Probing the Lewis basicity of the metalloligand [Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$] on tin substrates by electrospray mass spectrometry

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Introduction

Mass spectrometry has been applied to the characterization of inorganic and organometallic substances for many years, but the traditional electron impact method of ionization is generally limited to thermally robust, neutral compounds of low molecular mass.[i] Electrospray mass spectrometry (ESMS) is a relatively new ionization method introduced in the mid-1980's, largely by Fenn and co-workers.[ii] Its gentle ionization process easily supercedes the more established mass spectrometric techniques, including fast atom bombardment (FAB). ESMS was quickly exploited by researchers working with biomolecules because proteins and other high-mass, thermally-sensitive substrates could be readily analyzed.[iia,iii] Only recently has there been corresponding interest from inorganic chemists.[iv,v] Our main interests in the area of inorganic ESMS lie in the development of the technique to monitor chemical reactions. In a parallel study, we have demonstrated its utility of the technique in probing the chemistry of Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$.[vi] While there is a substantial chemistry reported on Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$,[vii] studies on the coordination chemistry of the

{Pt$_2$Se$_2$} core have been little studied. The nucleophilicity of the selenide centres is poorly understood whilst the ability of Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$ to interact with different metal species is potentially rich. In this paper, we discuss the ESMS-monitored reactions between Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$ **1** with tin(IV) substrates. A prime objective of this work is to establish a potentially facile route to assemble heterometallic selenide aggregates and clusters which are relatively rare in the current literature.[viii]

Results and discussion

ESMS-monitored reactions

General observations

The reactions of the metalloligand Pt$_2$(μ-Se)$_2$(PPh$_3$)$_4$ **1** with a range of tin(IV) complexes have been examined using electrospray mass spectrometry (ESMS). Tin has a strong affinity for both sulfur and selenium.[ix] ESMS data for reactions between **1** and the tin substrates are summarized in Table 1. Although hydrolysis by the protic solvent (MeOH) on the Sn-Cl species would be expected to occur, no Sn-OMe species was detected.

Displacement of one or two labile halide ligands through nucleophilic attack of the Se atoms of **1** is commonly observed, which then leads to the formation of cationic aggregates. Most reactions gave both mono- and di-cations through loss of one and two ligands respectively. Di-cations became the dominant species when more substrate was added to these reaction mixtures. As the cone voltage was increased, mono-cations were the common dominant peaks in the spectra. Cone voltages were varied up to a maximum of 80 V, beyond which as fragmentation was observed. The major fragmentation route involves loss of PPh$_3$ ligands at high cone voltages of 60 or 80 V. Detection of peaks at *m/z* 799 and 1598, assigned as [**1**+2H]$^{2+}$ and [**1**+H]$^+$ respectively, were normally observed when reactions did not occur,

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or **1** was in excess. A similar trend was observed in the study using $Pt_2(\mu_2\text{-}S)_2(PPh_3)_4$ **2** through detection of peaks pertaining to $[\mathbf{2}+2H]^{2+}$ and $[\mathbf{2}+H]^{+}$.[vi]

At low cone voltages (5-20 V), the predominant products detected in the reaction between **1** and $SnMeCl_3$ were $[\mathbf{1}(SnMeCl)]^{2+}$ **3** and $[\mathbf{1}(SnMeCl_2)]^{+}$ **4** at *m/z* 883 and 1802 respectively. Fragmentation started to occur at 60 V through loss of a PPh_3 ligand from $[\mathbf{1}(SnMeCl_2)]^{+}$, which resulted in detection of $[(\mathbf{1}\text{-}PPh_3)(SnMeCl_2)]^{+}$ at *m/z* 1540 with the former dominating as the most intense ion. At 80 V, fragmentation occurred to give $[(\mathbf{1}\text{-}PPh_3)(SnMeCl_2)]^{+}$ as the dominant ion. The ESMS-monitored reaction between **1** and $SnMe_2Cl_2$ paved similar observations to that of the previous reaction, with both reactions showing similar fragmentation patterns and similar peak intensities for their major ions.

Reaction between **1** and $SnMe_3Cl$ is much less spontaneous compared to the two mentioned methyl tin substrates, consistent with the reduced Lewis acidity of $SnMe_3Cl$. At a low cone voltage (20 V), $[\mathbf{1}+2H]^{2+}$, $[\mathbf{1}+H]^{+}$ and $[\mathbf{1}(SnMe_3)]^{+}$ were detected. $[\mathbf{1}+H]^{+}$ appeared as the dominant ion, even with the addition of excess $SnMe_3Cl$. At 40 V, fragmentation began, resulting in detection of $[(\mathbf{1}\text{-}PPh_3)(SnMe_3)]^{+}$ by loss of a PPh_3 ligand. Further increasing the cone voltage to 60 V eliminated $[\mathbf{1}+2H]^{2+}$, with $[\mathbf{1}+H]^{+}$ still dominating as the major ion.

