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Research paper

The coordination chemistry of sulfonyl-substituted thioureas towards the d^8 metal centres platinum(II), palladium(II), nickel(II) and gold(III)

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ABSTRACT

Reactions of the complexes *cis*-$[PtCl_2(PPh_3)_2]$, $[PtCl_2(dppp)]$ (dppp = $Ph_2P(CH_2)_3PPh_2$), $[MCl_2(dppe)]$ (dppe = $Ph_2P(CH_2)_2PPh_2$, M = Ni, Pd), $[PdCl_2(bipy)]$ (bipy = 2,2′-bipyridine) and $[AuCl_2(bp)]$ (bp = cyclometallated 2-benzylpyridine) with *p*-$TolSO_2NHC(S)NHPh$ and Et_3N in refluxing methanol gave a series of new thiourea complexes containing the ligand bound as a dianion through the S and the NPh groups. The related thioureas $RSO_2NHC(S)NHPh$ (R = Me, Et) and *p*-$TolSO_2NHC(S)NHCH_2CH{=}CH_2$ were also reacted with *cis*-$[PtCl_2(PPh_3)_2]$ to form the corresponding complexes $[Pt\{RSO_2NC(S)NPh\}(PPh_3)_2]$ and $[Pt\{TolSO_2NC(S)NCH_2CH{=}CH_2\}(PPh_3)_2]$ respectively. X-ray structure determinations were carried out on the thiourea $MeSO_2NHC(S)NHPh$ and its platinum complex $[Pt\{MeSO_2NC(S)NPh\}(PPh_3)_2]$, as well as $[Pt\{TolSO_2NC(S)NPh\}(PPh_3)_2]$. Both complexes form the *distal* isomer with a remote NSO_2R group, and no evidence was observed for isomerisation of these platinum complexes in solution. The palladium complexes $[Pd\{TolSO_2NC(S)NPh\}L_2]$ [L_2 = $Ph_2PCH_2CH_2PPh_2$ (dppe), or 2,2′-bipyridine (bipy)] undergo decomposition in solution to form the sulfide-bridged aggregates $[Pd_3S_2(L_2)_3]^{2+}$, identified by ESI MS and ^{31}P NMR.

1. Introduction

Thioureas are versatile ligands, capable of coordination to a wide array of metal centres, through the sulfur and/or nitrogen centres. Simple disubstituted or trisubstituted thioureas can be readily synthesised by reaction of an isothiocyanate such as commercially available PhNCS with a primary or secondary amine, respectively. A common coordination mode involves chelation of the metal centre, forming a four-membered M—S—C—N ring system. In contrast, acylthioureas of the type $RC(O)NHC(S)NR_1R_2$, derived from an isothiocyanate RC(O)NCS and primary or secondary amine, show a rather different typical binding mode. These generally, but not exclusively,[1,2] coordinate through sulfur and oxygen, forming a six-membered ring system. This different pattern of behaviour is clearly a consequence of the C═O functionality, and the ability of the acylthiourea ligand to form a delocalised, six-membered ring. Complexes of acylthioureas have attracted considerable attention, on account of their coordination chemistry,[3] biological activity,[4] and potential applications such as metal ion recovery processes.[5]

We wished to explore the effects of replacing the C═O functionality of an acylthiourea RC(O)NHC(S)NHR with a related, but distinctly different, sulfonyl (SO_2) group, i.e. ligands of the type $RS(O)_2NHC(S)NHR$, and to explore the effects of this substitution on the coordination chemistry of such ligands. The coordination chemistry of sulfonylthiourea ligands is in its infancy compared to acylthioureas. Some coordination complexes of sulfonylthioureas are known containing *N,S*-coordination e.g. in copper(I) and silver(I) clusters,[6,7] and *N*-dansyl-*N*'-alkylthioureas have been used for the complexation of a range of metal ions [8] including fluorometric quantification.[9,10] Some six-membered *S,O*-chelated complexes are also known.[11] However, no X-ray structures of sulfonylthiourea complexes appear to have been reported to date in a search of the Cambridge Structural Database (Conquest version 5.41 August 2020 update). Here we report our preliminary investigations into the coordination chemistry of such ligands towards d^8 metal complexes of platinum(II), palladium(II), nickel(II) and gold(III).

2. Results and discussion

2.1. Synthesis and characterisation of sulfonylthiourea ligands

Sulfonyl thioureas can be prepared by the reaction of a sulfonamide

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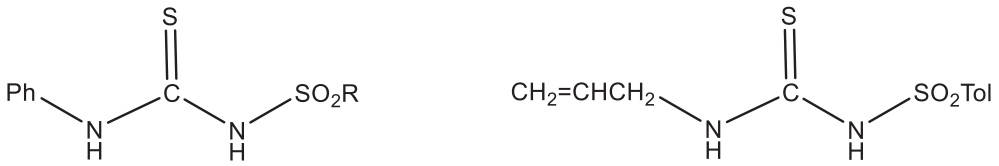
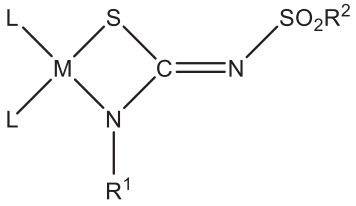


1a, R = *p*-Tol
1b, R = Me
1c, R = Et

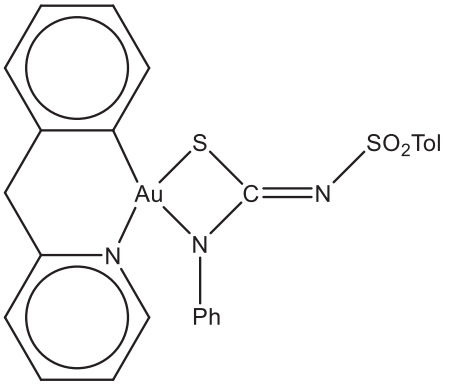
1d

Scheme 1. The sulfonylthiourea ligands used in this study.

with an isothiocyanate under alkaline conditions. Initial investigations centred on the thiourea *p*-TolSO_2NHC(S)NHPh **1a** (Scheme 1) which can be synthesised from commercially available and inexpensive *p*-toluenesulfonamide. Thus, reaction of *p*-TolSO_2NH_2 with PhNCS in acetone with aqueous sodium hydroxide, followed by acidification with acetic acid, resulted in the target ligand **1a** together with a by-product.



Complex	M	L/L_2	R^1	R^2
2a	Pt	PPh_3	Ph	*p*-Tol
2b	Pd	$Ph_2P(CH_2)_2PPh_2$ (dppe)	Ph	*p*-Tol
2c	Pd	2,2'-bipyridine (bipy)	Ph	*p*-Tol
2d	Pt	$Ph_2P(CH_2)_3PPh_2$ (dppp)	Ph	*p*-Tol
2e	Ni	dppe	Ph	*p*-Tol
2f	Pt	PPh_3	Ph	Me
2g	Pt	PPh_3	Ph	Et
2h	Pt	PPh_3	$CH_2CH{=}CH_2$	*p*-Tol



2i

Scheme 2. Complexes of the sulfonylthiourea ligands prepared in this study.

