A rapid screening, 'combinatorial-type' survey of the metalloligand chemistry of $Pt_2(PPh_3)_4(\mu\text{-}S)_2$ using electrospray mass spectrometry

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Electrospray mass spectrometry is a rapid and powerful technique for a combinatorial-like survey of the chemistry of the metalloligand $Pt_2(PPh_3)_4(\mu\text{-}S)_2$, leading to the successful isolation and crystallographic characterisation of the novel protonated species $Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SH)$ together with a range of metallated derivatives.

The sulfido complex $Pt_2(PPh_3)_4(\mu\text{-}S)_2$ **1** has attracted much interest in recent years, particularly for its ability to act as a metalloligand in the assembly of a diverse range of sulfido-bridged higher nuclearity aggregates.[1,2] In this communication, we describe how electrospray mass spectrometry (ESMS) can be used as a rapid, powerful combinatorial-type tool for surveying the metalloligand chemistry of **1** with a range of metal substrates. The utility of ESMS as a general technique for the characterisation of coordination and organometallic complexes is well known,[3] but as far as we are aware there are no previous extensive studies which have used ESMS as the primary screening tool for surveying the reactivity of coordination complexes, the results of which are then used to target subsequent synthetic efforts. Advantages of this approach include the need for only minute amounts of material, rapid screening of potential substrates for further study, and the accepted general agreement between mass spectrometric data and solution speciation.[3] In parallel studies, we are investigating the reactivity of the selenide analogue $Pt_2(PPh_3)_4(\mu\text{-}Se)_2$.[4]

The positive-ion ES spectrum of **1** in methanol gives ions due to protonated **1**, $[\mathbf{1} + 2H]^{2+}$ (*m/z* 752) and $[\mathbf{1} + H]^+$ (*m/z* 1504), together with ions $[(\mathbf{1})_2 + Ag + H]^{2+}$ (*m/z* 1557) and $[(\mathbf{1})_2 +$
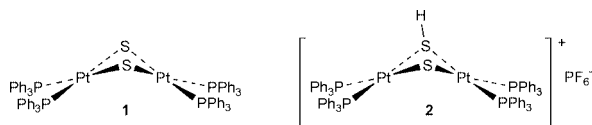
$2Ag]^{2+}$ (*m/z* 1611) formed by adventitious Ag^+ ions in the spectrometer. Addition of a small quantity of formic acid increased the intensity of the *m/z* 752 ion. The novel mono-protonated complex $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SH)]PF_6$ **2** was subsequently obtained by titration of **1** with HCl, followed by metathesis with NH_4PF_6. This complex, which is related to the monomethyl complex $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]^+$,[5] has not been isolated previously. Complex **2** gives two distinct ^{31}P NMR signals [δ 20.2, $^1J(PtP)$ 2705 and 23.0, $^1J(PtP)$ 3582, $^2J(PP)$ 15] together with a resonance for the SH proton at δ 3.48 in the ^1H NMR spectrum. Confirmation of its identity was obtained from an X-ray diffraction study, Fig. 1.[†] The dihedral angle of the four-membered Pt_2S_2 ring is 135°, which is similar to the methylated analogue $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]^+$ (138°).[5] There have only been two previous structural determinations on underivatised $Pt(\mu\text{-}sulfide)_2Pt$ systems, with $[(dppe)Pt(\mu\text{-}S)_2Pt(dppe)]$ being folded (140.2°)[6] and $[(dppy)_2Pt(\mu\text{-}S)_2Pt(dppy)_2]$ (dppy = 2-diphenylphosphinopyridine)[7] being
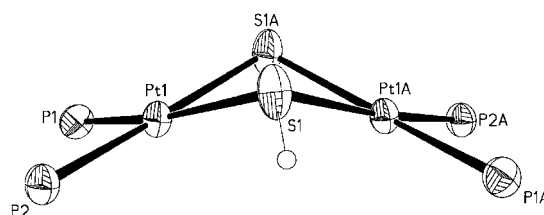