$[\mathbf{1}(SnEt_2)]^{2+}$ and $[\mathbf{1}(SnEt_2Cl)]^{+}$ were detected in the reaction between **1** and $SnEt_2Cl_2$ at cone voltages between 20 and 40 V. Fragmentation started to occur at 60 V through loss of a PPh_3 ligand, which resulted in detection of $[(\mathbf{1}\text{-}PPh_3)(SnEt_2)]^{2+}$ and $[(\mathbf{1}\text{-}PPh_3)(Sn)]^{2+}$ with $[\mathbf{1}(SnEt_2Cl)]^{+}$ still dominating as the most intense ion. Increasing the cone voltage to 80 V resulted in disappearance of all di-cations and emergence of a peak at *m/z* 1547 pertaining to $[(\mathbf{1}\text{-}PPh_3)(SnEt_2Cl)]^{+}$.

Reactions of **1** with $SnRCl_3$ (R = Bu, Ph) gave very clean spectra. At cone voltages between 20 and 60 V, $[\mathbf{1}(SnRCl_2)]^{+}$ and $[\mathbf{1}(SnRCl)]^{2+}$ were detected (shown in Fig. 1). The

dominance of $[\mathbf{1}(\text{SnRCl})]^{2+}$ as the most intense ion changed to $[\mathbf{1}(\text{SnRCl}_2)]^+$ when the cone voltage was further increased.

For the reaction between $\mathbf{1}$ and SnBu_2Cl_2, $[\mathbf{1}(\text{SnBu}_2)]^{2+}$ and $[\mathbf{1}(\text{SnBu}_2\text{Cl})]^+$ at 20 V with relative intensities 2:1. As the cone voltage was increased from 20 to 60 V, the mono-cations became progressively dominant. At 80 V, the expected loss of a PPh_3 ligand occurred to give $[(\mathbf{1}\text{-PPh}_3)(\text{SnBu}_2\text{Cl})]^+$. The di-cation was absent.

$\mathbf{1}$ reacted with SnPh_2Cl_2 to give $[\mathbf{1}(\text{SnPh}_2)]^{2+}$ and $[\mathbf{1}(\text{SnPhCl}_2)]^+$ at cone voltage of 20 V. Increasing the cone voltage (40-60 V) afforded the dominance of $[\mathbf{1}(\text{SnPhCl}_2)]^+$ over $[\mathbf{1}(\text{SnPh}_2)]^{2+}$. At 80 V, loss of a PPh_3 ligand from the mono-cation occurred to give $[(\mathbf{1}\text{-PPh}_3)(\text{SnPh}_2\text{Cl})]^+$. $[(\mathbf{1}\text{-PPh}_3)(\text{SnPh}_2\text{Cl})]^+$ emerged as the dominant charged species with absence of the dication at the cone voltage of 100 V.

Reaction between $\mathbf{1}$ and SnPh_3Cl afforded $[\mathbf{1}(\text{SnPh}_3)]^+$ as the major ion, together with minor ions $[\mathbf{1}(\text{SnPh}_2\text{Cl})]^+$ and $[\mathbf{1}(\text{SnPh}_2)]^{2+}$ between 20 to 60 V (relative intensities 20:3:8 respectively). The detection of $[\mathbf{1}(\text{SnPh}_2\text{Cl})]^+$ was due to SnPh_2Cl_2 being a contaminant in the substrate, rather than a preference of phenyl ligand displacement over a chloride ligand. ^{31}P NMR analysis of the isolated product from the bench-performed reaction confirmed that SnPh_2Cl_2 was indeed the contaminant (discussed under the NMR studies section). Some fragmentation was observed when the cone voltage was raised to between 80 to 120 V. These fragments were accounted for by $[(\mathbf{1}\text{-PPh}_3)(\text{SnPh}_2\text{Cl})]^+$ and $[(\mathbf{1}\text{-PPh}_3)(\text{SnPh}_3)]^+$, which emerged as more intense ions over the other two between 100-120 V.

