X-Ray Photoelectron Spectroscopic Characterization of $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2PtCl_2]$, $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-dppf})][PF_6]_2$ [dppf = $Fe(C_5H_4PPh_2)_2$] and other Heterometallic Aggregates derived from $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$†

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Lewis acid–base reactions between $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ and $[\{Cu(NO_3)(\mu\text{-dppf})\}_2]$–$NH_4PF_6$ [dppf = $Fe(C_5H_4PPh_2)_2$] and $[PtCl_2(NCMe)_2]$ gave hexanuclear $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-dppf})][PF_6]_2$ and trinuclear $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2PtCl_2]$ respectively. X-Ray photoelectron spectroscopic (XPS) studies of these sulfur aggregates were made together with other known alkylated complexes $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SR)]X$ (R = Me, X = I; R = CH_2Cl, X = Cl; R = $CHCl_2$, X = PF_6; R = CH_2Ph, X = PF_6) and metallated complexes $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_xML]^{n+}nX^-$ [M = Ni, L = $Ph_2PCH_2CH_2PPh_2$ (dppe), X = PF_6, $x = 1$; M = Pd_2, L = $(\mu\text{-}Cl)_2$, X = PF_6, $x = 2$; M = Ag_2, X = NO_3, $x = 2$; M = Au, L = PPh_3, X = PF_6, $x = 1$; M = Hg, X = PF_6, $x = 2$; M = Hg, L = dppe, X = PF_6, $x = 1$; $n = 2$ for all M except Au where $n = 1$]. The observed binding energies are related to the charge distribution and nucleophilicity of the sulfur centres. The possibility of using multinuclear XPS [S(2p), P(2p), Cl(2p), Pt(4f)] to distinguish chemically inequivalent nuclei is examined.

A series of heterometallic complexes of general formula $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_xML_y]^{n+}$ has been synthesized based on Lewis acid–base reactions between the highly nucleophilic $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ **1**[1] and MX_nL_z (or $[ML_z]^{n+}$) (*e.g.* M = Au, L = PPh_3, X = Cl, $n = 1$, $x = 1$, $y = 1$, $z = 1$; M = Hg, L = PPh_3, X = Cl, $n = 2$, $x = 1$, $y = 2$, $z = 2$).[2] Depending on the nature of the heterometal M (especially its stereogeometry and co-ordination number), a range of species with various nuclearities and structures results. These polynuclear structures, despite their polymetallic nature, are strictly not 'clusters', due to the absence of M–M interactions, but 'aggregates', a term Mingos[2a,d] advocated. They are constructed based entirely on the bridging and capping properties of sulfur. The electronic properties of the individual metal fragments therefore depend on the extent of charge transmission by these sulfur links. Such charge distribution directly affects the chemical stability of these aggregate structures. We have recently extended these syntheses to hybrids of p- and d-block metals.[3] As a prerequisite for further structural and electronic studies, we need to understand the charge-distribution ability of the sulfur ligand, and its electronic impact on the individual metals and their associated ligands. This can be conveniently studied by X-ray photoelectron spectroscopy (XPS). Some related work has been reported by Battistoni *et al.*[4] We are extending it to other thiolato and heterometallic complexes. These species are suitable models for correlation work by 'multinuclear XPS' owing to the many different sites in the complex framework which can be studied. Complex **1** is practically insoluble in all common organic solvents without decomposition (or derivatization). The XPS spectra of its solid powder thus provide valuable spectroscopic information. We have discussed recently other transition-metal complexes which are suitable for XPS modelling studies.[5]

Results and Discussion

All the sulfur complexes in this work are synthesized from the parent complex $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ **1** which is the only one with sulfur exclusively in the doubly bridging state. For comparison, *cis*-$[PtCl_2(PPh_3)_2]$ **2** and $[PtCl_2(dppe)]$ **3** (dppe = $Ph_2PCH_2CH_2PPh_2$) are included. Alkylation of **1** gives the monoalkylated products $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SR)]X$ (R = Me, X = I **4**; R = CH_2Cl, X = Cl **5**; R = $CHCl_2$, X = PF_6 **6**; R = CH_2Ph, X = PF_6 **7**). Metallation of **1** gives $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_xML]^{n+}nX^-$ [M = Ni, L = dppe, X = PF_6, $x = 1$ **8**; M = Pd_2, L = $(\mu\text{-}Cl)_2$, X = PF_6, $x = 2$ **9**; M = Ag_2, X = NO_3, $x = 2$ **10**; M = Au, L = PPh_3, X = PF_6, $x = 1$ **11**; M = Hg, X = PF_6, $x = 2$ **12**; M = Hg, L = dppe, X = PF_6, $x = 1$ **13**; $n = 2$ except for Au when $n = 1$). Complexes **10** and **12** have no subsidiary ligands on the heterometals.

