www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 602 (2000) 15–23

Dimethylaluminium enolates and alkoxides derived from trimethylaluminium and aromatic ketones: a synthetic, structural and theoretical investigation

John F. Allan [a], William Clegg [b], Mark R.J. Elsegood [b], Kenneth W. Henderson [a,*], Arlene E. McKeown [a], Paul H. Moran [a], Igor M. Rakov [a]

[a] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK*
[b] *Department of Chemistry, University of Newcastle upon Tyne, Newcastle, NE1 7RU, UK*

Received 19 January 2000; received in revised form 9 February 2000

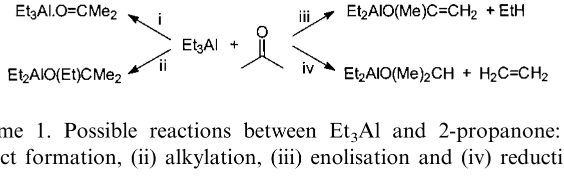
Abstract

Reaction of Me_3Al with a series of aromatic ketones results in the precipitation of either dimethylaluminium enolates or alkoxides. In situ ^1H-NMR spectroscopic studies of the reaction between Me_3Al and acetophenone reveal a complex mixture of products whereas under the same conditions 2,4,6-trimethylacetophenone reacts cleanly to give the corresponding enolate. The enolate compounds $[Me_2AlOC(2,4,6\text{-}Me_3\text{–}C_6H_2)\text{=}CH_2]$ (**2**) and $[Me_2AlOC(C_6Me_5)\text{=}CH_2]$ (**4**) were isolated and **2** as well as the representative alkoxide $[Me_2AlOCMe_2Ph]$ (**6**) were characterised by X-ray crystallography. Both **2** and **6** form dimers with a central Al_2O_2 core. Ab initio molecular orbital calculations (HF/6-31G*) indicate that both **2** and **6** are the thermodynamic products of their reactions. For 2,4,6-trimethylacetophenone enolisation is preferred over alkylation by 4.70 kcal mol^{-1} whereas for acetophenone alkylation is preferred by 25.39 kcal mol^{-1} over enolisation. Disubstitution of the *ortho* positions on the aromatic ring by methyl groups results in the relative destabilisation of the alkoxide compared to the enolate due to steric crowding around the quaternary carbon atom. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Enolates; Alkylations; Aluminium; Ab initio calculations; Crystal structure

1. Introduction

The reactions between trialkylaluminium compounds (R_3Al) and carbonyl containing species have been the subject of intensive study over many years [1]. In summary, these reactions may result in adduct formation, alkylation, reduction or enolisation, depending on the nature of the ketone and also the alkyl group attached to aluminium (Scheme 1). Moreover, aluminium compounds are important in the stereoselective formation of carbon–carbon bonds and recently there has been renewed interest in the chemistry of organoaluminiums in combination with a second organometallic (heterobimetallic species) to mediate a number of addition reactions [2,3]. Rather surprisingly, there have been relatively few studies into the mechanistic and structural aspects of enolisation reactions mediated by organoaluminium compounds. In part, this is due to the reported difficulty in the isolation and structural identification of aluminium enolates [4]. Herein, we report the reactions of Me_3Al with a variety of aromatic ketones. In addition, the solid-state structures of the enolate $[Me_2AlOC(2,4,6\text{-}Me_3\text{–}C_6H_2)\text{=}CH_2]$ and the alkoxide $[Me_2AlOCMe_2Ph]$ have been elucidated and will be discussed. Finally, an ab initio molecular orbital computational study into the factors governing the relative energies of enolisation and alkylation reactions mediated by Me_3Al is detailed [5].



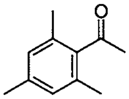
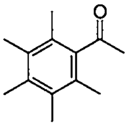
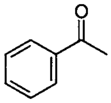
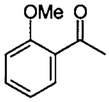
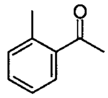
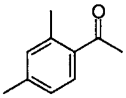
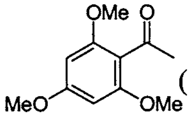
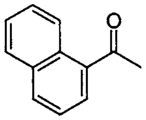
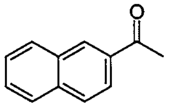
Scheme 1. Possible reactions between Et_3Al and 2-propanone: (i) adduct formation, (ii) alkylation, (iii) enolisation and (iv) reduction.

---

[*] Corresponding author. Tel.: +44-141-548 2351; fax: +44-141-552 0876.
E-mail address: k.w.henderson@strath.ac.uk (K.W. Henderson)

PII: S0022-328X(00)00111-X

Table 1
Solids isolated from the reaction of Me_3Al with various ketones

Entry	Ketone	Isolated Product
1	 (**1**)	$[Me_2AlOC(2,4,6\text{-}Me_3\text{-}C_6H_2){=}CH_2]$ (**2**)
2	 (**3**)	$[Me_2AlOC(C_6Me_5){=}CH_2]$ (**4**)
3	 (**5**)	$[Me_2AlOCMe_2Ph]$ (**6**)
4	 (**7**)	$[Me_2AlOC\{2\text{-}(MeO)\text{-}C_6H_4\}Me_2]$ (**8**)
5	 (**9**)	$[Me_2AlOC(2\text{-}Me\text{-}C_6H_4)Me_2]$ (**10**)
6	 (**11**)	$[Me_2AlOC(2,4\text{-}Me_2\text{-}C_6H_3)Me_2]$ (**12**)
7	 (**13**)	$[Me_2AlOC\{2,4,6\text{-}(MeO)_3\text{-}C_6H_2\}Me_2]$ (**14**)
8	 (**15**)	$[Me_2AlOC(1\text{-}C_{10}H_7)Me_2]$ (**16**)
9	 (**17**)	$[Me_2AlOC(2\text{-}C_{10}H_7)Me_2]$ (**18**)

2. Results and discussion

2.1. Reactivity studies

Each reaction was carried out in a similar fashion. The ketone was added to a toluene solution of Me_3Al cooled to −78°C, followed by slow warming to ambient temperature. The solution was then heated to reflux for 3 h, cooled to ambient temperature and the solvent removed in vacuo and replaced by hexane. Each solution was then cooled to −28°C to precipitate the products and these are listed in Table 1. As expected [1], the most common reaction is direct alkylation across the carbonyl, resulting in the formation of dimethylaluminium alkoxides. However, the reactions involving 2,4,6-trimethylacetophenone (**1**) and pentamethylacetophenone (**3**) yielded the enolate compounds $[Me_2AlOC(2,4,6\text{-}Me_3\text{–}C_6H_2){=}CH_2]$ (**2**) and $[Me_2AlOC(C_6Me_5){=}CH_2]$ (**4**), respectively, as the sole products [6]. It is interesting to note that the reaction with 2,4,6-trimethoxyacetophenone (**13**) also results in alkylation even though its steric properties resemble those of **1**.