For the reaction between $\mathbf{1}$ and SnBz_2Br_2 at low cone voltages of 20-40 V, only two ions, $[\mathbf{1}(\text{SnBz}_2\text{Br})]^+$ and $[\mathbf{1}(\text{SnBz}_2)]^{2+}$, were detected. At 60 V, an intense peak pertaining to $[\mathbf{1}(\text{Sn})]^{2+}$ was observed, possibly due to fragmentation of $[\mathbf{1}(\text{SnBz}_2)]^{2+}$ as there was a corresponding drop in intensity of the latter peak. $[\mathbf{1}(\text{SnBz}_2)]^{2+}$ and $[\mathbf{1}(\text{Sn})]^{2+}$ gave minor

peaks while $[\mathbf{1}(SnBz_2Br)]^+$ was the most intense ion at cone voltage of 80 V, relative intensities 4:5:50.

Syntheses and characterization of these {PtSeSn(IV)} charged aggregates were followed up, along with the postulations of major products made from this series of ESMS studies. The isolated products elucidated through elemental, NMR and single-crystal X-ray diffraction analyses corresponded to the respective species postulated in ESMS, which demonstrated that ESMS not only can help to monitor the progress of reactions but also provide a preliminary "screening" of the feasibility of reactions prior to lab-scale syntheses.

NMR studies

NMR analysis has been performed on the newly synthesized {Pt$_2$Se$_2$Sn(IV)} aggregates. We were unable to observe any distinct ^2J(P-Se), which is probably too small to be detected because of the small magnitude of the coupling and low abundance of ^{77}Se (15.3%). Interestingly, the ^1J(Pt-P) values decrease in the order: $[\mathbf{1}(SnRCl_2)]^+$ (R = Me, Ph; 3212, 3223 Hz) > $[\mathbf{1}(SnR_2Cl)]^+$ (R = Me, Ph; 3151, 3178 Hz) > $[\mathbf{1}(SnR_3)]^+$ (R = Me, Ph; 3037, 3124 Hz). This trend may be explained by considering that SnR_3^+ is less Lewis acidic than SnR_2Cl^+ which is less than $SnRCl_2^+$. Thus, the {SnRCl$_2$} moiety, being the most electron withdrawing, causes the strongest coordination of the phosphine ligands to the Pt atoms (highest ^1J(Pt-P) values) when coordinated to the metalloligand $\mathbf{1}$. A similar trend was observed in the study using Pt$_2$(μ_2-S)$_2$(PPh$_3$)$_4$ $\mathbf{2}$.[vi] In the reaction between $\mathbf{1}$ and SnPh$_3$Cl, ^{31}P NMR analysis confirms the identity of the impurity as $[\mathbf{1}(SnPh_2Cl)]^+$. From the spectra shown in Fig. 2, the chemical shift of the impurity corresponds identically to the only product isolated from the separate reaction between $\mathbf{1}$ and SnPh$_2$Cl$_2$.

Structural results

A structural analysis was carried out to investigate the effects on the $\{Pt_2Se_2\}$ core of **1** upon coordination to tin substrates. Crystallographic data for compounds **5b**, **7a·3.5CHCl₃** and **7b** are given in Table 2, while their pertinent bond distances and angles are in Tables 3-5. Figs. 3-5 illustrate the cationic structures of all the compounds with atomic numbering schemes. Fig. 3 shows the structure of the cationic aggregate of **5b**. X-ray analysis revealed that compound **5b** consists of an $\{SnMe_2Cl\}$ moiety coordinated to the metalloligand $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$, forming a distorted square-based pyramidal aggregate. The two center Pt(II) atoms are slightly distorted from their square-planar geometry. The average Pt-Se-Pt bond angle in $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ is $100.39°$[xiii] but upon coordination to the $\{SnMe_2Cl\}$ moiety, the bond angle retracts to $88.53°$. This directly causes the dihedral angle between the two planes to deviate from near planar to $130.8°$, thus adopting a bent conformation. This phenomenon agrees with the theoretical calculations previously done by Bencini *et al.*[xiii]

The structure of compound **7a·3.5CHCl₃** is shown in Fig. 4. As described in the experimental section, significant disorder of the PF_6^- counter anion and the 3.5 CHCl₃ solvates present in four regions of the asymmetric unit are observed in compound **7a·3.5CHCl₃**. For the disorder of the F atoms, two models are resolved with occupancies of 0.7/0.3 and common isotropic thermal parameters are refined. Compound **7a** adopts a distorted square-based pyramidal structure with the Sn atom making an acute angle of $72.46°$ with the two Se atoms. Upon coordination to the $\{SnBuCl_2\}$ moiety, the $\{Pt_2Se_2\}$ core bends from planarity, giving a dihedral angle of $128.0°$. The C-Sn-Se bond angle of compound **7a** ($96.7°$) is insignificantly $\sim 2\%$ wider than that of compound **5b** ($94.6°$), consistent with the low steric bulk of the ⁿBu group.

