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# New cyclometallated platinum(II) compounds with thiosemicarbazones: crystal and molecular structure of $[\text{Pt}\{4\text{-MeC}_6\text{H}_3\text{C}(\text{Me})=\text{NN}=\text{C}(\text{S})\text{NH}_2\}(\text{PPh}_3)]$

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## Abstract

Treatment of the thiosemicarbazones 3- $\text{CH}_3(\text{CH}_2)_5\text{OC}_6\text{H}_4\text{C}(\text{Me})=\text{NN}(\text{H})\text{C}(\text{S})\text{NH}_2$  (**a**), 4- $\text{MeC}_6\text{H}_4\text{C}(\text{Me})=\text{NN}(\text{H})=\text{C}(\text{S})\text{NH}_2$  (**b**),  $\text{C}_6\text{H}_5\text{C}(\text{Et})=\text{NN}(\text{H})=\text{C}(\text{S})\text{NH}_2$  (**c**),  $\text{C}_6\text{H}_5\text{C}\{\text{CH}_3(\text{CH}_2)_{10}\}=\text{NN}(\text{H})=\text{C}(\text{S})\text{NH}_2$  (**d**) and 4- $\text{MeC}_6\text{H}_4\text{C}(\text{Me})=\text{NN}(\text{H})=\text{C}(\text{S})\text{NHMe}$  (**e**) with  $\text{K}_2[\text{PtCl}_4]$  gives tetranuclear platinum(II) compounds **1a–1e** with deprotonation of the  $-\text{NH}-$  group and with the ligand acting as a terdentate [C,N,S] moiety. Reaction of **1a–1e** with  $\text{PPh}_3$  and of **1a** with  $\text{P}(4\text{-MeOC}_6\text{H}_4)_3$  yielded mononuclear species **2a–2e** and **3a**, respectively. Treatment of **1a** with the diphosphines  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm),  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (dppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$  (dppp),  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$  (dppb),  $\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$  (dpppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$  (dpph), and 1,1'-ferrocenebis(diphenylphosphine) (dppf) gives dinuclear compounds **4a–10a**. In all cases the  $\text{Pd}-\text{S}_{\text{chelating}}$  bond is strong enough to withstand reaction with the phosphorus ligands without bond cleavage. The molecular structure of **2b** has been determined by X-ray crystallography. Mononuclear units are held together by hydrogen bonding, forming dimers in the solid state. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Cyclometallated; Thiosemicarbazone; Platinum; Schiff bases

## 1. Introduction

Cyclometallation has become a relevant part of organometallic chemistry and several reviews covering the subject have appeared [1–5]. Cyclometallated compounds show significant applications, such as their use in regioselective organic and organometallic synthesis [6], in insertion reactions [7], in the synthesis of new metal mesogenic compounds [8] and in catalytic materials [9]. In previous work we have shown that potentially terdentate ligands such as Schiff bases **I** [10,11], semicarbazones **II** [12] and thiosemicarbazones **III** [13] undergo facile metallation with palladium(0), palladium(II) and platinum(II) to give compounds with two five-membered fused rings at the metal centre (Fig. 1).

When [C,N,O] and [C,N,N] derivatives are treated with neutral ligands, such as tertiary phosphines, breakage of the oxygen–metal or nitrogen–metal bonds occurs prior to ring-opening of the five-membered metacycle upon continued reaction with the corresponding phosphine. If the cyclometallated compound is treated with a silver(I) salt previous to treatment with the phosphine, the chloride ligand is removed from the coordination sphere of palladium as silver chloride and its position occupied by the phosphine.

In the present work, we describe the synthesis of the first cyclometallated platinum(II) compounds derived from thiosemicarbazone terdentate ligands. These cyclometallated compounds present a tetranuclear structure similar to that found in analogous palladium(II) complexes [13], having  $\text{Pt}-\text{S}_{\text{chelating}}$  and  $\text{Pt}-\text{S}_{\text{bridging}}$  bonds.

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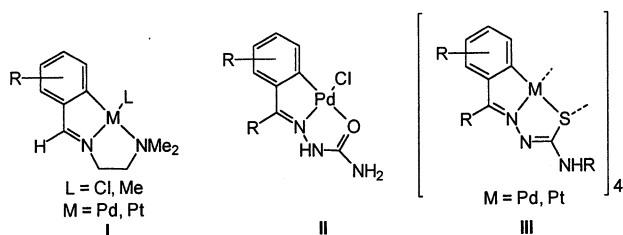


Fig. 1.

When the cyclometallated complexes are reacted with the tertiary monophosphine  $\text{PPh}_3$ , the  $\text{Pt-S}_{\text{bridging}}$  bond is cleaved and mononuclear complexes, in which the platinum atom is bonded to the thiosemicarbazone ligand, through the carbon, nitrogen and sulfur atoms and to the monophosphine through the phosphorus, are obtained. The crystal structure of one of these compounds is described. The reaction of the cyclometallated complexes with the tertiary diphosphines  $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$  (dpph),  $\text{Ph}_2\text{P}(\text{CH}_2)_5\text{PPh}_2$  (dpppe),  $\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$  (dppb),  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$  (dppp),  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$  (dppe),  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) and 1,1'-ferrocenebis(diphenylphosphine) (dppf) results in novel dinuclear complexes with the diphosphine bridging two palladium centres. The potentially beneficial biological activity of thiosemicarbazones and of their metal complexes has been discussed [14], a feature we are studying at present, in order to develop compounds of pharmaceutical importance.

