

# Inter- and hetero-metallic assembly of palladium sulfide aggregates: crystal and molecular structures of $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 3\text{CH}_2\text{Cl}_2$ and $[\text{Ag}_2\text{Pd}_2(\text{NO}_3)_2(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 2\text{CH}_2\text{Cl}_2$

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## Abstract

Lewis acid/base addition between  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  and  $\text{MX}_n$  [ $\text{M} = \text{In(III)}, \text{Ga(III)}, \text{Tl(I)}, \text{Pb(II)}, \text{Sn(IV)}, \text{Bi(III)}, \text{Ag(I)}$  and  $\text{Au(I)}$ );  $\text{X} = \text{halide}$  or pseudohalide;  $\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene] gives rise to a range of neutral or cationic intermetallic aggregates with the  $\{\text{Pd}_2\text{MS}_2\}$  or  $\{\text{Pd}_2\text{M}_2\text{S}_2\}$  core. Effectively  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  functions as a chelating or bridging dithio metallo-ligand. Two representative crystal structures, viz.  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 3\text{CH}_2\text{Cl}_2$  and  $[\text{Ag}_2\text{Pd}_2(\text{NO}_3)_2(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 2\text{CH}_2\text{Cl}_2$  are described and discussed. The former features an intermetallic  $\{\text{InPd}_2\}$  triangle whereas the latter displays a heterometallic  $\{\text{Ag}_2\text{Pd}_2\}$  metal plane. Both of them are sustained and supported by capping sulfides without significant or direct metal–metal bonds.

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**Keywords:** Ferrocenyl; Palladium; Metalloligand; Heterometallic; Structure; Phosphine; Sulfide

## 1. Introduction

The use of  $\text{Pt}_2\text{L}_4(\mu\text{-S})_2$  ( $\text{L} = \text{phosphine}$ ) as a precursor to homo- and heterometallic aggregates and clusters is well established [1]. Progress on the palladium analogues has been seriously handicapped by problems associated with lability, dissociation, polymerization and insolubility. Some of these limitations can be alleviated through the use of chelating phosphines [2]. We have earlier com-

municated on the “decoration” of the  $\{\text{Pd}_2\text{S}_2\}$  plane with silver “molecular tails” [3d]. In view of emerging significance of these and related complexes such as  $[\text{Pd}_3(\text{Bu}_2\text{bpy})_3(\mu_3\text{-S})_2]^{2+}$  ( $\text{Bu}_2\text{bpy} = 4,4'$ -di-tert-butyl-2,2'-bipyridine),  $[\text{Pd}_3(\text{dppm})_3(\mu_3\text{-S})_2]^{2+}$  [4], and  $[\text{Pd}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2(\text{CuPPh}_3)]_2(\text{W}_6\text{O}_{19})$  [5] as well as their potential importance in non-linear optical applications [6], we herein demonstrate that the inter- and heterometallic chemistry of  $\text{Pd}_2\text{L}_4(\mu\text{-S})_2$  ( $\text{L} = \text{phosphine}$ ) can be developed in parallel to that of the  $\text{Pt(II)}$  analogues [7]. Accordingly, we could develop an array of heterometallic ( $d\text{-}d$  metals) and intermetallic ( $d\text{-}p$  metals) aggregates based on the  $\{\text{Pd}_2\text{S}_2\}$  core. The crystal structures of two representative forms are described and discussed.

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Reaction of  $\text{InCl}_3$  with  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  ( $\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene [8]) in a molar ratio of 1:1 or 1:2 yields an orange-red crystalline product formulated as  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2]$ , **1**. The  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum shows a single resonance peak at 26.1 ppm, suggesting that all phosphines are chemically equivalent. X-ray diffraction study of a single-crystal of **1** (Fig. 1) revealed an addition compound formed between  $\text{InCl}_3$  and  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$ , with the latter serving as a neutral 4-electron donor through the nucleophilic sulfur (thio) centers. Effectively, this results in a  $\{\text{Pd}_2\text{In}\}$  intermetallic triangle bicapped by sulfide to give a pseudo-tbp framework for the  $\{\text{Pd}_2\text{InS}_2\}$  core. The 5-coordinate In(III) takes up a distorted sbp (Fig. 2) whereas the Pd(II) keeps its usual sq planar geometry. The analogous  $\text{InPt}_2\text{Cl}_3(\text{PPh}_3)_4(\mu_3\text{-S})_2$  structure, which was reported earlier [9], shows an unusual sbp (cf.  $\text{InCl}_3(\text{thf})_2$  is tbp [10]). Although this geometry is still apparent in **1**, with  $\text{Cl}(2)\cdots\text{Cl}(3)\cdots\text{S}(1)\cdots\text{S}(2)$  forming the basal plane, the apical  $\text{In}\cdots\text{Cl}(1)$  (2.403(3) Å) is comparable to the other  $\text{In}\cdots\text{Cl}$  bonds ( $\text{In}(1)\cdots\text{Cl}(2)$  2.417(3),  $\text{In}(1)\cdots\text{Cl}(3)$  2.432(3) Å) and hence is no longer unique. This is distinctly different from that in the  $\{\text{InPd}_2\}$  analogue in which the apical  $\text{In}\cdots\text{Cl}$  bond is significantly shorter (2.131(5) Å). No Pd–Pd or Pd–In bonds are envisaged although the

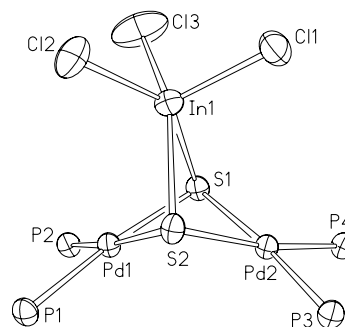


Fig. 2. Perspective view of the core in compound (**1**) and thermal ellipsoids are plotted at 30% probability level.

$\text{M}\cdots\text{M}$  separations [ $\text{Pd}\cdots\text{Pd}$  (3.2028 Å) and  $\text{Pd}\cdots\text{In}$  (3.1959 Å)] are close to bonding distances. There is no evidence for cross-metal migration for the chloride or phosphines.

