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s-Block metal complexes of a bulky, donor-functionalized allyl ligand†

Sophia A. Solomon, Christopher A. Muryn and Richard A. Layfield*

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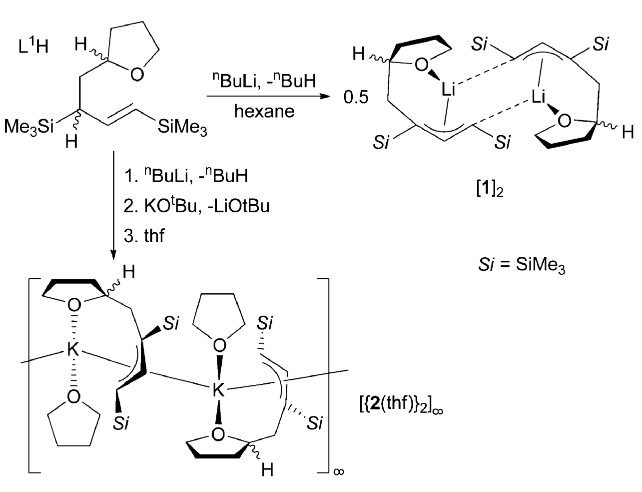
Crystallographic and NMR spectroscopic studies on allyl complexes of lithium, potassium and magnesium containing an *O*-donor functionality are described.

The introduction of heteroatom donor groups into organometallic ligand frameworks often allows control to be exerted over the structures and reactivities of organometallic compounds.[1] Donor-functionalized metal allyls are particularly interesting in this respect since their use in synthesis introduces the possibility of regioselectively converting metallated allyl silanes into functionalized products.[2] It is noteworthy, however, that fundamental studies on donor functionalized metal allyls are quite rare. Fraenkel and co-workers have reported a series of investigations on lithium allyls containing [bis(2-methoxyethyl)amino] and related donor groups tethered to the allyl C2 position, which revealed that notionally delocalized allyl anions may in some cases be conjugated to an extent that depends on the position of the counter cation relative to the plane of the allylic carbons. In turn, the position of the counter cation is determined by the short length of the tether to the pendant donor functionality, which can prevent lithium from occupying a position perpendicular to the centre of the allyl C_3 plane, resulting in partially localized allyl anions.[3] As a continuation of our work on the coordination chemistry of silyl–allyl ligands[4] and with the aim of increasing insight into the structural properties of donor-functionalized metal allyls, we report herein crystallographic and preliminary NMR spectroscopic studies on allyl complexes of lithium, potassium and magnesium in which the s-block metals are internally solvated by a tetrahydrofurfuryl functionality.

The new ligand L^1H was prepared as a mixture of diastereomers from the reaction of tetrahydrofurfuryl tosylate with $[Li\{C_3H_3(SiMe_3)_2\}]$. Deprotonation of L^1H by ^nBuLi in hexane afforded the corresponding lithium allyl complex, which was crystallized as a racemic mixture of the homochiral dimers (*R*,*R*)/(*S*,*S*)-$[L^1Li]_2$ ($[\mathbf{1}]_2$) with the *R* or *S* assignments referring to the configuration at C(5) and C(19) (Scheme 1 and Fig. 1).† Each lithium in $[\mathbf{1}]_2$ is complexed by the allyl component of L^1 in an η^3-manner with the Li(1)–C(1), Li(1)–C(2) and Li(1)–C(3) distances being 2.313(5), 2.194(5) and 2.489(5) Å, respectively, and the Li(2)–C(15), Li(2)–C(16) and Li(2)–C(17) distances being 2.310(5), 2.198(5) and 2.470(5) Å, respectively. The longer Li(1)–C(3) and Li(2)–C(17) bonds in $[\mathbf{1}]_2$ are adjacent to relatively short C(2)–C(3) and C(16)–C(17) bonds of 1.376(4) and 1.380(4) Å, whereas the shorter Li(1)–C(1) and Li(2)–C(15) bonds are adjacent to relatively long C(1)–C(2) and C(15)–C(16) bonds of 1.431(4) and 1.428(4) Å, respectively. The trimethylsilyl substituents adopt *exo*, *exo* orientations and significant deviations of Si(1) and Si(3) from the plane of the allyl carbons to which they are bonded are revealed by Si(1)–C(1)–C(2)–C(3) and Si(3)–C(15)–C(16)–C(17) torsional angles of 150.3(2) and 150.5(2)°, respectively. The Si(2)–C(3)–C(2)–C(1) and Si(4)–C(17)–C(16)–C(15) connectivities are near-planar, as shown by their torsional angles of 178.2(2) and 178.6(2)°, respectively. Internal solvation by the *O*-donor produces Li(1)–O(1) and Li(2)–O(2) distances of 1.870(5) and 1.871(5) Å, respectively, and relative to the $[Li_2C_2]$ core in $[\mathbf{1}]_2$ the pendant donor groups are mutually *cis*. Molecules of $[L^1Li]$ assemble into the dimer $[\mathbf{1}]_2$ by means of μ:η^1-bridging interactions to produce Li(1)–C(15) and Li(2)–C(1) bond distances of 2.272(5) and 2.260(5) Å, respectively, resulting in each lithium being 4-coordinate. The geometric parameters within the allyl components of $[\mathbf{1}]_2$ suggest that their negative charges are partially localized at C(1) and C(15), due to a combination of the μ-bridging modes of these carbons and also to coordination of the tetrahydrofurfuryl groups to the lithiums.