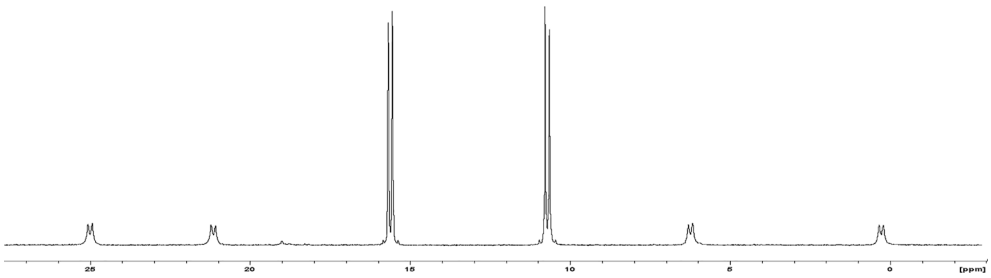


Fig. 1. $^{31}P\{^{1}H\}$ NMR spectrum of the complex [Pt{$TolSO_2NC(S)NPh$}$(PPh_3)_2$] **2a.**

The by-product was subsequently confirmed by ^{1}H NMR and ESI MS to be *N,N'*-diphenylthiourea, PhNHC(S)NHPh. Successful separation of the target sulfonylthiourea ligand was achieved by two consecutive crystallisations from hot EtOH and multiple washings with cold EtOH, resulting in a large loss of yield. Evaporation of the crystallisation filtrate yielded diphenylthiourea as a white crystalline solid. Additional confirmation of its identity was obtained by reaction with *cis*-$[PtCl_2(PPh_3)_2]$ to produce the known platinum thiourea complex [Pt{PhNC(S)NPh}$(PPh_3)_2$] [12] which gave an $[M + H]^+$ ion (*m/z* 946) in the ESI mass spectrum. Although seldom reported, examples of the synthesis of 1,3-disubstituted thioureas from isothiocyanates in the absence of amines are known.[13,14]

The methanesulfonylthiourea $CH_3SO_2NHC(S)NHPh$ **1b** was also prepared following an analogous procedure, using $CH_3SO_2NH_2$ and PhNCS. The product was isolated by acidification using acetic acid followed by precipitation with water. Although diphenylthiourea by-product was also observed in the ESI MS of the crude product, there was a sufficiently large difference in solubility between **1b** and diphenylthiourea to permit purification by simple recrystallisation. However, when the method was extended to the synthesis of the ethyl- and allyl-substituted thioureas $EtSO_2NHC(S)NHPh$ **1c** and $TolSO_2NHC(S)NHCH_2CH{=}CH_2$ **1d** respectively, pure compounds could not be obtained using the same acidification workup, and ESI MS indicated substantial decomposition. Instead, these ligands were isolated prior to acidification, by slow evaporation of the reaction mixtures, to give what are presumed to be the triethylammonium salts of the (deprotonated) thioureas. These were successfully used in subsequent syntheses, as described in the next section. The presence of the triethylammonium cation in the isolated solids of **1c** and **1d** was confirmed by positive ion ESI MS (see Supplementary Figures S6-S9). The structures of the various thioureas used in this study are shown in Scheme 1.

3. Synthesis and characterisation of sulfonylthiourea metal complexes

Initial reactions of **1a** were carried out with a selection of platinum (II), palladium(II), nickel(II) and gold(III) complexes (each containing two *cis* chloride ligands) in hot methanol with triethylamine base. The products were isolated by precipitation with water; in some cases the addition of an excess of sodium chloride and vigorous stirring was required to coagulate the precipitate to facilitate filtration. The corresponding triphenylphosphine platinum complexes formed from the thioureas $RSO_2NHC(S)NHPh$ (R = Me, Et) and *p*-$TolSO_2NHC(S)NHCH_2CH{=}CH_2$ were also prepared in the same way; in the case of reactions using **1c** and **1d**, the triethylammonium salts were used (*vide supra*). The structures of the synthesised complexes are shown in Scheme 2.

The $^{31}P\{^{1}H\}$ NMR spectra of the platinum phosphine complexes **2a**, **2d** and **2f-h** show the expected AB doublet of doublets with the corresponding satellites due to coupling to ^{195}Pt. For example, the $^{31}P\{^{1}H\}$ NMR spectrum of **2a** is shown in Fig. 1, and those of **2d** and **2f-h** in Supplementary Figures S1-S4. The $^{1}J(PtP)$ coupling constants for **2a** are 3038 Hz (tentatively ascribed to PPh_3 *trans* to S) and 3380 Hz (PPh_3 *trans* to N). These values are consistent with the expected S—N bidentate coordination mode, since an *O*-donor sulfonylthiourea ligand would be expected to display a much lower *trans* influence, resulting in a considerably larger value of $^{1}J(PtP)$ for the *trans* phosphorus. The sulfur atom is expected to have a slightly higher *trans* influence and is therefore used to assign the phosphorus with the smaller coupling constant to the sulfur *trans* position. The $^{1}J(PtP)$ coupling constant values for the series of triphenylphosphine-platinum complexes have relatively narrow ranges; 3308–3380 Hz (for P *trans* to N) and 3038 to 3059 Hz (for P *trans* to S).

Examination of the initial $^{31}P\{^{1}H\}$ NMR spectrum of complex **2a** in $CDCl_3$ revealed a single set of peaks, indicating the presence of a single isomer. After 8 days (with a spectrum recorded after every 48 h) no isomerisation was observed, indicating that there is only one stable isomer in solution. Likewise, $^{31}P\{^{1}H\}$ NMR investigation of the other phosphorus-containing platinum complexes identified only a single isomer in solution, *viz.* a single pair of AB doublets. For an *N,S*-chelated sulfonylthiourea, two isomers are possible, with a coordinated NSO_2Tol group (termed the *proximal* isomer) or with a coordinated NPh group (termed the *distal* isomer). From the X-ray structure determination on complexes **2a** and **2f** (*vide infra*) the latter isomer is identified, i.e. the NPh group is coordinated to platinum. In contrast, studies on mixed alkyl-aryl thiourea complexes of platinum(II) have explored the presence of both isomers in these systems.[15] It would appear from this present study that the presence of the sulfonyl group promotes the formation of only a single isomer in the corresponding complexes. Corresponding palladium(II) complexes of ligand **1a** with chelating bipy or dppe ligands, and the Ni-dppe complex, were also synthesised following the method used for the corresponding platinum complexes. The dppe complexes showed a single pair of doublets in their $^{31}P\{^{1}H\}$ NMR spectra, consistent with the formation of a single isomer.

By analogy with the structures of other cycloaurated complexes with thiourea ligands,[16] the cycloaurated benzylpyridyl (bp) complex **2i** is assumed to have a structure with mutually *cis* S and C donor atoms. The structure is also proposed to be the same *distal* isomer with a coordinated AuNPh group. The ^{1}H NMR spectrum of **2i** showed a single broad singlet for the CH_2 protons of the benzylpyridyl ligand, but in contrast, the ^{1}H NMR spectrum of the [$AuCl_2$(bp)] starting material shows an AB pattern of two doublets (see Supplementary Figure S5). This is due to slow inversion of the boat conformation of the six-membered Au(bp) chelate ring at room temperature, which allows protons in the axial and equatorial environments to be resolved.[17,18] The chemical shift of the singlet peak observed for complex (**2i**) is approximately at the midpoint of the two doublets observed for [$AuCl_2$(bp)].

