

Exploring the Lewis basicity of the metalloligand [Pt₂(μ-Se)₂(PPh₃)₄] on metal substrates by electrospray mass spectrometry. Synthesis, characterization and structural studies of new platinum selenido phosphine complexes containing the {Pt₂Se₂} core

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Introduction

Electrospray mass spectrometry (ESMS) is a soft ionization technique that has been employed extensively in the analysis of biomolecules such as proteins and oligonucleotides.¹ It has also been increasingly applied in the characterization of a range of inorganic and organometallic systems.^{2,3} Recently, we discussed the development of ESMS as a rapid and convenient method to probe the chemistry of [Pt₂(μ-S)₂(PPh₃)₄] **2** with a wide range of metal substrates.⁴ This chemistry using Pt₂(μ-S)₂(PPh₃)₄ as a metalloligand is now very established,⁵ but little is known until very recently on similar coordination chemistry of the {Pt₂Se₂} core⁶. In this paper, we repeat a parallel methodology applied to the selenide system. There are important materials as they are possible precursors for semiconducting materials.⁷ Our effort could add a fresh pool of novel intermetallic selenide aggregates and clusters which are relatively rare in the current literature.⁸ Using an approach aided by ESMS, we are able to identify and synthesize an array of polynuclear selenide structures.

Results and discussion

(I) Reactivity of $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$

Although the decomposition of **2** in chlorinated solvents have been long investigated,⁹ reports on $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ **1** have only recently surfaced¹⁰. Besides their decomposition pathway and products, no other characteristics on these metalloligands have been investigated. It was very recently that we reported the acid titration on **2** in lieu to investigate its Lewis basicity, yielding a novel mono-protonated complex $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SH})(\text{PPh}_3)_4][\text{PF}_6]$ upon metathesis with NH_4PF_6 .¹¹ Initial reaction of **1** with a Lewis acid $[\text{Ga}(\text{ClO}_4)_3]$ unexpectedly yielded a di-protonated product $[\text{Pt}_2(\mu\text{-SeH})_2(\text{PPh}_3)_4][\text{ClO}_4]_2$ **3** which was structurally characterized (Fig. 1). The analogous product from **2** was a subject of speculation, but till to date, it has not been isolated. The proton source (from H_2O) was most probably generated by the Lewis acid in its commercially available solution form. Protonation of $\mu\text{-E}$ ligands ($\text{E} = \text{S}, \text{Se}$) is a general route to compounds containing $\mu\text{-EH}$ groups.¹² The structure of **3** shows a hinged $\{\text{Pt}_2\text{Se}_2\}$ core with the two protons attached facing away from one another. The dihedral angle of the four-membered Pt_2Se_2 ring is 71.9° , in large contrast to those in tin(IV)- $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ complexes⁶ and also $[\text{Pt}_2(\mu\text{-S})(\mu\text{-SH})(\text{PPh}_3)_4][\text{PF}_6]$ ¹¹. This might be due to the bulky metal centres and ligands, which in the latter case hinder the bending of the $\{\text{Pt}_2\text{Se}_2\}$ core. Acid titration using HCl was subsequently performed on **1** and the NMR analysis of the product matched that obtained from Ga^{3+} . The identity of the di-protonated complex is reconfirmed by subsequent reaction of **1** with H_2PF_6 . Careful addition of acid to **1** (1:1 ratio) yielded a mixture of both mono- and di-protonated products.

(II) Three-step synthesis strategy employing ESMS as probe

The reactions of the metalloligand $\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4$ **1** with a wide range of metal complexes have been initially screened using electrospray mass spectrometry (ESMS). The trends observed from our recent report involving **1** and Sn(IV) substrates⁶ are also seen in this series of ESMS-monitored reactions. The general observations include: (i) Displacement of one or two labile ligands on the metal substrates through nucleophilic attack of the Se atoms of **1** which then leads to the formation of cationic aggregates. (ii) 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 commonly the dominant peaks in the spectra. (iii) The common fragmentation route (when high cone voltages of 60 or 80 V are applied) involves loss of PPh_3 ligands. (iv) Detection of peaks at m/z 799 and 1598, assigned as $[\mathbf{1}+2\text{H}]^{2+}$ and $[\mathbf{1}+\text{H}]^+$ respectively, were normally observed when reactions did not occur, or **1** was in excess. In this report, only those reactions that give unexpected and interesting products and fragmentation pathways are singled out and discussed in detail. Schlenk-flask syntheses and characterization of these charged aggregates and those inferred from the ESMS spectra were followed up. The isolated products were characterized by the conventional NMR and single-crystal X-ray diffraction analyses. The results demonstrate that ESMS is valuable not only in monitoring the progress of reactions, it also provides a preliminary "screening" of the feasibility of reactions prior to preparative scale syntheses. All reactions performed under ESMS and lab-scale conditions are summarized in the tables and experimental section.

