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Dinuclear sulfide–thiolate complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ as cationic metalloligands

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Abstract

The cationic monoalkylated derivatives of the well-known metalloligand $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$, *viz.* $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ (R = n-Bu, CH_2Ph) are themselves able to act as metalloligands towards the Ph_3PAu^+ and $R'Hg^+$ (R' = Ph or ferrocenyl) fragments, by reaction with Ph_3PAuCl or $R'HgCl$ respectively. The resulting dicationic products $[Pt_2(\mu\text{-}$

SR)(μ-SAuPPh$_3$)(PPh$_3$)$_4$]$^{2+}$ and [Pt$_2$(μ-SR)(μ-SHgR')(PPh$_3$)$_4$]$^{2+}$ are readily isolated as their hexafluorophosphate salts, and have been fully characterised by spectroscopic techniques and an X-ray structure determination on [Pt$_2$(μ-SR)(μ-SHgFc)(PPh$_3$)$_4$](PF$_6$)$_2$.

Keywords: Platinum complexes; Thiolate complexes; Sulfide complexes; Crystal structure; Electrospray mass spectrometry; Metalloligand

Introduction

The metalloligand properties of platinum(II) complexes containing the {Pt$_2$(μ-S)$_2$} core, primarily phosphine derivatives [Pt$_2$(μ-S)$_2$L$_4$] [L = PPh$_3$[1,2] or L$_2$ = Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 2 or 3)[3] Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$[4] *etc.*] have been extensively documented. Two strongly electron-rich sulfide ligands, together with the flexible hinge of the {Pt$_2$S$_2$} core, results in these metalloligands forming coordination complexes with a diverse range of metal fragments, including transition metals, main group metals and the actinide uranium. The high nucleophilicity of complexes with the {Pt$_2$S$_2$} core also makes them susceptible to attack by organic electrophiles such as alkyl halides. While this reactivity has been known for many years,[5,6,7] it has not, until recently, been more widely exploited. We have been exploring the reactivity of {Pt$_2$S$_2$} complexes towards alkylating and arylating agents with a view to the synthesis of novel thiolato complexes, and have recently reported[8] on a systematic survey of this chemistry, using the technique of electrospray ionisation mass spectrometry (ESI MS), which offers efficiencies in terms of scale and convenience. Using this methodology we have been able to add, stepwise, two different alkyl groups onto the $\{Pt_2S_2\}$ core, to form unsymmetrical dithiolate-bridged species with $\{Pt_2(\mu\text{-}SR)(\mu\text{-}SR')\}^{2+}$ cores.[9] We are also interested in exploiting the high reactivity of the $\{Pt_2S_2\}$ system in order to develop novel synthetic routes, ideally catalytic in nature, to organosulfur compounds.[10,11] This chemistry was initially explored using the more reactive selenido analogue $[Pt_2(\mu\text{-}Se)_2(PPh_3)_4]$.[12,13]

In contrast to the extensive coordination chemistry of the di(μ-sulfido) systems, nothing is known about the potential metal-coordinating ability of monoalkylated systems containing the $\{Pt_2(\mu\text{-}S)(\mu\text{-}SR)\}^+$ core, for which, somewhat surprisingly, only a small handful of examples are known. Their cationic nature would tend to decrease the coordinating ability, but it is noteworthy in this context that methods for the dialkylation of the $\{Pt_2S_2\}$ core giving $[Pt_2(\mu\text{-}SR)_2]^{2+}$ have been demonstrated,[9] and, cationic ligands are known in the literature. A good example is $[Co(\eta^5\text{-}C_5H_5PPh_2)_2]^+$. In this paper we report on initial investigations into the coordination chemistry of mono-alkylated derivatives of the type $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$.

Results and discussion

Synthesis and characterisation of monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$

Given the paucity of examples of isolated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ in the literature, where R is a simple unfunctionalised alkyl group, we initially set out to extend the range of compounds of this general type. Reactions were carried out by addition of an excess of the alkylating agent to $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ in methanol suspension; progress of the reaction is readily monitored using positive-ion ESI MS and occurs with dissolution of the sparingly soluble platinum-sulfide complex, giving yellow solutions. In these reactions, alkyl bromides were the preferred alkylating agents, because an excess of alkyl bromide can conveniently be used, without forming dialkylated products (as occurs with alkyl iodides). Using this route, the new complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ **1** [R = n-butyl (**1a**) and n-octyl (**1b**)] were prepared and isolated as their hexafluorophosphate salts. As expected, the rate of alkylation reactions are considerably slower when alkyl chlorides are used, and the corresponding tetraphenylborate salt of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ (**1c**) was also prepared in low yield using 1-chlorobutane. The complexes are soluble and stable in chlorinated hydrocarbon solvents. ESI MS of the isolated products showed a single $[M]^+$ ion at the expected *m/z* values (see Experimental), with no evidence for dialkylation, consistent with the weak alkylating properties of alkyl-chlorides and -bromides.

