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Platinum thiosemicarbazide and thiourea complexes: the crystal structure of [PtCl(dppe){SC(NHMe)NHNMe$_2$-*S*}](PF$_6$) and the influence of intramolecular hydrogen bonding on ligand co-ordination mode

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Abstract

The reaction of [PtCl$_2$(dppe)] [dppe=1,2-bis(diphenylphosphino)ethane] with two equivalents of the thioureas NHRC(S)NHR (R=H, Me, Et) in the presence of NH_4PF_6 led to substitution of both chlorides and formation of the complexes [Pt(dppe){SC(NHR)$_2$}$_2$](PF$_6$)$_2$ (**1a**, R=H; **1b**, R=Me; **1c**, R=Et). In contrast, the reaction of [PtCl$_2$(dppe)] with one equivalent of the potentially bidentate thiosemicarbazides NHRC(S)NHNR$'_2$ (R=Me, R′=H; R=Et, R′=H; R=Ph, R′=H; R=Me, R′=Me) in the presence of NH_4PF_6 led to substitution of only one chloride and formation of the complexes [PtCl(dppe){SC(NHR)NHNR$'_2$-*S*}](PF$_6$) (**2a**, R=Me, R′=H; **2b**, R=Et, R′=H; **2c**, R=Ph, R′=H; **2d**, R=Me, R′=Me). An X-ray analysis of complex **2d** revealed that an intramolecular N–H···Cl hydrogen bond [N(2)···Cl(1)=3.29(2) Å] helps to stabilise the monodentate co-ordination mode. The chloride ligand can be abstracted from complex **2d** by treatment with $TlPF_6$, and this reaction led to formation of [Pt(dppe){SC(NHMe)NHNMe$_2$-*S*,*N*}](PF$_6$)$_2$ **3d**. Reaction of [PtCl$_2$(dppe)] with unsubstituted thiosemicarbazide $NH_2C(S)NHNH_2$ in the presence of NH_4PF_6 resulted in a mixture of products containing mono- and bidentate co-ordinated ligands, [PtCl(dppe){SC(NH$_2$)NHNH$_2$-*S*}](PF$_6$) **2e** and [Pt(dppe){SC(NH$_2$)NHNH$_2$-*S*,*N*}](PF$_6$)$_2$ **3e**. [PtCl$_2$(dppe)] also reacts with two equivalents of $NHMeC(S)NHNMe_2$ in the presence of NH_4PF_6 to yield [Pt(dppe){SC(NHMe)NHNMe$_2$-*S*}$_2$](PF$_6$)$_2$ **1d**, in which the thiosemicarbazide is acting as an *S*-donor, directly analogous to the thiourea ligands in complexes **1a–c**.

Keywords: Platinum; Thiosemicarbazide; Thiourea; Hydrogen bonding; X-ray crystal structure; Phosphine

1. Introduction

Thiourea has a long history as a ligand in co-ordination chemistry being able to co-ordinate to a metal via either sulphur or nitrogen. Our original interest in thioureas and the related thiosemicarbazides arose as these ligands allow the retention of a hydrogen-bonding surface [1] within a complex following co-ordination. We have previously reported the use of the two parallel N–H hydrogen bond donor groups present in co-ordinated thiosemicarbazides together with the two parallel hydrogen bond acceptors in carboxylates as part of our crystal engineering studies of nickel [2,3] and zinc [4] complexes. Similar hydrogen bonds have been exploited as the basis of carboxylate receptors [5,6] and for the effect they have on C–N bond rotation [7]. In this paper we report the reactions of the platinum complex [PtCl$_2$(dppe)] with substituted thiosemicarbazides and thioureas in the presence of the metathesising agent NH_4PF_6. The thioureas and thiosemicarbazides used were of the general formulae NHRC(S)NHR and NHRC(S)NHNR$'_2$, respectively, in order to retain the required hydrogen bonding surface on complexation.

2. Results and discussion

Addition of an ethanol solution containing two equivalents of the thiourea NHRC(S)NHR (R=H, Me, Et) to a dichloromethane solution of [PtCl$_2$(dppe)], followed by an excess of NH_4PF_6 in ethanol gave the complexes [Pt(dppe){SC(NHR)$_2$}$_2$](PF$_6$)$_2$ (**1a**, R=H; **1b**, R=Me; **1c**, R=Et) in high yield. The symmetrical nature of complexes **1a–c** was confirmed by the $^{31}P\{^1H\}$ NMR spectra which showed one dppe-based phosphorus resonance, with ^1J(P,Pt) satellites between 3028 and 3059 Hz, and a septet arising from the hexafluorophosphate counter ion. The

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proposed formulae were confirmed by microanalyses and FAB mass spectra. In the FAB mass spectra, the two most intense peaks in each case were assigned to $[M+PF_6]^+$ and $[M-SC(NHR)_2]^+$, respectively, where M is $[Pt(dppe)\{SC(NHR)_2\}_2]$. The related compound $[Pt(PPh_3)_2\{SC(NHEt)_2\}_2](hfac)_2$ (hfac=1,1,1,5,5,5-hexafluoro-2,4-pentanedionate) has been prepared previously [8] from $[Pt(hfac)(PPh_3)_2](hfac)$ and 1,3-diethylthiourea, and the considerably lower $^1J(P,Pt)$ coupling constant for this complex (2436 Hz) may be consistent with the ligands adopting a *trans* geometry which is not accessible for complexes **1a–c** because of the chelating phosphine ligand. Complexes **1a–c** contain four hydrogen bond donor groups, and hydrogen bonding studies are currently in progress.

