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The key role of sulfur in thiosemicarbazone compounds. Crystal and molecular structure of $[Pd\{4\text{-}MeOC_6H_4C(Me)=NN=C(S)NHPh\}_2]$

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Abstract

The reaction of thiosemicarbazones 4-$MeOC_6H_4C(H)=NN(H)C(=S)NHMe$ (**a**), 4-$MeOC_6H_4C(H)=NN(H)C(=S)NHEt$ (**b**) and 4-$MeOC_6H_4C(H)=NN(H)C(=S)NHPh$ (**c**), with $Li_2[PdCl_4]$, $K_2[PdCl_4]$ or $Pd(AcO)_2$ leads to the tetranuclear palladium(II) compounds, $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHMe\}]_4$ (**1a**), $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHEt\}]_4$ (**1b**) and $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHPh\}]_4$ (**1c**); the ligands are terdentate through the [C, N, S] atoms and they are deprotonated at the –NH– group. Reaction of thiosemicarbazones 3-$MeOC_6H_4C(H)=NN(H)C(=S)NHMe$ (**d**) and 3-$MeOC_6H_4C(H)=NN(H)C(=S)NHEt$ (**e**), with $Li_2[PdCl_4]$ or $K_2[PdCl_4]$ gave the mononuclear palladium(II) compounds $[Pd\{3\text{-}MeOC_6H_4C(H)=NN=C(S)NHMe\}_2]$ (**1d**) and $[Pd\{3\text{-}MeOC_6H_4C(H)=NN=C(S)NHEt\}_2]$ (**1e**); the ligands are bonded only through the azomethine nitrogen and sulfur atoms. Treatment of thiosemicarbazone 4-$MeOC_6H_4C(Me)=NN(H)=C(S)NHPh$ (**f**) with $Li_2[PdCl_4]$ gave the tetranuclear compound $[Pd\{4\text{-}MeOC_6H_3C(Me)=NN=C(S)NHPh\}]_4$ (**1f**), which upon treatment with bis(-diphenylphosphino)methane, dppm in 1:2 molar ratio gave the dinuclear species $[\{Pd[4\text{-}MeOC_6H_3C(Me)=NN=C(S)NHPh]\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**2f**). The recrystallization of **2f** gave the chiral compound $[Pd\{4\text{-}MeOC_6H_4C(Me)=NN=C(S)NHPh\}_2]$ (**3f**). The molecular structure has been determined by single-crystal diffraction, showing O···H and S···H hydrogen bonding.

Keywords: Sulfur; Thiosemicarbazone compounds; Crystal and molecular structures

1. Introduction

Sulfur forms a wide variety of compounds, such as sulfides, oxides and oxoacids among others; sulfuric acid being one of the major inorganic industrial chemicals [1]. The sulfur atom can act as a ligand and many sulfur containing compounds are also known that are ligands in inorganic and organometallic chemistry [2]. An important and versatile type of ligands are the thiosemicarbazones due to the number and variety of donor atoms they may possess, among which sulfur is of paramount importance in the metal–ligand linkage; a comprehensive review on the coordination chemistry of thiosemicarbazones has been given [3]. Furthermore, there has been considerable interest in these ligands because of the potentially biological activity of thiosemicarbazones and of their metal complexes [4] and they have been screened for potential antitumor and antiviral activity [5].

In previous work we have shown that potentially terdentate ligands such as Schiff bases [6,7], semicarbazones [8] and thiosemicarbazones [9,10] undergo facile metallation with palladium(0), palladium(II) and platinum(II) yielding compounds with two five-membered fused rings at the metal center. Treatment of the corresponding [C, N, O] and [C, N, N] compounds with nucleophiles, e.g. tertiary phosphines, produces cleavage of the oxygen–metal or nitrogen–metal bonds, prior to ring-opening of the five-membered metallacycle

