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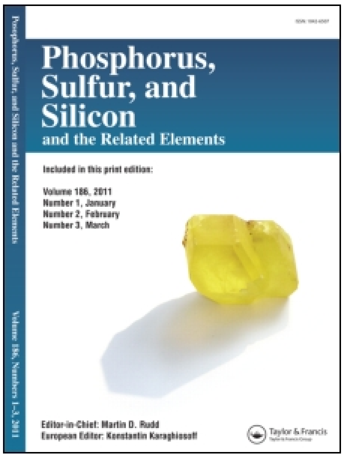

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Novel Metal Complexes Containing 1-Azaallyl and β-Diketiminato Ligands

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The bis[β-diketiminato(dimethyl)aluminium] complex $\{Me_2Al[N(R)C(Ar)]_2CH\}_2CH_2$ ($Ar = C_6H_4Me$-4, $R = SiMe_3$) **1** and the bis[lithium β-diketiminate]s $\{Li[N(R)C(Ar)]_2CH\}_2CH_2$ **2**($Ar = C_6H_5$) and **3** ($Ar = C_6H_4Me$-4) were prepared and fully characterised. The X-ray structures of **1** and **2** are reported, showing different features; **2** has the unexpected fused bicyclic structure of two 8-membered rings.

The adamantyl-substituted lithium 1-azaallyl complex $\{Li[N(R)C(Ad)C(H)R]\}_2$ **4** and the lithium β-diketiminates $\{Li[N(R)C(Ad)C(H)C(Ar)N(R)]\}_2$ **5** ($Ar = C_6H_5$) and **6** ($Ar = C_6H_4Me$-4) were synthesised. Each was reacted either with $AlMeCl_2$ (for **4**) or $AlMe_2Cl$ (for **5**), yielding the aluminium derivatives $MeAl[N(R)C(Ad)C(H)R][N(R)C(Ad){=}C(H)R]$ **7** and $Me_2Al[N(R)C(Ad)C(H)C(Ar)N(R)]$ **8**, respectively.

Keywords: 1-azaallyl; β-diketiminate; metal complex; adamantyl

There is much current interest in bi- and tri- dentate nitrogen-centred spectator ligands, which often are a component of electrophilic neutral or cationic metal alkyls. Aluminium complexes have become prominent, following the disclosure of Coles and Jordan that certain cationic amidinatoaluminium methyls are active catalysts for the polymerisation of ethylene [1]. We recently described the synthesis and X-ray molecular structures of a series of neutral and cationic β-diketiminatoaluminium methyls [2].

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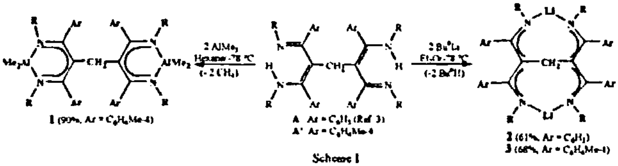
Here we report on the synthesis of new 1-azaaallyl- and β-diketiminato- metal complexes, which may be of interest as catalysts for olefin polymerisation or related reactions; for earlier publications, see refs. [2] and [3].

One aspect of the present study deals with the synthesis of new bis(β-diketiminatometal) complexes, based on the interesting bis[β-diketimine]s $\{H[N(R)C(Ar)]_2CH\}_2CH_2$ (Ar = C_6H_5, R = $SiMe_3$), **A** [4] and **A'** (Ar = C_6H_4Me-4).

Treatment of **A'** with two equivalents of $AlMe_3$ afforded the bis[β-diketiminato(dimethyl)aluminium] complex **1** (Scheme 1), which was X-ray-characterised. The synthesis of the bis[lithium β-diketiminate]s **2** and **3** has been accomplished by reacting two equivalents of $LiBu^n$ with **A** and **A'**, respectively (Scheme 1). The molecular structures for **1** and **2** were determined by single crystal X-ray diffraction.



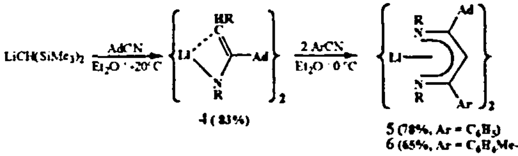
Scheme 1

It is interesting to note the difference between the molecular structures of the crystalline complexes 1 and 2. Whereas 1 allows free rotation around $-CH_2-$, in 2 the presence of the fused bicyclic structure (the $-CH_2-$ being 'trapped') confers rigidity to this molecule.

Another contribution deals with the synthesis of metal complexes based on a new 1-azaallyl ligand containing the adamantyl (Ad) substituent $[N(R)C(Ad)C(H)R]^-$ (R = $SiMe_3$), **B**.

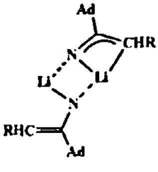
B

The lithium derivative $\{Li[N(R)C(Ad)C(H)R]\}_2$ **4** was obtained by reaction of $Li[CH(SiMe_3)_2]$ with one equivalent of the 1-adamantane-carbonitrile (1-AdCN), following the experimental procedure (Scheme 2) previously established for the synthesis of $[Li\{N(R)C(Bu^t)C(H)R\}]_2$ [5]. The reaction of **4** with either benzonitrile or *p*-tolunitrile yielded the new unsymmetrical lithium β-diketiminates **5** or **6** (Scheme 2).



Scheme 2

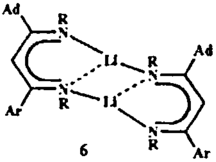
Both complexes **4** and **6** have been X-ray-characterised, crystalline **4** is dinuclear with the two ligands presenting different coordination modes, one being of 1-azaallyl and the other of enamido type (Figure 1).



4

Figure 1

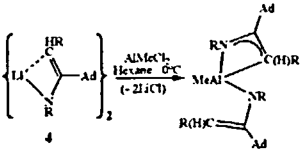
Compound **6** has a dimeric ladder-type structure with the central Li_2N_2 rhombus being planar (Figure 2).



6

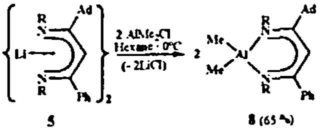
Figure 2

The reaction of (i) one equivalent of $AlMeCl_2$ with **4** and (ii) two equivalents of $AlMe_2Cl$ with **5**, afforded aluminium complexes MeAl[N(R)C(Ad)C(H)R]$_2$ **7** (Scheme 3) and Me$_2$Al[N(R)C(Ad)C(H)C(Ph)N(R)] **8** (Scheme 4), respectively.



4 **7** (66%)

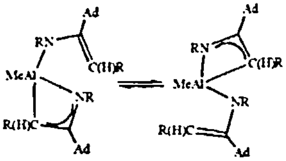
Scheme 3



5 **8** (65%)

Scheme 4

NMR spectroscopic solution studies showed that for **7** the two 1-azaallyl ligands exchange rapidly on the NMR time scale (Scheme 5); the ^{1}H NMR spectral coalescence temperature Tc = 300 K corresponds to $\Delta G^{\neq}_{300\ K}$ = 61.4 kJ mol^{-1}. Similar behaviour was observed [3] for the tert-butyl analogue of **7** (i.e., **7** with Bu^t in place of Ad), having Tc = 302 K corresponding to $\Delta G^{\neq}_{302\ K}$ = 60.7 kJ mol^{-1}.



Scheme 5

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