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Synthesis and characterisation of adducts of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with organo-palladium and platinum-hydride substrates

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ABSTRACT

The reactions of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a range of palladium(II) complexes containing organometallic ligands (cyclopalladated N-donor ligands, η^3-allyl, phenyl) have been explored, leading to the formation of a series of cationic, trinuclear sulfido-bridged aggregates containing $\{Pt_2PdS_2\}$ cores. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also reacts with the platinum(II) hydride complex *trans*-$[PtHCl(PPh_3)_2]$ giving the adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]^+$. X-ray crystal structure determinations on the complexes $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]PF_6$ and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]PF_6$ are reported, and show the expected bis μ_3-sulfido aggregates with three square-planar metal centres.

1. Introduction

The metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ displays considerable and varied reactivity towards a wide variety of metal- and organic-based electrophiles [1]. A range of palladium adducts of $\{Pt_2S_2\}$ metalloligands have been previously reported [2–6], but few are organometallic derivatives. The pentafluorophenyl adducts $[Pt_2(\mu\text{-}S)_2L_4Pd(C_6F_5)_2]$ [L = PPh_3, PMe_2Ph or $L_2 = Fe(\eta^5\text{-}C_5H_4PPh_2)_2$] have been prepared by reaction of the appropriate $\{Pt_2S_2\}$ metalloligand with the labile palladium precursor $[Pd(C_6F_5)_2(NCMe)_2]$ [7]. The cyclo-octa-1,5-diene (cod) adducts $[Pt_2(\mu\text{-}S)_2(PPh_3)_4M(cod)]^{2+}$ (M = Pd, Pt) have been prepared by reaction with $[MCl_2(cod)]$ substrates, resulting in displacement of chloride ligands and coordination of the $M(cod)^{2+}$ group [8]. The related triplatinum complex $[Pt_2(\mu\text{-}S)_2(dppp)_2Pt(cod)]^{2+}$ [dppp = $Ph_2P(CH_2)_3PPh_2$] has interestingly been found to undergo deprotonation of a CH_2 group instead of the more usual nucleophilic attack of solvent-derived methoxide ion at a coordinated alkene [9].

In developing the chemistry of $\{Pt_2S_2\}$ metalloligands, the technique of electrospray ionisation mass spectrometry (ESI-MS) [10] has proved to be extremely useful, being rapid and requiring only miniscule amounts of material. Information on the range of species present in solution is then used to target subsequent macroscopic syntheses [11–14]. We have recently used ESI-MS to screen the reactivity of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards a range of palladium(II) and platinum(II) halide substrates [8]. In this contribution we report on the application of this methodology to the synthesis of some organo-palladium(II) complexes, including complexes containing cyclometallated ligands. Previously we have reported analogous derivatives of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with gold(III) centres containing various cycloaurated *N,C*-donor ligands [15,16].

2. Results and discussion

$[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ reacts readily with a series of chloride- and acetate-bridged dinuclear palladium(II) substrates containing cyclopalladated ligands (*C,N*) $[PdCl(dmamp)]_2$ (dmamp = dimethyaminomethyphenyl) and substituted analogues, $[PdCl(phimid)]_2$ (phimid = 2-phenylimidazolyl), $[PdCl(bzpy)]_2$ (bzpy = 2-benzylpyridyl) and $[Pd(OAc)(\eta^2\text{-}C_6H_4PPh_2=NPh\text{-}C,N)]_2$, in methanol to give solutions containing the trimetallic aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(C,N)]^+$ **1**–**4**, respectively. $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ also reacts readily with the palladium η^3-allyl complex $[PdCl(\eta^3\text{-}C_3H_5)]_2$, the 2-pyridyl complex *trans*-$[PdBr(C_5H_4N)(PMePh_2)_2]$ and the phenyl derivative *trans*-$[PdBrPh(PPh_3)_2]$ in methanol to give the mixed-metal aggregates $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(\eta^3\text{-}C_3H_5)]^+$ **5**, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4Pd(NC_5H_4)(PMePh_2)]^+$ **6** and $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PdPh(PPh_3)]^+$ **7**, respectively. Precipitation of the cations was achieved by addition of excess NH_4PF_6, yielding the appropriate salts in reasonably good yields. The complexes are all stable and soluble in chlorinated hydrocarbon solvents such as CH_2Cl_2 and $CHCl_3$, and represent an

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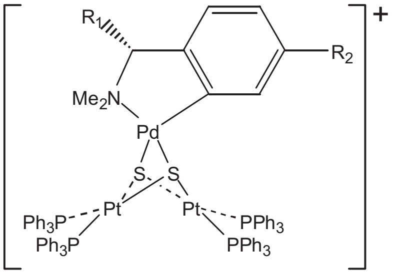
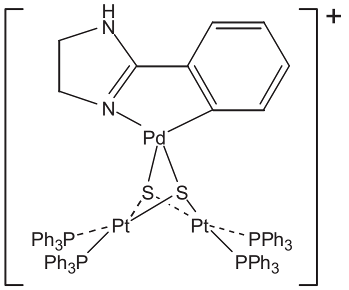
addition to the wide range of trinuclear complexes containing $\{M_3(\mu\text{-}S)_2\}$ cores (M = Pt, Pd) [3,17–20].