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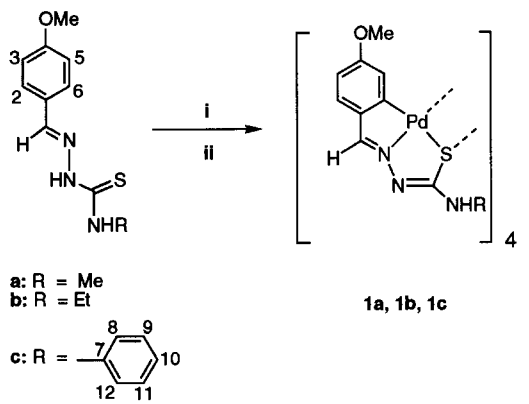
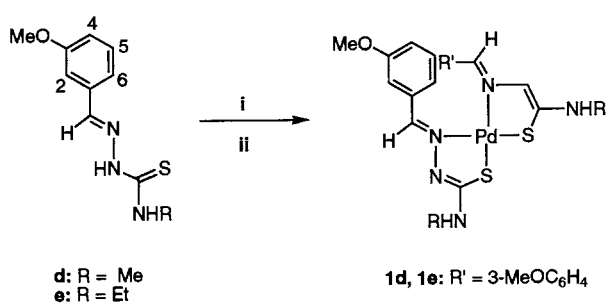
upon continued reaction with the corresponding phosphine. However, the use of a 'softer' base, in the terms of Pearson's concept [11], strengthens the bond of the metal to the chelate ring thus preventing its breakage. This is the case when the ligand has a sulfur donor atom bonded to the metal center.

In the present work we describe the reactions of thiosemicarbazone ligands with palladium(II) salts to give two types of compounds: (a) tetranuclear palladium(II) species, bearing two fused chelate rings at the metal, one of which contains a σ palladium–carbon bond; (b) coordination compounds with one chelate ring at palladium, which only show palladium–nitrogen and palladium–sulfur bonds; in the second case attempts to produce similar tetranuclear species as in (a) failed. Indeed the most important feature of the compounds is the strength of the palladium–sulfur bond (palladium–$\text{sulfur}_{\text{chelating}}$ bond in the case of the tetranuclear species). This is put forward in the decomposition of compound **2f** where the strong Pd–S bond retains the thiosemicarbazone ligand preventing its cleavage from the palladium atom to give a chiral bis-chelate complex **3f** which shows extended hydrogen-bonding yielding a three-dimensional array; the crystal structure of one such compound is also described.



Scheme 1. (i) $Li_2[PdCl_4]$–NaAcO–MeOH or $Pd(AcO)_2$–glacial acetic acid for **1a**, **1b**; (ii) $K_2[PdCl_4]$–EtOH for **1c**.



Scheme 2. (i) $Li_2[PdCl_4]$–MeOH for **1d**; (ii) $Li_2[PdCl_4]$–EtOH or $K_2[PdCl_4]$–EtOH for **1e**.

