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Exploring the chelating potential of 1,3-bis(furyl)-1,1,3,3-tetramethyldisilazides

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Dedicated to Professor M.F. Lappert FRS in recognition of his diverse and distinguished contributions to organometallic chemistry, and with sincere thanks for his help and encouragement over the years.

Abstract

A range of furyl-substituted silylamides of the group 1 metals have been isolated and structurally characterized. The lithium salts of the neutral compounds $(RMe_2Si)_2NH$ [**1**H, R = furyl; **2**H, R = 2-methylfuryl; **3**H, R = 2-trimethylsilylfuryl] are formed directly in a one-pot reaction between the chloraminosilane, $(ClMe_2Si)_2NH$ and three equivalents of the appropriate furyl lithium species. Conversion of the Li-salts to the neutral compounds **1**H and **2**H by quenching with NH_4Cl, and reaction of the unpurified products with KNH_2 afforded the corresponding potassium salts K{**1**} and K{**2**}. The crystal structures of $[Li\{\mathbf{2}\}]_2$, $[Li\{\mathbf{3}\}]_2(THF)$, $[K\{\mathbf{1}\}(toluene)]_2$ and $[K\{\mathbf{2}\}(toluene)]_2$ have been determined, in which, as predicted, the ability of the furyl group to coordinate to the metal is related to the size of the substituent in the 2-position.

Keywords: Lithium amide; Potassium amide; Silazide; Furyl; Crystal structure

1. Introduction

The search for alternative ancillary ligand frameworks to the ubiquitous cyclopentadienyl skeleton in group 4 metal catalysed olefin polymerization catalysis is an ongoing concern in many research groups worldwide [1]. Amongst the most successful new systems are those based on the amide ligand which, upon formation of the target bis(ligand) complex, $M(NR_2)_2X_2$, (M = group 4 metal, X = halide/alkyl) form a highly electron-deficient precatalyst with a formal electron count of 14. To help ensure that the ligands function in their desired supporting role, without causing adverse effects on the polymerization behaviour of the activated system through unwanted side-reactions, a combination of one or more of the following approaches have typically been adopted: (i) the use of sterically demanding *N*-substituents (**a**, Ar = 2,6-$^i Pr_2C_6H_3$, Fig. 1) [2]; (ii) formation of a chelating diamide system (**b**–**e**, Fig. 1) [3–5] (iii) incorporation of additional donor groups within the ligand framework [5,6]. (Fig. 1).

The use of silicon-based substituents, both in the N-terminal position and as a component of the bridging group between the two amide functionalities, have been liberally used in fulfillment of these objectives. In the latter cases, a higher activity in olefin polymerization has been observed compared with the hydrocarbon linked systems, attributed to reduced electron density at the metal arising from the 'silicon effect' [3].

We have developed a potential ligand system based on the bulky hexamethyldisilazide anion in which one of the methyl substituents has been replaced by a (substituted) furyl ring. We hypothesize that such ligands will be able to adopt a number of different coordination modes at a metal centre, highly dependant on the nature of the furyl substituent and the coordination requirements of the metal

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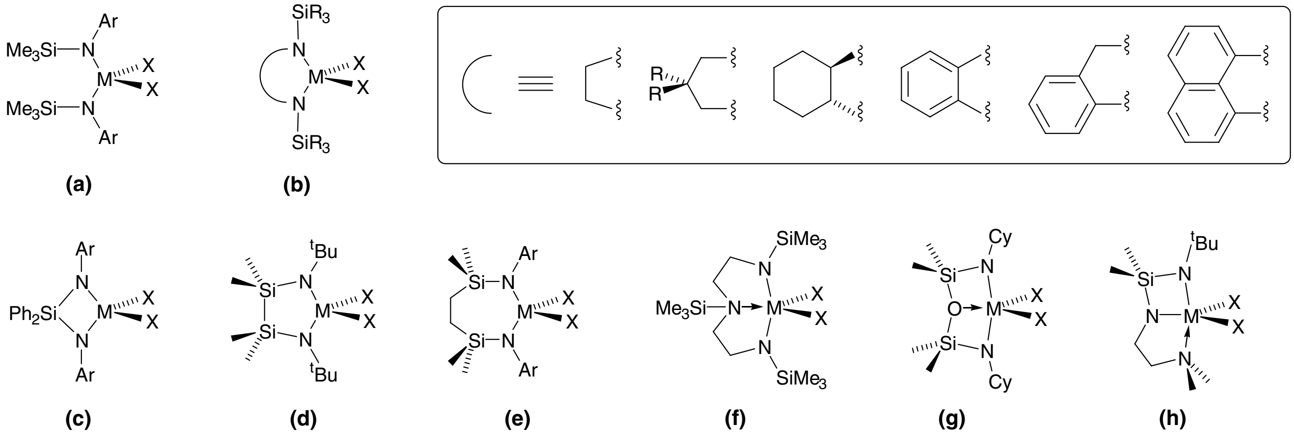