(a) Reactions between 1 and gold substrates

The ESMS data for this series of reactions are summarized in Table 1. The ease of displacement of chloride ligands on the gold substrates by **1** depends on the electron-donating as well as chelating ability of the ligands on the substrates.

Reaction between **1** and AuCl(PPh₃) gave a clean spectrum with a peak at m/z 2056 at moderately low cone voltages (20-40 V), attributed to $\{\mathbf{1}[\text{Au}(\text{PPh}_3)]\}^+$. When the cone voltage was further increased to 60 V, fragmentation occurred through loss of one PPh₃ ligand, resulting in either the detection of mono-cation $\{(\mathbf{1}\text{-PPh}_3)[\text{Au}(\text{PPh}_3)]\}^+$ or $[\mathbf{1}(\text{Au})]^+$. Phosphine mobility occurring on the Au atom is less likely because discrete signals are observed in the ³¹P NMR spectrum. At a cone voltage of 80 V, $\{(\mathbf{1}\text{-PPh}_3)[\text{Au}(\text{PPh}_3)]\}^+$ or $[\mathbf{1}(\text{Au})]^+$ dominated over $\{\mathbf{1}[\text{Au}(\text{PPh}_3)]\}^+$ and consecutive loss of another PPh₃ ligand yielded $\{(\mathbf{1}\text{-2PPh}_3)[\text{Au}(\text{PPh}_3)]\}^+$ or $[(\mathbf{1}\text{-PPh}_3)(\text{Au})]^+$.

Reaction of **1** with Au(anpy)Cl₂ **I** (anpy = cyclometallated 2-anilinopyridyl) resulted in detection of $\{\mathbf{1}[\text{Au}(\text{anpy})]\}^{2+}$ and $\{(\mathbf{1}\text{-PPh}_3)_2[\text{Au}(\text{anpyH})]\}^{3+}$ **4** at cone voltages between 20 and 60 V. The proposed structure of **4** is shown in Fig. 2, together with the observed and calculated isotope patterns. The identity of the tri-cation is clearly demonstrated by the corresponding match between the two isotope patterns. Protonation by the solvent presumably takes place on the nitrogen atom of the formerly cyclometallated anilinopyridine ligand to give **4**. Such protonation of the cyclometallated ligands on Au(III) ions has been observed previously.¹³

For the reaction between **1** and Au(tolpy)Cl₂ **II** (tolpy = cyclometallated *p*-tolylpyridyl), $\{\mathbf{1}[\text{Au}(\text{tolpy})]\}^{2+}$ was detected at 20 V. Further increasing the cone voltage to 40 V gave a significant peak at m/z 1288 (41% relative intensity c.f. the most intense peak $\{\mathbf{1}[\text{Au}(\text{tolpy})]\}^{2+}$), possibly attributed to $\{(\mathbf{1}\text{-PPh}_3)[\text{Au}(\text{tolpyH})][\text{PtSe}_2(\text{PPh}_3)_2]+\text{H}\}^{2+}$ **5**. Solvent protonation thus appears to occur again on the nitrogen atom of the tolylpyridine-derived ligand. At 60 V, loss of another PPh₃ ligand yielded $\{(\mathbf{1}\text{-}$

$2\text{PPh}_3[\text{Au}(\text{tolpyH})][\text{PtSe}_2(\text{PPh}_3)_2+\text{H}]^{2+}$. At a high cone voltage (80 V), there was still no sign of any fragmentation (through loss of a PPh_3 ligand) from $\{\mathbf{1}[\text{Au}(\text{tolpy})]\}^{2+}$ but it had ceased to be the dominant cation. $\{(\mathbf{1}-2\text{PPh}_3)[\text{Au}(\text{tolpyH})][\text{PtSe}_2(\text{PPh}_3)_2+\text{H}]\}^{2+}$ had emerged as the most intense cation at high cone voltage.