Two new complexes are included in this work, *viz.* $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2PtCl_2]$ **14** and $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-dppf})][PF_6]_2$ **15** [dppf = 1,1′-bis(diphenylphosphino)ferrocene]. The former, prepared by coupling **1** and $[PtCl_2(NCMe)_2]$, is a triplatinum complex with two chemically inequivalent platinum(II) moieties in a 2 : 1 abundance ratio. It is the only heterometallic complex which is neutral in this study. Complex **15**, prepared from **1** and $[\{Cu(NO_3)(\mu\text{-dppf})\}_2]$[6] followed by anion exchange with NH_4PF_6, is hexanuclear with two equivalent halves of $\{Pt_2S_2Cu\}$ singly bridged by dppf. There are ample examples in the literature which illustrate dppf in this bridging mode.[7] An *anti* orientation for the cyclopentadienyl phosphine groups can minimize any steric interaction between the two metalloligands **1**. Spectroscopic evidence of **14** and **15** is obtained from their ^{31}P NMR spectra which show a single resonance for **14** and two distinct resonances for **15**. Complex **15** is formed as the major product in both 1 : 1 and 2 : 1 stoichiometric ratios of **1** and $[\{Cu(NO_3)(\mu\text{-dppf})\}_2]$. The 1 : 1 addition complex $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-dppf})_2]^{2+}$ has so far eluded isolation. It presumably undergoes rapid ligand exchange of dppf with the metalloligand **1** to give **15**. The co-ordination flexibility of a capping sulfur

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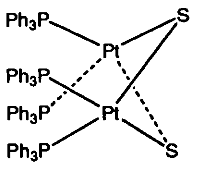
† *Non-SI units employed:* eV ≈ 1.60 × 10^{-19} J, bar = 10^5 Pa.



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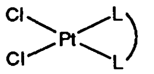
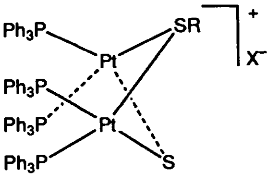
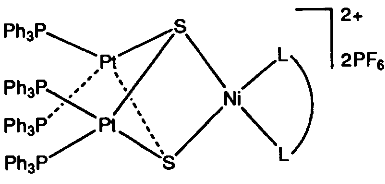


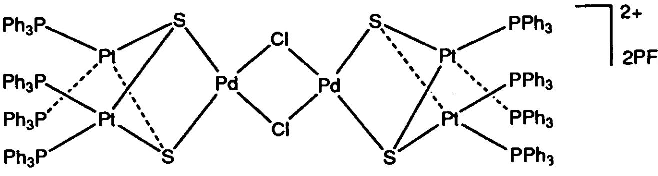
L⌒L = 2PPh$_3$ **2** or dppe **3**



	R	X
4	Me	I
5	CH$_2$Cl	Cl
6	CHCl$_2$	PF$_6$
7	CH$_2$Ph	PF$_6$



8 (L⌒L = dppe)



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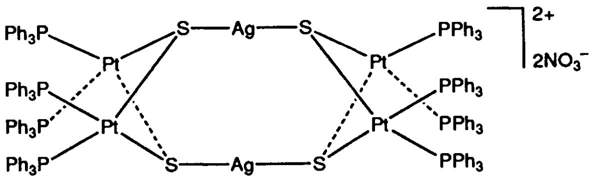

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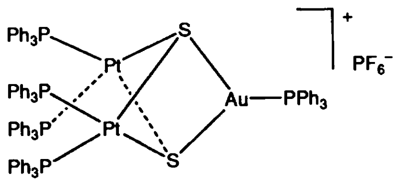