The metal thiourea complexes showed no unusual features in their positive ion ESI mass spectra, showing $[M + H]^+$ ions and in some cases the corresponding sodiated ions $[M + Na]^+$ and the aggregate ion $[2\,M + Na]^+$. The IR spectra also show no unexpected features; the most noteworthy point is the observation of the expected two strong stretching bands for the SO_2 group, for example for **2a** at 1312 and 1098 cm^{-1}.

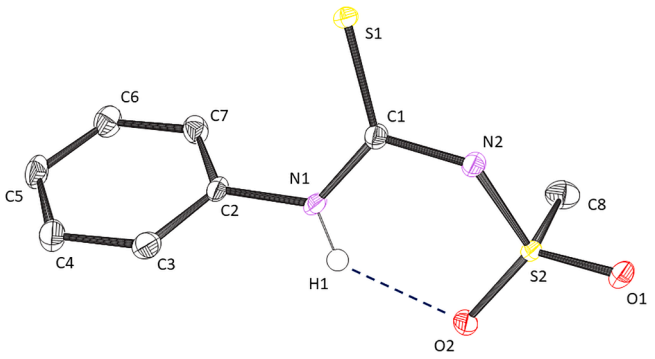


Fig. 2. Molecular structure of the sulfonylthiourea PhNHC(S)NHSO$_2$Me **1b**, showing the intramolecular hydrogen bond; hydrogens (other than H1) are omitted and thermal ellipsoids are at the 50% probability level.

Table 1
Selected bond lengths (Å) and angles (°) for PhNHC(S)NHSO$_2$Me **1b.**

C1 – N1	1.327(2)	C1 – N2	1.387(2)
S1 – C1	1.6758(17)	N2 – S2	1.6530(14)
S2 – C8	1.7533(18)	N1 – *C2*	1.4316(19)
S1 – C1 – N1	124.55(12)	S1 – C1 – N2	118.17(12)
C1 – N1 – *C2*	125.38(14)	N1 – C1 – N2	117.21(14)
C1 – N2 – S2	129.72(12)	N2 – S2 – C8	104.25(8)

4. X-ray structure determinations

Single crystals of the methanesulfonyl thiourea **1b** were grown by slow evaporation of a dichloromethane solution. While sulfonylthiourea ligands have been known since 1950 [19] there are only a small number of reported crystal structures, of which 3 are of the type H_2L. This is unlike the structurally similar and more extensively studied acylthioureas which have numerous reported crystal structures, including that of the acyl analogue of ligand **1b**, i.e. $CH_3C(O)NHC(S)NHPh$.[20] The molecular structure of **1b** is shown in Fig. 2, while selected bond lengths and angles are given in Table 1. The structure shows the standard trigonal planar geometry of the thiourea carbon with S1-C1, C1-N1 and C1-N2 bond lengths of 1.675, 1.327 and 1.387 Å respectively, and S1-C1-N1, S1-C1-N2 and N1-C1-N2 bond angles of 124.55, 118.17 and 117.21° respectively, close to the expected 120° trigonal planar bond angles. Interestingly, the sulfonyl group is facing in the opposite direction with respect to S1, with a C1-N2-S2 bond angle of 129.72°. This orentation of S2 is most likely due to intramolecular N—H···O═S hydrogen bonding (N1···O2 2.788(2) Å, N1-C1···S2-O2 torsion -2.6(1)°) which results in a hydrogen bond-stabilised pseudo 6-membered ring motif. Hydrogen bonding of this type has been observed for the acylthiourea analogues, including the methyl substituted analogue $CH_3C(O)NHC(S)NHPh$. This has N—H···O═C intramolecular hydrogen bonding between the thiourea N — H and the amidic O donor atom of the acyl group.[20] The geometry of **1b** reveals a nearly flat thiourea S—C—N1/N2 moiety, with a large deviation of S2 (which lies 0.57 Å from the thiourea plane defined by the mean positions of S1, C1, N1 and N2). The phenyl ring has an inter-plane angle of 61.24° to the thiourea plane, and the methyl substituent sits below the thiourea plane with a N2-S2-C8 bond angle of 104.25°.

Confirmation of the structure of the triphenylphosphine platinum complex **2a** was obtained by means of an X-ray structure determination. The molecular structure of the complex is shown in Fig. 3, while selected bond lengths and angles are given in Table 2. The platinum centre has a slightly distorted square planar geometry, coordinated by the S and NPh groups of the bidentate chelating thiourea ligand, as well as two triphenylphosphine ligands. The structure confirms the complex to have a coordinated NPh group. The metallacyclic bond distances [S1-Pt 2.322 (2), N1-Pt 2.105(5), C1-N1 1.330(8), C1-S1 1.770(6) Å] are similar to

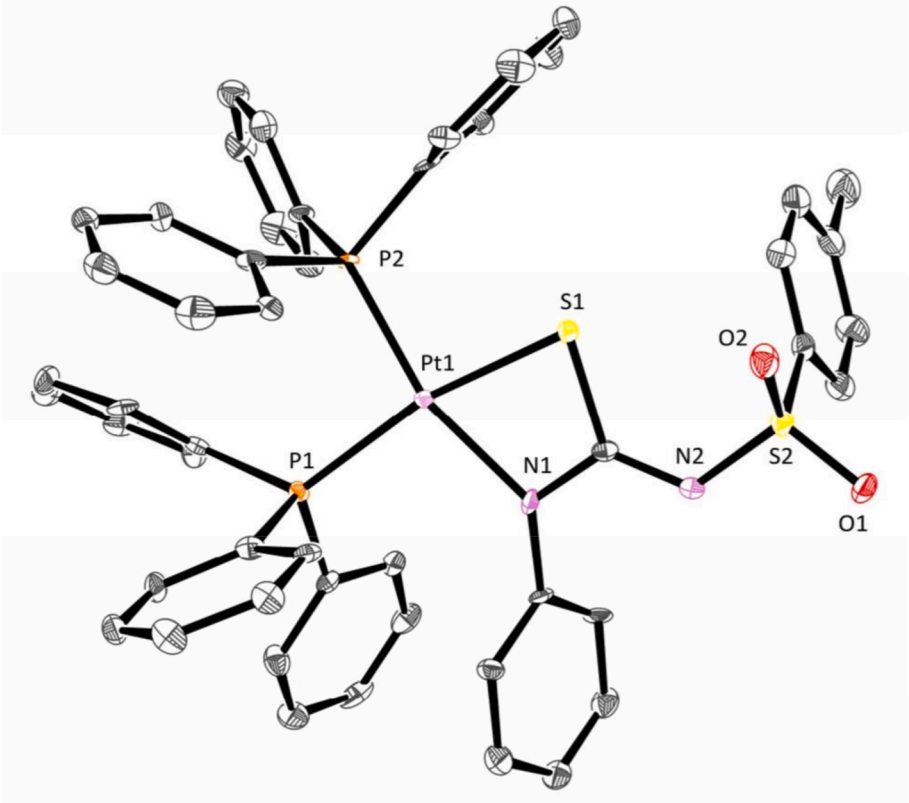


Fig. 3. ORTEP structure of the complex [Pt{TolSO$_2$NC(S)NPh}(PPh$_3$)$_2$] **2a** showing a partial atom numbering scheme. Hydrogens are omitted for clarity and ellipsoids are shown at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for the platinum complexes [Pt{*p*-$TolSO_2NC(S)NPh$}$(PPh_3)_2$] **2a** and [Pt{$MeSO_2NC(S)NPh$}$(PPh_3)_2$] **2f.**

