Tin Phosphides Supported by Nitrogen-Based Ligands

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Abstract

Synthetic route to a series of tin compounds incorporating nitrogen-based chelating ligands are described. The β-diketiminatotin chloride precursor was utilised to isolate the first tin-phosphorus tin compound using this ligand, $[(HC\{C(Me)NAr\}_2)SnPPh_2]$. The reactivity of the tin-phosphorus bond was probed by reaction with elemental selenium, resulting in direct insertion into the bond. A diamide ligand was employed to investigate this type of ligand in tin II and IV compounds. Two tin(IV) compounds, $[(Me_2Si\{ArN\}_2)SnPh_2]$ and $[Li(OEt)_2](Me_2Si\{ArN\}_2)SnPh_2]$, were formed via reaction of the lithiatedpreligand, $[Me_2Si\{ArNLi\}_2]$, with $SnCl_4$. And finally a novel Sn(II) N-heterocyclic stannylene compound was formed by reaction of the preligand with $SnCl_2$.

Keywords: Nitrogen-based chelating ligands, [(HC{C(Me)NAr}$_2$)SnPPh$_2$] ligand and diamide ligand.

الخلاصة

يتم وصف الطرق الاصطناعية لسلسلة من مركبات القصدير المدموجة بروابط النيتروجين المخلبية. تم استخدام كلوريد القصدير β–diketiminato لعزل أول قصدير الفوسفور ، باستخدام هذا الليكند ، $[(HC\{C(Me)NAr\}_2)SnPPh_2]$. حيث يعمل هذا الليكند ثنائي الأميد للتحقيق من مركبات القصدير (II) و (IV). تم توظيف متسلسلة الاواصر ثنائية الامايد للتحقق عن القصدير الثنائي والرباعي. وتم تحضير نوعين من القصدير الثنائي والرباعي عن طريق تفاعل متسلسل الاواصر الاولي المعوض بالليثيوم $[Me_2Si\{ArNLi\}_2]$ مع $SnCl_4$. وبالنهاية الحصول على مركب *N*–heterocyclic stannylene Sn(II).

ولقد وجد ان متسلسل الاواصر ثنائي الامايد مناسبا لمركبات القصدير Sn(IV)و Sn(II) . والمركب الناتج من التفاعل هو $[Li(OEt_2)_2][LSnCl_3]$والذي تم توصيفه وتحليله على انه الجسر الرابط للمركب المطلوب chloro–bridged lithium chloride.

للحصول على معلومات اكثر عن هذا التفاعل ، لقد تم اعادة التفاعل باستخدام $SnCl_2Ph_2$ لتحقيق القصدير التناظري والذي تم تحضيره بدون مشاكل. التفاعل استخدم لتحضير فسفور القصدير الثنائي الاصرة. وكان التفاعل لانتاج المركب–*N*

heterocylicstannylene مثيرة للاهتمام للغاية، وهذا المركب لديه امكانات كبيرة لغرض اجراء المزيد من التفاعلات وبشكل مستقل بما يتعلق بهدف هذا المنتج في هذا البحث، من اجل أنتاج القصدير الفوسفور ذو الروابط المتعددة.

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]. 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 stabilise low valent metal centres 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 synthesize 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 stabilised 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).

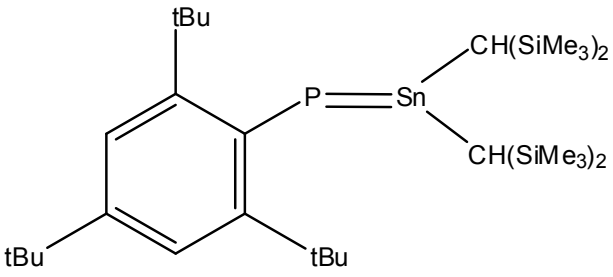

Figure 1: First stable Stannophosphene

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 *i*Pr2C6H3 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.

Experimental work

All experiments were conducted under dry nitrogen or in aMBraun 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, THF: potassium, 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, toluene, unless otherwise stated. The spectrometer frequencies for each nuclei are tabulated below. And finally all carbon NMR undertaken was proton decoupled unless stated otherwise.