## 2. Results and discussion

The thiosemicarbazones **a**, **b**, **c**, **d** and **e** were prepared by reaction of thiosemicarbazide or 4-methyl-3-thiosemicarbazide with the appropriate ketone (see Section 3 and Table 1). The  $\text{NH}_2$  protons (**a**, **b**, **c** and **d**) gave two characteristic broad resonances in the  $^1\text{H-NMR}$  spectra due to the restricted rotation about the  $\text{C-NH}_2$  bond, which was attributed to the formation of hydrogen bonding between the  $\text{C=N}$  nitrogen and one of the  $\text{NH}_2$  hydrogen atoms. The  $\text{NH}$  proton showed a broad signal ca.  $\delta$  8.8–9. The reaction of the thiosemicarbazones with potassium tetrachloroplatinate in ethanol–water at  $60^\circ\text{C}$  gave the cyclometallated complexes,  $[\text{Pt}\{3\text{-CH}_3(\text{CH}_2)_5\text{OC}_6\text{H}_3\text{C}(\text{Me})=\text{NN}=\text{C}(\text{S})\text{NH}_2\}]_4$  (**1a**),  $[\text{Pt}\{4\text{-MeC}_6\text{H}_3\text{C}(\text{Me})=\text{NN}=\text{C}(\text{S})\text{NH}_2\}]_4$  (**1b**),  $[\text{Pt}\{6\text{-H}_4\text{C}(\text{Et})=\text{NN}=\text{C}(\text{S})\text{NH}_2\}]_4$  (**1c**),  $[\text{Pt}\{6\text{-H}_4\text{C}(\text{CH}_3(\text{CH}_2)_{10})=\text{NN}=\text{C}(\text{S})\text{NH}_2\}]_4$  (**1d**) and  $[\text{Pt}\{4\text{-MeC}_6\text{-H}_3\text{C}(\text{Me})=\text{NN}=\text{C}(\text{S})\text{NHMe}\}]_4$  (**1e**), as orange air-stable solids (see Scheme 1). Preparative details, characterising microanalytical and IR data are discussed in Section 3.  $^{31}\text{P}\{-^1\text{H}\}$ - and  $^1\text{H-NMR}$  data are in Table 1. The products were characterised by elemental analysis (C, H, N and S) and the mass (FAB) spectra showed peaks at  $m/z$  1947 (**a**), 1600 (**b**, **c**), 2106 (**d**) and 1657 (**e**) whose

isotopic patterns are in agreement with a tetranuclear formulation. Related cyclometallated tetranuclear complexes of palladium(II) have been reported by us [13]. The absence of the  $-\text{NH}-$  signal in the  $^1\text{H-NMR}$  spectra was indicative of deprotonation of thiosemicarbazone ligands. This behaviour has been observed in coordination compounds of related ligands [14a]. The importance of the deprotonation of the  $-\text{NH}-$  groups is put forward in the reaction between similar 2-methyl-3-thiosemicarbazones and potassium tetrachloroplatinate, which does not take place under similar conditions to those for ligands **a–e**. The  $\text{NH}_2$  protons gave rise to a broad signal in the  $^1\text{H-NMR}$  spectra, shifted to higher field by ca. 1.5 ppm as observed in similar palladium(II) cyclometallated complexes [13]. The  $^1\text{H-NMR}$  spectra shows that metallation has taken place and the metallated carbon is the C6 in all cases. In the  $^1\text{H-NMR}$  spectra the H5 signal shows the coupling to  $^{195}\text{Pt}$  with  $^3J_{\text{PtH}}$  in the range 45.9–61.5 Hz (a value in agreement with those reported for platinum(II) cyclometallated compounds [15]).

In compounds **1c** and **1d** the  $^1\text{H-NMR}$  spectra showed the  $-\text{CH}_2\text{CH}_3$  and  $-\text{CH}_2(\text{CH}_2)_9\text{CH}_3$  resonances as a doublet of quartets and as a doublet of triplets, respectively, instead of the expected quartet and triplet patterns. This is probably due to restricted rotation around the  $\text{C-Et}$  and  $\text{C-CH}_2(\text{CH}_2)_9\text{CH}_3$  bonds as a consequence of the tetrameric structure of the compounds, which brings these groups and a neighbouring metallated phenyl ring of the tetramer sufficiently close together to give steric hindrance. In the  $^1\text{H-NMR}$  of compounds **1a**, **1b** and **1e** the  $\text{N=C-CH}_3$  protons resonance is shifted to lower frequency by ca. 0.5 ppm. Probably due to the tetrameric structure of the complexes, the methyl groups lie in the shielding area of a metallated phenyl ring that belongs to an adjacent metallated thiosemicarbazone ligand.

The  $\nu(\text{C=N})$  bands are neither shifted or only slightly shifted to lower wavenumbers upon complex formation [16], a trend that is opposed to the one observed in other thiosemicarbazone complexes where this shift is towards higher wavenumbers [17]. In the present complexes, we suggest this could be attributed to the  $\text{C=N}$  moiety being part of a five-membered metallacycle, as has been found by us and others [18,19]. The bands involving the  $\text{C=S}$  group are often difficult to assign. Coordination by sulfur induces changes in the position and intensity of these bands, although the degree of  $\nu(\text{C=S})$  in each band and the proximity of phenyl ring bands in the IR spectra (especially in complexes with phosphine ligands) makes a clear assignation of the vibration modes difficult. Nevertheless, in our opinion the  $\nu(\text{C=S})$  mode in the free ligands may be assigned to the band at  $820\text{--}845\text{ cm}^{-1}$  (Section 3), even if the bands observed at ca.  $1100\text{--}1000\text{ cm}^{-1}$  also contribute to the  $\text{C=S}$  stretching mode. This band disappears in

Table I  
<sup>31</sup>P-<sup>a</sup> and <sup>1</sup>H-NMR <sup>b</sup> data <sup>c,d,e</sup>

