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Inorganica Chimica Acta 320 (2001) 101–109

Inorganica Chimica Acta

# Platinum(II) complexes of chelating and monodentate thiourea monoanions incorporating chiral, fluorescent or chromophoric groups

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Received 14 March 2001; accepted 27 April 2001

## Abstract

The reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with trisubstituted thioureas $[R^1R^2NC(=S)NHR^3]$ in refluxing methanol with triethylamine base, followed by addition of $NaBPh_4$ gives the salts $[Pt\{SC(=NR^1R^2)NR^3\}(PPh_3)_2]BPh_4$ in high yield; a range of thiourea substituents, including chiral, fluorescent and chromophoric groups can be incorporated. The azo dye-derived complex $[Pt\{SC(=N(CH_2CH_2)_2O)NC_6H_4N{=}NC_6H_4NMe_2\}(PPh_3)_2]BPh_4$ has been characterised by a single-crystal X-ray diffraction study. The formation of a fluorescein-derivatised platinum–thiourea complex is also described. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with PhNHC(S)NHPh or EtNHC(S)NHEt, triethylamine and $NaBPh_4$ gives, respectively, $[Pt\{SC(=NHPh)NPh\}(PPh_3)_2]^+$ and the known cation $[Pt\{SC(=NHEt)NEt\}(PPh_3)_2]^+$, isolated as tetraphenylborate salts. Reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with an excess of Na[MeNHC(S)NCN] in methanol gives the bis(thiourea monoanion) complex *trans*-$[Pt\{SC(=N{-}CN)NHMe\}_2(PPh_3)_2]$, characterised by NMR spectroscopy and an X-ray crystal structure determination. When *cis*-$[PtCl_2(PPh_3)_2]$ is reacted with 1 equiv. of Na[MeNHC(S)N–CN] in methanol, with added $NaBPh_4$, a mixture of isomers of the $[Pt\{SC(=NHCN)NMe\}(PPh_3)_2]^+$ cation is obtained. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Crystal structures; Platinum complexes; Thiourea complexes

## 1. Introduction

Thioureas are versatile ligands, able to coordinate to metal centres either as neutral ligands, as monoanions, or as dianions [1–4]. An attractive feature of their chemistry is their ease of synthesis, and the ready modification of the substituents on nitrogen and hence their physical and chemical properties. There have been many studies of benzoyl-substituted thioureas and related ligands coordinated to platinum(II) [5], and other metals [6], where the ligand typically bonds as a monoanion through S and O, giving a six-membered ring system, though complexes with neutral ligands are also known [7]. Platinum–thiourea complexes have attracted interest for their biological activity [8]. Metal cluster complexes with coordinated thiourea monoanions are also well-known [9]. However, there are relatively few examples of mononuclear metal complexes of simple alkyl- or aryl-substituted thiourea monoanions, containing N,S-chelated ligands; examples include complexes of chromium(III) [10], rhodium(III) [11], technetium(III) [12], rhenium(V) [13,14], aluminium [15], ruthenium [16,17], osmium [17] and iridium [17]. For platinum(II), the topic of this paper, the reaction of the thiourea dianion complex $[Pt\{SC(=NEt)NEt\}(PPh_3)_2]$ with *p*-toluenesulfonic acid ($TsOH{\cdot}H_2O$) gave the thiourea monoanion complex $[Pt\{SC(=NHEt)NEt\}(PPh_3)_2]OTs$ [18]. The complex was also prepared by reaction of $[Pt(hfac)(PPh_3)_2](hfac)$ [hfac = $CF_3C(O)CHC(O)CF_3$] with 1,3-diethylthiourea [18]. Palladium complexes containing monodentate and N,S-chelating thiourea monoanions have also been described [19].

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0020-1693/01/$ - see front matter

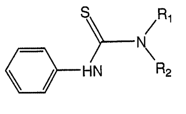
PII: S0020-1693(01)00473-X

In this paper, we report the synthesis of a series of platinum(II) complexes containing thiourea monoanions, bonded in either N,S-chelating mode (with four-membered Pt–N–C–S rings) or in an S-bonded monodentate mode. These complexes contrast with those of trisubstituted thioureas containing benzoyl substituents, which commonly bond as monoanions to platinum(II) through S and O giving six-membered rings [5]. The ease of synthesis of thioureas allows the synthesis of derivatives containing various chiral, fluorescent or chromophoric groups, and in this paper we demonstrate the simplicity of using thioureas to incorporate such functionalities into platinum complexes.

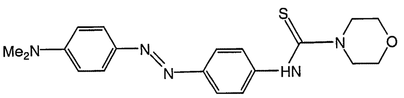
## 2. Results and discussion

### 2.1. Synthesis and characterisation of complexes of trisubstituted thiourea monoanions

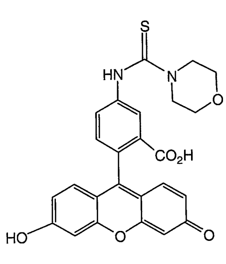
The thioureas **1a**–**1f** were readily synthesised in good yields by addition of the appropriate amine to PhNCS in diethyl ether solution, or by addition of morpholine to either 4-[(4-isothiocyanatophenyl)azo]-*N*,*N*-dimethylaniline or fluorescein isothiocyanate, isomer I. Reactions of the complex *cis*-[$PtCl_2(PPh_3)_2$] with the trisubstituted thioureas **1a**–**1e** in refluxing methanol, with added triethylamine base gives clear solutions containing cationic platinum–thiourea monoanion complexes. Addition of $NaBPh_4$ to the hot solutions results in precipitation of the tetraphenylborate salts in good to high yields, giving complexes **2a**–**2e**, respectively. Using this general method, a range of functionalised thiourea complexes can easily be prepared, including derivatives containing chiral (**2c**), fluorescent (**2d**) or chromophoric (**2e**) labels.



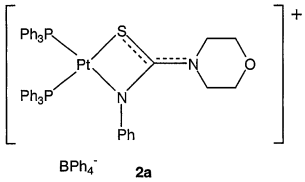
**1a**, $R_1R_2 = (CH_2CH_2)_2O$
**1b**, $R_1 = R_2 = CH_2Ph$
**1c**, $R_1 = CH_2Ph$, $R_2 = CH(Me)Ph$
**1d**, $R_1 = Me$, $R_2 = CH_2$(9-anthracenyl)