Reaction between **1** and $\text{Au}(\text{tolpyH})\text{Cl}_3$ **III** or $[\text{AuCl}_4][\text{NMe}_4]$ is less spontaneous compared to the three earlier mentioned gold substrates. At a low cone voltage (20 V), $[\text{Pt}(\text{PPh}_3)_2\text{Cl}]^+$, $[(\mathbf{1})_2\text{Au}]^{3+}$, $[(\mathbf{1}-\text{PPh}_3)_2(\text{AuCl}_2)+\text{H}]^{2+}$ and $[\mathbf{1}(\text{AuCl}_2)]^+$ were detected. At this voltage, $[\text{Pt}(\text{PPh}_3)_2\text{Cl}]^+$ and $[\mathbf{1}(\text{AuCl}_2)]^+$ were equally dominant. $[(\mathbf{1})_2\text{Au}]^{3+}$ **6**, being surprisingly detected at reasonable intensity, might be attributed to the preferred stabilization of the 'naked' Au^{3+} ion through coordination with two units of $\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4$ over the oxidation of the former¹⁴. Such stabilization has been observed in cyclometallated gold(III) complexes which form stable derivatives with thiolate¹⁵ and thiolate-type¹³ ligands. At a high cone voltage (60 V), $[\text{Pt}(\text{PPh}_3)_2\text{Cl}]^+$ became the dominant ion, together with the platinum cation containing a cyclometallated triphenylphosphine ligand, $\{\text{Pt}(\text{PPh}_3)[\text{PPh}_2(\text{C}_6\text{H}_4)]\}^+$. This cation was discussed in detail in a recent paper.³ Further elevation of the cone voltage to 80 V gave $\{\text{Pt}(\text{PPh}_3)[\text{PPh}_2(\text{C}_6\text{H}_4)]\}^+$ as the most intense cation.

(b) Reactions between 1 and group 12 metal (mercury, cadmium) substrates

Group 12 metals, especially mercury,¹⁶ have a very strong affinity for both sulfur and selenium. ESMS data for reactions between **1** and group 12 metal substrates are summarized in Table 2.

Reaction between **1** and thiomersal **IV** ($\text{EtHgSC}_6\text{H}_4\text{CO}_2\text{Na}$) was not straightforward. Thiomersal is a conveniently handled source of the $[\text{HgEt}]^+$ cation. At low cone voltages (20-40 V), the expected ions $[\mathbf{1}(\text{HgEt})]^+$ **7** and $[\mathbf{1}(\text{HgEt})_2]^{2+}$ **8** were detected along with $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SC}_6\text{H}_4\text{CO}_2)+\text{H}]^+$ and $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SC}_6\text{H}_4\text{CO}_2)+\text{Na}]^+$. The detection of the

mononuclear platinum thiosalicylate ions can be explained by Scheme 1, with $\text{Se}(\text{HgEt})_2$ being a proposed byproduct. The synthesis and characterization of $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SC}_6\text{H}_4\text{CO}_2)]$ was reported in a recent paper,³ including the thiolate exchange reaction between *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ and thiomersal, giving $[\text{Pt}(\text{PPh}_3)_2(\eta^2\text{-SC}_6\text{H}_4\text{CO}_2)]$ (and presumably HgEtCl).¹⁷

Complex **1** reacts with ferrocenyl mercury chloride **V** to give $[\mathbf{1}(\text{HgFc})]^+$, $[\mathbf{1}(\text{HgFc})_2]^{2+}$ and $[(\mathbf{1})_2\text{Hg}]^{2+}$ **9** at a cone voltage of 20V. Although $[(\mathbf{1})_2\text{Hg}]^{2+}$ was detected as a minor product under ESMS conditions, we have managed to isolate this cationic product as its PF_6^- salt under lab-scale conditions, solely from the decomposition of $[\mathbf{1}(\text{HgFc})][\text{PF}_6]$ in CH_2Cl_2 after a week. The formation of $[(\mathbf{1})_2\text{Hg}][\text{PF}_6]_2$ resulted from a 'naked' Hg^{2+} ion coordinating with two molecules of **1**. The source of this Hg^{2+} cation originated from the cleavage of the Hg-Fc bond in **V**, which was purified prior to use, rather than from an impurity. A similar observation was absent in our parallel study with **2**.⁴ $\{[\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_4]_2(\text{Hg})\}^{2+}$ has been reported by Mingos *et al.*,¹⁸ however, there is no report on the selenium analogue. At the high cone voltage of 80 V, only $[\mathbf{1}(\text{HgFc})]^+$ was detected. Complex **1** also reacted with $\text{HgCl}_2(\text{PPh}_3)_2$ or $\text{HgBr}_2(\text{dppe})$ to give **9**, observed at cone voltages in the range of 20-60 V. $\text{Hg}(\text{ClO}_4)_2$ was also used as a substrate for **1**, with the intention to isolate **9** cleanly. At cone voltage of 20 V, the reaction gave the only distinct peak at m/z 1698 pertaining to **9**. Fragmentation was absent even when the cone voltage was increased to 60 V.

