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Cycloplatination of Thiosemicarbazones Derived from Furane. Crystal and Molecular Structure of [{Pt[(OC_4H_2)C(Me)=NN=C(S)NHEt]}$_2${μ-$Ph_2P(CH_2)_2PPh_2$}]

Luis Adrio[a], José M. Antelo[a], Juan M. Ortigueira[a], Darío Lata[a], Mª Teresa Pereira[a], Margarita López-Torres[b], José M. Vila[a,*]

[a] Santiago de Compostela, Spain, Universidad de Santiago de Compostela Departamento de Química Inorgánica,
[b] A Coruña / Spain, Universidad de A Coruña, Departamento de Química Fundamental

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Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 65th Birthday

Abstract. Treatment of thiosemicarbazones (OC_4H_3)C(Me)=NN(H)C(=S)NHR (R: Me, **a**; Et, **b**) with [*cis*-$PtMe_2$(cod)] afforded the tetranuclear compounds [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}]$_4$ (R: Me, **1a**; Et, **1b**). The reaction of **1a** and **1b** with triphenylphosphine in 1:4 molar ratio gave rise to the mononuclear compounds [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}(PPh_3)] (**2a**, **2b**). Treatment of **1a** and **1b** with large-bite diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 2, dppe; n = 3, dppp; n = 4, dppb) afforded the dinuclear compounds [{Pt[(OC_4H_2)C(Me)=NN=C(S)NHR]}$_2${μ-$Ph_2P(CH_2)_nPPh_2$}], (**3a−5a**, **3b−5b**), with the diphosphine in a bridging mode. Similar reactions with the short-bite diphosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PC(=CH_2)PPh_2$ (vdpp) yielded the mononuclear compounds [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}-($Ph_2PCH_2PPh_2$-*P*)] (**6a**, **6b**) and [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}(Ph_2P-C($=CH_2$)PPh_2-*P*)] (**7a**, **7b**) with the diphosphine in a monodentate coordination. Treatment of **1a** and **1b** with [$W(CO)_5(Ph_2CH_2PPh_2)$] gave the novel heterodinuclear species [{Pt[(OC_4H_2)C(Me)=NN=C(S)NHR]}{$W(CO)_5(Ph_2CH_2PPh_2$-*P*)}] (**8a**, **8b**), which could also be synthesized by reaction of **6a** and **6b** with [$W(CO)_5$(THF)]. ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR and IR data are given. The crystal structure of compound **3b** has been determined by X-ray crystallography.

Keywords: Platinum; Metallation; Thiosemicarbazone; Furane; Phosphorus ligands; Crystal structures

1 Introduction

The cyclometallation reaction, *i.e.* the intramolecular activation of aromatic C-H bonds by transition metals in coordinated ligands, has been widely investigated, especially in the case of phenyl rings. The ease of metallation is dependent on the directing influence of the ring substituents, as well as on steric factors [1]. The main interest in this type of compounds stems from their salient applications, such as for instance, to serve as intermediates in organic and organometallic synthesis [2], as active catalysts [3], liquid crystals [4], analytical tools [5], to allow the resolution of racemic mixtures [6], and for the design of metal complexes with promising anticancer [7] or photochemical properties [8]. In particular, nitrogen, phosphorus or sulfur containing platinacycles [9] also offer attractive applications as catalysts in the assymmetric aldol-type condensation of isocyanides and aldehydes in the presence of ^{i}Pr$_2$NEt [10], in Michael and Diels-Alder reactions for C-C bond formation [11], or as highly tunable photooxidants or photoreductants [12]. Recently, platinum species have represented an important class of complexes particularly from the point of view of their luminescent properties, and the usage of the phosphorescent complexes as emitters in light-emitting diodes (LEDS) [13].

Cyclometallation reactions of heterocyclic derivatives have been less extensively studied, in spite that heterocycles are expected to possess unique properties in applied fields of chemistry and pharmacy [14], not encountered in phenyl derivatives. Work related to cyclometallated complexes derived from simple five-membered heterocycles such as furane, thiophene and pyrrole [15], or benzo fused five-membered heterocycles [16], have been reported. Thus, treatment of the appropriate ligands with $Li_2[PdCl_4]$ or $K_2[PtCl_4]$ gave chloro-bridged dinuclear complexes; whilst reaction with palladium(II) acetate (the most commonly used palladium(II) salt in metallation processes) did not afford the well known acetato-bridged dimer complexes [17]; instead, unexpected mononuclear nitro complexes were formed *via* oxidation of the acetonitrile used as solvent.

Furthermore, thiosemicarbazones and semicarbazones have been known to form stable complexes with many transition metal ions [18]. Our interest in cyclometallated compounds has been, in part, focused on the study of complexes derived from [*C,N,S*] terdentate ligands such as thiosemicar-

* Prof. Dr. José M. Vila
Universidad de Santiago de Compostela
Departamento de Química Inorgánica
E-15782 Santiago de Compostela / Spain
Fax: +34/981-595012
E-mail: qideport@usc.es

bazones or Schiff base ligands with additional sulfur donor atoms, which react readily with $M_2[PdCl_4]$ (M = Li, K), $Pd(OAc)_2$ or $K_2[PtCl_4]$ to give mono- or tetranuclear compounds (see Figure 1) [19], depending on the nature of the starting ligand. All complexes showed a metallated carbon atom belonging to a phenyl ring as depicted in Figure 1,

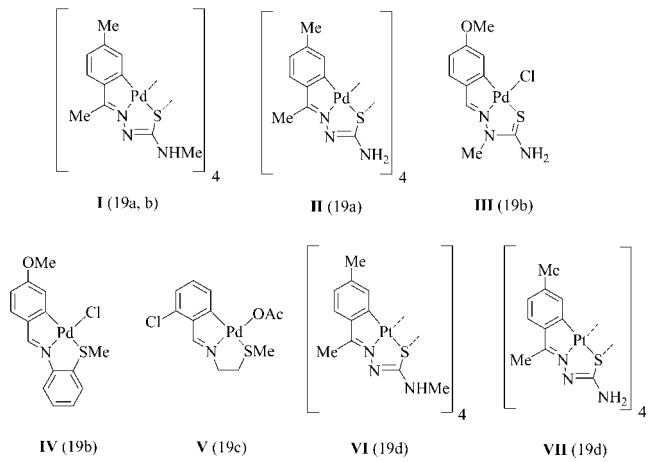


Figure 1

However, work concerning the heteroaromatic thio- and semicarbazone derivatives are scarce, mainly due to the large number of potential coordination sites they present, which usually gives rise to a complex chelation chemistry. In the present paper we report the synthesis of new cycloplatinated compounds derived from thiosemicarbazones in which the metallated carbon atom belongs to a furane ring, as well as the preliminary results concerning novel heterodinuclear platinum-tungsten compounds.

2 Experimental Section

General procedures

All solvents were distilled prior to use from appropriate drying agents [20]. Chemicals were used as supplied from commercial sources. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago, with a Carlo-Erba Elemental Analyser 1108. IR spectra were recorded as KBr pellets or Nujol mulls with a Perkin-Elmer 1330 and with a Mattson spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C-{^1H}) or 85 % H_3PO_4 (^{31}P-{^1H}); and were recorded on a Bruker WM250 and AMX 300 spectrometers (200.0 MHz for ^1H, 50.3 MHz for ^{13}C-{^1H}, 81.0 MHz for ^{31}P-{^1H}). Electrospray mass spectra were recorded on a Finnigan Navigator spectrometer with acetonitrile as the solvent.