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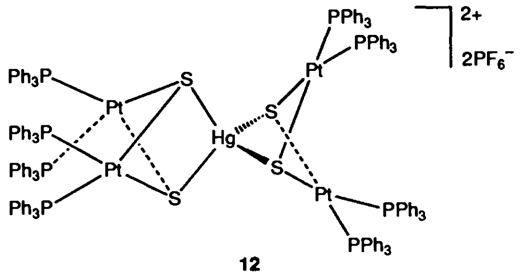

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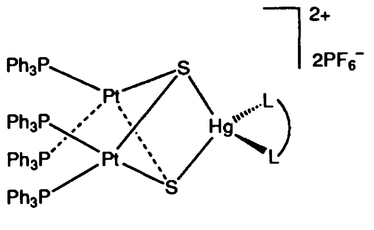
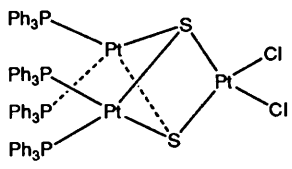


13 (L⌒L = dppe)



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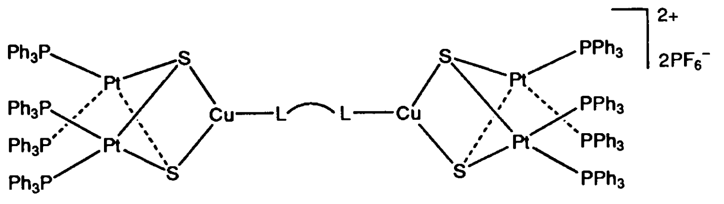

15 (L⌒L = dppf)

allows it to stabilize a heterometal in a linear (**10**), trigonal-planar (**11** and **15**), square-planar (**8**, **9** and **14**) or tetrahedral geometry (**12** and **13**). The two sulfur centres of each complex studied are identical except in the alkylated complexes **4**–**7** which bear thio and thiolato bridges.

The S(2p$\frac{3}{2}$) and S(2p$\frac{1}{2}$) spin–orbit components differ in energy by 1 eV.[8] These spin doublets are resolved in all S(2p) spectra to give two peaks in the area ratio of 2:1 for each sulfur environment. These data are summarized in Table 1. For clarity only the S(2p$\frac{3}{2}$) values are discussed. Among the complexes studied, the substituted sulfur in the thiolato complexes invariably gives higher binding energy (b.e.) (163.0–163.3 eV) than sulfur in the parent complex **1** (160.8 eV). This is significant when one considers that, for a particular nucleus in a metal complex, the core b.e.s from XPS are rarely sensitive to the environmental changes of the nucleus unless there is a change

Table 1 Core-level binding energies (eV) (referenced to hydrocarbon peak at 285.0 eV; f.w.h.m. values in parentheses)