Complex **1** reacts with $\text{HgCl}(\text{BzNMe}_2)$ **VI** at 20 V to give $\{\mathbf{1}[\text{Hg}(\text{BzNMe}_2)]_2\}^{2+}$ and $\{\mathbf{1}[\text{Hg}(\text{BzNMe}_2)]\}^+$, the latter further being protonated (by the solvent) to give $\{\mathbf{1}[\text{Hg}(\text{BzNHMe}_2)]\}^{2+}$ at m/z 966. Increasing the cone voltage to 40 V eliminated $\{\mathbf{1}[\text{Hg}(\text{BzNMe}_2)]_2\}^{2+}$, and further eliminated $\{\mathbf{1}[\text{Hg}(\text{BzNHMe}_2)]\}^{2+}$ at 80 V to give $\{\mathbf{1}[\text{Hg}(\text{BzNMe}_2)]\}^+$ as the dominant ion. Similar protonation on the amino group was also observed for the reaction between **1** and $\text{HgCl}(p\text{-OMe-BzNMe}_2)$ **VII**. However, the

protonated ion was dominant over $\{\mathbf{1}[\text{Hg}(p\text{-OMe-BzNMe}_2)]\}^+$ at low cone voltages. At 60 V, competition came between these two ions and at 80 V, $\{\mathbf{1}[\text{Hg}(p\text{-OMe-BzNMe}_2)]\}^+$ emerged as the dominant ion.

For the reaction between **1** and CdCl_2 , a single dominant ion $[\mathbf{1}(\text{CdCl})]^+$ was observed between 20-60 V. A further increase of the cone voltage to 80 V only gave an insignificant peak at m/z 1483 (5% relative intensity c.f. the most intense peak $[\mathbf{1}(\text{CdCl})]^+$) attributed to $[(\mathbf{1}\text{-PPh}_3)(\text{CdCl})]^+$. The synthesis and characterization of this reaction (discussed under the experimental section) was followed up on a preparative scale and instead of obtaining the expected cationic product $[\mathbf{1}(\text{CdCl})][\text{Cl}]$, a neutral compound was prepared and structurally characterized as $[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4(\text{CdCl}_2)]$ **11e** (with a disordered CH_2Cl_2 and two H_2O solvates). The neutral compound was re-analyzed under ESMS conditions (dissolved in CH_2Cl_2 , using MeOH as mobile phase) and the results matched those as discussed above. Fig. 3 shows the structure of **11e** and its pertinent bond distances and angles are depicted in Table 3. X-ray analysis revealed that compound **11e** consists of an $\{\text{CdCl}_2\}$ moiety coordinated to the metalloligand $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$, forming a distorted square-based pyramidal aggregate (cadmium atom on the $\{\text{Pt}_2\text{Se}_2\}$ core) with a 2-fold symmetry along the center axis (referenced to the cadmium atom). The dissociation of one chloride from compound **11e** with the detection of $[\mathbf{1}(\text{CdCl})]^+$ as the dominant ion under ESMS conditions is further supported by our recent work on $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_4[\text{CdCl}(\text{bipy})]\} \{\text{PF}_6\}$ ¹⁹ where only one chloride on the coordinated cadmium was substituted by a bipyridyl ligand. Similar halide dissociation from a range of neutral metal complexes to give $[\text{M-Cl}]^+$ under ESMS conditions has also been reported recently.²⁰ We are currently investigating the development of compound **11e** as a building block for multi-metallic materials, taking advantage of its spontaneous dissociation of chloride which provides an active site for coordination.

(c) Reactions between **1** and Group 13 (gallium, indium, thallium), Group 14 (germanium, lead) and Group 15 (antimony, bismuth) substrates

ESMS data for displacement reactions with group 13, 14 and 15 complexes are reported in Tables 4, 5 and 6 respectively. All reactions shown in the tables were repeated on a preparative scale and the respective isolated products reported under the experimental section.

Detection of $[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4(\text{Pb})]^{2+}$ and $\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Pb}(\text{NO}_3)]\}^+$ (m/z 902 and 1866 respectively) in the reaction between **1** and $\text{Pb}(\text{NO}_3)_2$ illustrated the lability of the nitrate ligands. The re-run of this reaction after standing in solution over time showed a decrease in the intensity of the peak at m/z 1866 with a simultaneous increase in that at m/z 902 that further suggested the ease of nitrate ligand dissociation. However, $\{[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4]_2(\text{Pb})\}^{2+}$ was absent even when excess $\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4$ was added. We have managed to isolate and fully characterize the product as $\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Pb}(\text{NO}_3)]\} \{\text{NO}_3\}$ **13b** from the reaction performed on a preparative scale, and its structure is shown in Fig. 4. Compound **13b** consists of a $\{\text{Pb}(\text{NO}_3)\}$ moiety resting on top of the metalloligand $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$ and the NO_3^- ligand is terminally bonded to the Pb atom. The second NO_3^- ligand is only weakly bonded. The bonding modes of the two NO_3^- ligands are further supported by IR data in the experimental section. Among the four Pb-O bond lengths, only one $[\text{Pb}(1)\text{-O}(1)$ 2.559 Å] suggests a strong Pb-O interaction. This NO_3^- ligand is best described as terminal and the coordination sphere of Pb(II) is [3+3]. The other three Pb-O bonds (aver. 2.817 Å), though not as strong as Pb(1)-O(1), are still within bonding distance when compared to a selection of Pb- NO_3 structures (< 3 Å) obtained from CCDC²¹. Upon coordination to the $\{\text{Pb}(\text{NO}_3)\}$ moiety, the $\{\text{Pt}_2\text{Se}_2\}$ core bends from planarity, giving a dihedral angle of 132.5°. Similar observations are found in the sulfur analog, *viz.* $\{\text{Pt}_2(\mu_3\text{-S})_2(\text{PPh}_3)_4[\text{Pb}(\text{NO}_3)]\} \{\text{NO}_3\}$,²² and the structural parameters of these two structures are