The reaction of $[PtCl_2(dppe)]$ with one equivalent of a thiosemicarbazide $NHRC(S)NHNR'_2$ (R=Me, R′=H; R=Et, R′=H; R=Ph, R′=H; R=Me, R′=Me) in the presence of NH_4PF_6 was expected to lead to the complex $[Pt(dppe)\{SC(NHR)NHNR'_2\text{-}S,N\}](PF_6)_2$, containing two parallel hydrogen bond donor groups. The reactions, carried out under similar conditions to those that gave rise to complexes **1a–c**, yielded only one product in each case (complex **2a** for R=Me, R′=H; **2b** for R=Et, R′=H; **2c** for R=Ph, R′=H; **2d** for R=Me, R′=Me). Although the presence of two dppe-based phosphorus signals in the $^{31}P\{^1H\}$ NMR spectrum, both with $^1J(P,Pt)$ satellites, was consistent with the formulation above, the microanalysis results were not accordant with this proposed structure. Moreover the FAB mass spectra demonstrated that the metathesis reactions had only replaced one of the two chlorides, suggesting the empirical formula $PtCl(dppe)\{NHRC(S)NHNR'_2\}(PF_6)$. This formulation was also more consistent with the $^{31}P\{^1H\}$ NMR spectra than the structure originally proposed: not only does it contain the two inequivalent phosphine phosphorus atoms necessary to explain the observed coupling pattern, but integration over the phosphine and PF_6^- chemical shift ranges suggest a dppe:PF_6^- ratio of 1:1 as opposed to 1:2 in the originally proposed structure.

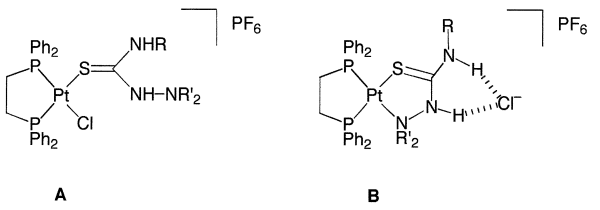


Fig. 1. Possible structural isomers for complexes **2a–d**.

There are two possible structural isomers for $PtCl(dppe)\{NHRC(S)NHNR'_2\}(PF_6)$ consistent with the spectroscopic data. The thiosemicarbazide could be monodentate, with a chloride still bound to the metal (**A** in Fig. 1), or bidentate with a chloride strongly hydrogen bonded to the two hydrogen bond donors on the thiosemicarbazide (**B** in Fig. 1). There is precedent for the bonding mode in **B** in the halide sensors developed by Beer et al. [9].

In order to determine whether **A** or **B** was the observed structure, a single crystal X-ray analysis was undertaken. Suitable crystals of the $NHMeC(S)NHNMe_2$ adduct **2d** were grown from the diffusion of diethyl ether into an acetone solution of the complex. The crystal structure (Fig. 2) confirmed structure **A**. The co-ordination sphere around

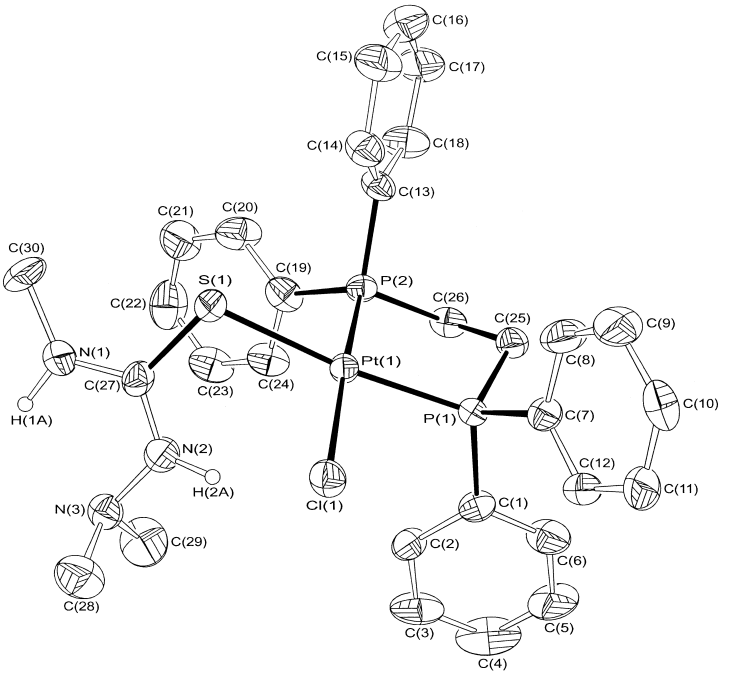


Fig. 2. Solid-state structure of the cationic complex present in **2d**. Thermal ellipsoids are illustrated at 30% probability.

the platinum atom is distorted square planar consisting of two phosphorus atoms, a chloride and a sulphur atom from a monodentate thiosemicarbazide ligand. Selected bond lengths and angles are given in Table 1. The *cis* angles range from 86.9(2) to 93.4(2)°, and the distortion from planarity is such that the chloride lies slightly above the plane defined by Pt(1), P(1) and P(2) [0.241(7) Å] whereas the sulphur atom lies slightly below [0.266(7) Å]. The C=S, C–N and N–N bond lengths are unexceptional with respect to comparative parameters for substituted thiosemicarbazides.

