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Towards an understanding of the conjugate addition of organolithium reagents to α,β-unsaturated ketones: the isolation and solid-state structure of a monomeric lithium aluminate with very short agostic Li···HC interactions[1]

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Abstract

Reaction of methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), **1**, with alkyllithium reagents, R′Li (R′ = Me, *n*-Bu or *t*-Bu), yields the solvent-dependent products lithium bis(2,6-di-*tert*-butyl-4-methylphenoxide)-THF complex, **2**·THF, lithium dimethylbis(2,6-di-*tert*-butyl-4-methylphenoxide)aluminate, **3**, a new type of lithium aluminate in which the lithium centre is stabilised by very short agostic Li···H(*t*-Bu) interactions, and tris(alkyl)aluminium. The observation of these products suggests an explanation for the tendency of α,β-unsaturated ketones to undergo conjugate (rather than 1,2-) addition in the presence of MAD and organolithium reagents. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aluminium; α,β-Unsaturated ketone; Conjugate addition; Lithium; Solid-state structure

1. Introduction

While the synthetic utility of organolithium reagents in 1,2-addition reactions to carbonyl groups is well established [1], it has proven less easy to use such hard nucleophiles in 1,4-conjugate additions to α,β-unsaturated ketones. Recent reports have detailed the development of new asymmetric hetero-bimetallic species [2] capable of catalytically promoting such reactions. Further work has employed the non-catalytic addition of Lewis acids such as tri-coordinate aluminium species [3], notably the sterically-crowded organoaluminium methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide), $MeAl(OR)_2$, **1**, (MAD; $R = t\text{-}Bu_2C_6H_2Me$; Scheme 1) [4,5]. Addition to this in non-polar media of an α,β-unsaturated ketone is followed, upon subsequent treatment with an organolithium reagent, by 1,4- rather than 1,2-addition. Why this is so has not been explained, other than to note that the oxygenophilic aluminium species may electrophilically activate the enone. Given this uncertainty, we have investigated the reactions between MAD and the organolithium reagents (R′ = Me, *t*-Bu and *n*-Bu). In these instances common products, LiOR, **2**, and $Me_2Al(\mu_2\text{-}OR)_2Li$, **3**, are observed *irrespective* of which organolithium is used. More generally, the isolation of **3** suggests that while the addition of R′Li to a system containing enone and an aluminium oxygenophile yields a new hetero-bimetallic species in situ, the persistent observation of a *dimethyl*aluminium moiety in **3** demonstrates that it is

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[1] Dedicated to Professor Brian Johnson on the occasion of his 60th birthday and in recognition of his outstanding and ongoing contributions to organometallic chemistry.

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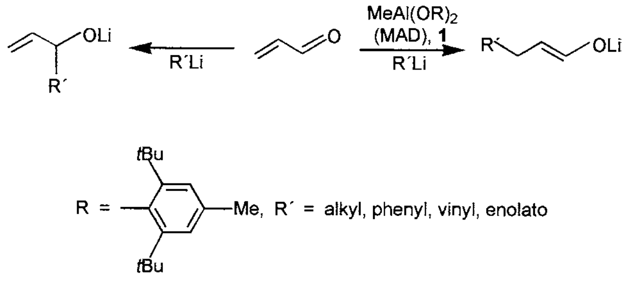


Scheme 1.

not this species which directly causes 1,4-addition to the enone. Nevertheless, an understanding of the structure of **3** and how it comes about does shed light on the probable route for conjugate addition to the enone, and, furthermore suggests that **3** does, in fact, play an indirect but crucial role in this process.

2. Results and discussion

The 1:2 reaction of trimethylaluminium with 2,6-di-*tert*-butyl-4-methylphenol in toluene at −80°C generates methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD), **1**. Its crystal structure reveals a monomer (Fig. 1 and Table 1) in which the aluminium centre is tri-coordinate by virtue of the bulky 2,6-di-*tert*-butyl-4-methylphenoxide ligands [6].

Addition of *t*-BuLi to **1** at −80°C, followed by warming to room temperature, gives a suspension which can be dissolved in two ways. Treatment with THF leads to colourless crystals which X-ray crystallography shows to be the simple dimeric [7] lithium 2,6-di-*tert*-butyl-4-methylphenoxide-THF complex, **2** · THF (Fig. 2 and Table 2).