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

X-ray crystallographic analysis was performed by Dr. M. P. Coles using a Nonius Kappa CCD diffractometer.

Tin Complexes of the Amidine Ligand $[PhC\{NAr\}_2]^-$

Synthesis of $[\{PhC(NAr)_2\}SnCl]$

^{n}BuLi (mL, mmol) was added dropwise at -78 °C to a dark orange solution of *N,N'*-bis(2,6-Diisopropylphenyl)benzamidine (mg, mmol) to yield a dark orange solution which was stirred for 2 hours. The lithiated solution was added dropwise to a colourless solution of $SnCl_2$ (mg, mmol) in THF (ca. 20 mL) and stirred for 22 hours. The solvent was removed *in vacuo*and the product extracted in pentane.

Reaction of *in situ* generated $[\{PhC(NAr)2\}SnCl]$ with $LiPPh_2$

MeLi (3.42mL, 1.14mmol) was added dropwise at -78 °C to a dark orange solution of *N,N'*-bis(2,6-Diisopropylphenyl)benzamidine (503 mg, 1.14 mmol) to yield a dark orange solution which was stirred for 2 hours. The lithiated solution was added dropwise to a colourless solution of $SnCl_2$ (217.0 mg, 1.14 mmol) in THF (ca. 20 mL) and stirred for 20 hours. MeLi (3.42 mL, 1.14 mmol) was added dropwise at -78°C to a solution of $HPPh_2$ in

THF (ca. 15mL) and stirred for 2 hours. The resulting solution was then added dropwise to the solution of[{PhC(NAr)$_2$}SnCl] to give a dark red solution which became darker over time. After 17 hours the solvent was removed *in vacuo* and the product extracted in pentane. A mixture of orange and yellow crystals were mechanically separated.

- **Orange product yield = 15 mg**
- **Yellow product yield = 19 mg**

Orange crystals

^{1}H NMR: δ 7.77-7.73 and 7.16-7.12 (m, 20H, (P*Ph$_2$*)$_2$)

^{31}P{^{1}H} NMR: δ -14.9 (s, (*P*Ph$_2$)$_2$)

Yellow crystals:

^{1}H NMR: δ 7.30-7.02 and 6.81-6.72 (m, 36H, Ar*H*), 4.15 (sept, 2H, C*H*Me$_2$), 3.93 (sept, 2H, C*H*Me$_2$), 3.79 (sept, 2H, C*H*Me$_2$), 3.63 (sept, 2H, C*H*Me$_2$), 3.54 (sept, 2H, C*H*Me$_2$), 4.46 (sept, 2H, C*H*Me$_2$), 1.65 (d, 6H,), 1.57 (d, 6H, CH*Me$_2$*) 1.50, (d, 6H, CH*Me$_2$*), 1.47 (d, 6H, CH*Me$_2$*), 1.13 (d, 6H, CH*Me$_2$*), (d, 6H, CH*Me$_2$*), 0.89 (br s, 12H, *Me*), 0.67 (s, 6H, *Me*)

^{31}P{^{1}H} NMR: δ -14.9 (s, (*P*Ph$_2$)$_2$)

Tin Complexes of the β-Diketiminato Ligand [HC{C(Me)NAr}$_2$]$^-$

BDI = β-diketiminato

Synthesis of (BDI)SnPPh$_2$

A solution of MeLi (2.15 mL, 0.717 mmol) in THF (ca. 15 mL) was added dropwise at 78°C to HPPh$_2$ (134 mg, 0.717 mmol) in THF (ca. 15 mL) resulting in a rapid colour change from a colourless to a vibrant orange solution. A solution of (BDI)SnCl (410 mg, 0.717 mmol) in THF (ca. 15 mL) was added dropwise to the reaction mixture at -78 °C, resulting in a red solution. The reaction was allowed to warm to room temperature and stirred for 2.5 hours. The volatiles were removed under vacuum and the product was extracted with pentane. Concentration of the reaction mixture was resulted in spontaneous growth of red crystals of(BDI)SnPPh$_2$.

Yield = 350.4 mg, 68 %.