Compound	<sup>31</sup> P	Aromatic	Others
<b>a</b>		7.28[m, 3H, H <sup>2</sup> , H <sup>5</sup> , H <sup>6</sup> ] 6.95[dt, 1H, H <sup>4</sup> , 7.3 <sup>f</sup> , 2.9 <sup>i</sup> ]	8.7[br, 1H, NH] 7.4[s, 1H, NH <sub>2</sub> ] 6.4[s, 1H, NH <sub>2</sub> ] 3.99[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.92[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.26[s, 3H, Me]
<b>1a</b>		7.44[d, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 46.4 <sup>k</sup> ] 6.66[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.9 <sup>i</sup> ] 6.33[d, 1H, H <sup>2</sup> , 2.9 <sup>i</sup> ]	5.3[br, 2H, NH <sub>2</sub> ] 3.89[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.86[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 1.87[s, 3H, Me]
<b>2a</b>	22.7 s, 3880 <sup>r</sup>	6.63[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.21[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 43.5 <sup>k</sup> , 1.9 <sup>q</sup> ] 6.11[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.0[br, 2H, NH <sub>2</sub> ] 3.79[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.90[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.41[s, 3H, Me]
<b>3a</b>	17.6 s, 3869 <sup>r</sup>	6.61[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.24[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 44.4 <sup>k</sup> , 1.9 <sup>q</sup> ] 6.14[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.1[br, 2H, NH <sub>2</sub> ] 3.79[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.88[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.38[s, 3H, Me] 7.57 <sup>q</sup> [dd, 2H, 11.2 <sup>q</sup> , 8.8 <sup>f</sup> ] 6.88 <sup>q</sup> [dd, 2H, 1.7 <sup>q</sup> , 8.8 <sup>f</sup> ] 3.80[s, 3H, MeO <sup>phosphine</sup> ]
<b>4a</b> <sup>1</sup>	11.6 s, 3943 <sup>r</sup>	6.41[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.24[d, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 56.4 <sup>k</sup> ] 6.14[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.2[br, 2H, NH <sub>2</sub> ] 3.70[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.89[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.31[s, 3H, Me]
<b>5a</b>	17.7 s, 3843 <sup>r</sup>	6.64[d, 1H, H <sup>2</sup> , 2.6 <sup>i</sup> ] 6.22[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 43.9 <sup>k</sup> , 1.9 <sup>q</sup> ] 6.13[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.6 <sup>i</sup> ]	5.1[br, 2H, NH <sub>2</sub> ] 3.80[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.89[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.41[s, 3H, Me]
<b>6a</b>	13.3 s, 3941 <sup>r</sup>	6.61[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.27[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 39.6 <sup>k</sup> , 1.5 <sup>q</sup> ] 6.16[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.0[br, 2H, NH <sub>2</sub> ] 3.79[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.89[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.38[s, 3H, Me]
<b>7a</b>	15.2 s, 3813 <sup>r</sup>	6.61[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.27[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 45.8 <sup>k</sup> , 1.5 <sup>q</sup> ] 6.18[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.0[br, 2H, NH <sub>2</sub> ] 3.79[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.88[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.38[s, 3H, Me]
<b>8a</b>	15.4 s, 3819 <sup>r</sup>	6.60[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.29[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 45.4 <sup>k</sup> , 1.9 <sup>q</sup> ] 6.18[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.2[br, 2H, NH <sub>2</sub> ] 3.77[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.87[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.36[s, 3H, Me]
<b>9a</b>	15.2 s, 3815 <sup>r</sup>	6.60[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.29[dd, 1H, H <sup>5</sup> , 8.3 <sup>f</sup> , 45.7 <sup>k</sup> , 1.7 <sup>q</sup> ] 6.17[dd, 1H, H <sup>4</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.0[br, 2H, NH <sub>2</sub> ] 3.79[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.88[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.37[s, 3H, Me]
<b>10a</b> <sup>m</sup>	13.4 s, 3870 <sup>r</sup>	6.63[d, 1H, H <sup>2</sup> , 2.4 <sup>i</sup> ] 6.16[m, 2H, H <sup>4</sup> , H <sup>5</sup> , 8.3 <sup>f</sup> , 2.4 <sup>i</sup> ]	5.1[br, 2H, NH <sub>2</sub> ] 3.80[t, 2H, -CH <sub>2</sub> O <sup>o</sup> ] 0.89[t, 3H, CH <sub>3</sub> - <sup>p</sup> ] 2.41[s, 3H, Me]
<b>b</b>		7.60[d, 2H, H <sup>2</sup> , H <sup>6</sup> , 8.2 <sup>f</sup> ] 7.21[d, 2H, H <sup>3</sup> , H <sup>5</sup> , 8.2 <sup>f</sup> ]	8.8[br, 1H, NH] 6.8[br, 1H, NH <sub>2</sub> ] 7.4[br, 1H, NH <sub>2</sub> ] 2.38[s, 3H, Me] 2.28[s, 3H, Me]
<b>1b</b>		7.40[s, 1H, H <sup>5</sup> , 50.7 <sup>k</sup> ] 6.71[d, 1H, H <sup>3</sup> , 7.6 <sup>f</sup> ] 6.60[d, 1H, H <sup>2</sup> , 7.6 <sup>f</sup> ]	5.2[br, 2H, NH <sub>2</sub> ] 2.35[s, 3H, Me <sup>h</sup> ] 1.80[s, 3H, Me]
<b>2b</b>	23.0 s, 3854 <sup>r</sup>	6.88[d, 1H, H <sup>2</sup> , 7.6 <sup>f</sup> ] 6.63[d, 1H, H <sup>3</sup> , 7.6 <sup>f</sup> ] 6.13[s, 1H, H <sup>5</sup> , 48.4 <sup>k</sup> ]	4.9[br, 2H, NH <sub>2</sub> ] 2.39[s, 3H, Me] 1.73[s, 3H, Me <sup>h</sup> ]

Table 1 (Continued)

