Heteropolymetallic aggregates from $[Pd_2(dppf)_2(\mu\text{-}S)_2]$. Bonding and structural analysis of $[Ag_2Pd_2Cl_2(dppf)_2(\mu_3\text{-}S)_2]\cdot 4CH_2Cl_2$ [dppf = $Fe(C_5H_4PPh_2)_2$]—a flat $\{Pd_2S_2\}$ core with two AgCl 'tails' †

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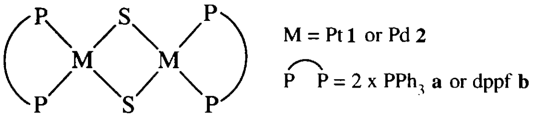
Nucleophilic addition of the heterometallic complex $[Pd_2(dppf)_2(\mu\text{-}S)_2]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene] to $[AgCl(PPh_3)]$ or AgCl gave $[Ag_2Pd_2Cl_2(dppf)_2(\mu_3\text{-}S)_2]$, the first example of a heteropolymetallic aggregate based on a $\{Pd_2S_2\}$ core and whose crystal structure shows a planar $\{Pd_2S_2\}$ ring with two protruding AgCl fragments.

Ever since Mingos and co-workers[1] reported the nucleophilicity of $[Pt_2(PPh_3)_4(\mu\text{-}S)_2]$[2] **1a** towards $AgBF_4$, giving an unusual hexanuclear complex with a Ag^I–Ag^I bond, a host of hetero-[3] and inter-metallic[4] aggregates based on the $\{Pt_2S_2\}$ core has emerged. Such facile entry to mixed-metal materials makes **1a** an invaluable metalloligand and probably the most versatile precursor in the synthesis of heterometallic sulfide complexes.[5] The development of an electrochemically active ferrocenyl phosphine [1,1′-bis(diphenylphosphino)ferrocene = dppf] derivative[6] **1b** fuels further research in this area. The Pd analogue of **1a**, on the contrary, is poorly characterized[7] and its chemistry virtually unknown. In view of the fascinating structural diversity and catalytic potential of these mixed-metal aggregates,[5,8] we intend to develop similar heterometalloligand chemistry of the Pd analogues on the basis that electronically related Pd and Pt clusters are rarely isostructural. We herein report the synthesis of a suitable Pd precursor, $[Pd_2(dppf)_2(\mu\text{-}S)_2]$ **2b**, and demonstrate a direct entry into heteropolymetallic aggregate chemistry using Ag^+ as a model. The distinctive structural features of the Ag–Pd aggregate are described.

Attempts to prepare pure $[Pd_2(PPh_3)_4(\mu\text{-}S)_2]$ **2a** were plagued by the lability of the phosphine. This problem was circumvented by replacing PPh_3 with a chelating phosphine, dppf, which is an established co-catalyst.[9] A suspension of $[PdCl_2(dppf)]$ with Na_2S in benzene readily yields **2b**.‡ Like its Pt analogues, its decomposition in chlorinated solvents gives the first indication of its high nucleophilicity.[10] With AgCl, **2b** gives a heterometallic aggregate formulated as $[Ag_2Pd_2Cl_2(dppf)_2(\mu_3\text{-}S)_2]$ **3**.§ Single-crystal X-ray crystallographic analysis shows an unusual structure consisting of a $\{Pd_2S_2\}$ molecular square with two AgCl 'tails' dangling from the sulfur sites on opposite faces of the plane (Fig. 1).¶ It may be viewed as a $\{Pd_2S_2\}$ metalloligand bridging two AgCl moieties or collectively as a $\{Ag_2Pd_2S_2\}$ near-octahedral frame. With a chelating dppf molecule on each Pd atom, the complex is formally hexametallic comprising three different metals. Without active M–M bonds, **3** is best described as an 'aggregate'[14] instead of a cluster.