	S			Pt		
Complex	$2p_{\frac{3}{2}}$	$2p_{\frac{1}{2}}$	P	$4f_{\frac{7}{2}}$	$4f_{\frac{5}{2}}$	Others
1 $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$	160.8 (1.8)	162.2 (1.8)	131.5 (1.9)	72.3 (1.8)	75.7 (1.8)	
2 *cis*-$[PtCl_2(PPh_3)_2]$			132.1 (1.8)	73.4 (1.5)	76.7 (1.5)	199.5 (1.6) $[Cl(2p_{\frac{3}{2}})]$
3 $[PtCl_2(dppe)]$			132.0 (1.9)	73.3 (1.8)	76.9 (1.6)	
4 $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]I$	163.1 (1.8), 161.3 (1.8)	164.1 (1.8), 162.3 (1.8)	132.2 (1.6), 131.4 (1.6)	72.8 (1.5)	76.2 (1.5)	
5 $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$	163.0 (1.8), 161.8 (1.8)	164.0 (1.8), 162.8 (1.8)	132.2 (1.6), 131.7 (1.6)	73.0 (1.6)	76.4 (1.5)	199.7(1.5), 197.8 (1.5) $[Cl(2p_{\frac{3}{2}})]$
6 $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCHCl_2)]PF_6$	163.2 (1.8), 161.2 (1.8)	164.2 (1.8), 162.2 (1.8)	132.2 (1.6), 131.6 (1.6), 136.2 (1.6)	72.9 (1.6)	76.2 (1.4)	
7 $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCH_2Ph)]PF_6$	163.3 (1.8), 161.7 (1.8)	164.3 (1.8), 162.7 (1.8)	132.4 (1.6), 131.7 (1.6), 136.7 (1.4)	73.1 (1.6)	76.6 (1.5)	
8 $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2Ni(dppe)][PF_6]_2$	162.3 (1.5)	163.5 (1.5)	131.9 (1.8), 136.4 (1.7)	73.2 (1.6)	76.5 (1.6)	854.8 (1.6) $[Ni(2p_{\frac{3}{2}})]$
9 $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Pd\}_2(\mu\text{-}Cl)_2][PF_6]_2$	162.1 (1.6)	163.1 (1.6)	131.8 (1.8), 136.2 (1.5)	72.9 (1.6)	76.2 (1.6)	198.2 (1.5) $[Cl(2p_{\frac{3}{2}})]$ 337.3 (1.5) $[Pd(3d_{\frac{5}{2}})]$
10 $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_2Ag_2][NO_3]_2$	161.8 (1.6)	162.9 (1.6)	131.9 (1.8)	72.9 (1.6)	76.2 (1.6)	368.7 (1.5) $[Ag(3d_{\frac{5}{2}})]$
11 $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2Au(PPh_3)]PF_6$	161.7 (1.7)	162.9 (1.7)	131.8 (1.8), 136.3 (1.5)	72.8 (1.6)	76.1 (1.6)	85.0 (1.6) $[Au(4f_{\frac{7}{2}})]$
12 $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2\}_2Hg][PF_6]_2$	161.8 (1.6)	162.8 (1.6)	131.8 (1.7), 136.7 (1.6)	73.0 (1.6)	76.3 (1.6)	100.6 (1.5) $[Hg(4f_{\frac{7}{2}})]$
13 $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2Hg(dppe)][PF_6]_2$	162.0 (1.6)	163.0(1.6)	131.9 (1.8), 136.7 (1.6)	73.0 (1.6)	76.3 (1.6)	101.0 (1.8) $[Hg(4f_{\frac{7}{2}})]$
14 $[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2PtCl_2]$	161.8 (1.6)	162.9 (1.6)	131.6 (1.7)	71.7 (1.5), 72.6 (1.6)	75.0 (1.5), 75.9 (1.6)	197.2 (1.5) $[Cl(2p_{\frac{3}{2}})]$
15 $[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-}dppf)][PF_6]_2$	161.7 (1.6)	162.9 (1.6)	131.8 (1.8), 136.4 (1.5)	72.8 (1.6)	76.2 (1.6)	933.2 (1.6) $[Cu(2p_{\frac{3}{2}})]$

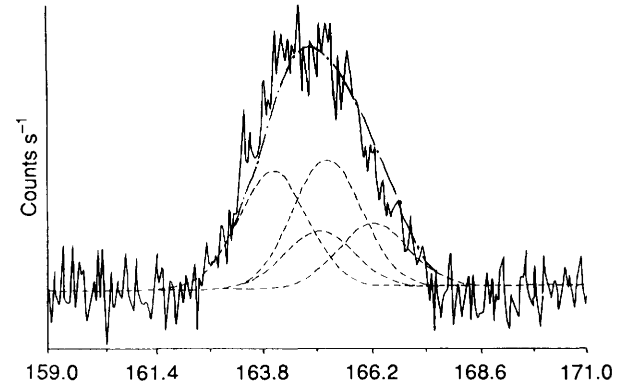

Fig. 1 Experimental (——), deconvoluted (- - - -) and simulated (— · — · —) S(2p) XPS spectra of $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCH_2Cl)]Cl$ **5** showing a 1:1 doublet for each 2:1 spin doublet ($2p_{\frac{3}{2}}$:$2p_{\frac{1}{2}}$). The deconvoluted spectra were produced by a peak-synthesis procedure described in the Experimental section to achieve a best fit of the experimental spectra