	2a	2f
P1 – Pt	2.2964(15)	2.2913(9)
P2 - Pt	2.2627(15)	2.2551(9)
S1 - Pt	2.3222(15)	2.3453(8)
N1 - Pt	2.105(5)	2.088(3)
C1 – N1	1.331(8)	1.326(5)
C1 – S1	1.770(6)	1.791(4)
C1 – N2	1.325(8)	1.327(5)
P1 – Pt – P2	98.19(5)	97.53(3)
S1 – Pt – N1	69.29(15)	69.04(8)
S1 – C1 – N1	108.1(4)	107.0(3)
C1 – N2 – S2	121.2(5)	122.9(3)

the corresponding distances of the closely related diphenylthiourea complex [Pt{PhNC(S)NPh}$(PPh_3)_2$] which are 2.331(1), 2.054(3), 1.348(7) and 1.782(5) Å, respectively. The S1-C1-N2 bond angle of 121.1(4)° is close to the expected trigonal planar bond angle of 120°, however, the S1-C1-N1 bond angle [108.1(4)°] is less obtuse, due to bonding with the platinum metal centre. A significant feature of difference between **2a** and [Pt{PhNC(S)NPh}$(PPh_3)_2$] concerns the exocyclic C═N bond distance, which is 1.326(8) Å for **2a**, and significantly shorter [1.277(6) Å] for Pt{PhNC(S)NPh}$(PPh_3)_2$]. The NPh group is approximately parallel to one of the triphenylphosphine aromatic rings, in an almost π- π stacked manner, with a distance between the two ring centroids of 3.650 Å.

The structure of the methanesulfonyl derivative **2f**, which crystallised as a partial hydrate, was also determined; selected bond parameters are given in Table 2, and the structure is shown in Fig. 4. The structural parameters of the two triphenylphosphine complexes **2a** and **2f** are nearly identical, which is not surprising given that the position of difference (the sulfonyl substituent) is remote from the coordination centre.

5. Formation of trinuclear palladium(II) sulfido aggregates from sulfonylthiourea palladium complexes

During $^{31}P\{^1H\}$ NMR characterisation of the complex [Pd{$TolSO_2NC$(S)NPh}(dppe)] **2b** over a period of four weeks (to observe possible isomerisation), a second AB pair of doublets, and then a singlet at *ca.* δ51 were seen to increase in intensity, with a concomitant reduction in intensity of the AB doublets due to **2b**. The series of spectra is shown in Fig. 5. The palladium chloride complex [$PdCl_2$(dppe)] was readily ruled out as the identity of the singlet peak, since its chemical shift is reported as 68.3 ppm.[21]

The degradation of complex **2b** was then monitored by ESI MS. The spectrum of a freshly prepared methanol solution of **2b** was compared to the NMR sample at the end of the 4 week duration to observe the formation of any new ions. The spectra revealed a large intensity drop of the $[\mathbf{2b} + H]^+$ ion (*m/z* 809), with the appearance of doubly-charged ions in the NMR sample. The most notable of these was a dication at *m/z* 788, therefore a mass of 1576 Da. This indicated an aggregation, rather than a fragmentation process was occurring. A fresh solution of **2b** was dissolved in methanol and the ESI mass spectrum was recorded. The solution was then refluxed for 7 h to promote the decomposition of the complex **2b**. ESI mass spectra were recorded at the beginning, and after 3 and 7 h intervals, as shown in Fig. 6. The mass spectra reveal a decrease in intensity for the $[M + H]^+$ ion of complex **2b** and a dramatic increase in intensity for the dication at *m/z* 788. These spectra indicate a relationship between the two ions of interest.

The dication was readily identified as the sulfido species [Pd_3(μ-

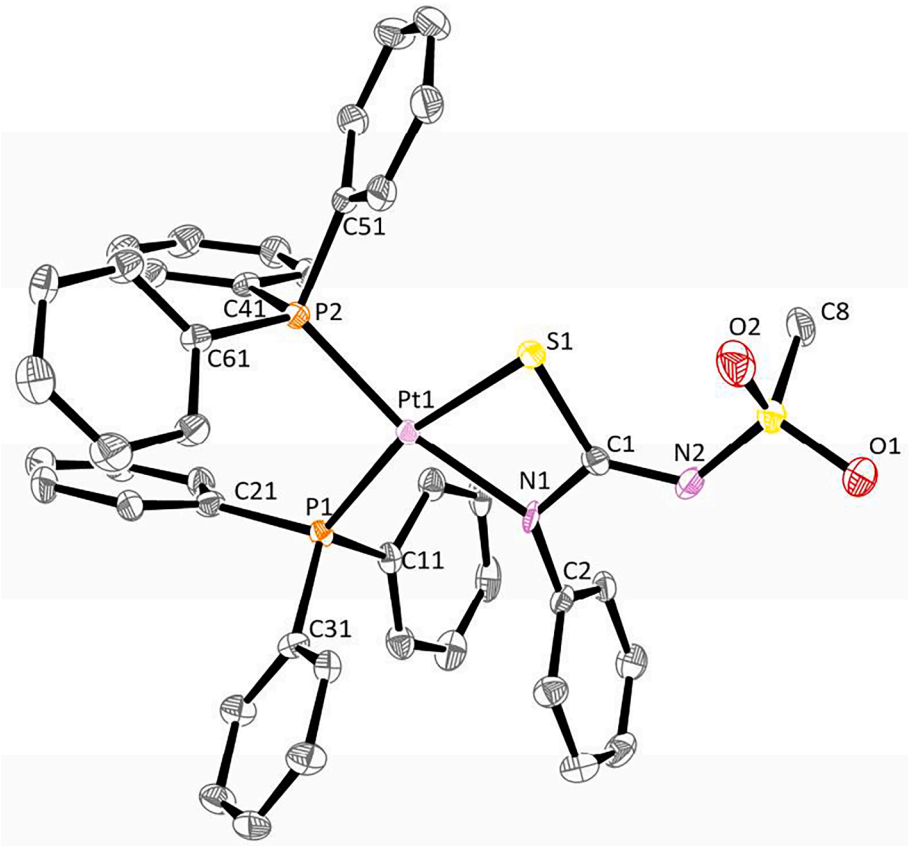


Fig. 4. ORTEP structure of the complex [Pt{$MeSO_2NC(S)NPh$}$(PPh_3)_2$] **2f** showing a partial atom numbering scheme. Hydrogens and a water molecule of crystallisation are omitted for clarity and ellipsoids are shown at the 50% probability level.