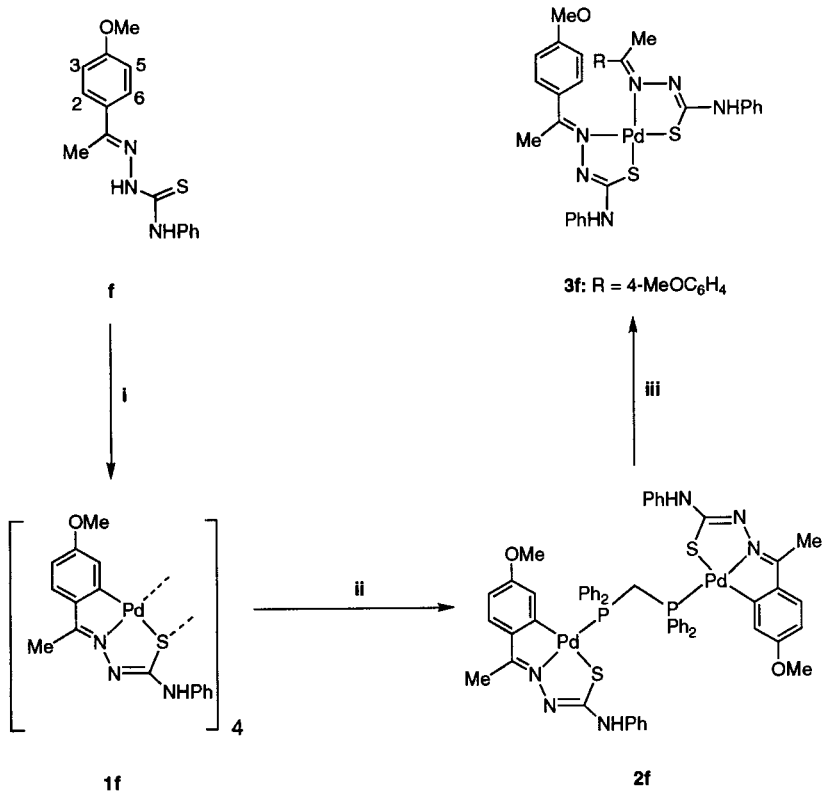
2. Results and discussion

2.1. Cyclometallated and coordination compounds

The thiosemicarbazones **a**–**f** were prepared by reaction of 4-methoxybenzaldehyde, 3-methoxybenzaldehyde or 4-methoxyacetophenone with 4-methyl-3-thiosemicarbazide, 4-ethyl-3-thiosemicarbazide or 4-phenyl-3-thiosemicarbazide, as appropriate (see Section 4, Schemes 1–3 and Table 1). The NH proton gave a resonance ca. δ 9.3–10.3 and the NHR proton gave a broad signal ca. δ 7.4–9.2. Treatment of lithium tetrachloropalladate or of potassium tetrachloropalladate in methanol or ethanol with the corresponding thiosemicarbazone ligand, **a**–**c**, gave clear solutions from which complexes $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHMe\}]_4$ (**1a**), $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHEt\}]_4$ (**1b**) and $[Pd\{4\text{-}MeOC_6H_3C(H)=NN=C(S)NHPh\}]_4$ (**1c**), were isolated as air-stable solids, with the ligand in the *E*,*Z* configuration (method 1). Compounds **1a** and **1b** could also be made by reaction of the corresponding thiosemicarbazone ligand with palladium(II) acetate in glacial acetic acid (method 2); (see Section 4; method 1 was preferred due to the low yields of method 2). The products were characterized by elemental analysis (C, H and N), IR and ^1H and $^{13}C-\{^1H\}$- (**1a**, **1b**) NMR data (see Section 4 and Table 1). Similar tetranuclear compounds have been observed before by us [9,10] and others [12,13], however, these are the first tetranuclear species with thiosemicarbazones derived from aldehydes as opposed to previous compounds with thiosemicarbazones made from ketones. The shift of the ν(C=N) stretch towards lower wavenumbers [14,15] and the upfield shift of the HC=N resonance in the ^1H-NMR spectra ca. 1.0 ppm supports nitrogen coordination to the metal center [16]. Metallation of the ligand is clear from the absence of the AA′XX′ system of the *para*-substituted phenyl ring; three protons were assigned for each metallated aromatic ring (see Table 1). The $^{13}C-\{^1H\}$ data (**1a**, **1b**) reveal the upfield shift of the N*C*S nucleus relative to the free ligands, whilst the C=N, C1 and C6 resonances reveal lowfield shifts in the complexes, confirming metallation of the phenyl ring [17]. In the ^1H-NMR spectrum for **1a** the $-NHCH_3$ resonance shows a doublet and for **1b** the $-CH_2CH_3$ resonance shows a doublet of quartets. The N*H*Me (**1a**), N*H*Et (**1b**) and N*H*Ph (**1c**) resonances show a strong upfield shifts ca. 2.4 ppm.

The band at 850–830 cm^{-1} may be assigned to the ν(C=S) mode in the free ligands (Section 4), even if the bands observed at ca. 1100–1000 cm^{-1} also contribute to the C=S stretching mode. This band disappears in the complexes, in accordance with loss of the double bond character upon deprotonation of the NH group[1].