Synthesis

Preparation of $(OC_4H_3)C(Me)=NN(H)C(=S)NHMe$ (a). – To a solution obtained by heating methyl-thiosemicarbazide (0.500 g, 4.755 mmol) and 1 cm^3 of acetic acid in 25 cm^3 of water a solution of 2-acetylfurane (0.524 g, 4.759 mmol) in 25 cm^3 of ethanol was added. The resulting mixture was heated under reflux for 6 h. After cooling to room temperature the white solid formed was filtered off, washed with water, dried *in vacuo* and recrystallized in etanol. Yield 749 mg, 80 %. Anal. Found: C, 49.1; H, 5.5; N, 21.1; S, 16,0; $C_8H_{11}N_3OS$ (197.26 g/mol) requires C, 48.7; H, 5.6; N, 21.3; S, 16.3 %.

IR /cm^{-1}: ν(C=N) 1631w, ν(C=S) 824w. **^1H NMR** ($CDCl_3$, δ, *J* Hz): 8.59 (s, NH); 7.64 (b, N*H*Me); 7.48 (d, H5, ^3J(H4H5) 1.9); 6.72 (d, H3, ^3J(H4H3) 3.5); 6.46 (dd, H4, ^3J(H4H3) 3.5, ^3J(H4H5) 1.9); 3.25 (d, NH*Me*, ^3J(MeH) = 4.7); 2.18 (s, CMe). **^{13}C NMR** ($CDCl_3$, δ, *J* Hz): 178,99 (s, $C_{C=S}$); 149,50 (s, C2); 144,87 (s, $C_{C=N}$); 144,54 (s, C5); 112,33 (s, C3); 111,56 (s, C4); 31,64 (s, CMe); 21,20 (s, NMe).

Ligand **b** was prepared similarly.

$(OC_4H_3)C(Me)=NN(H)C(=S)NHEt$ (b). – Yield: 739 mg, 83 %. Anal. Found: C, 51.4; H, 6.0; N, 20.0; S, 15.3; $C_9H_{13}N_3OS$ (211.28 g/mol) requires C, 51.2; H, 6.2; N, 19.9; S, 15.2 %.

IR (cm^{-1}): ν(C=N) 1611w, ν(C=S) 814w. **^1H NMR** ($CDCl_3$, δ, *J* Hz): 8,51 (s, NH); 7.58 (b, N*H*Et); 7.49 (d, H5, ^3J(H4H5) = 1.6); 6,73 (d, H3, ^3J(H3H4) = 3.5); 6.47 (dd, H4, ^3J(H3H4) = 3.5; ^3J(H4H5) = 1.6); 3.76 (qd, NCH_2Me, ^3J(HH) = 5.5, ^3J(HH) = 8.1); 2.19 (s, CMe); 1.31 (t, NCH_2Me, ^3J(HH) = 8.1). **^{13}C NMR** ($CDCl_3$, δ, *J* Hz): 177,79 (s, $C_{C=S}$); 149,52 (s, C2); 144,86 (s, $C_{C=N}$); 144,52 (s, C5); 112,34 (s, C3); 111,42 (s, C4); 39,89 (s, NCH_2); 21,21 (s, CMe); 14,84 (s, NCH_2Me).

***Preparation of* $[Pt\{(OC_4H_2)C(Me)=NN=C(S)NHMe\}]_4$ (1a). –** Ligand **a** (65 mg, 0.330 mmol) and [*cis*-$PtMe_2$(cod)] (100 mg, 0.300 mmol) were refluxed in 25 cm^3 of anhydrous *n*-octane for 2 h under nitrogen. After cooling to room temperature, the orange solid formed was filtered and dried *in vacuo*. Yield: 67 mg, 57 %. Anal. Found: C, 24.8; H, 2.4; N, 10.6; S, 8.4; $C_{32}H_{36}N_{12}O_4Pt_4S_4$ (1561.28 g/mol) requires C, 24.6; H, 2.3; N, 10.8; S, 8.2 %.

IR /cm^{-1}: ν(C=N) 1618sh. **^1H NMR** ($CDCl_3$, δ, *J* Hz): 7.29 (s, H5); 6.41 (s, H4); 5.02 (q, N*H*Me, ^3J(MeH) = 4.9); 3.01 (d, NH*Me*, ^3J(MeH) = 4.9); 1.97 (s, CMe). **ESI-MS**: m/z = 1561 $[M]^+$; 390 $[M/4]^+$.

Compound **1b** was prepared analogously.

$[Pt\{(OC_4H_2)C(Me)=NN=C(S)NHEt\}]_4$ (1b). – Yield: 69 mg, 57 %. Anal. Found: C, 27.0; H, 2.9; N, 10.3; S, 7.8; $C_{36}H_{44}N_{12}O_4Pt_4S_4$ (1617.38 g/mol) requires C, 26.7; H, 2.7; N, 10.4; S, 7.9 %.

IR /cm^{-1}: ν(C=N) 1590sh. **^1H NMR** ($CDCl_3$, δ, *J* Hz): 7.28 (d, H5, ^3J(H4H5) = 1.6); 6.40 (d, H4, ^3J(H4H5) = 1.6); 5.04 (t, N*H*Et, ^3J(HH) = 5.9); 3.43 (qd, NCH_2Me, ^3J(HH) = 5.9, ^3J(HH) = 9.3); 1.96 (s, CMe); 1.22 (t, NCH_2Me, ^3J(HH) = 9.3). **ESI-MS**: m/z = 1617 $[M]^+$; 404 $[M/4]^+$.

***Preparation of* $[Pt\{(OC_4H_2)C(Me)=NN=C(S)NHMe\}(PPh_3)]$ (2a). –** To **1a** (20 mg, 0.013 mmol) in chloroform (10 cm^3), PPh_3 (14 mg, 0.053 mmol) was added in a complex/phosphine 1:4 molar ratio. The resulting mixture was heated under nitrogen for 10 min. The solvent was removed under reduced pressure and the residue recrystallized from chloroform/n-hexane. Yield: 19 mg, 56 %. Anal. Found: C, 48.1; H, 3.9; N, 6.3; S, 5.1. $C_{26}H_{24}N_3OPPtS$ (652.61 g/mol) requires C, 47.9; H, 3.7; N, 6.4; S, 4.9 %.

IR /cm^{-1}: ν(C=N) 1610sh. **^1H NMR** ($CDCl_3$, δ, *J* Hz): 6.97 (s, H5); 4.99 (s, H4); 4.65 (q, N*H*Me, ^3J(MeH) = 4.7); 2.96 (d, NH*Me*); 2.34 (s, CMe). **^{31}P-{^1H} NMR** ($CDCl_3$, δ, *J* Hz): 16.60 (s, ^1J(PtP) = 3743.4).

Compound **2b** was prepared in a similar manner.

$[Pt\{(OC_4H_2)C(Me)=NN=C(S)NHEt\}(PPh_3)]$ (2b). – Yield: 16 mg, 49 %. Anal. Found: C, 48.4; H, 4.1; N, 6.2; S, 4.6; $C_{27}H_{26}N_3OPPtS$ (666.63 g/mol) requires C, 48.7; H, 3.9; N, 6.3; S, 4.8 %.

IR /cm^{-1}: ν(C=N) 1595sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.98 (d, H5, ^3J(H4H5) = 1.6); 5.01 (d, H4, ^3J(H4H5) = 1.6); 4.66 (b, N*H*Et); 3.37 (qd, N*CH*$_2$Me, ^3J(HH) = 5.2, ^3J(HH) = 8.5); 2.34 (s, CMe); 1.12 (t, NCH$_2$*Me*, ^3J(HH) = 8.5). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 16.65 (s, ^1J(PtP) = 3743.4).

