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The Influence of Substituents at C^2 Carbon Atom of Thiosemicarbazones $\{R(H)C^2{=}N^3\text{-}N^2(H)\text{-}C^1(=S)\text{-}N^1H_2\}$ on their Dentacy in Pt^{II}/Pd^{II} Complexes: Synthesis, Spectroscopy, and Crystal Structures

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Abstract. The coordination chemistry of platinum(II) with a series of thiosemicarbazones $\{R(H)C^2{=}N^3\text{-}N^2(H)\text{-}C^1(=S)\text{-}N^1H_2$, R = 2-hydroxyphenyl, H_2stsc; pyrrole, H_2ptsc; phenyl, Hbtsc$\}$ is described. Reactions of *trans*-$PtCl_2(PPh_3)_2$ precursor with H_2stsc (or H_2ptsc) in 1 : 1 molar ratio in the presence of Et_3N base yielded complexes, $[Pt(\eta^3\text{-}O, N^3, S\text{-stsc})(PPh_3)]$ (**1**) and $[Pt(\eta^3\text{-}N^4, N^3, S\text{-ptsc})(PPh_3)]$ (**2**), respectively. Further, *trans*-$PtCl_2(PPh_3)_2$ and Hbtsc in 1 : 2 (M : L) molar ratio yielded a different compound, $[Pt(\eta^2\text{-}N^3, S\text{-btsc})(\eta^1\text{-}S\text{-btsc})(PPh_3)]$ (**3**). Complex **1** involved deprotonation of hydrazinic ($-N^2H-$) and hydroxyl (-OH) groups, and $stsc^{2-}$ is coordinating via O, N^3, S donor atoms, while complex **2** involved deprotonation of hydrazinic ($-N^2H-$) and $-N^4H$ groups and $ptsc^{2-}$ is probably coordinating via N^4, N^3, S donor atoms. Reaction of $PdCl_2(PPh_3)_2$ with Hbtsc-Me $\{C_6H_5(CH_3)C^2{=}N^3\text{-}N^2(H)\text{-}C^1(=S)\text{-}N^1H_2\}$ yielded a cyclometallated complex $[Pd(\eta^3\text{-}C, N^3, S\text{-btsc-Me})(PPh_3)]$ (**4**). These complexes have been characterized with the help of analytical data, spectroscopic techniques {IR, NMR (^1H, ^{31}P), U.V} and single crystal X-ray crystallography (**1**, **3** and **4**). The effects of substituents at C^2 carbon of thiosemicarbazones on their dentacy and cyclometallation are emphasized.

Keywords: Platinum; Salicylaldehyde thiosemicarbazone; Pyrrole-2-carbaldehyde thiosemicarbazone; Benzaldehyde thiosemicarbazone; Cyclometallation; Deprotonation

Introduction

Thiosemicarbazones (structure I, Chart 1) are an important class of organic ligands [1], and are currently being explored for their analytical applications [2], variable bonding modes [3] and for their biological relevance [4−5]. Palladium(II) and platinum(II) complexes of thiosemicarbazones have exhibited antitumor, antibacterial and antifungal activities [4−10]. For example, a square planar complex [PtLCl] containing 2-acetylpyridine thiosemicarbazone-N-Me displayed cytotoxicity against the cisplatin resistant and sensitive ovarian cancer cell lines, A2780 and A2780/Cp8 [8].

A literature survey reveals that the thiosemicarbazone chemistry of palladium(II) has been more widely investigated than that of platinum(II). Chart 1 depicts the reported mononuclear square planar Pt^{II} complexes [6−10]. Pyridine based thiosemicarbazones (structure I) are uninegative tridentate in [PtLCl] (**4**-**6**) [6, 8] and $[PtL_2]$ (**7**) [9]. Thiosemicarbazones based on phenyl rings with substituents formed complexes [PtLCl] (**8**), $[PtL(H_2L)]$ (**9**) [7] and $[PtL(PPh_3)]$ (**10**) [10]. A ligand (L) is uninegative tridentate coordinating via N^4, N^3, S in **4**-**7**, P, N^3, S in **8** and it is dinegative tridentate coordinating via O, N^3, S or C, N^3, S donor atoms in complexes **9** and **10**, respectively. Fourth site is occupied by the halogen atoms (**4** - **6**, **8**), PPh_3 (**10**) or S atom of anionic (**7**) or neutral (**9**) thiosemicarbazone ligands. It was observed that the phenyl rings with the donor substituents at C^4 position were involved in the coordination to the metal (**8**, **9**), whereas its absence led to the cyclometallation in complex **10**.