Dissolution of the suspension resulting from the reaction of **1** with *t*-BuLi can alternatively be effected by the dropwise addition of toluene, storage at room temperature affording lithium dimethylbis(2,6-di-*tert*-butyl-4-methylphenoxide)aluminate, **3**. Retention of the aluminium centre is demonstrated by ^{1}H-NMR spectroscopy in [$^2H_8$]toluene, which shows a singlet at −0.45 ppm, characteristic of an aluminium-attached methyl group. Intriguingly, however, integrals show a 1:1 ratio of 2,6-di-*tert*-butyl-4-methylphenolate to aluminium-attached methyl. Unsurprisingly, the same result is observed if MeLi is employed in place of *t*-BuLi, but the fact that the reaction undergone by *t*-BuLi is not an anomaly is established by the isolation of **3** if *n*-BuLi is employed instead. That **3** contains a dimethylated aluminium centre is borne out by X-ray crystallography which shows it to be the monomeric ate complex lithium dimethylbis(2,6-di-*tert*-butyl-4-methylphenoxy)aluminate (Fig. 3). At the core of the structure is an AlO_2Li four-membered ring (Al–O1 = 1.8457(17) Å, Al–O2 = 1.8425(17) Å, Li–O1 = 1.848(5) Å, Li–O2 = 1.888(4) Å). Although this motif has been observed before, in all but one of these previous five

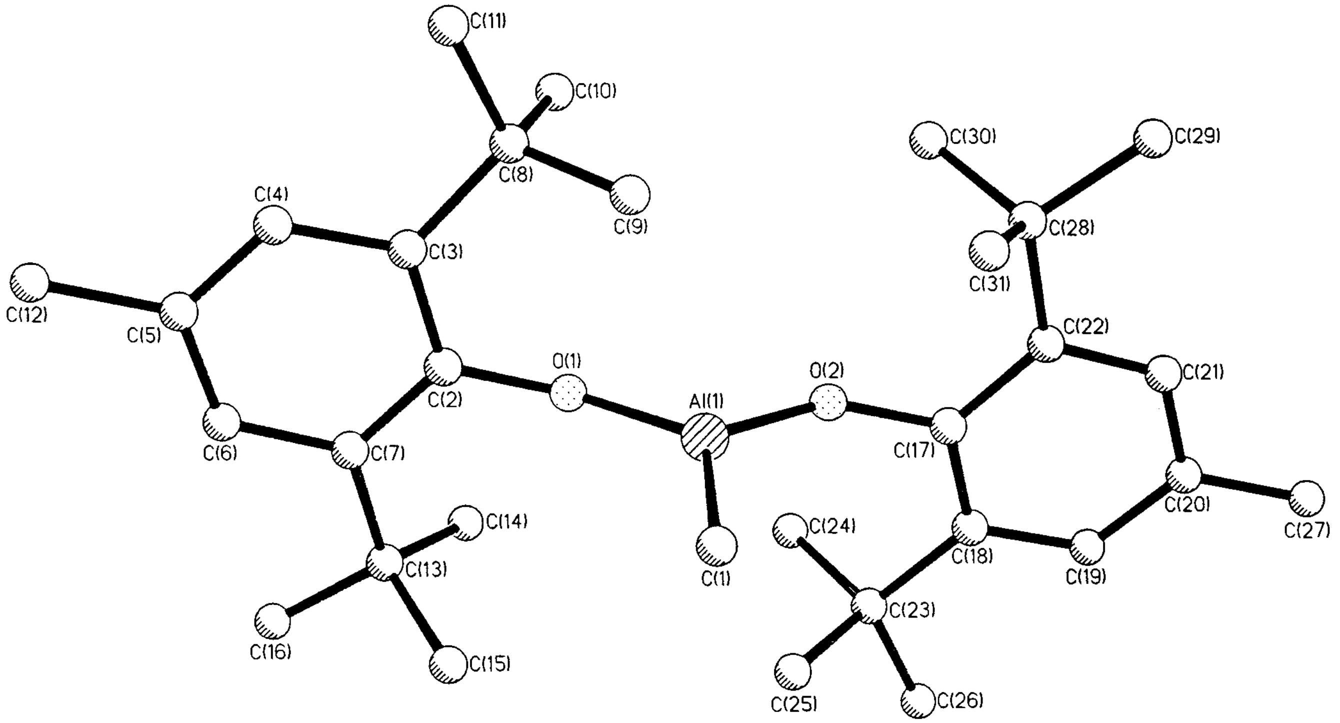


Fig. 1. Structure of the monomeric reagent MAD, **1**, with key atoms labelled; hydrogen atoms omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for MAD, **1**