^{1}H NMR: δ 7.10-7.55 (m, 16H, P*Ph$_2$*and 2,6-*i*-Pr$_2$C$_6$*H$_3$*), 5.08 (s, 1H, γ-C*H*), 4.45 (sept, *J* = 6.82, 2H, C*H*Me$_2$), 3.53 (sept, *J* = 6.78, 2H, C*H*Me$_2$), 2.04 (d, *J* = 6.82, 6H, CH*Me$_2$*), 1.89 (s, 6H, *Me*), 1.60 (d, *J* = 6.89, 6H, CH*Me$_2$*), 1.48 (d, *J* = 6.80, 6H, CH*Me$_2$*), 1.31 (d, *J* = 6.83, 6H, CH*Me$_2$*).

^{13}C NMR: δ 167.1 (N*C*Me), 143.7, 143.1, 128.0, 127.9, 126.6, 125.4, 124.7, 124.5 (P*PH$_2$*and 2,6-*i*-Pr$_2$*C$_6$*H$_3$), 96.8 (s, γ-*C*H), 28.8 (s, *C*HMe$_2$), 28.0 (*C*HMe$_2$), 25.8 (s, CH*Me$_2$*), 24.8 (CH*Me$_2$*), 24.3 (CH*Me$_2$*), 24.2 (CH*Me$_2$*), 23.1 (s, *Me*).

^{31}P NMR: δ -30.8 (s, ^{1}J$_{Sn117-P}$ = 936 Hz, ^{1}J$_{Sn119-P}$ = 978 Hz, LSn*P*Ph$_2$)

^{117}Sn NMR:δ 120 (d, ^{1}J$_{Sn-P}$ = 924 Hz)

^{119}Sn NMR:δ 125 (d, ^{1}J$_{Sn-P}$ = 978Hz)

Anal.Calcd. For C$_{41}$H$_{50}$N$_2$SnP (721.27): C, 68.21 %; H, 6.99 %; N, 3.88 %.

Found: C, 68.10 %; H, 7.18 %; N, 3.95 %.

M.P: 94.9-110.4 °C. (Decomposed)

NMR scale:

Elemental selenium (2.6 mg, 0.033 mmol) was added to a solution of **3** (23.7 mg, 0.033 mmol) in C$_6$D$_6$ (ca. 0.75 mL).

^{31}P{^{1}H} NMR:

(0 h)δ 4.1 (s, ^{1}J$_{Sn117-P}$ = 723 Hz, ^{1}J$_{Sn119-P}$ 755 Hz, ^{1}J$_{Se-P}$ =214 Hz), -14.9 (s, (*P*Ph$_2$)$_2$), -30.7 (s, ^{1}J$_{Sn117-P}$ = 936 Hz, ^{1}J$_{Sn119-P}$ = 978 Hz, LSn*P*Ph$_2$),

(72 h)δ 19.5 (s, ^{1}J$_{Sn117-P}$ = 198 Hz, ^{1}J$_{Sn119-P}$ = 210 Hz ^{1}J$_{Se-P}$ = 571 Hz), 4.1(s, ^{1}J$_{Sn117-P}$ = 723 Hz, ^{1}J$_{Sn119-P}$ = 755 Hz, ^{1}J$_{Se-P}$ = 214 Hz,), -14.9 (s, (*P*Ph$_2$)$_2$)

^{117}Sn NMR(C_6D_6): δ 201 (s), -10 (d, $^1J_{Sn-P}$ = 723 Hz), δ -165 (d, $^1J_{Sn-P}$ = 198 Hz)
^{119}Sn NMR(C_6D_6): δ 225 (s), 20 (d, $^1J_{Sn-P}$ = 755 Hz), -140 (d, $^1J_{Sn-P}$ = 210 Hz)
^{77}Se NMR(C_6D_6): δ 94 (d, $^1J_{Se-P}$ = 214 Hz), 92 (d, $^1J_{Se-P}$ = 571 Hz),

NMR scale (excess Se):
Elemental Selenium (11.4 mg, 0.14 mmol) was added to the red solution of **3** (20.6 mg, 0.028 mmol) in C_6D_6 (ca. 0.75 mL)