Fig. 1 Molecular structure of $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SH)]PF_6$ **2**. The phenyl rings of the PPh_3 ligands have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt(1)–S(1) 2.3289(8), Pt(1)–S(1A) 2.3536(8), Pt(1)–P(1) 2.2965(8), Pt(1)–P(2) 2.2712(8), Pt(1)–S(1)–Pt(1A) 91.01(3), Pt(1)–S(1A)–Pt(1A) 91.01(3), S(1)–Pt(1)–S(1A) 78.91(4), S(1)–Pt(1A)–S(1A) 78.91(4), P(1)–Pt(1)–P(2) 98.97(3), P(1)–Pt(1)–P(2) 98.97(3), P(1)–Pt(1)–S(1) 167.60(3), P(2)–Pt(1)–S(1) 92.88(3), P(1)–Pt(1)–S(1A) 89.06(3), P(2)–Pt(1)–S(1A) 171.27(3).

3a   **3b**
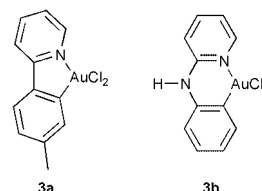
planar. Structural features of such $\{M_2S_2\}$ systems has attracted recent interest.[1,8] The structure of **2** is the first containing the Pt–SH–Pt moiety, although μ-SH complexes of other metals such as palladium[9] and nickel[10] have been structurally characterised.