[1] For a more detailed study of the IR bands see Ref. [9] and refs. therein.



Scheme 3. (i) $Li_2[PdCl_4]$–EtOH; (ii) $Ph_2PCH_2PPh_2$, acetone, water; (iii) recrystallization from $CDCl_3$. Ph numbering scheme samse as for **c**.

Treatment of lithium tetrachloropalladate or of potassium tetrachloropalladate in methanol or ethanol with the corresponding thiosemicarbazone ligand **d**, **e**, gave clear solutions from which complexes [Pd{3-$MeOC_6H_4C(H)$=NN=C(S)NHMe}$_2$] (**1d**) and [Pd{3-$MeOC_6H_4C(H)$=NN=C(S)NHEt}$_2$] (**1e**), were isolated as air-stable solids. The products were fully characterized by elemental analysis (C, H and N), IR and ^{1}H- and ^{13}C–{^{1}H}-NMR data (see Section 4 and Table 1). The phenyl ring was not metallated as shown by the clear assignment of the four aromatic protons in the ^{1}H-NMR spectra (see Table 1) and no significant lowfield shift of the C1 and C6 resonances was observed in the ^{13}C–{^{1}H}-NMR spectra. However, the ^{1}H-NMR spectra reveal absence of the hydrazinic resonance and a slight upfield shift of the HC=N signal, ca. 0.3 ppm, while the N*H*Me (**1d**) and N*H*Et (**1e**) resonances showed strong upfield shifts ca. 2.5 ppm. The ^{13}C–{^{1}H} data showed the lowfield shift of the C=N resonance. These findings are indicative of deprotonation of the thiosemicarbazone ligands and subsequent formation of a five-membered chelate ring containing the palladium atom; this not only seems to be a typical behavior of thiosemicarbazones [12,13,18], as opposed to the related [C, N, N] and [C, N, O] ligands (see above), leading to the formation of coordination complexes as those depicted here, but also puts forward the important role of the sulfur atom which supports the negative charge of the deprotonated ligand in the thiolato form [18]. Attempts to metallate ligands **d** and **e** have been, so far, unsuccessful.

The relevant role of sulfur in these compounds was asserted by the final product which was obtained in the reaction sequence using ligand **f**. Thus, treatment of lithium tetrachloropalladate in methanol with thiosemicarbazone **f** gave the tetranuclear compound [Pd{4-$MeOC_6H_3C(Me)$=NN=C(S)NHPh}]$_4$ (**1f**), which was fully characterized (see Experimental section and Table 1). Further reaction of **1f** with bis(diphenylphosphino)methane in 1:2 molar ratio gave the dinuclear species [{Pd[4-$MeOC_6H_3C(Me)$=NN=C(S)NHPh]}$_2$(μ-$Ph_2PCH_2PPh_2$)] (**2f**) (see Section 4 and Table 1) as a yellow air-stable solid. The ^{31}P–{^{1}H}-NMR spectrum showed a singlet resonance in agreement with the existence of equivalent phosphorus nuclei. The decomposition product [Pd{4-$MeOC_6H_4C(Me)$=NN=C(S)-NHPh}$_2$] (**3f**), precipitated out when compound **2f** was left to stand for recrystallization from a chloroform solution (see Scheme 3). Earlier results showed that metallated complexes bearing phosphine ligands at the metal center may decompose in solution to give typical phosphine coordination compounds. To name but a few, [$PdCl(PEt_3)_2L$] gave [$PdCl_2(PEt_3)_2$] and L [19]; [$PdBr_2${$Ph_2PC(Me)PPh_2$}] was obtained from a solution of [{Pd[*o*-C_6H_4C=NC(H)=C(H)NMe](Br)}$_2${μPh_2PC-(Me)PPh_2}] [20]; [{1,4-{Pd[2,3,4-$(MeO)_3C_6HC$-