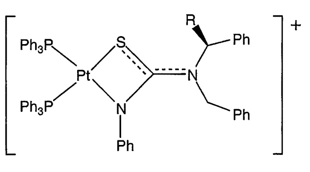
**1e**



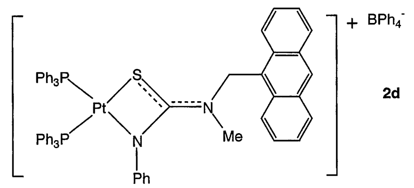
**1f**



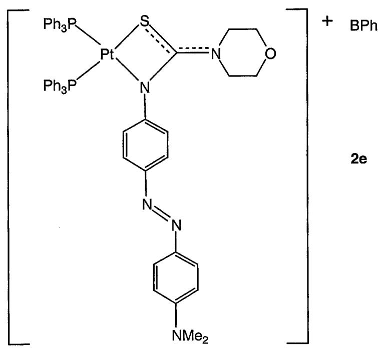
**2a**



**2b**, R = H
**2c**, R = Me



**2d**

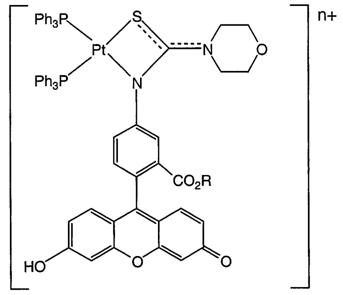


**2e**

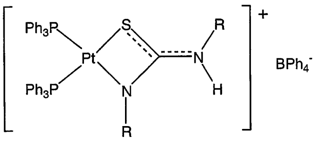
The formation of the expected platinum–thiourea cations is readily confirmed by positive-ion electrospray ionisation mass spectrometry (ESMS) in methanol solution, which in all cases gives an intense, single $M^+$ ion for the cation, at the expected $m/z$ values. The $^{31}P\{^1H\}$ NMR spectra of complexes **2a**–**2e** show the expected AB doublet of doublets for two inequivalent $PPh_3$ ligands, with coupling to $^{195}Pt$ in the ranges 3241–3265 Hz ($PPh_3$ ligands *trans* to S) and 3401–3444 Hz ($PPh_3$ ligands *trans* to N). It is noteworthy that for the complexes **2c** and **2d**, where two possible isomers could be formed, only a single set of $^{31}P$ NMR resonances was seen, suggesting the formation of a single isomer, presumably with the bulkiest substituent *cis* to sulfur. Satisfactory microanalytical data were observed for all complexes. The UV–Vis spectrum of the anthracenyl complex **2d** shows similar absorptions as the parent thiourea **1d**, while for the azo dye derivative **2e**, the absorption maximum (430 nm) is shifted from 420 nm in the free thiourea **1e**, presumably due to conjugation of the azo chromophore and platinum centres. In **2d**, the anthracenyl moiety is remote and not conjugated to the platinum centre.

When the fluorescein-derived thiourea **1f** is reacted under analogous conditions, the corresponding cation **2f** is formed, as shown by ESMS ($m/z$ 1195), but the attempted precipitation using $NaBPh_4$ was not successful, presumably because the complex is zwitterionic (with a deprotonated carboxylic acid or phenol group) in the basic reaction medium. In a separate preparation (without added $NaBPh_4$), addition of water, and prolonged standing, resulted in formation of a bright orange solid **2g**. The observation of a single *m*/*z* 1195 ion in the positive-ion ES mass spectrum, together with very similar $^{31}P\{^1H\}$ NMR coupling constants (3241 and 3453 Hz) to the other complexes **2**, suggests that the complex **2g** also contains an N,S-chelated thiourea monoanion ligand, though satisfactory microanalytical data could not be obtained for this complex.

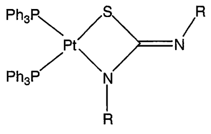
The N,S-chelate binding of the thiourea monoanion to the platinum(II) centre appears to be strong, since the addition of excess $PPh_3$ to a $CDCl_3$ solution of complex **2a** resulted in no reaction after standing for 24 h.



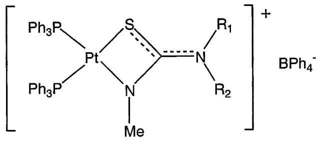
**2f**; R = H; n = 1
**2g**; R = -; n = 0



**3a**, R = Ph
**3b**, R = Et



**4a**, R = Ph
**4b**, R = Et



**5a**, $R_1$ = CN, $R_2$ = H
**5b**, $R_1$ = H, $R_2$ = CN

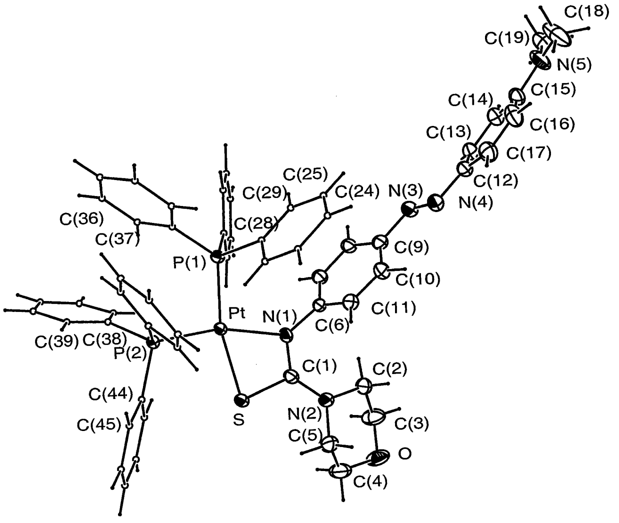


Fig. 1. Molecular structure and numbering scheme of the cation of $[Pt\{SC(=N(CH_2CH_2)_2O)NC_6H_4N=NC_6H_4NMe_2\}(PPh_3)_2]BPh_4$ (**2e**), containing an N,S-chelated thiourea monoanion incorporating an azo dye.

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

| | | | |
|---|---|---|---|
| Pt–N(1) | 2.135(2) | Pt–P(1) | 2.2897(7) |
| Pt–P(2) | 2.2595(7) | Pt–S | 2.3439(7) |
| S–C(1) | 1.758(3) | N(1)–C(1) | 1.328(4) |
| N(1)–C(6) | 1.432(4) | N(2)–C(1) | 1.339(4) |
| N(2)–C(2) | 1.473(4) | N(2)–C(5) | 1.476(4) |
| N(3)–N(4) | 1.255(4) | N(3)–C(9) | 1.436(4) |
| N(4)–C(12) | 1.426(4) | | |
| N(1)–Pt–P(2) | 163.02(7) | N(1)–Pt–P(1) | 98.05(7) |
| P(2)–Pt–P(1) | 97.42(3) | N(1)–Pt–S | 68.68(7) |
| P(2)–Pt–S | 95.14(3) | P(1)–Pt–S | 165.47(3) |
| C(1)–S–Pt | 81.22(10) | C(1)–N(1)–Pt | 100.20(18) |
| N(1)–C(1)–S | 109.5(2) | | |

When PhNHC(S)NHPh is reacted with *cis*-$[PtCl_2(PPh_3)_2]$ and excess triethylamine in refluxing methanol, a clear, pale yellow solution is formed, and addition of $NaBPh_4$ results in precipitation of the salt $[Pt\{SC(=NHPh)NPh\}(PPh_3)_2]BPh_4$ (**3a**) as a pale yellow solid on cooling. Similarly, the reaction with EtNHC(S)NHEt gives the analogous complex $[Pt\{SC(=NHEt)NEt\}(PPh_3)_2]BPh_4$ (**3b**) as a white solid. The cation $[Pt\{SC(=NHEt)NEt\}(PPh_3)_2]^+$ has been isolated previously as its hfac salt [18]. The $^{31}P\{^1H\}$ NMR spectrum of complex **3b** shows two resonances at $\delta$ 16.2 and 11.1 with $^1J(PtP)$ values of 3233 and 3352 Hz, which compare with the literature values of $\delta$ 15.7 and 10.4 with $^1J(PtP)$ 3226 and 3318 Hz, respectively [18]. The diphenylthiourea analogue $[Pt\{SC(=NHPh)NPh\}(PPh_3)_2]BPh_4$ (**3a**) shows similar $^1J(PtP)$ coupling constants of 3198 and 3490 Hz. By comparison, the $^1J(PtP)$ coupling constants for the thiourea dianion analogues $[Pt\{SC(=NPh)NPh\}(PPh_3)_2]$ (**4a**) (3103 and 3261 Hz) [3] and $[Pt\{SC(=NEt)NEt\}(PPh_3)_2]$ (**4b**) (3164 and 3152 Hz) [18] and are slightly smaller, reflecting the slightly higher *trans*-influence for the dianionic ligands. For both complexes **3a** and **3b** a single set of resonances was observed in the $^{31}P\{^1H\}$ NMR spectra, and the complexes are assigned as the isomer with the substituent on the imine nitrogen *cis* to the sulfur atom, which is the expected isomer on steric grounds, and is observed in other complexes of chelated thiourea monoanions [15] and dianions [3,18]. Complex **3a** is stable in $CDCl_3$ solution in the presence of added pyridine; no conversion to the dianion complex **4a** was observed after 24 h.