The reactivity of complex **1** towards a range of halide-containing main group (*e.g.* Sn and Hg) and transition metal (*e.g.* Au) complexes can conveniently be monitored by ESMS, and allows the identification of novel, sulfide-bridged aggregates. As an illustrative example, the reaction of **1** with the organogold(III) complexes $AuCl_2(tolpy)$ **3a**[11] and $AuCl_2(pap)$ **3b**[12] monitored by positive-ion ESMS shows a single major peak in each case, due to the aggregate cations $[Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Au(tolpy)]^{2+}$ and $[Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Au(pap)]^{2+}$, as illustrated for the pap system in Fig. 2, with excellent agreement between observed and calculated isotope patterns. On a synthetic scale, metathesis of the $AuCl_2(tolpy)$ reaction solution with NH_4BF_4 gave yellow $[Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Au(tolpy)][BF_4]_2$ **4**, Fig. 3.[‡] While there have been several studies on aggregates with $\{M_3S_2\}$ cores containing Pt and Pd,[1,13] this is the first time that the isoelectronic gold(III) centre has been incorporated, though gold(I) and silver(I) derivatives of the $\{Pt_2S_2\}$ core have been known for some time.[1,14] The isolation of silver(I) halide aggregates containing the isoelectronic $\{Au^{III}_2S_2\}$ core has been reported.[15] The successful formation of **4** is facilitated by the increased stability towards reduction (by sulfur-based ligands) of gold(III) complexes bearing *N,C*-cyclometallated ligands.[16] The structure confirms the formulation of **4** as the
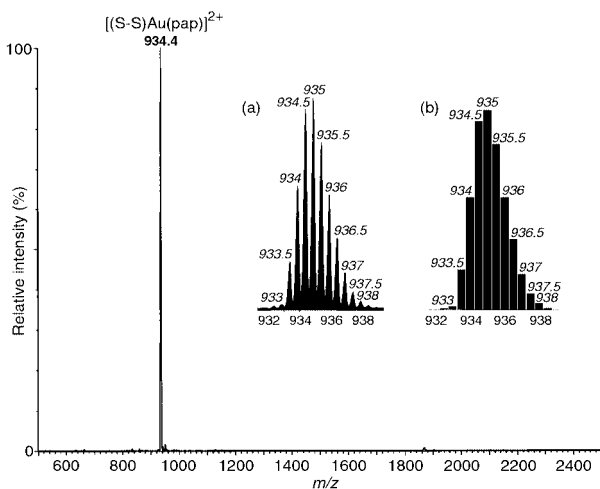
Fig. 2 Positive ion ES spectrum of a 1:1 mixture of **1** and AuCl₂(pap) **3b** in MeOH at a cone voltage of 20 V, demonstrating the facile and exclusive formation of [Pt₂(PPh₃)₄(μ₃-S)₂Au(pap)]²⁺. The inset shows (a) observed and (b) calculated isotope patterns for the dication.
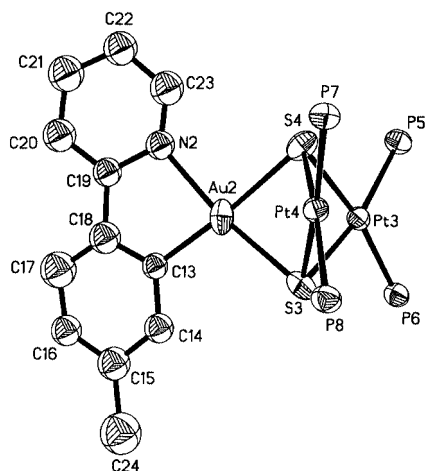
Fig. 3 Molecular structure of one of the cations of [Pt₂(PPh₃)₄(μ₃-S)₂Au(tolpy)][BF₄]₂ **4** with thermal ellipsoids at the 50% probability level. The phenyl rings of PPh₃ have been omitted for clarity. Selected bond distances (Å) and angles (°): Pt(3)–S(3) 2.371(3), Pt(3)–S(4) 2.362(3), Pt(4)–S(3) 2.377(3), Pt(4)–S(4) 2.360(3), Au(2)–S(3) 2.357(4), Au(2)–S(4) 2.371(4), Pt(3)–P(5) 2.302(3), Pt(3)–P(6) 2.274(3), Pt(4)–P(7) 2.269(3), Pt(4)–P(8) 2.296(3), Au(2)–C(13) 1.94(3), Au(2)–N(2) 2.18(2), Pt(3)–S(3)–Pt(4) 87.66(11), Pt(3)–S(4)–Pt(4) 88.25(11), Pt(3)–S(3)–Au(2) 82.81(11), Pt(3)–S(4)–Au(2) 82.68(11), Pt(4)–S(3)–Au(2) 82.42(11), Pt(4)–S(4)–Au(2) 82.46(11), S(3)–Pt(3)–S(4) 78.20(12), S(3)–Pt(4)–S(4) 78.12(12), P(5)–Pt(3)–P(6) 99.92(12), P(7)–Pt(4)–P(8) 98.92(12), P(5)–Pt(3)–S(3) 167.06(12), S(3)–Au(2)–S(4) 78.31(11), C(13)–Au(2)–N(2) 81.0(9).

first heterometallic aggregate of the {Pt₂S₂} core containing gold(III), and the presence of the methyl group allows for unambiguous assignment of N(1) and C(1) on the square-planar gold atom. The {Pt₂S₂} ring is, as expected, puckered (126.8°) with average Au–S bond distances 2.358(2) Å.

The successful isolation and characterisation of the novel species, initially identified by mass spectrometry experiments, clearly demonstrates the power of this methodology. It helps researchers to identify possible products before they are synthesized on a macroscopic scale. This pre-synthesis scanning helps to cut down wastage and increases the chance of achieving successful syntheses. Extension to organotin(IV) halides leads to the successful isolation of a range of adducts of complex **1** with SnMeCl₂⁺, SnMe₂Cl⁺, and SnPhCl₂⁺ moieties (derived from SnMeCl₃, SnMe₂Cl₂ and SnPhCl₃, respectively), their formulation being confirmed by single crystal X-ray diffraction studies. Full details will be reported in due course. Although **1** is a good model for this methodology, it is neither unique nor exclusive. One can anticipate similar success in other systems.

