Synthesis and reactivity of alkaline-earth stannane complexes by hydride-mediated distannane metathesis and organostannane dehydrogenation†

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The synthesis of heteroleptic complexes with calcium– and magnesium–tin bonds is described. The dimeric β-diketiminato calcium hydride complex, \([\text{[BDI]}\text{Ca}[\mu-H]\text{]}_2\) (I Ca), reacts with \(\text{Ph}_3\text{Sn-SnPh}_3\) to provide the previously reported \(\mu_2\)-H bridged calcium stannane dimer, \([\text{[BDI]}_2\text{Ca}_2(\text{SnPh}_3)_2[\mu-H]]\) (3). Computational assessment of this reaction supports a mechanism involving a hypervalent stannate intermediate formed by nucleophilic attack of hydride on the distannane. Mononuclear calcium stannanes, \([\text{[BDI]}\text{Ca(SnPh}_3)_2\text{OPPh}_3]\) (8·OPPh3) and \([\text{[BDI]}\text{Ca(SnPh}_3)_2\text{TMTHF}]\) (8-TMTHF), were obtained from I Ca and \(\text{Ph}_3\text{Sn-SnPh}_3\), after addition OPPh3 or TMTHF. Both complexes were also synthesised by deprotonation of \(\text{Ph}_3\text{SnH}\) by I Ca in the presence of the Lewis base. The calcium and magnesium THF adducts, \([\text{[BDI]}\text{Ca(SnPh}_3)_2\text{THF}_2]\) (8-THF2) and \([\text{[BDI]}\text{Mg(SnPh}_3)_2\text{THF}]\) (9-THF), were similarly prepared from \([\text{[BDI]}\text{Ca}[\mu-H]\text{]}(\text{THF})_2\) (I Ca-THF2) or \([\text{[BDI]}\text{Mg}[\mu-H]\text{]}_2\) (I Mg) and \(\text{Ph}_3\text{SnH}\). An excess of THF or TMTHF was essential in order to obtain 8-TMTHF, 8-THF2 and 9-THF in high yields whilst avoiding redistribution of the phenyl-tin ligand. The resulting \(\mu_2\)-Sn complexes were used as a source of \(\text{[Ph}_3\text{Sn]}^\text{−}\) in salt metathesis, to provide the known tristannane \(\text{Ph}_3\text{Sn-Sn(\text{t-Bu})}_2-\text{SnPh}_3\) (11). Nucleophilic addition or insertion with N,N′-di-isopropylcarbodiimide provided the stannyl-amidinate complexes, \([\text{[BDI]}\text{Mg}\{\text{iPrN}_2\}_2\text{CsSnPh}_3]\) (12) and \([\text{[BDI]}\text{Ca}\{\text{iPrN}_2\}_2\text{CsSnPh}_3]\text{-L}\) (13-TMTHF, 13-THF, L = TMTHF, THF). The reactions and products were monitored and characterised by multinuclear NMR spectroscopy, whilst for compounds 8, 9, 12, and 13-THF, the X-ray crystal structures are presented and discussed.

Introduction

Although Grignard’s ubiquitous organomagnesium compounds have been widely used as synthetic reagents for over a century, the catalytic potential of alkaline-earth (AE) reagents was largely overlooked until the past two decades.1,2 By analogy to well-established lanthanide(III)-based catalysis,3 AE2+ centres participate in redox-neutral catalytic cycles that are assembled from fundamental steps such as polarised \(2\pi–2\sigma\) insertion- and \(2\sigma–2\pi\) metathesis.2 In many cases, reactivity is better described by non-concerted processes involving attack of an AE-bound nucleophile on a substrate, such as a silane, that is capable of expanding its coordination sphere.4–7 As such, the heavier alkaline earths (Mg–Ba) are adept at mediating catalytic dehydrocoupling,5,8–15 hydrofunctionalisation,16–23 and even reductive hydrogenation reactions.24–26 We have previously reported the use of silylboranes to perform the catalytic ‘disilacoupling’ of amines and boranes; a non-dehydrogenative process thought to be dependent on AE-mediated redox-neutral metathesis of N–H and Si–B σ-bonds (Scheme 1, top).27 A model reaction between a β-diketiminato (BDI) magnesium butyl complex and the silylborane, PhMe2Si-Bpin (Bpin = pinacolatoboryl), resulted in elimination of nBu-Bpin and isolation of the magnesium silanide complex, 1 (Scheme 1, bottom).27 Computational assessment has suggested that this reaction is best described by nucleophilic attack of a butyl group on the boron centre to provide a borane intermediate from which the silyl group is subsequently transferred to magnesium.28 Bis[pinacolato]diboron (B2pin2), which contains a non-polar B–B σ-bond, was shown to react in a similar way with...
[(BDI)MgBu] to provide an isolable diboranate complex, 2a (Scheme 1, bottom). Treatment of 2a with 4-dimethylaminopyridine (DMAP) promoted heterolysis of the B–B bond and delivered the terminal magnesium boryl species, 2b, which is a source of the nucleophilic [Bpin]− anion.