A series of in situ ^{1}H-NMR spectroscopic experiments were conducted on the reaction mixtures obtained from the addition of either **1** or acetophenone (**5**) to one equivalent of Me_3Al in toluene solution. In both reactions the reagents were mixed at − 78°C, followed by slow warming to ambient temperature and then stirred for 1 h. Analysis of the reaction mixtures at this stage showed significant differences between the reactivity of the ketones. The mixture involving **1** contained only Me_3Al and the ketone, indicating the formation of an adduct, $[Me_3Al{\cdot}O{=}CMe(2,4,6\text{-}Me_3-C_6H_2)]$. In contrast, a complex mixture was formed in the reaction involving **5**, however, the major species present was determined to be the alkylated product $[Me_2AlOCMe_2Ph]$ (**6**) and no characteristic olefinic–CH_2 signals from an enolate were present. Both reaction mixtures were heated to reflux in toluene solution for 2.5 h and re-analysed. The reaction of **1** showed almost quantitative conversion to the enolate **2** which is consistent with the high yield (93.3%) of pure solid precipitated from solution using this ketone. After heating the reaction containing **5** the alkylated product **6** was again determined to be present as part of a mixture. Analysis of the remaining species present is consistent with the formation of self-coupled aldolate from identification of the characteristic *gem*-CH_2 signals. On precipitation of solids from the reactions involving **5** only the alkylated product **6** was obtained, which is most likely a result of the relative solubilities of the species present. Previously, Barron and co-workers found that the bulky alkoxide $EtAl(BHT)_2$ (BHT−H is butylated hydroxytoluene) reacts with a variety of ketones to yield aldol addition products (Eq. (1)) [7].

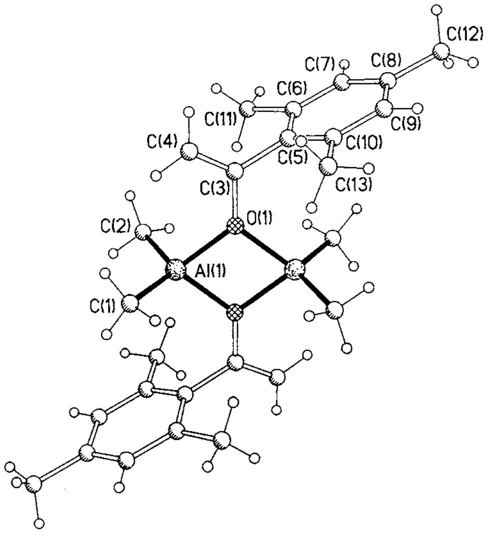


Fig. 1. Molecular structure of $[\{Me_2AlOC(2,4,6\text{-}Me_3C_6H_2){=}CH_2\}_2]$ (**2**).

$$EtAl(BHT)_2 + 2Bu^tCOMe \rightarrow [EtAl(BHT)\{Bu^tC{=}OCH_2C(Me)(Bu^t)O\}] + BHT{-}H \quad (1)$$

No enolates were identified even when equimolar amounts of reactants were used, suggesting fast reaction of the enolate with ketone to form the thermodynamically stable aldolates. The ability to prepare and isolate enolate **2** is likely due to the difficulty in forming the self-coupled aldol product derived from the sterically hindered ketone **1**[1].

Since only very limited information is available on the solid-state structures of aluminium enolates, an X-ray crystallographic study of **2**, and for comparison the alkylated compound **6**, was undertaken [4,9]. Furthermore, analysis of the products from the enolisation and alkylation reactions may aid in rationalising the reactivity differences between **1** and **5**[2].

2.2. X-ray crystallography

To our knowledge, the only aluminium enolate to be structurally characterised is the α-amino ester enolate $[\{Me_2Al(MeO)OC{=}(H)CNMe_2\}_2]$ (**19**) and its complex with Me_2AlCl $[Me_2Al(MeO)OC{=}(H)CNMe_2{\cdot}Me_2AlCl]$ (**20**) [4]. These enolates were prepared by transmetallation of the corresponding lithium enolates with Me_2AlCl. Compound **19** crystallises as an oxygen-bridged dimer, with each metal chelated by a dimethylamido unit, resulting in two five-coordinate aluminium centres. Complex **20** adopts a dinuclear geometry, where the Me_2AlCl unit binds to the enolate oxygen, and internal chelation by the dimethylamido unit to the remaining metal gives two four-coordinate aluminium centres. Although a few simple aluminium enolates have been characterised by spectroscopic techniques, determination of their solid-state structures has proved elusive [11].

As can been seen from Fig. 1, compound **2** adopts dimeric aggregation in the solid-state by bridging through the enolate oxygens. Each metal is four-coordinate by binding to two methyl groups and two oxygens, with the average of the angles at the metal being 108.1°, which range between 78.87(7)° for O–Al–O, to 121.56(10)° for C(1)–Al–C(2). Both the ^{1}H- and ^{13}C-NMR spectra of **2** in C_6D_6 solution are consistent with symmetrical dimeric association.

In general, **2** and **19** display similar geometric parameters (key bond lengths and angles are given in Table 2). However, notable exceptions are the Al–O

---

[1] Self-coupled aldolates of methyl ketones can be prepared through the use of magnesium amides [8].