Al(1)–O(1)	1.695(2)	Al(1)–O(2)	1.684(2)
Al(1)–C(1)	1.926(3)		
O(2)–Al(1)–O(1)	111.97(11)	O(2)–Al(1)–C(1)	123.57(14)
O(1)–Al(1)–C(1)	123.84(14)	C(2)–O(1)–Al(1)	140.0(2)
C(17)–O(2)–Al(1)	147.3(2)		

structures stabilisation of the lithium centre has been effected by external solvation [5,8]; in the remaining case [9] there is internal stabilisation via Li ← F interactions. It is, therefore, significant to note that **3** shows stabilisation of the otherwise merely two-coordinate lithium centre via extensive agostic Li···H(Me) bonding which renders the overall coordination sphere of the metal pseudo-octahedral (Fig. 4). Even though the Li–O distances observed in **3** (mean = 1.868 Å) represent the shortest of any yet observed in monomeric lithium aluminates of this type, the four short Li···C distances (Li···C8 = 2.732(7) Å, Li···C9 = 2.458(7) Å, Li···C28 = 2.823(7) Å, Li···C30 = 2.415(7) Å) are similar to those previously attributed to strong agostic interactions in compounds containing formally two-coordinate lithium (e.g. 2.787 Å in $[(Me_3Si)_2NLi]_2$ ([10]a) 2.482 Å (mean) in $[(Me_3Si)_2NLi]_3$ ([10]a) and 2.82–3.05 Å in *anti*-$[(Et_2O)Li]_2[(t\text{-Bu})_6Al_6(O)_6Me_2]$ ([10]b)). Further, the Li···H interactions seen in **3** are all exceptionally short (Li···H8C = 2.017 Å, Li···H9C = 1.868 Å, Li···H28C = 2.127 Å, Li···H30C = 1.885 Å; all other Li···H distances are ≥ 2.35 Å) ([10]b). For the purposes of computing the agostic Li···distances relevant C–H bond lengths were increased from 0.98 Å, appropriate to X-ray diffraction, to 1.08 Å by simple displacement along the bond (Table 3).

It is not surprising that the reaction of **1** with MeLi yields a product containing two aluminium-attached methyl groups. However, that **3** results also from the use of *n*- or *t*-BuLi is altogether more intriguing and is best rationalised in terms of the isolation of **2** · THF. The suggestion is clearly that in this instance BuLi (*n*- or *t*-) undergoes a 3:1 reaction with **1** yielding tris(butyl)aluminium *and* MeLi in situ, the combination of the latter intermediate with a further equivalent of MAD giving **3** (Scheme 2). The observation that MAD is monomeric in solution and that it fails to act as a precursor to $Al(OR)_3$ [11] rules out the alternative possibility that dimeric MAD acts as a source of Me_2AlOR and $Al(OR)_3$ in situ, the latter species undergoing a 1:3 reaction with R′Li (R′ = Me, *n*-Bu or *t*-Bu) to afford LiOR which could then combine with Me_2AlOR.

Our findings may have significance regarding the mechanism of the 1,4-addition of R′Li reagents (R′ = Me, *n*-Bu or *t*-Bu) to enones in the presence of aluminium species. Previously, the effect of such species had been consigned mostly, and rather vaguely, to that of electrophilic activation of the enone. One study had noted the possibility of lithium aluminate intermediates during conjugate additions to cyclopentenones [12]. For the specific case of MAD, **1**, as the aluminium species in question, however, experimental evidence was produced against the intermediacy of an ate complex [4]. Crucially, though, that study involved reacting R′Li, MAD and enone in *ethereal* solution; in such cases 1,2- and not 1,4-addition (as is observed in non-polar solvents) was observed. In fact, that is perhaps unsurprising. If an ate complex such as **3**, produced by reacting MAD with R′Li, was involved directly in conjugate addition, it would likely operate via the enone coordinating to the formally two-coordinate Li^+ centre of the ate complex, displacing the *t*-Bu···Li^+ interactions noted above. The resulting ate-enone complex would then be primed to deliver R′ to the 4-position (Fig. 5(a)). In ethereal solvents, however, the ether would compete with the enone for the Li^+ coordination site, thereby fully or partly blocking this mechanism. In fact, there is some evidence that ethers are better Lewis bases than enones. For example, we find that addition of 2-cyclohexenone (O=CHex) to MAD, **1**, in toluene affords the 1:1 complex **1** · O=CHex but that dissolution of this complex by THF addition results in the etherate complex **1** · THF. The suggestion is clearly that evidence gained in polar, coordinating solvents against the intermediacy of lithium aluminate species in 1,4-additions can be discounted. Our evidence, in contrast, shows quite definitively that an ate complex *cannot* be involved *directly* in such additions. Thus, we find that MAD, **1**, and R′Li reagents give one *common* product, the lithium dimethylaluminate, **3**, irrespective of whether R′ is Me or *t*-Bu or *n*-Bu. Obviously, this product could deliver only MeLi in 1,4-fashion to an enone, and yet it is proven that these mixtures *do* deliver MeLi or *t*-BuLi or *n*-BuLi in such a way. There seem to be two possible conclusions to be drawn from these findings. The first, and rather negative one, is that an ate complex such as **3** plays no role whatsoever in these conjugate additions even though it is isolated in reasonably high yields from R′Li and MAD mixtures. The second possible conclusion is that **3** is involved in an indirect (but crucial) way in accomplishing the 1,4-addition of R′Li to an enone. In particular, when **3** is produced from MAD, **1**, and R′Li we have shown that it is so, along with LiOR, **2**, and, by implication, R'_3Al (Scheme 2). Clearly, when such a mixture is treated with enone, the only possible sources of R′ are unreacted R′Li (which, on its own, undergoes 1,2-addition) and this R'_3Al co-product. Thus, one mechanistic scenario is that **3**, formed in non-polar solvent from R′Li and MAD, is coordinated at Li^+ by subsequently added enone. Such coordination would presumably displace the (*t*-Bu)H···Li interactions found in **3** but