The Ae-centred manipulation of boron-, silicon-, and organic substrates has, thus, received significant attention. In contrast, comparable reports of Ae-mediated reactivity suitable for the construction of catalytic cycles involving organostannanes, which could provide an attractive route towards materials such as polystannanes or act as sources of organostannane cross-coupling reagents, are lacking. The majority of published Ae-mediated organotin chemistry focusses on the irreversible, stoichiometric reaction between the group 2 element and organotin halides, distannanes and silastannanes. We recently reported that the BDI-calcium stannanide complexes 3 and 4 may be accessed through deprotonation of commercially available triphenylstannane by the soluble calcium hydride complex, ICa (Scheme 2a). Crystallographically characterised examples of Ae–Sn bonds were previously limited to the calcium and magnesium complexes 5 and 6, and the barium species 7 (Scheme 2b). Compound 5 was readily prepared by the oxidative-addition of hexamethyldistannane to calcium metal, the synthesis of 6 and 7 utilised salt metathesis routes from group 1-metalated precursors. Neither of these strategies, however, is likely to be amenable to incorporation into catalytic cycles. Since the formation of 3 and 4 is redox neutral at calcium and generates H2 instead of insoluble salts as a by-product, therefore, it holds attractive potential for the development of Ae-based catalysts for processes such as hydrostannylation or stannane dehydrocoupling.

Distannanes are synthetically useful precursors to organotin radicals as well as 1,2-distannylated alkanes and alkenes via transition metal-catalysed distannylation of alkynes. Such organotin compounds are valuable cross-coupling reagents in organic synthesis. Although the heterogeneous reaction of distannanes with solid alkali metals is well-known, the manipulation of distannanes by soluble s-block complexes has not been described. By analogy to the nucleophilic substitution-like process operative in the formation of Mg-silyl and -boryl species 1 and 2a/2b, we speculated that molecular calcium hydride and alkyl derivatives may react with Ph3Sn–SnPh3, providing an alternative route to nucleophilic calcium stannanide complexes. These investigations were motivated by the limitations encountered during our previously described synthesis of 3 and 4. Firstly, ICa also promotes redistribution of the organotin substrate, culminating in the generation of homoletic SnPh4 and (presumably) SnH4, the latter of which rapidly decomposes to give Sn0 and H2. Secondly, the strongly bound dimer of 3 retains a μ2-hydride ligand and the sub-
sequent formation of 4 is low-yielding and slow, impeding any rational assessment of the reactivity of these unusual compounds. In this contribution, therefore, we describe the facile and high yielding synthesis of well-defined, monomeric Aes-tannanide complexes and a preliminary assessment of their nucleophilic reactivity.

Results and discussion

Reaction of 1^Ca with Ph3Sn-SnPh3 and synthesis of compound 3

When 1^Ca was dissolved in C6D6 with an equimolar quantity of Ph3Sn–SnPh3, the reaction mixture bubbled gently and darkened from pale-yellow to orange brown over the course of six hours. The respective μ-hydride and BDI-γ-CH proton resonances of 1^Ca at δ 4.27 and 4.83 ppm in the in situ 1H NMR spectrum were replaced by two new singlets of relative intensity 2:1 at δ 4.75 and 3.83 ppm. The latter signal displayed unresolved 117/119Sn satellites with γ(117/119Sn–H) = 94 Hz, while the corresponding 119Sn(1H) NMR spectrum revealed complete consumption of the distannane and the appearance of a signal at δ −139.8 ppm, which was accompanied by the generation of Ph3Sn (δ −126 ppm).57 These observations were consistent with the formation of the μ-H-bridged dimeric calcium stannanide, 3, whilst the brown colouration was assigned to formation of colloidal tin.42 Although the slow formation of compound 4 was identified by its resonance at δ −158.5 ppm in the 119Sn(1H) NMR spectrum after a further five days at room temperature, complete conversion to this product was not obtained (Scheme 3).