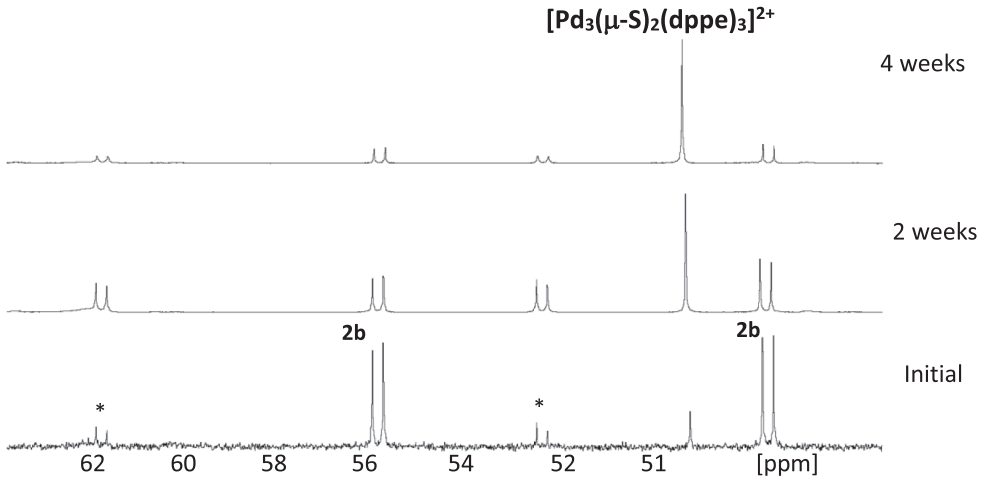


Fig. 5. $^{31}P\{^{1}H\}$ NMR spectra of the complex [Pd{TolSO$_2$NC(S)NPh}(dppe)] **2b** in $CDCl_3$, recorded over a period of 4 weeks, showing the formation of $[Pd_3S_2(dppe)_3]^{2+}$. The peaks marked * are due to an unidentified species.

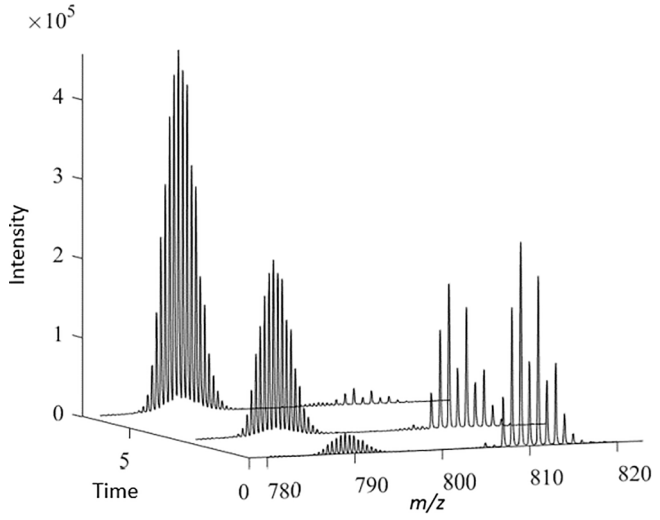


Fig. 6. A series of partial mass spectra obtained from a refluxing solution of complex **2b** in methanol, showing the conversion of **2b** ($[M + H]^+$ ion at *m/z* 809) to $[Pd_3S_2(dppe)_3]^{2+}$ (*m/z* 788).

$S)_2(dppe)_3]^{2+}$, from its *m/z* value, and 0.5 *m/z* separation of peaks in the isotope pattern, which gave an excellent match with the calculated pattern. The $^{31}P\{^{1}H\}$ NMR spectrum of the isolated product is also in agreement with $[Pd_3(\mu\text{-}S)_2(dppe)_3]^{2+}$. This species has been reported to have a single ^{31}P NMR environment at δ 52.9 for the chloride salt $[Pd_3(\mu\text{-}S)_2(dppe)_3]Cl_2$ in d^6-DMSO.[22] The cation $[Pd_3(\mu\text{-}S)_2(dppe)_3]^{2+}$ is one of a set of many such well-known species $[M_3(\mu\text{-}S)_2L_6]^{2+}$ [23,24]; $[Pd_3(\mu\text{-}S)_2(dppe)_3]^{2+}$ has also been structurally characterised.[21]

The palladium bipyridine complex **2c** might also be expected to form a trinuclear aggregate in the same manner as complex **2b**. A gently-warmed solution of **2c** in methanol was left for a duration of 7 h, and the solution monitored by ESI MS (since ^{31}P NMR was clearly not applicable). The expected ion at *m/z* 427 due to $[Pd_3S_2(bipy)_3]^{2+}$ increased in intensity over the duration of the experiment, as the $[M + H]^+$ ion for **2c** decreased; selected MS data are shown in Supplementary Figures S10-S13. Examples of palladium bipyridine sulfide aggregates are also known in the literature.[21,25]

The literature synthesis of $[Pd_3(\mu\text{-}S)_2(dppe)_3]Cl_2$ by Capdevila *et al* [22] was achieved by reaction of $[PdCl_2(dppe)]$ with Na_2S. In contrast, the synthesis of the same aggregate reported here is by decomposition of the sulfonylthiourea metal complex **2b** by C—S bond cleavage. Examples of dinuclear (M_2S_2) and trinuclear (M_3S_2) aggregates forming from thiourea cleavage have been described in the literature.[26–29] It is also well known that thioureas (but not, to date, sulfonylthioureas) may act as a source of sulfide in reactions with metal ions.[30,31] The synthetic route of these aggregates from the sulfonylthiourea complexes can be expected to be a result of desulfurisation resulting from the hydrolysis of the C—S thiourea bond of the metal complex. While desulfurisation has been demonstrated for thioureas, the electron withdrawing sulfonyl group of the sulfonylthiourea ligand might promote hydrolysis due to a reduction of electron density around the carbon making it more susceptible to nucleophilic attack by water and/or hydroxide. While the identity of the $[Pd_3S_2(dppe)_3]^{2+}$ cation from the degradation of **2b** is clear, the identity of the counteranion was not determined.

6. Conclusions

Following on from preceding studies on the coordination chemistry of substituted thiourea ligands towards platinum triad metals and gold, we have extended these studies to sulfonylthiourea ligands. In all cases, a single isomer was formed. X-ray structure determinations of two platinum triphenylphosphine complexes confirm that the observed isomer is *distal*, with a remote SO_2R group, and a coordinated *N*-alkyl/aryl. In addition, the structure determinations and ^{31}P NMR spectroscopy confirm that the thiourea ligands bind through S and N, with no evidence for oxygen coordination. This contrasts with the coordination chemistry of acylthiourea ligands, which have been shown in the literature to have a very strong tendency to show *S,O* chelation, forming six-membered rings.