in its oxidation state or some radical changes in the complex structure or charge distribution.[9] Similar reports on the S(2p) b.e.s of sulfur-containing complexes generally do not give shift differences greater than ≈2 eV.[10] The S(2p) b.e. of **1** is also significantly lower than that reported by Battistoni *et al.**[,4] Such a low b.e. is in agreement with the highest electron density being on the sulfur centres in **1**, and hence its well documented nucleophilic character.[11] The correlation of b.e. to atomic charge, bond polarity and charge distribution is established and discussed elsewhere.[12] An increase in b.e. is also observed upon metallation ($\mu\text{-}S \longrightarrow \mu_3\text{-}S$) (to give **8**–**15**) but the effect is less pronounced. In general, these increases are consistent with the expected charge dissipation to the C–S or M–S bond upon alkylation or metallation of the thio (unsubstituted sulfur) centres. The observed higher b.e.s of the thiolato complexes compared to those of the metallated species is indicative of possible d_π–d_π bonding between the capping sulfur and its associated metal centres. This M→S back donation causes the sulfur to be more electron rich compared to the thiolato sulfur in which the π bonding between R and S is negligible.† This significantly higher b.e. upon alkylation considerably broadens the sulfur bands of **4**–**7**. It allows a Gaussian deconvolution and extraction of two doublets associated with two chemically inequivalent sulfurs [163.2 for μ-SR *vs.* 161.5 eV for μ-S (mean)]. A typical spectrum is illustrated in Fig. 1 for complex **5**. A similar observation was made by Battistoni *et al.*‡[,4] This spectroscopic differentiation of binary sulfur from its derivative SR holds promise in view of the great difficulties

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* The S(2p) data from Battistoni *et al.* apply to the unresolved spin doublet whilst we are reporting the resolved $2p_{\frac{3}{2}}$ and $2p_{\frac{1}{2}}$ bands. The unresolved S(2p) band of complex **1** also shows a lower b.e.

† This is in general valid although it must be pointed out that for certain substituted methanethiolato systems, e.g. XCH_2SH, hyperconjugation is invoked to explain π interaction between R and S.[13]

‡ Battistoni *et al.* reported this S(2p) peak broadening for a complex of formula '$[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]$'. This formula is incorrect. The actual complex is cationic, $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]^+$, with the anion either I^-, BF_4^-, or PF_6^-. If it is I^-, it would be the same as complex **4**.

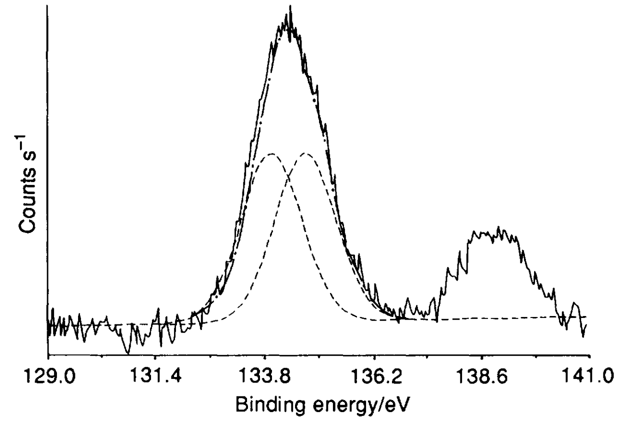

Fig. 2 Experimental (——) and simulated (— · — · —) P(2p) XPS spectra of [$Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SCH_2Ph)$]$PF_6$ **7** showing a deconvoluted 1:1 intensity doublet (- - - -) for two inequivalent Pt-bound phosphines and a high-energy P(2p) band due to PF_6^-

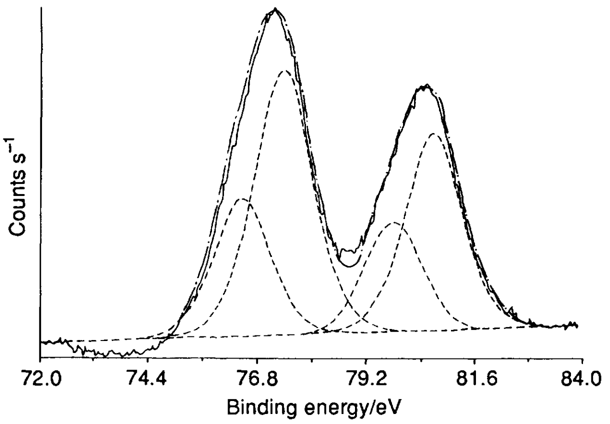

Fig. 3 Experimental (——), deconvoluted (- - - -) and simulated (— · — · —) Pt(4f) XPS spectra of [{$Pt(PPh_3)_2(\mu_3\text{-}S)$}$_2PtCl_2$] **14** showing the 2:1 doublets for both 4f$_{7/2}$ and 4f$_{5/2}$ spin–orbit components

encountered in the use of other direct techniques such as ^{33}S NMR spectroscopy.[14] Another interesting observation is the slight but consistently higher b.e.s for the thio centres in **4**–**7** than for those in the parent complex **1** [161.5 (mean) *vs.* 160.8 eV]. This points to a lower charge of the former which is consistent with the observed reduced basicity of the sulfur atom when its neighbouring sulfur bridge is alkylated. These XPS data thus fully concur with equation (1).