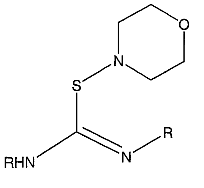
The attempted synthesis of the cyanothiourea analogue $[Pt\{SC(=NHCN)NMe\}(PPh_3)_2]BPh_4$ gave a product which yielded a single intense ion at $m/z$ 865 in the positive-ion ESMS spectrum, and gave good elemental microanalytical data, but which $^{31}P\{^1H\}$ NMR showed to be a mixture of isomers in a 4:1 ratio. The $^1J(PtP)$ coupling constants for both isomers are very similar (major isomer **5a** 3032 and 3205 Hz, minor isomer **5b** 3031 and 3182 Hz) and in the $^1H$ NMR spectrum the NMe groups of both isomers show phosphorus coupling of approximately 5 Hz, indicating that the NMe group in both isomers is coordinated to platinum. By comparison, the thiourea dianion complex $[Pt\{SC(=N–CN)NMe\}(PPh_3)_2]$ shows $^1J(PtP)$ values of 3171 and 3308 Hz, and an NMe resonance at $\delta$ 2.16 in the $^1H$ NMR spectrum, showing coupling to phosphorus of 4 Hz [2]. On the basis of the spectroscopic evidence, the two isomers are assigned as **5a** and **5b**, with the major isomer tentatively assigned as the isomer with the larger cyano substituent *cis* to sulfur. The observation of two isomers may arise due to the small size of the thiourea substituents in this complex.

### 2.2. X-ray crystal structure of the azo dye derivative $[Pt\{SC(=N(CH_2CH_2)_2O)NC_6H_4N=NC_6H_4NMe_2\}(PPh_3)_2]BPh_4$ (**2e**)

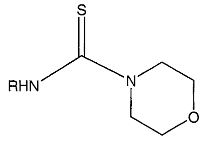
Confirmation of the nature of thiourea coordination was obtained by a single-crystal X-ray structure determination on complex **2e**. The molecular structure is shown in Fig. 1, which also gives the atom numbering scheme. Selected bond lengths and angles are given in Table 1. To date, there have been ten structure determinations on compounds containing the $R_2N–C_6H_4–N=N–C_6H_4–N$ fragment, but the structure of **2e** is the first of a metal derivative of such an azo dye.

The thiourea is bonded in N,S-chelating mode, forming a four-membered Pt–S–C–N ring system. The geometry about platinum is the expected square-planar, with two different Pt–P bond lengths: Pt–P(1) 2.2897(7) and Pt–P(2) 2.2595(7) Å. This indicates that the sulfur donor atom has the slightly higher *trans* influence, consistent with the $^{31}P$ NMR assignments. The same trend is seen in the related platinum(II) thiourea dianion complex $[Pt\{SC(=NPh)NPh\}(PPh_3)_2]$ (**4a**) [Pt–P 2.308(1) and 2.247(1) Å] [3], but not in the diethylthiourea analogue $[Pt\{SC(=NEt)NEt\}(PPh_3)_2]$ (**4b**) [Pt–P 2.274(6) and 2.269(6) Å] [18]. The Pt–S and Pt–N bond lengths of **2e** [2.3439(7) and 2.135(2) Å, respectively] are longer than the corresponding bond lengths in **4a** [2.331(1) and 2.054(3) Å] and **4b** [2.332(8) and 2.05(3) Å], reflecting tighter binding of the dianionic ligand in the complexes **4**.

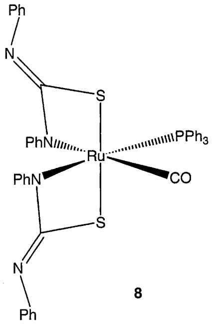
The thiourea core of the ligand, defined by the atoms N(1), C(1), N(2) and S, is planar to within 0.01 Å. Examination of the S–C and C–N bond lengths of **2e** strongly suggests considerable electronic delocalisation in the thiourea ligand. Thus, the C–S bond distance in **2e** [1.758(3) Å] is shorter than in the thiourea dianion complexes **4a** [1.782(5) Å] and **4b** [1.77(2) Å], while C–S bond lengths in the thiourea derivatives **6** [20] and **7** [21], containing, respectively, single and double C–S bonds, are 1.801(3) and 1.691(3) Å. In comparison, the average C=S bond length in thioureas is around 1.681 Å [22]. Likewise, the exocyclic C(1)–N(2) bond in **2e** [1.339(4) Å] is longer than the exocyclic C–N bond of **4a** [1.277(6) Å], while that of **4b** is similar [1.31(3) Å]. Comparison of the metallacyclic C–N bonds reveals the opposite trend, with that of **2e** [1.328(4) Å] being shorter than those of **4a** [1.348(7) Å] and **4b** [1.42(4) Å]. In the isothiourea **6**, the double and single C–N bond lengths are 1.267(3) and 1.355(3) Å. Taken together, these data suggest that in complex **2e**, there is partial double bond character in both the C–S and C–N bonds. A similar electron delocalisation and double bond character has been described for the structure of complex **8**, which contains two thiourea monoanions also bonded in an N,S-chelating mode [17]. In complex **8** the two C–S bond lengths, 1.736(5) and 1.738(5) Å, are somewhat shorter than the C–S bond length in **2e**, while the metallacyclic C–N bond lengths of **8** [1.330(6) and 1.314(6) Å] are similar to that of **2e**.