The similar chemical and structural behaviors between  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  and  $\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2$  towards  $\text{InCl}_3$  suggest that the intermetallic chemistry of  $\{\text{Pt}_2\text{S}_2\}$  can be extended to the  $\{\text{Pd}_2\text{S}_2\}$  core using  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  as the Lewis basic substrate. The less labile  $\text{dppf}$  (relative to  $\text{PPh}_3$ ) helps to alleviate the dissociative problems in Pd(II) phosphines. This is illustrated by the reactions of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  with other  $p$ -block metals.

Reaction between  $\text{GaCl}_3$  and  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (ca 1:2) gives a red crystalline product formulated as an ionic complex  $[\text{GaPd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2](\text{GaCl}_4)$ , **2**. It probably arises from direct addition between the substrates viz.  $[\text{Cl}_3\text{GaPd}_2(\text{dppf})_2(\mu_3\text{-S})_2]$ , followed by intermolecular chloride transfer between the adduct and  $\text{GaCl}_3$ . Its  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum shows that all phosphines are equivalent (single peak at 30.4 ppm). Molar conductivity measurement indicates that **2** is a 1:1 electrolyte in methanol. The proposed molecular structure is similar to that of the  $\{\text{GaPt}_2\}$  analogue reported earlier [11].

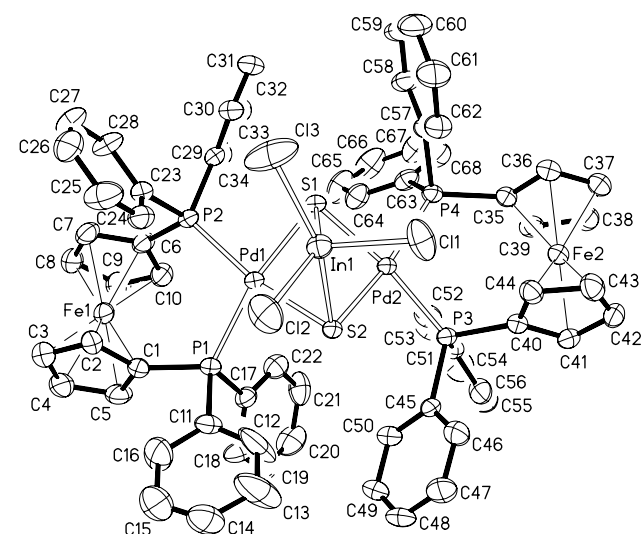
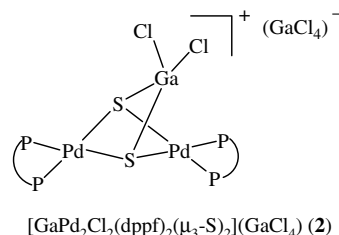
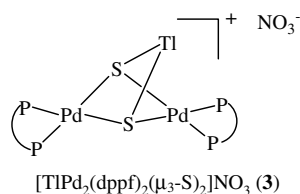


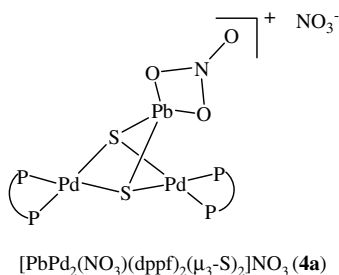
Fig. 1. ORTEP plot of the molecular structure of (**1**) (30% thermal ellipsoids and solvate removed for clarity). Selected bond distances (Å) and angles (°):  $\text{In}(1)\cdots\text{Cl}(1)$  2.403(3),  $\text{In}(1)\cdots\text{Cl}(2)$  2.417(3),  $\text{In}(1)\cdots\text{Cl}(3)$  2.432(3),  $\text{In}(1)\cdots\text{S}(1)$  2.567(2),  $\text{In}(1)\cdots\text{S}(2)$  2.6255(19),  $\text{In}(1)\cdots\text{Pd}(1)$  3.1959(8),  $\text{Pd}(1)\cdots\text{P}(1)$  2.3420(18),  $\text{Pd}(1)\cdots\text{S}(2)$  2.3521(18),  $\text{Pd}(1)\cdots\text{P}(2)$  2.3308(19),  $\text{Pd}(1)\cdots\text{S}(1)$  2.3517(18),  $\text{Pd}(1)\cdots\text{Pd}(2)$  3.2028(8),  $\text{Pd}(2)\cdots\text{P}(4)$  2.3342(19),  $\text{Pd}(2)\cdots\text{P}(3)$  2.3164(18),  $\text{Pd}(2)\cdots\text{S}(1)$  2.3471(18),  $\text{Pd}(2)\cdots\text{S}(2)$  2.3207(18);  $\text{Cl}(1)\cdots\text{In}(1)\cdots\text{Cl}(2)$  103.58(12),  $\text{Cl}(1)\cdots\text{In}(1)\cdots\text{Cl}(3)$  102.16(18),  $\text{Cl}(2)\cdots\text{In}(1)\cdots\text{Cl}(3)$  91.79(15),  $\text{Cl}(1)\cdots\text{In}(1)\cdots\text{S}(1)$  110.59(9),  $\text{Cl}(2)\cdots\text{In}(1)\cdots\text{S}(1)$  144.32(11),  $\text{Cl}(3)\cdots\text{In}(1)\cdots\text{S}(1)$  90.87(12),  $\text{Cl}(1)\cdots\text{In}(1)\cdots\text{S}(2)$  100.68(10),  $\text{Cl}(2)\cdots\text{In}(1)\cdots\text{S}(2)$  93.01(10),  $\text{Cl}(3)\cdots\text{In}(1)\cdots\text{S}(2)$  154.84(14),  $\text{S}(1)\cdots\text{In}(1)\cdots\text{S}(2)$  71.20(5),  $\text{Cl}(1)\cdots\text{In}(1)\cdots\text{Pd}(1)$  140.88(8),  $\text{Cl}(2)\cdots\text{In}(1)\cdots\text{Pd}(1)$  99.29(10),  $\text{Cl}(3)\cdots\text{In}(1)\cdots\text{Pd}(1)$  108.45(14),  $\text{S}(1)\cdots\text{In}(1)\cdots\text{Pd}(1)$  46.60(4),  $\text{S}(2)\cdots\text{In}(1)\cdots\text{Pd}(1)$  46.39(4).