^{31}P{^{1}H} NMR:
(0 h):δ 4.1 (s, $^1J_{Sn117-P}$ = 723 Hz, $^1J_{Sn119-P}$ 755 Hz, $^1J_{Se-P}$ =214 Hz), -14.9 (s, (PPh$_2$)$_2$), -30.7 (s, $^1J_{Sn117-P}$ = 936 Hz, $^1J_{Sn119-P}$ = 978 Hz, LSnPPh$_2$),
(18 h): δ 19.5 (s), 4.1(s, $^1J_{Sn117-P}$ = 722 Hz, $^1J_{Sn119-P}$ = 755 Hz, $^1J_{Se-P}$ = 215 Hz), -14.9 (s, (PPh$_2$)$_2$)
(42 h): δ 19.5 (s, $^1J_{Sn117-P}$ =199 Hz, $^1J_{Sn119-P}$ =208 Hz, $^1J_{Se-P}$ =571 Hz), 4.1(s, $^1J_{Sn117-P}$ = 722 Hz, $^1J_{Sn119-P}$ = 755 Hz, $^1J_{Se-P}$ = 215 Hz), -14.9 (s, (PPh$_2$)$_2$)
(144 h):δ 19.5 (s, $^1J_{Sn117-P}$ =199 Hz, $^1J_{Sn119-P}$ =208 Hz, $^1J_{Se-P}$ =571 Hz), -14.9 (s, (PPh$_2$)$_2$)

Scaled up (excess Se):

A solution of **3** (110.2 mg, 0.15 mmol) in toluene (ca. 10 mL) was added to a solution of Se (60.4mg, 0.77 mmol) in toluene (ca. 10mL) and left to stir over night for 17 hours. The orange solution was filtered *in vacuo* to remove unreacted Se. The volatiles were removed *in vacuo* and the product was dissolved in pentane to form a clear yellow solution. No crystals were formed at –30, -50 or –80 °C.

Results and Discussion

Monoanionic ligands

Tin Complexes of the Amidine Ligand [PhC{NAr}$_2$]$^-$

Synthesis: Deprotonation of *N,N'*-bis(2,6-diisopropylphenyl)benzamidine using ^{n}BuLi at -78 °C afforded an orange solution of the lithium amidinate ligand. Reaction with $SnCl_2$ generated the Sn(II) compound, [{PhC(NAr)$_2$}SnCl]. Although this compound has been previously fully characterised by X-ray, NMR and elemental analysis, it has proved extremely difficult to isolate in a satisfactory yield whilst scaling up. Therefore *in situ* generated[{PhC(NAr)$_2$}SnCl] was treated with $LiPPh_2$, assuming 100 % conversion to the tin(II) amidinate, in a one pot reaction to afford a dark red solution. Crystallisation of the product from pentane afforded a mixture of orange and yellow crystals, both of which were unsuitable for X-ray diffraction.

NMR data: The ^{1}H NMR spectrum of the orange crystals only showed a multiplet in the aromatic region, which inferred that the ligand was not present. ^{31}P NMR showed one singlet at -14.9 ppm, which was assigned to be the dimeric species, tetraphenyldiphosphene (Ph_2P=PPh_2)[10] The ^{1}H NMR spectrum of the yellow product confirms the presence of the amidine ligand, but also shows deviations from that of the starting material. The ^{31}P NMR spectrum of the yellow species also shows a single at -14.9 ppm, highlighting the presence of tetraphenyldiphosphene.

Mass Spec data: The mass spectrum of the yellow product highlights the presence of an amidine tin bond.

Table 1: Mass spectra Abundances of the yellow product

m/z	Assignment
559	$PhC\{NAr\}_2Sn$
440	$PhC\{NAr\}_2$
397	$PhC\{NAr\}NSn$
264	PhCNAr

In theory the compound could be $[PhC\{NAr\}_2Sn]^+$, where the tin is of II oxidation state and therefore has an empty p-orbital. An empty orbital of this nature would be readily filled with electrons from another species, X. By looking at all species present in the reaction, X could be Cl^-, PPh_2, AmidineSn or THF. X is unlikely to be THF and $PhC\{NAr\}_2Sn$ as these would result in a Sn(I) species. If the desired product was synthesised, tin satellites should be apparent in the ^{31}P spectrum, however only one singlet corresponding to $(PPh_2)_2$ is seen. It is most likely from both NMR and mass spec, that the yellow product is a combination of the starting material andtetraphenyldiphosphene.