Complex **3** has two unique structural features among the established Pt-based heteropolymetallics: (*i*) the $\{Pt_2S_2\}$ core is almost invariably hinged along the S···S axis|| whereas the $\{Pd_2S_2\}$ core is strictly flat; (*ii*) the bonding mode of $\{M_2S_2\}$ in **3** is open-bridging but is predominantly chelating in the Pt complexes.[5] These differences are best illustrated by comparing **3** with $[Ag_2Pt_4(PPh_3)_8(\mu_3\text{-}S)_4][BF_4]_2$ **4** which is similarly obtained



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‡ Compound **2b** was obtained in 65% yield from a reaction between $[PdCl_2(dppf)]$ (1.29 g, 1.77 mmol) and $Na_2S\cdot 9H_2O$ (0.43 g, 1.77 mmol) in benzene (30 cm^3) (Found: C, 58.80; H, 4.25; Fe, 7.30; P, 7.80; Pd, 14.75; S, 4.70. $C_{34}H_{28}Fe_2P_2Pd_2S_2$ requires C, 58.90; H, 4.05; Fe, 8.10; P, 8.95; Pd, 15.35; S, 4.60%). The solubility is so poor in common solvents that no satisfactory NMR data have been obtained.

§ Compound **3** was obtained in 65% yield from a reaction between **2b** (0.14 g, 0.10 mmol) and AgCl (0.03 g, 0.20 mmol) in tetrahydrofuran (20 cm^3) (Found: C, 48.65; H, 3.75; Ag, 9.60; Cl, 4.50; Fe, 6.20; P, 7.25; Pd, 11.65; S, 4.00. $C_{68}H_{56}Ag_2Cl_2Fe_2P_4Pd_2S_2$ requires C, 48.80; H, 3.35; Ag, 12.90; Cl, 4.25; Fe, 6.70; P, 7.40; Pd, 12.75; S, 3.85%). ^1H NMR ($CDCl_3$): δ 7.65–7.26 (m, 40 H, C_6H_5), 4.26 (s, 16 H, C_5H_4). ^{31}P-{H} NMR ($CDCl_3$): δ 25.5 (s). Similar reactions with $[AgCl(PPh_3)]$ gave the same product in 70% yield.

¶ Crystal data: $C_{68}H_{56}Ag_2Cl_2Fe_2P_4Pd_2S_2\cdot 4CH_2Cl_2$, crystal dimensions 0.06 × 0.08 × 0.18 mm, $M = 2012$, monoclinic, $P2_1/c$ (no. 14), $a = 13.090(1)$, $b = 20.539(1)$, $c = 15.744(1)$ Å, $\beta = 113.16(1)°$, $U = 3892(2)$ Å^3, $Z = 2$, $F(000) = 1992$, $T = 298$ K, $\rho_{calc} = 1.717$ g cm^{-3}, $\mu = 1.828$ mm^{-1}. Data collection (7755 unique data) was carried out on an MSC/Rigaku RAXI-II imaging plate system using graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) (oscillation IP photos; 60 frames in total, $\varphi = -30$ to $+150°$, $\Delta\varphi = 3°$). The structure was solved with the Patterson superposition method and refined anisotropically on F using absorption corrected data to give $R_F = 0.047$, $R_w = 0.067$, $R_F = \Sigma||F_o - |F_o||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ using 6196 observed intensities $[|F_o| \geq 4\sigma(|F_o|)]$ $[w^{-1} = \sigma^2(F) + 0.0006F^2]$. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generated geometrically (C–H 0.95 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All computations were performed with the SHELXTL PLUS-PC program package.[11] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[12] Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/309.

|| The only crystallographically established exception is $[Au_2Pt_2Cl_2(PPh_3)_4(\mu_3\text{-}S)_2]$ which shows a flat $\{Pt_2S_2\}$ core.[15]

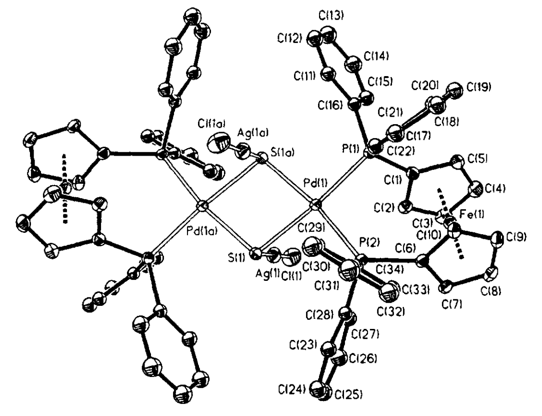
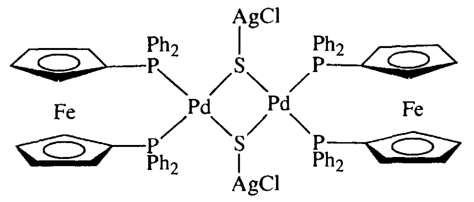