[2] For information on the related structural studies of lithium enolates, see Ref. [10].

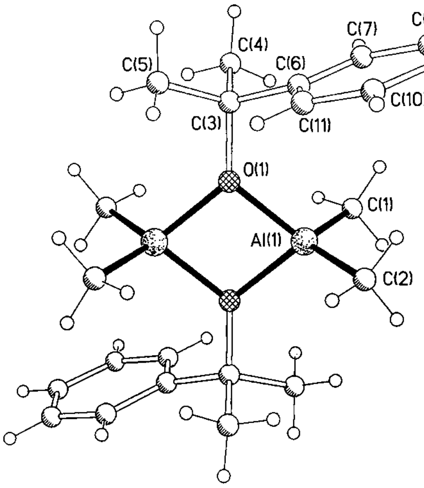


Fig. 2. Molecular structure of [$\mathrm{Me_2AlOCMe_2Ph}$] (**6**).

Table 2
Key bond lengths (Å) and angles (°) for [{$\mathrm{Me_2AlOC(2,4,6\text{-}Me_3\text{–}C_6H_2){=}CH_2}$}$_2$] (**2**) [a]

Al(1)–O(1)	1.8720(15)	Al(1)–O(1′)	1.8638(14)
Al(1)–C(1)	1.945(2)	Al(1)–C(2)	1.947(2)
O(1)–C(3)	1.386(2)	C(3)–C(4)	1.312(3)
C(3)–C(5)	1.488(3)		
O(1)–Al(1)–O(1′)	78.87(7)	C(1)–Al(1)–O(1′)	115.00(8)
O(1)–Al(1)–C(1)	112.89(8)	C(2)–Al(1)–O(1′)	111.79(8)
O(1)–Al(1)–C(2)	108.68(8)	C(1)–Al(1)–C(2)	121.56(10)
C(3)–O(1)–Al(1′)	130.20(12)	Al(1)–O(1)–C(3)	128.56(12)
Al(1)–O(1)–Al(1′)	101.13(6)	O(1)–C(3)–C(4)	121.2(2)
C(4)–C(3)–C(5)	125.3(2)	O(1)–C(3)–C(5)	113.46(15)

[a] Symmetry operator for primed atoms: $1-x$, $1-y$, $1-z$.

Table 3
Key bond lengths (Å) and angles (°) for [$\mathrm{Me_2AlOCMe_2Ph}$] (**6**)

Al(1)–O(1)	1.8445(5)	Al(1)–O(1′)	1.8464(5)
Al(1)–C(2)	1.9415(9)	Al(1)–C(1)	1.9456(9)
O(1)–C(3)	1.4608(9)	C(3)–C(4)	1.5163(13)
C(3)–C(5)	1.5233(12)	C(3)–C(6)	1.5252(11)
O(1)–Al(1)–O(1′)	80.28(2)	O(1)–Al(1)–C(2)	113.94(3)
C(2)–Al(1)–O(1′)	112.70(3)	O(1)–Al(1)–C(1)	113.61(4)
C(1)–Al(1)–O(1′)	112.93(3)	C(1)–Al(1)–C(2)	117.68(4)
Al(1)–O(1)–C(3)	129.17(4)	Al(1′)–O(1)–C(3)	130.16(4)
Al(1)–O(1)–Al(1′)	99.72(2)	O(1)–C(3)–C(4)	107.78(7)
O(1)–C(3)–C(5)	107.60(6)	C(4)–C(3)–C(5)	109.89(8)
O(1)–C(3)–C(6)	106.59(6)	C(4)–C(3)–C(6)	112.86(7)
C(5)–C(3)–C(6)	111.86(7)		

bond distances. The two independent Al–O bond lengths in **2** are similar at 1.8638(14) and 1.8720(15) Å, whereas in **19** one short and one long Al–O distance of 1.853(3) and 2.055(3) Å are found. This feature in **19** is a consequence of steric repulsions induced by neighbouring methoxy and dimethylamido units adjacent to the dimethylaluminium centres. The Al–C, O–C and C=C bond lengths in **2** conform to those expected for such species [4,12].

The separation of 3.292 Å between C(4) of the alkene group in **2** and the metal appears too long to involve any significant bonding interaction [13]. Such interactions have been found for a variety of metal enolates but are usually only present in coordinatively unsaturated species [14], for example, in lithium pinacolate, [{$\mathrm{LiO(Bu}^t\mathrm{)C{=}CH_2}$}$_6$], where the distance between the lithium atoms and the terminal carbon of the olefins range between 2.3 and 2.6 Å [15]. In **2** the olefin bond sits almost in the same plane as the dimeric $\mathrm{Al_2O_2}$ ring, with C(3) and C(4) sitting 0.064 and 0.310 Å, respectively out of the plane; the torsion angle Al–O–C(3)–C(4) is 23.3°. Similarly, the *ipso*-carbon of the aromatic group is also close to the $\mathrm{Al_2O_2}$ ring plane, with the torsion angle Al(1′)–O(1)–C(3)–C(5) being 19.5°, and the Al′–C(5) distance is 3.216 Å.

For comparison, the crystal structure of the alkylation product **6** was determined and is shown in Fig. 2 (key bond lengths and angles are given in Table 3). In contrast to the scant information on aluminium enolates, the structural chemistry of dialkylaluminium alkoxides is relatively well established[3]. Again the expected dimeric structural motif is seen which is consistent with the ^{1}H- and ^{13}C-NMR spectroscopic solution data. The two independent Al–O distances in the dimer are of similar length at 1.8445(5) and 1.8464(5) Å, these are shorter by ~0.02 Å than those in **2** (typically such Al–O distances are approximately 1.87 Å)[4].

Internal $\mathrm{Al_2O_2}$ ring angles are smaller at the metals and larger at the oxygens, which is consistent with sp^2 hybridisation for the bridging oxygens. Both methyl groups and the *ipso*-carbon of the aromatic ring are staggered with respect to the central $\mathrm{Al_2O_2}$ ring, with torsion angles of 39.0, 82.5 and 159.1° for Al–O–C(3)–C(6), Al–O–C(3)–C4 and Al–O–C(3)–C(5), respectively.