Compound	<sup>31</sup> P	Aromatic	Others
<b>c</b>		7.70–7.41 m	8.9[br, 1H, NH] 7.2[br, 1H, NH <sub>2</sub> ] 6.6[br, 1H, NH <sub>2</sub> ] 2.74[q, 2H, CH <sub>2</sub> CH <sub>3</sub> , 7.7 <sup>f</sup> ] 1.21[t, 3H, Et, CH <sub>2</sub> CH <sub>3</sub> , 7.7 <sup>f</sup> ]
<b>1c</b>		7.60[d, 1H, H <sup>5</sup> , 7.2 <sup>f</sup> , 61.5 <sup>k</sup> ] 7.02[t, 1H, H <sup>3</sup> , 7.2 <sup>f</sup> ] 6.89[t, 1H, H <sup>4</sup> , 7.2 <sup>f</sup> ] 6.68[d, 1H, H <sup>2</sup> , 7.2 <sup>f</sup> ]	5.3[br, 2H, NH <sub>2</sub> ] 2.62[dq, 1H, CH <sub>2</sub> CH <sub>3</sub> , 7.6 <sup>f</sup> , 12.6 <sup>j</sup> ] 1.76[dq, 1H, CH <sub>2</sub> CH <sub>3</sub> , 7.6 <sup>f</sup> , 12.6 <sup>j</sup> ]
<b>2c</b>	22.8 s, 3857 <sup>r</sup>	7.01[dd, 1H, H <sup>2</sup> , 7.5 <sup>f</sup> , 1.2 <sup>i</sup> ] 6.85[dt, 1H, H <sup>3</sup> , 7.5 <sup>f</sup> , 1.4 <sup>i</sup> ] 6.52[dt, 1H, H <sup>4</sup> , 7.5 <sup>f</sup> , 1.2 <sup>i</sup> ] 6.39[m, 1H, H <sup>5</sup> , 7.5 <sup>f</sup> , 1.4 <sup>i</sup> , 1.4 <sup>g</sup> , 47.4 <sup>k</sup> ]	0.96[t, 3H, CH <sub>2</sub> CH <sub>3</sub> , 7.6 <sup>f</sup> ] 4.9[br, 2H, NH <sub>2</sub> ] 2.86[q, 2H, CH <sub>2</sub> CH <sub>3</sub> , 7.6 <sup>f</sup> ] 1.25[t, 3H, CH <sub>2</sub> CH <sub>3</sub> , 7.6 <sup>f</sup> ]
<b>d</b>		7.7–7.1 m	9.0[br, 1H, NH] 7.2[br, 1H, NH <sub>2</sub> ] 6.4[br, 1H, NH <sub>2</sub> ] 2.74[q, 2H, –CH <sub>2</sub> –C <sup>iminic</sup> , 7.8 <sup>f</sup> ]
<b>1d</b>		7.59[d, 1H, H <sup>5</sup> , 7.3 <sup>f</sup> , 48.0 <sup>k</sup> ] 7.00[t, 1H, H <sup>3</sup> , 7.3 <sup>f</sup> ] 6.88[t, 1H, H <sup>4</sup> , 7.3 <sup>f</sup> ] 6.66[d, 1H, H <sup>2</sup> , 7.3 <sup>f</sup> ]	5.2[br, 2H, NH <sub>2</sub> ] 2.60[dt, 1H, –CH <sub>2</sub> –C <sup>iminic</sup> , 7.8 <sup>f</sup> , 12.4 <sup>j</sup> ] 1.60[dt, 1H, –CH <sub>2</sub> –C <sup>iminic</sup> , 7.8 <sup>f</sup> , 12.4 <sup>j</sup> ]
<b>2d</b>	21.7 s, 4071 <sup>r</sup>	6.99[dd, 1H, H <sup>2</sup> , 7.8 <sup>f</sup> , 1.5 <sup>i</sup> ] 6.85[dt, 1H, H <sup>3</sup> , 7.8 <sup>f</sup> , 1.1 <sup>i</sup> ] 6.52[dt, 1H, H <sup>4</sup> , 7.8 <sup>f</sup> , 1.5 <sup>i</sup> ] 6.39[m, 1H, H <sup>5</sup> , 7.8 <sup>f</sup> , 1.1 <sup>i</sup> , 1.7 <sup>g</sup> , 46.9 <sup>k</sup> ]	4.9[br, 2H, NH <sub>2</sub> ] 2.86[q, 2H, –CH <sub>2</sub> –C <sup>iminic</sup> , 7.8 <sup>f</sup> ]
<b>e</b>		7.59[d, 2H, H <sup>2</sup> , H <sup>6</sup> , 8.5 <sup>f</sup> ] 7.19[d, 2H, H <sup>3</sup> , H <sup>5</sup> , 8.5 <sup>f</sup> ]	8.7[br, 1H, NH] 7.6[br, 1H, NHCH <sub>3</sub> ] 3.25[d, 3H, NHCH <sub>3</sub> , 4.9 <sup>f</sup> ] 2.38[s, 3H, Me.] 2.28[s, 3H, Me.]
<b>1e</b>		7.39[s, 1H, H <sup>5</sup> , 45.9 <sup>k</sup> ] 6.73[m, 2H, H <sup>3</sup> , H <sup>2</sup> ]	5.2[br, 1H, NHCH <sub>3</sub> ] 2.36[s, 3H, Me <sup>h</sup> ] 1.72[s, 3H, Me]
<b>2e</b>	21.7 s, 4107 <sup>r</sup>	6.91[d, 1H, H <sup>2</sup> , 7.7 <sup>f</sup> ] 6.65[dd, 1H, H <sup>3</sup> , 7.7 <sup>f</sup> , 1.2 <sup>i</sup> ] 6.13[d, 1H, H <sup>5</sup> , 48.3 <sup>k</sup> , 1.5 <sup>g</sup> ]	3.06[d, 3H, NHCH <sub>3</sub> , 4.9 <sup>f</sup> ] 4.7[br, 1H, NHCH <sub>3</sub> ] 2.44[s, 3H, Me] 1.75[s, 3H, Me <sup>h</sup> ] 2.96[d, 3H, NHCH <sub>3</sub> , 4.9 <sup>f</sup> ]

<sup>a</sup> In CDCl<sub>3</sub>, unless otherwise stated. Measured at 80.9 MHz (ca. ± 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>.

<sup>b</sup> In CDCl<sub>3</sub>, unless otherwise stated. Measured at 200 MHz; chemical shifts (δ) in ppm (± 0.01) to high frequency of SiMe<sub>4</sub>.

<sup>c</sup> Coupling constants in Hz.

<sup>d</sup> s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt doublet of triplets; q, quadruplet; m, multiplet; br, broad.

<sup>e</sup> in DMSO-*d*<sup>6</sup>.

<sup>f</sup> <sup>3</sup>J<sub>HH</sub>.

<sup>g</sup> J<sub>PH</sub>.

<sup>h</sup> C(4)–Me.

<sup>i</sup> <sup>4</sup>J<sub>HH</sub>.

<sup>j</sup> <sup>2</sup>J<sub>HH</sub>.

<sup>k</sup> J<sub>195P,HH</sub>.

<sup>l</sup> δ(PCH<sub>2</sub>P) = 4.09, [t, 2H, <sup>2</sup>J<sub>CH<sub>2</sub>P</sub> = 11.2].

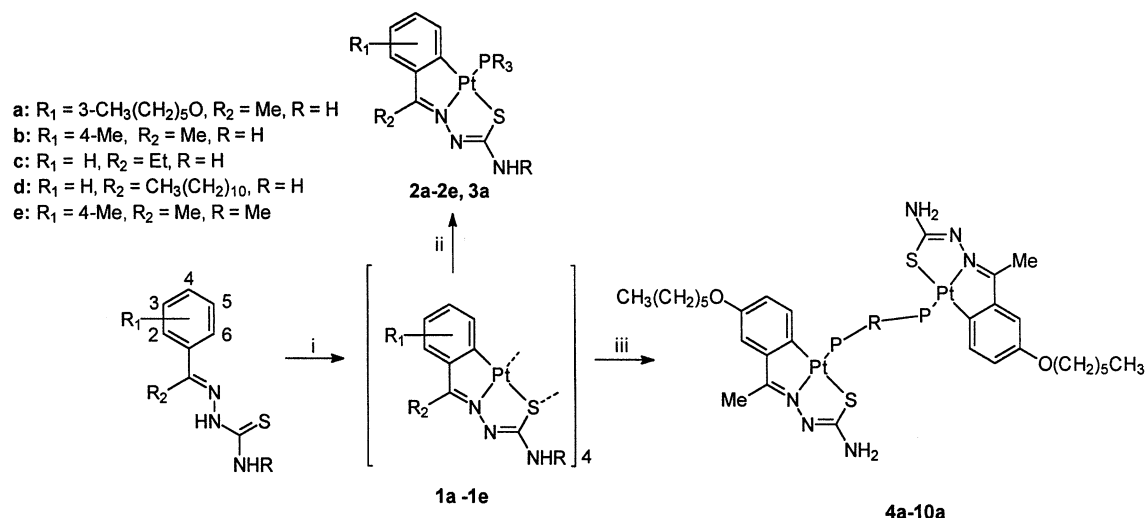
<sup>m</sup> δ(CH<sup>Ferrocene</sup>) = 5.0 [br, 2H], 4.3 [m, 2H].