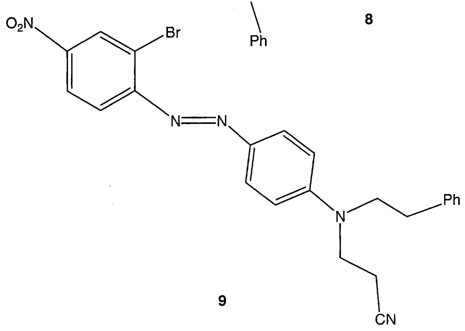
**6**, R = o-tolyl



**7**, R = o-tolyl



**8**



**9**

The geometry of the azo dye part of the molecule appears normal, with the N=N bond distance [1.255(4) Å] similar to that in related azo compounds, such as **9** [1.263(7) Å] [23]. The phenyl ring C(6)–C(11), which is planar to ± 0.01 Å, is inclined at an angle of 60.9° to the N(1)–C(1)–N(2)–S thiourea plane. The two azo

Table 2
Selected bond lengths (Å) and bond angles (°) for molecule 1 of **10a**

| | | | |
|---|---|---|---|
| Pt–P(1) | 2.333(1) | Pt–P(2) | 2.340(1) |
| Pt–S(1) | 2.338(1) | Pt–S(2) | 2.337(1) |
| S(1)–C(1) | 1.757(5) | S(2)–C(4) | 1.756(5) |
| N(1)–C(2) | 1.326(7) | N(1)–C(1) | 1.334(6) |
| N(2)–C(2) | 1.159(7) | N(3)–C(1) | 1.321(6) |
| N(3)–C(3) | 1.455(6) | N(4)–C(5) | 1.308(7) |
| N(4)–C(4) | 1.320(6) | N(5)–C(5) | 1.159(7) |
| N(6)–C(4) | 1.430(7) | N(6)–C(6) | 1.458(7) |
| P(1)–Pt–S(1) | 86.55(4) | P(1)–Pt–S(2) | 92.55(4) |
| S(2)–Pt–S(1) | 173.13(4) | P(2)–Pt–P(1) | 169.49(4) |
| C(1)–S(1)–Pt | 108.3(2) | C(4)–S(2)–Pt | 109.7(2) |

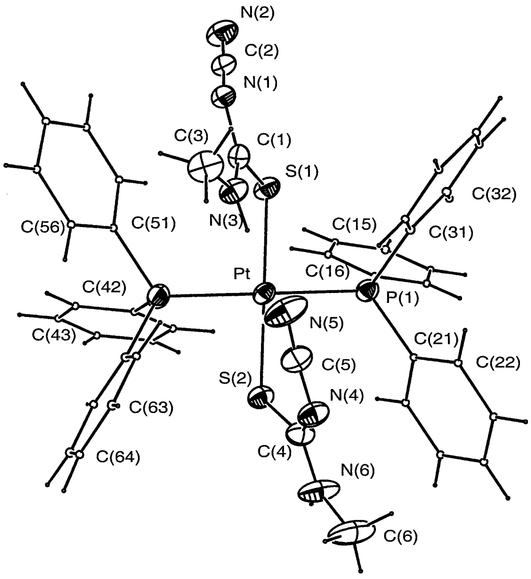
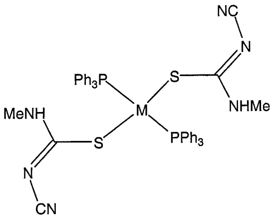


Fig. 2. Molecular structure of one of the two independent molecules (molecule 1) of *trans*-[Pt{SC(=N(CN)NHMe}$_2$(PPh$_3$)$_2$] (**10a**) showing the atom numbering scheme.

phenyl rings are not coplanar, the angle between the planes defined by C(6)–C(11) and C(12)–C(17) being 24.4°, due to a twisting of the phenyl rings, combined with bending of the azo moiety, primarily at N(3) which lies 0.54 Å out of the C(12)–C(17) phenyl plane [N(4) lies 0.18 Å out of the same plane].

### *2.3. Synthesis and characterisation of bis(thiourea monoanion) complexes*

Reaction of *cis*-[PtCl$_2$(PPh$_3$)$_2$] with a large excess of Na[MeNHC(S)NCN] in methanol at room temperature affords a very pale yellow solution, from which the complex *trans*-[Pt{SC(=NCN)NHMe}$_2$(PPh$_3$)$_2$] (**10a**) can be isolated as an off-white solid in high yield by precipitation with water. The bright yellow palladium complex **10b** can be prepared in analogous fashion. $^{31}$P{$^1$H} NMR spectroscopy of **10a** showed 2 equiv. phosphine ligands at $\delta$ 15.5, showing a small coupling to $^{195}$Pt of 2627 Hz, suggesting that the complex is the *trans* isomer. In comparison, the thiourea dianion complex [Pt{SC(=NCN)NMe}(PPh$_3$)$_2$], with PPh$_3$ *trans* to S, shows $^1J$(PtP) values of 3171 and 3308 Hz [2]. A small resonance at $\delta$ 17.1 was observed in one preparation of **10a**, showing a similar $^1J$(PtP) to **10a**, 2648 Hz, and is therefore tentatively assigned to a monosubstituted derivative *trans*-[PtCl{SC(=NCN)NHMe}-(PPh$_3$)$_2$]. Complex **10b** showed a single $^{31}$P resonance at $\delta$ 21.6. The presence of NH protons was indicated by a broad resonance in the $^1$H NMR spectrum (e.g. at $\delta$ 6.35 for **10a**), which disappeared on shaking the solution with D$_2$O.



**10a**, M = Pt
**10b**, M = Pd

Single crystals of complex **10a** were obtained by diffusion of diethyl ether into a dichloromethane solution of the complex, and an X-ray diffraction study was carried out. The complex crystallises with two independent molecules, and the bond lengths and angles are similar for both. Selected bond lengths and angles for molecule 1 are given in Table 2, and the molecular structure and atom numbering scheme are given in Fig. 2. The structure confirms the *trans* geometry of the complex with two S-bonded thiourea monoanions. The Pt–P [2.333(1) and 2.340(1) Å] and Pt–S [2.337(1) and 2.338(1) Å] bond lengths are as expected, when compared to the related structure of *trans*-[Pt(pyridine-2-thiolate)$_2$(PPh$_3$)$_2$] [Pt–P 2.315(1), Pt–S 2.343(2) Å] [24], and are longer than the Pt–P bond lengths in **2e**. The Pt–S bond lengths in the dianion complex [Pt{SC(=N–CN)NMe}(cod)] (cod = cyclo-octa-1,5-diene) are 2.318(3) and 2.303(3) Å (for two independent molecules) [2]. As with this structure, the cyano substituent is directed towards the S atom (rather than the NHMe group). The C–S bond lengths of **10a** [molecule 1, 1.757(5); molecule 2, 1.751(6) Å] are very comparable with **2e** [1.758(3) Å], consistent with the bonding as a thiourea monoanion.

In both molecules of **10a**, the cyano substituent [C(5)–N(5)] of one thiourea lies over the platinum, and accepts a hydrogen bond from the N(3)–H(3) group of the second thiourea monoanion, with N(3) − H(3) = 0.880 Å, N(5)···H(3) = 2.065 Å, and N(3) − H(3A)··· N(5) = 151.19°. There are also intermolecular hydrogen bonds involving the cyano and NH groups not involved in intramolecular hydrogen bonding [N(6′) − H(6′) = 0.880 Å, H(6′)···N(2) = 2.084 Å, N(6′) − H(6′)···N(2) =

163.7°; $N(6)-H(6)=0.880$ Å, $H(6)-N(2')=2.073$ Å, $N(6)-H(6)\cdots N(2')=154.4°$].