1a; $R_1 = R_2 = H$
1b; $R_1 = H$, $R_2 = OMe$
1c; $R_1 = Me$, $R_2 = H$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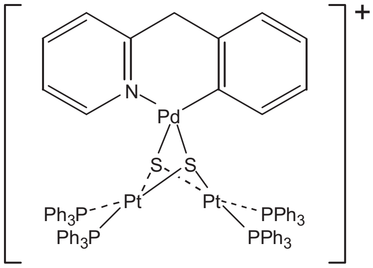
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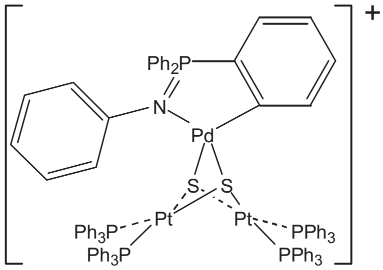
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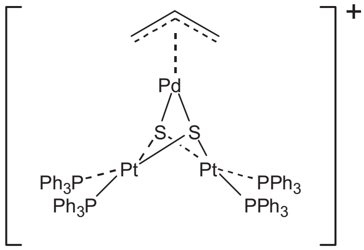
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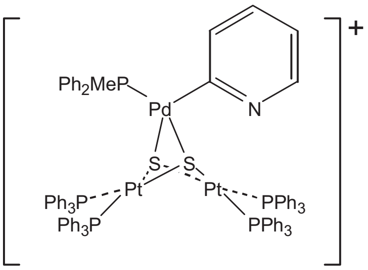
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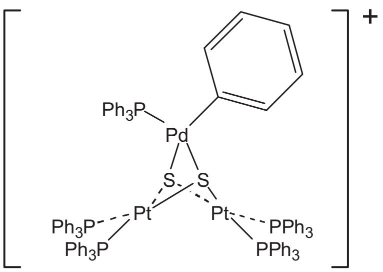
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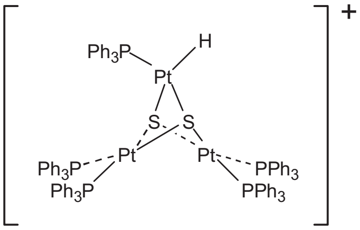
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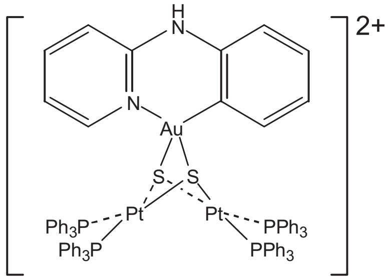
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Using the same methodology, reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with *trans*-$[PtHCl(PPh_3)_2]$ gave the new platinum-hydride adduct $[Pt_2(\mu\text{-}S)_2(PPh_3)_4PtH(PPh_3)]^+$, though the reaction proceeded slowly, and a considerable amount of unreacted $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ remained (as the bright yellow methanol solvate [21]). Refluxing the reaction mixture resulted in moderate conversion of the reactants, and the complex **8**·PF_6 was isolated from the reaction filtrate by precipitation with NH_4PF_6 as a cream powder in modest (34%) yield.

The complexes – with one exception – all show a single intense $[M]^+$ ion in their positive-ion ESI-MS spectra at low cone voltages (e.g. 20 V). The exception is complex **6** which shows an M^{2+} ion due to protonation of the pyridine nitrogen, however, microelemental analytical data support the formulation of the isolated product as being unprotonated, with a single hexafluorophosphate anion overall. At high cone voltages (e.g. 100 V) complex **6** showed the base peak at *m/z* 1887 for the $[M]^+$ ion, together with $[M{-}PMePh_2]^+$ at *m/z* 1687. The selective loss of the palladium-bound phosphine is consistent with the greater lability of palladium(II) compared to platinum(II). The other monocations are generally stable up to moderate cone voltages of 60–80 V, with the first fragmentations being either a loss of PPh_3 from the $\{Pt_2S_2PdL\}$ core (L = supporting palladium ligand), or the loss of the palladium supporting ligand and a PPh_3 resulting in $[Pt_2S_2(PPh_3)_2Pd(Ph_2PC_6H_4)]^+$ through cyclometallation of a PPh_3 ligand. To illustrate this, the effect of increasing cone voltage on complex **1c**·PF_6 is shown in Fig. 1.

The ^{31}P NMR spectra of complexes **1a**, **1b**, **2** and **3** give a single phosphorus signal with the characteristic satellites due to coupling to ^{195}Pt. Even though the organo-palladium centres in these complexes are not symmetrical with respect to the $\{Pt_2S_2\}$ ring the asymmetry is not sufficient to give rise to two distinct sets of phosphorus signals, though in each case one of the ^{195}Pt satellites is broader than the other, suggesting slightly different coupling constants. However, the chiral derivative **1c** appears to show four distinct P environments (though still with considerable overlapping of peaks) as a result of all four PPh_3 ligands being inequivalent in this complex. The presence of the chiral CHMe group therefore appears to have a significant effect on the environments of the PPh_3 phosphorus atoms. The pyridyl and phenyl complexes **6** and **7** also show distinct Pt-PPh_3 resonances for the $Pt_2S_2(PPh_3)_4$ core, with