The potassium complex of L^1 was synthesized by adding freshly prepared $[L^1Li]$ to KO^tBu in hexane to give a viscous solution. Evaporating the hexane solvent afforded a red–brown powder which was recrystallized from thf to afford single crystals of $[\{L^1K(thf)\}_2]_\infty$, $[\{\mathbf{2}(thf)\}_2]_\infty$, a zigzag coordination polymer consisting of two unique, repeating molecules of $[L^1K(thf)]$ in which the configuration at the



Scheme 1

School of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL.
E-mail: Richard.Layfield@manchester.ac.uk

† Electronic supplementary information (ESI) available: Synthetic and spectroscopic details for all compounds. Crystallographic data for **1** (CCDC 678934), **2** (678935) and **3** (678936). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b803364a

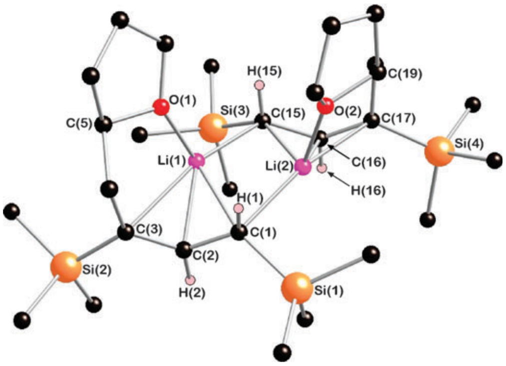


Fig. 1 Structure of (*R*,*R*)-[**1**]$_2$ shown with allylic hydrogens only. Selected bond lengths (Å) and angles (°): Li(1)–C(1) 2.313(5), Li(1)–C(2) 2.194(5), Li(1)–C(3) 2.489(5), Li(2)–C(15) 2.310(5), Li(2)–C(16) 2.198(5), Li(2)–C(17) 2.470(5), Li(1)–C(15) 2.272(5), Li(2)–C(1) 2.260(6), Li(1)–O(1) 1.870(5), Li(2)–O(2) 1.871(5), C(1)–C(2) 1.431(4), C(2)–C(3) 1.376(4), C(15)–C(16) 1.428(4), C(16)–C(17) 1.380(4); C(1)–C(2)–C(3) 132.1(2), C(15)–C(16)–C(17) 131.8(2).

tetrahydrofurfuryl CH group alternates from *R* to *S* along the polymer (Scheme 1 and Fig. 2). The K–C bond distances in $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ are within the range 3.009(4)–3.348(4) Å (average 3.133 Å), which is typical of η^n-coordination of organometallic ligands to potassium.[1a] The asymmetry in the bonding of the allyl component of L^1 to K(1) and K(2) is of a similar nature to the potassium–carbon bonding in other structurally characterized potassium allyls, in which the metal ions are complexed *inter*molecularly by Lewis bases.[5] Individual molecules of [L^{1}K(thf)] aggregate by means of μ:η^3:η^3-allyl interactions to result in a zigzag structure with K(1) and K(2) alternating to generate a K(1)–K(2)–K(1) angle of 141.3°. Each potassium cation is complexed additionally by a pendant *O*-donor group and one thf ligand to become formally 6-coordinate. The allyl C–C bond lengths in $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ are in the range 1.394(5)–1.412(5) Å, and with the range of Si–C–C–C torsional angles around the allyl carbons being only 174.3(3)–179.6(3)° this suggests that the formal negative charge within the allyl components of L^1 in $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ is essentially delocalized.