7. Experimental

7.1. Materials

The following chemicals were used as supplied from commercial sources: *p*-toluenesulfonamide and *N,N'*-diphenylthiourea (BDH), phenyl isothiocyanate, methanesulfonic acid and ethanesulfonic acid (Sigma Aldrich), thionyl chloride (Scharlau) and methanesulfonyl chloride (Riedel-de Haën AG). Allyl isothiocyanate was sourced from Fluka and steam distilled before use.

The complexes *cis*-$[PtCl_2(PPh_3)_2]$, $[PdCl_2(dppe)]$ and $[PtCl_2(dppp)]$ were prepared by ligand substitution of the cycloocta-1,5-diene (cod) ligand of $[MCl_2(cod)]$ (M = Pd [32], Pt [33]) with the stoichiometric quantity of phosphine in dichloromethane.[34] The complexes $[PdCl_2(bipy)]$,[35] $[NiCl_2(dppe)]$ [36] and $[AuCl_2(bp)]$ [16] were

prepared by the literature methods, or minor variations thereof.

8. Instrumentation

^{31}P and ^{1}H NMR spectra were recorded at room temperature using a 400 MHz Bruker Avance DRX400 FT-NMR spectrometer using $CDCl_3$ as the solvent. Spectra were processed using Bruker topspin software. ESI mass spectra were recorded in methanol using a Bruker Daltonics MicrOTOF electrospray ionisation mass spectrometer. Sodium formate solution was used for calibration. Samples were prepared in Eppendorf tubes by dissolving the solid sample in 1 drop of dichloromethane and making up to 1.5 mL with methanol. Samples were centrifuged before use to ensure separation of undissolved solids. Spectra were recorded with a *Capillary Exit* voltage of 150 V and a *Skimmer 1* voltage of 50 V unless otherwise stated. Infrared spectra were recorded using a Perkin Elmer Spectrum 100 Fourier transform IR spectrometer with an observed range of 4000–450 cm^{-1}; samples were prepared as KBr disks. Melting points were recorded on a Reichert-Jung Thermovar as solid samples placed on glass slides; temperatures were recorded at the first signs of liquifying. Elemental analysis was performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand.

Synthesis of p-TolSO$_2$NHC(S)NHPh **1a**

The thiourea was synthesised using a procedure adapted from that of Shah *et al.*[37] *p*-Toluenesulfonamide (10 g) was dissolved in acetone (70 mL) and a solution of NaOH (2.34 g) dissolved in distilled water (20 mL) was added. The resulting slightly cloudy pale-yellow solution was stirred for 10 min., followed by the portionwise addition of phenyl isothiocyanate (7.89 g). The resulting yellow solution was stirred at room temperature for 48 h, filtered to remove any unwanted solids, followed by acidification of the filtrate with glacial acetic acid to achieve a pH of 4. A white solid precipitate was obtained by addition of excess distilled water (approx. 200 mL). The product was isolated by suction filtration and washed with distilled water (2 × 30 mL) followed by cold ethanol (2 × 30 mL). The solid was recrystallised from hot ethanol to give a white crystalline solid (6 g, 35%). M.p. 145–148 °C (lit.[38] 144–146 °C). ESI MS: Capillary exit voltage 90 V, *m/z* $[M + H]^+$ 307, $[M + Na]^+$ 330; ^{1}H NMR (400.13 MHz, chloroform-d_1), δ ppm 2.47 (3H, s, CH_3), 7.30–7.86 (m, 9H, aromatic CH), 8.86 (1H, s, NH), 9.79 (1H, s, NH); FTIR (cm^{-1}): υ(NH) 3304(m) and 1597(w), υ(S═O) 1381(s) and 1146(s), υ(CN) 1481(m) and 1179(m).

9. Synthesis of N,N'-diphenylthiourea by the self-reaction of phenyl isothiocyanate in basic aqueous conditions

A solution of NaOH (2.34 g) in distilled water (20 mL) was added to a solution of phenyl isothiocyanate (7.89 g) in acetone (70 mL). The resulting clear yellow solution was left to sit for 48 h, followed by acidification with glacial acetic acid to a pH of 4. The product was separated as a white solid by precipitation with excess distilled water (approx. 200 mL) and recovered by filtration. The resulting white solid was dried in vacuum (7.6 g, 58%). ESI MS: capillary exit voltage 90 V, *m/z* $[M + H]^+$ 229.

Table 3
Synthesis details for sulfonylthiourea complexes.

		Starting metal complex		Thiourea			Yield
	Product	mg	mmol	mg	mmol	mg	%
cis-$[PtCl_2(PPh_3)_2]$	**2a**	100	0.127	40	0.131	101	78*
$[PdCl_2(dppe)]$	**2b**	100	0.174	54	0.176	112	80
$[PdCl_2(bipy)]$	**2c**	100	0.300	95	0.310	97	57*
$[PtCl_2(dppp)]$	**2d**	100	0.147	45	0.147	108	81
$[NiCl_2(dppe)]$	**2e**	100	0.189	60	0.189	126	88
cis-$[PtCl_2(PPh_3)_2]$	**2f**	80	0.101	23	0.100	70	74
cis-$[PtCl_2(PPh_3)_2]$	**2 g**	40	0.051	17¶	0.049	37	79
cis-$[PtCl_2(PPh_3)_2]$	**2 h**	40	0.051	18¶	0.048	39	82
$[AuCl_2(bp)]$	**2i**	100	0.229	71	0.232	115	75*

* NaCl was used in the isolation of the complex from solution (refer to text)
¶ The triethylammonium salt of the initially prepared thiourea was used in this reaction

10. Synthesis of methanesulfonamide $CH_3SO_2NH_2$

Methanesulfonyl chloride (15 g, 0.13 mol) was added dropwise into rapidly stirred, concentrated aqueous ammonia (150 mL, excess). The temperature of the mixture was allowed to rise to 80 °C during the addition. Once the addition was completed, the mixture was stirred at 80 °C for 1 h and while still warm (*ca.* 50 °C) the product was isolated by two consecutive liquid–liquid separations into acetonitrile (2 × 150 mL). The combined organic phases were evaporated to dryness to give methanesulfonamide (8 g, 64%), which was used without further purification.

11. Synthesis of MeSO$_2$NHC(S)NHPh 1b

Methanesulfonamide (5 g, 0.052 mol) was dissolved in acetone (50 mL) and sodium hydroxide (1.5 g dissolved in 5 mL water) was added. The mixture was stirred for 15 min. followed by the addition of phenyl isothiocyanate (7.1 g, 0.052 mol, in approximately 1 mL portions). The mixture was allowed to stand at room temperature for 48 h, followed by acidification with glacial acetic acid (15 mL). A white solid was precipitated using excess water (200 mL), filtered under suction, and washed with cold ethanol (2 × 25 mL). Yield 7.38 g, 60%. ESI MS: Capillary exit voltage 90 V, *m/z* $[M + H]^+$ 231.06 (calculated *m/z* 231.03).