2.3. Theoretical calculations

An ab initio molecular orbital computational study (HF/6-31G*) was undertaken to investigate the energetics of the enolisation and alkylation reactions between $\mathrm{Me_3Al}$ and ketones **1** and **5**[5]. Scheme 2 shows the alkylation and enolisation reactions for the ketones and the relative energies involved for each transformation (dimeric aggregation is assumed for the organometallic species calculated)[6]. Fig. 3 shows the optimised geo-

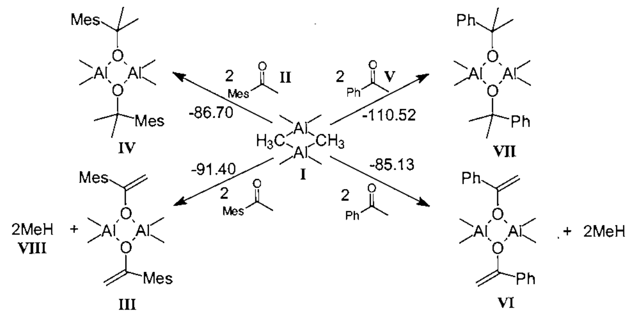
---

[3] For related structures, see Ref. [16].

[4] As found from a search of the Cambridge Structural Database [17].

[5] For other ab initio studies on aluminium systems, see Ref. [18].

[6] For reviews on aluminium structural chemistry, see Ref. [19].



Scheme 2. Energetics of enolisation and alkylation reactions for ketones **1** and **5**. Energies are quoted in kcal mol^{-1} and Mes = 2,4,6-Me_3–C_6H_2.

metries for the alkoxides and enolates **III**, **IV**, **VI** and **VII**. The geometric parameters within **III** and **VII** compare favourably with the experimentally determined crystal structures of **2** and **6** [18].

Both the alkylation and enolisation reactions are highly exothermic for each ketone. However, the enolisation route is preferred by 4.70 kcal mol^{-1} for ketone **II**, whereas alkylation is preferred by 25.39 kcal mol^{-1} for ketone **V**. Therefore, the calculations indicate that both **III** and **VII**, representing **2** and **6**, are the thermodynamic products of their respective reactions, i.e. the outcome of the reaction (alkylation or enolisation) is not necessarily controlled by kinetic factors.

Significantly, there is also a large difference in the relative energies within each type of reaction for the ketones. While the energy difference between the enolisation reactions is only 6.27 kcal mol^{-1}, the alkylation reactions differ by 23.82 kcal mol^{-1}. The large difference in the relative energies of the alkylation reactions can be attributed to the increased steric bulk of the alkoxide in **IV** compared to that in **VII**. Steric crowding around the quaternary carbon (O*C*Me_2Ar) is significantly greater in **IV** compared to **VII**, as a consequence of the methyl groups in the 2- and 6-positions of the aromatic ring. The difference between the energies of the enolisation reactions can mainly be attributed to the higher Brönsted acidity of **II** compared to **V**. The energy required to deprotonate ketones **II** and **V** to form the corresponding enolate anions [2,4,6-Me_3–$C_6H_2C(O){=}CH_2]^-$ (**IX**) and $[PhC(O){=}CH_2]^-$ (**X**) was