Although a tertiary amine group (NH*N*Me_2) would be expected to be a poorer ligand than a primary amine group (NH*N*H_2) the gain in entropy on chelate formation might still be expected to favour the bidentate co-ordination mode. Indeed bidentate nickel(II) complexes of NHMeC(S)NHNMe_2 have been crystallographically characterised and have not been observed to be labile even in competitive solvents [3]. However, in the platinum complex, monodentate co-ordination of the thiosemicarbazide is stabilised by formation of a weak intramolecular N–H···Cl hydrogen bond [N(2)···Cl(1) 3.29(2) Å, H(2A)···Cl(1) 2.40(7) Å, N(2)–H(2A)···Cl(1) 151(11)°], giving rise to an S(6) ring. There is precedence for N–H···Cl hydrogen bond formation in platinum complexes: the complex *cis*-bis(*N*-benzoyl-*N′*-propylthiourea)dichloroplatinum(II) contains N···Cl distances of 3.2 Å [10], although in this case the hydrogen atoms were not located crystallographically. Like the thiosemicarbazide ligands, the *N*-benzoyl-*N′*-propylthiourea ligand is also potentially bidentate, and the lack of chelate formation through acyl oxygen co-ordination was attributed to intramolecular N–H···O hydrogen bond formation which removes the oxygen atom from the vicinity of the metal.

Since the thiosemicarbazide complexes **2a–d** have many features in common such as similar ^{31}P chemical shifts and coupling constants, and similar fragments observed in their FAB mass spectra, all can be assigned the formulae [PtCl(dppe){SC(NHR)NHNR′$_2$-*S*}](PF_6) (**2a** R = Me, R′ = H; **2b** R = Et, R′ = H; **2c** R = Ph, R′ = H; **2d** R = Me, R′ = Me). In the FAB mass spectra of complexes **2a–c**, the molecular ion peak is observed at $[M+3H]^+$, where *M* is [PtCl(dppe){SC(NHR)NHNR′$_2$-*S*}], though there is precedence for observing multiple protonation using FAB-MS [11,12].

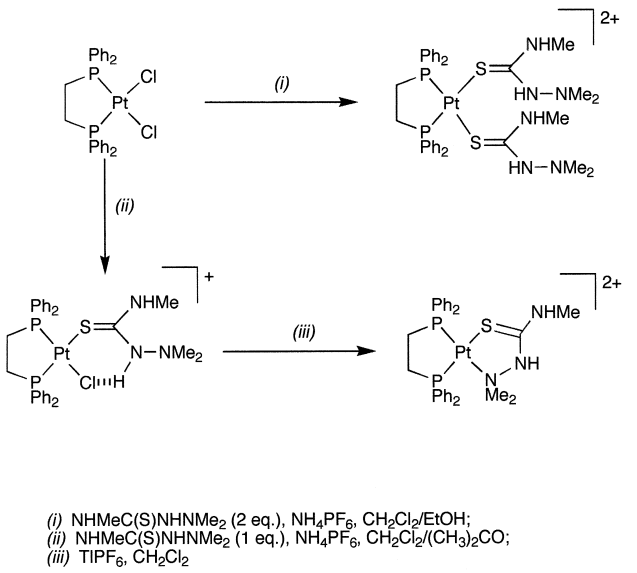
Table 1
Selected bond lengths (Å) and angles (°) for complex **2d**

Pt(1)–P(2)	2.217(4)	P(1)–Pt(1)–Cl(1)	89.2(2)
Pt(1)–P(1)	2.249(4)	P(2)–Pt(1)–S(1)	91.1(2)
Pt(1)–Cl(1)	2.361(4)	P(1)–Pt(1)–S(1)	173.3(2)
Pt(1)–S(1)	2.383(4)	Cl(1)–Pt(1)–S(1)	93.4(2)
S(1)–C(27)	1.73(2)	C(27)–S(1)–Pt(1)	106.2(6)
N(1)–C(27)	1.31(2)	C(27)–N(1)–C(30)	123(2)
N(1)–C(30)	1.46(3)	C(27)–N(2)–N(3)	121(2)
N(2)–C(27)	1.31(2)	N(2)–N(3)–C(28)	112(2)
N(2)–N(3)	1.42(2)	N(2)–N(3)–C(29)	108(2)
N(3)–C(28)	1.43(3)	C(28)–N(3)–C(29)	113(2)
N(3)–C(29)	1.46(3)	N(1)–C(27)–N(2)	118(2)
P(2)–Pt(1)–P(1)	86.9(2)	N(1)–C(27)–S(1)	121.1(14)
P(2)–Pt(1)–Cl(1)	173.0(2)	N(2)–C(27)–S(1)	120.4(13)