The electrospray mass spectrum of a freshly prepared MeOH solution of **10a** showed major peaks at *m*/*z* 833 [$M$ − MeNHC(S)NCN]$^+$, 865 [$M$ − MeNHC(S)NCN + MeOH]$^+$, together with lower intensity ions at *m*/*z* 948 [$M$ + H]$^+$ and *m*/*z* 1050 [$M$ + Et$_3$NH]$^+$, formed from adventitious Et$_3$NH$^+$ ions in the spectrometer. After standing for 30 min the *m*/*z* 865 ion was the base peak, with a small *m*/*z* 833 ion only, while after several hours, the *m*/*z* 865 ion was the only one observed, suggesting that solvolysis was occurring. $^{31}$P NMR analysis, however, indicates that complex **10a** was stable in CDCl$_3$ solution for 24 h in the presence of added methanol. Interestingly, compound **10a** melts to a yellow liquid at 160–162 °C, which then resolidifies and melts again at 210–214 °C. However, the $^{31}$P NMR spectrum of a sample of **10a** heated to 180 °C for 5 min showed predominantly **10a**.

## 3. Experimental

### 3.1. General experimental procedures

$^{31}$P{$^1$H}, $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker AC300P instrument in CDCl$_3$ solution (unless otherwise stated), at 121.51, 300.133 or 75.47 MHz, respectively, with chemical shifts relative to external 85% H$_3$PO$_4$ ($^{31}$P) or external SiMe$_4$ ($^1$H, $^{13}$C). Electrospray (ES) mass spectra were recorded in positive-ion mode on a VG Platform II instrument, in methanol solvent (unless otherwise stated); further details of the instrumentation have been given previously [2]. Isotope patterns were calculated using the Isotope program [25]. Melting points were recorded on a Reichert Jung hotstage apparatus and are uncorrected. UV–Vis spectra were recorded in methanol solution on a Perkin–Elmer Lambda 11 spectrophotometer.

Reactions were carried out in LR grade methanol as the solvent, without prior purification. Dichloromethane and diethyl ether were purified by distillation from calcium hydride and sodium-benzophenone ketyl, respectively.

### 3.2. Materials

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] was prepared by ligand displacement of the labile 1,5-*cyclo*-octadiene (cod) ligand of [PtCl$_2$(cod)] [26] with 2 equiv. of PPh$_3$ in dichloromethane [27]. The complex [PdCl$_2$(PPh$_3$)$_2$] was prepared similarly from [PdCl$_2$(cod)] [28]. EtNHC(S)NHEt (1,3-diethylthiourea), PhNHC(S)NHPh (1,3-diphenylthiourea), and the sodium salt Na[MeNHC(S)NCN] were used as supplied by Aldrich, and NaBPh$_4$ was from BDH. Other thioureas were prepared in high yields by addition of the appropriate secondary amine to a solution of either PhNCS (BDH), 4-[(4-isothiocyanatophenyl)azo]-*N*,*N*-dimethylaniline (Aldrich) or fluorescein isothiocyanate, isomer I (Aldrich).

PhNHC(S)N(CH$_2$CH$_2$)$_2$O (**1a**) [21,29] from PhNCS and morpholine (BDH) in diethyl ether, colourless crystals, (m.p. lit. 132 °C), ESMS; *m*/*z*: 223 [$M$H]$^+$.

PhNHC(S)NBz$_2$ (**1b**) from PhNCS and dibenzylamine (BDH) in diethyl ether, m.p. 138–140 °C. ESMS; *m*/*z*: 333 [$M$H]$^+$.

PhNHC(S)N(Bz)CHMePh (**1c**) from PhNCS and (*R*)-(+)-benzyl α-methylbenzylamine (Aldrich) in diethyl ether, m.p. 186–188 °C. ESMS; *m*/*z*: 347 [$M$H]$^+$.

PhNHC(S)N(Me)CH$_2$Anth (**1d**) from PhNCS and 9-(methylaminomethyl)anthracene (AnthCH$_2$NHMe, Aldrich) in diethyl ether, pale yellow crystals, yield 93%, m.p. 166–168 °C. UV–Vis: $\lambda_{max}$ (nm): 350, 368, 388.

Me$_2$NC$_6$H$_4$N=NC$_6$H$_4$NHC(S)N(CH$_2$CH$_2$)$_2$O (**1e**) from 4-[(4-isothiocyanatophenyl)azo]-*N*,*N*-dimethylaniline and morpholine in 5:1 diethyl ether–tetrahydrofuran, orange microcrystals, yield 84%, m.p. 192–194 °C. ESMS; *m*/*z*: 370 [$M$H]$^+$. UV–Vis: $\lambda_{max}$ (nm): 420.

FluorNHC(S)N(CH$_2$CH$_2$)$_2$O (**1f**) from fluorescein isothiocyanate, isomer I (FluorNCS) and morpholine in 1:1 tetrahydrofuran–diethyl ether, red powder, yield 87%, m.p. 226–230 °C. ESMS; *m*/*z*: 477 [$M$H]$^+$. UV–Vis: $\lambda_{max}$ (nm): 456, 482.

### 3.3. Synthesis of [Pt{SC(=N(CH$_2$CH$_2$)$_2$O)NPh}(PPh$_3$)$_2$]BPh$_4$ (**2a**)

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (200 mg, 253 mmol), PhNHC(S)N(CH$_2$CH$_2$)$_2$O (**1a**) (62 mg, 279 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (25 ml) for 5 min to give a colourless solution. NaBPh$_4$ (88 mg, 257 mmol) was added giving a white precipitate. The reaction mixture was cooled in ice, the product filtered and washed with water (5 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 285 mg (90%) of **2a** as a white powder. M.p. 222–224 °C. *Anal.* Found: C, 67.4; H, 5.0; N, 2.3. Calc. for C$_{71}$H$_{63}$N$_2$BOP$_2$PtS: C, 67.7; H, 5.0; N, 2.2%. ESMS; *m*/*z* (cone voltage 20 V): 940 [$M$]$^+$. $^1$H NMR: $\delta=7.6$–6.1 (m, Ph), 3.4 (m, CH$_2$O), 3.0 (m, CH$_2$N); $^{31}$P{$^1$H} NMR: $\delta=15.5$ (d, $^1J$(PtP) = 3241 Hz, $^2J$(PP) = 23 Hz, P *trans* S), 10.0 (d, $^1J$(PtP) = 3431 Hz, P *trans* N); $^{13}$C{$^1$H} NMR: $\delta=178.5$ (t, $J$(PC) = 3 Hz, $J$(PtC) = 99 Hz, C=N), 164.5 (m, *ipso* C of BPh$_4$), 144.1–121.7 (m, Ph), 65.8 (s, CH$_2$O), 46.6 (s, CH$_2$N).

### 3.4. Synthesis of [Pt{SC(=NBz$_2$)NPh}(PPh$_3$)$_2$]BPh$_4$ (**2b**)

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (300 mg, 379 mmol), PhNHC(S)NBz$_2$ (**1b**) (126.5 mg, 380 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (20 ml) for 5 min to give a colourless solution. $NaBPh_4$ (130 mg, 381 mmol) was added giving a white precipitate. The reaction mixture was cooled in ice, the product filtered and washed with methanol (5 ml), water (5 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 380 mg (73%) of **2b** as a white powder. M.p. 120–122 °C. *Anal.* Found: C, 70.5; H, 5.1; N, 2.2. Calc. for $C_{81}H_{69}N_2BP_2PtS$: C, 71.0; H, 5.1; N, 2.0%. ESMS; $m/z$ (cone voltage 20 V): 1051, $[M]^+$. $^1$H NMR: $\delta = 7.5–5.9$ (m, Ph); 4.04 (s, br, $CH_2$); $^{31}P\{^1H\}$ NMR: $\delta = 15.5$ (d, $^1J(PtP) = 3241$ Hz, $^2J(PP) = 23$ Hz, P *trans* S), 10.0 (d, $^1J(PtP) = 3420$ Hz, P *trans* N).