Fig. 1. Examples of amide-based ligand systems, incorporating silicon, that have been used in the synthesis of group 4 metal olefin polymerization precatalysts. For references, refer to text.

fragment in question. Several advantages over existing systems are evident, including the ease of synthesis and steric manipulation associated with this system, and the ability of the ligand to function as either an [X]-, [XL]- or [XL$_2$]-type electron donor, depending on the number of furyl rings bonding to the metal. Herein we report a series of structural results on the group 1 (Li, K) salts of the target compounds, enabling information to be gained on the ability of the O-donor group to interact with the N-bound metal centre.

2. Experimental

2.1. General considerations

All manipulations were carried out under dry argon using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox. Solvents were dried over appropriate drying agent and degassed prior to use. NMR spectra were recorded using a Bruker Advance DPX 300 MHz spectrometer at 300.1 (^{1}H), 75.4 (^{13}C{^{1}H}) and 116.6 (^{7}Li{^{1}H}) MHz and a Bruker AMX 500 MHz spectrometer at 500.1 (^{1}H), 125.7 (^{13}C{^{1}H}), 194.3 (^{7}Li{^{1}H}) and 99.3 (^{29}Si{^{1}H}) MHz, from samples at 25 °C in [^{2}H$_6$]-benzene, unless otherwise stated. Coupling constants are quoted in Hz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances; lithium was referenced externally to LiCl (aq) and silicon was referenced to SiMe$_4$. All samples were exposed to high vacuum before submission for combustion analysis (performed by S. Boyer at London Metropolitan University); formulae are therefore calculated for the desolvated compounds.

1,3-Dichloro-1,1,3,3-tetramethyldisilazane [7] and 2-trimethylsilylfuran [8] were synthesized according to the literature procedures. The furyl-lithium reagents were prepared in situ from the reaction of the corresponding furan ring and ^{n}BuLi at 0 °C [9]. Li{**1**} was made by the procedure described below; all data were in agreement with the previously reported compound [10].

2.2. Lithium 1,3-bis(furyl)-1,1,3,3-tetramethyldisilazide (Li{*1*})

A solution of furan (9.61 mL, 134 mmol) in THF (80 mL) was cooled to 0 °C and *n*-butyllithium (51.0 mL of a 2.61 M solution in hexane) was added dropwise over approximately 10 min. The resulting solution was stirred at 0 °C for a further 30 min before being allowed to warm to ambient temperature. The solution was then cooled to −78 °C, and neat 1,3-dichloro-1,1,3,3-tetramethyldisilazane (8.50 mL, 45 mmol) was added. The mixture was allowed to warm to ambient temperature, and the volatile components were removed in vacuo. The solid residue was extracted with toluene (80 mL) and filtered to exclude lithium chloride. The toluene extract was concentrated in vacuo to approximately 20 mL, and cooled to −45 °C. The crystalline product was isolated by filtration, washed with 40–60 petroleum ether (3 × 10 mL) and dried in vacuo to afford the pure product as a white powder. Yield: 3.50 g (29%). Characterising data for this compound can be found in the literature [10].

2.3. Lithium 1,3-bis(2-methylfuryl)-1,1,3,3-tetramethyldisilazide (Li{*2*})

The same procedure was used as described for compound Li{**1**}, using 2-methylfuran (8.14 mL, 90 mmol), *n*-butyllithium (34.60 mL of a 2.61 M solution in hexane) and 1,3-dichloro-1,1,3,3-tetramethyldisilazane (5.72 mL, 30 mmol). The product was isolated as an off-white solid. Yield: 6.30 g (70%).

Anal. Calc. for $C_{14}H_{22}NLiSi_2O_2$ (299.45): C, 56.16; H, 7.40; N, 4.68. Found: C, 56.30; H, 7.32; N, 4.54%. ^{1}H NMR: δ 6.27 (d, $^3J_{HH}$ 3.3, 2H, furyl-4*H*), 5.82 (m, 2H, furyl-3*H*), 2.10 (s, 6H, furyl-C*H*$_3$), 0.28 (br s, 12H, SiC*H*$_3$).