Although one chloride is retained in the thiosemicarbazide complexes following metathesis with NH_4PF_6, it is possible that the co-ordination mode of the thiosemicarbazide ligand may be changed from mono- to bidentate by the reaction of [PtCl(dppe){SC(NHR)NHNR′$_2$-*S*}](PF_6) with a halide abstracting agent. In order to test this premise, a dichloromethane solution of **2d** was stirred with $TlPF_6$ at room temperature for 18 h. After this time, the ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed the disappearance of the peaks for **2d** and the presence of signals for a new complex, **3d**. Two sets of doublets with ^{1}J(P,Pt) satellites showed that, like **2d**, complex **3d** contains inequivalent phosphorus environments, and both the integration of dppe:PF_6^- signals and the microanalysis were consistent with the abstraction of chloride, co-ordination of the NMe_2 nitrogen atom and formation of [Pt(dppe){SC(NHMe)NHNMe$_2$-*S,N*}](PF_6)$_2$.

In contrast to the reaction of the substituted thiosemicarbazides with [$PtCl_2$(dppe)] which gave only one product, the reaction with unsubstituted thiosemicarbazide, $NH_2C(S)NHNH_2$, gave rise to two complexes, as observed in the ^{31}P{^{1}H} NMR spectrum. Each complex has two signals in the dppe region with ^{1}J(P,Pt) satellites confirming the presence of inequivalent phosphorus atoms. One of these complexes had chemical shifts and ^{1}J(P,Pt) coupling constants very close to those observed for **2a–d** and, as with these complexes, the ^{2}J(P,P) coupling is too small to be resolved: this complex was therefore tentatively identified as [PtCl(dppe){SC(NH$_2$)NHNH$_2$-*S*}](PF_6) (**2e**). The second species had chemical shifts and both ^{1}J(P,Pt) and ^{2}J(P,P) coupling constants very close to those observed for **3d** and was tentatively identified as [Pt(dppe){SC(NH$_2$)NHNH$_2$-*S,N*}](PF_6)$_2$ (**3e**). Hence, in contrast to the reactions with substituted thiosemicarbazides, thiosemicarbazide itself gives a mixture of the mono- and bidentate thiosemicarbazide complexes.

In the structure of complex **2d**, the 1,1,4-trimethylthiosemicarbazide ligand can be likened to a thiourea ligand since co-ordination occurs only via the sulphur atom. This suggests that thiosemicarbazides might be able to act in a similar manner to the thioureas in complexes **1a–c** and that bis(thiosemicarbazide) complexes could be formed. Since the hydrogen bonding observed in the structure of **2d** involves an N–H group bonded to the carbon, this interaction is also possible in complexes of the general formula [PtCl(dppe){SC(NHR)$_2$}]$^+$ which are presumably intermediates in the formation of [Pt(dppe){SC(NHR)$_2$}$_2$]$^{2+}$ from [$PtCl_2$(dppe)]. In order to test whether bis(thiosemicarbazide) complexes could be formed, a dichloromethane solution of [$PtCl_2$(dppe)] was reacted with two equivalents of NHMeC(S)NHNMe_2 followed by an excess of NH_4PF_6 to give the complex



(i) $NHMeC(S)NHNMe_2$ (2 eq.), NH_4PF_6, CH_2Cl_2/EtOH;
(ii) $NHMeC(S)NHNMe_2$ (1 eq.), NH_4PF_6, CH_2Cl_2/$(CH_3)_2CO$;
(iii) $TlPF_6$, CH_2Cl_2

Scheme 1. Interconversion of platinum complexes of $NHMeC(S)NHNMe_2$.

$[Pt(dppe)\{SC(NHMe)NHNMe_2\text{-}S\}_2](PF_6)_2$ (**1d**) in high yield. The symmetrical nature of complex **1d** was confirmed by the $^{31}P\{^1H\}$ NMR spectrum which showed one dppe-based phosphorus resonance, with a $^1J(P,Pt)$ coupling constant of 3097 Hz, and a septet from the hexafluorophosphate counter ion. The proposed formula was confirmed by a FAB mass spectrum in which the two most intense peaks, as with complexes **1a–c**, could be assigned to $[M+PF_6]^+$ and $[M-SC(NHMe)NHNMe_2]^+$ where *M* is $[Pt(dppe)\{SC(NHMe)NHNMe_2\}_2]$. The reactions of $[PtCl_2(dppe)]$ with 1,1,4-trimethylthiosemicarbazide are summarised in Scheme 1, and the $^{31}P\{^1H\}$-NMR data for the compounds **1a–d**, **2a–e** and **3d–e** are given in Table 2. The magnitude of the $^1J(P,Pt)$ coupling constants clearly reflects the nature of the donor atom *trans* to the phosphorus atom, with those atoms having the largest *trans* influence showing the smallest coupling constants. Hence, the phosphorus atoms *trans* to sulphur atoms of thioureas and thiosemicarbazides have smaller coupling constants than those *trans* to thiosemicarbazide nitrogen atoms, whereas the largest coupling constants are for those phosphorus atoms *trans* to chloride.

