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Investigation of Sn(IV) and Sn(II) by dianionicligand compounds Supported by Nitrogen-Based Ligands

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Abstract

Synthetic routes to a series of tin compounds incorporating nitrogen-based chelating ligands are described. The β-diketiminato tin chloride precursor was utilized to isolate the first tin-phosphorus tin compound using this ligand, $[(HC\{C(Me)NAr\}_2)SnPPh_2]$. A diamide ligand was employed to investigate tin (II) and (IV) compounds. Two tin (II) and (IV) compounds, $[(Me_2Si\{ArN\}_2)SnPh_2]$ and $[Li(OEt)_2](Me_2Si\{ArN\}_2)SnPh_2]$, were formed *via* reaction of the lithiated preligand, $[Me_2Si\{ArNLi\}_2]$+Sn(IV). Finally a novel Sn(II) *N*-heterocyclic stannylene compound was formed by reaction of the preligand with $SnCl_4$.

The diamide ligand was found to be suitable for both Sn(IV) and Sn(II) compounds. Reaction to obtain the tin dichloride compound resulted in the formation of $[Li(OEt_2)_2][LSnCl_3]$, which was characterised to be the chloro-bridged lithium chloride adduct of the desired compound. To gain more information on this reaction it was repeated with $SnCl_2Ph_2$ to attain the tin diphenyl analogue, which was established with no problems. Reaction to generate a *N*-heterocylic stannylene was extremely interesting, as this compound has great potential for further reactivity both independently and with regards to the aim of this product, which was to generate a tin-phosphorus multiple bond.

Keywords: Tin(IV) compounds, $SnCl_2Ph_2$, A diamide ligand, β-diketiminato tin chloride

تحليل مركبات Sn(IV) وSn(II) بواسطة الليكند ثنائية الايون المدعومه بليكندات قواعد النتروجين

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الخلاصة

تم توصيف الطرق التحضيرية لسلسلة من مركبات القصدير من خلال دمج الليكندات المخلبية النيتروجينية. حيث تم توظيف متسلسل ثنائي الامايد للكشف عن مركبات القصدير الثنائي والرباعي Sn(IV)وSn(II. وقد تم تحضير المركبات الاخيرةعن طريق تفاعل متسلسل الاواصر الاولي المعوض بالليثيوم $[Me_2Si\{ArNLi\}_2]$ مع $SnCl_4$ للحصول على معقدات القصديرالثنائية Sn(II) *N*–heterocyclic stannylene.

وتم تشخيص هذه المركبات او المعقدات المحضرة باستخدام تقنيات HNMR، ومطيافية الكتلة Mass spectroscopyو وتقنية حيود الاشعة السينية XRD ومن خلال هذه التقنيات وجد ان المركب الناتج من التفاعل هو $[Li(OEt_2)_2][LSnCl_3]$على انه الجسر الرابط للمركب chloro–bridged lithium chloride.

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ومن الممكن اجراء المزيد من التفاعلات للمركب *N*-heterocylic stannylene لانتاج القصدير الفسفوري ذو الجسورالمتعددة.

Introduction

Extensive studies on the synthesis and reactivity of metal amides have been carried out since the pioneering work of Lappert and co-workers in the 1970's [1,a,b]. Although tin amides can be prepared in both II and IV oxidation states, the majority of complexes tend to involve Sn(IV). Divalent stannyl compounds can be isolated using sterically demanding substituted chelating amides. The bulky chelating ligands stabilize low valent metal centers via back donation of electron density through the nitrogen atoms whilst providing steric saturation in order to prevent further reaction to generate the more thermodynamically stable Sn (IV) compounds. A series of divalent group 14 metal LMX compounds have been reported [2,3] (L= *N*-heterocyclic chelating ligand; X= halide, amide, alkoxide, phosphanide). These compounds have sparked interest as potential single-site initiators for the polymerisation of lactides and/or as Lewis acid catalysts for ring opening polymerisations [4]. The high reactivity of the M-X bond means that they are precursors for further reactions at this site.