Computational and mechanistic investigation of 1^Ca mediated Ph3Sn–SnPh3 activation

In order to assess the mechanism of Ph3Sn–SnPh3 activation, the reaction between 1^Ca and Ph3Sn–SnPh3 was investigated by density functional theory (DFT, Fig. 1a, BP86 optimised, see ESI† for full details of computational methodology). Although we cannot, at this juncture, discount the operation of competitive single electron-based processes, consistent with the reported reactivity of compound 1^Ca thus far,25 these calculations are suggestive of a metathesis-based reactivity. Following the initial formation of a van der Waals encounter complex (A, ΔG = +8.7 kcal mol−1), the distannane is subjected to nucleophilic attack by one of the μ2-hydride ligands (H2) via transition state TSAB (Fig. 1b, ΔG‡ = +12.7 kcal mol−1), at which the Sn^a–Sn^b bond is marginally elongated from 2.85 Å (calculated for Ph3Sn–SnPh3) to 2.87 Å. Inspection of the Ca^a–H2 and H2–Sn^b bond lengths (2.30 Å and 2.14 Å, respectively) in the subsequent intermediate, B (Fig. 1c, ΔG = +5.2 kcal mol−1), is suggestive of the transfer of H2 to Sn^b and the formation of a hypervalent stannate anion with a Sn^a–Sn^b distance of 2.95 Å. The Sn^a–Sn^b distance elongates to 3.55 Å in the transition state TSBC (ΔG‡ = +8.2 kcal mol−1), facilitating cleavage of the stannane anion and concerted formation of a Ca^a–Sn^b bond (distance in TSBC = 2.24 Å) to give intermediate C (ΔG = +2.5 kcal mol−1). Subsequent dissociation of Ph3Sn^aH2 provides 3, at ΔG = −5.2 kcal mol−1. Whilst the overall process is only moderately exergonic, the modest kinetic barrier is consistent with the room temperature reaction conditions. Meanwhile, rapid consumption of the resultant molecule of Ph3SnH provides a thermodynamic driving force, yielding H2 and a second molecule of 3.

Experimental evidence in support of this mechanism was obtained by carrying out the analogous reaction between Ph3Sn–SnPh3 and the n-hexyl-calcium complex [[BDI]Ca(He)], (II). The relatively poor solubility of both substrates in C6D6 and the greater steric demand of the hexyl ligand compared to the hydride of 1^Ca resulted in sluggish reaction kinetics. Nevertheless, after gentle heating to 40 °C for 48 hours, the characteristic triplet corresponding to the α-CH2 protons of II at δ −0.71 ppm was all but absent from the 1H NMR spectrum. Although this observation was accompanied by almost complete redistribution to [[BDI]Ca]28 as the only soluble BDI-containing product, a resonance at δ −98.2 ppm in the corresponding 119Sn(1H) NMR spectrum revealed Ph3Sn(He) as the predominant tin-containing species.29 The absence of any unambiguously identifiable alkyl or stannyl-calcium species, such as a n-hexyl-containing analogue of 3, may be attributed to the likely low thermal stability of such intermediates. Formation of Ph3Sn(He), however, can be rationalised by attack of a calcium-bound n-hexyl-nucleophile on the distannane, with subsequent transfer of [Ph3Sn]^− to calcium and elimination of Ph3Sn(He) (Scheme 4). Whereas the tetraorgano-nostannane is inert towards further reactivity under these conditions, a similar reaction with 1^Ca would yield Ph3SnH, which is rapidly deprotonated by a second molecule of 1^Ca to provide 3.