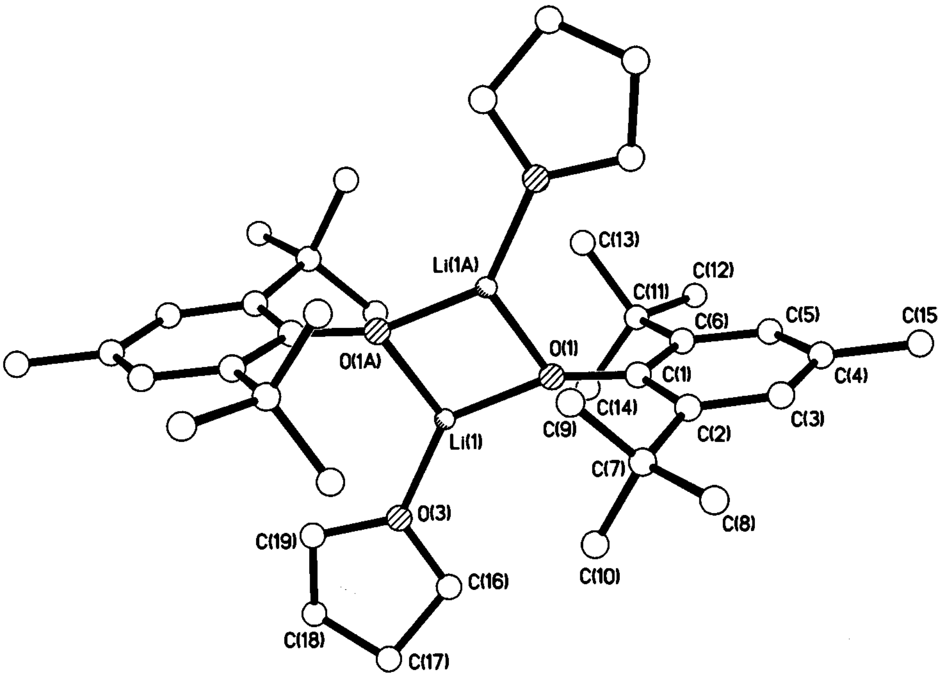


Fig. 2. The structure of one of the two crystallographically independent centrosymmetric dimeric molecules of **2** · THF with key atoms labelled; hydrogen atoms omitted for clarity.

nonetheless the space around the Li$^+$, the O of the enone, and its attached carbon centre (C-2) would be extremely crowded. This coordination and the resulting crowding might then direct the co-product R'_3Al to attack the much more exposed C-4 position of the enone (Fig. 5(b)).

We are exploring these mechanistic possibilities further by NMR experiments designed to deduce the solution species present in mixtures of MAD and R′Li reagents and, in particular, by synthetic and NMR studies in which isolated **3** is reacted with enones and then the characterised and isolated products of these reactions are in turn reacted with tris(alkyl)aluminium reagents. These results will be reported in a subsequent paper.

