminum, is seen by a downfield shift of the resonance in the ^{13}C NMR spectrum ($\Delta\delta = 5$–25 ppm) [4,9]. A similar effect may be observed for MMA. As can be seen from Table 1 and Fig. 2, the ^{13}C NMR resonances of the carbonyl carbon (i.e., α-carbon

O=C), methene (γ-carbon, C=CH$_2$), and to a lesser extent the methoxide (OCH$_3$) are shifted down field (deshielded) upon coordination. In contrast the β-carbon shows an upfield shift consistent with shielding. The relative magnitude of the $\Delta\delta$ values suggests that the contributions of the resonance form is in the following order: IX > VIII > X. This is therefore consistent with the observed reactivity of the aluminum aryloxides as initiators for the polymerization of MMA.

It should be noted that the effect on MMA is greater upon complexation to AlMe(BHT)$_2$ than AlR$_2$(BHT), while the effect of R = Me versus Et is negligible. This trend is in line with the general observation that increased activation of the polymerization catalyst systems occurs in the order AlR(OR)$_3$ > AlR(OR)$_2$ > AlR$_2$(OR) [1].

Table 1. Selected IR and ^{13}C NMR spectroscopic data for aluminum–MMA compounds

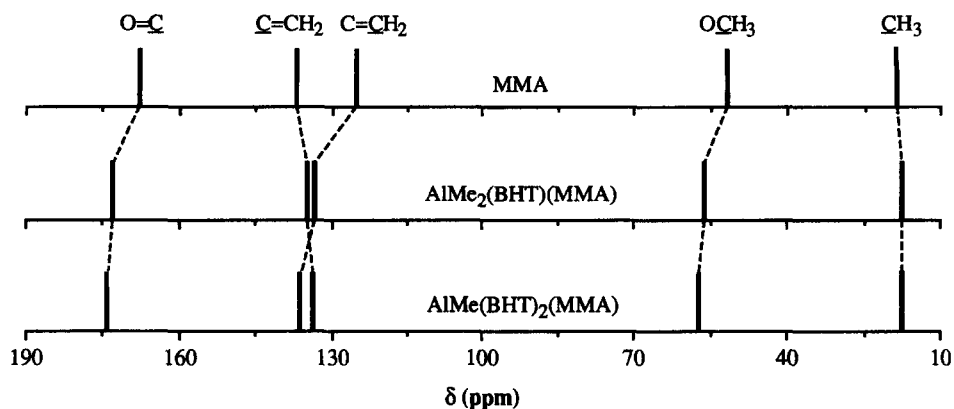| Compound	IR (cm^{-1})		^{13}C NMR (ppm)	
	v(C=O)	v(C=C)	δ(O=C)	δ(C=CH$_2$)
MMA	1724	1639	167.8	125.1
AlMe$_2$(BHT)(MMA) (1)	1661	1620	172.8	133.7
AlEt$_2$(BHT)(MMA) (2)	1660	1620	173.7	133.9
AlMe(BHT)$_2$(MMA) (3)	1650	1616	174.3	133.8

Fig. 2. Schematic representation of the changes in chemical shifts (ppm) in the ^{13}C NMR spectra of methylmethacrylate (MMA) upon complexation to AlMe₂(BHT) and AlMe(BHT)₂.

REFERENCES

1. Aida, T. and Inoue, S., *Acc. Chem. Res.*, 1996, **29**, 39.
2. (a) Kuroki, M., Watanabe, T., Aida, T. and Inoue, S., *J. Am. Chem. Soc.*, 1991, **113**, 5903. (b) Adachi, T., Sugimoto, H., Aida, T. and Inoue, S., *Macromolecules*, 1993, **26**, 1238.
3. Maruoka, K., Akakura, M. and Yamamoto, H., *Synlett*, 1995, 81.
4. Power, M. B., Bott, S. G., Atwood, J. L. and Barron, A. R., *J. Am. Chem. Soc.*, 1990, **112**, 3446.
5. Stern, A. J., Rohde, J. J. and Swenton, J. S., *J. Org. Chem.*, 1989, **54**, 4413.
6. Healy, M. D., Power, M. B. and Barron, A. R., *Coord. Chem. Rev.*, 1994, **130**, 63.
7. Healy, M. D., Power, M. B. and Barron, A. R., *J. Coord. Chem.*, 1990, **21**, 363.
8. Starowieyski, K. B., Pasynkiewicz, S. and Skowronska-Ptasinska, M., *J. Organomet. Chem.*, 1975, **90**, C43.
9. Power, M. B., Bott, S. G., Clark, D. L., Atwood, J. L. and Barron, A. R., *Organometallics*, 1990, **9**, 3086.
10. Barron, A. R., *Polyhedron*, 1995, **14**, 3197.
11. Haalan, A., in Coordination Chemistry of Aluminum, Ch. 1, Ed. G. H. Robinson, VCH, New York, (1993).
12. Shreve, A. P., Mulhaupt, R., Fultz, W., Calabrese, J., Robbins, W. and Ittel, S. D., *Organometallics*, 1988, **7**, 409.
13. Sharma, V., Simard, M. and Wuest, J. D., *J. Am. Chem. Soc.*, 1992, **114**, 7931.
14. See for example (a) Kakkonen, H. J., Pursiainen, J., Pakkanen, T. A., Ahlgrén, M. and Iiskola, E., *J. Organomet. Chem.*, 1993, **453**, 175. (b) Kolb, U., Drager, M. and Jousseaume, B., *Organometallics*, 1991, **10**, 2737. (c) Adama, R. D., Chen, L. and Huang, M., *Organometallics*, 1994, **13**, 2696.