The aim of this project was to synthesis compounds containing a tin phosphorus bond, which could act as precursors for an elimination reaction to form a tin-phosphorus multiple bond. Heavy metal multiple bonds are difficult to achieve due to their weak π bonds. In 1981 revolutionary Si=C,[5] Si=Si[6] and P=P[7] bonds were prepared by employing bulky ligands. The first stable compound containing a tin phosphorus double bond was isolated by Couret *et al.* in 1984 [8]. The compound, shown in Figure-1, is stabilized by bulky groups on both the tin and the phosphorus atoms. The double bond was formed by elimination of HF from the tin-phosphorus single bond compound, $R_2Sn(F)$-PAr(H).

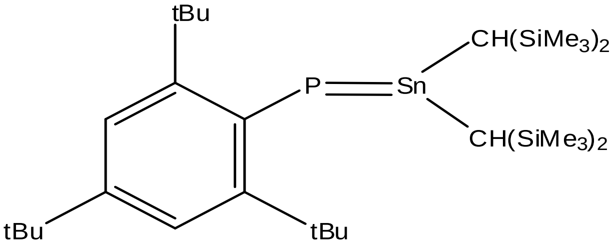


Figure 1-First stable Stannophosphene

In order to achieve a tin-phosphorus multiple bonded species, it is essential that a stable tin-phosphorus single precursor is formed. This compound must be able to be isolated in a yield satisfactory for further reaction as well as stable enough to accommodate the weak π bond once a double bond was formed. To achieve this, nitrogen based ligands with bulky $iPr_2C_6H_5$.(*iPr- iso*propyl) substituents, abbreviated as Ar in this report, were employed. By manipulation of the ligand, the position of the bulky, sterically protecting aryl groups can be controlled in order to achieve the desired degree of steric protection. Figure-2 illustrates two different nitrogen based ligands where the position of the bulky Ar group is altered by the size of the metallacyclic ring

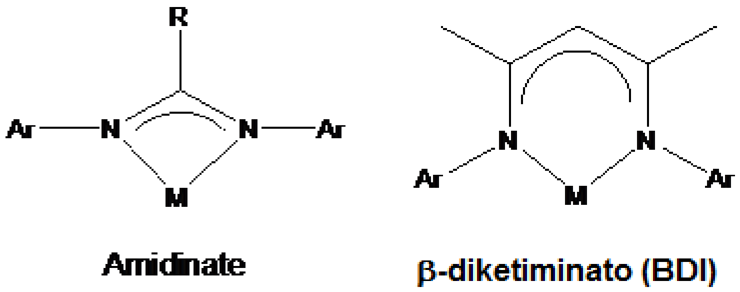
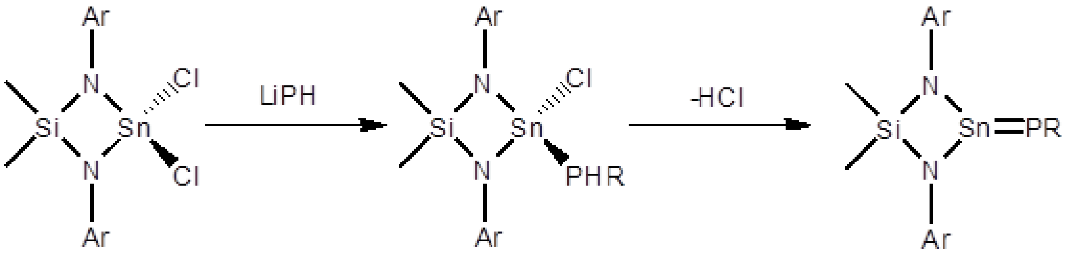


Figure 2-Projection of Ar groups by different ligands, where it forms with amidinate tetragonal cyclic while a hexagonal cyclic with a metal in case of BDI