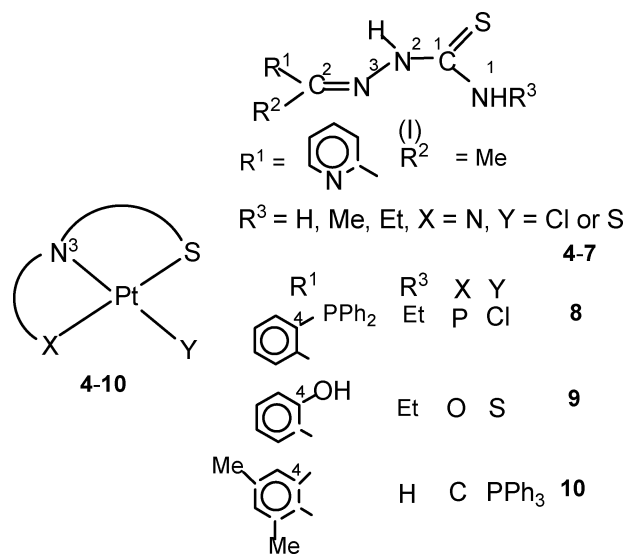

Chart 1

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In the present paper, we report the bonding behaviour of thiosemicarbazones with different rings (R^1 = 2-hydroxyphenyl, pyrrole, phenyl; R^2= H) as shown in Chart 2.The rings may coordinate or undergo metallation process after activation of C^4-H bond. The fourth site (Y) was kept constant and was occupied by PPh_3. The work has been extended to Pd^{II} to study the influence of a bulkier R^2 substituent (e.g. Me in place of H). This study is a part of our interest in the chemistry of platinum group metals with the N, S donors and earlier we reported [Pd(η^3-O, N^3, S-stsc)(PPh_3)] and [Pd(η^3-N^4, N^3, S-ptsc)(PPh_3)] with above mentioned ligands [11, 12].

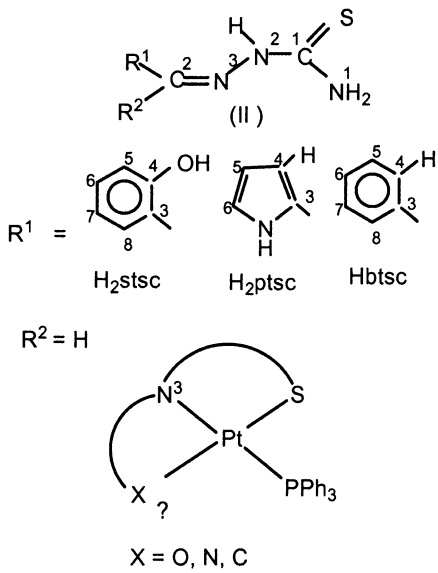


Chart 2

Experimental Section

Materials and Techniques

Platinum(II) dichloride, salicylaldehyde, pyrrole-2-carbaldehyde and benzaldehyde were obtained from Sigma Aldrich Ltd. The thiosemicarbazone ligands were prepared by the reported methods [13]. The starting platinum precursor $PtCl_2(PPh_3)_2$ was prepared by stirring a mixture of $PtCl_2$ and PPh_3 in acetonitrile for 2 h [14]. Elemental analyses for C, H and N were carried out using Thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. U.V spectra were recorded using UV-160 Shimadzu spectrophotometer. The IR spectra were recorded using KBr pellets on a Pye−Unicam SP3-300 spectrophotometer. The ^{1}H NMR spectra were recorded on a JEOL AL 300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. The ^{31}P NMR spectra were recorded at 121.5 MHz with TMP {$(CH_3O)_3P$} as the external reference taken as zero position.

Synthesis of the complexes

[Pt(η^3-O,N^3,S-stsc)(PPh_3)] (1). To $PtCl_2(PPh_3)_2$ (0.05 g, 0.06 mmol) suspended in toluene (15 mL) was added solid H_2stsc (0.012 g, 0.06 mmol) followed by the addition of Et_3N base (1 mL), and the mixture was stirred for 3 h during which a clear light orange-yellow solution was formed along with the formation of solid $Et_3NH^+Cl^-$ at the bottom of the flask. The contents were filtered to remove $Et_3NH^+Cl^-$ and the filtrate allowed to evaporate at room temperature. The yellow orange crystals of product **1** were formed. Yield: 0.026 g, 76 %; m.p. 220-222 °C. *Anal.*Calcd for $C_{26}H_{23}N_3OPPtS\cdot C_7H_8$($C_{33}H_{31}N_3OPPtS$): C, 53.29; H, 4.17; N, 5.6; Found: C, 53.0; H, 4.10; N, 5.41 %.