The molecular cationic structure of compound **7b** (illustrated in Fig. 5) shows the coordination of the metalloligand $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$ to the $\{SnBu_2Cl\}$ fragment with the butyl groups on the Sn atom pointing away from one another, as well as from the phenyl

rings on the $\{Pt_2Se_2\}$ core. The absence of any steric hindrance from the butyl groups on the tin is further supported through comparison of bond angles of compounds **5b** and **7b**. This observation can be rationalized by considering the availability of space above the $\{Pt_2Se_2\}$ core that allows the butyl groups to orientate themselves so that they are not within close proximity to the phenyl rings. The very slight steric effect displayed by butyl groups (in compound **7b**) over the methyl groups (in compound **5b**) is debatable by the difference of ~ 2° in Se(1)-Sn(1)-Se(2) bond angle.

Conclusions

The powerful ability of ESMS to monitor the progress of reactions of selenide species has been demonstrated. Before the start of a reaction, ESMS is used to check whether the reaction is spontaneously feasible and the number of major products formed. After starting the reaction, ESMS further monitors its progress till the point where the product is isolated. The indispensable ability of ESMS to monitor solution chemistry has been further emphasized through successful displacement experiments demonstrated by $Pt_2(\mu\text{-Se})_2(PPh_3)_4$ on tin substrates where different Sn-Se interactions are studied and the resultant heterometallic aggregates identified and subsequently confirmed by synthetic studies and single-crystal X-ray diffraction analyses. The major fragmentation route involves loss of PPh_3 ligands at high cone voltages of 60 or 80 V. Full characterization of the products isolated from lab-scale syntheses corresponded to the respective species postulated from the ESMS data. From structural studies, there is a significant effect on the $\{Pt_2Se_2\}$ core when $[Pt_2(\mu\text{-Se})_2(PPh_3)_4]$ is coordinated to the tin substrates, resulting in the core adopting a bent conformation, in agreement with theoretical calculations previously reported. It is our hope that more inorganic chemists will apply ESMS to their own field of research, or to develop

new fields, previously inaccessible due to the absence of suitable definitive analytical techniques.

Experimental

Mass spectrometry

Samples for ESMS analysis were prepared by dissolving **1** and substrate (both 10-100 μg) in 1 mL MeOH. Electrospray mass spectra were obtained with a VG Platform II mass spectrometer with the methanol mobile phase driven at 0.02 mL min^{-1} using a Thermo Separation products SpectraSystem P1000 LC pump. Samples were injected *via* a Rheodyne valve fitted with a 10 μL sample loop. The source temperature was 60°C. The capillary potential tip was 3500 V, with nitrogen used both as a drying and a nebulizing gas. The skimmer cone voltage was usually 5 V when clean parent ions were required, and was varied up to 80 V to investigate fragmentation processes. Peaks were assigned from the *m/z* values and from the isotope distribution patterns that were simulated using the ISOTOPE program.[x] The *m/z* values given are for the most intense peak in the envelope in each case.

Materials

The substrates used for analysis were $SnMeCl_3$, $SnMe_2Cl_2$, $SnMe_3Cl$, $SnEt_2Cl_2$, $SnBuCl_3$, $SnBu_2Cl_2$, $SnPhCl_3$, $SnPh_2Cl_2$, $SnPh_3Cl$ and $SnBz_2Br_2$. All tin substrates are commercially available from Strem except for $SnEt_2Cl_2$[xi] and $SnBz_2Br_2$.[xii]

$Pt_2(\mu\text{-}Se)_2(PPh_3)_4$ **1** was prepared by modification of the literature method.[xiii] To a stirred mixture of Se (1.840 g, 23.31 mmol) in 40 mL deionized and deoxygenated water, was added $NaBH_4$ (1.014 g, 26.77 mmol).[xiv] The reaction flask was cooled in ice. A colorless solution of NaHSe was obtained after 15 min. and transferred into a 50 mL benzene suspension of *cis*-$[PtCl_2(PPh_3)_2]$[xv] (4.742 g, 6.00 mmol) under nitrogen. The suspension turned yellow upon

addition of NaHSe and further darkened to give a brown suspension after a day. The brown suspension was filtered and the solid was washed successively with 100 mL each of deionized water and MeOH, and dried (yield = 4.653 g, 49%). ^{31}P-$\{^1H\}$ NMR (d_7-DMF) δ_p 10.2 ppm [t, ^1J(P-Pt) = 3889 Hz]. ^2J(P-Se) was too small to be detected. All reactions were performed under a positive pressure of purified argon unless otherwise stated, and solvents were distilled and degassed before use. ^1H NMR spectra were recorded at 300 MHz at 25°C on a Bruker ACF 300 spectrometer. Chemical shifts are reported in ppm to high frequency with Me_4Si as internal standard for ^1H NMR spectra. The ^{31}P NMR spectra were recorded at 121.39 MHz with 85% H_3PO_4 as external reference. Elemental analyses were performed by the microanalytical laboratory of the Department of Chemistry at the National University of Singapore.