Table 2
Selected bond lengths (Å) and angles (°) for the two crystallographically independent molecules of **2** · THF

O(1)–C(1)	1.3364(15)	O(1)–Li(1)	1.818(3)
O(1)–Li(1A)	1.874(3)	O(2)–C(20)	1.3388(16)
O(2)–Li(2)	1.852(3)	O(2)–Li(2B)	1.834(3)
Li(1)–O(3)	1.883(3)	Li(2)–O(4)	1.884(3)
C(1)–O(1)–Li(1)	158.48(11)	C(1)–O(1)–Li(1A)	120.31(11)
Li(1)–O(1)–Li(1A)	80.77(12)	O(1)–Li(1)–O(1A)	99.23(12)
C(20)–O(2)–Li(2)	132.24(11)	C(20)–O(2)–Li(2B)	147.08(12)
Li(2)–O(2)–Li(2B)	80.33(12)	O(2)–Li(2)–O(2B)	99.67(12)

Symmetry operators: A, $-x$, $1-y$, $-z$; B, $1-x$, $2-y$, $-z$.

3. Experimental

3.1. General experimental

Standard inert-atmosphere Schlenk techniques were employed using a dual nitrogen/vacuum line. Schlenk tubes were pre-dried at 180°C prior to evacuation to less than 0.1 Torr three times, being filled with dry nitrogen from the house supply between each evacuation. Reagents were used as received from the Aldrich Chemical Company. 2,6-Di-*tert*-butyl-4-methylphenol

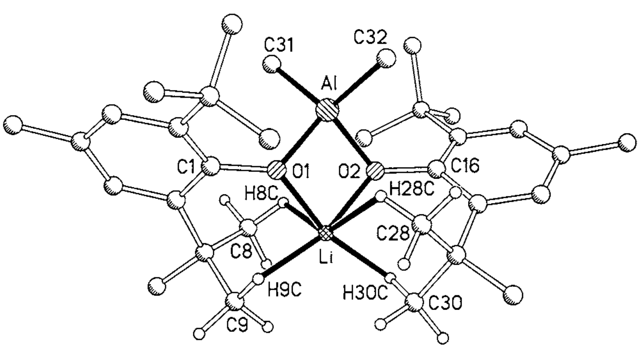


Fig. 3. Structure of the monomeric lithium aluminate **3** with key atoms labelled; hydrogen atoms (except for the methyl groups involved in agostic interactions with the lithium centre) omitted for clarity.

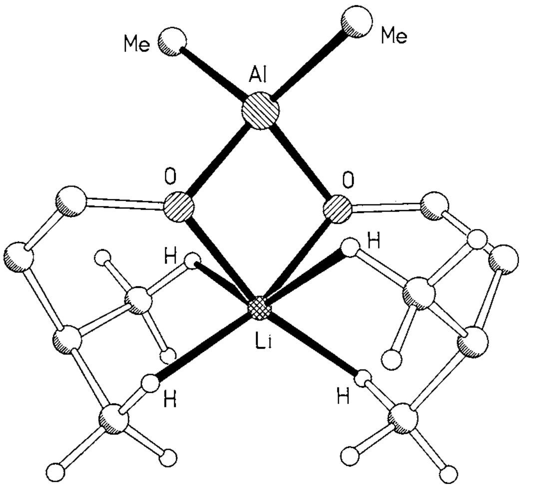


Fig. 4. The core of **3** emphasising the pseudo-octahedral coordination of the lithium centre.

was weighed into the Schlenk tube prior to purging, while toluene (freshly distilled and maintained at reflux over sodium), hexane (freshly distilled and maintained at reflux over sodium–potassium amalgam), trimethylaluminium, methyllithium, *n*-butyllithium, *t*-butyllithium and 2-cyclohexenone were added direct to the nitrogen-filled Schlenk tube using standard syringe techniques.

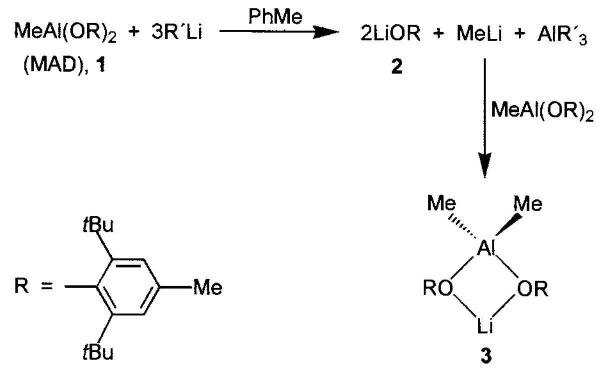
All ^{1}H-NMR spectra were recorded at room temperature using a Bruker AM 400 FT-NMR spectrometer.