The results reported in this paper demonstrate that thiosemicarbazides are very versatile ligands in platinum co-ordination chemistry as they are able to bind to the metal in a number of different modes. They can be monodentate, bound solely through the sulphur atom as in **1d**, they can be bidentate, bound through sulphur and nitrogen as in **3d–e**, or they can be monodentate but chelating through an intramolecular N–H···Cl hydrogen bond as in **2a–e**. The formation of this intramolecular hydrogen bond has a considerable effect on the hydrogen bonding surface presented by the cation.

3. Experimental

3.1. General

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen using dioxygen-free solvents, but no special precautions were taken to exclude oxygen during workup procedures. Microanalyses (C, H and N) were carried out by Mr. Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet 510P spectrometer as KBr pellets or nujol mulls. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM-EX270 spectrometer operating at 270 MHz referenced to TMS and 109.4 MHz referenced to H_3PO_4, respectively. $^{31}P\{^1H\}$ NMR data are given in Table 2. FAB mass spectra were recorded on a VG AutoSpec-Q spectrometer using 3-nitrobenzyl alcohol as the matrix. $[PtCl_2(cod)]$ (cod = cycloocta-1,5-diene) was prepared by the standard literature method [13]. Thioureas and thiosemicarbazides were purchased from Aldrich Chemical and used without purification, with the exception of 1,1,4-

Table 2
$^{31}P\{^1H\}$-NMR data for complexes **1a–d**, **2a–e** and **3d–e**

Complexes $[Pt(dppe)X_2]$		$\delta(P)^a$	$^1J(P,Pt)^b$			
$[PtCl_2(dppe)]^c$		41.9	3622			
$[Pt(dppe)\{SC(NH_2)_2\}_2](PF_6)_2$ [d,f]	**1a**	49.6	3030			
$[Pt(dppe)\{SC(NHMe)_2\}_2](PF_6)_2$ [d,f]	**1b**	49.3	3028			
$[Pt(dppe)\{SC(NHEt)_2\}_2](PF_6)_2$ [d,f]	**1c**	50.4	3059			
$[Pt(dppe)\{SC(NHMe)NHNMe_2\text{-}S\}_2](PF_6)_2$ [c,f]	**1d**	49.0	3097			
Complexes $[Pt(dppe)XY]$		$\delta(P_a)^a$	$\delta(P_b)^a$	$^1J(P_a,Pt)^b$	$^1J(P_b,Pt)^b$	$^2J(P_a,P_b)^b$
$[PtCl(dppe)\{SC(NHMe)NHNH_2\text{-}S\}](PF_6)$ [d,f]	**2a**	49.9	47.6	3149	3528	[e]
$[PtCl(dppe)\{SC(NHEt)NHNH_2\text{-}S\}](PF_6)$ [c,f]	**2b**	48.2	46.2	3126	3551	[e]
$[PtCl(dppe)\{SC(NHPh)NHNH_2\text{-}S\}](PF_6)$ [c,f]	**2c**	48.1	45.6	3129	3548	[e]
$[PtCl(dppe)\{SC(NHMe)NHNMe_2\text{-}S\}](PF_6)$ [c,f]	**2d**	47.9	45.5	3149	3541	[e]
$[PtCl(dppe)\{SC(NH_2)NHNH_2\text{-}S\}](PF_6)$ [c,f]	**2e**	48.5	45.2	3119	3558	[e]
$[Pt(dppe)\{SC(NHMe)NHNMe_2\text{-}S,N\}](PF_6)_2$ [c,f]	**3d**	49.4	37.6	3075	3122	7
$[Pt(dppe)\{SC(NH_2)NHNH_2\text{-}S,N\}](PF_6)_2$ [c,f]	**3e**	47.0	39.9	2911	3266	8

[a] a, ppm; b, Hz; c, $CDCl_3$; d, d_6-acetone; e, not resolved; f, PF_6^- also observed [$\delta(P)$–143.0, septet, $^1J(P,F)$ 712 Hz].

trimethylthiosemicarbazide which was prepared by the literature method [14]. {$\delta_H(CDCl_3)$ 7.32 [s, 1H, NH, (br)], 7.05 [s, 1H, NH, (br)] 3.12 [d, ^3J(HH) 6 Hz, 3H, CH_3], 2.53 [s, 6H, CH_3]}. With the exception of the reaction between [$PtCl_2$(dppe)], thiosemicarbazide and NH_4PF_6 (see below) the products were the only compounds observed in the NMR spectra, and were recovered after recrystallisation in 65–80% yield.

