Ansa-tris(allyl) complexes of alkali metals: tripodal analogues of cyclopentadienyl and *ansa*-metallocene ligands†‡

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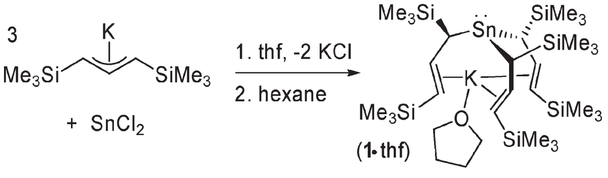
Alkali metal complexes of two types of *ansa*-tris(allyl) ligand are reported; a monoanionic *ansa*-tris(allyl) ligand containing tin(II) is formally valence isoelectronic to the cyclopentadienyl ligand and a trianionic *ansa*-tris(allyl) ligand containing silicon(IV) is formally valence isoelectronic to an *ansa*-metallocene ligand; the potential wider use of these tripodal ligands in coordination chemistry is discussed.

Transition metal complexes of the unsubstituted allyl ligand, $[(\eta^3\text{-}C_3H_5)_nM]$, have been known for almost half a century.[1] Thermal instability and high chemical reactivity are common in compounds of this type and it has been possible to isolate very few examples. More recently, however, the use of bulky, silyl-substituted allyl ligands, such as $[\{\eta^3\text{-}1,3\text{-}(R_3Si)_2C_3H_3\}]$, has allowed the detailed characterization of a range of kinetically stabilized allyl complexes of several transition metals.[2] Many examples of alkali, alkaline earth[3] and f-block metal silylallyl complexes and their *ansa*-*bis*(allyl) relatives are also known.[4] Silylallyl complexes of the lanthanides have been shown to be efficient catalysts for the polymerization of functionalized olefins such as acrylates and lactones.

The p-block metals are conspicuous by their absence from the growing roll-call of silylallyl complexes, which is somewhat surprising given the propensity of the p-block elements to form stable η^n-cyclopentadienyl complexes, particularly in the case of the heavier congeners in their low-valent form.[5] Thus, an application of silylallyl ligands in this setting seemed timely. At the outset, our aim was to prepare a sterically hindered η^3-allyl complex of tin(II). However, addition of $[K\{(Me_3Si)_2C_3H_3\}]$ to $SnCl_2$ in 3 : 1 stoichiometry proceeded according to Scheme 1.

Storage of a concentrated hexane solution of **1**·thf at −15 °C afforded yellow single crystals suitable for X-ray diffraction.§



Scheme 1

Compound [**1**·thf] exists as contact ion pairs in which a tripodal tris(allyl)stannate anion complexes a potassium cation by means of cation–π interactions (Fig. 1). The molecular C_3-axis coincides with Sn(1) and K(1), hence Sn(1) resides in a pyramidal environment with an Sn(1)–C(1) bond distance of 2.344(7) Å and C–Sn–C bond angles of 96.7(2)°, the latter parameter suggesting that the tin-centred electron lone-pair possesses appreciable s-character. The K(1)–C(2) and K(1)–C(3) distances are 3.164(8) and 3.065(8) Å, respectively, and although the K(1)–C(1) distance of 3.201(7) Å is typical for a potassium organometallic, the proximity of C(1) to K(1) is coincidental and not indicative of a chemical bond since C(1) is sp^3-hybridized. In contrast, C(2) and C(3) are sp^2-hybridized, with the C(2)–C(3) distance being 1.337(10) Å, and H(2), H(3) and *exo*-Si(2) showing only slight deviations from the allylic mean plane. These data suggest an unusual μ:η^2:η^1-bonding mode of the allyl groups to K(1) and Sn(1). K(1) is therefore best regarded as being encapsulated within an *ansa*-tris(η^2-olefin) ligand, with its coordination environment being completed by a disordered thf molecule and possible K(1)–H(1) and K(1)–H(3) agostic bonds with distances of 2.73(6) and 2.80(7) Å, respectively. Compound **1**·thf is the first crystallographically characterized tin(II) allyl and its structure is reminiscent of the tris(allyl)zincate