Preparation of [{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe]}$_2${μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$}] (3a). − To a suspension of **1a** (20 mg, 0.013 mmol) in chloroform (10 cm^3) 1,2-bis(diphenylphosphino)-ethane (10 mg, 0.025 mmol) was added and the resulting mixture was heated under nitrogen for 10 min. The solvent was removed at reduced pressure and the residue recrystallized from chloroform/n-hexane. Yield: 16 mg, 53 %. Anal. Found: C, 42.5; H, 3.7; N, 7.0; S, 5.46. $C_{42}H_{42}N_6O_2P_2Pt_2S_2$ (1178.16 g/mol) requires C, 42.8; H, 3.6; N, 7.1; S, 5.44 %.

IR /cm^{-1}: ν(C=N) 1615sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.95 (b, H5); 5.05 (b, H4); 4.65 (q, N*H*Me, ^3J(MeH) = 4.7), 3.01 (d, NH*Me*, ^3J(MeH) = 4.7); 2.34 (s, CMe). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 12.56 (s, ^1J(PtP) = 3692.6).

Compounds **4a**, **5a**, and **3b**−**5b** were synthesized following a similar procedure.

[{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe]}$_2${μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (4a). − Yield: 18 mg, 60 %. Anal. Found: C, 43.5; H, 3.9; N, 6.9; S, 5.3. $C_{43}H_{44}N_6O_2P_2Pt_2S_2$ (1193.08 g/mol) requires C, 43.3; H, 3.7; N, 7.0; S, 5.4 %.

IR /cm^{-1}: ν(C=N) 1610sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.98 (s, H5); 5.13 (s, H4); 3.24 (d, NH*Me*, ^3J(MeH) = 4.7); 2.74 (s, CMe); 2.74 (b, PCH$_2$); 2.40 (b, PCH$_2$*CH*$_2$). **^{31}P-{^{1}H}** NMR ($CDCl_3$, δ, *J* Hz): 8.11 (s, ^1J(PtP) = 3672.2).

[{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe]}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] (5a). − Yield: 23 mg, 73 %. Anal. Found: C, 43.7; H, 4.0; N, 7.2; S, 5.5. $C_{44}H_{46}N_6O_2P_2Pt_2S_2$ (1207.11 g/mol) requires C, 43.8; H, 3.8; N, 7.0; S, 5.3 %.

IR /cm^{-1}: ν(C=N) 1610sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.99 (s, H5); 5.14 (s, H4); 4.71 (q, N*H*Me, ^3J(MeH) = 4.9); 2.98 (d, NH*Me*); 2.46 (b, PC*H*$_2$CH$_2$); 2.31 (s, CMe); 1.99 (b, PCH$_2$*CH*$_2$). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 7.33 (s, ^1J(PtP) = 3692.6).

[{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt]}$_2${μ-Ph$_2$P(CH$_2$)$_2$PPh$_2$}] (3b). − Yield: 23 mg, 77 %. Anal. Found: C, 43.6; H, 3.9; N, 7.2; S, 5.1; $C_{44}H_{46}N_6O_2P_2Pt_2S_2$ (1206.19 g/mol) requires C, 43.8; H, 3.8; N, 7.0; S, 5.3 %.

IR /cm^{-1}: ν(C=N) 1591sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.95 (b, H5); 5.07 (b, H4); 4.71(b, N*H*Et); 3.41 (qd, N*CH*$_2$Me, ^3J(HH) = 5.1, ^3J(HH) = 7.8); 2.86 (b, PCH$_2$); 2.33 (s, CMe); 1.17 (t, NCH$_2$*Me*, ^3J(HH) = 7.8). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 12.56 (s, ^1J(PtP) = 3743.4).

[{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt]}$_2${μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$}] (4b). − Yield: 24 mg, 79 %. Anal. Found: C, 44.5; H, 3.9; N, 7.1; S, 5.4.; $C_{45}H_{48}N_6O_2P_2Pt_2S_2$ (1221.14 g/mol) requires C, 44.3; H, 4.0; N, 6.9; S, 5.3 %.

IR /cm^{-1}: ν(C=N) 1590sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.98 (s, H5); 5.15 (s, H4); 4.68 (b, N*H*Et); 3.42 (qd, N*CH*$_2$Me, ^3J(HH) = 5.2, ^3J(HH) = 8.4); 2.75 (b, PC*H*$_2$CH$_2$); 2.47 (b, PCH$_2$*CH*$_2$); 2.31 (s, CMe); 2.09 (b, PCH$_2$*CH*$_2$); 1.16 (t, NCH$_2$*Me*, ^3J(HH) = 8.4). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 8.14 (s, ^1J(PtP) = 3662.2).

[{Pt[(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt]}$_2${μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$}] (5b). − Yield: 19 mg, 61 %. Anal. Found: C, 44.9; H, 4.2; N, 7.0; S, 5.0. $C_{46}H_{50}N_6O_2P_2Pt_2S_2$ (1235.16 g/mol) requires C, 44.7; H, 4.1; N, 6.8; S, 5.2 %.

IR /cm^{-1}: ν(C=N) 1586sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.97 (d, H5, ^3J(H4H5) = 1.6, ^4J(PtH5) = 10.6); 5.15 (d, H4, ^3J(H4H5) = 1.6, ^3J(PtH4) = 11.3); 4.70 (t, N*H*Et); 3.38 (qd, N*CH*$_2$Me, ^3J(HH) = 5.9, ^3J(HH) = 9.1); 2.46 (b, PC*H*$_2$CH$_2$); 2.30 (s, CMe); 1.76 (b, PCH$_2$*CH*$_2$); 1.14 (t, NCH$_2$*Me*, ^3J(HH) = 9.1). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 7.28 (s, ^1J(PtP) = 3680.4).

Preparation of [Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe}-(Ph$_2$PCH$_2$PPh$_2$-*P*)] (6a). To a suspensión of **1a** (20 mg, 0.013 mmol) in chloroform (10 cm^3) 1,1-bis(diphenylphosphino)-methane (dppm, 20 mg, 0.052 mmol) was added and the resulting mixture was heated under nitrogen for 10 min. The solvent was removed under reduced pressure and the residue recrystallized in chloroform/n-hexane. Yield: 16 mg, 41 %. Anal. Found: C, 50.9; H, 4.2; N, 5.5; S, 4.3. $C_{33}H_{31}N_3OP_2PtS$ (774.71 g/mol) requires C, 51.2; H, 4.0; N, 5.4; S, 4.1 %.

IR /cm^{-1}: ν(C=N) 1616sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.94 (s, H5); 5.08 (s, H4); 4.72 (d, N*H*Me, ^3J(MeH) = 5.2); 3.37 (d, PC*H*$_2$); 3.00 (d, NH*Me*, ^3J(MeH) = 5.2); 2.28 (s, CMe). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 6.15d, ^2J(PP) = 71.2; ^1J(PtP) = 3723.2; −27.90d, ^1J(PP) = 71.2.

Compounds **7a**, **6b** and **7b** were synthesized following a similar procedure.

[Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe}{Ph$_2$PC(=CH$_2$)PPh$_2$-*P*}] (7a). − Yield: 23 mg, 56 %. Anal. Found: C, 51.6; H, 4.2; N, 5.1; S, 4.0. $C_{34}H_{31}N_3OP_2PtS$ (786.72 g/mol) requires C, 51.9; H, 4.0; N, 5.3; S, 4.1 %.