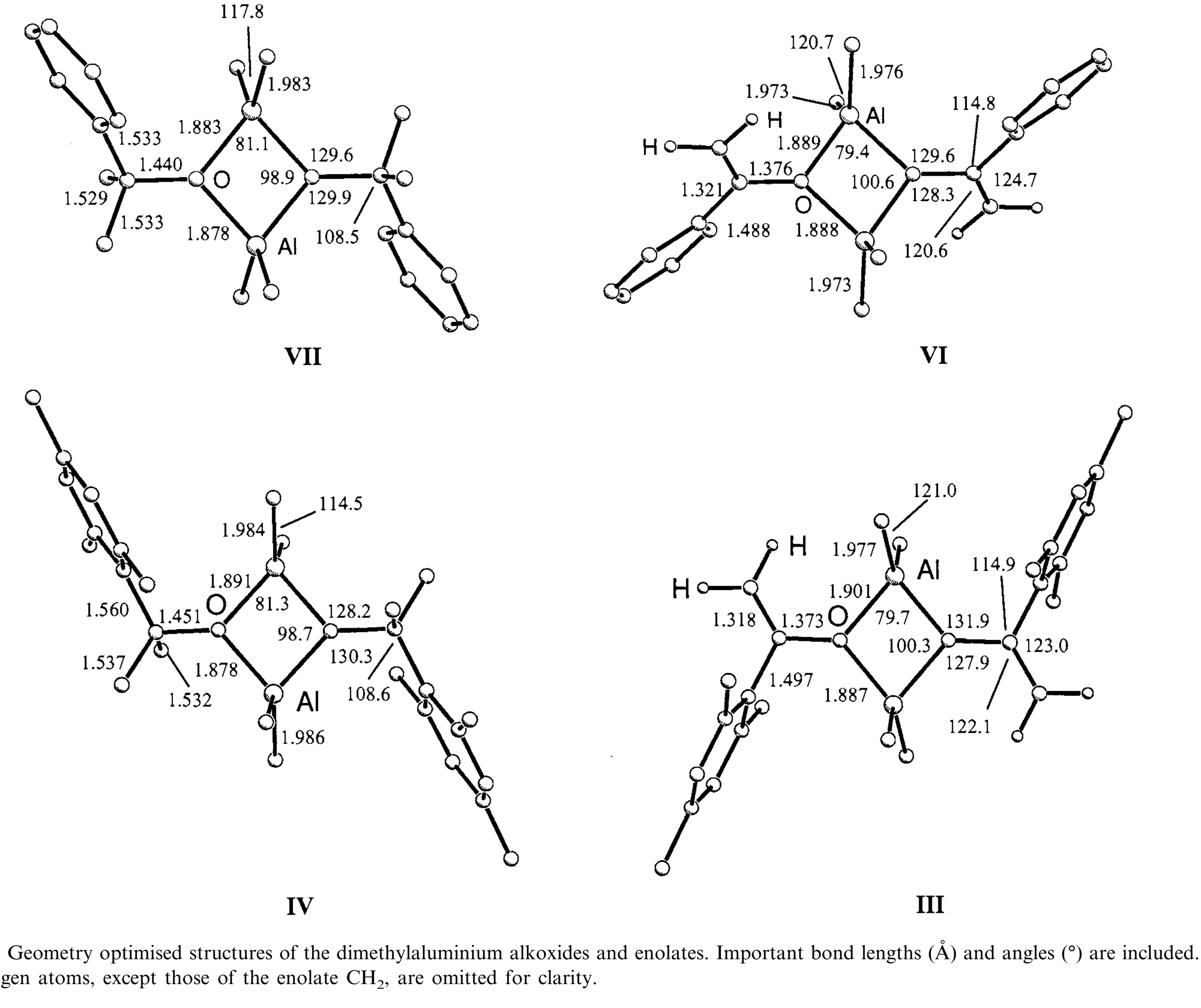


Fig. 3. Geometry optimised structures of the dimethylaluminium alkoxides and enolates. Important bond lengths (Å) and angles (°) are included. Hydrogen atoms, except those of the enolate CH_2, are omitted for clarity.

calculated to be 389.06 and 392.98 kcal mol^{-1}, respectively, i.e. methylation of the aromatic ring increases the acidity of the ketone.

Comparing the dimensions between the alkoxides **IV** and **VII** reveals slightly longer bond lengths associated with the atoms in close proximity to the aromatic ring, i.e. the difference between the C–C bonds joining the aromatic ring and the quaternary carbon is 0.027 Å, and between the C–O bonds is 0.011 Å. Other dimensions within the structures, including the bond angles, are similar. Almost no differences in dimensions are discernible between the enolates **III** and **VI**.

The bond lengths associated with the α-carbon (O*C*) decrease significantly comparing the alkoxides and the enolates. As expected the formation of the olefinic bond shortens one C–C length. However, the O–C and the C–C(*ipso*) bonds also shorten significantly. It is pertinent to note that this contraction is greater for the more substituted anion, i.e. O–C shortens by 0.078 Å for **III** and by 0.064 Å for **VI**, and C–C(*ipso*) shortens by 0.063 Å for **III** and by 0.045 Å for **VI**. These results support the assessment that steric crowding induced by the *ortho* methyl groups is an important factor in determining the stability of complexes **III** and **IV**.

The olefinic group of the enolate in **III** sits almost perfectly in the same plane as the dimeric ring (with a torsion angle of 0.0° for Al–O–C–C between the metal centre and the enolate group). No local minimum was found for a geometry where the enolate ligands are orthogonal to the Al_2O_2 plane. Placing the enolates in a *pseudo-syn* orientation with respect to each other resulted in the location of an energy minimum, **XI**, with essentially the same absolute energy as **III** (with a torsion angle of 19.7° for Al–O–C–C between the metal centre and the enolate group). No minimum was located for an 'in-plane' orientation for **VI**. In this case the ligands rotate to adopt staggered conformations with respect to the Al_2O_2 ring (with a torsion angle of 59.5° for Al–O–C–C between the metal centre and the enolate group). In combination, these results suggest that any agostic interactions between the enolate anion and the metal are small, if present at all, and that the conformation adopted by the ligands is mainly governed by steric factors.

3. Conclusions

The most common reaction between the aryl ketones and Me_3Al is alkylation across the carbonyl to give dimethylaluminium alkoxides. The ^{1}H-NMR spectroscopic studies of the reaction between Me_3Al and **5** reveal that a complex mixture of products are formed and although alkylation is the major reaction, enolisation is a competitive side reaction. Formation of aldolate indicates that any enolate formed reacts with available ketone, as has been seen previously for the reactions of $EtAl(BHT)_2$ [7]. In contrast, alkylation is suppressed in the reactions of Me_3Al with **1** and **3** which yield the enolate products **2** and **4**, respectively. No trace of aldolate was formed in these reactions which is a consequence of the steric bulk of the anion. The calculations confirmed that the enolate and alkoxide compounds **2** and **6**, formed in the reactions using **1** and **5**, respectively, are indeed the thermodynamic products of their reactions. Although the electronics of the ligand may play a role, it appears that steric influences are the major contributing factor in determining the outcome of the reaction between the ketones and Me_3Al. It also appears from the reactions of **9** and **11** that substitution by methyl groups on both *ortho* positions of the aromatic ring is necessary to lead to significantly different reactivity for these ketones.

Finally, the 2,4,6-trimethoxy substituted ketone **13** reacts with Me_3Al to give the alkylated product **14**. The reactivity of **13** may be due to the Lewis base nature of the attached methoxy substituents which in conjunction with the carbonyl initially coordinate to the aluminium of Me_3Al to give a pentacoordinate metal geometry, and direct the transformation in favour of alkylation [16b,20].

4. Experimental

4.1. General experimental conditions

All syntheses were conducted in Schlenk-type glassware under a blanket of argon gas. Glassware was dried in an oven overnight and flame-dried under vacuum before use. All metallated compounds isolated are highly air- and moisture-sensitive, and were handled in an argon-filled glove box fitted with a recirculating column [21]. Ketones were distilled over CaH_2 and stored over 4 Å molecular sieves before use. All solvents were distilled over sodium/benzophenone prior to use and used directly from the still. Trimethylaluminium was supplied as a 2 M solution in toluene from Aldrich and used as received. NMR spectroscopy was run on a Bruker AMX 400 MHz spectrometer at 300 K in C_6D_6 solutions unless otherwise stated.