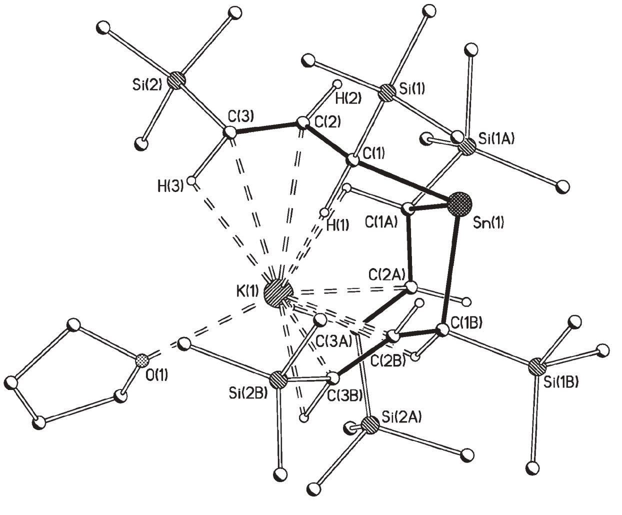


Fig. 1 Molecular structure of **1**·thf. For clarity, only the allylic hydrogens are shown and symmetry equivalents of H(1), H(2) and H(3) are not labeled. Selected distances (Å): Sn(1)–C(1) 2.344(7), C(1)–C(2) 1.499(9), C(2)–C(3) 1.337(10), K(1)–C(2) 3.164(8), K(1)–C(3) 3.065(8), K(1)–H(1) 2.73(6), K(1)–H(3) 2.80(7), K(1)–O(1) 2.767(11). Symmetry operations used to generate equivalent atoms: (A) = $-y$, $1 + x - y$, $+z$; (B) = $1 - x + y$, $-x$, $+z$.

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† This paper is dedicated to the memory of Dr Alex D. Hopkins.

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[Zn{1,3-(Me$_3$Si)$_2$C$_3$H$_3$}$_3$K].[6] The σ-bonding of the allyl ligand to Sn(1) in **1**·thf is similar to that found in allyl derivatives of magnesium[7] and the η^n-allyl bonding to K(1) is similar to that found in other potassium π-organometallics.[5]

An NMR spectroscopic study of [**1**·thf] revealed that the solid-state structure persists in solution. The resonance for Sn(1) was a single, broad peak at $\delta(^{119}\text{Sn}) = -132.9$ ppm. The room-temperature ^{13}C and ^{1}H NMR spectra revealed three unique allylic carbons and two trimethylsilyl environments. A doublet of doublets at $\delta(^{1}\text{H}) = 6.43$ ppm was assigned to H(2) and an HMQC spectrum allowed C(2) to be assigned to $\delta(^{13}\text{C}) = 159.2$ ppm. A resonance at $\delta(^{13}\text{C}) = 39.7$ ppm was accompanied by ^{117}Sn and ^{119}Sn satellites due to coupling with C(1), allowing C(3) to be assigned at 112.8 ppm. Consequently, in the ^{1}H NMR spectrum H(1) resonates as a doublet at 1.20 ppm and H(3) as a doublet at 4.42 ppm. The ^{1}H NMR spectrum was temperature-independent in the range 180–298 K. The static solution-phase structure of [**1**·thf] contrasts to the behaviour of the related metal allyls [Zn{1,3-(Me$_3$Si)$_2$C$_3$H$_3$}$_3$K][6] and [Ga{(1,3-Me$_3$Si)$_2$C$_3$H$_3$}$_3$][8] which undergo facile allylic rearrangements. We attribute the differing behaviour of [**1**·thf] to a combination of chemically relatively robust Sn–C bonds and a degree of structural rigidity afforded by the potassium cation interacting with the anionic framework of the tripodal ligand and with the π-component of three olefinic ligand groups. These observations support the idea that [**1**·thf] may be regarded as containing a monoanionic *ansa*-tris(allyl) ligand in which the olefinic donor groups are connected by a tin(II) bridgehead, indicated by the solid bonds in Fig. 1.

The broader significance of the monoanionic *ansa*-tris(allyl) ligand in **1**·thf is its valence isoelectronic relationship with the well-known cyclopentadienyl (Cp) ligand (Fig. 2).

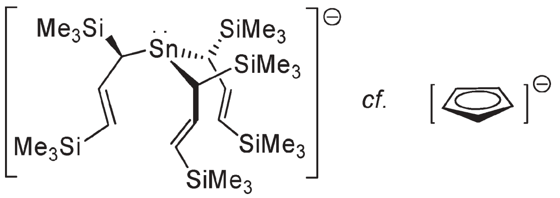


Fig. 2 Monoanionic *ansa*-tris(allyl) and Cp ligands.