The monoanionic amidinate ligand forms a four membered ring on coordination to a metal, whereas the monoanionic BDI ligand forms a six membered ring. The less strained BDI-metal complex projects the Ar groups towards the coordinated metal to a greater extent than in the amidinate-metal complex, resulting in a higher degree of steric shielding at the metal Centre. Extensive reactions of (BDI)$SnCl_2$ have been carried out [9], although none involved any phosphorus species. It is only in the last two years that Dreiss et al. have carried out studies on group 14 metal BDI compounds to generate species containing a group 14 metal phosphorus bond [10, 11], Interestingly, tin is omitted from these studies and hence is an intriguing area of research to complement existing literature. A tin(II) compound, (BDI)Sn-PPh_3 was synthesised and fully characterized [12]. The reactivity of the stable Sn-P bond was then probed by reaction with elemental selenium [13].

The stable tin(II) compound (BDI)$SnPPh_2$ synthesised, achieved good comparisons with analogous compounds. However, unfortunately (BDI)$SnPPh_2$ compound was not a prominent precursor for an elimination reaction to form the desired tin-phosphorus double bond due to the lack of labile substituents on the tin ion. To address this, a different nitrogen based ligand was employed to generate a tin(IV) species. A chelating silyl diamide ligand [4], evoked interest as a ligand in a precursor for a Sn-P containing species. The dianionic ligand was used to generate the tin(IV) complex ($Me_2Si\{NAr\}_2$)$SnPh_2$, in order to gain information on the predictably less stable $LSnCl_2$ species.

In an attempt to generate the chlorine analog compound $[Li(OEt_2)_2][LSnCl_3]$, $[Li(OEt_2)_2][Me_2Si\{(NArLi)_2\}Cl_3]$ was isolated. In an effort to generate the desired product clearly, the carbene analog was synthesised similarly to complexes published by [14]. N-heterocyclic carbens are commonly known for high stability as a result of their strong N-C carbene π-donation, resulting in large electron density in π orbitals of the carben, carbon atom. Analogous species containing group 14 metals at the carben centre have been successfully synthesised for M= Si[15], Ge[16] and more recently Pb[17] and Sn[18]. Although more work has been carried out on the lighter group 14 metals, divalent heavier metal analogs are predicted to be more stable due to the inert pair effect. Since the tin atom of N-heterocyclic stannylenes have large potential as a catalytic site, the aim of this work is to employ it as a site for addition of halide ions. The tin(II) centre can be oxidized to a tin(IV) ion by the addition of two halides, to generate the desired product clearly. This dihalide tin(IV) complex would hold great potential in both catalytic terms, but more importantly with respect to this project, could act as a starting material for a Sn-P and furthermore a Sn=P containing complex, due to the readily replaceable halide ions. As shown in Scheme-1.



Scheme 1-Postulated reaction of Diamide $SnCl_2$ to generate Sn-P bonds [19]

Result and discussion

Synthesis: The Reaction $[Me_2Si\{(NArLi)_2\}]$ of with 1 equiv of $SnCl_2Ph_2$ in Et_2O, provided colourless crystals of $[Me_2Si\{ArNLi\}(ArNH)]_2$ upon recrystallization in toluene. Analysis of the crystals by X-ray diffraction however, identified the compound to be the monolithiated adduct of the initial ligand, where one lithium atom was replaced by a proton. This was suspected to be caused by the tin reagent having degraded over time and hence become hydrated. Therefore a sample of $SnCl_2Ph_2$ was recrystallised from toluene, to generate clean white crystals. The reaction was repeated in Et_2O to generate a yellow solution which was stirred for 20 hours. The product was extracted in hot toluene and recrystallised at -80 °C. The clear, colourless, moisture and air sensitive crystals of $[(Me_2Si\{ArN\}_2)SnPh_2]$ underwent thermal shock, to become opaque, upon mounting onto the X-ray diffractometer and were therefore no longer suitable for X-ray diffraction. The product was however, fully characterised by NMR, mass spectroscopy and elemental analysis.