Synthesis and NMR characterisation of monomeric alkaline-earth stannanides 8 and 9-THF

Compound 4 could only be accessed in low yields following fractional crystallisation of the crude products obtained from

Scheme 3  Synthesis of 3 and 4 by reaction of 1^Ca with Ph2Sn–SnPh3 in C6D6. Ar = 2,6-di-isopropylphenyl.
reaction of $\text{I}^{\text{Ca}}$ with $\text{Ph}_3\text{SnH}_4$ or $\text{Ph}_2\text{Sn-SnPh}_3$. It was also anticipated that the $\mu_2$-hydride of 3 would provide a likely complication in subsequent efforts to assess the reactivity of the Ca–Sn bond. With this in mind, we speculated that addition of a Lewis base would encourage fragmentation of the dimer, result in reaction of both hydride ligands, and provide a high-yielding route towards a well-defined monomeric calcium stannanide. Similar strategies have previously been applied successfully to achieve, for example, the isolation of monomeric magnesium complexes comprising terminal hydride and boryl ligands.29,60,61

To this end, the reaction between $\text{I}^{\text{Ca}}$ and $\text{Ph}_3\text{Sn-SnPh}_3$ was repeated and, after quantitative conversion of $\text{I}^{\text{Ca}}$ was ascertained by $^1\text{H}$ NMR spectroscopy, an equimolar equivalent of Ph$_3$PO was added to the $\text{in situ}$ generated solution of 3 (Scheme 5). Upon standing at room temperature for 24 hours,
the reaction mixture took on an opaque dark-brown appearance and, in addition to several minor species, a major new BDI-γ-CH resonance was observed to have emerged at δ 5.23 ppm. The $^{119}\text{Sn}$($^1\text{H}$) NMR spectrum displayed a doublet at δ −146 ppm, whose coupling constant of 10 Hz is consistent with the sparse number of $^3J(^{117}/^{119}\text{Sn})$ coupling constants that have been reported.\textsuperscript{62,63} Notwithstanding some minor peaks at δ 88–89 ppm and 71 ppm, consistent with this observation, the $^{31}\text{P}$($^1\text{H}$) NMR spectrum was free of evidence for any unligated phosphate oxide. The spectrum also comprised a major resonance at δ 36.4 ppm, which displayed unresolved $^{117/119}\text{Sn}$ satellites with an approximate coupling constant consistent with that observed in the $^{119}\text{Sn}$($^1\text{H}$) NMR spectrum. Recrystallisation of the crude product mixture from toluene/hexane provided single-crystals of the monomeric Ph$_3$PO-adduct $^8\text{OPPH}_3$ in low yield, from which the molecular structure was determined by X-ray diffraction analysis (Fig. 2a). Crystals of the known compound [(BDI)Ca(OPPh$_2$)$_2$]$^\text{ff}$ were also obtained from the same sample and identified from the unit cell-parameters determined by X-ray diffraction.\textsuperscript{64} This observation is consistent with the calcium hydride-mediated reduction chemistry previously reported for phosphine oxides,\textsuperscript{64} and helps to account for the low yield and poor selectivity of this reaction. Compound $^8\text{OPPH}_3$ was, however, obtained cleanly from the single-step reaction of $^1\text{Ca}^\text{ff}$ with two equivalents each of Ph$_3$SnH and Ph$_3$PO in C$_6$D$_6$. Although high solubility of the crystalline product obtained from this reaction provided a low, unoptimised isolated yield, it displayed identical NMR resonances to those described above.

Mindful of phosphine oxide reactivity towards reductive and/or nucleophilic alkaline-earth complexes,\textsuperscript{61,64} it was decided that 2,2,5,5-tetramethyltetrahydrofuran (TMTHF) would be a better choice of Lewis-base. Westerhausen and co-workers have recently reported the use of TMTHF to prepare monomeric amide complexes [Ae[N(SiMe$_3$)$_2$]$_2$·TMTHF] (Ae = Mg, Ca, Sr, Ba), in which the TMTHF ligand is highly labile in solution.\textsuperscript{65} We reasoned that, whilst coordination of TMTHF would encourage monomerisation, its relatively labile binding compared to more common bases such as THF or DMAP, might enhance the reactivity of the resultant calcium stannanide complex. Hence, $^1\text{Ca}^\text{ff}$ was dissolved in C$_6$D$_6$ with two equivalents each of Ph$_3$Sn–SnPh$_3$ and TMTHF (Scheme 6). Analysis of the crude reaction mixture by $^1\text{H}$ NMR spectroscopy showed complete conversion of the starting materials after two days at room temperature. A new product, $^8\text{TMTHF}$, was characterised by a broadened resonance at δ 5.21 ppm corresponding to the γ-CH of the BDI ligand backbone. The $^{119}\text{Sn}$($^1\text{H}$) NMR spectrum comprised a resonance at δ −170.6 ppm in addition to a signal which was readily assigned as Ph$_4$Sn at δ −126 ppm. Colourless block-like single crystals deposited from the reaction mixture overnight and were shown to be the monomeric TMTHF-solvated calcium stannanide, compound $^8\text{TMTHF}$, by X-ray diffraction analysis (Fig. 2b).