$$[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2] \xrightarrow[\text{rapid}]{MeI} \underset{\mathbf{1}}{} [Pt_2(PPh_3)_4(\mu\text{-}S)(\mu\text{-}SMe)]I \xrightarrow{MeI} \!\!\!\!\!\!\!\!\times\;\;\;\; [Pt_2(PPh_3)_4(\mu\text{-}SMe)_2]I_2 \quad (1)$$

1 **4**

Despite their obvious merit, the S(2p) values must be used with caution. First, their insensitivity towards the alkyl substituents in complexes **4**–**7** (±0.3 eV) despite the disparity of the latter in electron-withdrawing abilities epitomizes an inherent problem of XPS. Secondly, a cationic complex strictly should have a higher ionization potential and higher b.e. than those of its neutral analogue. A direct comparison of **1** with its cationic derivatives would hence be limited in scope. However, since these spectra are referenced to the same C(1s) b.e., this ionic effect has been taken into consideration. A comparison between **1** and **14**, which is also neutral, also shows that the S(2p$_{3/2}$) b.e. of the latter is still substantially (1 eV) higher. These results provide a justification for the above comparisons as well as the following ones.

The energy difference between the two P(2p) spin–orbit components is too small for their resolution. Every phosphine environment would give a single peak; the observed full width at half-maximum (f.w.h.m.) ranges between 1.6 for the alkylated to 1.7–1.8 eV for the metallated derivatives. Complex **1** gives a b.e. of 0.5–0.6 eV less than that of **2** or **3**. This reflects the higher *trans* influence of sulfide as a ligand compared to chloride which makes the phosphine a better σ donor when it is *trans* to chloride than when *trans* to sulfide. When **1** is alkylated to give **4**–**7** the P(2p) bands show a high-energy shift and slight broadening. This energy shift is in line with the lower *trans* influence of thiolate compared to thio. Attempts to deconvolute these bands give two peaks of spacing ≈0.65 eV (mean). While the peak broadening is indicative of the chemical inequivalence of the phosphines owing to their differing *trans* ligands, we are reluctant to put too much significance in expressing the inequivalence in quantitative terms. The fact that the f.w.h.m. of the resolved bands is 0.3 eV less than that of **1** restrict the significance of these peak differentiations. A similar scenario is faced in the heterometallic complexes. For complexes **8**, **11**, **13** and **15** the P(2p) signal arising from the phosphine on the heterometal is not resolved from that of the platinum phosphines since the peak broadening is only very marginal. Another observation is that the shift difference between complexes **1** [P(2p) 131.5 eV] and **14** (131.6 eV) is insignificant. One may hence deduce that the metallation at the sulfur site is too remote to impart any influence on the phosphines. The observed b.e. differences between other heterometallics and **1** [0.34 eV (mean)] however suggest, besides the charge effect mentioned earlier, a small enhancement in P(2p) b.e. upon metallation. All cationic complexes with PF_6^- as the counter ion exhibit a discrete high-energy band due to P^V. A typical example is found for complex **7** in Fig. 2. This unmistakable identification of a PF_6^- salt complements the established infrared or NMR evidence.

The spin–orbit components, separated by 3.4 eV, are well resolved in the platinum(4f) spectra. For discussion purposes only the low-energy 4f$_{7/2}$ values are quoted. Upon alkylation or metallation the Pt(4f) b.e.s increases by an average of 0.62 eV. This reflects a reduction in the electron dissipation from S to Pt upon increase of the sulfur co-ordination number. Note that this effect is slightly more conspicuous in the Pt(4f) than in the P(2p) spectra, and possibly indicates a proximity effect of S on Pt.