Main **I.R.** bands (KBr, cm^{-1}), ν(NH), 3431s, 3290s, ν(C-H) 3047w, ν(C=N) + δNH_2 + ν(C=C) 1627s, 1600s, 1583s, ν(C-S) 813s, ν(P-C) 1099s. **UV-Vis spectrum** (CH_2Cl_2, $\lambda_{max/nm}$, ε/L mol^{-1} cm^{-1}): 413 (5.51 x 10^3), 365 (9.08 x 10^3), 239 (8.44 x 10^3). **^{1}H NMR** (δ, $CDCl_3$), δ = 8.54 (d, 1H, C^2H, *J* = 11.7), 7.63-7.76 (m, 8H, *o*-Ph+$C^{4,6}$), 7.41-7.55 (m, 10H, *m*, *p*-Ph), 6.73 (dd, 1H, C^5H, *J* = 8.7), 4.82 (s, 2H, NH_2). **^{31}P NMR** ($CDCl_3$),δ = −78.533 [^1J(PtP) = 4868 Hz].

Compound **2** was prepared similarly.

[Pt(η^3-N^4,N^3,S-ptsc)(PPh_3)] (2) Yield: 72 %; m.p. 190 °C. *Anal.*-Calcd for $C_{24}H_{21}N_4PPdS$: C, 46.08; H, 3.36; N, 8.96; Found: C, 46.12; H, 3.59; N, 8.11 %.

Main **I.R.** bands (KBr, cm^{-1}), ν(NH) 3495s, 3292s, ν(C-H) 3050w, ν(C=N) + δNH_2 + ν(C=C) 1606s, 1589s, 1514s, ν(C-S) 819s, ν(P-C) 1095s. **UV-Vis spectrum** (CH_2Cl_2, $\lambda_{max/nm}$, ε/L mol^{-1} cm^{-1}) 430 (1.04 x 10^4), 314 (1.56 x 10^4), 245 (2.08 x 10^4). **^{1}H NMR** (δ, $CDCl_3$, *J*, Hz), δ = 7.90 (d, 1H, C^2H, *J* = 7.8), 7.45-7.69 (m, 16H, o, *m*, *p*-Ph+C^4), 6.62 (d, 1H, C^6H, *J* = 3), 5.88 (dd, 1H, C^5H, *J* = 2.1), 5.71 (s, 2H, NH_2). **^{31}P NMR** ($CDCl_3$), δ = −94.4 [^1J(PtP) = 3530 Hz]

[Pt(η^2-N^3,S-btsc)(η^1-S-btsc)(PPh_3)] (3). To $PtCl_2(PPh_3)_2$ (0.05 g, 0.06 mmol) suspended in toluene (15 mL) was added solid Hbtsc (0.023 g, 0.12 mmol) followed by the addition of Et_3N base (2 mL), and the mixture was stirred for 3 h during which a clear lightyellow solution was formed along with the formation of solid $Et_3NH^+Cl^-$ at the bottom of the flask. The contents were filtered to remove $Et_3NH^+Cl^-$ and the filtrate allowed to evaporate at room temperature. The yellow orange crystals of product **3** were formed. Yield: 76 %; m.p. 215 °C. *Anal.*Calcd for $C_{34}H_{31}N_6PPtS_2$: C, 50.18; H, 3.8; N, 10.30; Found :C, 50.55; H, 4.01; N, 10.42 %.

Main **I.R.** bands (KBr, cm^{-1}), ν(NH) 3443s, 3340s, 3267w, 3245w ν(C-H) 3070w, 3081, ν(C=N) + δNH_2 + ν(C=C) 1600s, 1569s, 1541s, ν(C-S) 800s, ν(P-C) 1097s. **UV-Vis spectrum** (CH_2Cl_2, $\lambda_{max/nm}$, ε/L mol^{-1} cm^{-1}) 366 (1.69 x 10^4), 300 (2.21 x 10^4), 249 (2.19 x 10^4). **^{1}H NMR** (δ, $CDCl_3$), δ = 9.05 (s, 2H, C^2H), 7.18-7.74 (m, Ph-H + ring protons of tsc), 5.08 (s, 2H, NH_2). **^{31}P NMR** ($CDCl_3$), δ = −102.02.

[Pd(η^3-C,N^3,S-btsc-Me)(PPh_3)] (4) To $PdCl_2(PPh_3)_2$ precursor (0.05 g, 0.07 mmol) suspended in toluene (15 mL) was added solid Hbtsc-Me (0.014 g, 0.14 mmol), followed by the addition of Et_3N base (1 mL), and the mixture was stirred for 3 h during which a clear light orange solution was formed along with $Et_3NH^+Cl^-$, separating in solution at the bottom of the flask. The solution was filtered to remove $Et_3NH^+Cl^-$ and allowed to evaporate at room temperature, and after evaporation, yellow orange crystals of product were formed Yield 76 %, mp 250 °C. *Anal.*Calcd. for $C_{27}H_{24}N_3PPdS$: C 57.86, H 4.28, N 7.50; Found: C 57.53, H, 4.5, N 7.08 %.