Reactivity of monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ towards metal halide complexes

The reactivity of the monoalkylated complexes towards a selection of metal-halide complexes has been explored. The simple alkyl derivative $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ **1a**, and the previously reported[7] benzylated derivative $[Pt_2(\mu\text{-}S)(\mu\text{-}CH_2Ph)(PPh_3)_4]PF_6$ **1d** were used; no studies were carried out with the octyl derivative **1b**. In these initial studies the reactivity towards Ph_3PAuCl and RHgCl [R = Ph or ferrocenyl, Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)] species have been investigated. These were chosen because the parent [$Pt_2(\mu\text{-}S)_2(PPh_3)_4$] itself is well-known to undergo single- or double-addition of gold(I)[14,15,16] or mercury(II)[17,18,19] fragments, in the case of gold giving species such as [$Pt_2(\mu\text{-}SAuCl)_2(PPh_3)_4$] and [$Pt_2(\mu\text{-}SAuPPh_3)_2(PPh_3)_4$]$^{2+}$. Similar reactivity has been observed with [$Pd_2(\mu\text{-}S)_2(dppf)_2$] [dppf = 1,1'-bis(diphenylphosphino)ferrocene].[20]

Reaction of a yellow methanolic suspension of [$Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4$]$PF_6$ **1a** with one equivalent of Ph_3PAuCl proceeded quickly, with the solids dissolving to give a clear pale yellow solution, which then deposited a white solid. Precipitation of the product was facilitated by addition of solid NH_4PF_6, which resulted in the deposition of more product, identified as the adduct [$Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4$]$(PF_6)_2$ **2a**. The reaction of [$Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4$]$PF_6$ **1d** with Ph_3PAuCl proceeded in a similar manner, giving [$Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4$]$(PF_6)_2$ **2b**, also as a white solid.

The isolated gold adducts **2a** and **2b** show the expected dications as the dominant base peaks in their positive-ion ESI mass spectra, at *m/z* 1026.5 for [$Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4$]$^{2+}$ and at *m/z* 1009.5 for [$Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4$]$^{2+}$. The ^{31}P-{^{1}H} NMR spectra of these complexes consist of two multiplets for the two types inequivalent Pt-PPh_3 ligands and a singlet for the Au-PPh_3 ligand; in both complexes the ^{1}J(PtP) coupling constants for the phosphines *trans* to $SAuPPh_3$ and to SR are very similar [e.g. 2960 and 2942 Hz in **2a**]. The reaction of [$Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4$]$PF_6$ with Cy_3PAuCl (Cy = cyclohexyl) was explored on a micro-scale using ESI mass spectrometry, and yielded the analogous species [$Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPCy_3)(PPh_3)_4$]$^{2+}$ at *m/z* 1018.5. The dicationic nature of these ions was readily confirmed by matching the observed and predicted isotope patterns. Minor ions at *m/z* 2197 and 2164 are assigned to the ion pairs $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4(PF_6)]^+$ and $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4(PF_6)]^+$ respectively. Fragmentation has been investigated for the benzyl derivative $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$ (M^{2+}): on raising the cone voltage to 50 V, two new but relatively low intensity ions at *m/z* 721 and 895.5 are assigned to $[Au(PPh_3)_2]^+$ and $[M - PPh_3]^{2+}$ respectively. At 80 V, $[Au(PPh_3)_2]^+$ was the dominant peak in the spectrum. The absence of fragmentation to $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ suggests that the gold centre is reasonably strongly bound to the $\{Pt_2S_2\}$ core. The binding affinity of the $AuPPh_3$ moiety towards the metalloligand was qualitatively investigated by the addition of an excess of a neutral ligand [tetrahydrothiophene (tht) or PPh_3] to a solution of $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4](PF_6)_2$. In the case of tht, the reaction solution remained colourless, and the ESI mass spectrum was essentially unchanged, with only a trace of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ observed. In contrast, the yellow PPh_3 solution showed $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ as the sole platinum species in the ESI mass spectrum, together with $[Au(PPh_3)_2]^+$ (*m/z* 721, base peak) and $[Au(PPh_3)_3]^+$ (*m/z* 983). Thus, strongly coordinating PPh_3 is able to displace the gold from $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$, but the weaker donor ligand tht cannot. Interestingly, the reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ with AuCl(tht) results in decomposition of the dinuclear species, with the formation of $[PtCl(PPh_3)_2(tht)]^+$ as the base peak in the ESI mass spectrum, with $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuCl)(PPh_3)_4]^+$ observed as a low intensity ion at *m/z* 1792.

The attempted synthesis of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$ from the known complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SAuPPh_3)(PPh_3)_4]PF_6$ by reaction with excess $PhCH_2Cl$ in dichloromethane-methanol solution was not successful in giving a pure product. After standing overnight, the initial yellow solution of $[Pt_2(\mu\text{-}S)(\mu\text{-}SAuPPh_3)(PPh_3)_4]PF_6$ faded to pale yellow, with positive-ion ESI MS revealing the presence of various ions, the most intense of which were $[Pt_2(\mu\text{-}SAuPPh_3)_2(PPh_3)_4]^{2+}$ (base peak; *m/z* 1210.5), $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ (*m/z* 1594), and the target product $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$ (*m/z* 1026.5).