compared in Table 7. From the bond parameters, it can be observed that the coordinating nitrate ligand in **13b** adopts the terminal mode whereas that in the sulfur analog prefers the chelating mode. This can be rationalized through the Lewis basicity of the selenium atoms in **13b** (over the sulfur atoms), thus causing the center lead atom to be more electron rich and less willing to accept the chelating mode of the coordinating nitrate ligand.

Conclusions

The ability of ESMS and its simplicity to monitor solution chemistry has been emphasized through successful displacement experiments demonstrated by $\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4$ on a wide range of metal substrates where the resulting intermetallic aggregates are identified and subsequently confirmed by synthetic studies and single-crystal X-ray diffraction analyses. Full characterization of the products isolated from preparative scale syntheses corresponded to the respective species postulated from the ESMS data. These results suggest that there is a clear link between species observed by ESMS and isolable products. This emphasizes our belief that more synthetic chemists should take advantage of this ESMS-directed synthetic methodology of materials of their interest. Our next target is to study the material properties of these intermetallic selenides, especially as precursors to optoelectronically active materials.

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 μ L 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.²³ The m/z values given are for the most intense peak in the envelope in each case.

Materials

The substrates used were AuCl(PPh₃),²⁴ Au(anpy)Cl₂ (anpy = cyclometallated 2-anilinopyridyl),²⁵ Au(tolpy)Cl₂ (tolpy = cyclometallated *p*-tolylpyridyl),²⁶ Au(tolpyH)Cl₃ (tolpyH = *p*-tolylpyridine),²⁶ HgFcCl,²⁷ HgCl₂(PPh₃)₂,²⁸ HgBr₂(dppe),²⁹ HgCl(BzNMe₂),³⁰ HgCl(*p*-OMe-BzNMe₂),³⁰ [NMe₄][AuCl₄] is commercially available from Strem; HgPhCl from Fluka; EtHgSC₆H₄CO₂Na (thiomersal) and SbCl₃ from BDH; Ga(ClO₄)₃, Hg(ClO₄)₂, fluorescein[Hg(OAc)]₂ and InBr₃ from Aldrich; Ga(NO₃)₃ and GeI₄ from Johnson Matthey; TlNO₃ and Pb(NO₃)₂ from Merck; and BiCl₃ from TCI. **CAUTION:** perchlorate salts combined with organic ligands are potentially explosive and should be handled in small quantity and with the necessary precautions,³¹ Hg(II) compounds are highly toxic and any skin contact must be avoided. A modified preparation of Pt₂(μ -Se)₂(PPh₃)₄ **1** was adapted from our recent report.⁶ 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. The ³¹P NMR spectra were recorded at 121.39 MHz with 85% H₃PO₄ as external reference, PF₆⁻ resonances at around -144 ppm (heptet, ¹J(P-F) = 713 Hz) are omitted from ³¹P NMR reports for clarity. Infrared spectra were recorded in the range 4000–400 cm⁻¹, on a Perkin Elmer

FTIR spectrometer. Elemental analyses were performed by the microanalytical laboratory of the Department of Chemistry at the National University of Singapore.

Synthesis of di-protonated $[\text{Pt}_2(\mu\text{-Se})_2(\text{PPh}_3)_4]$

$[\text{Pt}_2(\mu\text{-SeH})_2(\text{PPh}_3)_4][\text{ClO}_4]_2$ (**3**). $\text{Ga}(\text{ClO}_4)_3$ (14.5 mg, 2.20 μL , 0.0395 mmol) was added to a brown suspension of **1** (57.8 mg, 0.0362 mmol) in MeOH (20 mL). The resultant orange suspension was stirred for 24 h and filtered. The solid washed successively with 100 mL portions of deionized water and Et_2O , and dried under vacuum yielding an orange powder of **3** (0.0514 g, 79%). Found: C, 47.7; H, 3.4; P, 6.1. Calc. for $\text{C}_{72}\text{H}_{62}\text{Cl}_2\text{O}_8\text{Se}_2\text{P}_4\text{Pt}_2$: C, 48.1; H, 3.5; P, 6.9%. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CDCl_3): δ_{p} 5.4 ppm [t, $^1J(\text{P-Pt}) = 3910$ Hz]. ^1H NMR (CDCl_3): δ_{H} 1.25 (s, 2H, 2SeH), 7.10-7.80 (m, 60H, 12C₆H₅).