Complex **14** is a good model for XPS identification of chemically inequivalent platinum nuclei. Gaussian extraction from the broad bands gives two peaks in 2:1 intensity ratio for both spin–orbit components (Fig. 3). A satisfactory deconvolution is achieved only when the higher-energy pair belongs to the more intense signals. Its higher intensity gives the first indication of its affiliation to the phosphine-bound platinum. This assignment is supported by the observed b.e. (72.6 eV) which compares well with the b.e.s of phosphine-bound platinum for other metallated products (**8**–**13** and **15**) (72.8–73.2 eV). The lower-energy peak at 71.7 eV, corresponding to the distinctive $PtCl_2$ moieties, is unique as it represents the only Pt(4f) b.e. which is lower than that of the parent complex **1**. This lower b.e. is attributed to the negligible Pt→Cl back bonding as compared to Pt→PPh_3. The effect, which is reinforced by the σ-donating property of chloride, gives a higher charge accumulation on the Pt. In this context one may understand why the $Pt(PPh_3)_2$ moieties in **14** give the lowest b.e. compared to those of all the other metallated derivatives. This higher accumulation of charge on Pt in $PtCl_2$ limits further charge influx from the sulfur ligands and in turn promotes electron donation to the platinum sites in $Pt(PPh_3)_2$. Such enhanced electron donation is reflected in the lower b.e.

This uneven charge distribution by the capping sulfur also effectively maintains the three platinum centres in an effective oxidation state of +2 despite their different ligand characteristics. The Pt(4f) b.e.s in **14** are typical of Pt^{II}.[15] These values lend support to the ability of sulfur as a bridging/capping ligand to distribute its charge according to the needs of individual metal fragments. The stability of many heterometallic sulfur aggregates and clusters is well known.[16]

The higher chlorine($2p_{\frac{3}{2}}$) b.e. for complex **9** compared to that of **14** indicates a higher charge dissipation for a bridging chloride. This observation is supported by some literature work[17] but debated elsewhere.[18] The small f.w.h.m. of the Cl(2p) band of **14** is also consistent with the proposed structure with equivalent chlorides. Band broadening would be expected if chloride dissociation occurs which would give rise to a cationic complex with bridging and ionic chloride such as in **9** (obtained from the metathesis of NH_4PF_6 with its parent cationic complex which contains ionic chloride). All the heterometals, *viz.* Ni, Pd, Ag, Au, Hg and Cu, give b.e.s characteristic of their usual oxidation states.

Conclusion

Despite its limitations, XPS offers a convenient means to study the charge distribution in heterometallic compact aggregates. The syntheses of these macromolecules is a step towards the molecular design of solids and surfaces. As XPS is an established technique in surface and solid analysis, it is an inevitable extension that one should apply, and understand, this technique to macromolecular analysis. Our recent research is therefore directed at these parallel studies of micro- and macro-molecular and inorganic solid systems by XPS.

Experimental

General.—All the preparations were carried out in standard Schlenk flasks under a dry argon atmosphere. Solvents were distilled and degassed before use. The NMR spectra were recorded on either a Bruker AC 300F or a JEOL FX90Q spectrometer, the ^{31}P spectra being externally referenced to 85% H_3PO_4. Infrared spectra (KBr disc) were recorded on a Shimadzu IR-470 spectrometer. All the known platinum thio and thiolato compounds, $[\{Cu(NO_3)(\mu\text{-dppf})\}_2]$ and $[PtCl_2(NCMe)_2]$[19] were prepared according to literature methods. The identity and purity of samples were checked by IR, NMR and microanalyses. Elemental analyses were carried out in the Microanalytical Laboratory of the Chemistry Department of National University of Singapore. Platinum analysis was carried out on a sample solution in a mixture of concentrated $HClO_4$–HNO_3–H_2SO_4 by flame emission spectroscopy using an inductively coupled plasma torch.