Preliminary studies indicate that the same metalloligand chemistry can be extended to silver(I) species; reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ with AgCl and PPh_3, followed by precipitation with NH_4PF_6 gave an off-white solid, that showed the ions $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgPPh_3)(PPh_3)_4]^{2+}$ (*m/z* 964, 100%), $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ (*m/z* 1560, 10%), and $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgCl)(PPh_3)_4]^+$ (*m/z* 1703, 20%) in the ESI mass spectrum. The coordination of a neutral AgCl moiety is an alternative to coordination of the cationic $AgPPh_3^+$, as has been observed in previous studies on $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ itself.**[21]** An attempt at synthesising the AgCl adduct $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgCl)(PPh_3)_4]^+$ by reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ with a large excess of AgCl in methanol for several days only appeared to result in about 60% conversion to the adduct.

Organomercury adducts have also been synthesised. Upon stirring yellow $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]PF_6$ **1d** and an excess of PhHgCl in methanol for 4 days, a pale yellow suspension was formed, and the ESI mass spectrum confirmed that an incomplete reaction to give $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4]^{2+}$ had occurred, with starting $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ still observed at about 25% relative intensity. Addition of excess NH_4PF_6 appeared to effect conversion, with the formation of a white solid, which was isolated by filtration and washing, and confirmed by ^{31}P NMR as the hexafluorophosphate salt **3a**. The ESI mass spectrum of this material dissolved in dichloromethane-methanol shows $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4]^{2+}$ as the base peak, with $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ now at 50% relative intensity. Similarly, reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ with FcHgCl showed a mixture of starting material and product $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4]^{2+}$ cations. The resulting product (isolated as its hexafluorophosphate salt **3b**) showed a single set of resonances in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, consistent with the complete formation of the expected adduct. When analysed by ESI MS in dichloromethane-methanol, the material showed a greater amount of free $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ when compared to the reaction mixture containing excess FcHgCl. These observations suggest that (i) the reactions between $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ and RHgCl in methanol are equilibria, driven to completion by addition of excess PF_6^-, which precipitates the dicationic adduct; (ii) isolated $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgR)(PPh_3)_4](PF_6)_2$ dissociate in methanolic solution but remain intact in non-coordinating solvents dichloromethane and chloroform, as indicated by ^{31}P NMR.

The reactivity of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ towards other organomercury derivatives $PhN{=}NC_6H_4HgCl$ and $AcOHgC_6H_4NMe_2\text{-}4$ has also been explored by ESI MS, and found to produce analogous dicationic adducts $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SHgR)(PPh_3)_4]^{2+}$ [R = $PhN{=}NC_6H_4$, *m/z* 971.0 and R = $C_6H_4NMe_2\text{-}4$, *m/z* 940.5].

The reactivity of a selection of other metal systems with $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ has been explored using ESI MS. No reaction was observed between $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ and $TlNO_3$, $[RhCl_2(\eta^5\text{-}C_5Me_5)]_2$ or Ph_3SnCl. With $[PtCl_2(cod)]$ (cod = 1,5-cyclo-octadiene), a low intensity ion adduct ion was identified as $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SPtClcod)(PPh_3)_4]^{2+}$. The cationic metalloligands therefore appear to show a strong preference for binding to relatively strong Lewis acids that form two-coordinate adducts, possibly for reasons of steric crowding.

X-ray structure determination on $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4](PF_6)_2$ 3b

Orange crystals of **3b** suitable for an X-ray study were obtained by recrystallisation from dichloromethane-diethyl ether. The structure of the cation is shown in Figure 1, together with the atom numbering scheme, and selected bond lengths and angles are given in Table 1. The structure confirms adduct formation, with the HgFc unit coordinated to the formerly free sulfide atom, on the same side of the puckered $\{Pt_2S_2\}$ core as the benzyl group. We have recently carried out an X-ray structure determination on the parent complex **1d**[22] and the structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SHgFc)(PPh_3)_4]^+$ has also been previously reported.[17] Together, these complexes provide useful comparisons.

The fold angle (the angle between the two PtS_2 planes) of the $\{Pt_2S_2\}$ core of **3b** is 138.1°, which compares extremely favourably with that of **1d** (140°). Unsurprisingly, the Pt-S(sulfide) bonds are lengthened upon coordination to Hg. Thus, in **3b** the Pt(1)-S(1) and Pt(2)-S(1) bond distances to the S-Hg group [2.350(3) and 2.355(3) Å respectively] compare with 2.3209(13) and 2.3363(13) Å in **1d**. The Pt-S(thiolate) bond distances in **3b** [2.369(3) and 2.384(3) Å] compare with values of 2.3667(13) and 2.3594(13) Å in **1d**. The mercury is coordinated exclusively to sulfide S(1), with a Hg(1)-S(1) bond length of 2.349(3) Å. In contrast, in $[Pt_2(\mu\text{-}S)(\mu\text{-}SHgFc)(PPh_3)_4]^+$ the Hg atom has a distorted T-shaped geometry, with a relatively strong interaction [2.381(2) Å] to one sulfide, and a much weaker, longer interaction [3.0001(18) Å] with the other, as also found in the structure of $[Pt_2(\mu\text{-}S)(\mu\text{-}SHgPh)(PPh_3)_4]BPh_4$.**[19]** As a consequence, in $[Pt_2(\mu\text{-}S)(\mu\text{-}SHgFc)(PPh_3)_4]^+$ there is one essentially linear S-Hg-C bond angle [179.3(2)º for the main interaction]. The S(1)-Hg(1)-C(11) bond angle in **3b** is not, however, perfectly linear [174.5(4)º] with bending away from the benzyl group presumably as a result of steric interactions. The benzyl and HgFc substituents on the two sulfurs are slightly twisted to avoid eclipsing about the S(1)···S(2) axis, as indicated by the torsion angle C(31)-S(2)-S(1)-Hg(1) = 11.1° and the S(1)···S(2) distance of 3.126 Å is widened from 3.098 Å in the monoderivatised parent complex $[Pt_2(\mu\text{-}S)(\mu\text{-}SHgFc)(PPh_3)_4]^+$.