Reaction of  $\text{TlNO}_3$  with  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  in a molar ratio of 1:1 or 1:2 yields red crystalline  $[\text{TlPd}_2(\text{dppf})_2(\mu_3\text{-S})_2]\text{NO}_3$  (**3**) which metathesizes easily with  $\text{NH}_4\text{PF}_6$  in methanol to give orange-red precipitate of  $[\text{TlPd}_2(\text{dppf})_2(\mu_3\text{-S})_2]\text{PF}_6$ . Its  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum shows equivalent phosphines ( $\delta = 22.0$  ppm). IR

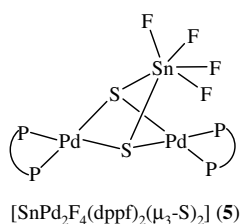
analysis (ionic nitrate at  $1384\text{ cm}^{-1}$ ) and conductivity measurement both indicate the 1:1 ionic nature of the compound. The structure is hence analogous to those of  $[\text{TiPt}_2(\text{PP})_2(\mu_3\text{-S})_2]\text{NO}_3$  (PP = dppf or  $2 \times \text{PPh}_3$ ) [12].



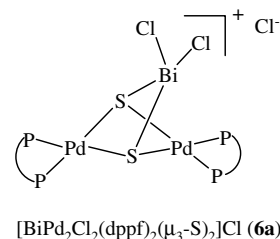
Similar to the  $\{\text{Pd}_2\text{Ti}\}$  complex, reaction between  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  in either 1:1 or 1:2 molar ratio gives similar orange-red crystalline product,  $[\text{PbPd}_2(\text{NO}_3)(\text{dppf})_2(\mu_3\text{-S})_2]\text{NO}_3$  (**4a**). The  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR spectrum shows a single resonance at 23.5 ppm. The IR spectrum (KBr) suggests that nitrate exists in both ionic ( $\nu\ 1384\text{ cm}^{-1}$ ) and coordinated ( $\nu\ 1276\text{ cm}^{-1}$ ) forms. This is consistent with molar ionic conductivity measurement, which shows a typical 1:1 electrolyte. The solid-state crystal structure of its platinum analogue shows a covantly-bound and a weakly coordinative nitrate. In solution, the latter dissociates readily to give a 1:1 ionic complex, which is consistent with that proposed for **4a**. Metathesis of **4a** with  $\text{NH}_4\text{PF}_6$  in MeOH conveniently gives an orange-red precipitate of  $[\text{PbPd}_2(\text{NO}_3)(\text{dppf})_2(\mu_3\text{-S})_2](\text{PF}_6)$ , **4b**.



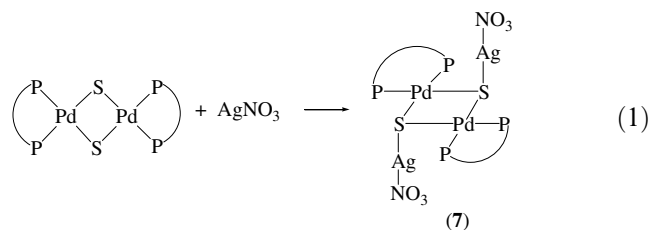
$\text{SnF}_4$  and  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (1:1) react similarly to give orange-red  $[\text{SnF}_4\text{Pd}_2(\text{dppf})_2(\mu_3\text{-S})_2]$  (**5**). The single  $^{31}\text{P}\text{-}\{^1\text{H}\}$  NMR resonance ( $\delta\ 27.5\text{ ppm}$ ) infers that the phosphines are equivalent. Molar conductivity measurement indicates that it is neutral in MeOH. These pointed to a direct adduct rather than redox or dissociative product.



$\text{BiCl}_3$  reacts readily with  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (1:1) to give orange  $[\text{BiPd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]\text{Cl}$  (**6a**). The phosphines are equivalent ( $\delta\ ^{31}\text{P}\ 26.1\text{ ppm}$ ). Conductivity in MeOH shows that it is a typical 1:1 electrolyte. It can be metathesized with  $\text{NH}_4\text{PF}_6$  to give a red precipitate viz.  $[\text{BiPd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2](\text{PF}_6)$  ( $\delta\ ^{31}\text{P}\ 26.2\text{ ppm}$ ) (**6b**). Similar reaction of  $\text{BiCl}_3$  with  $[\text{Pt}_2(\text{PPh}_3)_4(\mu\text{-S})_2]$  gave both neutral adduct  $[\text{BiPt}_2\text{Cl}_3(\text{PPh}_3)_4(\mu_3\text{-S})_2]$  and ionic product  $[\text{BiPt}_2\text{Cl}_2(\text{PPh}_3)_4(\mu_3\text{-S})_2]\text{Cl}$  [13].



We have reported earlier that late-metal precursors LMX (M = Ag(I), Au(I); L = 2-e donors e.g.  $\text{PR}_3$  and  $\text{Me}_2\text{S}$ ; X = halide or pseudohalide) react with  $\text{Pt}_2\text{L}_4(\mu\text{-S})_2$  to give the corresponding  $d^8\text{-}d^{10}$  heterometallic species [14]. To verify that similar Pd(II) species can be assembled, we selected two reactions as representative studies that could give the  $\{\text{Pd}_2\text{M}_2\text{S}_2\}$  (M = Ag (**7**) and Au (**8**)) core.  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  was treated with  $\text{AgNO}_3$  in a molar ratio of 1:2 (Eq. 1) to give  $\text{Ag}_2\text{Pd}_2(\text{NO}_3)_2(\text{dppf})_2(\mu_3\text{-S})_2$  (**7**) which is identified by NMR, IR, conductivity and elemental analyses. The coordinated nitrate groups are verified by a strong IR band at  $1384\text{ cm}^{-1}$ . The molar conductivity measurements in MeOH shows the neutral nature of the compound. The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonance peak of the Pd-coordinated phosphines occurs at 26.1 ppm. The single resonance peak infers that all phosphine groups are palladium-bound, equivalent and there is no facile migration to the Ag(I) centers.