4.2. Synthesis of the complexes

Each compound was prepared in a similar manner. The synthesis of $[Me_2AlOC(2,4,6\text{-}Me_3{-}C_6H_2){=}CH_2]$ (**2**) is given as an example. In most instances the products were highly soluble in hydrocarbon solvents, leading to low yields of isolated solid precipitates. The samples using ketones **9**, **11** and **15** were contaminated by a small quantity ($<5\%$) of the corresponding enolate. Purification of the mixtures was achieved through fractional crystallisation.

4.2.1. [$Me_2AlOC(2,4,6\text{-}Me_3\text{–}C_6H_2)\text{=}CH_2$] (**2**)

2,4,6-Trimethylacetophenone (1.46 g, 0.009 mol) was added dropwise to a −78°C cooled solution of Me_3Al (0.011 mol) in 12 ml of toluene. The reaction mixture was allowed to warm slowly to ambient temperature with constant stirring and subsequently heated to reflux for 3 h. Solvents were removed in vacuo, the residue dissolved in 5 ml of hexane and a crystalline product was obtained on cooling the mixture to −28°C for 24 h. Yield, 93.3%; m.p., 131–132°C. ^{1}H-NMR spectrum, δ −0.51 (s, 6H, AlCH_3), 2.02 (s, 3H, p-CH_3), 2.33 (s, 6H, o-CH_3), 4.04 (d, $^2J = 2.3$ Hz, 1H, C=CH_2), 4.80 (d, 1H, C=CH_2), 6.68 (s, 2H, m-H, C_6H_2). ^{13}C-NMR spectrum, δ −9.05 (AlCH_3), 20.90 (o, m-CH_3), 21.66 (p-CH_3), 96.35 (C=CH_2), 129.28 (m-C, C_6H_2), 153.68 (OC=CH_2), 133.72, 137.65 and 139.78 (i-, o- and p-C, C_6H_2). X-ray quality crystals were prepared by sublimation of the sample under high vacuum (< 0.1 Torr) using a 2 cm diameter Schlenk tube. A temperature gradient between 5 and 82°C was established along 20 cm of the tube by means of a copper jacket fitted with a water cooling element at one end and immersing the other end in a heated oil bath.

4.2.2. [$Me_2AlOC(C_6Me_5)\text{=}CH_2$] (**4**)

Yield, 60.0%; m.p., 210–214 °C with decomposition. ^{1}H-NMR spectrum, δ −0.54 (s, 6H, AlCH_3), 1.97 (s, 3H, p-CH_3), 2.02 (s, 6H, m-CH_3), 2.35 (s, 6H, o-CH_3), 4.13 (d, $^2J = 2.2$ Hz, 1H, C=CH_2), 4.83 (d, 1H, C=CH_2). ^{13}C-NMR spectrum, δ −9.20 (AlCH_3), 17.02 (m-CH_3), 17.31 (p-CH_3), 19.22 (o-CH_3), 96.01 (C=CH_2), 132.96, 133.46 (o- and m-C, C_6Me_5), 134.59, 136.71 (i- and p-C, C_6Me_5), 155.35 (OC=CH_2).

4.2.3. [$Me_2AlOCMe_2Ph$] (**6**)

Yield, 8.9%; m.p., 82–84°C. ^{1}H-NMR spectrum, δ −0.58 (s, 6H, AlCH_3), 1.61 (s, 6H, OCCH_3), 7.07 (t, 1H, p-H, Ph), 7.17 (s, 2H, m-H, Ph), 7.41 (d, 2H, o-H, Ph). ^{13}C-NMR spectrum, δ −5.29 (AlCH_3), 31.62 (C–CH_3), 77.50 (C–CH_3), 126.68, 129.28, 129.88 (o-, m- and p-C, Ph), 145.75 (i-C, Ph). X-ray quality crystals were grown from a hexane solution of the sample which was cooled to −28°C for 24 h.

4.2.4. [$Me_2AlOC\{2\text{-}(MeO)\text{–}C_6H_4\}Me_2$]

Yield, 37.2%; m.p., 112–114°C. ^{1}H-NMR spectrum, δ −0.54 (s, 6H, AlCH_3), 1.85 (s, 6H, OCCH_3), 3.42 (s, 3H, OCH_3), 6.53 (d, 1H, m'-H, C_6H_4), 6.80 (t, 1H, m-H, C_6H_4), 7.07 (t, 1H, p-H, C_6H_4), 7.36 (d, 1H, o-H, C_6H_4). ^{13}C-NMR spectrum, δ −5.55 (AlCH_3), 30.58 (OCCH_3), 54.59 (OCH_3), 77.24 (C-CH_3), 112.12 (m'-C, C_6H_4), 120.50 (m-C, C_6H_4), 127.50, (o-C, C_6H_4), 129.92 (p-C, C_6H_4), 132.96 (i-C, C_6H_4), 158.57 (o'-C, C_6H_4).

4.2.5. [$Me_2AlOC(2\text{-}Me\text{–}C_6H_4)Me_2$] (**10**)

Yield, 26.3%; m.p., 158–160°C. ^{1}H-NMR spectrum, δ −0.68 (s, 6H, AlCH_3), 1.61 (s, 6H, OCCH_3), 2.52 (s, 3H, o-CH_3), 6.88 (m, 3H, m- and p-H, C_6H_4), 7.19 (d, $^3J = 7.7$ Hz, 1H, o-H, C_6H_{40}). ^{13}C-NMR spectrum, δ −5.30 (AlCH_3), 23.50 (C_6H_4–CH_3), 31.30 (OC–CH_3), 78.92 (OCCH$_3$), 126.40, 126.79, 129.24, 134.01, 138.64 and 142.19 (o-, m-, p- and i-C, C_6H_4).