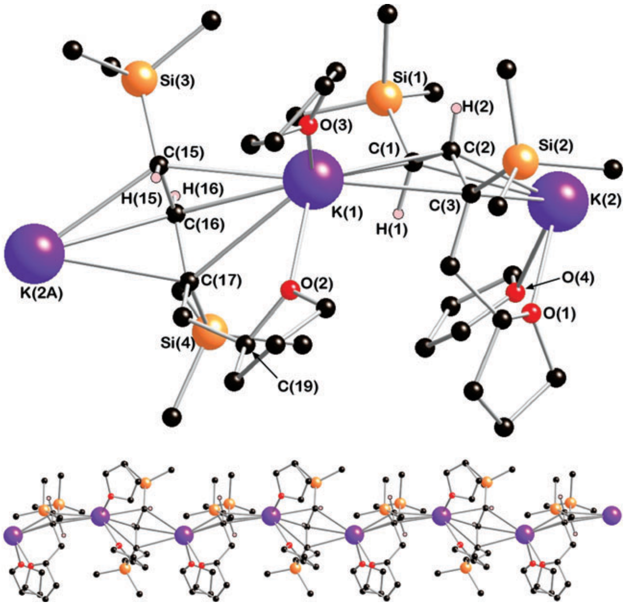
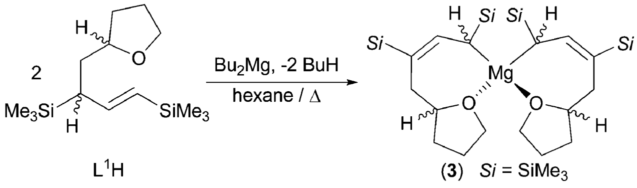


Fig. 2 Structure of $[\{\mathbf{2}(\text{thf})\}_2]_\infty$: Detail of the structure (upper) and an extended segment of the polymer chain (lower). Selected bond lengths (Å) and angles (°): K(1)–C(1) 3.120(4), K(1)–C(2) 3.058(4), K(1)–C(3) 3.186(4), K(1)–C(15) 3.102(4), K(1)–C(16) 3.014(3), K(1)–C(17) 3.348(4), K(2)–C(15) 3.075(3), K(2)–C(16) 3.048(3), K(2)–C(17) 3.216(4), K(2)–C(1) 3.084(4), K(2)–C(2) 3.009(4), K(2)–C(3) 3.334(4), K(1)–O(2) 2.665(3), K(1)–O(3) 2.731(3), K(2)–O(1) 2.659(3), K(2)–O(4) 2.728 (averaged due to disorder), C(1)–C(2) 1.412(5), C(2)–C(3) 1.394(5), C(15)–C(16) 1.412(5), C(16)–C(17) 1.397(5); C(1)–C(2)–C(3) 130.9(4), C(15)–C(16)–C(17) 131.4(3), K(1)–K(2)–K(1), 141.3.

The polymeric zigzag motif in $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ is often seen in the structures of potassium cyclopentadienyls,[1a] some of which are donor-functionalized,[6] and although the structure of $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ is reminiscent of these compounds it is also the first crystallographically characterized donor-functionalized potassium allyl. The different aggregation states of [**1**]$_2$ and $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ evidently stem from the differing radii of the metal ions, with the larger radius of K$^+$ leading to the metal raising its coordination number as far as steric constraints permit.

The magnesium complex of L^1, [(L^1)$_2$Mg] (**3**), was prepared according to Scheme 2. Molecules of **3** are C_2-symmetric and the two L^1 ligands coordinate to magnesium *via* a carbon atom of an η^1-allyl group and the oxygen atom of a pendant tetrahydrofurfuryl group, with Mg(1)–C(1) and Mg(1)–O(1) being 2.173(4) and 2.063(2) Å, respectively, resulting in two seven-membered chelate rings (Fig. 3) whose formation suggests that the initial deprotonation step is followed by a 1,3-sigmatropic rearrangement. The C(1)–Mg(1)–C(1), C(1)–Mg(1)–O(1) and O(1)–Mg(1)–O(1) bond angles in **3** are 138.9(2), 100.65(12) and 91.52(13)° (average 110.4°), respectively, affording a highly distorted tetrahedral geometry at Mg(1). The two chiral carbons within each L^1 in [**3**], C(1), C(5) and symmetry equivalents, adopt the same absolute configuration, with the (*S*,*S*)(*S*,*S*) form being shown in Fig. 3.

Magnesium allyls are widely used in synthesis as sources of the allyl anion and although their structures have been less studied than their alkali metal analogues, a few examples have been crystallographically characterized and display interesting structural properties.[7] In contrast to the η^3-allyl bonding mode that is common in alkali metal complexes of this ligand[8] and the observation of η^3-allyl coordination in $[\text{Ca}\{\eta^3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2(\text{thf})_2\}]$,[9] a noteworthy feature of magnesium allyls is the apparent preference for η^1-allyl coordination, as seen in **3**. This observation is particularly interesting in light of the regular occurrence of η^5-coordination in magnesium cyclopentadienyls,[1a] suggesting that η^3-coordination of the allyl ligand to magnesium is intrinsically disfavoured. The η^1- or σ-coordination of the allyl component of L^1 to magnesium in **3** means that it is closely related to the family of