IR bands (KBr pellets, cm^{-1}) ν(N-H), 3516b, 3448sh, 3334w (-NH_2), ν(C=N) + δNH_2 + ν(C=C) 1588s, 1508b; $\nu_{(C-S)}$, 840s; ν(P-C_{Ph}) 1089s. **^{1}H NMR** ($CDCl_3$) /δ: 7.64-7.70 (m, *o*-H, 6H), 7.35-7.46 (m, *m*, *p*-H, 9H), 6.29 (q, C^5H, 1H, *J* = 4.5), 6.49 (t, C^6H, 1H, *J* = 6), 6.85 (t, C^7H, 1H, *J* = 7.8), 7.08 (d, C^8H, 1H, *J* = 7.5), 4.86 (s, -NH_2, 2H), 2.35 (s, CH_3, 3H)

Table 1 Crystal Data and Refinement details for **1**, **3** and **4**.

	1	**3**	**4**
Empirical formula	$C_{33}H_{31}N_3OPPtS$	$C_{34}H_{31}N_6PPt\,S_2$	$C_{27}H_{24}N_3PPdS$
M	743.73	813.83	559.92
T/K	295(2)	100(2) K	100(2)
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions			
a/Å	9.740(5)	10.0108(6)	9.8710(12)
b/Å	11.878(5)	10.1951(6)	11.3204(13)
c/Å	13.619(5)	16.2316(10)	12.3388(15)
α/°	75.410(5)	105.2090(10)	89.603(2)
β/°	75.810(5)	90.2280(10)	74.098(2)
γ/°	87.130(5)	98.2820(10)	67.0721(2)
V/Å^3	1478.2(11)	1580.41(16)	1213.0(3)
Z	2	2	2
D_{calcd} /mg m^{-3}	1.788	1.710	1.533
μ/mm^{-1}	12.972	4.657	0.938
Reflections collected	14681	16481	12626
Unique reflections	4131	7823	6003
R indices (all data)	R1 = 0.0636, wR2 = 0.1313	R1= 0.0234, wR2 = 0.0552	R1= 0.0272, wR2 = 0.0727
Final R indices [I>2σ(I)]	R1 = 0.0528, wR2 = 0.1250	R1 = 0.0250, wR2 = 0.0561	R1= 0.0258, wR2 = 0.0712
Largest diff. peak and hole /e Å^{-3}	0.887 and −1.830	2.625 and −1.150	0.41 and −0.492

X-ray crystallography

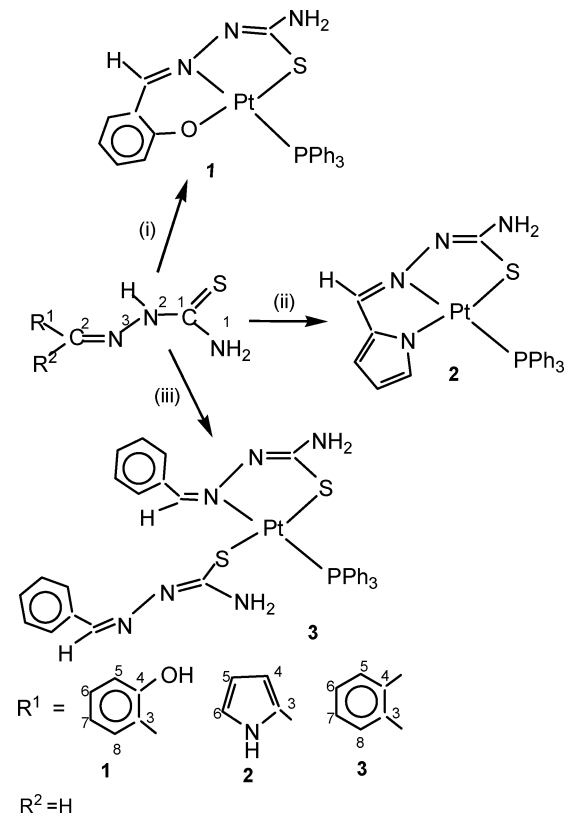
The data for compound **1** was collected at 293 K, on a Siemens P4 diffractometer. The θ−2θ technique was used to measure the intensities up to a maximum of 2θ = 50° with graphite monochromatized Mo-Kα radiator (λ = 0.71073 Å). Cell parameters were refined in the θ range, 10-12.5° using XSCANS [15]. The data were corrected for Lorentz and polarization factors. An empirical psi absorption correction was applied. The structure was solved by the direct methods, and refined by the full matrix least squares methods based on F^2. All the nonhydrogen atoms were refined anisotropically, and hydrogen atoms were assigned calculated positions. Scattering factors from the International Tables for X-ray crystallography were used [16]. Data reduction, structure solution, refinement and molecular graphics were performed using SHELXTL-PC [17] and WinGX [18].