3.2. Synthesis of methylaluminium bis(2,6-di-tert-butyl-4-methylphenoxide) (MAD), ***1***

Trimethylaluminium (1.5 ml, 2.0 M in toluene, 3.0 mmol) was added to a stirred suspension of 2,6-di-*tert*-butyl-4-methylphenol (1.32 g, 6.0 mmol) in toluene (2 ml) under nitrogen at −78°C and the resulting solution was stirred for 1 h at room temperature. Removal of the solvent afforded a white powder which was dissolved in hexane (3 ml) and the minimum of hot toluene. Storage at room temperature for 12 h afforded large colourless crystals of **1**, m.p., 171–173°C; yield, 89%. Found: C 76.48, H 9.97. Calc. for $C_{31}H_{49}AlO_2$: C 77.50, H 10.21. ^{1}H-NMR spectroscopy (400.137 MHz, 25°C, [${}^{2}H_6$]benzene), δ 7.18 (s, 4H, Ar), 2.30 (s, 6H, *p*-CH_3), 1.58 (s, 36H, *o*-CCH_3), −0.26 (s, 3H, $AlCH_3$).

Table 3
Selected bond lengths (Å) and angles (°) for **3**

Al–O(1)	1.8457(17)	Al–O(2)	1.8425(17)
Al–C(31)	1.969(3)	Al–C(32)	1.968(3)
Li(1)–O(1)	1.848(5)	Li(1)–O(2)	1.888(4)
O(1)–C(1)	1.390(3)	O(2)–C(16)	1.384(3)
Li···C8	2.732(7)	Li···C9	2.458(7)
Li···C28	2.823(7)	Li···C30	2.415(7)
O(1)–Al–O(2)	89.40(7)	C(31)–Al–C(32)	115.39(13)
Al–O(1)–Li(1)	91.92(15)	Al–O(2)–Li(1)	90.72(15)
O(1)–Li(1)–O(2)	87.96(19)	C(1)–O(1)–Al	125.16(16)
C(16)–O(2)–Al	127.40(14)	C(1)–O(1)–Li(1)	129.7(2)
C(16)–O(2)–Li(1)	130.86(19)		



Scheme 2.

3.3. Synthesis of MAD-(2-cyclohexenone) complex, ***1*** *· O=CHex*

Trimethylaluminium (1.5 ml, 2.0 M in toluene, 3.0 mmol) was added to a stirred suspension of 2,6-di-*tert*-butyl-4-methylphenol (1.32 g, 6.0 mmol) in toluene (2 ml) under nitrogen at −78°C and the resulting solution was stirred for 1 h at room temperature. The solution was cooled to −78°C and 2-cyclohexenone (0.29 ml, 3.0 mmol) was added, yielding a deep orange suspension. Warming to room temperature afforded a yellow suspension which was dissolved by gentle heating. Storage at +5°C for 1 day yielded bright yellow micro-crystals of **1** · O=CHex, m.p., 250–251°C (dec.); yield, 24%. Found: C 77.87, H 9.62. Calc. for $C_{39}H_{57}AlO_3$: C 78.00, H 9.50. ^{1}H-NMR spectroscopy (400.137 MHz, 25°C, [${}^{2}H_6$]benzene), δ 7.25 (s, 4H, **1**, Ar), 7.13–7.00 (m, 3H, 2/3tol.), 6.23 (dt, 1H, O=CHex, 3-CH, ${}^{3}J_{\mathrm{C(H)=CH}} = 9.95$ Hz, ${}^{3}J_{\mathrm{C(H)-CH}} = 4.02$ Hz), 6.07 (dt, 1H, O=CHex, 2-CH, ${}^{3}J_{\mathrm{C(H)=CH}} = 9.97$ Hz), 2.33 (s, 6H, **1**, *p*-CH_3), 2.11 (s, 2.08H, 2/3tol.), 2.07 (t, 1H, O=CHex, 6-CH_2, ${}^{3}J_{\mathrm{C(H)-CH}} = 6.81$ Hz), 1.67 (s, 36H, **1**, *o*-CCH_3), 1.20 (quart., 1H, O=CHex, 4-CH_2, ${}^{3}J_{\mathrm{C(H)-CH}} = 5.60$ Hz), 0.97 (dt., 1H, O=CHex, 5-CH_2, ${}^{3}J_{\mathrm{C(H)-CH}} = 6.40$ Hz), 0.00 (s, 3H, **1**, $AlCH_3$).