The monoanionic *ansa*-tris(allyl) and Cp ligands are capable of donating up to 6 electrons and are both formally terdentate, suggesting that the ligand in [**1**·thf] may have interesting applications in transition metal chemistry. Furthermore, triply deprotonating the three acidic C–H bonds of an *ansa*-tris(allyl) ligand would result in a tripodal, trianionic analogue of an *ansa*-metallocene ligand, since both ligands are potentially hexadentate and 12-electron donors (Fig. 3).

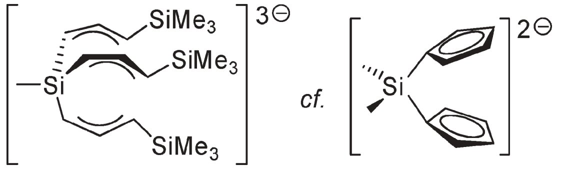
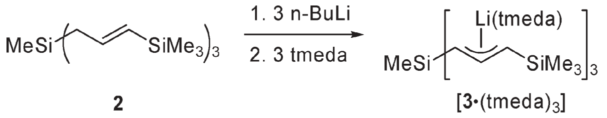


Fig. 3 Trianionic *ansa*-tris(allyl) and *ansa*-metallocene ligands.



Scheme 2

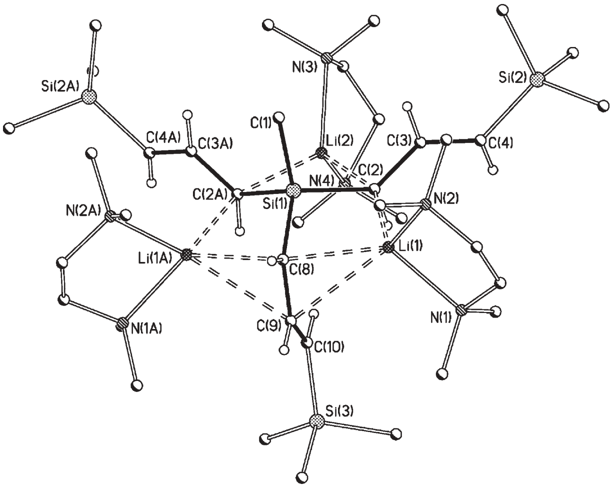


Fig. 4 Molecular structure of [**3**·(tmeda)$_3$]. Hydrogen atoms, except those bonded to the allylic carbons, are omitted for clarity. Selected distances (Å): Si(1)–C(2) 1.851(3), Si(1)–C(8) 1.858(5), C(2)–C(3) 1.416(4), C(3)–C(4) 1.384(4), C(8)–C(9) 1.401(7), C(9)–C(10) 1.383(7), Li(1)–C(2) 2.289(6), Li(1)–C(8) 2.283(5), Li(1)–C(9) 2.696(6), Li(2)–C(2) 2.258(7), Li(1)–N(1) 2.088(7), Li(1)–N(2) 2.171(6), Li(2)–N(3) 2.169(11), Li(2)–N(4) 2.017(10). Symmetry operation used to generate equivalent atoms: $+1/2 - x, +y, +z$.