Fig. 1 ORTEP[13] plot (30% thermal ellipsoids) of $[Ag_2Pd_2Cl_2(dppf)_2(\mu_3\text{-}S)_2]\cdot 4CH_2Cl_2$ **3** (solvate removed for clarity). Selected bond distances (Å) and angles (°) Ag(1)–Cl(1) 2.348(2), Ag(1)–S(1) 2.397(1), Pd(1)–S(1) 2.382(1), Pd(1)–S(1a) 2.355(1), Pd(1)–P(1) 2.334(1), Pd(1)–P(2) 2.339(1), Cl(1)–Ag(1)–S(1) 178.1(1), S(1)–Pd(1)–S(1a) 82.7(1), P(1)–Pd(1)–P(2) 98.1(1), P(1)–Pd(1)–S(1a) 91.5(1), P(2)–Pd(1)–S(1) 87.7(1), P(2)–Pd(1)–S(1a) 169.6(1), Ag(1)–S(1)–Pd(1) 79.5(1), Ag(1)–S(1)–Pd(1a) 82.9(1), Pd(1)–S(1)–Pd(1a) 97.3(1)



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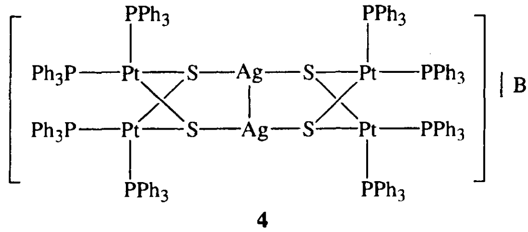

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from **1a** and $AgBF_4$ and has been crystallographically characterized.[1a] Complex **4** is ionic and comprises two $\{Pt_2S_2\}$ butterflies close-bridging two M–M bonded Ag^I atoms. The *trans* disposition of the AgCl moieties in **3**, which is covalent, forbids any direct M–M interaction. The Ag–Cl length [2.348(2) Å] is typical of a strong Ag–Cl covalent bond.[16] Complex **3** does not dissociate to give **2b** and AgCl in solution. It is formed in good yield (70%) even when AgCl is replaced by $[AgCl(PPh_3)]$ in the synthesis. Absence of the expected products $[\{(Ph_3P)Ag\}_n(\mu_3\text{-}S)_2Pd_2(dppf)_2]^{n+}nCl^-$ ($n = 1$ or 2) shows the thermodynamic stability of **3** and covalence of the Ag–Cl bond. Although **4** is easily prepared, air-stable and resistive to chlorinated solvents, we have insofar failed to isolate its Pd relative $[Ag_2Pd_4(dppf)_4(\mu_3\text{-}S)_4]^{2+}$.

In an attempt to understand the differences between **3** and **4**, some theoretical considerations based on Fenske–Hall molecular orbital calculations are discussed below.[17] Previous calculations[18] have shown that the sulfur lone pairs are directed perpendicular to the $\{M_2S_2\}$ moiety when the latter is planar. This result is consistent with the observed orientation of the AgCl fragments in **3**. On the other hand, in **4** the lone pairs must be tilted slightly inward for Ag–Ag bond formation to occur, which could partially account for the way in which the $\{Pt_2S_2\}$ moieties are hinged.

It should be noted that the introduction of Ag^I causes electron density to be drawn away from S, and hence indirectly from the Pd and P atoms as well. Since the Ag–Ag bond is an electron density sink, this flow occurs to a greater extent in the structure of **4** than in **3**, and then in the Pd- more than the Pt-analogue.[19] The latter may be an indication of the relative instability of the Pd analogue of **4**,* and perhaps accounts for the difficulty in its isolation.

Isolation of **3** demonstrates that the rich heteropolymetallic chemistry based on the $\{Pt_2S_2\}$ core can be extended to the Pd system. Our immediate task is to explore the chemical implications of the resultant aggregates which are structurally distinctive.

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* A similar result was obtained for Pt and Pd phosphine acetates,[20] Pd phosphine acetates are known to be unstable.

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