An X-ray structure determination on the gold adduct $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4](PF_6)_2$ **2a** was also attempted, from crystals obtained from dichloromethane-diethyl ether. Due to poor crystal quality, a well-defined structure determination could not be obtained however the positions of the heavy atoms confirmed the overall structure, with gold-phosphine coordination to the non-alkylated sulfide.

Conclusions

In this paper we have established for the first time that the monoalkylated derivatives $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ are able to act as monodentate metalloligands through the sulfido group. Complexes $[Pt_2(\mu\text{-}S)(\mu\text{-}SR)(PPh_3)_4]^+$ with simple R derivatives (n-butyl and n-octyl) are readily available through selective monoalkylation reactions from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and excess alkyl halide. The bromides are found to be sufficiently reactive, but not so reactive as to result in dialkylated products, as previously observed with alkyl iodides.**[8]**

Although not previously demonstrated, it is not unexpected that the monoalkylated derivatives should act as metalloligands, since the parent sulfide complexes containing $\{Pt_2(\mu\text{-}S)_2\}$ cores are able to: (i) be dialkylated; (ii) act as bidentate chelating ligands towards a range of mono- and di-cationic metal fragments, and (iii) coordinate two separate metal fragments. In the latter cases, the linear nature of the appended metal fragments probably permits double addition, consistent with the formation of adducts in this study with linear $MPPh_3^+$ (M = Ag, Au) and HgR^+ fragments, but not with more bulky groups such as $SnPh_3^+$. The general principles defined herein should also be applicable to more highly functionalised derivatives, where the alkyl group itself possesses coordinating ability. This could lead to the synthesis of a wide range of designer metalloligands, containing a soft sulfido donor together with an ancillary alkyl-appended donor group, with different donor atom and ligand bite characteristics, potentially able to act as bidentate ligands. This current work also develops options for our long term goal of building up large polymetallic assemblies based on functionalised $\{Pt_2S_2\}$ cores. We are currently exploring these possibilities.

Experimental

Water was distilled prior to use, while methanol was LR grade and used as supplied. Reactions were carried out without regard for the exclusion of air, light or moisture. The complex $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was prepared by the literature procedure, from *cis*-$[PtCl_2(PPh_3)_2]$ and $Na_2S.9H_2O$ in benzene suspension.[7] The compounds FcHgCl,[23] Ph_3PAuCl,[24] Cy_3PAuCl,[25] thtAuCl,[26] $PhN{=}NC_6H_4HgCl$,[27] and $AcOHgC_6H_4NMe_2$-4[28] were prepared by the literature procedures, and $[Pt_2(\mu\text{-}S)(\mu\text{-}CH_2Ph)(PPh_3)_4]PF_6$ was prepared by reaction of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ with excess $PhCH_2Cl$ in methanol, followed by precipitation with NH_4PF_6, using a modification of the literature procedure.[5] $[Pt_2(\mu\text{-}S)(\mu\text{-}SAuPPh_3)(PPh_3)_4]PF_6$ was prepared from $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and Ph_3PAuCl as reported previously.[15] The following chemicals were used as supplied from commercial sources: 1-chlorobutane (Riedel-de Haën), 1-bromobutane (BDH), 1-bromooctane (BDH), ammonium hexafluorophosphate (Aldrich), phenyl mercury chloride (Aldrich), thallium(I) nitrate (BDH), silver chloride (BDH), tetrahydrothiophene (BDH), and triphenylphosphine (Riedel-de Haën).

Positive-ion ESI mass spectra were recorded using a VG Platform II mass spectrometer. Solid samples were prepared for ESI MS analysis by dissolution of the solid product in 2 drops of dichloromethane, followed by dilution with methanol. Reaction mixtures were analysed directly, following dilution to give a total dissolved solids concentration of *ca.* 0.1 mg mL^{-1}. Spectra were typically an average of at least 10 scans and were typically acquired using a cone voltage of 20 V, though in some cases this was varied. Assignment of all major species was confirmed by recording the high resolution isotope pattern of the ion; this was used to confirm the charge on the species. These were compared with theoretical isotope patterns obtained using the ISOTOPE program.[29]

NMR spectra were recorded in $CDCl_3$ solution (unless otherwise stated) on a Bruker AC300P spectrometer at 300.13 (^1H) and 121.49 MHz (^{31}P) respectively, and were referenced to $CHCl_3$ or external H_3PO_4 respectively.