X-ray data: The monolithiated product $[Me_2Si\{ArNLi\}(ArNH)]_2$ isolated, shown in Figure-3, is reminiscent of the known dilithiated species in the sense that it crystallises as discrete dimeric molecules. Both lithium atoms in the X-ray structure are coordinated by three nitrogen atoms. One nitrogen from each monomer bonds to a lithium ion from another monomer as well as its associated lithium ion, whilst the other nitrogen atom binds to the lithium ion associated with the monomer and one proton. This forms a trigonal-pyramidal geometry around the three coordinate metal ions in both complexes, allowing a distortion parameter to be calculated. In the compound the average degree of pyramidalization (DP) of the two metal ions is 20.1 % which is small compared to that of the dilithiated complex, 53.2 %. By replacing one lithium ion with a proton, the crystal structure is relaxed, forming a more planar core around the lithium ions.

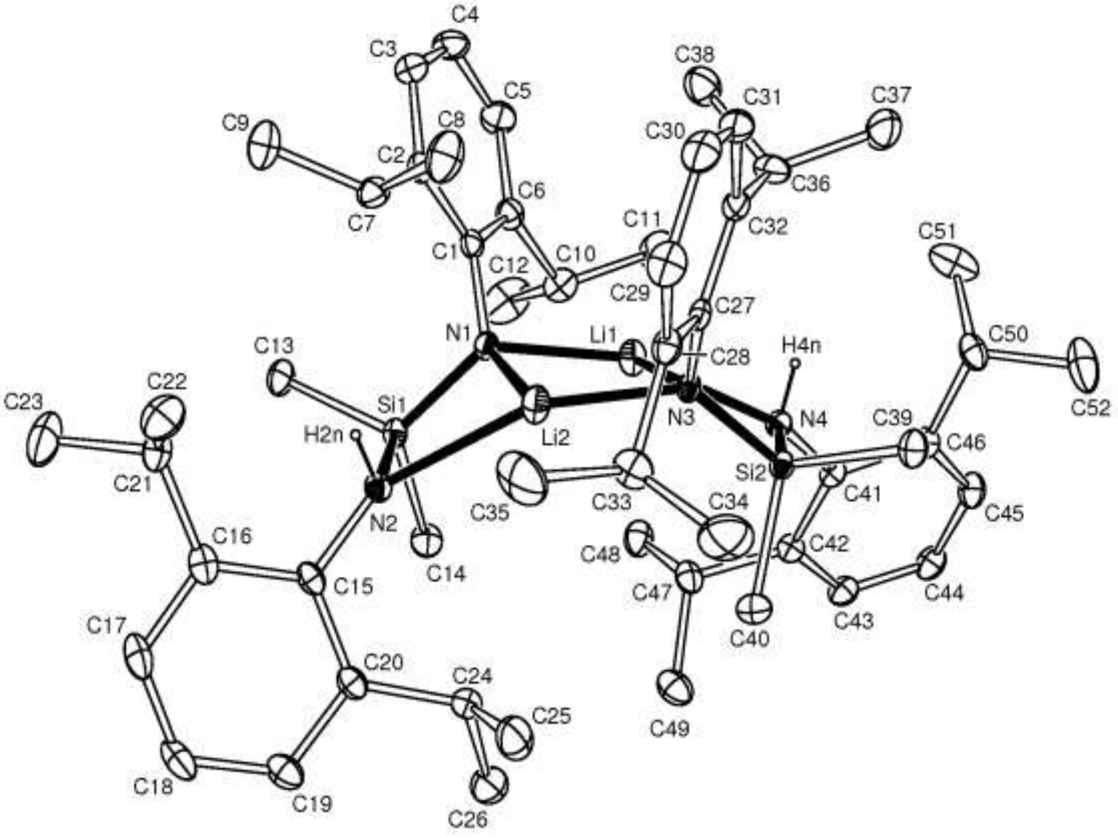


Figure 3-Monolithiated product rendered from Oak Ridge Thermal Ellipsoid Plot (ORTEP)