The crystal structure of **7** reveals a flat  $\{\text{Pd}_2\text{S}_2\}$  core with two  $\text{AgNO}_3$  “residues” anchored at the basic sulfur atoms above and below the plane (Fig. 3). The *anti* arrangement of the two  $\text{AgNO}_3$  groups precludes Ag–Ag bond formation. An alternative view of the aggregate is a planar tetranuclear (Fig. 4)  $\{\text{Ag}_2\text{Pd}_2\}$  aggregate in which two isosceles  $\{\text{AgPd}_2\}$  triangles are juxtaposed above and below by the two  $\mu_3\text{-sulfide}$  without direct

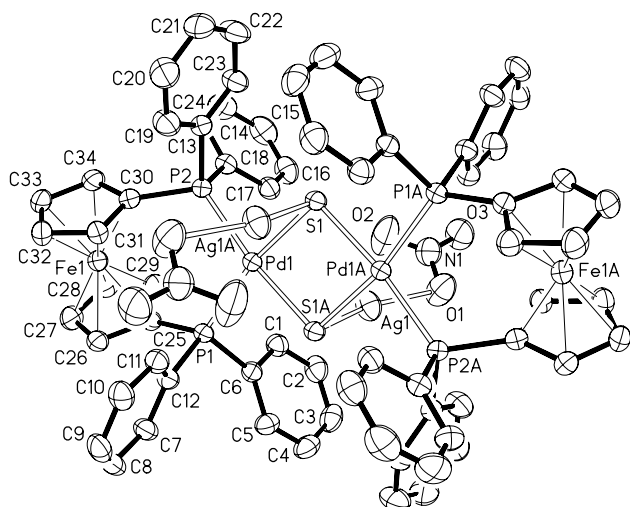


Fig. 3. ORTEP plot of the molecular structure of (7) (30% thermal ellipsoids and solvate removed for clarity). Selected bond distances (Å) and angles (°): Pd(1)–P(2) 2.3210(8), Pd(1)–P(1) 2.3326(9), Pd(1)–S(1) 2.3614(9), Pd(1)–S(1A) 2.3690(8), Pd(1)–Ag(1A) 3.0753(6), Pd(1)–Ag(1) 3.2305(6), Ag(1)–O(1) 2.250(4), Ag(1)–S(1A) 2.3732(10), Ag(1)–Pd(1A) 3.0753(6); S(1)–Pd(1)–S(1A) 81.95(3), Pd(1)–S(1)–Pd(1A) 98.05(3), S(1)–Pd(1)–Ag(1A) 49.66(3), S(1A)–Pd(1)–Ag(1A) 80.62(3), P(2)–Pd(1)–Ag(1) 130.15(2), P(1)–Pd(1)–Ag(1) 94.66(3), S(1)–Pd(1)–Ag(1) 77.44(3), S(1A)–Pd(1)–Ag(1), 47.11(2), Ag(1A)–Pd(1)–Ag(1) 111.058(14), S(1A)–Ag(1)–Pd(1A) 49.33(2), S(1A)–Ag(1)–Pd(1) 47.01(2), Pd(1)–S(1)–Ag(1A) 81.01(3), Pd(1A)–S(1)–Ag(1A) 85.88(3).

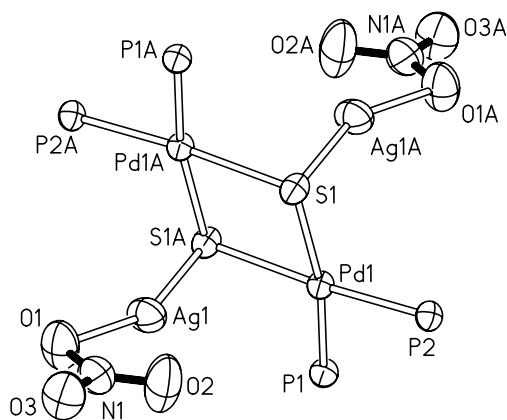
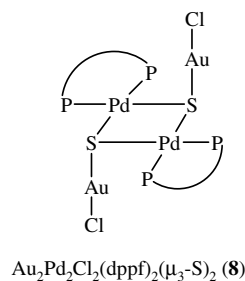


Fig. 4. Perspective view of the core in compound (7) and thermal ellipsoids are plotted at 30% probability level.

metal–metal bond. The dppf maintains at chelating positions at the Pd(II), instead of the alternative of bridging the heterometallic Ag··Pd axis. The  $[\text{Ag}_2\text{Pd}_2\text{S}_2]$  molecular frame thus collectively forms a distorted octahedral core. The stability of this frame is mainly achieved through the strong Ag–S (2.3732(10) Å) and Pd–S (2.3614 Å, ave.) bonds. The former is notably stronger than the Ag–S bonds in  $[\text{AgPt}_2\text{Cl}(\text{CO})(\text{PPh}_3)_3(\mu_3\text{-S})]$  [3a] (2.427(3) Å) and  $[\text{AgPt}_2(\text{PPh}_3)_5-$

$(\mu_3\text{-S})_2]\text{PF}_6$  (2.479(1) and 2.585(1) Å) [3a], whereas the latter is comparable to the Pd–S bonds in  $[\text{Ag}_2\text{Pd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]$  (2.397(1) Å). Likewise, the Ag–O bond (2.250(4) Å) is shorter, and presumably stronger, than covalent Ag–O bonds in  $[\text{Ag}(\text{NO}_3)(\text{dppf})_2 \cdot \text{CHCl}_3]$  (2.476(8), 2.80(1) and 2.873(7) Å) [15]. The short Ag··Pd contacts  $[\text{Ag}(1) \cdots \text{Pd}(1)$  3.2305(6) Å,  $\text{Ag}(1\text{A}) \cdots \text{Pd}(1)$  = 3.0753(6) Å] are common among these aggregates and not necessarily indicative of active M–M bonds.

Complex 7 and  $[\text{Ag}_2\text{Pd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]$  share a common feature in that they are assembled by functionalizing a  $\{\text{Pd}_2\text{S}_2\}$  metal plane with two Ag(I) “molecular tails”. Kinetically, the formation of 7 is more facile compared to that of  $[\text{Ag}_2\text{Pd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]$ , largely because of the better solubility of  $\text{AgNO}_3$  than  $\text{AgCl}$ . This plane-metallation strategy can be extended to the Au(I) residues. Similar experiments on  $\text{Pd}_2(\text{dppf})_2(\mu_3\text{-S})_2$  with  $\text{AuCl}(\text{SMe}_2)$  also yields an orange-red crystalline  $\text{Au}_2\text{Pd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2$  (8). The  $^{31}\text{P}\{-^1\text{H}\}$  NMR, conductivity measurement and elemental analyses suggest that it is analogous to its Ag(I) analogue.