Synthesis of [Pt$_2$(μ-S)(μ-SBu)(PPh$_3$)$_4$]PF$_6$ **1a** *from BuBr*

[Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] (208 mg, 0.138 mmol) in methanol (30 mL) with 1-bromobutane (1 mL, excess) was stirred at room temperature for 20 h giving a cloudy yellow solution. After refluxing for 40 min., the resulting clear yellow solution was cooled to room temperature, and solid NH$_4$PF$_6$ (200 mg, 1.23 mmol) added, giving a yellow precipitate. Water (30 mL) was added to complete the precipitation, and the product was isolated by filtration, washed with water (2 x 20 mL) and dried under vacuum to give **1a** as a yellow powder (182 mg, 77%). Found: C, 53.3; H, 4.3. $C_{76}H_{69}F_6P_5Pt_2S_2$ requires C, 53.5; H, 4.1%. ESI MS: [Pt$_2$(μ-S)(μ-SBu)(PPh$_3$)$_4$]$^+$ (*m/z* 1561, 10%). ^{31}P-{^{1}H} NMR, δ 25.0 [m, ^{1}J(PtP) 3235], 24.3 [m, ^{1}J(PtP) 2634]. ^{1}H NMR, δ 7.49 – 6.89 (m, Ph), 2.29 (m, SCH_2), 0.79 (m, SCH$_2$CH$_2$CH_2), 0.61 (m, CH_2CH$_2$CH_3).

Synthesis of [Pt$_2$(μ-S)(μ-SOct)(PPh$_3$)$_4$]PF$_6$ **1b**

[Pt$_2$(μ-S)$_2$(PPh$_3$)$_4$] (277 mg, 0.184 mmol) in methanol (30 mL) with 1-bromooctane (1 mL, excess) was stirred at room temperature for 18 h, and then refluxed for 2 h, giving a clear yellow solution. Solid NH$_4$PF$_6$ (200 mg, 1.23 mmol) was added with stirring, giving a yellow precipitate. Water (30 mL) was added dropwise to complete the precipitation, and the solid was isolated by filtration, washed with water (2 x 10 mL), and dried under vacuum to give **1b** (255 mg, 79%). Found: C, 54.3; H, 4.7. $C_{80}H_{77}F_6P_5Pt_2S_2$ requires C, 54.5; H, 4.4%. ESI MS: [Pt$_2$(μ-S)(μ-SOct)(PPh$_3$)$_4$]$^+$ (*m/z* 1616, 100%). ^{31}P-{^{1}H} NMR, δ 24.9 [m, ^{1}J(PtP) 3219], 24.4 [m, ^{1}J(PtP) 2612]; ^{1}H NMR, δ 7.62-7.06 (m, Ph), 2.3-0.6 (m, octyl).

Synthesis of [Pt_2(μ-S)(μ-SBu)(PPh_3)$_4$]BPh_4 **1c** *from BuCl*

This complex was prepared similarly to **1b** in 16% yield from [Pt_2(μ-S)$_2$(PPh_3)$_4$] and 1-chlorobutane. M.p. 242-245 ºC. Found: C, 63.3; H, 4.7. $C_{100}H_{89}BP_4Pt_2S_2$ requires C, 63.9; H, 4.8%.

Synthesis of [Pt_2(μ-SBu)(μ-SAuPPh_3)(PPh_3)$_4$](PF_6)$_2$ **2a**

A mixture of [Pt_2(μ-S)(μ-SBu)(PPh_3)$_4$]PF_6 **1a** (233 mg, 0.137 mmol) and Ph_3PAuCl (69 mg, 0.140 mmol) was suspended in methanol (25 mL) and stirred. The initial yellow suspension quickly dissolved in a few minutes, giving a clear pale yellow solution which then deposited a white solid. After stirring for 2 h, NH_4PF_6 (150 mg, 0.92 mmol) was added, resulting in the deposition of more white solid. After stirring for 2 days, the off-white solid was filtered, washed with water (10 mL) and dried under vacuum to give **2a** 268 mg, 85%). Found: C, 48.6; H, 3.8. $C_{94}H_{84}AuF_{12}P_7Pt_2S_2$ requires C, 48.9; H, 3.7%. Recrystallisation by vapour diffusion of diethyl ether into a dichloromethane solution produced colourless crystals that were investigated by single-crystal X-ray diffraction; unfortunately the crystals rapidly lost solvent upon isolation from the mother liquor, preventing collection of an acceptable data set. ESI MS: [Pt_2(μ-SBu)(μ-SAuPPh_3)(PPh_3)$_4$]$^{2+}$ (*m/z* 1009.5, 100%), [Pt_2(μ-SBu)(μ-SAuPPh_3)(PPh_3)$_4PF_6$]$^+$ (*m/z* 2164, 3%). $^{31}P-\{^1H\}$ NMR, δ 34.3 (s, AuPPh_3), 23.0 [m, PtPPh_3, ^1J(PtP) 2960], 20.7 [m, PtPPh_3, ^1J(PtP) 2942].