12. Synthesis of EtSO$_2$NHC(S)NHPh 1c

Ethanesulfonyl chloride (5 g, 0.038 mol) was added dropwise to concentrated aqueous ammonia (150 mL, excess) with rapid stirring. The temperature was allowed to rise to 80 °C during the addition and held at this temperature for 1 h. While still warm (*ca.* 50 °C), the product was isolated by two consecutive liquid–liquid separations into acetonitrile (2 × 150 mL). The combined organic phases were evaporated to near dryness to give ethanesulfonamide $EtSO_2NH_2$ as an off-white oil. Dichloromethane (100 mL) was added to dissolve the product followed by triethylamine (5 g). The solution was stirred for 20 min., followed by the dropwise addition of phenyl isothiocyanate (6 g, 0.044 mol) with stirring. The reaction mixture was allowed to evaporate slowly over 42 h to give the target ligand as its crystalline triethylammonium salt, which was then filtered under suction and washed with isopropyl alcohol (15 mL) and cold ethanol (25 mL). The solid was used without further purification. Yield, 3.7 g. Negative ion ESI MS: Capillary exit voltage −90 V, *m/z* $[M-H]^-$ 243.08 (calculated, 243.03).

13. Synthesis of p-TolSO$_2$NHC(S)NHCH$_2$CH = CH$_2$ 1d

p-Toluenesulfonamide (5 g, 0.029 mol) was dissolved in CH_2Cl_2 (150 mL) followed by the addition of triethylamine (3 g). The solution was heated to reflux followed by the addition of allyl isothiocyanate (2.9 g, 0.029 mol) with stirring. The reaction mixture was refluxed for 30 min. and without delay evaporated to dryness by rotary evaporation to give an off-white solid. This was filtered, washed with isopropyl alcohol (25 mL) and cold ethanol (25 mL) resulting in a white powder which was expected to be the triethylammonium salt of the target ligand, used without further purification. Yield 4.17 g. Negative ion ESI MS: Capillary exit voltage −90 V, *m/z* $[M-H]^-$ 269.01 (calculated 269.04).

Table 4
Crystallographic data for $MeSO_2NHC(S)NHPh$ **1b**, and the platinum complexes [Pt{*p*-$TolSO_2NC(S)NPh$}$(PPh_3)_2$] **2a** and [Pt{$MeSO_2NC(S)NPh$}$(PPh_3)_2$] **2f.**

	1b				**2a**				**2f**
Formula	$C_8H_{10}N_2O_2S_2$			$C_{50}H_{42}N_2O_2P_2PtS_2$		$C_{44}H_{39}N_2O_2P_2PtS_2.{}^2/_3H_2O$			
Formula weight	230.31			1024.06			959.947		
Crystal system	monoclinic			monoclinic			triclinic		
Space group	$P2_1/c$			$P2_1/n$				P-1	
a/Å	5.63542 (12)			9.69052 (13)			11.9104 (4)		
b/Å	8.87072 (18)			20.4713 (3)			12.7126 (6)		
c/Å	20.3842 (4)			21.2268 (3)			14.9487 (6)		
α/°	90				90				67.617 (4)
β/°	91.4698 (17)			96.9343 (12)			87.901 (3)		
γ/°	90				90				69.376 (4)
Volume/Å^3	1018.68(4)			4180.12(10)			1946.29 (15)		
Z	4				4				2
ρ_{calc} g/cm^3	1.502			1.627				1.638	
μ/mm^{-1}	4.564				8.284				8.861
Crystal size/ mm^3	0.18 × 0.093 × 0.071		0.079 × 0.038 × 0.030		0.185 × 0.071 × 0.047				
Radiation	Cu Kα (λ 1.54184 Å)			Cu Kα (λ 1.54184 Å)		Cu Kα (λ 1.54184 Å)			
2θ range for data collection/°	8.68 to 148.16			8.40 to 147.78		7.98 to 148.00			
Reflections collected	5704			23,539			21,882		
Independent reflections	1997 [R_{int} 0.0186, R_{sigma} 0.0179]	8188 [R_{int} 0.0378, R_{sigma} 0.0421]	7614 [R_{int} 0.0301, R_{sigma} 0.0321]						
Data/ restraints/ parameters	1997/0/ 128		8188/0/ 533		7614/0/ 491				
Goodness-of-fit on F^2	1.033			1.044			1.042		
Final R indexes [I ≥ 2σ (I)]	R_1 0.0279, wR_2 0.0714		R_1 0.0379, wR_2 0.1021	R_1 0.0253, wR_2 0.0606					
Final R indexes [all data]	R_1 0.0306, wR_2 0.0731		R_1 0.0507, wR_2 0.1086	R_1 0.0286, wR_2 0.0645					
Largest diff. peak/hole (eÅ^{-3})	0.40/-0.55			2.36/- 2.31			1.15/- 1.23		

14. General procedure for the synthesis of platinum(II), palladium(II), nickel(II) and gold(III)

14.1. Complexes of sulfonylthioureas

Equimolar amounts of the ligand and metal starting material were suspended in MeOH (30 mL) with stirring. The mixture was brought to reflux, followed by the addition of triethylamine (0.8 mL, excess). The solution was refluxed for 10 min. followed by the addition of distilled water (40 mL) to precipitate any solid. The mixture was cooled rapidly using an ice bath to facilitate precipitation and coagulation. Where stated in Table 3, solid NaCl (0.4 g) was added and allowed to stir for 1 h to aid coagulation of the precipitate. The solid was filtered and washed with hot water (2 × 20 mL, or 4 × 50 mL if NaCl added) and dried under vacuum. Details pertaining to each compound are given in Table 3. Elemental analytical data for complexes **2b** and **2c** were not obtained due to the instability of these products and formation of trinuclear sulfido aggregates.

[Pt{TolSO$_2$NC(S)NPh}(PPh$_3$)$_2$] **2a** Pale yellow solid. Elemental analysis: Found (%) C 58.89; H 4.73; N 2.72. Calculated (%) C 58.65; H 4.14; N 2.74. M.p. 279 °C. ESI MS: *m/z* $[M + H]^+$ 1025. FTIR (cm^{-1}): 3204(w,br), 3047(w,br), 1600(s), 1563(vs), 1486(s), 1434(s), 1312(s), 1098(s), 754(s), 693(vs), 544(s). NMR: $^{31}P\{^1H\}$, δ (ppm) 15.6 [d, $^1J_{PtP}$ 3039, $^2J_{PP}$ 21] and 10.7 [d, $^1J_{PtP}$ 3380, $^2J_{PP}$ 22]; ^1H, δ 7.7–6.2 (m, aromatic), 2.35 (3H, s, CH_3).

[Pd{TolSO$_2$NC(S)NPh}(dppe)] **2b**. Orange-brown solid. M.p. 129 °C. ESI MS: *m/z* $[M + H]^+$ 808. FTIR (cm^{-1}): 1589(w), 1471(vs), 1446(s), 1325(s), 1276(w), 1140(s), 1103(m), 1089(s), 691(s), 530(m). NMR: $^{31}P\{^1H\}$, δ (ppm) 56.9 (d, $^2J_{PP}$ 34) and 49.5 (d, $^2J_{PP}$ 35); ^1H, δ 8.0–6.5 (m, aromatic), 2.34 (3H, s, CH_3).