<sup>n</sup> CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>2</sub>O–.

<sup>p</sup> CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>O–.

<sup>q</sup> Shifts for phenyl protons of phosphine ligand.

<sup>r</sup> J<sub>195P,IP</sub>.



Scheme 1. (i)  $\text{K}_2[\text{PtCl}_4]/\text{EtOH}/\text{H}_2\text{O}$ ; (ii)  $\text{PR}_3$  (acetone, 4:1 ratio); (iii) diphosphine (acetone 2:1 molar ratio).

the complexes, in accordance with the loss of the double bond character upon deprotonation of the NH group. This is shown in the lengthening of the C–S bond in the structure of **2b**. No  $\nu(\text{Pt}–\text{Cl})$  band was found in the IR spectra of the complexes indicating the absence of a chlorine ligand in the coordination geometry of the platinum atom; furthermore, when **1a–1e** were treated with a silver(I) salt, in order to remove possible existing chlorine bonded to platinum, no precipitation of silver chloride was observed.

### 2.1. Reactivity of the complexes

Treatment of the cyclometallated complexes with tertiary monophosphines gave mononuclear species in which the bond at platinum to the  $\text{S}_{\text{bridging}}$  atom was cleaved. The  $\text{Pt}–\text{S}_{\text{chelating}}$  bond of the terdentate thiosemicarbazone ligand remains, even when large excess of monophosphine is used. We believe this is due to the presence of the stronger  $\text{Pt}–\text{S}$  bond in terms of Pearson's concept [20]. This was observed when complexes **1a–1e** and **1a** were reacted with  $\text{PPh}_3$  and  $(4\text{-MeOC}_6\text{H}_4)_3\text{P}$ , respectively, in 1:4 molar ratio. The  $^1\text{H}$ -NMR spectra showed the H5 resonance in compounds **2a**, **3a**, **2c**, **2d** and **2e** shifted to a lower frequency and coupled to the phosphorus nuclei ( $^4J_{\text{PtH}} \approx 1.5$  Hz; this coupling was not observable in complex **2b**). This coupling is smaller, considerably, than the one found in related thiosemicarbazone complexes of palladium(II). The H5 signals also showed coupling to  $^{195}\text{Pt}$  ( $^3J_{\text{PtH}}$  in the range 43.5–48.4 Hz). The  $\text{N}=\text{C}–\text{Me}$  resonance for **2a**, **3a**, **2b** and **2e** is shifted slightly with respect to the corresponding free ligand, whilst the  $–\text{CH}_2\text{CH}_3$  (**2c**) and  $–\text{CH}_2(\text{CH}_2)_9\text{CH}_3$  (**2d**) resonances appear as a quartet and a triplet, respectively, in agreement with free rotation about the C–Et

and C– $\text{CH}_2(\text{CH}_2)_9\text{CH}_3$  bonds consequent upon cleavage of the tetranuclear structure in **1a–1e**. The C4–Me resonance was shifted to lower frequency relative to the free ligands due to shielding of phosphine phenyl ring, as we have shown before in related complexes [21], confirming the relative *trans* disposition of the nitrogen atom and the phosphine ligand.

Treatment of **1a** with tertiary diphosphines in a 2:1 molar ratio afforded dinuclear complexes of formula  $[\{\text{Pt}[3\text{-CH}_3(\text{CH}_2)_5\text{OC}_6\text{H}_3\text{C}(\text{Me})=\text{NN}=\text{C}(\text{S})\text{NH}_2]\}_2(\mu\text{-L})]$  (**4a**, L = dpmm; **5a**, L = dppe; **6a**, L = dppp; **7a**, L = dppb; **8a**, L = dppe; **9a**, L = dpbh; **10a**, L = dppf) as pure air stable solids, which were fully characterised (see Section 3 and Table 1). The  $^1\text{H}$ - and  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of the compounds have been fully assigned. They show phosphorus *trans* to nitrogen coordination. There was only one set of signals for each cyclometallated moiety in the  $^1\text{H}$ -NMR spectra and only one singlet for the two  $^{31}\text{P}$  nuclei in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra, which suggests the compounds to be centrosymmetric as we have shown before in related compounds [12].

### 2.2. Molecular structure of complex **2b**

The crystal structure has been determined (Figs. 2 and 3) and confirms the geometry predicted from spectroscopic studies. Selected bond lengths and angles are listed in Table 2.

The crystal structure comprises a molecule of complex **2b**. The platinum shows an approximately square planar coordination and is bonded to a terdentate thiosemicarbazone system through the aryl C(1) carbon, the imine N(1) nitrogen and the thioamide S(1) sulfur atoms, and to a phosphorus atom of the triphenylphosphine. The angles between adjacent atoms

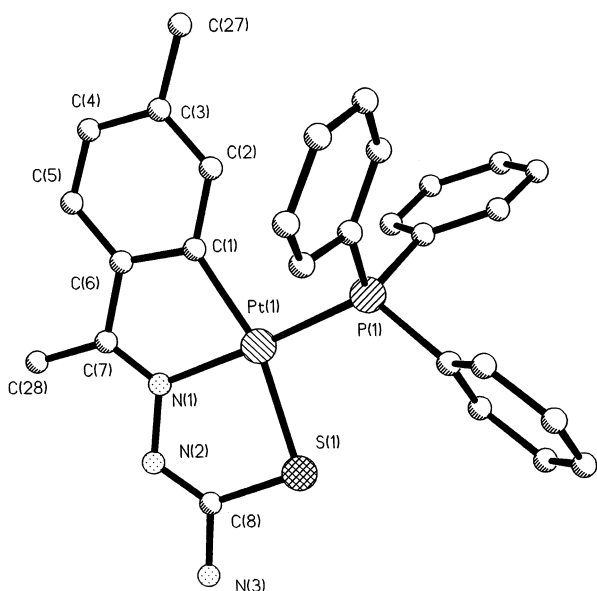


Fig. 2. X-ray crystal structure of **2b** (hydrogens have been omitted for clarity).

Table 2  
Selected bond lengths [Å] and angles [°] for **2b**.