Compound $^8\text{TMTHF}$ could also be obtained by reacting $^1\text{Ca}^\text{ff}$ with two equivalents of Ph$_3$SnH in toluene (Scheme 6). Organostannane redistribution to Ph$_4$Sn was completely circumvented by use of a ten-fold excess of TMTHF, and $^8\text{TMTHF}$ was deposited as colourless crystals on standing at room temperature overnight in 68% yield.

Once crystallised, $^8\text{TMTHF}$ is sparingly soluble in aromatic solvents but is readily soluble in THF. The $^1\text{H}$ NMR spectrum in d$_8$-THF displayed a single, well-defined BDI environment, while resonances observed at δ 1.80 and 1.16 ppm suggested displacement of TMTHF from the calcium centre by the NMR solvent. The resultant $^{119}\text{Sn}$($^1\text{H}$) chemical shift was also substantially perturbed with a single resonance appearing at δ −137.3 ppm. Despite poor solubility, attempts to obtain NMR spectra of isolated and vacuum-dried crystals of $^8\text{TMTHF}$ in
C₆D₆ were successful, albeit the resonances were weak and broadened. Nevertheless, we were interested to find that two species were clearly discernible by ¹H NMR spectroscopy. Although both species were identifiable as 8·TMTHF by the BDI γ-CH resonance at δ 5.21 ppm and the Lewis base-free compound, 4 (δ 5.02 ppm for γ-CH of the BDI backbone), their contrasting solubility in aromatic solvents prevented any confident, quantitative analysis of their relative abundance in solution. The apparent lability of TMTHF under vacuum was, however, further supported by the low relative intensity of its associated ¹H resonances when vacuum-dried samples were redissolved in d₈-THF. In order to investigate the viability of 8·TMTHF as a convenient precursor to 4, therefore, isolated crystals were stirred in the solid state under vacuum at 80 °C for sixteen hours. The resultant pale-yellow powder was only partially soluble in d₈-toluene and, although the relative ratio of the two species determined by integration of the ¹H NMR spectrum was increased in favour of 4, substantial quantities of 8·TMTHF remained. Both species could be clearly discerned in the resulting ¹¹⁹Sn(¹H) NMR spectrum, which comprised two resonances at δ −160.5 (4) and −170.7 ppm (8·TMTHF).

The solution-state behaviour of 8·TMTHF was also investigated by variable temperature ¹H NMR in d₈-toluene. Whilst separate environments for 4 and 8·TMTHF could be discerned at 298 K, the γ-CH signals coalesced to a single broad resonance at δ 5.11 ppm above 318 K. Similarly, resonances

Fig. 2 X-ray crystal structures of (a) 8·OPPh₃, (b) 8·TMTHF, (c) 8·THF₂, (d) 9·THF. Ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity except for those bound to C33 in 8·TMTHF. Where disorder is present only the major component is shown.
assigned to free TMTHF experienced a pronounced and simultaneous upfield shift with increasing temperature. Although no more quantitative information could be extracted from these experiments, both of these observations suggest the establishment of a coordination-decoordination equilibrium when isolated 8-TMTHF samples are dissolved in arene solvents, facilitated by the lability of coordinated TMTHF.

The THF-solvated calcium hydride, [(BDI)CaH·THF]$_2$ (1$^\text{38}$-THF$_2$) was also reacted with two equivalents of Ph$_3$SnH under a ten-fold excess of THF in toluene. After stirring overnight at room temperature, volatiles were removed under vacuum to provide the bis-THF adduct, 8-THF$_2$, as a pale cream-coloured powder in high yield (Scheme 6). Its molecular structure (Fig. 2c) was determined by X-ray diffraction analysis performed on single crystals obtained by slow evaporation of a saturated toluene/THF solution. Compound 8-THF$_2$ is readily soluble in aromatic solvents and displays a well-defined $^1$H NMR spectrum in C$_6$D$_6$ or d$_6$-toluene. The single $^{119}$Sn environment resonates at $\delta$ = -138.4 ppm in C$_6$D$_6$. When dissolved in d$_8$-THF, the $^1$H and $^{119}$Sn$[^1$H$]$ NMR spectra of 8-THF$_2$ were identical to that of 8-TMTHF in the same solvent, supporting the hypothesis that TMTHF is readily displaced from the calcium centre in THF-solution.