Synthesis of Pt-Se-Sn aggregates

[Pt$_2$(μ_3-Se)$_2$(PPh$_3$)$_4$SnMeCl$_2$][PF$_6$] (5a). SnMeCl$_3$ (7.2 mg, 0.0299 mmol) was added to a reaction flask containing a brown suspension of **1** (47.6 mg, 0.0298 mmol) in 20 mL MeOH. A bright yellow solution was formed instantaneously and the reaction was allowed to stir for another 3 h before the addition of excess NH$_4$PF$_6$ (10.0 mg, 0.0614 mol), giving a light yellow suspension. It was allowed to stir for another 1 h, after which 50 mL of deionized water was added to induce precipitation. The suspension was filtered and the solid was washed successively with 100 mL each of deionized water and ether, and dried under vacuum yielding a light yellow powder of **5a** (0.0285 g, 49%). Found: C, 44.7; H, 3.3; P, 7.8. Calc. for C$_{73}$H$_{63}$Cl$_2$F$_6$Se$_2$P$_5$Pt$_2$Sn: C, 45.0; H, 3.3; P, 8.0%. ^{31}P-$\{^1H\}$ NMR (CDCl$_3$): δ_p 16.9 ppm [t, ^1J(P-Pt) = 3212 Hz]. ^1H NMR (CDCl$_3$): δ_H 1.28 (s, 3H, CH$_3$), 7.08-7.45 (m, 60H, 12C$_6$H$_5$).

[Pt₂(μ₃-Se)₂(PPh₃)₄SnMe₂Cl][PF₆] (5b). The procedure was similar to that detailed above for **5a**. Yellow-brown powder of **5b** was isolated in 34% yield (0.0209 g) from the reaction of $SnMe_2Cl_2$ (7.1 mg, 0.0323 mmol) and **1** (51.1 mg, 0.0320 mmol). Found: C, 46.0; H, 3.5; P, 7.6. Calc. for $C_{74}H_{66}ClF_6Se_2P_5Pt_2Sn$: C, 46.1; H, 3.5; P, 8.0%. $^{31}P\text{-}\{^1H\}$ NMR (CDCl₃): δ_p 17.6 ppm [t, ^1J(P-Pt) = 3151 Hz]. ^1H NMR (CDCl₃): δ_H 1.30 (s, 6H, 2CH₃), 7.08-7.50 (m, 60H, 12C₆H₅).

[Pt₂(μ₃-Se)₂(PPh₃)₄SnMe₃][PF₆] (5c). The procedure was similar to that detailed above for **5a** except that the mixture was allowed to stir overnight to ensure complete reaction. Yellow powder of **5c** was isolated in 59% yield (0.0337 g) from the reaction of SnMe₃Cl (6.0 mg, 0.0301 mmol) and **1** (47.7 mg, 0.0299 mmol) Found: C, 47.0; H, 3.8; P, 7.9. Calc. for $C_{75}H_{69}F_6Se_2P_5Pt_2Sn$: C, 47.3; H, 3.9; P, 8.1%. $^{31}P\text{-}\{^1H\}$ NMR (CDCl₃): δ_p 21.0 ppm [t, ^1J(P-Pt) = 3037 Hz]. ^1H NMR (CDCl₃): δ_H 1.32 (s, 9H, 3CH₃), 6.93-7.80 (m, 60H, 12C₆H₅).

[Pt₂(μ₃-Se)₂(PPh₃)₄SnEt₂Cl][PF₆] (6). The procedure was similar to that detailed above for **5a** except that the mixture was allowed to stir overnight to ensure complete reaction. Brown powder of **6** was isolated in 38% yield (0.0228 g) from the reaction of $SnMe_2Cl_2$ (7.5 mg, 0.0303 mmol) and **1** (48.4 mg, 0.0303 mmol). Found: C, 45.5; H, 3.4; P, 7.8. Calc. for $C_{74}H_{65}ClF_6Se_2P_5Pt_2Sn$: C, 45.5; H, 3.4; P, 7.9%. $^{31}P\text{-}\{^1H\}$ NMR (CDCl₃): δ_p 17.4 ppm [t, ^1J(P-Pt) = 3155 Hz]. ^1H NMR (CDCl₃): δ_H 1.27 (t, 6H, 2CH₃), 2.32 (q, 4H, 2CH₂), 7.12-7.34 (m, 60H, 12C₆H₅).