[Pd{TolSO$_2$NC(S)NPh}(bipy)] **2c**. Orange-red solid. M.p. 143 °C. ESI MS: *m/z* $[M + H]^+$ 567 and $[M + Na]^+$ 589. FTIR (cm^{-1}): 1601(w), 1487 (s), 1446(m), 1330(m), 1276(w), 1208(vw), 1140(s), 1088(s), 766(w), 692(w). NMR: ^1H, δ 8.4–6.8 (m, aromatic), 2.37 (3H, s, CH_3).

[Pt{TolSO$_2$NC(S)NPh}(dppp)] **2d**. Off white solid. M.p. 147–150 °C. ESI MS: *m/z* $[M + H]^+$ 912 and $[M + Na]^+$ 934. FTIR (cm^{-1}): 1590(w), 1473(vs), 1364(s), 1328(s), 1277(m), 1140(s), 1102(m), 1089(m), 690 (s), 545(m), 514(s). NMR: $^{31}P\{^1H\}$, δ (ppm) −2.9 [d, $^1J_{PtP}$ 2906, $^2J_{PP}$ 33] and −11.2 [d, $^1J_{PtP}$ 3024, $^2J_{PP}$ 33]; ^1H, δ 7.8–6.3 (m, aromatic), 2.35 (3H, s, CH_3). The complex was only characterised spectroscopically, and satisfactory microelemental analytical data could not be obtained.

[Ni{TolSO$_2$NC(S)NPh}(dppe)] **2e**. Orange solid. Elemental analysis: Found (%) C 63.01; H 4.82; N 3.53. Calculated (%) C 63.09; H 4.77; N 3.68. M.p. 140–145 °C. ESI MS: *m/z* $[M + H]^+$ 760.8. FTIR (cm^{-1}): 1626 (w), 1591(w), 1484(vs), 1435(s), 1328(s), 1289(m), 1126(s), 1097(s), 693(s). NMR: $^{31}P\{^1H\}$, δ (ppm) 58.4 (d, $^2J_{PP}$ 38) and 53.5 (d, $^2J_{PP}$ 38); ^1H, δ 8.1–6.4 (m, aromatic), 2.34 (3H, s, CH_3).

[Pt{CH$_3$SO$_2$NC(S)NPh}(PPh$_3$)$_2$] **2f**. Pale yellow solid. Elemental analysis: Found (%) C 55.72; H 3.54; N 2.77. Calculated (%) C 55.75; H 4.04; N 2.96. M.p. 260–266 °C. ESI MS: *m/z* $[M + H]^+$ 948.08 (calculated, 948.16), $[M + Na]^+$ 970.00 (calculated, 970.14). FTIR (cm^{-1}) 1591(w), 1484 (vs), 1436(s), 1131(s), 1098(m), 694(s), 526(s). NMR: $^{31}P\{^1H\}$, δ (ppm) 15.5 (d, $^1J_{PtP}$ 3059, $^2J_{PP}$ 22) and 10.4 (d, $^1J_{PtP}$ 3358, $^2J_{PP}$ 22). ^1H, δ 7.7–6.2 (m, aromatic), 2.88 (3H, s, CH_3).

[Pt{CH$_3$CH$_2$SO$_2$NC(S)NPh}(PPh$_3$)$_2$] **2g**. Pale yellow solid. M.p. 220–227 °C. ESI MS: *m/z* $[M + H]^+$ 962.34 (calculated, 962.17). FTIR (cm^{-1}): 3053(w), 2922(w), 1631(w, br), 1591(m), 1484(vs), 1328(s), 1289(s), 1126(vs), 1097(s), 997(m), 693(vs, br), 547(s). NMR: $^{31}P\{^1H\}$, δ (ppm) 15.6 (d, $^1J_{PtP}$ 3043, $^2J_{PP}$ 21) and 10.5 (d, $^1J_{PtP}$ 3366, $^2J_{PP}$ 21). ^1H, δ 7.7–6.2 (m, aromatic), 2.89 (2H, q, CH_2), 1.17 (3H, t, CH_3).

[Pt{TolSO$_2$NC(S)NCH$_2$CH=CH$_2$}(PPh$_3$)$_2$] **2h**. Pale yellow solid. M.p. 226–230 °C. ESI MS: *m/z* $[M + H]^+$ 989.27 (calculated, 989.18), $[M + Na]^+$ 1010.11 (calculated, 1010.17). FTIR (cm^{-1}): 1633(w, br), 1500(s), 1436(m), 1141(m), 1091(s), 693(s). NMR: $^{31}P\{^1H\}$, δ (ppm) 17.3 (d, $^1J_{PtP}$ 3038, $^2J_{PP}$ 21) and 12.1 (d, $^1J_{PtP}$ 3308, $^2J_{PP}$ 21). ^1H, δ 7.8 (Tol, d, 2H), 7.78 (Tol, d, 2H), 7.5–7.0 (PPh_3, m, 30H), 5.2 (allyl-CH, m, 1H), 4.5 (NCH_2, d, 2H), 4.2 (C=CH_2, m, 2H), 2.19 (Tol CH_3, s, 3H).

[Au{TolSO$_2$NC(S)NPh}(bp)] **2i**. Deep yellow solid. Elemental analysis: Found (%) C 46.14; H 3.31; N 6.22. Calculated (%) C 46.63; H 3.31; N 6.28. M.p. 121 °C. ESI MS: *m/z* $[M + H]^+$ 670 and $[M + Na]^+$ 692. FTIR (cm^{-1}): 1611(w), 1592(w), 1493(vs,br), 1447(m), 1336(s), 1281 (w), 1145(s), 1185(m), 690(m), 545(m). NMR: ^1H, δ 8.9–6.7 (m, aromatic), 3.41 (2H, s, CH_2) and 2.40 (3H, s, CH_3).

15. Formation of $[Pd_3(\mu\text{-}S)_2(dppe)_3]^{2+}$

The complex [Pd{*p*-TolSO$_2$C(S)NPh}(dppe)] **2b** (20 mg) was dissolved in methanol (20 mL) and heated slightly below boiling for 7 h. Alternatively, the same complex (20 mg) was dissolved in chloroform (0.5 mL), and allowed to stand at room temperature for 14 d. The solution was analysed by positive ion ESI MS.

16. X-ray crystal structure determinations

Crystals of the thiourea **1b** were grown by slow evporation of a dichloromethane solution, at room temperature. Crystals of the complexes **2a** and **2f** were obtained by slow diffusion of diethyl ether into a dichloromethane solution at room temperature. Intensity data were obtained on an Agilent SuperNova, Single source at offset, Atlas diffractometer with graphite-monochromated Cu—Kα radiation and corrected for absorption using a multi-scan procedure.[39] Using Olex2, [40] the structures were solved with the Olex2.solve [41] structure solution program using Charge Flipping and refined with the Olex2.refine [41] refinement package using Gauss–Newton minimisation. Crystal and refinement details are summarised in Table 4.

CRediT authorship contribution statement

Matthew C. Risi: Investigation, Formal analysis, Methodology, Writing - original draft. **Graham C. Saunders:** Formal analysis, Investigation, Methodology, Supervision, Writing - original draft. **William Henderson:** Conceptualization, Methodology, Project administration, Resources, Supervision, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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