Scheme 2

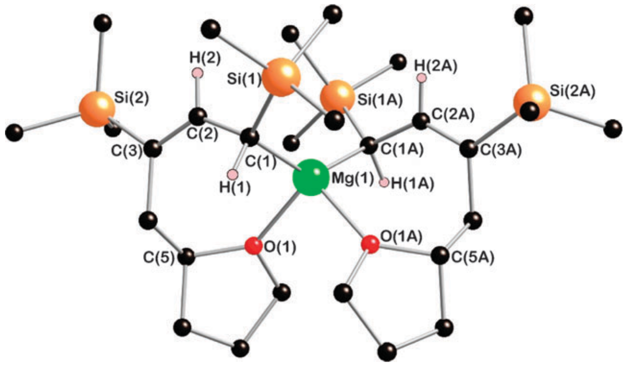


Fig. 3 Structure of (*S*,*S*)(*S*,*S*)-[**3**]. Selected bond lengths (Å) and angles (°): Mg(1)–C(1) 2.173(4), Mg(1)–O(1) 2.063(2), C(1)–C(2) 1.461(5), C(2)–C(3) 1.348(5); C(1)–Mg(1)–O(1) 100.65(12), C(1)–Mg(1)–C(1A) 138.9(2), O(1)–Mg(1)–O(1A) 91.52(13), C(1)–C(2)–C(3) 132.3(3). Symmetry transformations used to generate equivalent atoms: (A) = − *x* + 3/2, −*y* + 1/2, *z*.

structurally authenticated magnesium alkyls and aryls that feature intramolecular coordination to the metal by a range of *O*- or *N*-donor groups.[10]

NMR spectroscopy reveals that the solution-phase properties of $[\mathbf{1}]_2$, $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ and [**3**] are similar in several respects and therefore merit a collective discussion. The NMR properties of lithium allyls in particular have been studied in detail,[8a,b] and multinuclear NMR spectroscopic studies on internally solvated lithium allyls have shown that several rearrangement mechanisms, such as rotation about C–C and C–Si bonds, inversion at lithium, 1,3-sigmatropic rearrangements and bimolecular exchange of lithium, are possible.[3] Notwithstanding the intrinsically complicated behaviour of donor-functionalized lithium allyls, L^1 also contains four pairs of diastereotopic protons in the $[CH_2C_4H_7O]$ donor functionality. In the case of $[\mathbf{1}]_2$, the presence of two species in benzene-d_6 solution was revealed by four resonances in the ^{1}H and ^{13}C NMR spectra due to the $SiMe_3$ groups, eight ^{13}C resonances due to CH_2 groups and six ^{13}C resonances for the allylic carbons. The remaining ^{1}H resonances for $[\mathbf{1}]_2$ occur as a series of complex overlapping multiplets. The most likely explanation for these observations is the presence of two diastereomers in solution since the ^{1}H and ^{13}C resonances seemingly occur in pairs with only slight differences in chemical shift and resemble the spectra of the diastereomeric ligand precursor L^1H. The diastereomers of $[\mathbf{1}]_2$ are likely to involve both homochiral (*R*,*R*) and (*S*,*S*) enantiomeric pairs and their corresponding heterochiral diastereomers, *i.e.* (*R*,*S*) and (*S*,*R*), with respect to the tetrahydrofurfuryl methine group. Aggregation state equilibria are, in principle, possible, although the dimeric structure of $[\mathbf{1}]_2$ evidently remains intact in benzene, analogous to the parent compound $[Li(C_3H_5)]_2$, which is known to exist as a dimer in thf solution over a wide range of conditions.[11]

The ^{1}H and ^{13}C NMR spectra of [**2**(thf)] were recorded in benzene-d_6 solution and also provided evidence for two diastereomeric forms. The ^{1}H and ^{13}C NMR spectra of [**3**] were recorded in dmso-d_6 solution (a gelatinous precipitate forms in hydrocarbon solvents) and also revealed a second diastereomer in addition to the (*R*,*R*) and (*S*,*S*) enantiomeric pairs depicted in Fig. 3, presumably in which the configurations of the two chiral carbons within each L^1 are (*R*,*S*) or (*S*,*R*). The important question that remains to be addressed in the case of all three complexes of general formula $[(L^1)_nM]$ pertains to possible mechanisms through which the diastereomeric forms of $[\mathbf{1}]_2$, $[\{\mathbf{2}(\text{thf})\}_2]_\infty$ and [**3**] are interconverted. This work will be reported in a future full paper.

In summary, applications of a new donor-functionalized allyl ligand in s-block chemistry have been described, including the first structural studies on potassium and magnesium derivatives of such a ligand. These reagents have potential use in synthesis and our ongoing work will investigate both this aspect and their coordination chemistry with transition metals.

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