Synthesis of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4](PF_6)_2$ **2b**

A mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]PF_6$ **1d** (150 mg, 0.086 mmol) and Ph_3PAuCl (46 mg, 0.093 mmol) was suspended in methanol (25 mL) and stirred, giving a clear, colourless solution. After 20 min. NH_4PF_6 (200 mg, 1.23 mmol) was added, giving a white precipitate, which was filtered, washed with water (10 mL) and dried under vacuum to give **2b** (163 mg, 81%). Found: C, 49.3; H, 3.7. $C_{97}H_{82}AuF_{12}P_7Pt_2S_2$ requires C, 49.7; H, 3.5%. ESI MS: cone voltage 20 V, $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$ (*m/z* 1026.5, 100%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4PF_6]^+$ (*m/z* 2198, 2%); cone voltage 50 V, $[Au(PPh_3)_2]^+$ (*m/z* 721, 8%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4 - PPh_3]^{2+}$ (*m/z* 895.5, 18%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4]^{2+}$ (*m/z* 1026.5, 100%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4PF_6]^+$ (*m/z* 2198, 3%); cone voltage 80 V, $[Au(PPh_3)_2]^+$ (*m/z* 721, 100%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SAuPPh_3)(PPh_3)_4PF_6]^+$ (*m/z* 2198, 10%). $^{31}P\text{-}\{^1H\}$ NMR, δ 34.6 (s, $AuPPh_3$), 22.0 [m, $PtPPh_3$, $^1J(PtP)$ 3013], 20.6 [m, $PtPPh_3$, $^1J(PtP)$ 2937].

Synthesis of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4](PF_6)_2$ **3a**

A mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]PF_6$ **1d** (111 mg, 0.064 mmol) and PhHgCl (30 mg, 0.096 mmol) was suspended in methanol (25 mL) and stirred for 4 days, giving a pale yellow suspension. ESI MS showed the dicationic adduct $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4]^{2+}$ (*m/z* 936) as the major species, but with unreacted $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ at about 25% relative intensity. Solid NH_4PF_6 (200 mg, 1.23 mmol) was added, and the suspension stirred for 2 h, resulting in the precipitation of a considerable amount of a white solid. Water (20 mL) was added dropwise with stirring, and the solid was filtered off, washed with water (10 mL) and dried under vacuum to give

3a as a white solid (119 mg, 86%). Found: C, 47.0; H, 3.4. $C_{85}H_{72}F_{12}HgP_6Pt_2S_2$ requires C, 47.2; H, 3.5%. ESI MS: $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4]^{2+}$ (*m/z* 936, 100%), $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ (*m/z* 1594, 50%), $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgPh)(PPh_3)_4(PF_6)]^+$ (*m/z* 2017, 5%). $^{31}P\text{-}\{^1H\}$ NMR (d^6-DMSO), δ 20.8 [m, $^1J(PtP)$ 3082], 20.2 [m, $^1J(PtP)$ 2951].

Synthesis of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4](PF_6)_2$ **3b**

A mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]PF_6$ **1d** (106 mg, 0.061 mmol) and FcHgCl (26 mg, 0.062 mmol) was suspended in methanol (20 mL) and stirred, giving an orange suspension. After stirring for several hours a positive-ion ESI mass spectrum showed considerable unreacted starting complex; an additional 20 mg of FcHgCl was added, and the reaction mixture stirred overnight. ESI MS showed mainly $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)]^{2+}$ (*m/z* 990) but with a considerable amount of $[Pt_2(\mu\text{-}S)(\mu\text{-}SCH_2Ph)(PPh_3)_4]^+$ remaining. Solid NH_4PF_6 (200 mg, 1.23 mmol) was added, and after stirring for several hours, water (20 mL) was added. The orange product was filtered off, washed with water (10 mL) and dried under vacuum to give crude **3b** (107 mg). $^{31}P\text{-}\{^1H\}$ NMR, δ 21.4 [m, $^1J(PtP)$ 2895], 20.4 [m, $^1J(PtP)$ 3083].

Recrystallisation from dichloromethane-diethyl ether at room temperature produced bright orange crystals of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4](PF_6)_2$, suitable for an X-ray diffraction study, which lost solvent on isolation from the mother liquor. Found: C, 46.4; H, 3.5. $C_{89}H_{76}F_{12}FeHgP_6Pt_2S_2$ requires C, 47.1; H, 3.4%.

Reaction of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ with AgCl/PPh_3

A mixture of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ (100 mg, 0.059 mmol) and AgCl (8.4 mg, 0.059 mmol) was suspended in methanol (25 mL) and stirred for 10 min., giving a slightly cloudy yellow solution. Triphenylphosphine (17 mg, 0.065 mmol) was added, resulting in the rapid formation of a clear yellow solution. After stirring for 2 days, a white suspension was formed. Solid NH_4PF_6 (200 mg, 1.23 mmol) was added, and after stirring for 10 min. the resulting white solid was isolated by filtration, washed with water (10 mL) and dried under vacuum to give 92 mg of an off-white solid. ESI MS: $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgPPh_3)(PPh_3)_4]^{2+}$ (*m/z* 964, 100%), $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ (*m/z* 1560, 10%), $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgCl)(PPh_3)_4]^+$ (*m/z* 1703, 20%).