Notes and references

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

2 Selected recent references: Z. Li, X. Xu, S. B. Khoo, K. F. Mok and T. S. A. Hor, *J. Chem. Soc., Dalton Trans.*, 2000, 2901; H. Liu, C. Jiang, J. S. L. Yeo, K. F. Mok, L. K. Liu, T. S. A. Hor and Y. K. Yan, *J. Organomet. Chem.*, 2000, **595**, 276.

3 W. Henderson, B. K. Nicholson and L. J. McCaffrey, *Polyhedron*, 1998, **17**, 4291; R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79; I. I. Stewart, *Spectrochim. Acta, Part B*, 1999, **54**, 1649.

4 J. S. L. Yeo, J. J. Vittal, W. Henderson and T. S. A. Hor, *J. Chem. Soc., Dalton Trans*, 2001, 315.

5 C. E. Briant, C. J. Gardner, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1984, 2645.

6 M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. Gonzáles-Duarte, A. Lledós, J. Sola and G. Ujaque, *Chem. Commun.*, 1998, 597.

7 V. W.-W. Yam, P. K.-Y. Yeung and K.-K. Cheung, *J. Chem. Soc., Chem. Commun.*, 1995, 267.

8 M. Capdevila, W. Clegg, P. González-Duarte, A. Jarid and A. Lledós, *Inorg. Chem.*, 1996, **35**, 490.

9 S. Wirth and D. Fenske, *Z. Anorg. Allg. Chem.*, 1999, **625**, 2064.

10 R. J. Pleus, H. Waden, W. Saak, D. Haase and S. Pohl, *J. Chem. Soc., Dalton Trans.*, 1999, 2601.

11 S. J. Faville and W. Henderson, unpublished results.

12 Y. Fuchita, H. Ieda, A. Kayama, J. Kinoshita-Nagaoka, H. Kawano, S. Kameda and M. Mikuriya, *J. Chem. Soc., Dalton Trans.*, 1998, 4095.

13 Z. Li, H. Liu, K. F. Mok, A. S. Batsanov, J. A. K. Howard and T. S. A. Hor, *J. Organomet. Chem.*, 1999, **575**, 223; M. Capdevila, Y. Carrasco, W. Clegg, R. A. Coxall, P. González-Duarte, A. Lledós and J. A. Ramírez, *J. Chem. Soc., Dalton Trans.*, 1999, 3103.

14 H. Liu, A. L. Tan, C. R. Cheng, K. F. Mok and T. S. A. Hor, *Inorg. Chem.*, 1997, **36**, 2916; C. E. Briant, T. S. A. Hor, N. D. Howells and D. M. P. Mingos, *J. Organomet. Chem.*, 1983, **256**, C15; W. Bos, B. J. Bour, P. P. J. Schlebos, P. Hageman, W. P. Bosman, J. M. M. Smits, J. A. C. van Wietmarschen and P. T. Beurskens, *Inorg. Chim. Acta*, 1986, **119**, 141; V. W.-W. Yam, P. K.-Y. Yeung and K.-K. Cheung, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 739.

15 M. B. Dinger, W. Henderson, B. K. Nicholson and W. T. Robinson, *J. Organomet. Chem.*, 1998, **560**, 169.

16 Selected references: U. Abram, K. Ortner, R. Gust and K. Sommer, *J. Chem. Soc., Dalton Trans.*, 2000, 735; R. V. Parish, B. P. Howe, J. P. Wright, J. Mack, R. G. Pritchard, R. G. Buckley, A. M. Elsome and S. P. Fricker, *Inorg. Chem.*, 1996, **35**, 1659; M. A. Cinellu, G. Minghetti, M. V. Pinna, S. Stoccoro, A. Zucca and M. Manassero, *J. Chem. Soc., Dalton Trans.*, 1999, 2823.