NMR data: NMR data of $[Me_2Si\{ArN\}_2SnPh_2]$ provided evidence that the diamide ligand is bound to tin. Every resonance in the ^{1}H NMR were shifted to the left slightly in comparison to the starting material $[Me_2Si\{ArNLi\}_2]$, with one exception of the isopropyl doublet. This infers that each proton environment, bare the methyl groups on the *iso*propyl (iPr) are more deshielded, which is to be expected when lithium cations are replaced with a metal capable of donating electron density. Phenyl carbon environments, δ= 147.4, 137.7 and 131.0 ppm, assigned to be close to the tin atom show tin satellites in the ^{13}C spectrum. Interestingly the ^{119}Sn NMR showed a broad multiplet instead of the singlet predicted. The tin coupling seen in the proton NMR confirms that this multiplet is caused by coupling to the protons on the ortho carbons of the phenyl group. There are four ortho protons in this molecule which all couple to tin, hence the broad multiplet seen in the tin NMR is likely to be a quintet.

Mass Spec data: Both the parent compound and its fragments are seen in the mass spectrum of $[Me_2Si\{ArN\}_2SnPh_2]$ as shown in Table-1, thus proving that the Sn(IV) compound was formed.

Table 1-Mass spectra Abundances of [$Me_2Si\{ArN\}_2SnPh_2$]

m/z	Assignment
682	$Me_2Si(NAr)_2SnPh_2$
605	$Me_2Si(NAr)_2SnPh$
505	$MeSi(NAr)SnPh_2$
446	$Me_2Si(NAr)SnPh$
408	$Me_2Si(NAr)_2$

Synthesis: Reaction of the [$Me_2Si\{ArNLi\}_2$] with $SnCl_4$ generated solvated crystals of the desired tin(IV) compound, [$LSnCl_3$][$Li(Et_2O)_2$] at -30 °C from pentane. The yellow crystals were fully characterised using X-ray diffraction, NMR and mass spectroscopy. Some discrepancy was seen between the calculated and the observed elemental analysis values. This can be explained by partial loss of the coordinated diethyl ether solvent molecules, whilst pumping the crystals under vacuum.

X-ray data: The crystal structure shown in Figure 4, revealed a five coordinate Sn(IV) species. The geometry can best be described as distorted square based pyramidal, where Cl(1) forms the axial ligand and a square base is formed between the bidentate ligand and Cl(2) and Cl(3). Two of the three chlorine ligands are coordinated to a disolvated lithium ion, suggesting some lithium chloride side product still remained after the product was extracted in pentane. The Sn-Cl and Cl-Li bond lengths, shown in Table 2, the structure illustrated in Scheme 2 was deemed most plausible. The Sn-Cl(1) bond length is shorter than that between the other chlorine atoms which correlates with the fact that it is a terminal bond and the others are bridging chlorides. The Sn-Cl(2) bond is shorter than the Sn-Cl(3), this in conjunction with the longer Cl(2)-Li bond with respect to the Cl(3)-Li bond, infers that the Sn-Cl(3) and Cl(2)-Li bonds are both dative. The bite angle of the chelating ligand was smaller in comparison to that seen compound.[$(HC\{C(Me)NAr\}_2)SnPPh_2$] but consistent with a comparative Zr(IV) compound, [$LZrCl_2(THF)$] where the bite angle is 76.83(2) °[20]. Figure-3 it is obvious the coordinated ether molecules are disordered. This was caused by the solvent molecules being coordinated in several different orientations. Therefore the average atomic position within the unit cell for each solvent atom is more disordered than others within the compound.