Table 1
^{31}P [a]- and ^{1}H [b]-NMR data [c]

Compound	^{31}P	^{1}H	
		Aromatic	Others
a		7.58[d, 2H, H^2, H^6, 4.9 [d]]	9.66[s, 1H, NH]
		6.91[d, 2H, H^3, H^5, 4.9 [d]]	7.80[s, 1H, HC=N]
			7.56[br, 1H, N*H*Me]
			3.84[s, 3H, MeO]
			3.26[d, 3H, Me]
1a		7.07[d, 1H, H^5, 2.5 [f]]	6.78[s, 1H, HC=N]
		6.70[d, 1H, H^2, 8.4 [e]]	5.1[br, 1H, N*H*Me]
		6.45[dd, 1H, H^3, 8.4 [e], 2.5 [f]]	3.87[s, 3H, MeO]
			2.13[d, 3H, Me]
b		7.58[d, 2H, H^2, H^6, 8.8 [d]]	9.70[s, 1H, NH]
		6.91[d, 2H, H^3, H^5, 8.8 [d]]	7.81[s, 1H, HC=N]
			7.39[br, 1H, N*H*Et]
			3.84[s, 3H, MeO]
			3.76[dq, 2H, CH_2CH_3]
			1.31[t, 3H, CH_2CH_3]
1b		7.08[d, 1H, H^5, 2.3 [f]]	6.78[s, 1H, HC=N]
		6.68[d, 1H, H^2, 8.3 [e]]	5.04[br, 1H, N*H*Me]
		6.45[dd, 1H, H^3, 8.3 [e], 2.5 [f]]	3.86[s, 3H, MeO]
			3.40[dq, 2H, CH_2CH_3]
			1.22[t, 3H, CH_2CH_3]
c		7.62[d, 2H, H^2, H^6, 8.8 [d]]	10.30[s, 1H, NH]
		6.93[d, 2H, H^3, H^5, 8.8 [d]]	9.19[br, 1H, N*H*Me]
			7.93[s, 1H, HC=N]
			3.85[s, 3H, MeO]
1c		7.06[d, 1H, H^5, 2.6 [f]]	6.90[s, 1H, HC=N]
		6.83[d, 1H, H^2, 8.3 [e]]	6.87[br, 1H, N*H*Me]
		6.54[dd, 1H, H^3, 8.3 [e], 2.6 [f]]	3.59[s, 3H, MeO]
d		7.32[t, 1H, H^5, 7.9 [e]]	9.35[s, 1H, NH]
		7.21[d, 1H, H^2, 2.0 [f]]	7.76[s, 1H, HC=N]
		7.18[dd, 1H, H^6, 7.9 [e], 2.0 [f]]	7.46[br, 1H, N*H*Me]
		6.96[dd, 1H, H^4, 7.9 [e], 2.0 [f]]	3.85[s, 3H, MeO]
			3.27[d, 3H, Me]
1d		7.51[t, 1H, H^5, 7.9 [e]]	7.52[s, 1H, HC=N]
		7.23[m, 1H, H^2]	4.82[br, 1H, N*H*Me]
		6.98[m, 1H, H^6]	3.87[s, 3H, MeO]
		6.97[m, 1H, H^4]	2.93[d, 3H, Me]
e		7.30[t, 1H, H^5, 7.9 [e]]	10.20[s, 1H, NH]
		7.21[d, 1H, H^2, 1.9 [f]]	7.89[s, 1H, HC=N]
		7.18[m, 1H, H^6]	7.43[br, 1H, N*H*Et]
		6.93[dd, 1H, H^4, 7.9 [e], 1.9 [f]]	3.84[s, 3H, MeO]
			3.76[dq, 2H, CH_2CH_3]
			1.31[t, 3H, CH_2CH_3]
1e		7.48[m, 1H, H^5]	7.57[s, 1H, HC=N]
		7.22[m, 1H, H^2]	5.09[br, 1H, N*H*Et]
		6.97[m, 2H, H^4, H^6]	3.84[s, 3H, MeO]
			3.35[dq, 2H, CH_2CH_3]
			1.21[t, 3H, CH_2CH_3]
f		7.71[d, 2H, H^2, H^6, 8.2 [d]]	9.38[br, 1H, NH]
		6.95[d, 2H, H^3, H^5, 8.2 [d]]	8.76[br, 1H, N*H*Ph]
			3.85[s, 3H, MeO]
			2.33[s, 3H, Me]
1f		7.13[d, 1H, H^5, 8.5 [e], 2.5 [f]]	6.94[br, 1H, N*H*Ph]
		6.85[d, 1H, H^2, 8.5 [e]]	3.59[s, 3H, MeO]
		6.52[dd, 1H, H^3, 8.5 [e], 2.5 [f]]	1.92[s, 3H, Me]
2f	24.3s	6.83[d, 1H, H^2, 8.3 [e]]	6.67[br, 1H, N*H*Ph]
		6.17[dd, 1H, H^3, 8.3 [e], 2.8 [f]]	3.32[t, 2H, PCH_2P [h]]
		5.75[dd, 1H, H^5, 4.6 [g], 2.8 [f]]	3.12[s, 3H, MeO]
			2.29[s, 3H, Me]