Tin Complexes of the β-Diketiminato Ligand $[HC\{C(Me)NAr_2]^-$

Synthesis

In order to achieve greater stability in an attempt to generate an isolable Sn-P bond, the bulkier monoanionicβ-Diketiminato ligand was employed. The analogous precursor is therefore BDISnCl which can be easily prepared in good yield.[11]

Compound.$[(HC\{C(Me)NAr\}_2)SnCl]$ readily reacted with 1 molar equiv of $LiPPh_2$ to generate a dark red solution. Extraction in pentane provided a cherry red solution which on concentration spontaneously formed red crystals of the desired product, $BDISn\text{-}PPh_2$ in 68 % yield. The moisture and air sensitive compound was fully characterised by X-ray crystallography, NMR and elemental analysis.

X-ray data: The crystal structure determined using x-ray diffraction is illustrated in Figure 3. The overall structure of.$[(HC\{C(Me)NAr\}_2)SnPPh_2]$ is reminiscent of the starting material.$[(HC\{C(Me)NAr\}_2)SnCl]$[12] with a monomeric, three coordinate pyramidal tin centre. The Sn-N bond lengths increase slightly on formation of the Sn-P bond, from 2.180(2) and 2.185(2) Å in.$[(HC\{C(Me)NAr\}_2)SnCl]$ to 2.218(3) and 2.226(3) Å in .$[(HC\{C(Me)NAr\}2)SnPPh_2]$. This reaction also results in the bite angle N-Sn-N decreasing from 85.21(8) ° to 84.06(10) °. Corresponding structural data are shown in Table 3 along with data from comparative compounds. The Sn-P bond length is 2.6307(9) Å, which falls within the range shown for the similar group 14 compounds.[13,14]As expected the metal-P bond length increases as the group is

descended; the larger the metallic radii the worse the overlap between the metal p-orbital with the phosphorous p orbital, causing the σ bond to be weaker and hence longer. The Pb-P bond in the lead compound is however only slightly longer than that of the tin compound.[(HC{C(Me)NAr}$_2$)SnPPh$_2$] . This is due to the donating property of the TMS R groups, which push electron density back into the metal-phosphorous bond more than the phenyl R groups in the tin complex. The degree of pyramidalization (DP) was calculated to be 87 % using Equation 1, where α = the bond angles around tin. The high DP percentage infers large 5p character in the Sn-P sigma bond. It also suggests that the tin atom has retained large S character suggesting the lone pair of electrons is non-directional and thus relatively inert (inert pair effect). Although the lone pair on the tin atom is non-directional it is interesting that the compound is still bent, which can be seen in Figure 3. This is a result of the bonding *via* p orbitals between both the BDI ligand and tin, and the phosphine and tin.