4.2.6. [$Me_2AlOC(2,4\text{-}Me_2\text{-}C_6H_3)Me_2$] (**12**)

Yield, 50.9%; m.p., 118–120°C. ^{1}H-NMR spectrum, δ −0.57 (s, 6H, AlCH_3), 1.70 (s, 6H, OCCH_3), 2.03 (s, 3H, o-CH_3), 2.60 (s, 3H, p-CH_3), 6.78 (d, $^3J = 9.4$ Hz, 1H, m-H, C_6H_4), 6.85 (s, 1H, o'-H, C_6H_4), 7.18 (d, 1H, o-H, C_6H_4). ^{13}C-NMR spectrum, δ −5.32 (AlCH_3), 21.28 (o-CH_3), 23.44 (p-CH_3), 31.45 (OCCH_3), 78.78 (OCCH$_3$), 126.89, 127.02, 134.81, 138.50, 138.64, 139.47 (o-, m-, p- and i-C, C_6H_4).

4.2.7. [$Me_2AlOC(2,4,6\text{-}OMe\text{–}C_6H_2)Me_2$]

Yield, 40.1%; m.p., 138–140°C. ^{1}H-NMR spectrum, δ −0.47 (s, 6H, AlCH_3), 2.14 (s, 6H, OCCH_3), 3.34 (s, 3H, p-OCH_3), 3.40 (s, 6H, o-OCH_3, C_6H_4), 6.05 (s, 2H, m-H, C_6H_2). ^{13}C-NMR spectrum, δ −5.82 (AlCH_3), 33.60 (C–CH_3), 54.95 (p-OCH_3), 55.22 (o-OCH_3), 78.15 (C–CH$_3$), 92.44 (m-C, C_6H_2), 113.70 (i-C, C_6H_2), 161.21 and 161.50 (o- and p-C, C_6H_2).

4.2.8. [$Me_2AlOC(1\text{-}C_{10}H_7)Me_2$] (**16**)

Yield, 13.0%; slowly decomposes on heating. ^{1}H-NMR spectrum, δ −0.70 (s, 6H, AlCH_3), 1.87 (s, 6H, OCCH_3), overlapping signals covering the region 7.14–8.92 (m, 7H, naphthyl). ^{13}C-NMR spectrum in d_8-toluene, δ −6.10 (AlCH_3), 31.46 (OCCH_3), 78.69 (OCCH$_3$), overlapping signals 123.65–139.83 (aromatic naphthyl).

4.2.9. [$Me_2AlOC(2\text{-}C_{10}H_7)Me_2$] (**18**)

Yield 13.9%; m.p. 134–136°C. ^{1}H-NMR spectrum, δ −0.67 (s, 6H, AlCH_3), 1.60 (s, 6H, OCCH_3), overlapping signals covering the region 7.07–7.75 (m, 7H, naphthyl). ^{13}C-NMR spectrum, δ −5.41 (AlCH_3), 31.48 (OCCH_3), 77.59 (OCCH$_3$), overlapping signals 124.93–143.08 (aromatic naphthyl).

4.3. ^{1}H-NMR spectroscopic experiments

Ketone **1** or **5** (1.5 mmol) was added dropwise to a −78°C cooled solution of Me_3Al (1.7 mmol) in 3 ml of toluene. The reaction mixture was allowed to warm slowly to ambient temperature and stirred for 1 h. All solvents were removed in vacuo and a portion of the oily residue removed for spectroscopic analysis. The remaining oil was dissolved in 2 ml of toluene and the solution was heated to reflux for 3 h. Solvents were removed in vacuo and a portion removed for spectro-

Table 4
Crystallographic data

	2	**6**
Formula	$C_{26}H_{38}Al_2O_2$	$C_{22}H_{34}Al_2O_2$
M_r	436.52	384.45
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.320(2)	9.0532(9)
b (Å)	15.091(4)	15.2132(15)
c (Å)	12.153(3)	8.7909(9)
β (°)	102.447(16)	109.281(2)
V (Å^3)	1310.9(6)	1142.8(2)
Z	2	2
D_{calc} (g cm^{-3})	1.106	1.117
μ (mm^{-1})	1.131	0.140
T (K)	160	160
θ Range (°)	4.74–67.33	2.38–28.69
Measured reflections	4112	15 277
Unique reflections	2108	
Reflections with $I>2\sigma(I)$	1875	11 628
Goodness-of-fit (S)	1.071	1.062
R_{int}	0.0991	
R (F, $F^2>2\sigma$)	0.0454	0.0428
R_w (F^2, all data)	0.1180	0.1297

scopic analysis. The *gem*-CH_2 signals assigned to the self-coupled aldol reaction of **5** with Me_3Al were doublets located at δ 2.99 and 2.63 with $^2J = 17.1$ Hz.

4.4. X-ray crystallographic studies

Crystals of **2** and **6** were mounted onto glass fibres in an oil drop. For **2**, data were collected on a Stoe-Siemens four-circle diffractometer equipped with a novel microsource X-ray generator, tube and focussing optics [22]; the radiation was Cu–K_α ($\lambda = 1.54184$ Å). Intensities were measured with on-line profile fitting [23]. For **6**, data were collected on a Bruker AXS SMART CCD diffractometer with Mo–K_α radiation ($\lambda = 0.71073$ Å). Both data sets were measured at 160 K by use of a Cryostream cooler [24]. The crystal of **6** was found to be non-merohedrally twinned, and intensities were derived for both twin components, which were subsequently refined to a ratio close to 70:30. Crystal data are in Table 4; merging of symmetry equivalent reflections is not performed in the case of non-merohedral twinning, in order to retain the separate components for use in refinement. The structure solutions were by direct methods, with refinement on F^2 for all measured data [25].

4.5. Computational details

The GAUSSIAN 94 program (revision E.2), run on a Silicon Graphics Origin 200 workstation, was used for the calculations [5]. No symmetry constraints were imposed and all molecules were allowed to freely optimise. All calculations used the general basis set 6-31G* [26]. Absolute energies (Hartrees) for the calculated species: **I**, -721.51640; **II**, -499.57495; **III**, -1640.42162; **IV**, -1720.80446; **V**, -382.47637; **VI**, -1406.21446; **VII**, -1486.64526; **VIII**, 40.19517; **IX**, -498.95493; **X**, -381.85011; **XI**, -1640.42166.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 139425 and 139426. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We would like to thank the Royal Society for funding an Exquota Fellowship (I.R.) and a University Research Fellowship (K.W.H.). Thanks also to the EPSRC and Bede Scientific Instruments Ltd (microsource division) for equipment funding (W.C.).