### 3.5. Synthesis of [Pt{SC(=NBz(CHMePh))NPh}-(PPh$_3$)$_2$]BPh$_4$ (2c)

The complex *cis*-$[PtCl_2(PPh_3)_2]$ (200 mg, 253 mmol), PhNHC(S)NBz(CHMePh) (**1c**) (87.5 mg, 253 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (25 ml) for 5 min to give a colourless solution. $NaBPh_4$ (88 mg, 257 mmol) was added giving a white precipitate. The reaction mixture was cooled in ice, the product filtered and washed with water (5 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 250 mg (72%) of **2c** as a white powder. M.p. 132–134 °C. *Anal.* Found: C, 70.6; H, 5.2; N, 2.2. Calc. for $C_{82}H_{71}N_2BP_2PtS$: C, 71.1; H, 5.2; N, 2.0%. ESMS; $m/z$ (cone voltage 20 V): 1065 $[M]^+$. $^{31}P\{^1H\}$ NMR: $\delta = 15.8$ (d, $^1J(PtP) = 3265$ Hz, $^2J(PP) = 23$ Hz, P *trans* S), 10.0 (d, $^1J(PtP) = 3415$ Hz, P *trans* N).

### 3.6. Synthesis of [Pt{SC(=NPh)N(Me)(CH$_2$Anth)}-(PPh$_3$)$_2$]BPh$_4$ (2d)

The complex *cis*-$[PtCl_2(PPh_3)_2]$ (300 mg, 379 mmol), PhNHC(S)N(Me)($CH_2$Anth) (**1d**) (135 mg, 379 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (30 ml) for 5 min to give a pale yellow solution. $NaBPh_4$ (140 mg, 409 mmol) was added giving a pale yellow precipitate. The reaction mixture was cooled in ice, the product filtered and washed with water (10 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 485 mg (92%) of **2d** as a pale yellow powder. M.p. 230–232 °C. *Anal.* Found: C, 71.4; H, 5.0; N, 2.1. Calc. for $C_{83}H_{69}N_2BP_2PtS$: C, 71.5; H, 5.0; N, 2.0%. ESMS; $m/z$ (cone voltage 20 V): 1075 $[M]^+$. $^1$H NMR: $\delta = 8.4–6.2$ (m, aryl), 2.01 (s, NMe), 1.51 (s, $NCH_2$); $^{31}P\{^1H\}$ NMR: $\delta = 15.7$ (d, $^1J(PtP) = 3250$ Hz, $^2J(PP) = 23$ Hz, P *trans* S), 10.1 (d, $^1J(PtP) = 3401$ Hz, P *trans* N). UV–Vis: $\lambda_{max}$ (nm): 352, 368, 388.

### 3.7. Synthesis of [Pt{SC(=N(CH$_2$CH$_2$)$_2$O)-NC$_6$H$_4$N=NC$_6$H$_4$NMe$_2$}(PPh$_3$)$_2$]BPh$_4$ (2e)

The complex *cis*-$[PtCl_2(PPh_3)_2]$ (200 mg, 253 mmol), $Me_2NC_6H_4N{=}NC_6H_4NHC(S)N(CH_2CH_2)_2O$ (**1e**) (96 mg, 260 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (25 ml) for 5 min to give a bright orange solution. $NaBPh_4$ (95 mg, 278 mmol) was added giving an orange precipitate. The reaction mixture was cooled in ice, the product filtered and washed with water (10 ml), methanol (5 ml) and diethyl ether (10 ml) and dried to give 330 mg (93%) of **2e** as an orange powder. M.p. 236–238 °C. *Anal.* Found: C, 66.8; H, 5.2; N, 5.2. Calc. for $C_{79}H_{72}N_5BOP_2PtS$: C, 67.4; H, 5.2; N, 5.0%. ESMS; $m/z$ (cone voltage 20 V): 1088 $[M]^+$. $^1$H NMR: $\delta = 7.9–6.2$ (m, Ph), 3.4 (m, br, $CH_2O$), 3.1 (m, br, $CH_2N$), 3.08 (s, $NMe_2$); $^{31}P\{^1H\}$ NMR: $\delta = 15.5$ (d, $^1J(PtP) = 3243$ Hz, $^2J(PP) = 23$ Hz, P *trans* S), 10.0 (d, $^1J(PtP) = 3444$ Hz, P *trans* N). UV–Vis: $\lambda_{max}$ (nm): 430. X-ray quality crystals of the complex were grown by diffusion of diethyl ether into a dichloromethane solution at room temperature (r.t.).

### 3.8. Synthesis of the fluorescein complex (2g)

The complex *cis*-$[PtCl_2(PPh_3)_2]$ (100 mg, 126 mmol), thiourea **1f** (60 mg, 0.126 mmol) and triethylamine (1 ml, excess) in methanol (20 ml) was refluxed for 5 min to give a clear, fluorescent orange solution. Water (60 ml) was added, and the mixture evaporated to dryness. Water (60 ml) was added and the orange precipitate filtered, washed with water (2 × 20 ml) and diethyl ether (2 × 20 ml) and dried to give 152 mg of **2g**, m.p. > 300 °C. Satisfactory microanalytical data could not be obtained. *Anal.* Found: C, 58.5; H, 4.4; N, 2.3. Calc. for $C_{61}H_{48}N_2O_6P_2PtS$: C, 61.4; H, 4.1; N, 2.4%. ESMS; $m/z$ (cone voltage 20 V): 1195 $[M]^+$, 598 $[MH]^{2+}$. UV–Vis: $\lambda_{max}$ (nm): 456, 482. $^{31}P\{^1H\}$ NMR ($CDCl_3$ with 10% ethanol): $\delta = 14.5$ (d, $^1J(PtP) = 3241$ Hz, $^2J(PP)$ 23 Hz, P *trans* S), 10.1 (d, $^1J(PtP) = 3453$ Hz, P *trans* N).

### 3.9. Synthesis of [Pt{SC(=NHPh)NPh}(PPh$_3$)$_2$]BPh$_4$ (3a)

The complex *cis*-$[PtCl_2(PPh_3)_2]$ (300 mg, 379 mmol), PhNHC(S)NHPh (87 mg, 382 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (20 ml) for 5 min to give a pale yellow solution. $NaBPh_4$ (130 mg, 380 mmol) was added. On cooling in ice, a pale yellow solid was precipitated, which was filtered and washed with water (5 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 210 mg (44%) of **3a** as a pale yellow powder. M.p. 133–135 °C. *Anal.* Found: C, 68.2; H, 5.0; N, 2.5. Calc. for $C_{73}H_{61}N_2BP_2PtS$: C, 69.3; H, 4.9; N, 2.2%. ESMS; $m/z$ (cone voltage 20 V): 946 $[M]^+$. $^1$H NMR: $\delta = 7.3–6.2$ (m, Ph); $^{31}P\{^1H\}$ NMR: $\delta = 14.1$ (d, $^1J(PtP) = 3198$ Hz, $^2J(PP) = 22$ Hz, P *trans* S), 9.8 (d, $^1J(PtP) = 3490$ Hz, P *trans* N).