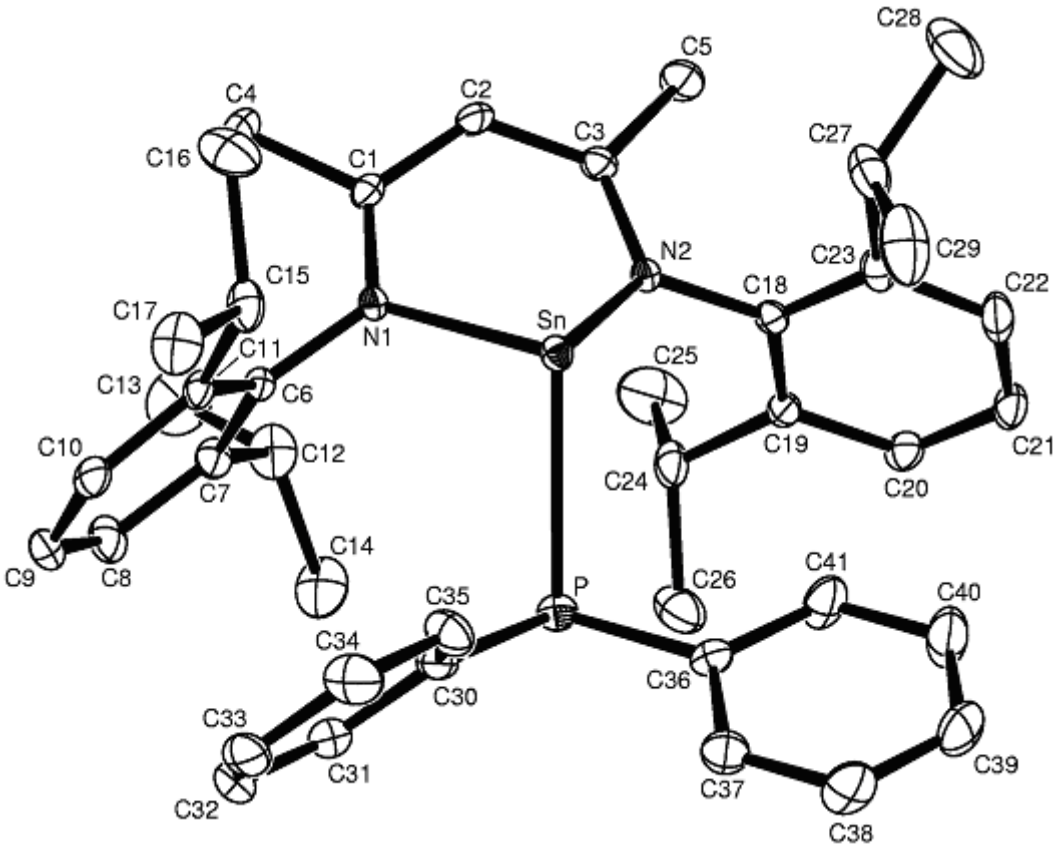

Figure 3: Compound (3) rendered from ORTEP

Table 2: Selected Crystal Data for compoun .[(HC{C(Me)NAr}$_2$)SnPPh$_2$]

Bond length/ Å		Bond angle/ °	
Sn-N(2)	2.218(3)	N(2)-Sn-N(1)	84.06(10)
Sn-N(1)	2.226(3)	N(2)-Sn-P	100.32(7)
Sn-P	2.6307(9)	N(1)-Sn-P	97.35(7)

Table 3: Selected Metrical Parameters for (BDI)Group14-PR$_2$ compounds

	LPb-P(TMS)$_2$	LSn-PPh$_2$	LGePH$_2$	LGeP(TMS)H	LGe(TMS)$_2$
M-P/ Å	2.671(1)	2.6307(9)	2.333(1)	2.426(7)	2.3912(8)
Folding angle/ °	43.9	40.6	26.0	40.8	22.1
Pyramidalization/ %	87	87	91	85	79

Lead compound[15], Germanium compounds[16]

NMR data: $^{31}P\{^1H\}$ NMR confirms the presence of a Sn-P bond; a singlet at -30.7 ppm with coupling constants of $^1J_{Sn-P}$= 936 and 978 Hz, proves the coupling of phosphorous through one bond to tin isotopes 117 and 119 respectively. ^1H NMR highlights the structural similarities of the BDI ligand in the complex to that of the precursor.[(HC{C(Me)NAr}$_2$)SnCl]; the splitting pattern and integration of each proton environment is identical, however each proton signal in the product is slightly more deshielded than its precursor analog. This can be explained by the greater electron density on the tin atom in the product due to the less electronegative PR_2 substituent which replaces the chlorine atom.

Reaction of a C_6D_6 solution of.[(HC{C(Me)NAr}$_2$)SnPPh$_2$] with excess selenium in an NMR tube generated a yellow solution. The reaction resulted in the generation of two species, A and B, observable in the ^{31}P NMR spectrum. Product B can be isolated by allowing the reaction to go to completion, followed by the removal of unreacted selenium. Extraction in pentane yields small yellow crystals unsuitable for X-ray diffraction.

NMR data: On addition of Se, a singlet at +4.1 ppm in the $^{31}P\{^1H\}$ spectrum immediately highlighted the formation of product **A**. Coupling constants of $^xJ_{Sn-P}$= 721, 754 Hz and $^xJ_{P-Se}$=215 Hz, indicated product **A** couples to both selenium and tin. After 18h the starting material was no longer present and a second product at 19.5ppm could be seen growing in. After 48h product **B** was abundant enough to resolve both tin and selenium satellites.