The Pd–S and Ag–S bonds as well as the M–S–M angles between  $[\text{Ag}_2\text{Pd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2]$  and 7 are similar. Their  $^{31}\text{P}\{-^1\text{H}\}$  NMR shifts ( $\delta = 25.5$  ppm to  $\delta = 26.1$  ppm when  $\text{Cl}^-$  is replaced by  $\text{NO}_3^-$ ) are also comparable. This group of complexes is isostructural, with the ligand on the heterometal viz. Ag(I) or Au(I) imposing little effect on the core structures. Other similar aggregates can be assembled and their functions can then be tailored by designing different ligands on the heterometals. The “molecular tails” are propagating along the same axis, roughly perpendicular to the Pd plane, but in opposite directions. This is fundamentally different from other  $d^8$ – $d^{10}$  aggregates [16] in which the heterometals  $M'$  ( $M' = d^{10}$  Au(I) and Ag(I)) are *syn* orientated with respect to the  $\{\text{M}_2\text{S}_2\}$  ( $M = d^8$  Pt(II) and Pd(II)) plane and hence permitting  $M'\text{--}M'$  bonding interactions. Such  $M'\text{--}M'$  active interaction would give more cluster traits to these aggregates. It also supplements the capping sulfides in contributing actively to their overall stability of the aggregate framework. The *syn* positioning of

the heterometals however do not necessarily impose the presence of M'–M' bonds, as evidenced in the  $d^8$ – $d^{12}$  assemblies [14].

The synthesis of **1** and other intermetallic assemblies between  $d^8$  and  $p^{1-3}$  metals suggest clearly that numerous metal combinations are possible, depending on functional needs. The value of such assemblies lies not only on the metal choice, but also the range of ligands that can be incorporated on the heterometal. This is further demonstrated in the heterometallic assembly between the  $d^8$  and  $d^{10}$  metals, although the resultant structural forms are different. These collectively point to a general strategy in which different moieties can be assembled on the metal aggregate (at the silver sites as in **7** or the indium site as in **1**), from which we can derive other functions and functionalities on the metal framework. Current initiatives at our laboratory are directed at harnessing the lability of the ligand on the heterometal, e.g. nitrate in **7** or chloride in **1**, from which we can expose and activate the metal center to receive other metal or non-metal fragments. Realization of this concept would lead us to the assembly of other polyhetero-intermetallic metal aggregates that are not accessible via the currently known methods.

## 2. Experimental

Although the compounds are generally air-stable, all manipulations were routinely carried out under dry argon atmosphere using freshly-distilled dried solvents. Preparation of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  was reported earlier [17]. Further experiments suggested that this complex has appreciable solubility in toluene. The preparation is therefore best carried out in toluene from which the product can be extracted and precipitated. Other substrates are commercially available materials and generally used as supplied. Infrared spectra were obtained from running the sample in KBr discs on the Shimadzu IR-470 spectrometer. All NMR spectra were recorded at 25 °C on a Bruker ACF 300 spectrometer.  $^1\text{H}$  spectra were run at 299.96 MHz and  $(\text{CH}_3)_4\text{Si}$  was used as an internal standard.  $^{31}\text{P}$   $\{^1\text{H}\}$  spectra were run at 121.49 MHz and 85%  $\text{H}_3\text{PO}_4$  was used as an external reference. Conductivities were measured using a Horiba ES-12 conductivity meter. Elemental analyses were performed by at the microanalytical laboratory of the National University of Singapore. The crystals of  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 3\text{CH}_2\text{Cl}_2$  (**1**) and  $[\text{Ag}_2\text{Pd}_2(\text{NO}_3)_2(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 2\text{CH}_2\text{Cl}_2$  (**7**) used for analysis was mounted inside a Lindemann glass capillary filled with Vaseline to prevent loss of co-crystallized solvent molecules. Intensity data were collected at The Chinese University of Hong Kong on an MSC/Rigaku RAXI IIC imaging plate system using graphite-monochromatized Mo- $\text{K}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) [18]. The determina-

tion of crystal class, orientation matrix and cell dimensions was performed according to established procedures. All data processings were performed on a PC 486 with the SHELXTL-PC program package [19]. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated [20]. The raw data were processed with the learnt-profile procedure [21] and absorption corrections were applied using an algorithm which based on the correction of equivalent reflections [22]. The structures were solved with the Patterson superposition method. The positions of all hydrogen atoms were generated geometrically (C–H bonds fixed at 0.096 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms. Crystal data, data collection parameters and the results of the analysis are listed in Table 1. The structure of **1** consists of well separated molecules of  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2]$  with occluded solvent molecules best modeled as  $3\text{CH}_2\text{Cl}_2$  molecules with partial occupancies. Complex **7** is crystallized in a space group  $P\bar{1}$  without any disorder.

### 2.1. Synthesis of $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2]$ (**1**)

A mixture of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (0.12 g, 0.09 mmol) and  $\text{InCl}_3$  (0.02 g, 0.09 mmol) was suspended in THF (20 ml) and stirred for 6 h at r.t. The suspension turned into an orange-red solution, which was filtered. The filtrate was stripped of the solvent under vacuum and the residue was extracted into  $\text{CH}_2\text{Cl}_2$  (20 ml), and filtered. Partial evaporation accompanied by hexane addition gave orange-red crystals of  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2]$ , **1**, which could be further purified from a mixture of  $\text{CH}_2\text{Cl}_2$ /hexane (0.056 g, 40%). Anal. Found: C, 50.05; H, 3.63; Cl, 6.93; Fe, 6.08; In, 6.62; P, 7.61; Pd, 11.31; S, 3.66. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{Cl}_3\text{Fe}_2\text{P}_4\text{Pd}_2\text{S}_2\text{In}$  (1606.9): C, 50.83; H, 3.51; Cl, 6.62; Fe, 6.95; In, 7.15; P, 7.71; Pd, 13.25; S, 3.99. The elemental analysis suggested the sample is  $[\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 1.5 \text{CH}_2\text{Cl}_2$ .  $^{31}\text{P}$ – $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 26.1$  ppm (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 7.87$ – $7.17$  ppm (m, 40H,  $\text{C}_6\text{H}_5$ ),  $\delta = 4.40$  ppm (s, 8H,  $\text{C}_3\text{H}_4$ ),  $\delta = 4.24$  ppm (s, 8H,  $\text{C}_5\text{H}_4$ ).  $\Lambda_m$  ( $10^{-3} \text{ M}$ , MeOH) =  $21.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ . Single crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of **1**.

