



Note

Reactivity studies of AlMe₂Cl with potentially tridentate O,N,L-type ligands



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ABSTRACT

Neutral tridentate O,N,L-type ligands *aeimp*-H, *quimp*-H and *ppimp*-H (*aeimp*-H = 2-((dimethylamino)ethylimino)methyl)-4,6-di-tert-butyl-phenol; *quimp*-H = 2-((quinolin-8-ylimino)methyl)-4,6-di-tert-butyl-phenol; *ppimp*-H = 2-((2-phenoxyphenylimino)methyl)-4,6-di-tert-butylphenol) readily reacted with AlMe₂Cl to afford the corresponding methyl-chloro aluminium derivatives (*aeimp*)AlMeCl (**2a**) (*quimp*)AlMeCl (**2b**) and (*ppimp*)AlMeCl (**2c**) with concomitant elimination of methane. DFT calculations suggested that the pendant donor arm in these species is weakly bounded to the metal centre. A fast chloride abstraction by Me₂AlCl from the neutral derivatives **2a** and **2b** produced the tetrahedral cationic species (η³-O,N,L)AlMe⁺ counterbalanced by the Me₂AlCl₂⁻ anion. Analogously direct treatment of *bpzmp*-H (*bpzmp*-H = 2,4-di-tert-butyl-6-(bis(3,5-dimethylpyrazol-1-yl)methyl)phenol) with two equivalents of Me₂AlCl afforded the Al cation [(*bpzmp*)AlMe][Me₂AlCl₂] (**3d**) as determined by single crystal X-ray analysis.

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1. Introduction

Recent years have witnessed a growing interest in the chemistry of organoaluminium compounds [1,2]. In addition to their use as catalyst component for poly-, co- and oligomerization of 1-olefins [3,4], organoaluminium compounds are extensively applied for the synthesis of various other organic compounds [5–8]. The use of aluminium compounds in applied chemistry generally relies on the fact that they are robust, highly soluble, and, above all, highly Lewis acidic species. Most of the investigated aluminium complexes have the general formula of LnAlR, where L is an ancillary ligand and R is an alkyl group. These complexes are generally prepared by alkane elimination reaction starting from the commercially available and easily handled solutions of aluminium alkyls. The generation of alkane adds the advantage of obviating to the byproduct removal step. However alkyl derivatives do not always represent the best initiator. For example, in the ring opening polymerization of cyclic esters, aluminium complexes bearing Al-alkyl bonds are generally inactive; they are able to initiate the ROP only in combination with aliphatic or benzylic alcohols [9–16]. Other aluminium precursors, including alkoxides [17–19], amides [20], halides [17,21,22], and alkyl halides [23], are also reported. In this context Al chloro species

may be of interest as they could exhibit an enhanced Lewis acidity vs. that of Al alkyls and thus be of potential use in catalysis.

Another class of aluminium complexes that has been studied for their potential use in catalysis is that of cationic alkyl–aluminium complexes [24]. These are highly electrophilic species that have already found application in ethylene, propylene oxide, ε-caprolactone and lactide polymerization catalysis [25–31]. Such cationic species can be generated by reaction of aluminium dialkyl precursors with [Ph₃C][B(C₆F₅)₄] or B(C₆F₅)₃, via alkyl abstraction at the metal centre or with ammonium salts [HNR₃][B(C₆F₅)₄] via alkane elimination [24]. The drawback of these approaches is the use of expensive reagents. Alternatively these cationic species could be synthesized through a chloride abstraction reaction of neutral alkyl–chloro complex. The ionization of {LX}Al(Cl)(R) derivatives with chloride abstracting agent has never been investigated although this approach might be a straightforward alternative for preparation of cationic aluminium complexes.

Schiff bases have been widely employed as heterobidentate ligands in the coordination chemistry of aluminium alkyl complexes. It is worth noting that phenoxy-imine based aluminium complexes are able to initiate the ROP of lactides and lactones [32,33]. Notable examples are the related salen aluminium complexes for their ability to promote stereoselective polymerization of *rac*-lactide. [34,35] While the majority of these aluminium complexes bears bidentate or tetradentate ligands, tridentate ligands have been much less explored for coordination to the aluminium centre.

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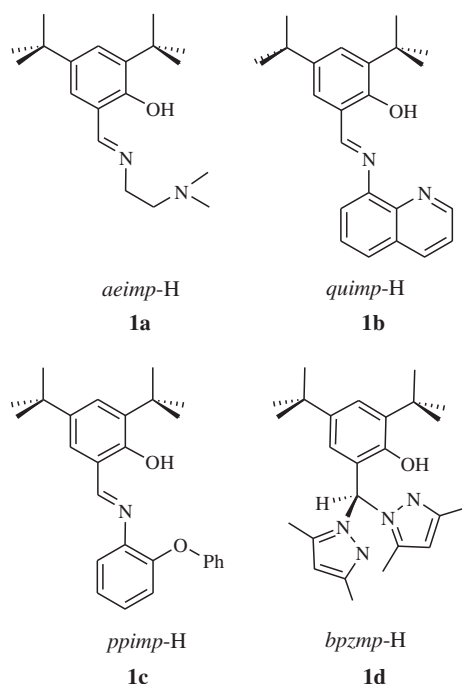
With this in mind, we were interested in exploring the reactivity of tridentate monoanionic Schiff base ligands toward AlMe_2Cl and in the characterization of the relative products of reaction. For our studies we selected the 2-((dimethylamino)ethylimino)methyl)-4,6-di-*tert*-butyl-phenol (*aeimp*-H **1a**), 2-((quinolin-8-ylimino)methyl)-4,6-di-*tert*-butyl-phenol (*quimp*-H **1b**) and 2-((2-phenoxypheylimino)methyl)-4,6-di-*tert*-butylphenol (*ppimp*-H **1c**) (Scheme 1). These ligands have salicylaldiminato skeleton and differ for the basicity of the pendant arm. We also included the heteroscorpionate 2,4-di-*tert*-butyl-6-(bis(3,5-dimethylpyrazol-1yl)methyl)phenol ligand (*bpzmp*-H **1d**) as a further example of a tridentate ligands bearing oxygen and nitrogen donors. All these ligands were successfully employed in the synthesis of neutral and cationic aluminium complexes [29,36]. Here we report the results of our reactivity studies.