3.2. Syntheses of complexes

3.2.1. Synthesis of [Pt(dppe){SC(NH_2)$_2$-S}$_2$](PF_6)$_2$, **1a**

Dppe (0.107 g, 0.269 mmol) was added to a solution of [$PtCl_2$(cod)] (0.100 g, 0.269 mmol) in dichloromethane (20 cm^3) to generate [$PtCl_2$(dppe)] in situ. After stirring for 10 min, a solution of thiourea (0.041 g, 0.539 mmol) in ethanol (10 cm^3) was added, and the reaction mixture was stirred for 1 h. After this time, a solution of NH_4PF_6 (0.175 g, 1.074 mmol) in acetone (10 cm^3) was added. After an additional 30 min stirring, the solvent was removed under reduced pressure. The product was extracted with dichloromethane, and recrystallised from acetone–diethyl ether to give a colourless solid. (Found: N, 5.41; C, 32.4; H, 3.40. $C_{28}H_{32}F_{12}N_4P_4S_2Pt$ requires N, 5.41; C, 32.5; H, 3.11%); ν_{max}/cm^{-1}(NH) 3457m, 3364m, δ_{max}/cm^{-1}(NH_2) 1634m, ν_{max}/cm^{-1}(PF_6) 835vs, ν_{max}/cm^{-1}(CS) 691m; δ_H(d_6-acetone) 8.0–7.4 [m, 20H, Ar], 2.7 [m, 4H, CH_2]; *m*/*z* 890 $[M+PF_6]^+$, 668 $[M-\{SC(NH_2)_2\}]^+$.

3.2.2. Synthesis of [Pt(dppe){SC(NHMe)$_2$-S}$_2$](PF_6)$_2$, **1b**

Synthesis as for complex **1a** using 1,3-dimethylthiourea (0.056 g, 0.538 mmol) instead of thiourea. (Found: N, 5.00; C, 37.3; H, 4.03. $C_{32}H_{40}F_{12}N_4P_4S_2Pt$–1.5$CH_3COCH_3$ requires N, 4.75; C, 37.2; H, 4.19%); ν_{max}/cm^{-1}(NH) 3386m (br), ν_{max}/cm^{-1}(amide) 1613m, 1510s, ν_{max}/cm^{-1}(PF_6) 839vs, ν_{max}/cm^{-1}(CS) 693m; δ_H(d_6-acetone) 7.9–7.4 [m, 20H, Ar], 2.6 [m, 4H, CH_2]; 2.80 [s, 12H, CH_3]; *m*/*z* 946 $[M+PF_6]^+$, 696 $[M-\{SC(NHMe)_2\}]^+$.

3.2.3. Synthesis of [Pt(dppe){SC(NHEt)$_2$-S}$_2$](PF_6)$_2$, **1c**

Synthesis as for complex **1a** using 1,3-diethylthiourea (0.071 g, 0.538 mmol) instead of thiourea. (Found: N, 4.87; C, 37.4; H, 4.28. $C_{36}H_{48}F_{12}N_4P_4S_2Pt$ requires N, 4.88; C, 37.7; H, 4.21%); ν_{max}/cm^{-1}(NH) 3446w, 3368m, ν_{max}/cm^{-1}(amide) 1607m, 1509s ν_{max}/cm^{-1}(PF_6) 839vs, ν_{max}/cm^{-1}(CS) 694m; δ_H(d_6-acetone) 8.0–7.4 [m, 20H, Ar], 3.45 [m, 8H, CH_2Me], 2.8 [m, 4H, CH_2P]; 1.13 [t, 12H, CH_3]; *m*/*z* 1003 $[M+PF_6]^+$, 724 $[M-\{SC(NHEt)_2\}]^+$.

3.2.4. Synthesis of [PtCl(dppe){SC(NHMe)NHNH$_2$-S}](PF$_6$), **2a**

Dppe (0.107 g, 0.269 mmol) was added to a solution of [$PtCl_2$(cod)] (0.100 g, 0.269 mmol) in dichloromethane (20 cm^3) to generate [$PtCl_2$(dppe)] in situ. After stirring for 10 min, a solution of 4-methylthiosemicarbazide (0.029 g, 0.276 mmol) in dichloromethane (10 cm^3) was added, and the reaction mixture was stirred for 24 h. After this time, a solution of NH_4PF_6 (0.175 g, 1.074 mmol) in acetone (10 cm^3) was added. After an additional 30 min stirring, the solvent was removed under reduced pressure. The product was extracted with dichloromethane before recrystallisation from acetone–diethyl ether to give a pale orange solid. (Found: N, 4.34; C, 40.9; H, 3.95. $C_{28}H_{31}ClF_6N_3P_3SPt\cdot 2CH_3COCH_3$ requires N, 4.22; C, 41.0; H, 4.35%); ν_{max}/cm^{-1}(NH) 3360m (br), ν_{max}/cm^{-1}(amide) 1586m, ν_{max}/cm^{-1}(PF_6) 839vs, ν_{max}/cm^{-1}(CS) 691s; $\delta_H(CDCl_3)$ 10.5 [s, NH (br)], 8.0–7.4 [m, 20H, Ar], 2.79 [d, ^3J(HH) 5, 3H, CH_3], 2.6 [m, 4H, CH_2]; *m*/*z* 737 $[M+3H]^+$, 629 $[M-\{SC(NHMe)NHNH_2\}]^+$.