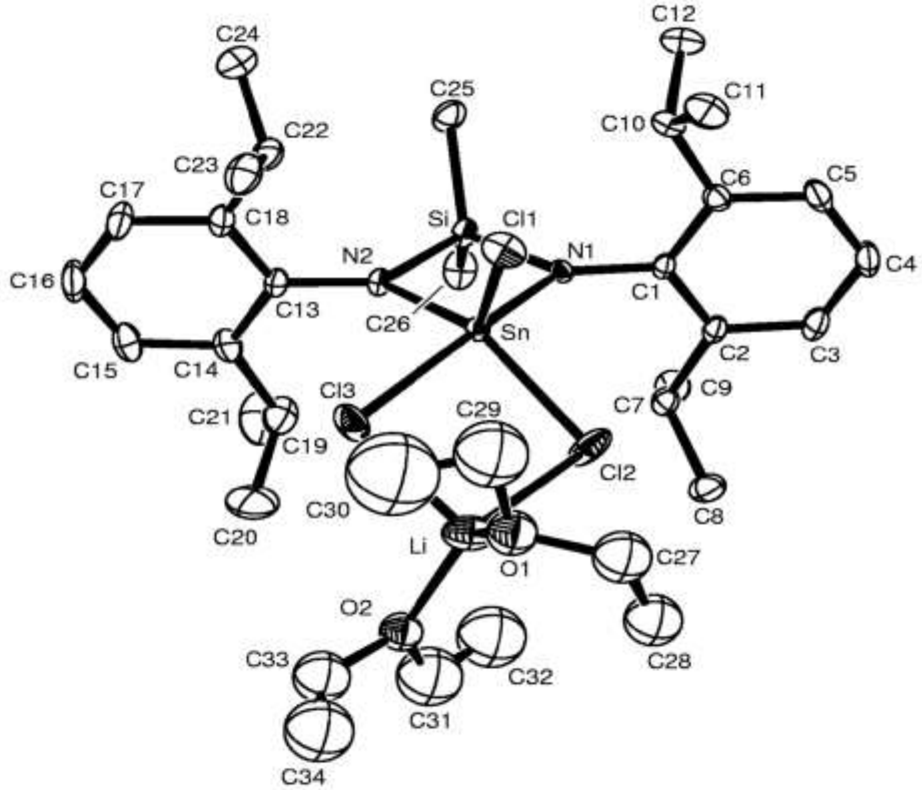
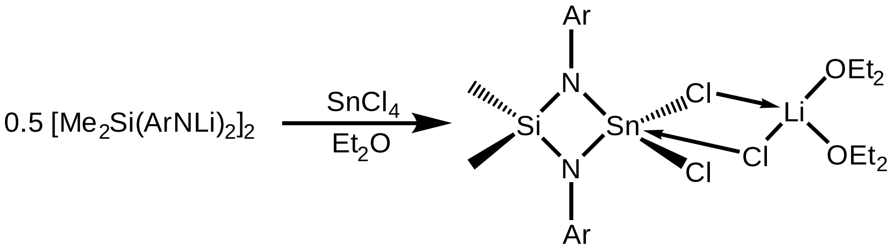


Figure 4-Compound (4) rendered from ORTEP

Table 2-Selected Crystal Data for compound .$[Li(OEt)_2][Me_2Si\{ArN\}_2SnCl_3]$

Bond length/ Å		Bond angle/ °	
Sn-Cl(1)	2.3464(16)	N(1)-Sn-N(2)	74.77(16)
Sn-Cl(2)	2.4176(16)	Cl(1)-Sn-Cl(2)	99.30(8)
Sn-Cl(3)	2.4703(16)	Cl(1)-Sn-Cl(3)	92.63(7)
Cl(2)-Li	2.437(15)	Cl(2)-Sn-Cl(3)	85.27(7)
Cl(3)-Li	2.389(15)		



Scheme 2-Formation of chloro-bridged lithium chloride adduct

NMR data: A characteristic quartet and triplet in the ^{1}H NMR indicated the presence of diethyl ether. The ^{7}Li NMR spectrum showed a strong singlet at -0.46 ppm, significantly different from.$[Me_2Si\{ArNLi\}_2]$ which is at +1.97 ppm. Therefore proving that the coordinated Li ion is unlikely to be bound directly to the ligand.