Bond lengths			
Pt(1)–C(1)	2.02(2)	Pt(1)–N(1)	2.03(2)
Pt(1)–P(1)	2.235(5)	Pt(1)–S(1)	2.335(5)
S(1)–C(8)	1.78(2)	N(1)–N(2)	1.45(2)
N(1)–C(7)	1.22(3)	N(3)–C(8)	1.36(3)
N(2)–C(8)	1.25(3)		
Bond angles			
C(1)–Pt(1)–N(1)	77.9(6)	C(1)–Pt(1)–P(1)	98.6(5)
N(1)–Pt(1)–P(1)	176.0(4)	C(1)–Pt(1)–S(1)	161.4(5)
N(1)–Pt(1)–S(1)	83.7(4)	P(1)–Pt(1)–S(1)	99.9(2)
C(8)–S(1)–Pt(1)	95.3(7)	C(9)–P(1)–C(15)	102.5(8)

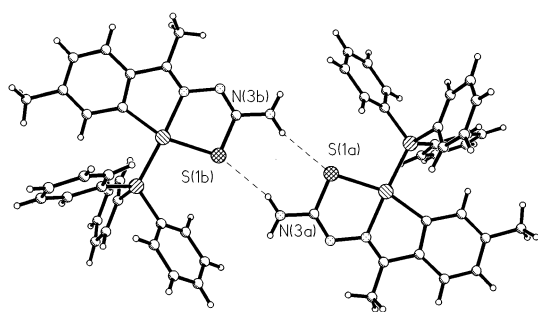


Fig. 3. Hydrogen bonding in **2b** X-ray structure.

in the coordination sphere are close to the expected value of 90°. The most noticeable distortion corresponds to angle C(1)–Pt(1)–N(1) 77.9(6)° consequent upon chelation. The N(1)–Pt(1)–S(1) angle of 83.7(4)° is also less than 90°; the angles C(1)–Pt(1)–P(1) and P(1)–Pt(1)–S(1) are thus greater than 90°. The sum of angles around platinum is 360.1°.

All the bond distances are within the expected range with allowance for the strong *trans* influence of the phosphorus donor ligand.

The Pt(1)–C(1) distance of 2.02(2) Å is similar to other platinum aryl carbon bond distances [11]. The Pt(1)–N(1) bond length of 2.03(2) Å is in agreement with values given earlier [15]. The Pt–P distance of 2.235(5) Å is similar to Pt–P (phosphorus *trans* to nitrogen) bond lengths found in related cyclometallated complexes [15,22,23].

The geometry around the platinum is planar (r.m.s = 0.032 Å; plane 1). The metallated ring [Pt(1), C(1), C(2), C(7), N(1)] and the coordination ring [Pt(1), N(1), N(2), C(8), S(1)] are also planar, (r.m.s. = 0.022 Å; plane 2) and (r.m.s. = 0.0017 Å; plane 3), respectively. Angles between planes are as follows: plane 1/plane 2, 3.3°; plane 1/plane 3, 1.6°; plane 2/plane 3, 4.1°.

The molecular units are stacked in dimers held together by intramolecular hydrogen bonding between one thioamide hydrogen atom and the sulfur atom, N(3)⋯S(1) 3.44 Å, H(3A)⋯S(1) 2.57 Å, N(3)–H(3A)⋯S(1) 167.2°, which forms dimers (Fig. 3).

### 3. Experimental

#### 3.1. Materials and instrumentation

Solvents were purified by standard methods [24]. Chemicals were reagent grade. Potassium tetrachloroplatinate(II) was purchased from Alfa Products. The phosphines (4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub> (dppm), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> (dppe), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>3</sub>PPh<sub>2</sub> (dppp), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>4</sub>PPh<sub>2</sub> (dppb), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>5</sub>PPh<sub>2</sub> (dpppe), Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>6</sub>PPh<sub>2</sub> (dpph), and 1,1'-ferrocenebis(diphenylphosphine) (dppf) were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba Elemental Analyser, model 1108. NMR spectra were obtained as CDCl<sub>3</sub> or DMSO-*d*<sup>6</sup> solutions and referenced to SiMe<sub>4</sub> (<sup>1</sup>H) or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P-<sup>1</sup>H}) and were recorded on a Bruker AaC-2005 spectrometer. All chemical shifts were reported downfield from standards.

#### 3.2. Preparations

##### 3.2.1. Preparation of 3-CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>C(Me)=NN(H)C(=S)NH<sub>2</sub> (**a**)

A mixture of thiosemicarbazide (1.00 g, 10.97 mmol) and hexyloxyacetophenone (2.417 g, 10.97 mmol) and 0.1 cm<sup>3</sup> of acetic acid in 50 cm<sup>3</sup> of ethanol was heated under reflux for 5 h. The mixture was then cooled to –10°C and the white crystalline solid that precipitated was washed with small portions of cold ethanol and

dried in air. Yield 85%. Anal. Found: C, 61.0; H, 7.7; N, 14.4; S 11.7.  $C_{15}H_{23}N_3OS$  Anal. Calc.: C, 61.4; H, 7.9; N, 14.3; S, 11.9%. IR:  $\nu(C=S)$  845  $m\text{ cm}^{-1}$ ;  $\nu(C=N)$  1620  $s\text{ cm}^{-1}$ .

Thiosemicarbazones **b–e** were prepared following a similar procedure.

### 3.2.2. 4-MeC<sub>6</sub>H<sub>4</sub>C(Me)=NN(H)=C(S)NH<sub>2</sub> (**b**)

Yield 80%. Anal. Found: C, 58.3; H, 6.3; N, 20.3; S 15.6.  $C_{10}H_{13}N_3S$  Anal. Calc.: C, 57.9; H, 6.3; N, 20.3; S, 15.5%. IR:  $\nu(C=S)$  820  $m\text{ cm}^{-1}$ ;  $\nu(C=N)$  1615 sh,  $s\text{ cm}^{-1}$ .

### 3.2.3. C<sub>6</sub>H<sub>5</sub>C(Et)=NN(H)=C(S)NH<sub>2</sub> (**c**)

Yield 75%. Anal. Found: C, 58.1; H, 6.5; N, 20.3; S 15.6.  $C_{10}H_{13}N_3S$  Anal. Calc.: C, 57.9; H, 6.3; N, 20.3; S, 15.5%. IR:  $\nu(C=S)$  820  $m\text{ cm}^{-1}$ ;  $\nu(C=N)$  1620  $s\text{ cm}^{-1}$ .

### 3.2.4. C<sub>6</sub>H<sub>5</sub>C{CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>}=NN(H)=C(S)NH<sub>2</sub> (**d**)

Yield 50%. Anal. Found: C, 68.1; H, 9.3; N, 12.8; S, 9.9.  $C_{19}H_{31}N_3S$  Anal. Calc.: C, 68.4; H, 9.4; N, 12.6; S, 9.6%. IR:  $\nu(C=S)$  825  $m\text{ cm}^{-1}$ ;  $\nu(C=N)$  1620 sh,  $s\text{ cm}^{-1}$ .