Product **B** showed significantly different coupling than observed in **A**; $^xJ_{Sn-P}$= 199, 208 Hz and $^xJ_{P-Se}$= 571 Hz. Difficulty in isolating and crystallising products **A** and **B** caused significant difficulty in obtaining characterisation. Possible identities postulated are shown in Figure 4. If one selenium atom was to oxidise the

phosphorous from +3 to +5 and form a terminal double bond, the one bond P-Se coupling constant is predicted to be approximately 800 Hz on the basis of literature examples.[17,18] This therefore is unlikely to be the structure of **A** as the observed P-Se coupling is too small. If in the other scenario one selenium atom was to oxidise the tin from +2 to +4 and form a terminal double bond, one would expect to observe selenium satellites in the tin NMR and tin satellites in the selenium NMR, which was not the case. If a selenium atom was to insert itself into the Sn-P bond, the P-Sn coupling would be through two bonds which is generally a magnitude of 10^2 in the literature example.[19]This is much smaller than the observed value of 721 and 754 Hz and hence is unlikely to be the conformation in solution. The most likely structure in solution is the resonance structure where the selenium atom is bonded to both tin and phosphorous, as both the Sn-P and Se-P coupling is through 1.5 bonds and hence is an intermediate between one and two bond couplings. Structure **B** formed after further reaction with excess selenium, it is therefore likely to contain two Se atoms. The Sn-P coupling in this compound is significantly smaller than of that seen in **A**. This suggests that the tin and phosphorous atoms are likely to be interacting through two bonds, rather than being directly bonded. The most logical position for another selenium atom is therefore likely to be a result of an insertion into the Sn-P bond, which results in the structure postulated in Figure 4. A similar structure illustrating this double selenium bridge between Sn and P has been derived analogously to our predictions and displays a similar Sn-P coupling, $^2J_{119Sn-P}$= 129.4 Hz, yet the Se-P coupling is much smaller, $^1J_{Se-P}$=88.2 Hz.[20]

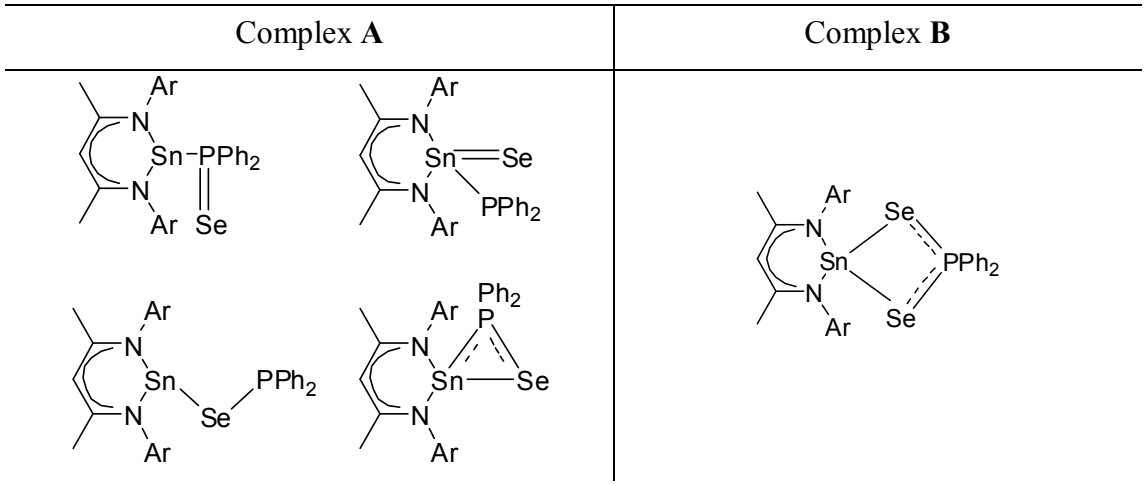

Figure 4: Possible Identities of A and B

The lack of crystalline products of **A** and **B** is believed to be due to two main factors. Firstly separating the two products is problematic, especially when trying to isolate A, because it is difficult to trap the reaction at the point before **B** is formed.