### 2.2. Synthesis of $[\text{GaPd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2][\text{GaCl}_4]$ (**2**)

A mixture of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (0.12 g, 0.09 mmol) and  $\text{GaCl}_3$  (0.03 g, 0.18 mmol) was suspended in THF (20 ml) and stirred for 4 h at room temperature. The resultant orange-red solution was treated similarly as above to yield  $[\text{GaPd}_2\text{Cl}_2(\text{dppf})_2(\mu_3\text{-S})_2][\text{GaCl}_4]$  (0.09 g, 60%). Anal. Found: C, 46.95; H, 3.29; Cl, 12.22; Fe, 5.90; Ga, 7.48; P, 7.42; Pd, 11.11; S, 3.59. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{Fe}_2\text{Ga}_2\text{Cl}_6\text{P}_4\text{Pd}_2\text{S}_2$  (1737.89): C, 47.00; H, 3.25;

Table 1

Crystallographic data for  $\text{InPd}_2\text{Cl}_3(\text{dppf})_2(\mu_3\text{-S})_2 \cdot 3\text{CH}_2\text{Cl}_2$  (**1**) and  $[\text{Ag}_2\text{Pd}_2(\text{NO}_3)_2(\text{dppf})_2(\mu_3\text{-S})_2] \cdot 2\text{CH}_2\text{Cl}_2$  (**7**)

	Compound <b>1</b>	Compound <b>7</b>
Molecular formula	$\text{C}_{71}\text{H}_{62}\text{Cl}_9\text{Fe}_2\text{InP}_4\text{Pd}_2\text{S}_2$	$(\text{C}_{35}\text{H}_{30}\text{AgCl}_2\text{FeNO}_3\text{P}_2\text{PdS})_2$
Molecular weight	1861.58	1895.24
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Triclinic
Space group	$P_1/n$	$P\bar{1}$
Unit cell parameters	$a = 13.517(10)$ Å, $\alpha = 90^\circ$ $b = 24.268(10)$ Å, $\beta = 92.03(10)^\circ$ $c = 22.648(10)$ Å; $\gamma = 90^\circ$	$a = 11.456(10)$ Å, $\alpha = 77.19(10)^\circ$ $b = 11.835(10)$ Å, $\beta = 78.81(10)^\circ$ $c = 14.287(10)$ Å, $\gamma = 68.09(10)^\circ$
Volume, Z	7424.6(7) Å <sup>3</sup> , 4	1739.1(2) Å <sup>3</sup> , 1
Density (calculated)	1.665 mg m <sup>-3</sup>	1.810 mg m <sup>-3</sup>
Absorption coefficient $\mu$	1.670 mm <sup>-1</sup>	1.824 mm <sup>-1</sup>
$F(0\ 0\ 0)$	3704	940
Crystal size	0.30 mm × 0.24 mm × 0.18 mm	0.25 mm × 0.22 mm × 0.18 mm
$\theta$ range for data collected	1.73 to 26.73°	2.19 to 27.18°
Limiting indices	$16 \geq h \geq 0$ , $30 \geq k \geq -30$ , $28 \geq l \geq -28$	$13 \geq h \geq -14$ , $0 \geq k \geq -14$ , $17 \geq l \geq -18$
Reflection collected	20430	6764
Independent reflection	12092 ( $R_{\text{int}} = 0.0569$ )	6764 ( $R_{\text{int}} = 0.0000$ )
Refinement method	Full-matrix least-squares on $F^2$	Full-matrix least-squares on $F^2$
Data/restraints/parameters	11966/2/821	6557/0/425
Goodness-of-fit on $F^2$	1.425	1.073
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0642$ , $wR_2 = 0.1952$	$R_1 = 0.0411$ , $wR_2 = 0.1130$
$R$ indices (all data)	$R_1 = 0.0663$ , $wR_2 = 0.1956$	$R_1 = 0.0424$ , $wR_2 = 0.1142$
Extinction coefficient	0.0034(3)	0.0369(18)
Largest differential peak and hole	1.042 and $-1.132$ e Å <sup>-3</sup>	0.633 and $-0.782$ e Å <sup>-3</sup>

Cl, 12.24; Fe, 6.43; Ga, 8.02; P, 7.13; Pd, 12.25; S, 3.69.  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta\delta = 30.4$  ppm (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 7.65\text{--}7.16$  ppm (m, 40H),  $\delta = 4.51$  ppm (4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.50$  ppm (4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.44$  ppm (4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.08$  ppm (4H,  $\text{C}_5\text{H}_4$ ).  $\Lambda\text{m}$  ( $10^{-3}$  M, MeOH) =  $74.8 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

### 2.3. Synthesis of $[\text{TlPd}_2(\text{dppf})_2(\mu_3\text{-S})_2]X$ (**3**) ( $X = \text{NO}_3, \text{PF}_6$ )

A mixture of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (0.10 g, 0.07 mmol) and  $\text{TlNO}_3$  (0.02 g, 0.07 mmol) in THF (20 ml) was stirred for 4 h at r.t. and treated as above to yield  $[\text{TlPd}_2(\text{dppf})_2(\mu_3\text{-S})_2][\text{NO}_3]$  (0.054 g, 45%). Found: C, 48.70; H, 3.57; Fe, 5.54; N, 0.64; P, 6.95; Pd, 11.13; S, 3.48; Tl, 10.94. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{Fe}_2\text{NO}_3\text{P}_4\text{Pd}_2\text{S}_2\text{Tl}$  (1652.12): C, 49.44; H, 3.42; Fe, 6.76; N, 0.85; P, 7.50; Pd, 12.88; S, 3.88; Tl, 12.37.  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 22.0$  ppm (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 7.54\text{--}7.14$  ppm (m, 40H,  $\text{C}_6\text{H}_5$ ),  $\delta = 4.34$  ppm (s, 8H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.16$  ppm (s, 8H,  $\text{C}_5\text{H}_4$ ). IR (KBr):  $1384 \text{cm}^{-1}$  (uncoordinated  $\text{NO}_3^-$ ).  $\Lambda\text{m}$  ( $10^{-3}$  M, MeOH) =  $83.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . The  $\text{PF}_6^-$  salt was prepared by metathesis with  $\text{NH}_4\text{PF}_6$  in MeOH. Anal. Found: C, 47.37; H, 3.16; S, 3.48. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{F}_6\text{Fe}_2\text{P}_5\text{Pd}_2\text{S}_2\text{Tl}$  (1735.07): C, 47.07; H, 3.25; S, 3.70.  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 22.1$  ppm (from dppf),  $\delta = -126.9$  ppm,  $\delta = -132.7$  ppm,  $\delta = -138.6$  ppm,  $\delta = -144.4$  ppm,  $\delta = -150.3$  ppm,  $\delta = 156.1$  ppm,  $\delta = -161.9$  ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 7.54\text{--}7.14$  ppm (m, 40H,  $\text{C}_6\text{H}_5$ ),