3.4. Synthesis of MAD-THF complex, ***1*** *· THF*

An identical procedure as for **1** · O=CHex was used except that dissolution was effected by the dropwise

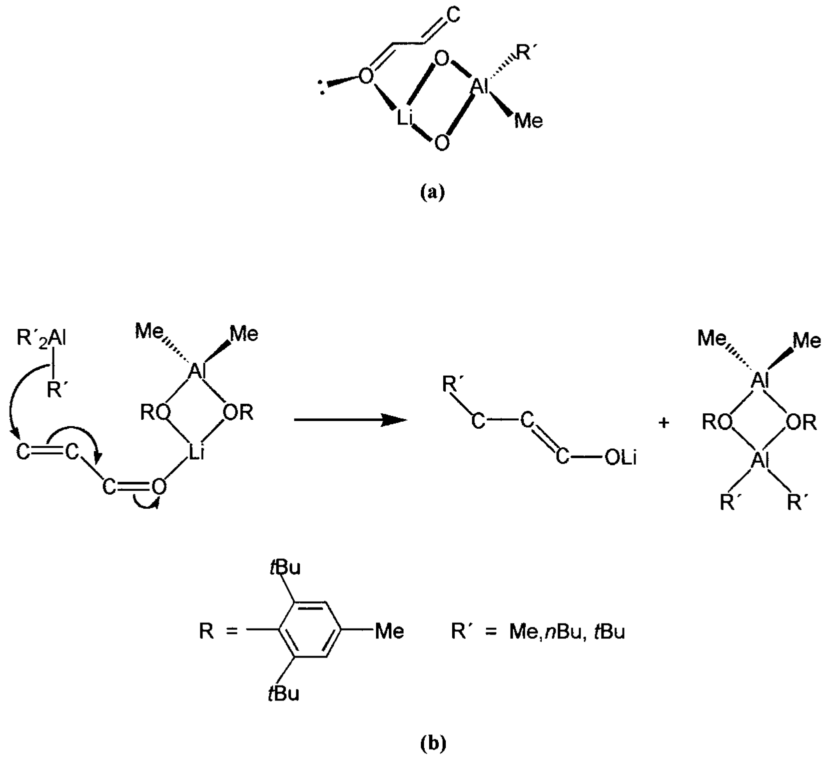


Fig. 5. (a) Schematic representation of a complex between enone and an ate complex such as **3**. (b) Schematic representation of a tris(alkyl)aluminium at the C-4 position of an enone coordinated to an ate complex such as **3**.

addition of THF (ca. 1 ml). Storage at + 5°C for 1 day afforded colourless crystals of **1** · THF, m.p., 176–178°C, yield, 59%. Found: C 75.87, H 10.44. Calc. for $C_{37}H_{57}AlO_3$: C 77.08, H 9.90. ^{1}H-NMR spectroscopy (400.137 MHz, 25 °C, [$^2H_8$]toluene), δ 7.21 (s, 4H, **1**, Ar), 3.69 (m, 4H, THF), 2.32 (s, 6H, **1**, *p*-CH_3), 1.52 (s, 36H, **1**, *o*-CCH_3), 0.98 (4H, THF), 0.03 (s, 3H, **1**, $AlCH_3$).

3.5. Synthesis of lithium bis(2,6-di-tert-butyl-4-methylphenoxide)-THF complex, 2 · THF

Trimethylaluminium (1.5 ml, 2.0 M in toluene, 3.0 mmol) was added to a stirred suspension of 2,6-di-*tert*-butyl-4-methylphenol (1.32 g, 6.0 mmol) in toluene (2 ml) under nitrogen at − 80°C and the resulting solution was stirred for 1 h at room temperature. To this solution of methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide), *t*-BuLi (1.77 ml, 1.7 M in hexane, 3.0 mmol) was added at − 80°C. Warming to room temperature afforded a suspension which was dissolved at reflux by the dropwise addition of THF (ca. 3 ml). Storage at room temperature for 2 days afforded colourless crystals of **2** · THF, m.p., 304–306°C; yield, 89% (with respect to *t*-BuLi, see Scheme 2). Found: C 75.64, H 10.35, Li 2.10. Calc. for $C_{19}H_{31}LiO_2$: C 76.51, H 10.40, Li 2.35. ^{1}H-NMR spectroscopy (400.137 MHz, 25°C, [$^2H_8$]toluene), δ 7.24 (s, 2H, Ar), 3.18 (m, 4H, THF), 2.39 (s, 3H, *p*-CH_3), 1.66 (s, 18H, *o*-CCH_3), 1.07 (m, 4H, THF).