Attempted synthesis of $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgCl)(PPh_3)_4]PF_6$

A suspension of $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]PF_6$ **1a** (145 mg, 0.085 mmol) and AgCl (500 mg, 3.49 mmol) in methanol (30 mL) was stirred in the dark for 3 days. The ESI mass spectrum of the reaction mixture showed $[Pt_2(\mu\text{-}S)(\mu\text{-}SBu)(PPh_3)_4]^+$ (*m/z* 1560, 90%), $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAgCl)(PPh_3)_4]^+$ (*m/z* 1703, 100%).

Reactivity of $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4](PF_6)_2$ towards neutral ligands

To solutions (*ca.* 1 mg mL^{-1}) of $[Pt_2(\mu\text{-}SBu)(\mu\text{-}SAuPPh_3)(PPh_3)_4](PF_6)_2$ **2a** in dichloromethane-methanol were added tetrahydrothiophene (tht, 2 drops) or triphenylphosphine (*ca.* 2 mg), and the mixtures shaken for 20 min. The colourless (tht) and pale yellow (PPh_3) reaction solutions were analysed by ESI MS.

X-ray crystallography

Orange crystals of **3b** as a dichloromethane solvate were obtained from dichloromethane-diethyl ether at room temperature. X-ray intensity data were collected on a Bruker CCD diffractometer using standard procedures and software. Empirical absorption corrections were applied (SADABS).[30] Structures were solved by direct methods and developed and refined on F_o^2 using the SHELX programmes[31] operating under WinGX.[32] Hydrogen atoms were included in calculated positions.

Crystal data: $C_{90}H_{78}Cl_2F_{12}FeHgP_6Pt_2S_2$ $M = 2354.98$, monoclinic, space group C2, $a = 20.8593(3)$, $b = 16.6485(2)$, $c = 25.5687(1)$ Å, $\beta = 100.801(1)^o$, $U = 8722.09(17)$ Å^3, T 83(2) K, $Z = 4$, $D_{calc} = 1.793$ g cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 5.406$ mm^{-1}, 26201 reflections collected with $1.58 < \theta < 26.54$, 13339 unique (R_{int} 0.0499) used after correction for absorption ($T_{max, min}$ 0.5632, 0.3129). Crystal dimensions 0.28 x 0.20 x 0.12 mm^3.

Refinement on F_o^2 converged at $R_1 = 0.0501$ [$I > 2\sigma(I)$] and $wR_2 = 0.1301$ (all data), GoF 1.072. The penultimate difference map revealed electron density associated with solvent molecule(s). This was severely disordered and was modelled as four fractional Cl atoms, summing to two, i.e. equivalent to one CH_2Cl_2 in total. The C and two H atoms were not included. The structure of **3b** is illustrated in Figure 1, with selected bond parameters summarised in Table 1.

Supplementary material

Crystallographic data (excluding structure factors) for the structure of **3b** described in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 649873. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 1 Selected bond lengths (Å) and angles (º) for $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4](PF_6)_2$

Pt(1)-P(2)	2.293(3)	Pt(1)-P(1)	2.308(3)
Pt(1)-S(1)	2.350(3)	Pt(1)-S(2)	2.369(3)
Pt(2)-P(3)	2.291(3)	Pt(2)-P(4)	2.290(4)
Pt(2)-S(1)	2.355(3)	Pt(2)-S(2)	2.384(3)
Hg(1)-C(11)	2.028(14)	Hg(1)-S(1)	2.349(3)
Fe(1)-C(23)	2.015(16)	Fe(1)-C(13)	2.017(17)
Fe(1)-C(24)	2.028(15)	Fe(1)-C(14)	2.034(14)
Fe(1)-C(12)	2.035(16)	Fe(1)-C(25)	2.034(15)
Fe(1)-C(22)	2.042(15)	Fe(1)-C(21)	2.058(14)
Fe(1)-C(15)	2.065(15)	Fe(1)-C(11)	2.066(13)
S(2)-C(31)	1.871(15)		
P(2)-Pt(1)-P(1)	100.21(11)	P(2)-Pt(1)-S(1)	167.09(13)
P(1)-Pt(1)-S(1)	83.51(11)	P(2)-Pt(1)-S(2)	92.93(11)
P(1)-Pt(1)-S(2)	166.49(11)	S(1)-Pt(1)-S(2)	82.98(11)
P(3)-Pt(2)-P(4)	99.73(13)	P(3)-Pt(2)-S(1)	90.75(12)
P(4)-Pt(2)-S(1)	169.07(12)	P(3)-Pt(2)-S(2)	173.10(12)
P(4)-Pt(2)-S(2)	86.88(12)	S(1)-Pt(2)-S(2)	82.55(11)
C(11)-Hg(1)-S(1)	174.5(4)	Hg(1)-S(1)-Pt(1)	119.59(14)
Hg(1)-S(1)-Pt(2)	100.14(11)	Pt(1)-S(1)-Pt(2)	91.80(11)
C(31)-S(2)-Pt(1)	105.5(5)	C(31)-S(2)-Pt(2)	102.7(4)
Pt(1)-S(2)-Pt(2)	90.61(11)	C(32)-C(31)-S(2)	109.4(9)

Captions to Figures

Figure 1 Molecular structure of the dication of $[Pt_2(\mu\text{-}SCH_2Ph)(\mu\text{-}SHgFc)(PPh_3)_4](PF_6)_2$ **3b** showing the atom numbering scheme. The phenyl rings of the PPh_3 ligands have been omitted for clarity.