$[\text{Pt}_2(\mu\text{-SeH})_2(\text{PPh}_3)_4][\text{PF}_6]_2$ (**3a**). Standard 0.5028M HCl (3.0 mg, 0.16 mL, 0.0823 mmol) was added to a brown suspension of **1** (44.4 mg, 0.0278 mmol) in MeOH (20 mL). The resulting orange solution was stirred for 3 h, after which excess NH_4PF_6 (10.0 mg, 0.0614 mol) was introduced to give an orange suspension. After stirring for 1 h, deionized water (50 mL) was added to induce precipitation. The suspension was filtered, the solid washed successively with 100 mL portions of deionized water and Et_2O , and dried under vacuum yielding an orange powder of **3a** (0.0252 g, 48%). Found: C, 45.4; H, 3.2; P, 9.1. Calc. for $\text{C}_{72}\text{H}_{62}\text{F}_{12}\text{Se}_2\text{P}_6\text{Pt}_2$: C, 45.8; H, 3.3; P, 9.8%. $^{31}\text{P}\text{-}\{^1\text{H}\}$ NMR (CDCl_3): δ_{p} 5.4 ppm [t, $^1J(\text{P-Pt}) = 3910$ Hz]. ^1H NMR (CDCl_3): δ_{H} 1.25 (s, 2H, 2SeH), 7.10-7.80 (m, 60H, 12C₆H₅). Alternatively, **3a** is better prepared by addition of HPF_6 to a MeOH suspension of **1** (90% yield).

Synthesis of heterometallic aggregates

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Au}(\text{PPh}_3)]\}\{\text{PF}_6\}$ (10a). AuCl(PPh₃) (15.8 mg, 0.0319 mmol) was added to a brown suspension of **1** (50.4 mg, 0.0316 mmol) in MeOH (20 mL). The resulting orange solution was stirred for 3 h, after which excess NH₄PF₆ (10.0 mg, 0.0614 mol) was introduced to give an orange-brown suspension. After stirring for 1 h, deionized water (50 mL) was added to induce precipitation. The suspension was filtered, the solid washed successively with 100 mL portions of deionized water and Et₂O, and dried under vacuum yielding an orange-brown powder of **10a** (0.0358 g, 52%). Found: C, 49.0; H, 3.3; P, 8.1. Calc. for C₉₀H₇₅F₆Se₂P₆AuPt₂: C, 49.1; H, 3.4; P, 8.4%. ³¹P-¹H NMR (CDCl₃): δ_p 19.0 ppm [t, ¹J(P-Pt) = 3117 Hz], 33.6 ppm [s, 1 P (PPh₃ on Au)].

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Au}(\text{anpy})]\}\{\text{PF}_6\}_2$ (10b). Following a similar procedure as described for **10a**, Au(anpy)Cl₂ (12.6 mg, 0.0288 mmol) and **1** (45.8 mg, 0.0287 mmol) gave an orange powder of **10b** (0.0313 g, 48%). Found: C, 45.0; H, 3.1; P, 8.4. Calc. for C₈₄H₇₀F₁₂Se₂NP₆AuPt₂: C, 44.8; H, 3.1; P, 8.2%. ³¹P-¹H NMR (CDCl₃): δ_p 13.5 ppm [t, ¹J(P-Pt) = 3273 Hz].

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4(\text{HgPh})\}[\text{PF}_6]$ (11a). Following a similar procedure as described for **10a**, HgPhCl (9.4 mg, 0.0300 mmol) and **1** (47.8 mg, 0.0299 mmol) gave an orange-brown powder of **11a** (0.0388 g, 64%). Found: C, 46.3; H, 3.2; P, 7.5. Calc. for C₇₈H₆₅F₆Se₂P₅HgPt₂: C, 46.4; H, 3.2; P, 7.7%. ³¹P-¹H NMR (CDCl₃): δ_p 19.6 ppm [t, ¹J(P-Pt) = 3120 Hz].

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4\text{HgEt}\}[\text{PF}_6]$ (11b). Following a similar procedure as described for **10a**, EtHgSC₆H₄CO₂Na (12.2 mg, 0.0301 mmol) and **1** (47.4 mg, 0.0297 mmol) gave a

yellow powder of **11b** (0.0178 g, 30%). Found: C, 44.9; H, 3.2; P, 7.8. Calc. for $C_{74}H_{65}F_6Se_2P_5HgPt_2$: C, 45.1; H, 3.3; P, 7.9%. $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ_p 20.1 ppm [$t, ^1J(P-Pt) = 3136$ Hz].