Whilst 1$^\text{44}$ reacts rapidly with two equivalents of Ph$_3$SnH to provide 3, the magnesium congener, [(BDI)MgH]$_2$ (1$^\text{4M}$) reacts much more slowly. Although, approximately 50% of the initial Ph$_3$SnH was observed to have redistributed to Ph$_4$Sn after five days at room temperature (Scheme 7), the $^1$H NMR spectrum showed no net consumption of 1$^\text{4M}$. In addition, no other significant BDI- or Sn-containing products could be detected by either $^1$H or $^{119}$Sn$[^1$H$]$ NMR spectroscopy. Repetition of the reaction in toluene with a 10-fold excess of THF, however, not only suppressed organostannane redistribution, but also accelerated consumption of Ph$_3$SnH. The monomeric magnesium stannanide complex, 9-THF, was, thus, obtained in near quantitative yield as a colourless powder after stirring for 16 hours at room temperature and removal of volatiles under vacuum (Scheme 7). Single-crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane vapour into a THF solution at −30 °C, providing confirmation of the solid-state structure (Fig. 2d). Compound 9-THF is readily soluble in aromatic solvents and THF and, albeit the $^1$H resonances associated with the iso-propyl resonances were substantially broadened in C$_6$D$_6$ at 25 °C, both the $^1$H and $^{13}$C$[^1$H$]$ NMR spectra were indicative of a single BDI-environment. Similarly, the $^{119}$Sn$[^1$H$]$ NMR spectrum displayed a single resonance at $\delta$ = -155.4 ppm in C$_6$D$_6$.

![Scheme 7 Synthesis of 9-THF. Ar = 2,6-di-isopropylphenyl.](Image)

X-ray diffraction analysis of 8-OPPh$_3$, 8-THF$_2$, 8-TMTHF and 9-THF Compounds 8-OPPh$_3$, 8-THF$_2$ and 9-THF each crystallise in the monoclinic space group, P2$_1$/c, whilst the crystal structure of 8-TMTHF adopts the P2$_1$/m space group (Fig. 2a–d; selected bond distances and angles are presented in Table 1). Whilst the geometries of the four-coordinate calcium centres in 8-OPPh$_3$ and 8-TMTHF are best described as distorted tetrahedra, 9-THF adopts a near trigonal-pyramidal geometry, with the magnesium centre situated 0.557(1) Å above an equatorial plane defined by the nitrogen and tin atoms ($\Sigma$ angles = 342°). The geometry of the five-coordinate calcium centre in 8-THF$_2$ can be considered as a heavily distorted trigonal bipyramid, with the [Ph$_4$Sn]$^-$ and one THF ligand in the axial positions and the BDI ligand and the second THF molecule occupying the equatorial sites. Compound 8-TMTHF is bisected through C3, the C16–C21 phenyl ring, and the furan ring by a mirror plane that is intrinsic to the space group, such that half a molecule is present per asymmetric unit. The methyl groups of the TMTHF ligand were disordered across the crystallographic mirror and a weak anagostic interaction was observed between one methyl group and the calcium centre.

With a series of well-defined monomeric Ae-stannanide derivatives in hand, we undertook an initial exploration of their reac-
tivity. The highly ionic nature of the Ae–Sn bond suggests that they can be considered as hydrocarbon-soluble salts of the Ph₃Sn⁻ anion. As such, compounds 8-TMTHF and 9-THF were reacted with 0.5 equivalents of t-Bu₂SnCl₂ in CaDM (Scheme 8). Both reactions provided a relatively clean ¹H NMR spectrum indicative of the formation of a single major BDI-containing product. A pair of resonances at δ ~ -76.9 and -137.20 ppm in the ¹¹Sn[¹H] NMR spectrum was consistent with formation of the alternating tristannane, Ph₃Sn–Sn(t-Bu)₂–SnPh₃ (11). The identity of this compound was confirmed by X-ray diffraction and NMR spectroscopic analysis performed on single crystals isolated by fractional recrystallisation of the crude product mixture from hexane/toluene. Unfortunately, a satisfactory sample of the calcium-containing by-product (10Ca) could not be isolated from the reaction involving 8-TMTHF. When 9-THF was used, however, colourless crystalline blocks were deposited from the reaction mixture and identified as the known chloride complex, [(BDI)Mg(μ-Cl)]²⁻ by comparison to the published unit cell parameters and NMR spectra.⁶⁶