3.6. Syntheses of lithium dimethylbis(2,6-di-tert-butyl-4-methylphenoxide)aluminate, 3

(a) An identical procedure as for **2** · THF was used except that dissolution was effected by the dropwise addition of toluene at room temperature (ca. 5 ml). Storage at room temperature for 4 days afforded colourless crystals of **3**, m.p., 232–234°C, yield, 53% (with respect to *t*-BuLi, see Scheme 2). Found: C 75.48, H 10.18, Li 1.28. Calc. for $C_{32}H_{52}AlLiO_2$: C 76.49, H 10.36, Li 1.39. ^{1}H-NMR spectroscopy (400.137 MHz, 25°C, [$^2H_8$]toluene), δ 7.11 (s, 2H, Ar), 2.25 (s, 3H, *p*-CH_3), 1.46 (s, 18H, *o*-CCH_3), −0.45 (s, 3H, $AlCH_3$).

(b) A solution of methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) was prepared as for **2** · THF. To this was added *n*-BuLi (1.88 ml, 1.6 M in hexane, 3.0 mmol) at − 80°C. Warming to room temperature afforded a suspension which was dissolved at reflux. Storage of the resultant colourless solution at room temperature for 1 day afforded colourless micro-crystals of **3**, yield, 45% (with respect to *n*-BuLi).

Table 4
Crystallographic data for **1**, **2** · THF and **3**

	1	**2** · THF	**3**
Formula	$C_{31}H_{49}AlO_2$	$C_{38}H_{62}Li_2O_4$	$C_{32}H_{52}AlLiO_2$
M_r	480.68	596.76	502.66
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	12.144(2)	11.5446(6)	10.8610(2)
b (Å	12.846(2)	15.7174(9)	11.6770(11)
c (Å)	11.014(2)	21.3907(11)	14.3324(13)
α (°)	102.63(1)	90	93.616(2)
β (°)	110.52(1)	103.607(2)	108.845(2)
γ (°)	68.18(1)	90	112.793(2)
V (Å^3)	1486.2(4)	3772.4(4)	1548.6(2)
Z	2	4	2
D_c (g cm^{-3})	1.074	1.051	1.078
Crystal size (mm)	0.40 × 0.30 × 0.20	0.80 × 0.60 × 0.30	0.56 × 0.38 × 0.37
Radiation (Å)	Mo–K$_\alpha$, 0.71069	Mo–K$_\alpha$, 0.71073	Mo–K$_\alpha$, 0.71073
μ (mm^{-1})	0.092	0.065	0.090
F(000)	528	1312	552
T (K)	180	160	160
Scan mode	ω-2θ	ω	ω
2θ range (°)	5.50–54.98	3.70–57.74	4.30–57.68
Measured reflections	7144	23149	11455
Unique reflections	6817	8870	6933
R_{int}	0.0643	0.0282	0.0373
Reflections with $I > 2\sigma(I)$	6816	6096	4257
Final $R(F)$, $wR(F^2)$	0.0627, 0.1994	0.0527, 0.1514	0.0641, 0.1789
Goodness-of-fit	0.991	1.033	0.974
Max. peak, hole (eÅ^{-3})	0.298, −0.394	0.350, −0.274	0.549, −0.299

(c) A solution of methylaluminium bis(2,6-di-*tert*-butyl-4-methylphenoxide) was prepared as for **2** · THF. To this was added MeLi (3.00 ml, 1.0 M in 90% cumene/10% THF, 3.0 mmol) at −80°C. Warming to room temperature afforded a suspension which was dissolved at reflux. Toluene (2 ml) was added and the colourless solution was stored at +5°C for 2 days, whereupon colourless crystals of **3** were deposited, yield, 38% (with respect to MeLi).

3.7. X-ray crystallography

Essential crystallographic details are given in Table 4. Data for **1** were collected on a Rigaku AFC5R four-circle diffractometer with data for **2** · THF and **3** being collected on a Bruker AXS SMART CCD diffractometer. All three structures were solved using direct methods and subsequent Fourier difference syntheses and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms [13]. All hydrogen atoms were placed in geometrically-idealised positions based on peaks found in a difference synthesis and refined using a riding model including free torsional rotation about X–Me bonds. Two-fold disorder was resolved for the THF ligands in one of the two independent molecules of **2** · THF. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

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