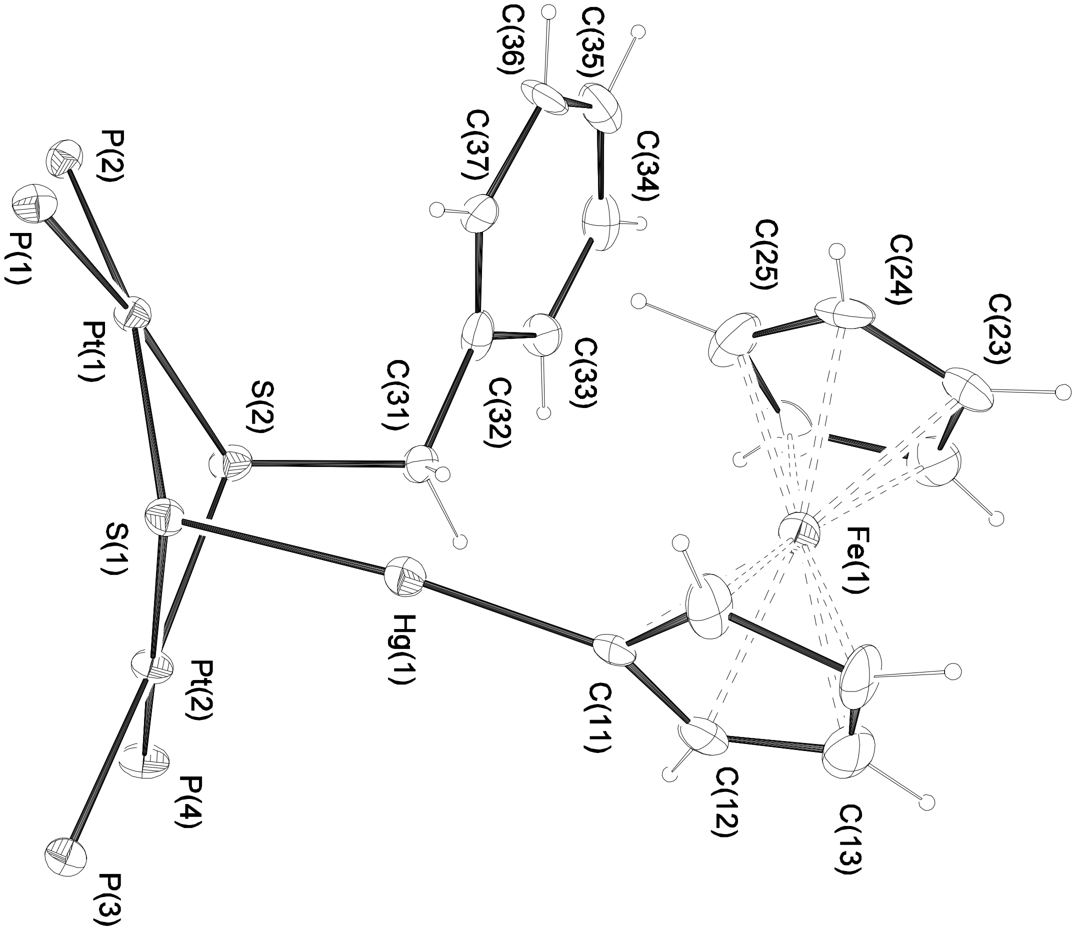
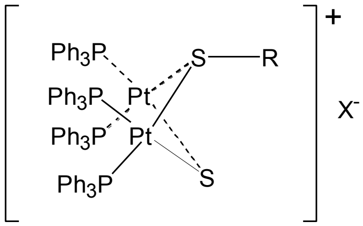
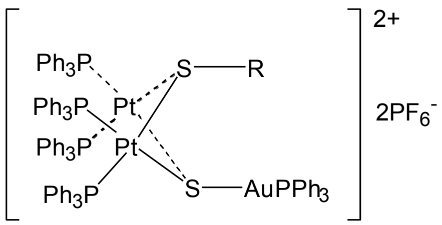

P(2)
P(1)
Pt(1)
S(2)
S(1)
Pt(2)
P(4)
P(3)
Hg(1)
C(31)
C(32)
C(33)
C(34)
C(35)
C(36)
C(37)
C(25)
C(24)
C(23)
Fe(1)
C(11)
C(12)
C(13)

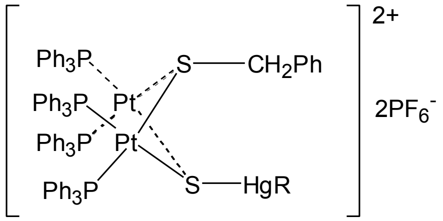
Figure 1



1a, R = n-C_4H_9, X = PF_6
1b, R = n-C_8H_{17}, X = PF_6
1c, R = n-C_4H_9, X = BPh_4
1d, R = CH_2Ph, X = PF_6



2a, R = n-C_4H_9
2b, R = CH_2Ph



3a, R = Ph
3b, R = Fc

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