IR /cm^{-1}: ν(C=N) 1615sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.97 (s, H5); 5.07 (s, H4); 6.81, 5.79 (dd, C=CH$_2$, *trans*-^3J(PH) = 27, *cis*-^3J(PH) = 16); 4.70 (d, N*H*Me, ^3J(MeH) = 4.7); 2.99 (d, NH*Me*, ^3J(MeH) = 4.7); 2.31 (s, CMe). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 23.00d, ^2J(PP) = 76.3, ^1J(PtP) = 3784.2; −12.55d, ^2J(PP) = 76.3.

[Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt}(Ph$_2$PCH$_2$PPh$_2$-*P*)] (6b). − Yield: 19 mg, 45 %. Anal. Found: C, 51.5; H, 4.4; N, 5.2; S, 4.1. $C_{34}H_{33}N_3OP_2PtS$ (788.74 g/mol) requires C, 51.8; H, 4.2; N, 5.3; S, 4.1 %.

IR /cm^{-1}: ν(C=N) 1596sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz) 6.94 (d, H5, ^3J(H4H5) = 1.6, ^4J(PtH5) = 10.6); 5.07 (d, H4, ^3J(PtH4) = 10.6); 4.73 (t, N*H*Et, ^3J(HH) = 5.6); 3.41 (qd, N*CH*$_2$Me, ^3J(HH) = 5.6, ^3J(HH) = 8.7); 2.27 (s, CMe); 1.79 (d, PC*H*$_2$); 1.15 (t, NCH$_2$*Me*, ^3J(HH) = 8.7). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 3.70d, ^2J(PP) = 73.2, ^1J(PtP) = 3717.0; −30.40d, ^2J(PP) = 73.2.

[Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt}{Ph$_2$PC(=CH$_2$)PPh$_2$-*P*}] (7b). − Yield: 18 mg, 46 %. Anal. Found: C, 52.2; H, 4.3; N, 5.4; S, 3.9. $C_{35}H_{33}N_3OP_2PtS$ (800.75 g/mol) requires C, 52.5; H, 4.2; N, 5.3; S, 4.0 %.

IR /cm^{-1}: ν(C=N) 1590sh. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 6.97 (s, H5); 6.84, 5.81dd (dd, C=CH$_2$, *trans*-^3J(PH) = 29, *cis*-^3J(PH) = 17); 5.09 (s, H4); 4.71 (b, N*H*Et); 3.41 (qd, N*CH*$_2$Me, ^3J(HH) = 5.3, ^3J(HH) = 8.4); 2.30 (s, CMe); 1.16 (t, NCH$_2$*Me*, ^3J(HH) = 8.4). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 23.10d, ^2J(PP) = 76.2, ^1J(PtP) = 3684.2; −12.50d, ^2J(PP) = 76.2.

Preparation of [Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHMe}{(WCO)$_5$-(Ph$_2$PCH$_2$PPh$_2$-*P*)}] (8a). − To a suspension of **1a** (20 mg, 0.012 mmol) in chloroform (10 cm^3) [W(CO)$_5$(Ph$_2$PCH$_2$PPh$_2$)] (35 mg, 0.049 mmol) was added and the resulting mixture was stirred under nitrogen for 15 min. The solvent was removed under reduced pressure and the residue recrystallized in chloroform/n-hexane. Yield: 40 mg, 71 %. Anal. Found: C, 41.9; H, 2.7; N, 3.6; S, 3.1. $C_{38}H_{31}N_3O_6P_2PtSW$ (1098.60 g/mol) requires C, 41.5; H, 2.8; N, 3.8; S, 2.9 %.

IR /cm^{-1}: ν(C=N) 1611m. **^{1}H NMR** ($CDCl_3$, δ, *J* Hz): 7.02 (s, H5); 5.23 (s, H4); 4.68 (b, N*H*Me); 3.00 (d, NH*Me*, ^3J(MeH) = 4.7); 2.28 (s, CMe); 2.01 (b, PCH$_2$). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, *J* Hz): 8.75d, ^2J(PP) = 25.4, ^1J(WP) = 245.7; 2.87d, ^1J(PP) = 25.4, ^1J(PtP) = 3784.2.

Compound **8b** was prepared analogously.

[Pt{(OC$_4$H$_2$)C(Me)=NN=C(S)NHEt}{(WCO)$_5$(Ph$_2$CH$_2$PPh$_2$-*P*)}] (8b). − Yield: 42 mg, 77 %. Anal. Found: C, 42.2; H, 3.1; N, 3.6;

S, 2.8. $C_{39}H_{33}N_3O_6P_2PtSW$ (1112.63 g/mol) requires C, 42.1; H, 3.0; N, 3.8; S, 2.9 %.

IR /cm^{-1}: ν(C=N) 1607m. **^{1}H NMR** ($CDCl_3$, δ, J Hz): 7.01 (d, H5, ^3J(H4H5) = 1.6); 5.22 (d, H4, ^3J(H4H5) = 1.6); 4.75 (b, N*H*Et); 3.42 (qd, N*CH*$_2$Me, ^3J(HH) = 5.7, ^3J(HH) = 8.9); 2.28 (s, C*Me*); 2.05 (b, PCH_2). 1.19 (t, NCH_2*Me*, ^3J(HH) = 8.9). **^{31}P-{^{1}H} NMR** ($CDCl_3$, δ, J Hz): 6.27d, ^2J(PP) = 24.9, ^1J(WP) = 246.3; 0.40d, ^2J(PP) = 24.9, ^1J(PtP) = 3772.0.

Crystal structure

Three-dimensional, room temperature X-ray data were collected on a Siemens SMART CCD diffractometer by the omega scan method. Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. Of the 42816 reflections measured, all of which were corrected from Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections (max./min. transmissions; 0.389, 0.076), 12823 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 $R = 0.0434$ ($wR_2 = 0.0924$, for all 12823 unique data; 626 parameters), with allowance for the thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final density −0.838 and 0.767 eA^{-3}. The structure solution and refinement were carried out using the program package SHELX-97 [21].

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 645840. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