### 3.2.5. 4-MeC<sub>6</sub>H<sub>4</sub>C(Me)=NN(H)=C(S)NHMe (**e**)

Yield 85%. Anal. Found: C, 59.5; H, 6.8; N, 18.9; S 14.6.  $C_{11}H_{15}N_3S$  Anal. Calc.: C, 59.7; H, 6.8; N, 19.0; S, 14.5%. IR:  $\nu(C=S)$  825  $s\text{ cm}^{-1}$ ;  $\nu(C=N)$  1620  $m\text{ cm}^{-1}$ .

### 3.2.6. Preparation of

#### [Pt{3-CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NH<sub>2</sub>}]<sub>4</sub> (**1a**)

To a stirred solution of potassium tetrachloroplatinate (200 mg, 0.48 mmol) in water (3  $\text{cm}^3$ ), ethanol was added (27  $\text{cm}^3$ ). The fine yellow suspension of potassium tetrachloroplatinate obtained was treated with 3-CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>4</sub>C(Me)=NN(H)C(=S)NH<sub>2</sub> (**a**) (160 mg, 0.55 mmol). The mixture was stirred for 48 h at 60°C. After cooling to room temperature, the orange precipitate formed was filtered off, washed with ethanol and dried in air. Yield 71%. Anal. Found: C, 37.0; H, 4.0; N, 8.4; S 6.5.  $C_{60}H_{84}N_{12}O_4S_4Pt_4$  Anal. Calc.: C, 37.0; H, 4.3; N, 8.6; S, 6.6%. IR:  $\nu(C=N)$  1620  $s\text{ cm}^{-1}$ .

Compounds **1b–1e** were obtained following a similar procedure as orange solids.

#### 3.2.7. [Pt{4-MeC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NH<sub>2</sub>}]<sub>4</sub> (**1b**)

Yield 66%. Anal. Found: C, 30.2; H, 2.9; N, 10.0; S, 8.4.  $C_{40}H_{44}N_{12}S_4Pt_4$  Anal. Calc.: C, 30.0; H, 2.8; N, 10.5; S 8.0%. IR:  $\nu(C=N)$  1610 sh,  $m\text{ cm}^{-1}$ .

#### 3.2.8. [Pt{C<sub>6</sub>H<sub>4</sub>C(Et)=NN=C(S)NH<sub>2</sub>}]<sub>4</sub> (**1c**)

Yield 70%. Anal. Found: C, 30.4; H, 3.0; N, 10.0; S, 8.2.  $C_{40}H_{44}N_{12}S_4Pt_4$  Anal. Calc.: C, 30.0; H, 2.8; N, 10.5; S 8.0%. IR:  $\nu(C=N)$  1610 sh,  $s\text{ cm}^{-1}$ .

#### 3.2.9. [Pt{C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>)=NN=C(S)NH<sub>2</sub>}]<sub>4</sub> (**1d**)

Yield 60%. Anal. Found: C, 43.4; H, 5.4; N, 7.7; S, 6.1.  $C_{76}H_{116}N_{12}S_4Pt_4$  Anal. Calc.: C, 43.3; H, 5.5; N, 8.0; S 6.1%. IR:  $\nu(C=N)$  1610  $s\text{ cm}^{-1}$ .

#### 3.2.10. [Pt{4-MeC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NHMe}]<sub>4</sub> (**1e**)

Yield 50%. Anal. Found: C, 31.9; H, 3.1; N, 10.2; S, 7.6.  $C_{44}H_{52}N_{12}S_4Pt_4$  Anal. Calc.: C, 31.9; H, 3.2; N, 10.1; S 7.7%. IR:  $\nu(C=N)$  1615  $s\text{ cm}^{-1}$ .

#### 3.2.11. Preparation of [Pt{3-CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NH<sub>2</sub>}](PPh<sub>3</sub>) (**2a**)

PPh<sub>3</sub> (27.0 mg, 0.103 mmol) was added to a suspension of **1a** (50.0 mg, 0.026 mmol) in acetone (15  $\text{cm}^3$ ). The solution was stirred for 4 h, the solvent removed in vacuo and the resulting yellow solid recrystallised from acetone–*n*-hexane. Yield 75%. Anal. Found: C, 52.9; H, 4.7; N, 5.7; S, 4.2.  $C_{33}H_{36}N_3OSPtP$  Anal. Calc.: C, 52.9; H, 4.8; N, 5.6; S, 4.3%. IR:  $\nu(C=N)$  1620  $s\text{ cm}^{-1}$ .

#### 3.2.12. [Pt{4-MeC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NH<sub>2</sub>}](PPh<sub>3</sub>) (**2b**)

Compound **2b** was synthesised following a similar procedure to that for **2a**, but after stirring the cyclometallated compound–phosphine mixture, an orange precipitate appeared which was filtered off and dried in vacuo.

Yield 80%. Anal. Found: C, 50.5; H, 4.0; N, 6.5; S, 4.7.  $C_{28}H_{26}N_3SPTP$  Anal. Calc.: C, 50.7; H, 3.9; N, 6.3; S, 4.8%. IR:  $\nu(C=N)$  1605 sh,  $s\text{ cm}^{-1}$ .

Compounds **3a** and **2e** were synthesised following a similar procedure to that for **2a** as orange solids.

Compounds **2c** and **2d** were synthesised following a similar procedure to that for **2b** as orange solids.

#### 3.2.13. [Pt{C<sub>6</sub>H<sub>4</sub>C(Et)=NN=C(S)NH<sub>2</sub>}](PPh<sub>3</sub>) (**2c**)

Yield 80%. Anal. Found: C, 50.5; H, 4.2; N, 6.6; S, 4.7.  $C_{28}H_{26}N_3SPTP$  Anal. Calc.: C, 50.7; H, 3.9; N, 6.3; S, 4.8%. IR:  $\nu(C=N)$  1580  $s\text{ cm}^{-1}$ .

#### 3.2.14. [Pt{C<sub>6</sub>H<sub>4</sub>C(CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>)=NN=C(S)NH<sub>2</sub>}](PPh<sub>3</sub>) (**2d**)

Yield 50%. Anal. Found: C, 57.0; H, 4.0; N, 5.4; S, 4.1.  $C_{37}H_{34}N_3SPTP$  Anal. Calc.: C, 57.1; H, 4.4; N, 5.4; S, 4.1%. IR:  $\nu(C=N)$  1605  $s\text{ cm}^{-1}$ .