Secondly, in the ^{31}P NMR spectrum of both the starting material and the selenium reactions, a resonance is seen at -14.9ppm which has been assigned to tetraphenyldiphosphene ($Ph_2P=PPh_2$).

This PPh_2 dimer decomposition product slowly is formed over time, and hence is interfered with crystallisation. The dimer could be a product of a radical reaction, where homolytic breakage of the Sn-P bond results in BDISn• and •PPh_2 radicals. These potentially generated radicals can either react again to form or can react with themselves to form dimers. The BDISn-SnBDI dimer however is not seen. In previous studies the BDI_2Sn complex was found to be too stericically hindered to be assessable[21] which could also be the case for the dimer complex. When left over time,[(HC{C(Me)NAr}$_2$)SnPPh$_2$]also degraded to elemental tin. Therefore it is possible that free ligand is also present in the solution.

In order to overcome this problem, a different R group was used instead of phenyl. This work was carried out by the collaborating Fulton group. Cyclohexyl R groups were chosen due to their similar sterics, yet the differences in electronics prevent the dimer decomposition. Analogous compounds of A and B were synthesised *via* identical procedures. The yellow solutions formed crystals which were suitable for x-ray diffractions, allowing molecular structures to be determined, Figure 5.

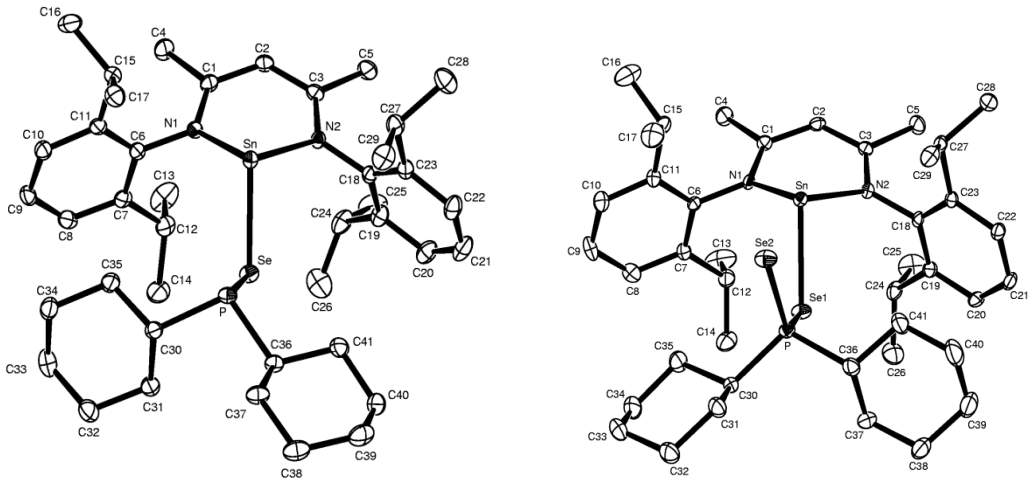

Figure 5: Analogous Compounds of A and B rendered from ORTEP[i]

The structures represent **A** and **B** in the solid state. Structure A does not agree with the coupling constants observed in solution state NMR, because as explained earlier the Sn-P coupling of ca. 740 Hz is far to large for this suggested two bond coupling. However, it is plausible that in solution a resonance structure, as suggested earlier, is adapted and when under transition to solid state the structure arranges to break this bond to achieve better packing. A similar argument can be used for structure B, because if this structure was true for the solution state the two selenium atoms would be in different environments which would be obvious in both the ^{31}P and ^{77}Se NMR spectra. However this is not the case, and therefore it is highly likely that both selenium atoms are bonded to tin in the solution state.

Conclusion

Reactivity with the amidinate ligand was found to be problematic due to difficultly during the scaling up process, which was primarily a result of the formation of tetraphenyldiphosphine. The BDI ligand was found to be much better for this reaction because it was able to provide sufficient steric bulk to stabilise the Sn-P bond. This therefore allowed to be isolated in good yield and fully characterised. The reactivity of the synthesised Sn-P bond was probed by reaction with elemental selenium, which resulted in the formation of two distinctly different products. Multinuclear NMR suggests that the reaction undergone was an insertion into the Sn-P bond, to form a fluxional mono and diselenide compounds in solution.

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