[Pt₂(μ₃-Se)₂(PPh₃)₄SnBuCl₂][PF₆] (7a). The procedure was similar to that detailed above for **5a**. Pale yellow powder of **7a** was isolated in 77% yield (0.0474 g) from the

reaction of SnBuCl$_3$ (14.9 mg, 8.78 μL, 0.0312 mmol) and **1** (49.6 mg, 0.0311 mmol). Found: C, 46.0; H, 3.5; P, 7.8. Calc. for C$_{76}$H$_{69}$Cl$_2$F$_6$Se$_2$P$_5$Pt$_2$Sn: C, 45.9; H, 3.5; P, 7.8%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ$_p$ 16.9 ppm [t, ^1J(P-Pt) = 3216 Hz]. ^{1}H NMR (CDCl$_3$): δ$_H$ 0.85 (t, 3H, CH$_3$), 1.26-1.35 (m, 4H, 2CH$_2$), 1.99 (t, 2H, CH$_2$), 7.16-7.32 (m, 60H, 12C$_6$H$_5$).

[Pt$_2$(μ$_3$-Se)$_2$(PPh$_3$)$_4$SnBu$_2$Cl][PF$_6$] (7b). The procedure was similar to that detailed above for **5a**. Light brown powder of **7b** was isolated in 56% yield (0.0356 g) from the reaction of SnBu$_2$Cl$_2$ (9.7 mg, 0.0319 mmol) and **1** (50.5 mg, 0.0316 mmol). Found: C, 47.7; H, 3.9; P, 7.7. Calc. for C$_{80}$H$_{78}$ClF$_6$Se$_2$P$_5$Pt$_2$Sn: C, 47.8; H, 3.9; P, 7.7%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ$_p$ 17.5 ppm [t, ^1J(P-Pt) = 3166 Hz]. ^{1}H NMR (CDCl$_3$): δ$_H$ 0.88 (t, 6H, 2CH$_3$), 1.18-1.33 (m, 8H, 4CH$_2$), 1.92 (t, 4H, 2CH$_2$), 7.12-7.32 (m, 60H, 12C$_6$H$_5$).

[Pt$_2$(μ$_3$-Se)$_2$(PPh$_3$)$_4$SnPhCl$_2$][PF$_6$] (8a). The procedure was similar to that detailed above for **5a** except that the mixture was allowed to stir overnight to ensure complete reaction. Pale yellow powder of **8a** was isolated in 54% yield (0.0347 g) from the reaction of SnPhCl$_3$ (17.8 mg, 9.68 μL, 0.0320 mmol) and **1** (50.8 mg, 0.0318 mmol). Found: C, 46.2; H, 3.2; P, 7.5. Calc. for C$_{78}$H$_{65}$Cl$_2$F$_6$Se$_2$P$_5$Pt$_2$Sn: C, 46.6; H, 3.3; P, 7.7%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ$_p$ 16.7 ppm [t, ^1J(P-Pt) = 3223 Hz]. ^{1}H NMR (CDCl$_3$): δ$_H$ 7.11-7.33 (m, 60H, 12C$_6$H$_5$), 7.48-7.76 (m, 5H, C$_6$H$_5$ on Sn).

[Pt$_2$(μ$_3$-Se)$_2$(PPh$_3$)$_4$SnPh$_2$Cl][PF$_6$] (8b). The procedure was similar to that detailed above for **5a**. Yellow powder of **8b** was isolated in 57% yield (0.0342 g) from the reaction of SnPh$_2$Cl$_2$ (10.1 mg, 0.0294 mmol) and **1** (46.5 mg, 0.0291 mmol). Found: C, 49.0; H, 3.4; P, 7.5. Calc. for C$_{84}$H$_{70}$ClF$_6$Se$_2$P$_5$Pt$_2$Sn: C, 49.2; H, 3.4; P, 7.6%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ$_p$

17.0 ppm [t, ^1J(P-Pt) = 3178 Hz]. ^{1}H NMR (CDCl$_3$): δ_H 7.06-7.31 (m, 60H, 12C$_6$H$_5$), 7.40-7.75 (m, 10H, 2C$_6$H$_5$ on Sn).