Compound 11 was first isolated in 33% yield (versus 78% in the current work) by Adams and Dräger in 1987 and synthesised by salt metathesis of the lithiated precursor, Ph₃SnLi, with t-Bu₂SnCl₂ in THF and/or toluene.⁵⁷ Notably, although selectivity could be improved by variation of reaction stoichiometry, solvent polarity and concentration, this earlier approach yielded a mixture of Ph₃Sn-capped tetra-, penta-, and hexastannanes such that the published crystal structure of 11 was as a component of a co-crystal with the tetrastannane, Ph₃Sn-
Sn(t-Bu)₂-Sn(t-Bu)₂-SnPh₃. For completeness, therefore, the crystal structure of the pure tristannane, 11, is included in the ESI (Fig. S1†). This reaction presents 8-TMTTHF and 9-THF as promising alternatives to group 1 metallated organostannanes in salt metathesis reactions.68-71

Insertion/nucleophilic addition of Ae-Sn bonds to N,N'-di-isopropylcarbodiiimide

As an initial assay of the potential utility of BDI-Ae stannylamidates to engage in catalytically relevant insertion reactions with unsaturated small molecules, 8-TMTTHF, 8-THF₂ and 9-THF were reacted with one equivalent of N,N’-di-isopropylcarbodiimide (DIC) in C₆D₆ (Scheme 9). To the best of our knowledge, the resultant compounds provide the first reported C-organostannyl analogues of the ubiquitous amidinate class of N,N-donor anions. Compound 9-THF required 48 hours to cleanly convert DIC into the stannylationimidate complex, 12, at room temperature. Compound 12 was characterised by an upfield-shifted resonance at δ ~186.9 ppm in the ¹¹⁹Sn{¹H} NMR spectrum and a characteristic resonance at δ 181.9 ppm in the ¹³C{¹H} NMR spectrum, corresponding to the central carbon atom of the Mg-ligated stannyl-amidinate ligand. The ¹H NMR spectrum was indicative of a single, symmetrical BDI environment, with equivalent N-isopropyl environments and characteristic SnPh₃ resonances with ¹¹⁹/¹¹⁷Sn satellites. THF was absent from the isolated product, which was obtained as a colourless powder by removal of volatiles under vacuum and which could be crystallised from methycyclohexane at ~30 °C. The resultant colourless blocks were subjected to single-crystal X-ray diffraction analysis to provide the molecular structure of compound 12 (Fig. 3).

The calcium complexes were more reactive towards DIC compared to 9-THF. Compound 8-TMTTHF provided a clear, colourless solution of the calcium stannylationimidate, 13-TMTTHF, after 60 minutes of sonication at room temperature. A further reaction at room temperature for 16 hours also provided quantitative spectroscopic conversion to 13-TMTTHF, and 13-THF was obtained in a similar manner from 8-THF₂ (Scheme 9). Compounds 13-TMTTHF and 13-THF were isolated as colourless powders after removing volatiles from the reaction mixture and displayed similar ¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra to 12. Compared to 12, the ¹¹⁹Sn{¹H} resonances of 13-TMTTHF and 13-THF exhibited slightly upfield shifts to δ ~193.8 and ~196.1 ppm, respectively, whilst the stannylationimidate ‘backbone’ carbon nuclei resonated at δ 179.1 and 177.1 ppm in the corresponding ¹³C{¹H} NMR spectra. The ¹¹⁹Sn and ¹¹⁷Sn satellites could also be clearly discerned for the tin-bonded amidinate ¹³C resonance of 13-TMTTHF to provide coupling constants of ¹J(¹ªSn) = 204.4 Hz and ¹J(¹¹ªSn) = 344.7 Hz. The BDI and stannylationimidate ligands of both complexes display a set of resonances indicative of high symmetry and, in contrast to 12, the presence of a single coordinated TMTTHF or THF was clearly discerned by ¹H NMR spectroscopy. Although attempts to acquire single crystals of 13-TMTTHF were unsuccessful, colourless plate-like single crystals suitable for X-ray analysis of 13-THF were obtained by cooling a hexane/methylcyclohexane solution to ~30 °C.