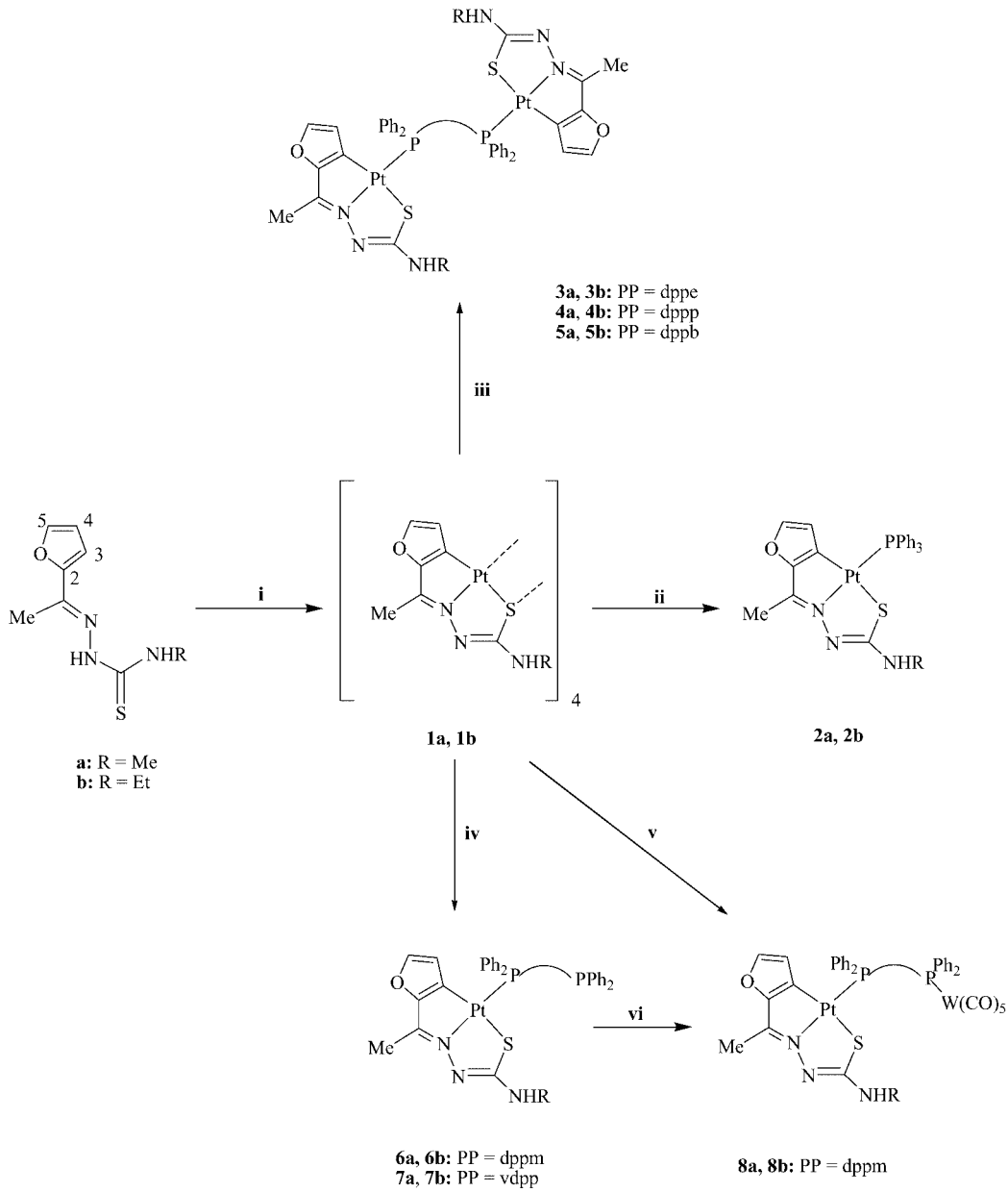
3 Results and Discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N), and by IR and ^{1}H, ^{31}P-{^{1}H} and (for the ligands) ^{13}C-{^{1}H} NMR spectroscopy.

The thiosemicarbazones **a** and **b** were obtained as air-stable solids by the reaction of 2-acetylfurane with methyl-thiosemicarbazide and ethyl-thiosemicarbazide, respectively, and were fully characterized. In the ^{1}H NMR spectra a singlet *ca.* 8.50 and a broad signal *ca.* 7.60 ppm, were assigned to the N*H* and N*H*Me resonances, respectively. Two doublets and a doublet of doublets *ca.* 7.5−6.5 ppm were assigned to the furane ring protons. The IR spectra showed the ν(C=N) stretches at 1631 (**a**) and 1611 cm^{-1} (**b**) [22], and the ν(N-H) bands due to the NH groups ca. 3200−3150 cm^{-1} [23]. Characteristic bands at 824 (**a**) and 814 cm^{-1} (**b**) were ascribed to the ν(C=S) stretching mode.

The reaction of **a** and **b** with [*cis*-$PtMe_2$(cod)] in refluxing n-octane gave the cyclometallated complexes, $[Pt\{(OC_4H_2)C(Me)=NN=C(S)NHR\}]_4$, (**1a**, R = Me; **1b**, R = Et), respectively, as air-stable solids with the ligand in the *E,Z* configuration. The elemental analysis were consistent with a $C_{32}H_{36}N_{12}O_4Pt_4S_4$, **1a**, $C_{36}H_{44}N_{12}O_4Pt_4S_4$, **1b**, formulations, but the FAB mass spectra only showed peaks at low values of m/z probably due to a fast fragmentation of the compounds. Nevertheless, the electrospray mass spectra registered the corresponding peaks at m/z 1561 (**1a**) and 1617 (**1b**) whose isotopic composition suggests a structure comprising four cyclometallated units [24]. A similar trend has been observed for other cyclometallated compounds of Pd^{II} and Pt^{II} derived from thiosemicarbazones by us [19a, 19b] and others [7a, 25]. The IR data were in agreement with deprotonation of the ligand at the hydrazynic nitrogen on complex formation [25, 26], and also showed the ν(C=N) band shifted to lower wavenumbers [26a, 27], contrary to the trend observed for other thiosemicarbazone complexes, with shift to higher wavenumbers [23]; likewise, the ν(C=S) band disappeared in agreement with loss of the double bond character upon deprotonation of the N*H* group. The ^{1}H NMR spectra showed absence of the N*H* group resonance, in agreement as well, with deprotonation as observed in other coordination and organometallic compounds of similar ligands [26]. The absence of the H3 resonance put forward metallation of the ligands and two singlets or two doublets, as appropriate, *ca.* 7.25 and *ca.* 6.40 ppm were assigned to the H5 and H4 proton resonances, respectively. The C*Me* resonance was upfield shifted *ca.* 0.2 ppm indicating a shielding effect which has not been observed in any other derivative of these ligands. These results were in agreement with a tetranuclear structure in which the coordination sphere at platinum is occupied by a carbon atom, a nitrogen atom and a sulfur atom of the thiosemicarbazone ligand, with the fourth coordination site being occupied by a sulfur atom of an adjacent cycloplatinated moiety. No coupling of the CMe group, nor of the H4 and H5 protons with the ^{195}Pt nucleus was observed, following the trend shown in related as with other cycloplatinated complexes [28].

Treatment of **1a** and **1b** with tertiary phosphines gave mono- or dinuclear species, as appropriate, where only the bond at palladium atom to the $S_{bridging}$ atom was cleaved. The Pd-$S_{chelating}$ bond of the tridentate thiosemicarbazone ligands remains, even when a large excess of monophosphine or diphosphine was used; in the latter case stabilization caused by the chelate effect of the bidentate phosphine did not promote $S_{chelating}$ bond cleavage. This is reminiscent of the trend observed in related cyclometallated thiosemicarbazone Pd_4 cluster complexes, and further supports the greater strength of the Pd-$S_{chelating}$ bond as compared to the Pd-$S_{bridging}$ bond [19a]. Thus, the reaction of **1a** and **1b** with tertiary phosphines in 1:4 or in 1:2 molar ratio, as appropriate, gave the mononuclear $[\{Pt[(OC_4H_2)C(Me)=NN=C(S)NHR]\}(PPh_3)]$ (**2a**, R = Me; **2b**, R = Et) or dinuclear $[\{Pt[(OC_4H_2)C(Me)=NN=C(S)NHR]\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$ (R = Me: n = 2, **3a**; n = 3, **4a**; n = 4, **5a**; R = Et: = 2, **3b**; n = 3, **4b**; n = 4, **5b**) compounds as pure air-stable solids, which were characterized by elemental analysis and spectroscopic methods (Scheme 1). In the ^{1}H NMR spectra the H4 resonance was upfield shifted *ca.* 1.5 ppm due to the shielding effect of



Scheme 1

i) *cis*-[$PtMe_2$(cod)], *n*-octane; ii) PPh_3 (1:4), $CHCl_3$; iii) $Ph_2(CH_2)_nPPh_2$, n = 2, 3, 4, (1:2), chloroform; iv) $Ph_2PCH_2PPh_2$; $Ph_2PC(=CH_2)PPh_2$ (1:4), $CHCl_3$; v) [$W(CO)_5(Ph_2CH_2PPh_2)$], $CHCl_3$; vi) [$W(CO)_5$(THF)]; $CHCl_3$.