References

[1] J.R. Zietz, G.C. Robinson, K.L. Lindsay, Chapter 46, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 7, Pergamon, Oxford, 1983.

[2] H. Yamamoto, K. Maruoka, Pure Appl. Chem. 60 (1988) 21.

[3] (a) S. Saito, M. Shiozawa, M. Ito, H. Yamamoto, J. Am. Chem. Soc. 120 (1998) 813. (b) D.A. Cogan, J.A. Ellman, J. Am. Chem. Soc. 121 (1999) 268. (c) S. Saito, T. Sone, K. Shimada, H. Yamamoto, Synlett (1999) 81. (d) S. Saito, H. Yamamoto, Chem. Commun. (1997) 1585.

[4] F.H. van der Steen, G.P.M. van Mier, A.L. Spek, J. Kroon, G. van Koten, J. Am. Chem. Soc. 113 (1991) 5742.

[5] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian Inc., Pittsburgh, PA, 1995.

[6] (a) S. Pasynkiewicz, E. Silwa, J. Organomet. Chem. 3 (1965) 121. (b) E.A. Jeffery, A. Meisters, T. Mole, J. Organomet. Chem. 74 (1974) 365.

[7] M.B. Power, A.W. Apblett, S.G. Bott, J.L. Atwood, A.R. Barron, Organometallics 9 (1990) 2529.

[8] J.F. Allan, K.W. Henderson, A.R. Kennedy, Chem. Commun. (1999) 1325.

[9] R.M. Waymouth, B.D. Santarsiero, R.H. Grubbs, J. Am. Chem. Soc. 106 (1984) 4050.

[10] (a) D. Seebach, R. Amstutz, J.D. Duntiz, Helv. Chim. Acta 64 (1981) 2622. (b) D. Seebach, Angew. Chem. Int. Ed. Engl. 27

(1988) 1624. (c) K.W. Henderson, A.E. Dorigo, Q.-Y. Liu, P.G. Williard, P.v.R. Schleyer, P.R. Bernstein, J. Am. Chem. Soc. 118 (1996) 1339. (d) P.G. Williard, Q.Y. Liu, J. Am. Chem. Soc. 115 (1993) 3380.

[11] (a) E.A. Jeffery, A. Meisters, T. Mole, J. Organomet. Chem. 74 (1974) 373. (b) E.A. Jeffery, A. Meisters, J. Organomet. Chem. 82 (1974) 307.

[12] P. Veya, P. Giorgio Cozzi, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 13 (1999) 4939.

[13] G. Erker, M. Albrecht, Organometallics 12 (1993) 4969.

[14] (a) W. Clegg, E. Lamb, S.T. Liddle, R. Snaith, A.E.H. Wheatley, J. Organomet. Chem. 573 (1999) 305. (b) R.J. Wehmschulte, W.J. Grigsby, B. Schiemenz, R.A. Bartlett, P.P. Power, Inorg. Chem. 35 (1996) 6694. (c) K.W. Henderson, A.E. Dorigo, P.G. Williard, P.R. Bernstein, Angew. Chem. Int. Ed. Eng. 35 (1996) 1322. (d) L.M. Jackman, M.M. Petrei, B.D. Smith, J. Am. Chem. Soc. 113 (1991) 3451. (e) M. Westerhausen, W. Schwarz, Z. Anorg. Allg. Chem. 619 (1993) 1053.

[15] P.G. Williard, G.B. Carpenter, J. Am. Chem. Soc. 108 (1986) 462.

[16] (a) M.L. Sierra, V.S.J. de Mel, J.P. Oliver, Organometallics 8 (1989) 2486. (b) H. Schumann, M. Frick, B. Heymer, F. Girgsdies, J. Organomet. Chem. 512 (1996) 117. (c) P.B. Hitchcock, H.A. Jasim, M.F. Lappert, H.D. Williams, Polyhedron 9 (1990) 245.

[17] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.

[18] (a) W. Clegg, S.T. Liddle, K.W. Henderson, F.E. Keenan, A.R. Kennedy, A.E. McKeown, R.E. Mulvey, J. Organomet. Chem. 572 (1999) 283. (b) D.R. Armstrong, F.J. Craig, A.R. Kennedy, R.E. Mulvey, J. Organomet. Chem. 550 (1998) 355. (c) D.R. Armstrong, F.J. Craig, A.R. Kennedy, R.E. Mulvey, Chem. Ber. 129 (1996) 1293. (d) I. Demachy, F. Volatron, Eur. J. Inorg. Chem. (1998) 1015. (e) M.G. Gardiner, G.A. Koutsantonis, S.M. Lawrence, F.-C. Lee, C.L. Raston, Chem. Ber. 129 (1996) 545.

[19] (a) J.J. Eisch, Chapter 6, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), vol. 1, Pergamon Press, Oxford, 1982. (b) G.H. Robinson, Coordination Chemistry of Aluminium, VCH, New York, 1993.

[20] (a) J. Lewinski, J. Zachara, I. Justyniak, Organometallics 16 (1997) 4597. (b) J. Lewinski, J. Zachara, K.B. Starowieyski, J. Chem. Soc. Dalton Trans. (1997) 4217.

[21] D.F. Schriver, M.A. Drezdon, The Manipulation of Air-Sensitive Compounds, Wiley, New York, 1986.

[22] U.W. Arndt, J.V.P. Long, P. Duncumb, J. Appl. Crystallogr. 31 (1999) 936.

[23] W. Clegg, Acta Crystallogr. Sect. A 37 (1981) 22.

[24] J. Cosier, A.M. Glazer, Appl. Crystallogr. 19 (1986) 105.

[25] G.M. Sheldrick, SHELXTL Version 5, Bruker AXS Inc, Madison, WI, USA, 1997.

[26] (a) W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257. (b) P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213. (c) J.D. Dill, J.A. Pople, J. Chem. Phys. 62 (1975) 2921.