A single crystal of compound **3** was mounted on a Bruker AXS SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 100(2) K. The structure was solved by the direct methods, and refined by the full matrix least square based on F^2 with anisotropic thermal parameters for the non-hydrogen atoms using Bruker SMART (data collection) and Bruker SAINT (cell refinement), Bruker SHELXTL (data reduction and computing molecular graphics, structure solution and (structure refinement)]. Amine hydrogen atoms were located in the difference density Fourier map, however the N-H distances were restrained to be 0.88 Å within a standard deviation of 0.02 Å. All other hydrogen atoms were placed in the calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.5 (methyl) or 1.2 times of hydrogen atoms at all other adjacent carbon atoms.

Results and Discussion

Synthesis

Reaction of $PtCl_2(PPh_3)_2$ with H_2stsc in the presence of triethylamine deprotonated hydrazinic (-N^2H-) and hydroxyl (-OH) groups, yielding the complex [Pt(stsc)(PPh_3)] (**1**) (Scheme 1). Similarly, the ligand H_2ptsc deprotonated hydrazinic (-N^2H-) and -N^4H groups, and yielded complex [Pt(ptsc)(PPh_3)] (**2**). The x-ray crystallography showed that $stsc^{2-}$ is coordinating via O, N^3, S donor atoms in **1** (vide infra). In compound **2**, the coordination by $ptsc^{2-}$ is prob-



Scheme 1 $PtCl_2(PPh_3)_2$ (i, ii); $^1/_2PtCl_2(PPh_3)_2$ (iii); Et_3N, toluene (i-iii).

ably occurring via N^4, N^3, S donor atoms. Thus, there was no activation of C-H bonds in both the complexes and the rings used their donor groups for coordination. Earlier it has been reported that Pd^{II} with H_2stsc and H_2ptsc has formed compounds similar to **1** and **2**, respectively [11].

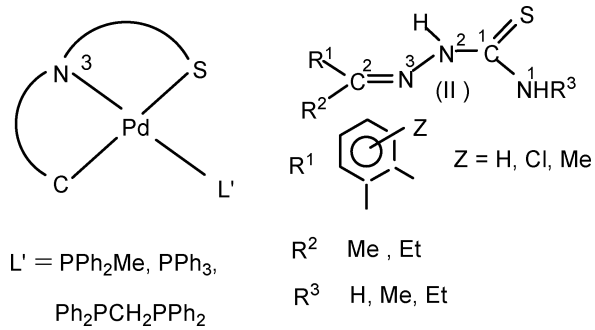
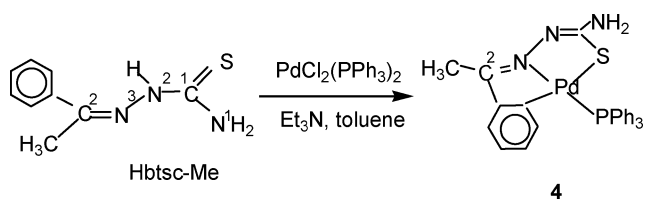


Chart 3

It is highlighted here that the reaction of $PtCl_2(PPh_3)_2$ with Hbtsc (R^1 = Ph, R^2 = H) in 1 : 1 molar ratio was carried out for obtaining the anticipated complex, [Pt(η^3-C^4, N^3, S-btsc)(PPh_3)] similar to compound **10**, but no isolable product could be obtained. However, further addition of one mole of Hbtsc yielded [Pt(btsc)$_2$(PPh_3)] (**3**), and X-ray crystallography has confirmed that one ligand (as $btsc^-$) is N^3, S chelating and second ($btsc^-$) is η^1-S-bonded (vide infra). Thus compound **3** has not involved cyclometallation as expected. A close analysis of complexes of Pd^{II}/Pt^{II} (Charts 1 and Chart 3) [10, 19] reveals that cyclometallation of aromatic rings (R^1) occurred only when R^2 substituent at C^2 is bulky group such as methyl or ethyl. In order to give further credence to this important observation, reaction of $PtCl_2(PPh_3)_2$ with a thiosemicarbazone for R^1 = Ph, R^2 = Me (see structure II, Chart 2) was carried out, but no crystalline product could be obtained. However, a similar reaction with palladium(II) yielded a cyclometallated product, [Pd(η^3-C^4, N^3, S-btsc-Me)(PPh_3)] (**4**) (Scheme 2) in which phenyl ring binds to Pd metal {Hbtsc-Me = Ph(Me)C^2=N^3-N^2(H)-C^1(=S)-N^1H_2}.



Scheme 2

The steric effect of R^2 group appears to push R^1 group closer to the metal for cyclometallation (see Chart 4). Since R^2 = H in Hbtsc, low steric effect may explain the lack of cyclometallation in compound **3**. But introduction of methyl group for R^2 again has led to cyclometallation as shown for Pd^{II} complex **4** (Scheme 2).