the adjacent phosphine phenyl rings. The ^{31}P-{^1H} NMR spectra showed a singlet *ca.* 16 ppm, **2a**, **2b**, and *ca.* 12−7 ppm, **3a−5a**, **3b−5b**, (downfield shifted from its position in the free ligand), in accordance with P-coordination to the platinum atom in a phosphorus *trans* to nitrogen disposition [29] with ^1J(Pt-P) *ca.* 3700 Hz, and in the line of the "transphobic effect" [30]. For the dinuclear compounds **3a−5a** and **3b−5b** the presence of only a set of signals in the ^1H NMR spectra and of a singlet in the ^{31}P-{^1H} NMR spectra put forward the equivalence of the cycloplatinated moieties, on the one hand, and of the phosphorus nuclei, on the other. In the ^1H NMR of compound **5b**, the ^4J(PtH5) and ^3J(PtH4) coupling constants, 10.6 and 11.3 Hz, respectively, could be unambiguously assigned. Reaction of **1a** and **1b** with the diphosphines in ≥ 1:4 molar ratio gave a mixture of the dinuclear compounds and free diphosphine; the strength of the Pt-$S_{chelating}$ bond impedes the formation of a chelate ring for the diphoshine ligand. This behaviour is in contrast with that shown by the related cyclometallated complexes derived from [*C,N,S*] terdentate Schiff base ligands [19c] and semicarbazones [31], where the M-$S_{chelating}$ and M-$O_{chelating}$ bonds were easily cleaved, respectively. The resolution of the molecular structure of compound **3b** (see below) confirmed these findings.

Reactions of **1a** and **1b** with short-bite diphosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PC(=CH_2)PPh_2$ (vdpp) yielded the mononuclear compounds [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}($Ph_2PCH_2PPh_2$-*P*)] (**6a**, R = Me; **6b**, R = Et) and [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}($Ph_2PC(=CH_2)PPh_2$-*P*)] (**7a**, R = Me; **7b**, R = Et) as air-stable solids. Notwithstanding, these short bite bidentate diphosphines were uncapable of splitting the Pd-$S_{chelating}$ bond, even when a large excess of the diphosphine was used, and the products obtained here were the mononuclear compounds with the thiosemicarbazone as terdentate [*C,N,S*] and with the diphosphine ligand acting as monocoordinate. The ^{31}P-$\{^1H\}$ NMR spectra showed two doublets assigned to the two inequivalent phosphorus nuclei, the resonance of the coordinated phosphorus nucleus appeared at higher frequency, and showed coupling to the platinum nucleus, with ^1J(Pt-P) *ca.* 3700 Hz. The ^1H NMR spectra showed an apparent doublet for the PCH_2P resonance (ABXY spin system); whereas a doublet of doublets *ca.* 5.8 ppm was assigned to the vinylidene protons.

Treatment of **1a** and **1b** with [$W(CO)_5(Ph_2CH_2PPh_2)$] gave the new heterodinuclear compounds [Pt{(OC_4H_2)C(Me)=NN=C(S)NHR}{$W(CO)_5(Ph_2CH_2PPh_2$-*P*)}] (**8a**, R = Me; **8b**, R = Et) as air-stable solids which were characterized by elemental analysis and spectroscopic methods. The most salient feature was the shift of the resonance of the non-coordinated phosphorus nucleus, in the ^{31}P NMR spectra, as compared to its position in the spectrum of the starting material, towards higher frequency upon coordination to the tungsten nucleus by *ca.* 30 ppm, with ^1J(W-P) *ca.* 245 Hz. Alternatively, compounds **8a** and **8b** could be synthesized by stirring equimolecular amounts of **6a** or **6b** with [$W(CO)_5$(THF)] in chloroform for 1 h. A new and vast range of bimetallic species, whether homo- or heteronuclear, may be obtained by this method employing compounds of type **6** and **7**, of which the results depicted herein are but the initial step, and ensuing preparations are currently in progress.

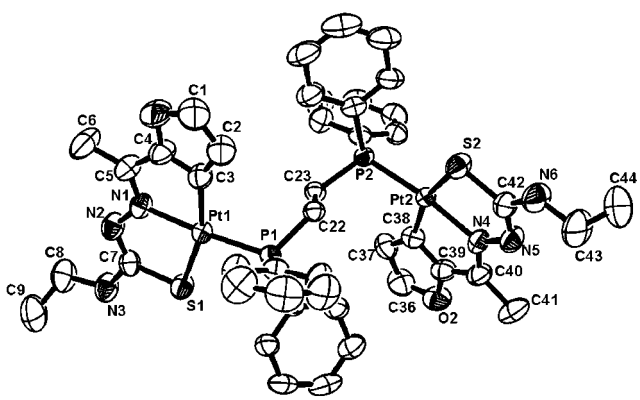


Figure 2 Molecular structure of [{Pt[(OC_4H_2)C(Me)=NN=C(S)NHEt]}$_2${μ-$Ph_2P(CH_2)_2PPh_2$}] (**3b**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Molecular structure of [{Pt[(OC_4H_2)C(Me)=NN=C(S)NH(CH_2Me)]}$_2${μ-Ph_2P-$(CH_2)_2PPh_2$}] (3b)

Suitable crystals of the title compound were grown by slowly evaporating a chloroform solution. The labeling scheme for the compound is shown in Figure 2. Crystallographic data and selected interatomic distances and angles are listed in Tables 1 and 2.

The crystal structure comprises a molecule of **3b**, and three molecules of $CHCl_3$ per asymmetric unit. The four-

Table 1 Crystal data and structure refinement data for compound **3b**.

Empirical formula	$C_{44}H_{46}N_6O_2P_2Pt_2S_2 \cdot 3CHCl_3$
Formula weight	1565.21
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 11.634(2) Å α = 90.090(3)°
	b = 15.890(3) Å β = 100.443(3)°
	c = 17.350(3) Å γ = 92.456(3)°
Volume	3151.2(10) Å^3
Z	2
Density (calculated)	1.650 Mg/m^3
Absorption coefficient	4.972 mm^{-1}
F(000)	1520
Crystal size	0.63 x 0.47 x 0.19 mm
θ range for data collection	1.28 to 26.40°
Index ranges	$-14< h< 14$, $-19< k< 19$, $0< l< 21$
Reflections collected	42816
Independent reflections	12823 [R(int) = 0.0255]
Completeness to θ = 26.40°	99.1 %
Max. and min. transmission	0.389 and 0.076
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12823 / 0 / 626
Goodness-of-fit on F^2	1.018
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0323, wR_2 = 0.0880
R indices (all data)	R_1 = 0.0434, wR_2 = 0.0924
Largest diff. peak and hole	0.767 and −0.838 e.Å^{-3}

Table 2 Selected bond distances /Å and angles /° for compound **3b**.