### 3.10. Synthesis of [Pt{SC(=NHEt)NEt}(PPh$_3$)$_2$]BPh$_4$ (**3b**)

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (300 mg, 379 mmol), EtNHC(S)NHEt (50 mg, 379 mmol) and triethylamine (1 ml, excess) were refluxed in methanol (20 ml) for 5 min to give a pale yellow solution. NaBPh$_4$ (130 mg, 380 mmol) was added. On cooling in ice, a white solid was precipitated, which was filtered and washed with water (10 ml), methanol (5 ml) and diethyl ether (10 ml) and dried to give 320 mg (72%) of **3b** as a white powder. M.p. softens > 120 °C, melting 214–216 °C. *Anal*. Found: C, 65.9; H, 5.3; N, 2.5. Calc. for $C_{65}H_{61}N_2BP_2PtS$: C, 66.7; H, 5.3; N, 2.4%. ESMS; $m/z$ (cone voltage 20 V): 850 $[M]^+$. $^{31}P\{^1H\}$ NMR: $\delta = 16.2$ (d, $^1J$(PtP) = 3233 Hz, $^2J$(PP) = 21 Hz, P *trans* S), 11.1 (d, $^1J$(PtP) = 3352 Hz, P *trans* N).

### 3.11. Synthesis of [Pt{SC(=NHCN)NMe}(PPh$_3$)$_2$]BPh$_4$ (**5a** and **5b**)

The complex *cis*-[PtCl$_2$(PPh$_3$)$_2$] (250 mg, 316 mmol) and Na[MeNHC(S)NCN] (45 mg, 328 mmol) were refluxed in methanol (20 ml) for 10 min to give a clear, pale yellow solution. NaBPh$_4$ (112 mg, 327 mmol) was added, resulting in formation of a white precipitate. The mixture was cooled in ice, and the product filtered, washed with methanol (5 ml), water (5 ml), methanol (5 ml) and diethyl ether (5 ml) and dried to give 320 mg (86%) of a white powder. *Anal*. Found: C, 65.6; H, 5.0; N, 3.5. Calc. for $C_{63}H_{54}N_3BP_2PtS$: C, 65.6; H, 4.7; N, 3.7%. ESMS; $m/z$ (cone voltage 20 V): 865 $[M]^+$. $^{31}P\{^1H\}$ NMR: Major isomer **5a**: $\delta = 22.2$ (d, $^1J$(PtP) = 3032 Hz, $^2J$(PP) = 25 Hz, P *trans* S), 10.7 (d, $^1J$(PtP) = 3205 Hz, P *trans* N). Minor isomer **5b**: $\delta = 21.2$ (d, $^1J$(PtP) = 3031 Hz, $^2J$(PP) = 26 Hz, P *trans* S), 12.4 (d, $^1J$(PtP) = 3182 Hz, P *trans* N).

### 3.12. Synthesis of trans-[Pt{SC(=N–CN)NHMe}$_2$-(PPh$_3$)$_2$] (**10a**)

To a suspension of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (222 mg, 0.281 mmol) in methanol (25 ml) was added an excess (255 mg) of Na[MeNHC(S)NCN] dissolved in water (3 ml). The platinum complex dissolved giving a clear, very pale yellow solution, which was stirred overnight at r.t. Concentration to approximately 6 ml on a rotary evaporator at approximately 40 °C, followed by addition of water (50 ml) afforded an off-white precipitate. This was filtered, washed with water (5 ml) and dried in vacuo to give complex **10a** (205 mg, 77%). M.p. melts and resolidifies to a yellow solid at 160–162 °C, then melts 210–214 °C. *Anal*. Found: C, 52.4; H, 4.2; N, 8.9. Calc. for $C_{42}H_{38}N_6P_2PtS$: C, 53.2; H, 4.0; N, 8.9%. ESMS; $m/z$ (cone voltage 20 V): 833 (90%) $[M - \text{MeNHC(S)NCN}]^+$, 865 (100%) $[M - \text{MeNHC(S)NCN} + \text{MeOH}]^+$, 948 (40%) $[M + H]^+$, 1050 (40%) $[M + Et_3NH]^+$. $^{31}P\{^1H\}$ NMR: $\delta = 16.4$ (s, $^1J$(PtP) = 2624 Hz); $^1H$ NMR: $\delta = 7.73$–7.38 (m, Ph), 6.35 (s, br, NH), 2.20 (s, br, Me). NH proton disappears on shaking with $D_2O$. $^{13}C\{^1H\}$ NMR: $\delta = 173.2$ (s, br, C=N, $J$(PtC) = approximately 35), 135.0–128.0 (m, Ph), 122 (s, C≡N), 30.4 (s, NMe). Crystals for an X-ray diffraction study were obtained by diffusion of diethyl ether into a dichloromethane solution.

### 3.13. Synthesis of trans-[Pd{SC(=N-CN)NHMe}$_2$-(PPh$_3$)$_2$] (**10b**)

Following the procedure for **10b**, [PdCl$_2$(PPh$_3$)$_2$] (350 mg, 0.499 mmol) with Na[MeNHC(S)NCN] (500 mg, 3.65 mmol) in methanol (20 ml) gave a bright yellow suspension which was stirred for 24 h. The product was filtered, washed with water (10 ml) and diethyl ether (10 ml) and dried in vacuo to give 390 mg (91%) of **10b**, m.p. 158–160 °C. *Anal*. Found: C, 57.7; H, 4.7; N, 9.8. Calc. for $C_{42}H_{38}N_6P_2PdS$: C, 58.7; H, 4.5; N, 9.8%. $^{31}P\{^1H\}$ NMR: $\delta = 21.6$ (s). $^1H$ NMR: $\delta = 7.69$–7.34 (m, Ph), 6.6 (s, br, NH), 2.23 (s, br, Me). $^{13}C\{^1H\}$ NMR: $\delta = 176.5$ (s, br, C=N), 134.7–128.1 (m, Ph), 122 (s, C≡N), 30.4 (s, NMe).

### 3.14. X-ray crystal structure determination of **2e**

*Crystal data:* $C_{79}H_{72}BN_5OP_2PtS$, $M_r = 1407.32$, monoclinic, space group $C2/c$, $a = 33.0259(4)$ Å, $b = 10.5148(1)$ Å, $c = 37.5592(5)$ Å, $\beta = 96.2750(10)°$, $V = 12964.7(2)$ A$^3$, $Z = 8$, $D_{calc} = 1.442$ g cm$^{-3}$, $\mu$ (Mo K$\alpha$) = 2.298 mm$^{-1}$, $T = 150(2)$ K, 63 277 reflections measured, 14 215 unique with $R_{int}$ 0.0377, 12 400 observed with $I > 2\sigma(I)$. $\theta$ range 1.56–27.16°. Final $wR_2 = 0.0646$, $R_1 = 0.0445$ (all data).