[Pt$_2$(μ$_3$-Se)$_2$(PPh$_3$)$_4$SnPh$_3$][PF$_6$] (8c). The procedure was similar to that detailed above for **5a**. Brown powder of **8c** was isolated in 37% yield (0.0229 g) from the reaction of SnPh$_3$Cl (11.5 mg, 0.0298 mmol) and **1** (46.9 mg, 0.0294 mmol). ^{31}P-{^{1}H} NMR (CDCl$_3$): δ_p 19.8 ppm [t, ^1J(P-Pt) = 3124 Hz] and 17.0 ppm [t, ^1J(P-Pt) = 3178 Hz] (contamination of SnPh$_2$Cl$_2$ in substrate resulted formation of **8b**). ^{1}H NMR (CDCl$_3$): δ_H 7.06-7.31 (m, 120H, 24C$_6$H$_5$ from **8b** and **8c**), 7.40-7.75 (m, 25H, 2C$_6$H$_5$ from **8b** and 3C$_6$H$_5$ from **8c**).

[Pt$_2$(μ$_3$-Se)$_2$(PPh$_3$)$_4$SnBz$_2$Br][PF$_6$] (9). The procedure was similar to that detailed above for **5a**. Yellow powder of **9** was isolated in 58% yield (0.0388 g) from the reaction of SnBz$_2$Br$_2$ (14.5 mg, 0.0315 mmol) and **1** (50.2 mg, 0.0314 mmol). Found: C, 48.8; H, 3.5; P, 7.5. Calc. for C$_{86}$H$_{74}$BrF$_6$Se$_2$P$_5$Pt$_2$Sn: C, 48.7; H, 3.5; P, 7.3%. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ_p 17.5 ppm [t, ^1J(P-Pt) = 3143 Hz]. ^{1}H NMR (CDCl$_3$): δ_H 3.14 (d, 2H, PhCH$_2$), 3.44 (d, 2H, PhCH$_2$), 6.50-6.68 (m, 10H, C$_6$H$_5$CH$_2$), 7.03-7.35 (m, 60H, 12C$_6$H$_5$).

Crystal structure determination and refinement

The data collection was performed on a Bruker AXS SMART diffractometer, equipped with a CCD area-detector using Mo-Kα radiation (λ = 0.71073 Å). The software SMART[xvi] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[xvi] for integration of intensity of reflections and scaling, SADABS[xvii] for empirical absorption correction, and SHELXTL[xviii] for space group and structure determination, refinements, graphics, and structure reporting. Hydrogen atoms were not located. The structures were refined by full-matrix least squares on F^2 with anisotropic

thermal parameters for non-hydrogen atoms, unless otherwise indicated [$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ (where $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$]. A summary of parameters for the data collections and refinements is given in Table 2. Supplementary material including non hydrogen and hydrogen atomic coordinates, thermal parameters for the non hydrogen atoms, and complete tables of bond distances and angles has been deposited at the Cambridge Crystallographic Data Centre (CCDC).

Suitable single crystals of [$Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4SnMe_2Cl$][$PF_6$] **5b** and [$Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4SnBu_2Cl$][$PF_6$] **7b** for structure determination were obtained by layering a CH_2Cl_2 solution of each compound with hexane, while those of [$Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4SnBuCl_2$][$PF_6$]·3.5CHCl$_3$ **7a** were obtained by layering a CHCl$_3$ solution with hexane.

Compound 5b. A suitable crystal of dimensions $0.24 \times 0.18 \times 0.08$ mm^3 was selected, wedged inside a glass capillary tube and flame-sealed. A total of 34409 reflections were collected in the θ range 1.82-26.37° (-22 < h < 25, -24 < k < 23, -22 < l < 18).

Compound 7a·3.5CHCl$_3$. A suitable crystal of dimensions $0.52 \times 0.44 \times 0.36$ mm^3 was selected, wedged inside a glass capillary tube and flame-sealed. A total of 32947 reflections were collected in the θ range 1.88-24.71° (-16 < h < 16, -19 < k < 18, -24 < l < 24). The F atoms in the PF_6^- counter anion are disordered. Two models are resolved (occupancies 0.7/0.3) and common isotropic thermal parameters are refined. There are 3.5 CHCl$_3$ solvate present in four regions of the asymmetric unit, most of them being disordered. Common isotropic thermal parameters are refined for these non-hydrogen atoms in the solvent.

Compound 7b. A suitable crystal of dimensions $0.40 \times 0.30 \times 0.22$ mm^3 was selected, wedged inside a glass capillary tube and flame-sealed. A total of 30600 reflections were collected in the θ range 1.55-29.38° (-16 < h < 16, -21 < k < 18, -29 < l < 29).

(1) M. I. Bruce, *Adv. Organomet. Chem.*, **1968**, *6*, 273; J. Lewis and B. F. G. Johnson, *Acc. Chem. Res.*, **1968**, *1*, 245; M. R. Litzow and T. R. Spalding, *Mass Spectrometry of Inorganic and Organometallic Compounds*; Elsevier, Amsterdam, **1973**.