Core-level spectra were obtained on the VG ESCALAB Mk II spectrometer using Mg-Kα radiation, operating on a fixed retardation ratio of 40, and covered the energy region for all the elements contained. With an ultimate base pressure of $\approx 5 \times 10^{-10}$ mbar, the normal operating pressure in the analysis chamber is $< 2 \times 10^{-9}$ mbar during the course of the measurements.[20] All the complexes studied are air-stable especially in the solid state. No surface oxidation was observed (or expected) under the high-vacuum operating conditions. No spectral changes due to sample decay were observed. The instrument was calibrated at high resolution on both the Au($4f_{\frac{3}{2}}$) peak at b.e. 84.0 eV and the Cu($3p_{\frac{3}{2}}$) peak at b.e. 932.7 eV. This procedure ensures that the error at mid-range of the energy scale will not exceed 0.05 eV.[21] The powder sample was sprinkled onto a double-sided Scotch tape mounted onto a standard VG holder. For insulating samples, energy referencing is necessary since these surfaces will be charged positively by the emission of electrons due to X-ray irradiation. In our system where oil diffusion pumps are used this is conveniently carried out by referencing the b.e. to the C(1s) peak at 285.0 eV which arises from adventitious hydrocarbon contamination present on the sample surfaces. A VGS2000 computer data system was used in the peak synthesis. The XPS core-level spectra, after background subtraction, were decomposed into a suitable number of Gaussian component peaks with the constraint that the full width at half-maximum for all the component peaks in a particular spectrum is maintained constant. Other variable fitting parameters including peak positions, intensities and separations were then continuously adjusted and refined until the overlap of the raw data and the sum of the convoluted peaks was optimized.[22] The b.e. results are reliable since they are chemically sound and consistent with data obtained for the various complexes studied. Based on the findings of our previous studies, an uncertainty of ±0.3 eV for the b.e. is estimated.[5] Surface atomic stoichiometric ratios were measured from peak-area ratios corrected with appropriate experimentally determined sensitivity factors.

Designed Syntheses.—$[\{Pt(PPh_3)_2(\mu_3\text{-}S)\}_2PtCl_2]$ **14**. The complex $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ (0.12 g, 0.080 mmol) was stirred with *cis*-$[PtCl_2(NCMe)_2]$ (0.028 g, 0.080 mmol) in MeCN (50 cm^3) at *ca.* 70 °C until it gave a clear chrome yellow solution ($\approx$2 h). It was filtered and carefully concentrated under vacuum to *ca.* 3 cm^3. Orange microcrystals formed upon cooling to −20 °C. This solid was analytically pure, but can be recrystallized from CH_2Cl_2–hexane mixture, followed by washing with Et_2O to give complex **14** (0.060 g, 42%) (Found: C, 48.65; H, 3.35; Cl, 4.10; P, 7.25; Pt, 29.90; S, 4.80. Calc. for $C_{72}H_{60}Cl_2P_4Pt_3S_2$: C, 48.85; H, 3.40; Cl, 4.00; P, 7.00; Pt, 33.05; S, 3.65%). $\delta_P(CDCl_3)$ 13.31[t, J(P–Pt) 3177 Hz]. Complex **14** can also be prepared in a one-pot reaction involving $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ and $PtCl_2$ in refluxing MeCN (2 h).

$[\{Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Cu\}_2(\mu\text{-dppf})][PF_6]_2$ **15**. The complex $[\{Cu(NO_3)(\mu\text{-dppf})\}_2]$ (0.034 g, 0.025 mmol) was added to a suspension of $[\{Pt(PPh_3)_2(\mu\text{-}S)\}_2]$ (0.075 g, 0.050 mmol) in MeOH (40 cm^3) and the mixture stirred for 30 min. The resultant yellow solution was filtered and an excess of NH_4PF_6 in MeOH added dropwise. The resultant yellow precipitate was filtered off and recrystallized from CH_2Cl_2–Et_2O to give complex **15** (0.056 g, 60%) (Found: C, 53.70; H, 3.80; Cu, 2.80; Fe, 1.60; P, 9.85; Pt, 18.90; S, 4.40. Calc. for $C_{178}H_{148}Cu_2F_{12}FeP_{12}Pt_4S_4$: C, 53.75; H, 3.75; Cu, 3.20; Fe, 1.40; P, 9.35; Pt, 19.65; S, 3.25%. $\nu(PF_6^-)$ 837 cm^{-1}. NMR: ^1H (CD_2Cl_2), δ 6.94–7.35 (m, 140 H, Ph), 4.24 (br s, 4 H, C_5H_4) and 3.79 (br s, 4 H, C_5H_4); $^{31}P\text{-}\{^1H\}$, δ 19.38 [t, P_{Pt}, J(P–Pt) 3095 Hz] and −7.01 (s, P_{Cu}).

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