#### 3.2.15. [Pt{4-MeC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NHMe}](PPh<sub>3</sub>) (**2e**)

Yield 30%. Anal. Found: C, 51.5; H, 4.2; N, 6.2; S, 4.6.  $C_{29}H_{28}N_3SPTP$  Anal. Calc.: C, 51.5; H, 4.2; N, 6.2; S, 4.7%. IR:  $\nu(C=N)$  1580  $s\text{ cm}^{-1}$ .

#### 3.2.16. [Pt{3-CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>OC<sub>6</sub>H<sub>3</sub>C(Me)=NN=C(S)NH<sub>2</sub>}-P(4-MeOC<sub>6</sub>H<sub>4</sub>)<sub>3</sub>]<sub>4</sub> (**3a**)

Yield 60%. Anal. Found: C, 51.5; H, 5.2; N, 5.2; S, 3.9.  $C_{36}H_{42}N_3O_4SPTP$  Anal. Calc.: C, 51.5; H, 5.0; N, 5.0; S, 3.8%. IR:  $\nu(C=N)$  1615  $s\text{ cm}^{-1}$ .

3.2.17. Preparation of  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)NH_2]\}_2(\mu-Ph_2PCH_2PPh_2)$  (**4a**)

$Ph_2PCH_2PPh_2$  (20.0 mg, 0.052 mmol) was added to a suspension of **1a** (50.0 mg, 0.026 mmol) in acetone (15 cm<sup>3</sup>). The solution was stirred for 4 h and the resulting orange solid filtered off and dried in air. Yield 70%. Anal. Found: C, 48.5; H, 4.7; N, 6.0; S, 4.9. C<sub>55</sub>H<sub>64</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 48.7; H, 4.7; N, 6.2; S, 4.7%. IR:  $\nu(C=N)$  1620 sh, s cm<sup>-1</sup>.

Compounds **5a–10a** were obtained as orange air-stable solids following a similar procedure.

3.2.18.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2P(CH_2)_2PPh_2)$  (**5a**)

Yield 62%. Anal. Found: C, 48.7; H, 4.7; N, 6.6; S, 4.6. C<sub>56</sub>H<sub>66</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 49.0; H, 4.8; N, 6.1; S, 4.7%. IR:  $\nu(C=N)$  1620 sh, m cm<sup>-1</sup>.

3.2.19.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2P(CH_2)_3PPh_2)$  (**6a**)

Yield 62%. Anal. Found: C, 49.4; H, 4.7; N, 6.2; S, 4.5. C<sub>57</sub>H<sub>68</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 49.4; H, 4.9; N, 6.1; S, 4.5%. IR:  $\nu(C=N)$  1620 s cm<sup>-1</sup>.

3.2.20.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2P(CH_2)_4PPh_2)$  (**7a**)

Yield 40%. Anal. Found: C, 50.0; H, 5.3; N, 6.0; S, 4.7. C<sub>58</sub>H<sub>70</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 49.8; H, 5.0; N, 6.0; S, 4.6%. IR:  $\nu(C=N)$  1620 sh, s cm<sup>-1</sup>.

3.2.21.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2P(CH_2)_5PPh_2)$  (**8a**)

Yield 70%. Anal. Found: C, 49.9; H, 5.1; N, 5.9; S, 4.7. C<sub>59</sub>H<sub>72</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 50.1; H, 5.1; N, 5.9; S, 4.5%. IR:  $\nu(C=N)$  1620 sh, s cm<sup>-1</sup>.

3.2.22.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2P(CH_2)_6PPh_2)$  (**9a**)

Yield 45%. Anal. Found: C, 50.2; H, 5.1; N, 6.1; S, 4.5. C<sub>60</sub>H<sub>74</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub> Anal. Calc.: C, 50.5; H, 5.2; N, 5.9; S, 4.5%. IR:  $\nu(C=N)$  1620 sh, s cm<sup>-1</sup>.

3.2.23.  $\{Pt[3-CH_3(CH_2)_5OC_6H_3C(Me)=NN=C(S)-NH_2]\}_2(\mu-Ph_2PC_5H_4FeC_5H_4PPh_2)$  (**10a**)

Yield 75%. Anal. Found: C, 49.9; H, 4.6; N, 5.4; S, 4.4. C<sub>64</sub>H<sub>70</sub>N<sub>6</sub>O<sub>2</sub>S<sub>2</sub>Pt<sub>2</sub>P<sub>2</sub>Fe Anal. Calc.: C, 50.3; H, 4.6; N, 5.5; S, 4.2%. IR:  $\nu(C=N)$  1615 sh, m cm<sup>-1</sup>.

### 3.3. Single-crystal X-ray diffraction analysis

Crystal data for C<sub>28</sub>H<sub>26</sub>N<sub>3</sub>PPtS:  $M = 662.64$  crystallises from chloroform as yellow blocks; crystal dimensions 0.66 × 0.43 × 0.22 mm. Monoclinic,  $a = 10.036(9)$ ,  $b = 11.152(7)$ ,  $c = 12.489(11)$  Å,  $\alpha = 91.52(6)^\circ$ ,  $\beta = 105.91(7)^\circ$ ,  $\gamma = 110.03(7)^\circ$ ,  $U = 1252(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc.}} = 1.758$  g cm<sup>-3</sup>, space group  $P\bar{1}$  (no. 2), Mo–K $\alpha$

radiation  $\lambda = 0.71073$  Å,  $\mu(\text{Mo–K}\alpha) = 5.775$  mm<sup>-1</sup>,  $F(000) = 648$ .

Three-dimensional, room-temperature X-ray data were collected in the range  $3.5 < 2\theta < 45^\circ$  on a Siemens P4 diffractometer by the omega scan method. Of the 3430 reflections measured, all of which were corrected for Lorentz and polarisation effects, 2652 independent reflections exceeded the significance level  $|F|/\sigma(|F|) > 4.0$ . The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$ . Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final  $R = 0.0957$  ( $wR_2 = 0.2550$  for all 2930 unique data, 168 parameters, mean and maximum  $\delta/\sigma$  0.000, 0.000), with allowance for the thermal anisotropy of Pt1, S1, P1 and N1 to N3 only. Minimum and maximum final electron density 3.900 and  $-5.851$  e Å<sup>-3</sup> (0.932 Å to Pt1). A weighting scheme  $w = 1/[\sigma^2(F_o^2) + (0.2201P)^2 + 1.1386P]$  where  $P = (F_o^2 + 2F_c^2)/3$  was used in the latter stages of refinement. Complex scattering factors were taken from the program package SHELXL-93 [25] as implemented on the Viglen 486dx computer.

## 4. Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 132969 for compound **2b**.

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