Thus, (1*E*,1′*E*,1″*E*)-3,3′,3″-(methylsilanetriyl)tris(prop-1-ene-3,1-diyl)tris(trimethylsilane) (**2**) can be prepared in *ca.* 80% yield, and subsequent treatment with *n*-butyllithium and tetramethylethylenediamine (tmeda) affords [**3**·(tmeda)$_3$] in an isolated yield of 32% (Scheme 2). The molecular structure of [**3**·(tmeda)$_3$] (Fig. 4) was determined by X-ray crystallography§ and contains a trianionic *ansa*-tris(allyl) ligand consisting of a central, tetrahedral silicon atom Si(1) and three allyl ligand groups, each of which is formally bonded to a [Li(tmeda)]$^+$ cation. Two allyl groups, containing C(2), C(3), C(4) and symmetry equivalents, are related by a mirror plane and feature terminal, *exo*-SiMe$_3$ groups and an *exo*-relationship to Si(1). The allyl group containing C(8), C(9) and C(10) also has an *exo*-relationship to its terminal SiMe$_3$ group but has an *endo*-relationship with Si(1). The allyl C–C distances in [**3**·(tmeda)$_3$] are in the range 1.383(7)–1.416(4) Å (average 1.396 Å) and are similar to those found in other structurally authenticated lithium allyls.[3b,c] Li(1) bridges two allyl groups that coordinate to the cation in a $\mu{:}\eta^1{:}\eta^2$ fashion, with the Li(1)–C(2) and Li(1)–C(8) distances of 2.289(6) and 2.283(5) Å, respectively, being typical for a lithium allyl and Li(1)–C(9) being considerably longer at 2.696(6) Å. Li(2) adopts a symmetrical bridge between C(2) and C(2A) with the allyl ligands bonding in a $\mu{:}\eta^1{:}\eta^1$ mode. Each Li$^+$ cation is also complexed by one bidentate tmeda ligand with one long (av. 2.170 Å) and one short (av. 2.064 Å) Li–N bond distance. Application of the SQUEEZE utility in PLATON[9] reveals a solvent-accessible void of 1360 Å^3 corresponding to 53 e$^-$. In our solution for [**3**·(tmeda)$_3$], the largest peaks of residual electron density are located close to **3**, while no solvent of crystallization could be located within the void spaces, hence any uncoordinated solvent is likely to be totally disordered.

In the NMR spectra of [**3**·(tmeda)$_3$], it was possible to assign the ^{1}H and ^{13}C environments of the *endo*-allyl group. The *exo*-allyl groups lose their solid-state equivalence in solution, as seen in the ^{1}H NMR spectrum by the presence of two triplets due to the central allylic hydrogens and four doublets due to the terminal allylic hydrogens. Broad, overlapping resonances in both the ^{1}H and ^{13}C spectra due to non-equivalent NMe_2 and CH_2 groups of tmeda were also observed, suggesting [**3**·(tmeda)$_3$] is fluxional to some extent in solution. Fluxional behaviour in solvated lithium allyls, such as [(tmeda)Li{$(Me_3Si)_2C_3H_3$}],[3c] is common and rearrangements pathways are frequently complicated, hence a detailed description of the NMR spectrum of [**3**·(tmeda)$_3$] will be reported in a future full paper.

In addition to the relationship between **1**·thf and [**3**·(tmeda)$_3$] and the Cp and *ansa*-metallocene ligands, respectively, the cation–π interactions in **1**·thf (in particular) and [**3**·(tmeda)$_3$] are also isoelectronic to the commonly observed η^6-coordination of arenes to alkali metals, such as the $[M^+]\cdots[(\eta^6\text{-arene})_n]$ (n = 1, 2) complexation modes found in the lithium, sodium and potassium complexes of calix[4]arenes.[10] According to our interpretation, compounds **1**·thf and [**3**·(tmeda)$_3$] provide the first examples of *ansa*-tris(allyl) ligands. Their ability to coordinate to alkali metals and the relationship of [**1**·thf] with the Cp ligand and [**3**·(tmeda)$_3$] with *ansa*-metallocene ligands creates potential for the use of these interesting tripodal ligands in the coordination chemistry of transition metals, and our ongoing work will address this prospect.

Notes and references

§ *Crystal data* for [**1**·thf]: $C_{31}H_{71}KOSi_6Sn$, M = 786.22, T = 180(2) K, rhombohedral, $R3c$, a = 17.4815(9), b = 17.4815(9), c = 27.596(2) Å, γ = 120°, V = 7303.5(8) Å^3, Z = 6, 7480 reflections collected, 1622 independent reflections (R_{int} = 0.0517), final R indices [$I > 2\sigma(I)$], $R1$ = 0.0312, $wR2$ = 0.0698, R indices (all data): $R1$ = 0.0483, $wR2$ = 0.0789, absolute structure parameter = −0.03(4).

Crystal data for [**3**·(tmeda)$_3$]: $C_{37}H_{87}Li_3N_6Si_4$, M = 749.31, T = 180(2) K, tetragonal, $P4_2/nmc$, a = 33.6787(3), b = 33.6787(3), c = 11.17300(10) Å, V = 12673.0(2) Å^3, Z = 8, 54441 reflections collected, 5735 independent reflections (R_{int} = 0.0579), final R indices [$I > 2\sigma(I)$], $R1$ = 0.0890, $wR2$ = 0.2242, R indices (all data): $R1$ = 0.1116, $wR2$ = 0.2374.

CCDC 656893 and 656894. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b712285c

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