Compounds 12 crystallises in the monoclinic space group, P2₁/c, with one molecule of the magnesium complex and one disordered solvent region, equating to two methycyclohexane molecules, per unit cell. The solid state structure of 12 (Fig. 3) consists of a four-coordinate distorted tetrahedral magnesium centre, bonded to a BDI ligand via N1 and N2, and to a stannylationimidate ligand via N3 and N4. Although the Mg-N distances are all of a similar length, the magnesium centre is co-planar to the latter ligand but projects out of the mean N1-C2-C3-C4-N2 plane of the BDI ligand by 0.7483(16) Å. The two bidentate ligands are effectively perpendicular,
such that the angle between the mean planes defined by N1–Mg1–N2 and N3–Mg1–N4–C30, is 90.47(6)°. Although no directly analogous stannyl-amidinate ligands have been reported previously, the C30–Sn1 bond length is unremarkable (2.203(12) Å). The C30–N3 and C30–N4 bond lengths (1.3353 (19), 1.3311(19) Å) are slightly longer, and the N3–C30–N4 angle (114.1(11)°) is slightly more acute, than those previously reported in homo- and heteroleptic N,N-di-iso-propylamidinate calcium complexes (ca. 121.3(2)°).72,73

Compound 13·THF crystallised in the monoclinic Cc space group and, unusually, contains four crystallographically independent molecules per unit cell (Fig. S2†). Because of this, and a fall-off in diffraction intensity at higher Bragg angles arising from the thin plate-like morphology of the crystal, a detailed discussion of the structure is unwarranted. The gross features of the compound are, however, unambiguous and the four molecules display only minor structural differences. The X-ray crystal structure of the Ca1/Sn1-containing molecule is shown in Fig. 4. The BDI, stannyl-amidinate and THF ligands are arranged about the five-coordinate calcium centre such that N1, N2 and N3 lie in an approximate equatorial plane, with O1 located axially. The two chelating ligands are arranged in a similar way to those in 12, with an average twist angle of approximately 93° between the mean planes defined by NBDI–Ca1–NBDI, and NmMg1–Nam–Ca1, respectively. Significant variations in the structural metrics pertaining to the stannyl-amidinate ligands of 12 and 13·THF were not unambiguously discernible, but the larger ionic radius and higher coordination number of calcium results in displacement of the metal centre by approximately 2.5 Å from the mean plane of the BDI ligand backbone.

**Conclusions**

In conclusion, dimeric calcium and magnesium hydrides I\(^{\text{Ca}},\) I\(^{\text{Ca}}\)-THF\(_2\), and I\(^{\text{Mg}}\)-deprotonate triphenylstannane in the presence of an excess of coordinating Lewis base to provide clean access to well-defined monomeric Ae-stannanide complexes in good yield. Calcium stannane complexes are also accessible through distannane heterolysis by nucleophilic attack of a calcium hydride. A preliminary exploration of the reactivity arising from the resultant compounds demonstrates their potential as well-defined, soluble sources of the [Ph\(_3\)Sn]\(^-\) anion in salt metathesis and nucleophilic addition reactions. Further work continues to explore the nature and reactivity of bonds between heavier p-block elements and the heavier alkaline earths.

**Conflicts of interest**

There are no conflicts to declare.

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**Fig. 4 X-ray crystal structure of compound 13·THF.** Ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity. Only one of the four crystallographically independent molecules present in the unit cell is shown. Selected bond lengths (Å) and angles (°): Sn1–C30 2.214(12), Sn1–C37 2.165(10), C30–N3 2.373(10), Ca1–O1 2.377(10), Ca1–N1 2.382(10), Ca1–N2 2.341(10), Ca1–N3 2.373(11), Ca1–N4 2.377(11), N3–C30 1.380(17), N4–C30 1.311(16), C37–Sn1–C30 120.5(5), C37–Sn1–C43 100.1(5), C43–Sn1–C30 113.7(5), C48–Sn1–C38 103.7(6), O1–Ca1–N1 189(1), O1–Ca1–N1 28(1), O2–Ca1–N3 146.0(4), O2–Ca1–N4 108.9(4), N3–Ca1–O1 150.4(4), N4–Ca1–N1 107.6(4), N3–C30–Sn1 123.7(13), N4–C30–Sn1 121.2(9), N4–C30–N3 114.1(11).
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