[Pt₂(μ_3 -Se)₂(PPh₃)₄HgFc][PF₆] (11c). Following a similar procedure as described for **10a**, HgFcCl (13.4 mg, 0.0318 mmol) and **1** (50.0 mg, 0.0313 mmol) gave an orange-brown powder of **11c** (0.0423 g, 64%). Found: C, 46.0; H, 3.2; P, 7.0. Calc. for $C_{82}H_{69}F_6Se_2P_5FeHgPt_2$: C, 46.3; H, 3.3; P, 7.3%. $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ_p 19.3 ppm [$t, ^1J(P-Pt) = 3117$ Hz].

{[Pt₂(μ_3 -Se)₂(PPh₃)₄]₂Hg}{ClO₄}}₂ (11d). Following a similar procedure as described for **10a** (with the exclusion of metathesis by NH_4PF_6), $Hg(ClO_4)_2 \cdot H_2O$ (5.8 mg, 0.0145 mmol) and **1** (46.6 mg, 0.0292 mmol) gave an orange-brown powder of **11d** (0.0382 g, 36%). Found: C, 48.0; H, 3.4; P, 6.6. Calc. for $C_{144}H_{120}Cl_2O_8Se_4P_8HgPt_2$: C, 48.1; H, 3.4; P, 6.9%. $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ_p 18.5 ppm [$t, ^1J(P-Pt) = 3113$ Hz].

[Pt₂(μ_3 -Se)₂(PPh₃)₄(CdCl₂)] (11e). $CdCl_2$ (21.0 mg, 0.1145 mmol) was added to a brown suspension of **1** (182.0 mg, 0.1140 mmol) in MeOH (30 mL). An immediate bright yellow suspension resulted and it was stirred for 2 h. The suspension was filtered, the solid washed successively with 30 mL of MeOH and 100 mL of Et_2O , and dried under vacuum yielding a bright yellow powder of **11e** (0.1356 g, 67%). Found: C, 48.5; H, 3.3; P, 6.7. Calc. for $C_{72}H_{60}Cl_2Se_2P_4CdPt_2$: C, 48.6; H, 3.4; P, 7.0%. $^{31}P\{-^1H\}$ NMR ($CDCl_3$): δ_p 21.1 ppm [$t, ^1J(P-Pt) = 3047$ Hz].

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Ga}(\text{NO}_3)_2]\}\{\text{PF}_6\}$ (12a). Following a similar procedure as described for **10a**, $\text{Ga}(\text{NO}_3)_3$ (8.2 mg, 0.0321 mmol) and **1** (50.0 mg, 0.0313 mmol) gave a brown powder of **12a** (0.0263 g, 43%). Found: C, 44.5; H, 3.0; N, 1.2; P, 7.7. Calc. for $\text{C}_{72}\text{H}_{60}\text{F}_6\text{O}_6\text{Se}_2\text{N}_2\text{P}_5\text{GaPt}_2$: C, 44.7; H, 3.1; N, 1.4; P, 8.0%. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ_{p} 18.7 ppm [t, $^1J(\text{P-Pt}) = 3216$ Hz].

$[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4\text{InBr}_2][\text{PF}_6]$ (12b). Following a similar procedure as described for **10a**, InBr_3 (11.2 mg, 0.0316 mmol) and **1** (50.0 mg, 0.0313 mmol) gave a brown powder of **12b** (0.0242 g, 38%). Found: C, 42.9; H, 3.0; P, 7.6. Calc. for $\text{C}_{72}\text{H}_{60}\text{Br}_2\text{F}_6\text{Se}_2\text{P}_5\text{InPt}_2$: C, 42.9; H, 3.0; P, 7.7%. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ_{p} 17.7 ppm [t, $^1J(\text{P-Pt}) = 3201$ Hz].

$[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4\text{Tl}][\text{NO}_3]$ (12c). Following a similar procedure as described for **10a** (with the exclusion of metathesis by NH_4PF_6), TlNO_3 (8.4 mg, 0.0315 mmol) and **1** (50.0 mg, 0.0313 mmol) gave a brown powder of **12c** (0.0242 g, 41%). Found: C, 46.3; H, 3.2; P, 6.3. Calc. for $\text{C}_{72}\text{H}_{60}\text{O}_3\text{Se}_2\text{NP}_4\text{Pt}_2\text{Tl}$: C, 46.4; H, 3.2; P, 6.6%. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ_{p} 20.1 ppm [t, $^1J(\text{P-Pt}) = 3017$ Hz].