2. Results and discussion

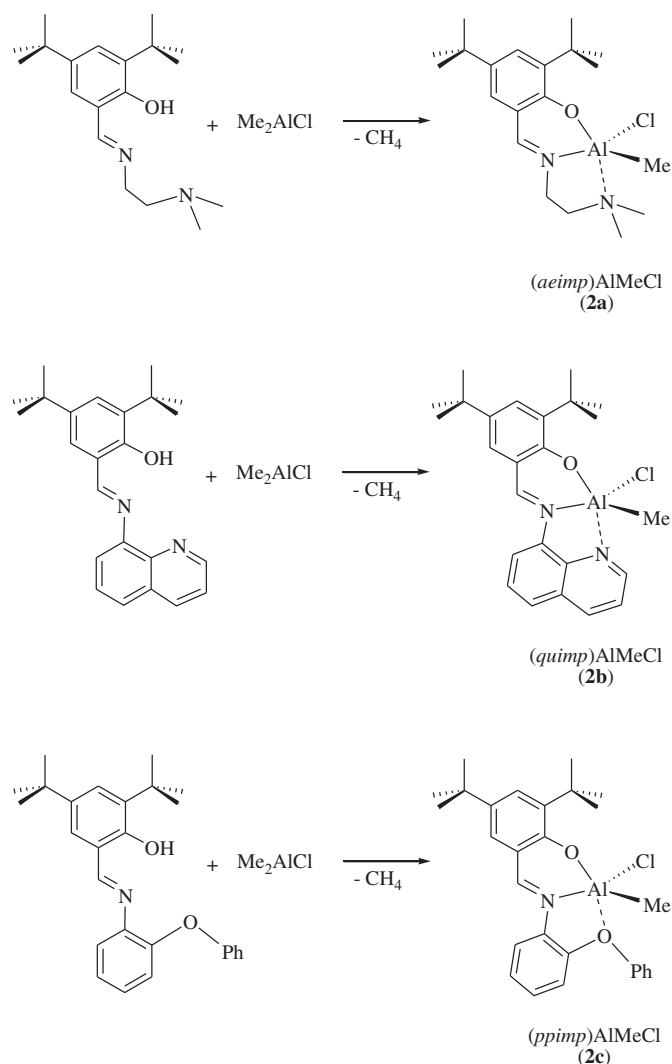
The ligands *aeimp*-H, *quimp*-H and *ppimp*-H were synthesized by reacting the 3,5-di-*tert*-butylsalicylaldehyde with the suitable amine according to the published procedure [36].

Treatment of a benzene solution of *aeimp*-H, *quimp*-H or *ppimp*-H with 1 equiv. of Me_2AlCl readily afforded the methyl-chloro aluminium derivatives (*aeimp*) AlMeCl (**2a**) (*quimp*) AlMeCl (**2b**) and (*ppimp*) AlMeCl (**2c**) (Scheme 2). The reactions were fast and quantitative on NMR scale. Solution ^1H NMR studies of the reactions performed in benzene- d_6 indicated the disappearance of the O–H signal of the free ligands and the appearance of a resonance for the protons of methyl group bound to the aluminium in the high-field region of the ^1H NMR spectra. The σ -bond metathesis reaction between alcoholic proligand and AlMe_2Cl , enabling methane elimination, is a well known synthetic procedure for the preparation of methyl chloro aluminium complexes [17,37,38].

The ^1H and ^{13}C NMR spectra of the obtained products were consistent with the presence of one phenoxy-imine ligand and one methyl ligand in 1:1 molar ratio. In the ^1H NMR spectra recorded in C_6D_6 , the methyl groups bound at aluminium centre appeared as a sharp singlet in the highfield region at -0.16 , 0.00 and -0.07 ppm



Scheme 1.



Scheme 2.

for **2a**, **2b** and **2c**, respectively. The resonances of the imine proton occurred at 7.33, 8.09 and 7.72 ppm for **2a**, **2b** and **2c**, respectively. It is worth noting that pattern of resonances suggested a κ^3 coordination of the ligands to the metal centre. As matter of fact in ^1H NMR spectrum of **2a** the backbone $=\text{NCH}_2\text{CH}_2\text{N}$ group gave rise to a typical pattern of resonances of diastereotopic protons as expected for a C_1 symmetric species resulting from the coordination of the ligands to the metal centre via the phenoxy group, the imino and amine nitrogen atoms (Fig. 1).

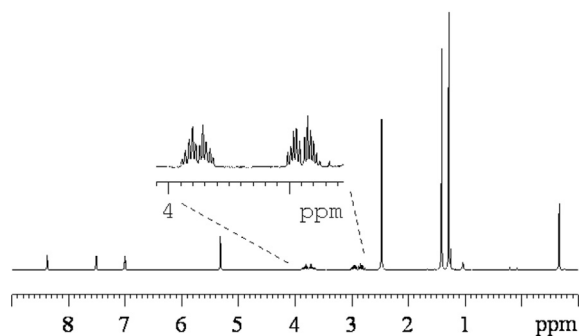


Fig. 1. ^1H NMR spectra of **2a** (CD_2Cl_2 , RT, 250 MHz).

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