### 3.15. X-ray crystal structure determination of **10a**

*Crystal data:* $C_{43.5}H_{40.5}Cl_3N_6P_2PtS_2$, $M_r = 1074.82$, monoclinic, space group $P2_1/c$, $a = 22.3802(5)$ Å, $b = 21.6501(4)$ Å, $c = 21.2258(5)$ Å, $\beta = 113.119(1)°$, $V = 9458.7(4)$ A$^3$, $Z = 8$, $D_{calc} = 1.510$ g cm$^{-3}$, $\mu$ (Mo K$\alpha$) = 3.329 mm$^{-1}$, $T = 150(2)$ K, 55 286 reflections measured, 19 142 unique with $R_{int} = 0.0279$, 16 665 observed with $I > 2\sigma(I)$. $\theta$ range 0.99–26.46°. The asymmetric unit consists of two independent molecules of the complex, together with three molecules of dichloromethane, one of which was not well defined. Some of the phenyl carbons have rather high thermal parameters, possibly due to disorder, which was not modelled. Final residuals $wR_2 = 0.0937$, $R_1 = 0.0499$ (all data).

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 155641 and 155642 for compounds **2e** and **10a**, respectively. Copies of this information may be obtained free of charge from 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).

## Acknowledgements

We thank the Universities of Waikato and Auckland for financial support, the New Zealand Lottery Grants Board for a grant towards the purchase of the mass spectrometer, and Johnson Matthey plc for a generous loan of platinum.

## References

[1] S.E. Livingstone, in: R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 2, Pergamon, Oxford, 1987, p. 639.

[2] W. Henderson, B.K. Nicholson, Polyhedron 15 (1996) 4015.

[3] W. Henderson, R.D.W. Kemmitt, S. Mason, M.R. Moore, J. Fawcett, D.R. Russell, J. Chem. Soc., Dalton Trans. (1992) 59.

[4] R.S. Pilato, K.A. Eriksen, E.I. Stiefel, A.L. Rheingold, Inorg. Chem. 32 (1993) 3799.

[5] (a) C. Sacht, M.S. Datt, S. Otto, A. Roodt, J. Chem. Soc., Dalton Trans. (1998) 727;
(b) K.R. Koch, S. Bourne, J. Mol. Struct. 441 (1998) 11;
(c) K.R. Koch, C. Sacht, C. Lawrence, J. Chem. Soc., Dalton Trans. (1998) 689;
(d) K.R. Koch, S.A. Bourne, A. Coetzee, J. Miller, J. Chem. Soc., Dalton Trans. (1999) 3157.

[6] (a) G. Kemp, A. Roodt, W. Purcell, K.R. Koch, J. Chem. Soc., Dalton Trans. (1997) 4481;
(b) I. Déchamps-Olivier, E. Guillon, A. Mohamadou, J.-P. Barbier, Polyhedron 15 (1996) 3617;
(c) A. Mohamadou, I. Déchamps-Olivier, J.-P. Barbier, Polyhedron 13 (1994) 3277.

[7] (a) K.R. Koch, Y. Wang, A. Coetzee, J. Chem. Soc., Dalton Trans. (1999) 1013;
(b) D. Cauzzi, M. Lanfranchi, G. Marzolini, G. Predieri, A. Tiripicchio, M. Costa, R. Zanoni, J. Organomet. Chem. 488 (1995) 115;
(c) K.R. Koch, T. Grimmbacher, C. Sacht, Polyhedron 17 (1999) 267.

[8] (a) E. Rodríguez-Fernández, E. García, M.R. Hermosa, A. Jiménez-Sánchez, M.M. Sánchez, E. Monte, J.J. Criado, J. Inorg. Biochem. 75 (1999) 181;
(b) J.J. Criado, E. Rodríguez-Fernández, E. García, M.R. Hermosa, E. Monte, J. Inorg. Biochem. 69 (1998) 113;
(c) U. Bierbach, T.W. Hambley, J.D. Roberts, N. Farrell, Inorg. Chem. 35 (1996) 4865;
(d) U. Bierbach, T.W. Hambley, N. Farrell, Inorg. Chem. 37 (1998) 708;
(e) U. Bierbach, J.D. Roberts, N. Farrell, Inorg. Chem. 37 (1998) 717;
(f) U. Bierbach, J. Reedijk, Angew. Chem., Int. Ed. Engl. 33 (1994) 1632.

[9] (a) R.D. Adams, M. Huang, J.H. Yamamoto, L. Zhang, Chem. Ber. 129 (1996) 137;
(b) U. Bodensieck, L. Hoferkamp, H. Stoeckli-Evans, G. Süss-Fink, J. Chem. Soc., Dalton Trans. (1993) 127;
(c) L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, Inorg. Chem. 34 (1995) 5786;
(d) L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, Organometallics 15 (1996) 1122;
(e) G. Süss-Fink, U. Bodensieck, L. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, J. Cluster Sci. 3 (1992) 469;
(f) E.W. Ainscough, A.M. Brodie, S.L. Ingham, T.G. Kotch, A.J. Lees, J. Lewis, J.M. Waters, J. Chem. Soc., Dalton Trans. (1994) 1.

[10] U. Bodensieck, Y. Carraux, H. Stoeckli-Evans, G. Süss-Fink, Inorg. Chim. Acta 195 (1992) 135.

[11] P. Piraino, G. Bruno, G. Tresoldi, G. Faraone, G. Bombieri, J. Chem. Soc., Dalton Trans. (1983) 2391.

[12] P.L. Watson, J.A. Albanese, J.C. Calabrese, D.W. Ovenall, R.G. Smith, Inorg. Chem. 30 (1991) 4638.

[13] M. Lipowska, B.L. Hayes, L. Hansen, A. Taylor Jr, L.G. Marzilli, Inorg. Chem. 35 (1996) 4227.

[14] M. Lipowska, L. Hansen, A. Taylor Jr., L.G. Marzilli, Inorg. Chem. 35 (1996) 4484.

[15] M.P. Coles, D.C. Swenson, R.F. Jordan, V.G. Young Jr., Organometallics 17 (1998) 4042.

[16] L.A. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Süss-Fink, Organometallics 15 (1996) 704.

[17] S.D. Robinson, A. Sahajpal, J.W. Steed, Inorg. Chim. Acta 306 (2000) 205.

[18] S. Okeya, Y. Fujiwara, S. Kawashima, Y. Hayashi, K. Isobe, Y. Nakamura, H. Shimomura, Y. Kushi, Chem. Lett. (1992) 1823.

[19] S. Okeya, H. Kameda, H. Kawashima, H. Shimomura, T. Nishioka, K. Isobe, Chem. Lett. (1995) 501.

[20] L. Sudha, J.S. Selvan, K. Subramanian, T. Steiner, G. Koellner, N. Srinivasan, K. Ramdas, Acta Crystallogr., Sect. C 52 (1996) 2047.

[21] A. Ramnathan, K. Sivakumar, N. Srinivasan, N. Janarthanan, K. Ramadas, H.-K. Fun, Acta Crystallogr., Sect. C 52 (1996) 1285.

[22] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. 2 (1987) S1.

[23] M.L. Glowka, Z. Olubek, Acta Crystallogr., Sect. C 50 (1994) 458.

[24] T.S. Lobana, R. Verma, A. Castineiras, Polyhedron 17 (1998) 3753.

[25] L.J. Arnold, J. Chem. Educ. 69 (1992) 811.

[26] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.

[27] D.L. Oliver, G.K. Anderson, Polyhedron 11 (1992) 2415.

[28] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52.

[29] M.F. Fegley, N.M. Borthick, C.H. McKeever, F.B. Farhum, J. Am. Chem. Soc. 79 (1957) 4734.