(2) J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Science*, **1989**, *246*, 64; J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Mass Spectrom. Rev.*, **1990**, *9*, 37.

(3) I. I. Stewart, *Spectrochim. Acta B*, **1999**, *54*, 1649; R. B. Cole, *Electrospray Ionisation Mass Spectrometry; Fundamentals, Instrumentation and Applications*, Wiley-Interscience, New York, **1997**; G. J. Langley and G. A. Mills, *Educ. Chem.*, **1997**, 14; R. Bakhtiar, S. A. Hofstadler and R. D. Smith, *J. Chem. Educ.*, **1996**, *73*, A118; M. Przybylski and M. O. Glocker, *Angew. Chem., Int. Ed. Engl.*, **1996**, *35*, 807; M. Mann and M. Wilm, *Trends Biochem. Sci.*, **1995**, *20*, 219; R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Barinaga and H. R. Udseth, *Mass Spectrom. Rev.*, **1991**, *10*, 359.

(4) J. -J. Gaumet and G. F. Strouse, *J. Am. Soc. Mass Spectrom.*, **2000**, *11*, 338; M. C. B. Moraes, J. G. A. Brito Neto and C. L. do Lago, *Int. J. Mass Spectrom.*, **2000**, *198*, 121; A. S. Batsanov, A. V. Churakov, M. A. M. Easson, L. J. Govenlock, J. A. K. Howard, J. M. Moloney and D. Parker, *J. Chem. Soc., Dalton Trans.*, **1999**, 323; J. W. Kriesel, S. König, M. A. Freitas, A. G. Marshall, J. A. Leary and T. D. Tilley, *J. Am. Chem. Soc.*,

1998, *120*, 12207; R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, **1995**, *14*, 79; I. I. Stewart and G. Horlick, *Trends Anal. Chem.*, **1996**, *15*, 80; C. E. C. A. Hop, and R. Bakhtiar, *J. Chem. Educ.*, **1996**, *73*, A165; A. Canty and R. Colton, *Inorg. Chim. Acta*, **1994**, *215*, 179; D. Dakternieks, H. Zhu, E. R. T. Tiekink and R. Colton, *J. Organomet. Chem.*, **1994**, *476*, 33.

(5) W. Henderson and M. J. Taylor, *Polyhedron*, **1996**, *15*, 1957; L. J. McCaffrey, W. Henderson, B. K. Nicholson, J. E. Mackay and M. B. Dinger, *J. Chem. Soc., Dalton Trans.*, **1997**, 2577; W. Henderson, B. K. Nicholson and L. J. McCaffrey, *Polyhedron*, **1998**, *17*, 4291.

(6) S. -W. A. Fong, W. T. Yap, J. J. Vittal, A. G. Oliver, C. E. F. Rickard, W. Henderson and T. S. A. Hor, manuscript in preparation.

(7)   S. -W. A. Fong and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, **1999**, 639.

(8) A. Bencini and S. Midollini, *Coord. Chem. Rev.*, **1992**, *120*, 87; L. C. Roof and J. W. Kolis, *Chem. Rev.*, **1993**, *93*, 1037.

(9) A. G. Davis and P. J. Smith, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, Pergamon Press, United Kingdom, **1982**, vol. 2, ch. 11.11.3, p. 606.

(10) L. J. Arnold, *J. Chem. Educ.*, **1992**, *69*, 811.

(11) R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, W. B Saunders Company, Philadelphia, **1969**, p. 153.

(12) Modifications from literature procedures, K. Sisido, Y. Takeda and Z. Kinugawa, *J. Am. Chem. Soc.*, **1961**, *83*, 538.

(13) A. Bencini, M. D. Vaira, R. Morassi and P. Stoppioni, *Polyhedron*, **1996**, *15*, 2079.

(14) D. L. Klayman and T. S. Griffin, *J. Am. Chem. Soc.*, **1973**, *95*, 197.

(15) Cavinato, G.; Toniolo, L. *Inorg. Chim. Acta* **1981**, *52*, 39.

(16) *SMART & SAINT Software Reference Manuals*, version 4.0, Siemens Energy &

Automation, Inc., Analytical Instrumentation, Madison, WI, **1996.**

(17) G. M. Sheldrick, *SADABS, a software for empirical absorption correction*, University of

Göttingen, **1993**.

(18) G. M. Sheldrick, *SHELXTL*, version 5.03, Siemens Energy & Automation, Inc.,

Analytical Instrumentation, Madison, WI, **1996.**