$[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4\text{GeI}_3][\text{PF}_6]$ (13a). Following a similar procedure as described for **10a**, GeI_4 (19.0 mg, 0.0327 mmol) and **1** (50.0 mg, 0.0313 mmol) gave an orange powder of **13a** (0.0188 g, 27%). Found: C, 39.3; H, 2.8; P, 7.0. Calc. for $\text{C}_{72}\text{H}_{60}\text{F}_6\text{I}_3\text{Se}_2\text{P}_5\text{GePt}_2$: C, 39.4; H, 2.8; P, 7.1%. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ_{p} 19.6 ppm [t, $^1J(\text{P-Pt}) = 3043$ Hz].

$\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Pb}(\text{NO}_3)_2]\}\{\text{NO}_3\}$ (13b). Following a similar procedure as described for **10a** (with the exclusion of metathesis by NH_4PF_6), $\text{Pb}(\text{NO}_3)_2$ (10.5 mg, 0.0317 mmol) and **1** (50.0 mg, 0.0313 mmol) gave a brown powder of **13b** (0.0208 g, 34%). Found:

C, 44.6; H, 3.1; N, 1.4; P, 6.1. Calc. for $C_{72}H_{60}O_6Se_2N_2P_4PbPt_2$: C, 44.8; H, 3.1; N, 1.5; P, 6.4%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ_p 15.9 ppm [t , $^1J(P\text{-}Pt) = 3143$ Hz]. $\nu(NO_3^-)$ in CH_2Cl_2 : 1381 (uncoordinated NO_3^-), 1272 (coordinated NO_3^-) cm^{-1} .

$[Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4SbCl_2][PF_6]$ (14a). Following a similar procedure as described for **10a**, $SbCl_3$ (7.3 mg, 0.0320 mmol) and **1** (50.0 mg, 0.0313 mmol) gave an orange-brown powder of **14a** (0.0400 g, 66%). Found: C, 44.7; H, 3.1; P, 8.1. Calc. for $C_{72}H_{60}Cl_2F_6Se_2P_5Pt_2Sb$: C, 44.7; H, 3.1; P, 8.0%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ_p 16.8 ppm [t , $^1J(P\text{-}Pt) = 3239$ Hz].

$[Pt_2(\mu_3\text{-}Se)_2(PPh_3)_4BiCl_2][PF_6]$ (14b). Following a similar procedure as described for **10a**, $BiCl_3$ (10.0 mg, 0.0317 mmol) and **1** (50.0 mg, 0.0313 mmol) gave an orange-brown powder of **14b** (0.0315 g, 50%). Found: C, 42.7; H, 2.9; P, 7.4. Calc. for $C_{72}H_{60}Cl_2F_6Se_2P_5BiPt_2$: C, 42.8; H, 3.0; P, 7.7%. $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$): δ_p 11.8 ppm [t , $^1J(P\text{-}Pt) = 3235$ Hz].

Crystal structure determination and refinement

The data collections were performed on a Bruker AXS SMART diffractometer, equipped with a CCD area-detector using Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The software SMART³² was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT³² for integration of intensity of reflections and scaling, SADABS³³ for empirical absorption correction, and SHELXTL³⁴ for space group and structure determination, refinements, graphics, and structure reporting. 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 $wR_2 = \{\Sigma[w(F_o^2 -$

$F_c^2)/\Sigma[w(F_o^2)^2]^{1/2}$ (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 8. 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 $[\text{Pt}_2(\mu\text{-SeH})_2(\text{PPh}_3)_4][\text{PF}_6]_2$ **3**, $[\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4(\text{CdCl}_2)]$ **11e**, $\{\text{Pt}_2(\mu_3\text{-Se})_2(\text{PPh}_3)_4[\text{Pb}(\text{NO}_3)]\} \{\text{NO}_3\}$ **13b** for structure determination were obtained by layering a CH_2Cl_2 solution of each compound with hexane.

Compound 3. A suitable crystal of dimensions $0.24 \times 0.18 \times 0.14 \text{ mm}^3$ was selected, wedged inside a glass capillary tube and flame-sealed. A total of 30240 reflections were collected in the θ range $1.68\text{-}25.00^\circ$ ($-15 < h < 15$, $-16 < k < 16$, $-28 < l < 28$).

Compound 11e. A suitable crystal of dimensions $0.36 \times 0.30 \times 0.20 \text{ mm}^3$ was selected, wedged inside a glass capillary tube and flame-sealed. A total of 19576 reflections were collected in the θ range $1.47\text{-}25.00^\circ$ ($-20 < h < 18$, $-14 < k < 13$, $-14 < l < 20$).

Compound 13b. A suitable crystal of dimensions $0.16 \times 0.12 \times 0.04 \text{ mm}^3$ was selected, wedged inside a glass capillary tube and flame-sealed. A total of 16730 reflections were collected in the θ range $2.01\text{-}25.00^\circ$ ($-14 < h < 13$, $-20 < k < 12$, $-20 < l < 19$).

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