Mass Spec data: Mass spec proves the presence of tin in the compound. Although the parent compound is not present suitable fragments confirm that the tin(IV) compound.$[Li(OEt)_2][Me_2Si\{ArN\}_2SnCl_3]$ was formed. It is not surprising that the parent compound was not seen, as the Li ion is bonded very weakly and hence will easily fragment upon bombardment with electrons as shown in Table-3.

Table 3-Mass spectra Abundances of.$[Li(OEt)_2][Me_2Si\{ArN\}_2SnCl_3]$

m/z	Assignment
634	$Me_2Si(NAr)_2SnCl_3$
598	$Me_2Si(NAr)_2SnCl_2$
528	$MeSi(NAr)_2Sn$
393	MeSiNAr
232	Me_2SiNAr
74	OEt_2

Due to the obstacle faced during the synthesis of the desired product without the lithium chloride adduct, a one container reaction of compound.$[Li(OEt)_2][Me_2Si\{ArN\}_2SnCl_3]$ generated *in situ* was reacted with $LiPPh_2$, in an attempt to generate a Sn-P bond from this species. The bright yellow solution of the resulting product(s) in pentane was stored at -30, -50 and -80 °C in an attempt to afford crystals. However, none were formed and due to time restraints the reaction was not repeated.

Experimental work

All experiments were conducted under dry nitrogen or in a MBraun 150B-G drybox. Standard Schlenk, vacuum line and cannula techniques were employed throughout. All solvents utilised were dried for a minimum of 72 hours before use by refluxing over an appropriate drying agent (diethyl ether, hexane: sodium/potassium alloy, potassium, and toluene: sodium). Dry solvents were degassed and stored under nitrogen over activated molecular sieves or potassium mirrors. All liquids were freshly distilled before use. NMR studies were carried out using a Varian VNMR 400 spectrometer at 30 °C in C_6D_6, unless otherwise stated. The spectrometer frequencies for each nuclei are tabulated below Table-4. And finally all carbon NMR undertaken was proton decoupled unless stated otherwise.

Table 4-Spectrum frequencies for nuclei of standard compounds

Nuclei	^{1}H	^{7}Li	^{13}C	^{29}Si	^{31}P	^{77}Se	^{117}Sn	^{119}Sn
Spectrometer Frequency/ Hz	399.50	155.26	100.46	79.37	161.72	76.19	142.42	148.99

Experimental Procedures for dianionic ligand compounds

Synthesis of the [$Me_2Si\{ArNLi\}_2$]

The [$Me_2Si\{(NArLi)_2\}$] preligand was synthesised from 2,6-diisopropylanaline and dimethylsilyl dichloride as reported by Hill and Hitchcock [21].

Synthesis of the [($Me_2Si\{ArN\}_2$)$SnPh_2$]

Addition of $SnCl_2Ph_2$ (410 mg, 1.19 mmol) in Et_2O (25-30 ml) dropwise at -78 °C to a solution of the[$Me_2Si\{ArNLi\}_2$] (502 mg, 0.59 mmol) in Et_2O resulted in a rapid colour change from colourless to clear yellow. The solution was stirred for 20 hours. The volatiles were removed in *vacuo* and the product was extracted in toluene (25-30 ml). Product compound was recrystallised from toluene at -80 °C .

Yield = 170mg, 41.9 %.

^{1}H NMR: δ 7.73 (d, *J* = 5.97, 4H, *o*-Ph), 7.21- 7.06 (m, 12H, *m*-Ph, *p*-Ph and Ar), 4.35 (sept, *J* = 6.77, 4H, C*H*Me_2), 1.18 (d, *J* = 6.69, 24H, CH*Me₂*), 0.56 (s, 6H, Si*Me₂*)

^{13}C NMR: δ 147.4 (s, C, *i*-Ph), 141.75 and 141.15 (s, CH, N*Ar*), δ 137.71(s, C, *o*-Ph), 131.04, 129.52 and 124.23 (s, CH, *m*-Ph and *p*-Ph and Ar), 28.29 (s, *C*HMe_2), 26.04 (s, CH*Me₂*), 5.22 (s, Si*Me₂*)

^{29}Si NMR: δ 8.7

^{119}Sn NMR: δ 68 (br m)

Elemental anal. Calcd. For $C_{38}H_{50}N_2SiSn$ (682.28): C, 66.84 %; H, 7.38 %; N, 4.10 %.