$\delta = 4.34$  ppm (s, 8H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.16$  ppm (s, 8H,  $\text{C}_5\text{H}_4$ ). IR (KBr):  $840 \text{cm}^{-1}$  ( $\text{PF}_6^-$ ).  $\Lambda\text{m}$  ( $10^{-3}$  M, MeOH) =  $80.4 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $\Lambda\text{m}$  ( $10^{-3}$  M,  $\text{CH}_3\text{NO}_2$ ) =  $86.7 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .

### 2.4. Synthesis of $[\text{PbPd}_2(\text{NO}_3)(\text{dppf})_2(\mu_3\text{-S})_2]X$ (**4**) ( $X = \text{NO}_3, \text{PF}_6$ )

A mixture of  $\text{Pd}_2(\text{dppf})_2(\mu\text{-S})_2$  (0.14 g, 0.10 mmol) and  $\text{Pb}(\text{NO}_3)_2$  (0.033 g, 0.10 mmol) in THF (20 ml) was stirred for 4 h at r.t. to give an orange-red solution and treated as above to yield  $[\text{PbPd}_2(\text{NO}_3)(\text{dppf})_2(\mu_3\text{-S})_2][\text{NO}_3]$  (0.11 g, 65%). Anal. Found: C, 47.33; H, 3.42; Fe, 5.83; N, 0.90; P, 7.15; Pb, 11.82; Pd, 10.97; S, 3.68. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{Fe}_2\text{N}_2\text{O}_6\text{P}_4\text{PbPd}_2\text{S}_2$  (1716.94): C, 47.57; H, 3.29; Fe, 6.51; N, 1.63; P, 7.22; Pb, 12.07; Pd, 12.40; S, 3.74.  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 23.6$  ppm (s).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 8.01\text{--}7.07$  ppm (m, 40H,  $\text{C}_6\text{H}_5$ ),  $\delta = 4.95$  ppm (s, 4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.47$  ppm (s, 4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 4.18$  ppm (s, 4H,  $\text{C}_5\text{H}_4$ ),  $\delta = 3.83$  ppm (s, 4H,  $\text{C}_5\text{H}_4$ ). IR (KBr):  $1384 \text{cm}^{-1}$  (uncoordinated  $\text{NO}_3^-$ ).  $\Lambda\text{m}$  ( $10^{-3}$  M, MeOH) =  $84.8 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . The  $\text{PF}_6^-$  salt was prepared by metathesis with  $\text{NH}_4\text{PF}_6$  in MeOH. Anal. Found: C, 45.32; H, 3.28; N, 0.07; S, 3.84. Calcd. For  $\text{C}_{68}\text{H}_{56}\text{F}_6\text{Fe}_2\text{NO}_3\text{P}_5\text{PbPd}_2\text{S}_2$  (1799.9): C, 45.38; H, 3.14; N, 0.78; S, 3.56.  $^{31}\text{P}\{-^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 23.5$  ppm (from dppf),  $\delta = -126.9$  ppm,  $\delta = -132.7$  ppm,  $\delta = -138.6$  ppm,  $\delta = -144.4$  ppm,  $\delta = -150.3$  ppm,  $\delta = 156.1$  ppm,  $\delta = -161.9$  ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta = 8.01\text{--}$

7.07 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 4.95 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.47 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.18 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 3.83 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>). IR (KBr): 840 cm<sup>-1</sup> (PF<sub>6</sub><sup>-</sup>).  $\Lambda_m$  (10<sup>-3</sup> M, MeOH) = 87.2  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.  $\Lambda_m$  (10<sup>-3</sup> M, CH<sub>3</sub>NO<sub>2</sub>) = 124.9  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

### 2.5. Synthesis of [Pd<sub>2</sub>SnF<sub>4</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub> (5)

A mixture of Pd<sub>2</sub>(dppf)<sub>2</sub>( $\mu$ -S)<sub>2</sub> (0.14 g, 0.10 mmol) and SnF<sub>4</sub> (0.02 g, 0.10 mmol) in THF (20 ml) was stirred for 6 h at r.t. to give a red solution, which was treated as above to give orange-red crystals of [Pd<sub>2</sub>SnF<sub>4</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>] · CH<sub>2</sub>Cl<sub>2</sub> (0.066 g, 40%). Anal. Found: C, 49.75; H, 3.64; F, 4.33; Fe, 6.10; Sn, 8.84; P, 7.82; Pd, 11.27; S, 3.81. Calcd. For C<sub>69</sub>H<sub>58</sub>Cl<sub>2</sub>F<sub>4</sub>Fe<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>S<sub>2</sub>Sn (1665.36): C, 49.76; H, 3.51; F, 4.56; Fe, 6.71; Sn, 7.13; P, 7.44; Pd, 12.78; S, 3.85. <sup>31</sup>P-<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 27.5 ppm (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 7.86–7.08 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 4.88 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.41 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.21 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 3.86 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>).  $\Lambda_m$  (10<sup>-3</sup> M, MeOH) = 24.6  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

### 2.6. Synthesis of [BiPd<sub>2</sub>Cl<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>]X (6) (X = Cl, PF<sub>6</sub>)