3.2.5. Synthesis of [PtCl(dppe){SC(NHEt)NHNH$_2$-S}](PF$_6$), **2b**

Synthesis as for complex **2a** using 4-ethylthiosemicarbazide (0.032 g, 0.269 mmol) instead of 4-methylthiosemicarbazide. The crude product was extracted with dichloromethane before recrystallisation from acetone–diethyl ether to give a colourless solid. (Found: N, 4.26; C, 41.4; H, 4.07. $C_{29}H_{33}ClF_6N_3P_3SPt$–1.5$CH_3COCH_3$ requires N, 4.16; C, 41.7; H, 4.49%); ν_{max}/cm^{-1}(NH) 3365m (br), ν_{max}/cm^{-1}(amide) 1576m, ν_{max}/cm^{-1}(PF_6) 835vs, ν_{max}/cm^{-1}(CS) 691s; $\delta_H(CDCl_3)$ 10.4 [s, NH (br)], 8.0–7.4 [m, 20H, Ar], 3.21 [m, ^3J(HH) 7, 2H, CH_2Me], 2.6 [m, 4H, CH_2], 1.06 [t, ^3J(HH) 7, 3H, CH_3]; *m*/*z* 751 $[M+3H]^+$, 629 $[M-\{SC(NHEt)NHNH_2\}]^+$.

3.2.6. Synthesis of [PtCl(dppe){SC(NHPh)NHNH$_2$-S}](PF$_6$), **2c**

Synthesis as for complex **2a** using 4-phenylthiosemicarbazide (0.045 g, 0.269 mmol) instead of 4-methylthiosemicarbazide. The crude product was extracted with dichloromethane before recrystallisation from acetone–diethyl ether to give a cream coloured solid. (Found: N, 4.03; C, 44.6; H, 4.07. $C_{33}H_{33}ClF_6N_3P_3SPt$–2$CH_3COCH_3$ requires N, 3.97; C, 44.3; H, 4.29%); ν_{max}/cm^{-1}(NH) 3260m, 3150w (br), ν_{max}/cm^{-1}(amide) 1557s, 1499m, ν_{max}/cm^{-1}(PF_6) 839vs, ν_{max}/cm^{-1}(CS) 691m; *m*/*z* 799 $[M+3H]^+$, 759 $[M-Cl]^+$, 629 $[M-\{SC(NHPh)NHNH_2\}]^+$.

3.2.7. Synthesis of [PtCl(dppe){SC(NHMe)NHNMe$_2$-S}](PF$_6$), **2d**

Dppe (0.107 g, 0.269 mmol) was added to a solution of [$PtCl_2$(cod)] (0.100 g, 0.269 mmol) in dichloromethane (20 cm^3) to generate [$PtCl_2$(dppe)] in situ. After stirring for 10 min, a solution of 1,1,4-trimethylthiosemicarbazide (0.036 g, 0.271 mmol) in dichloromethane (10 cm^3) was

added, and the reaction mixture was stirred for 24 h. After this time, a solution of NH_4PF_6 (0.175 g, 1.074 mmol) in acetone (10 cm^3) was added. After an additional 30 min stirring, the solvent was removed under reduced pressure. The product was extracted with acetone, and recrystallised by addition of diethyl ether to give colourless crystals. (Found: N, 4.89; C, 39.3; H, 3.99. $C_{30}H_{35}ClF_6N_3P_3SPt$ requires N, 4.63; C, 39.7; H, 3.86%); ν_{max}/cm^{-1}(NH) 3314m, 3142w, ν_{max}/cm^{-1}(amide) 1590m, 1402m, $\nu_{max}/cm^{-1}(PF_6)$ 837vs, ν_{max}/cm^{-1}(CS) 693m; $\delta_H(d_6$-acetone) 8.6 [1 H, s, NH, (br)], 8.3 [1 H, s, NH, (br)], 7.6–7.3 [20 H, m, Ph], 2.55 [3 H, d, Me, ^{3}J(HH) 5], 2.4 [4 H, m, CH_2] and 2.18 [6 H, s, Me]; *m/z* 761 $[M]^+$, 725 $[M-Cl]^+$, 629 $[M-\{SC(NHMe)NHNMe_2\}]^+$, 592 $[M-Cl-\{SC(NHMe)NHNMe_2\}]^+$.