Found: C, 67.07 %; H, 7.30 %; N, 3.92 %.

Synthesis of [$Li(OEt)_2$][($Me_2Si\{ArN\}_2$)$SnCl_3$]

Addition of $SnCl_4$ (380 mg, 1.46 mmol) in Et_2O, dropwise at -78 °C to a solution of [$Me_2Si\{(NArLi)_2\}$] (616 mg, 1.46 mmol) in Et_2O was carried out with continuous stirring for 20 hours. The solution was filtered and recrystallized in pentane at -30 °C to yield yellow needles of [$Li(OEt)_2$][($Me_2Si\{ArN\}_2$)$SnCl_3$].

Yield = 255 mg, 23.9 %.

^{1}H NMR: δ 7.09 (m, 6H, *m*-Ar and *p*-Ar), 4.01 (sept, *J* = 6.92, 4H, C*H*Me_2), 3.26 (q, *J* = 6.99, 4H, OC*H₂*CH_3), 1.30 (d, *J* = 6.69, 24H, CH*Me₂*), 1.08 (t, *J* = 6.99, 6H, OCH_2C*H₃*), 0.24 (s, 6H, Si*Me₂*)

^{13}C NMR: δ 148.0 (s, C, *i*-Ph and *o*-Ph), 126.4 and 124.6 (s, CH, *m*-Ar and *p*-Ar), 66.2 (s, OCH_2CH_3), 28.5 (s, C*H*Me_2), 25.7 (s, CH*Me₂*), 15.8 (s, OCH_2*C*H_3), 2.9 (s, Si*Me₂*)

^{7}Li NMR: δ -0.46 (s)

^{29}Si NMR: δ -22.2

^{119}Sn NMR: δ -383 (s)

Elemental anal. Calcd. For $C_{30}H_{50}Cl_3LiN_2O_2SiSn$ (730.19): C, 49.30 %; H, 6.90 %; N, 3.84 %.

Found: C, 48.43 %; H, 5.58 %; N, 5.13 %.

Reaction [$Li(OEt)_2$][($Me_2Si\{ArN\}_2$)$SnCl_3$] with LiPPh2

A solution of $SnCl_4$ (178.8 mg, 0.69 mmol) in Et_2O, was added dropwise at -78°C to a solution of [$Me_2Si\{ArNLi\}_2$] (290 mg, 0.69 mmol) in Et_2O and the mixture was stirred for 5 hours. MeLi (2.1 mL of a 0.33 M solution in Et_2O) was added dropwise at -78 °C to a solution of $HPPh_2$ (127.8 mg, 0.69 mmol) in Et_2O resulting in a bright yellow solution which was stirred for 2 hours. The LiPPh2 solution was added dropwise to the [$Li(OEt)_2$][($Me_2Si\{ArN\}_2$)$SnCl_3$] solution at -78 °C and stirred for 3 hours. The resulting product was filtered and dissolved in Et_2O. No crystalline product formed at -30, -50 or 80 °C.

Conclusions

The diamide ligand was found to be suitable for both Sn(IV) and Sn(II) compounds. Reaction to obtain the tin dichloride compound resulted in the formation of.$[Li(OEt)_2][(Me_2Si\{ArN\}_2)SnCl_3]$, To gain more information on this reaction it was repeated with $SnCl_2Ph_2$ to attain the tin diphenyl analog. Reaction to generate a *N*-heterocylic stannylene was extremely interesting, as this compound has great potential for further reactivity both independently and with regards to the aim of this product, which was to generate a tin-phosphorus multiple bond.

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