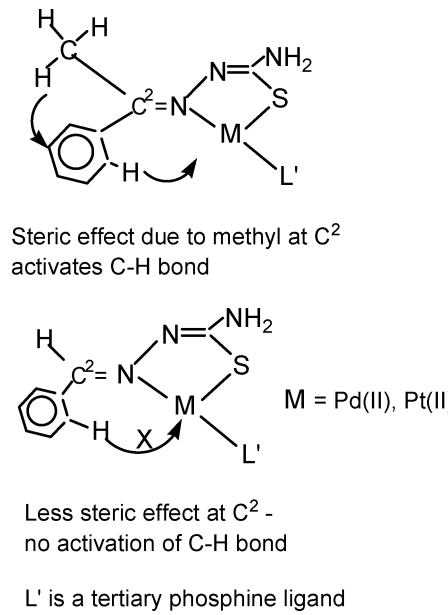


Chart 4

I.R. Spectroscopy

The IR spectra of the complexes reveal the presence of ν(N−H) bands due to (-NH_2) group in the range 3278−3495 cm^{-1}. The bands in the region 3100−3150 cm^{-1} expected due to −N^2H group in the free ligands [13] are found to be absent in the spectra of their complexes 1−3, and it supports the anionic form of the ligands. The ν(C−H) bands due to the aromatic ring are observed for all the complexes in the region near 3050 cm^{-1}. Further, δ(NH_2) + ν(C=N) + ν(C-C) vibration modes are unresolved, and are assigned in the range 1635−1515 cm^{-1}. The thioamide band, which contains considerable ν(CS) character is less intense in the complexes and is found at a lower frequency {ν(C-S), 800-819 cm^{-1}} suggesting coordination of the metal through sulfur [13, 19]. The presence of PPh_3 in complexes **1**-**4** is confirmed by the presence of a characteristic ν(C-P) bands in the range, 1095−1099 cm^{-1}.

Crystal structures of complexes

The atomic numbering schemes for **1** and **3** are given in Figures 1 and 2 respectively, and selected bond angles and bond lengths are listed in Table 2. Both the compounds crystallized in triclinic crystal systems with space groups $P\bar{1}$ in each case. A molecule of toluene is present as solvent of crystallisation in complex **1**, which is also supported by the elemental analysis. The ligand salicylaldehyde thiosemicarbazone is coordinating as a dianion ($stsc^{2-}$) after deprotonation of hydrazinic (-N^2H-) and hydroxyl (-OH) protons

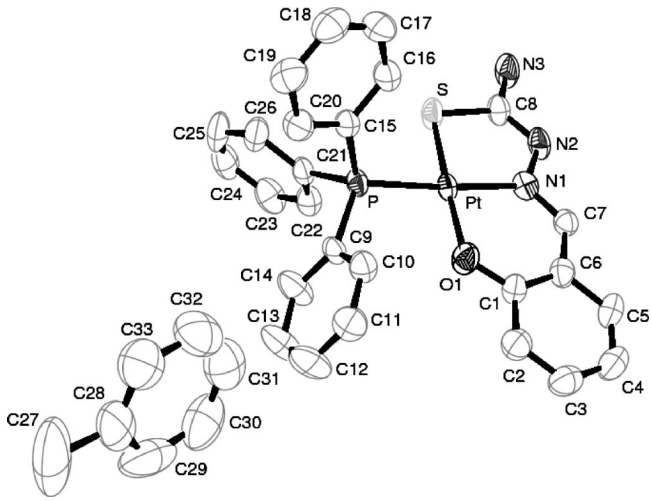


Figure 1 Structure of complex [Pt(η^3- O, N^3, S-stsc)(PPh_3)] (**1**) with atomic numbering Scheme.

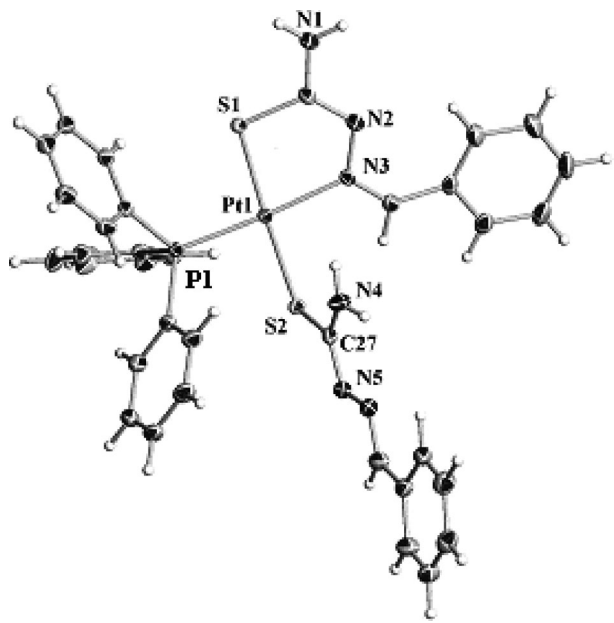


Figure 2 Structure of complex [Pt(η^2-N^3,S-btsc)(η^1-S-btsc)(PPh_3)] (**3**) with atomic numbering Scheme.