Pt(1)-C(3)	2.022(5)	Pt(2)-C(38)	2.033(4)
Pt(1)-N(1)	2.050(4)	Pt(2)-N(4)	2.052(4)
Pt(1)-S(1)	2.317(2)	Pt(2)-S(2)	2.319(1)
Pt(1)-P(1)	2.220(1)	Pt(2)-P(2)	2.229(1)
C(3)-C(4)	1.345(7)	C(38)-C(39)	1.357(6)
C(4)-C(5)	1.442(8)	C(39)-C(40)	1.433(7)
C(5)-N(1)	1.303(6)	C(40)-N(4)	1.298(6)
N(1)-N(2)	1.395(5)	N(4)-N(5)	1.387(6)
N(2)-C(7)	1.298(6)	N(5)-C(42)	1.322(7)
C(7)-S(1)	1.773(5)	C(42)-S(2)	1.759(5)
C(3)-Pt(1)-N(1)	80.42(2)	C(38)-Pt(2)-N(4)	80.17(18)
N(1)-Pt(1)-S(1)	82.00(12)	N(4)-Pt(2)-S(2)	82.08(12)
S(1)-Pt(1)-P(1)	103.00(4)	S(2)-Pt(2)-P(2)	103.93(4)
P(1)-Pt(1)-C(3)	94.60(15)	P(2)-Pt(2)-C(38)	93.66(14)
Pt(1)-C(3)-C(4)	108.6(4)	Pt(2)-C(38)-C(39)	108.8(3)
C(3)-C(4)-C(5)	124.1(5)	C(38)-C(39)-C(40)	123.2(4)
C(4)-C(5)-N(1)	109.3(4)	C(39)-C(40)-N(4)	110.5(4)
C(5)-N(1)-Pt(1)	117.4(3)	C(40)-N(4)-Pt(2)	117.3(3)
Pt(1)-N(1)-N(2)	123.7(3)	Pt(2)-N(4)-N(5)	124.0(3)
N(1)-N(2)-C(7)	112.7(4)	N(4)-N(5)-C(42)	111.3(4)
N(2)-C(7)-S(1)	126.2(4)	N(5)-C(42)-S(2)	126.6(4)
C(7)-S(1)-Pt(1)	95.99(16)	C(42)-S(2)-Pt(2)	95.96(18)
Pt(1)-P(1)-C(22)	112.37(14)	Pt(2)-P(2)-C(23)	108.92(14)

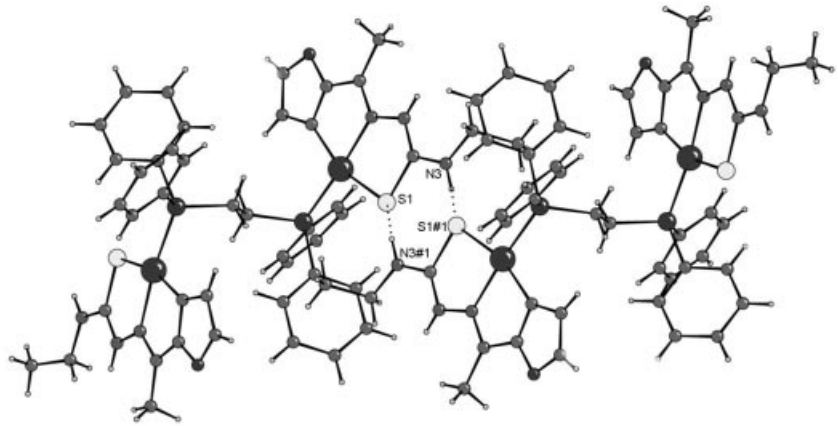


Figure 3 Hydrogen bond interactions in complex **3b**. The atoms involved have been labeled.

coordinated platinum(II) is bonded to an α-carbon atom of the furane ring, a nitrogen atom of the imine group and a thioamide sulfur atom (*trans* to C3) of the deprotonated thiosemicarbazone ligand. A phosphorus atom from the diphosphine ligand, which bridges the two metal atoms, completes the metal coordination sphere. The sum of angles about platinum is 360.04°, with the distortion most noticeable in the somewhat reduced "bite" angle of the metallated moiety consequent upon double *C,N* and *N,S* chelation. The requirements of the five-membered rings force the bond angles C(3)−Pt(1)−N(1) and N(1)−Pt(1)−S(1) to 80.42(2)° and 82.00(12)°, respectively. The configuration around the palladium atom is slightly distorted square-planar, the mean deviation from the least squares plane is 0.0044 Å, Pt(1) and 0.0622 Å, Pt(2).

The platinum-nitrogen bond lengths in the metallacycle, Pt(1)−N(1) 2.050(4) Å, Pt(2)−N(4) 2.052(4) Å, are longer than the predicted single bond value of 1.981 Å, based on the sum of covalent radii for nitrogen(sp^2) and platinum, 0.701 and 1.28 Å, respectively [32] and reflect the *trans* influence of the phosphorus atom [28]. The Pt−C and Pt−P bond lengths, Pt(1)−C(3) 2.022(5) Å, Pt(2)−C(38) 2.033(4) Å, and Pt(1)−P(1) 2.220(1) Å, Pt(2)−P(2) 2.229(1), respectively, are shorter than the expected values of 2.051 Å and 2.34 Å, also respectively, (based on the sum of the covalent radii for platinum, 1.28 Å, carbon(sp^2), 0.771 Å, and phosphorus, 1.06 Å) [33] suggesting a partial multiple-bond character [34]. The platinum-sulfur bond lengths, Pt(1)−S(1) 2.317(2) Å, Pt(2)−S(2) 2.319(1) Å, are within the expected ranges and reflect the strong *trans* influence of the furane carbon atoms. The C(7)−S(1) 1.773(5) Å and C(42)−S(2) 1.759(5) Å bond distances are consistent with increased single-bond character, and the N(2)−C(7) 1.298(6) Å and N(5)−C(42) 1.322 Å, with increased double-bond character in the deprotonated form of the thiosemicarbazone ligand. The cyclometallated moieties are nearly co-planar at an angle of 15.16°. The mean deviations from the least squares planes determined for the metallacycle (Pt1, C3, C4, C5, N1) and the metallated furane ring (O1, C1, C2, C3, C4) are 0.0211 and 0.0090 Å, respectively, with angle between planes of 5.01°. The N,S- chelate ring (Pt1, N1, N2, C7, S1) is also planar, r.m.s. 0.0136, and the angle between the two fused five-membered chelate rings is 1.38°.

The molecular units are stacked in dimers held together by intermolecular hydrogen bonding between the N*H*Et hydrogen atom and the sulfur atom with N(3)−H(3)···S(1)#1 3.499 Å, with an angle of 126.70° (see Figure 3).

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References

[1] (a) E. C. Constable, *Polyhedron* **1984**, *3*, 1037; (b) G. R. Newkome, W. E. Puckett, V. K. Gupta, G. E. Kiefer, *Chem. Rev.* **1986**, *86*, 451; (c) O. A. Dunina, V. M. Zalewskaya, V. M. Potapov, *Russ. Chem. Rev.* **1988**, *57*, 250; (d) I. Omae, "*Organometallic Intramolecular-Coordination Compounds*", in "Journal of Organometallic Chemistry Library", Elsevier, Amterdam, **1986**; (e) I. Omae, *Coord. Chem. Rev.* **1988**, *83*, 137.

[2] (a) L. Main, B. K. Nicholson, *Adv. Met. Org. Chem.* **1994**, *3*, 1; (b) J. Spencer, M. Pfeffer, *Adv. Met.-Org. Chem.* **1998**, *6*, 103.

[3] (a) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917; (b) L. Botella, C. Najera, *Angew. Chem.* **2002**, *114*; 187; *Angew. Chem. Int. Ed.* **2002**, *41*, 179.

[4] M. Marcos, in "*Metallomesogens. Synthesis, Properties and Applications*", J. L. Serrano (ed.), VCH, Weinheim, **1996**.

[5] (a) O. Cantin, C. Cativiela, M. D. Diaz-de-Villegas, R. Navarro, E. P. Urriolabeitia, *Tetrahedron Asymmetry* **1996**, *7*, 2695; (b) E. P. Urriolabeitia, M. D. Diaz-de-Villegas, *J. Chem. Educ.* **1999**, *76*, 77.

[6] (a) S. B. Wild, *Coord. Chem. Rev.* **1997**, *166*, 291; (b) J. Albert, J. M. Cadena, J. R. Granell, X. Solans, M. Font-Bardia, *Tetrahedron Asymmetry* **2000**, *11*, 1943.