3.2.8. Synthesis of [Pt(dppe){SC(NHMe)NHNMe$_2$-S}$_2$](PF$_6$)$_2$, **1d**

Dppe (0.107 g, 0.269 mmol) was added to a solution of $[PtCl_2(cod)]$ (0.100 g, 0.269 mmol) in dichloromethane (20 cm^3) to generate $[PtCl_2(dppe)]$ in situ. After stirring for 10 min, a solution of 1,1,4-trimethylthiosemicarbazide (0.072 g, 0.541 mmol) in ethanol (10 cm^3) was added, and the reaction mixture was stirred for 1 h. After this time, a solution of NH_4PF_6 (0.175 g, 1.074 mmol) in ethanol (10 cm^3) was added. After an additional 30 min stirring, the solvent was removed under reduced pressure. The product was extracted with dichloromethane, and recrystallised by addition of diethyl ether to give a colourless solid. (Found: N, 7.87; C, 34.9; H, 4.09. $C_{34}H_{46}F_{12}N_6P_4S_2Pt$ requires N, 7.31; C, 35.5; H, 4.03%); ν_{max}/cm^{-1}(NH) 3303m, ν_{max}/cm^{-1}(amide) 1617m, 1595s, $\nu_{max}/cm^{-1}(PF_6)$ 837vs, ν_{max}/cm^{-1}(CS) 693m; $\delta_H(d_6$-acetone) 7.8–7.3 [20 H, m, Ph], 2.82 [6 H, s, Me], 2.8 [4 H, m, CH_2] and 2.51 [3 H, m, Me]; *m/z* 1004 $[M+PF_6]^+$, 725 $[M-\{SC(NHMe)NHNMe_2\}]^+$.

3.2.9. Reaction of [PtCl(dppe){SC(NHMe)NHNMe$_2$-S}](PF$_6$), **2d**, with TlPF$_6$: synthesis of [Pt(dppe){SC(NHMe)NHNMe$_2$-S,N}](PF$_6$)$_2$, **3d**

Complex **2d** (0.100 g, 0.11 mmol) was dissolved in dichloromethane (20 cm^3), $TlPF_6$ (0.055 g, 0.16 mmol) added and the mixture stirred for 18 h. The solution was filtered, the solvent removed under reduced pressure, and the crude solid recrystallised from dichloromethane–diethyl ether. (Found: N, 4.03; C, 34.8; H, 3.49. $C_{30}H_{35}F_{12}N_3P_4PtS\cdot 0.5CH_2Cl_2$ requires N, 3.97; C, 34.6; H, 3.43%); ν_{max}/cm^{-1}(NH) 3398m, 3314m, ν_{max}/cm^{-1}(amide) 1614s, 1524s, $\nu_{max}/cm^{-1}(PF_6)$ 841vs, ν_{max}/cm^{-1}(CS) 700m; $\delta_H(d_6$-acetone) 7.8–7.3 [20 H, m, Ph], 2.96 [12 H, s, Me], 2.7 [4 H, m, CH_2] and 2.55 [6 H, s, Me]; *m/z* 725 $[M]^+$.

3.2.10. Reaction of [PtCl$_2$(dppe)] with thiosemicarbazide and NH$_4$PF$_6$

Synthesis as for complex **2a** using thiosemicarbazide (0.025 g, 0.270 mmol) instead of 4-methylthiosemicarbazide. The $^{31}P\{^1H\}$ NMR spectrum showed the presence of two complexes **2e** and **3e**, in a 70:30 ratio, identified as $[PtCl(dppe)\{SC(NH_2)NHNH_2\text{-}S\}](PF_6)$ and $[Pt(dppe)\{SC(NH_2)NHNH_2\text{-}S,N\}](PF_6)_2$, respectively.

3.3. Crystallography

Single crystals of complex **2d** suitable for analysis by X-ray crystallography were grown by diffusion of diethyl ether into an acetone solution of **2d**.

3.3.1. Crystal data

$[C_{30}H_{35}ClN_3P_2PtS]PF_6$, $M=907.12$, triclinic, space group $P\bar{1}$ (No. 2), $a=9.668(1)$, $b=11.211(2)$, $c=17.346(3)$ Å, $\alpha=107.56(1)$, $\beta=96.43(2)$, $\gamma=92.656(2)°$, $U=1774.8(5)$ Å^3, $Z=2$, $\mu=4.279$ mm^{-1}, a colourless crystal of dimensions $0.3\times0.3\times0.07$ mm was used.

3.3.2. Data collection and processing.

Data were collected at 293(2)K on an Enraf-Nonius CAD4 automatic four-circle diffractometer using graphite monochromated MoKα radiation ($\lambda=0.71069$ Å). 4321 reflections were collected ($2.12<\theta<21.93°$, $-10\le h\le10$, $-11\le k\le11$, $0\le l\le18$) and corrected for Lorentz, polarisation and absorption [15]. R(int) = 0.0313 (pre-DIFABS).

3.3.3. Structure solution and refinement

The solution (SHELX86 [16]) and refinement (SHELXL93 [17]; full-matrix least squares based on F^2) of the structure converged to a conventional [i.e. based on 3096 with $F_0>4\sigma(F_0)$] $R1=0.0446$ and $wR2=0.1175$[1] for the observed data and 418 parameters. In the final least squares cycle, all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant, except for H(1A) and H(2A) [attached to N(1) and N(2), respectively] which were located by examining an electron density map based on low Bragg angle data, and refined at a fixed distance of 0.98 Å from the relevant parent atoms. The structural diagram was produced using ORTEX [18].

Supplementary data

The crystal structure has been deposited at the CCDC. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number CCDC 116444.

[1] $R1=\Sigma\ \|F_o|-|F_c\|/\Sigma\ |F_o|$, $wR2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma\ w(F_o^2)^2]^{1/2}$.

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