in complex **1**. The thiosemicarbazone ligand is tridentate coordinating via O, N^3 and S donor atoms with Pt-O, Pt-N and Pt-S bond distances of 2.014(6), 2.032(6) and 2.234(2) Å, respectively. The Pt-N and Pt-S bond distances are longer than those observed in complexes of the type [Pt(L)Cl], where L is monoanion of the pyridine based thiosemicarbazones reported in the literature (ca. Pt-N, 1.95 and Pt-S, 2.25 Å) [6, 8]. The fourth site is occupied by phosphorus atom of the coordinating PPh_3 molecule with a Pt-P distance of 2.258(2) Å. The bite angles O-Pt-N^3 and N^3-Pt-S of 93.1(3)° and 83.8(2)° respectively are comparable with those of analogous complex [Pd(stsc)(PPh_3)] [11]. The two trans angles are quite close to linearity {O1-Pt-S, 176.6(2)° and N-Pt-P, 176.3(2)°} and the complex is square planar.

Table 2 Important bond lengths/Å and bond angles/° of complexes **1**, **3** and **4**.

		1	
N(1)-Pt	2.032(6)	S-Pt	2.234(2)
O(1)-Pt	2.014(6)	P-Pt	2.2576(19)
C(8)-S	1.731(8)	N1-N2	1.369(9)
C8-N2	1.302(11)	O1-C1	1.315(9)
O1-Pt-N1	93.1(3)	O1-Pt-P	89.91(17)
O1-Pt-S	176.60(16)	N1-Pt-P	176.34(18)
N1-Pt-S	83.79(19)	S-Pt-P	93.27(7)
		3	
P1-Pt1	2.2466(6)	Pt1-S2	2.3461(6)
Pt1-S1	2.2769(6)	N3-Pt1	2.118(2)
C19-N2	1.308(3)	C27-N5	1.314(3)
C19-S1	1.755(3)	C27-S2	1.7552(3)
N2-N3	1.396(3)	N5-N6	1.405(3)
N3-Pt-P1	176.51(6)	N3-Pt1-S2	95.13(4)
N3-Pt1-S1	82.28(6)	P1-Pt1-S2	88.26(2)
P1-Pt1-S1	94.32(2)	S1-Pt1-S2	177.20(2)
		4	
N(1)-Pd(1)	2.0326(15)	P(2)-Pd(1)	2.2513(5)
C(1)-Pd(1)	2.0411(19)	N(1)-N(2)	1.376(2)
Pd(1)-S(1)	2.3464(6)	C(9)-S(1)	1.758(2)
N(1)-Pd(1)-C(1)	81.47(7)	N(1)-Pd(1)-S(1)	82.26(5)
N(1)-Pd(1)-P(2)	177.05(5)	C(1)-Pd(1)-S(1)	163.45(6)
C(1)-Pd(1)-P(2)	95.83(6)	P(2)-Pd(1)-S(1)	100.493(18)

In the mononuclear complex **3**, platinum(II) is coordinating to two thiosemicarbazone ligands. One ligand is uninegative bidentate coordinating via N^3 and S donor atoms forming a five membered chelate ring with the Pt1-N3 and Pt1-S1 bond distances of 2.118(2) and 2.277(6) Å, respectively, with a the bite angle N^3-Pt-S of 82.28(6)°. The other thiosemicarbazone ligand in anionic form is coordinating

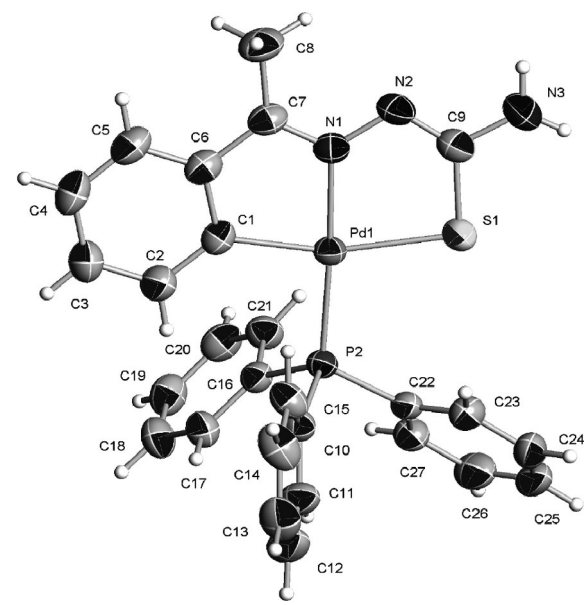


Figure 3 Structure of complex [Pd(η^3-C,N^3,S-btsc-Me)(PPh_3)] (**4**) with atomic numbering Scheme.

through S atom only with a longer Pt1-S2 bond distance, 2.3461(6) Å. A comparison of these bond lengths with complex **1** and literature reports reveal that both the Pt-S as well as Pt-N bond lengths are comparatively longer [6, 8]. The *trans* bond angles of complexes, {N-Pt-P, 176.51(6)°; S-Pt-S, 177.20(2)°}, are nearly linear and the geometry is distorted square planar.Figure 3 shows molecular structure of the cyclometallated product, [Pd(η^3-C^4, N^3, S-btsc-Me)(PPh_3].