[7] (a) A. G. Quiroga, J. M. Perez, I. Lopez-Solera, J. R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso, C. Navarro-Ranninger, *J. Med. Chem.* **1998**, *41*, 1399; (b) C. Navarro-Ranninger, I. Lopez-Solera, V. M. González, J. M. Pérez, A. Alvarez-Valdés, A. Martin, P. Raithby, *Inorg. Chem.* **1996**, *35*, 5181.

[8] (a) A. von Zelewski, P. Belser, P. Hayos, R. Dux, X. Hua, A. Suckling, H. Stoeckli-Evans, *Coord. Chem. Rev.* **1994**, *132*, 75; (b) D. Song, Q. Wu, A. Hook, I. Kozin, S. Wang, *Organometallics* **2000**, *20*, 4683.

[9] (a) M. D. Meijer, A. W. Kleij, B. S. Williams, D. Ellis, M. Lutz, A. L. Spek, G. P. M. van Klink, G. van Koten, *Organometallics* **2002**, *21*, 264; (b) L. R. Falvello, J. Forniés, A. Martín, V. Sicilia, P. Villarroya, *Organometallics* **2002**, *21*, 4604; (c) P. V. Bernhardt, C. Gallego, M. Martínez, T. Parella, *Inorg. Chem.* **2002**, *41*, 1747.

[10] Y. Motoyama, H. Kawakami, K. Shimozono, K. Aoki, H. Nishiyama, *Organometallics* **2002**, *21*, 3408.

[11] J. S. Fossey, C. J. Richards, *Organometallics* **2002**, *21*, 5259.

[12] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055.

[13] M. Akaiwa, T. Kanbara, H. Fukumoto, T. Yamamoto, *J. Organomet Chem.* **2005**, *690*, 4192.

[14] R. A. Katritzky, C. W. Rees, E. F. V. Scriven, "*Comprehensive Heterocyclic Chemistry II*", vol. 2, Elsevier, Oxford, **1996**.

[15] (a) M. Nonoyama, *J. Organomet. Chem.* **1984**, *262*, 407; M. Nonoyama, *Inorg. Chim. Acta* **1989**, *157*, 9; (b) M. Nonoyama, *Transit. Met. Chem.* **1990**, *15*, 366.

[16] (a) M. Nonoyama, K. Nakajima, H. Mizuno, S. Hayashi, *Inorg. Chim. Acta* **1994**, *215*, 91; (b) M. Nonoyama, K. Nakajima, *Polyhedron* **1998**, *18*, 533.

[17] (a) C. Navarro-Ranninger, F. Zamora, I. López-Solera, A. Monge, J. R. Masaguer, *J. Organomet. Chem.* **1996**, *506*, 149; (b) B. Teijido, A. Fernández, M. López-Torres, S. Castro-Juiz, A. Suárez, J. M. Ortigueira, J. M. Vila, J. J. Fernández, *J. Organomet. Chem.* **2000**, *598*, 71.

[18] S. Padhye, *Coord. Chem. Rev.* **1985**, *63*, 127.

[19] (a) J. M. Vila, M. T. Pereira, J. M. Ortigueira, M. Graña, D. Lata, A. Suárez, J. J. Fernández, A. Fernández, M. López-Torres, H. Adams, *J. Chem. Soc. Dalton Trans.* **1999**, 4193; (b) A. Amoedo, M. Graña, J. Martínez, T. Pereira, M. López-Torres, A. Fernández, J. J. Fernández, J. M. Vila, *Eur. J. Inorg. Chem.* **2002**, 613; (c) A. Fernández, D. Vázquez-García, J. J. Fernández, M. López-Torres, A. Suárez, S. Castro-Juiz, J. M. Ortigueira, J. M. Vila, *New J. Chem.* **2002**, *26*, 105; (d) D. Vázquez-García, A. Fernández, J. J. Fernández, M. López-Torres, A. Suárez, J. M. Ortigueira, J. M. Vila, H. Adams, *J. Organomet. Chem.* **2000**, *595*, 199.

[20] W. L. F. Armarego, D. D. Perrin, "*Purification of Laboratory Chemicals*", 4th ed., Butterworth-Heinemann, Oxford, **1997**.

[21] G. M. Sheldrick, SHELX-97, *An Integrated System for Solving and Refining Crystal Structures from Diffraction Data*, University of Göttingen, Germany, **1997**.

[22] K. Nakamoto, "*Infrared and Raman Spectra of Inorganic and Coordination Compounds*", 5th ed., Wiley & Sons, New York, 1997.

[23] T. S. Lobana, A. Sánchez, J. S. Casas, A. Castiñeiras, J. Sordo, M. S. García-Tasende, E. Vázquez-López, *J. Chem. Soc. Dalton Trans.* **1997**, 4289.

[24] (a) L. Tusek-Bozic, M. Curic, P. Traldi, *Inorg. Chim. Acta* **1997**, *254*, 49; (b) L. Tusek-Bozic, M. Komac, M. Curic, A. Lycka, M. Dálpaos, V. Scarcia, A. Furlani, *Polyhedron* **2000**, *19*, 937.

[25] K. Kawamoto, Y. Nagasawa, H. Kuma, Y. Kushi, *Inorg. Chem.* **1996**, *35*, 2427.

[26] (a) D. Kovala-Demertzi, A. Domopoulou, M. A. Demertzis, C. P. Raptopoulou, A. Terzis, *Polyhedron* **1994**, *13*, 1917; (b) F. Hueso-Ureña, N. A. Illán-Cabeza, M. Moreno-Carretero, A. M. Peñas-Chamorro, R. Faure, *Inorg. Chem. Commun.* **1999**, *2*, 323.

[28] (a) J. M. Vila, M. T. Pereira, J. M. Ortigueira, D. Lata, M. López-Torres, J. J. Fernández, A. Fernández, H. Adams, *J. Organomet. Chem.* **1998**, *566*, 93; (b) E. Ceci, R. Cini, J. Konopa, L. Maresca, G. Natile, *Inorg. Chem.* **1996**, *35*, 876.

[27] D. X. West, J. S. Ives, G. A. Bain, A. Liberta, J. Valdés-Martínez, K. H. Ebert, S. Hernández-Ortega, *Polyhedron* **1997**, *16*, 1995.

[29] (a) P. S. Pregosin, R. W. Kuntz; "*^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*", in: NMR Basic Principles and Progress, vol. 16, P. Diehl, E. Fluck, R. Kosfeld, (eds.), Springer-Verlag, Berlin, **1979**; (b) P. E. Garrou, *Chem. Rev.* **1981**, *81*, 229.

[30] J. Vicente, J. A. Abad, A. D. Frankland, M. C. Ramirez de Arellano, *Chem. Eur. J.* **1999**, *5*, 3066.

[31] A. Fernández, M. López-Torres, A. Suárez, J. M. Ortigueira, T. Pereira, J. J. Fernández, J. M. Vila, H. Adams, *J. Organomet. Chem.* **2000**, *598*, 1.

[32] L. Pauling, "The nature of the chemical bond", Cornell University Press, New York, 3rd edn., 1960.

[33] F. H. Allen, O. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc. Dalton Trans.* **1989**, S1.

[34] (a) J. Selbin, K. Abboud, S. F. Watkins, M. A. Gutierrez, F. R. Fronczek, *J. Organomet. Chem.* **1983**, *241*, 259; (b) C. Navarro-Ranninger, I. López-Solera, A. Álvarez-Valdés, J. H. Rodríguez-Ramos, J. R. Masaguer, J. L. García-Ruano, *Organometallics* **1993**, *12*, 4104.