A mixture of Pd<sub>2</sub>(dppf)<sub>2</sub>( $\mu$ -S)<sub>2</sub> (0.12 g, 0.09 mmol) and BiCl<sub>3</sub> (0.027 g, 0.09 mmol) in THF (20 ml) was stirred for 4 h at r.t. to give a red solution which was filtered and stripped of the solvent. The residue was washed twice with hexane (20 ml), dried and crystallized from CH<sub>2</sub>Cl<sub>2</sub>/hexane to obtain red crystalline [BiPd<sub>2</sub>Cl<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>]Cl · CH<sub>2</sub>Cl<sub>2</sub> (0.072 g, 50%). Anal. Found: C, 46.22; H, 3.38; Bi, 13.20; Cl, 9.88; Fe, 5.74; P, 6.94; Pd, 11.43; S, 4.11. Calcd. For: C<sub>69</sub>H<sub>58</sub>BiCl<sub>3</sub>Fe<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>S<sub>2</sub> (1786): C, 46.40; H, 3.27; Bi, 11.70; Cl, 9.93; Fe, 6.25; P, 6.94; Pd, 11.92; S, 3.59. <sup>31</sup>P-<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 26.1 ppm (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 7.9–7.1 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 5.1 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.5 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.38 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 3.9 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>).  $\Lambda_m$  (10<sup>-3</sup> M, MeOH) = 82.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. The PF<sub>6</sub><sup>-</sup> salt was prepared by metathesis with NH<sub>4</sub>PF<sub>6</sub> in MeOH. Anal. Found: C, 44.87; H, 3.01; S, 3.43. Calcd. For C<sub>68</sub>H<sub>56</sub>BiCl<sub>2</sub>F<sub>6</sub>Fe<sub>2</sub>P<sub>5</sub>Pd<sub>2</sub>S<sub>2</sub> (1810.58): C, 45.11; H, 3.12; S, 3.54. <sup>31</sup>P-<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 26.2 ppm (from dppf),  $\delta$  = -126.9 ppm,  $\delta$  = -132.7 ppm,  $\delta$  = -138.6 ppm,  $\delta$  = -144.4 ppm,  $\delta$  = -150.3 ppm,  $\delta$  = 156.1 ppm,  $\delta$  = -161.9 ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 7.9–7.1 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 5.1 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.5 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 4.38 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>),  $\delta$  = 3.9 ppm (s, 4H, C<sub>5</sub>H<sub>4</sub>). IR (KBr): 845 cm<sup>-1</sup> (PF<sub>6</sub><sup>-</sup>).  $\Lambda_m$  (10<sup>-3</sup> M, MeOH) = 79.6  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.  $\Lambda_m$  (10<sup>-3</sup> M, CH<sub>3</sub>NO<sub>2</sub>) = 90.3  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

### 2.7. Synthesis of [Ag<sub>2</sub>Pd<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>] · 2CH<sub>2</sub>Cl<sub>2</sub> (7)

A mixture of Pd<sub>2</sub>(dppf)<sub>2</sub>( $\mu$ -S)<sub>2</sub> (0.14 g, 0.10 mmol) and AgNO<sub>3</sub> (0.034 g, 0.20 mmol) was stirred in THF (20 ml) for 4 h at r.t. to give an orange-red solution, which was treated similarly as **1** to give [Ag<sub>2</sub>Pd<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>]. The product was purified by carefully layer hexane on a CH<sub>2</sub>Cl<sub>2</sub> solution of the sample, which eventually yielded crystalline [Ag<sub>2</sub>Pd<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub>] · 2CH<sub>2</sub>Cl<sub>2</sub> (0.085 g, 50%). Anal. Found: C, 43.91; H, 3.00; N, 1.09; Ag, 11.00; Fe, 5.66; P, 7.36; Pd, 9.93; S, 3.39. Calcd. For C<sub>70</sub>H<sub>60</sub>Ag<sub>2</sub>Cl<sub>4</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>P<sub>4</sub>Pd<sub>2</sub>S<sub>2</sub> (1895.34): C, 44.36; H, 3.19; N, 1.48; Ag, 11.38; Fe, 5.89; P, 6.54; Pd, 11.23; S, 3.38. <sup>31</sup>P-<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 26.1 ppm (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 7.62–7.36 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 4.28 ppm (s, 16H, C<sub>5</sub>H<sub>4</sub>). IR (KBr): 1384 cm<sup>-1</sup> (uncoordinated NO<sub>3</sub><sup>-</sup>), 1283 and 1267 cm<sup>-1</sup> (coordinated NO<sub>3</sub><sup>-</sup>).  $\Lambda_m$  (10<sup>-3</sup> M, MeOH) = 132.8  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. Single crystals of X-ray quality of **7** were grown by slow diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution of the compound.

### 2.8. Synthesis of Au<sub>2</sub>Pd<sub>2</sub>Cl<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub> (8)

A mixture of Pd<sub>2</sub>(dppf)<sub>2</sub>( $\mu$ -S)<sub>2</sub> (0.10 g, 0.07 mmol) and AuCl(SMe<sub>2</sub>) (0.04 g, 0.14 mmol) in THF (20 ml) was stirred for 3 h at r.t. and then treated similarly to **1** to yield Au<sub>2</sub>Pd<sub>2</sub>Cl<sub>2</sub>(dppf)<sub>2</sub>( $\mu_3$ -S)<sub>2</sub> (0.092 g, 50%). Anal. Found: C, 43.77; H, 2.85; Au, 17.02; Cl, 4.04; Fe, 5.43; P, 7.03; Pd, 10.24; S, 3.57. Calcd. For C<sub>68</sub>H<sub>56</sub>Au<sub>2</sub>Cl<sub>2</sub>Fe<sub>2</sub>P<sub>4</sub>Pd<sub>2</sub>S<sub>2</sub> (1850.57): C, 44.13; H, 3.05; Au, 21.29; Cl, 3.83; Fe, 6.04; P, 6.69; Pd, 11.50; S, 3.47. <sup>31</sup>P-<sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 20.7 ppm (s). <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  = 7.39 ppm (m, 40H, C<sub>6</sub>H<sub>5</sub>),  $\delta$  = 4.29 ppm (s, 16H, C<sub>5</sub>H<sub>4</sub>).

## 3. Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Centre, CCDC Nos. 252923 and 252922 for complexes **1** and **7**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2, 1EZ, UK (fax: +44-1233-336-033; e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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