The mononuclear complex **4** involves the cyclometallation of the phenyl ring at C^2 to Pd^{II}. Thus the ligand is dianionic coordinating via C, N^3, S donor atoms. The bond parameters lie in the usual range [11−12].

NMR spectroscopy

The signals due to $-N^2H$ protons which appear around 11.2 ppm in the free ligands [13] were absent in the spectra of their complexes **1**−**3**. It supports deprotonation during complexation in all these complexes. Additionally in complexes **1** and **2**, the absence of −OH (9.87 ppm, H_2stsc) and $-N^4H$- (11.34 ppm, H_2ptsc) proton signals respectively confirmed their deprotonation. Thus in complexes **1** and **2**, the thiosemicarbazone ligands are behaving as dianions. The $-NH_2$ protons appear as single peaks in all the complexes due to the free rotation of the N^1H_2 group along the C^1-N^1 bond axis. The free ligands exhibit two broad peaks due to the restricted rotation of the $-N^1H_2$ group along the C^1-N^1 bond axis at room temperature [13]. The peaks due to C^2H and ring protons are given in the experimental section, however, the phenyl ring (R^1) protons of complex **3** could not be identified due to their overlapping with the signals of PPh_3 group. The ^{31}PNMR of complexes **1** and **2** shows peaks at −78.8 and −94.4 ppm with ^{195}Pt satellites. The $^1J(^{195}Pt$-$^{31}P)$ coupling constants (4868 and 3530 Hz for complex **1** and **2** respectively) of both the complexes are in the usual range [20] though it is greater for complex **1** than for complex **2**. The obvious reason for this seems to be the difference in electronegativity of O atom in complex **1** vis-à-vis that of N atom in complex **2**. Due to low solubility of complex **3**, ^{195}Pt satellites could not be observed.

Electronic Absorption Spectroscopy

The electronic absorption spectra of platinum(II) complexes are indicative of their square planar geometry. In the visible region of the square planar Pt^{II} complexes, three spin allowed singlet-singlet d-d transitions are predicted [21]. The ground state is $^1A_{1g}$ and the excited states corresponding the three transitions are $^1A_{2g}$, $^1B_{1g}$ and ^1E_g in order of increasing energy. Strong charge transfer transitions interfere and prevent the observation of all the expected bands. The very intense band at 366-430 nm is assignable to a combination of sulfur→Pt^{II}, and charge transfer {(L(π)→MCT} and Pt^{II} d-d bands [6, 8]. The band at 300-365 nm is assignable to a combination of metal-ligand charge transfer (M→LCT) and d-d bands, the band at around 245 nm is assignable to thiosemicarbazone moiety (π→π*transitions).

Conclusion

The substituents at C^2 position affect the stoichiometry as well as the bonding modes of thiosemicarbazones. For example, in Pt^{II} complexes, the presence of a substituent (R^1) at C^2 with ionisable hydrogens (e.g. 2-hydorxyphenyl, **1**; pyrrole ring, **2**) made the ligands, H_2stsc and H_2ptsc to behave as dinegative tridentate ligands (O, N^3, S, **1** or N^4, N^3, S, **2**) after the loss of −OH and -N^2H (H_2stsc) or N^4H and N^2H (H_2ptsc) protons in the complexes. Fourth site of square plane is occupied by PPh_3 ligand.Complex **3** with R^1 as phenyl ring did not involve activation of C^4-H bond, rather two thiosemicarbazonates ($btsc^-$) coordinate in a different manner, one is η^1-S- bonded and the second is η^2-N^3, S-chelated. It is inferred from these studies that the bulky substituent R^2 at C^2 carbon(e. g. Me, Et, etc.) appears responsible for the activation of a C-H bond of aryl (R^1) ring followed by cyclometallation in complexes [10, 19]. For R^1 = phenyl, and R^2 = Me, palladium(II) has yielded a cyclometallated product, [Pd(η^3-C^4, N^3, S-btsc-Me)(PPh_3)] (**4**) in which phenyl ring metallates Pd metal {Hbtsc-Me = Ph(Me) C^2=N^3-N^2(H)-C^1(=S)-N^1H_2}. For R^1 = furan and R^2 = Me, cyclometallation is also encountered in Pt^{II} complexes [22].

Supplementary data is available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-12336033; e-mail: **deposit@ccdc.cam.ac.uk**) on request quoting the deposition number CCDC 662656, 662657 and 666777 for compounds **1**, **3** and **4** respectively.

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