[a] In $CDCl_3$ unless otherwise stated. Measured at 100.6 Mhz (ca. 20°C); chemical shifts (δ) in ppm (± 0.1) to high frequency of 85% H_3PO_4.

[b] In $CDCl_3$ unless otherwise stated. Measured at 250 or 300 MHz; chemical shifts (δ) in ppm (± 0.01) to high frequency of $SiMe_4$.

[c] Coupling constants in Hz. s, singlet; d, doublet; dd, doublet of doublets; t, triplet; dt doublet of triplets; dq, doublet of quadruplets; m, multiplet; br, broad.

[d] $N = {}^3J(HH) + {}^5J(HH)$.

[e] ${}^3J(HH)$.

[f] ${}^4J(HH)$.

[g] ${}^4J_{(HP)}$.

[h] ${}^2J_{(HP)} = 15.2$ Hz PCH_2P.

(H)=N](Br)}$_2$C$_6$H$_4$}$_2${μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$}$_2$] [21] rendered [PdBr$_2${Ph$_2$P(CH$_2$)$_3$PPh$_2$}] which was characterized by $^{31}P-\{^1H\}$- and ^1H-NMR (suitable crystals for single-crystal diffraction were grown from $PdCl_2$/KBr and $Ph_2P(CH_2)_3PPh_2$ [22]); and [Pd{C$_6$H$_4$C(H)=N(CH$_2$)$_2$NMe$_2$} –(*cis*-Ph$_2$PCH=CHPPh$_2$–*P*,*P*)][Cl] gave [PdCl$_2$(Ph$_2$PCH=CHPPh$_2$)] [6]. In all situations the organic ligand was detached from the palladium coordination sphere. However, in the present case the end product is the coordination product with two thiosemicarbazone ligands chelated to the palladium atom; the palladium–carbon bond was cleaved with loss of the five-membered metallacycle, but the chelate ring containing the palladium and sulfur atoms remained. We attribute this to the presence of the stronger palladium–sulfur bond as compared to the Pd–N and Pd–O bonds.

2.2. Molecular structure of complex *3f*

The crystal structure of the complex with the numbering scheme is shown in Fig. 1. Selected bonds lengths and angles are listed in Table 3. The molecule has approximate C_2 symmetry with the C_2 axis bisecting the S(1)–Pd(1)–S(2) angle. The structure of complex **3f**·0.5$CHCl_3$ comprises a molecule with the palladium(II) atom bonded to two thiosemicarbazone ligands in a distorted square planar coordination. The coordination sphere around palladium consists of two nitrogen atoms and two sulfur atoms from each of the two thiosemicarbazone ligands, N(1), S(1) and N(4), S(2), respectively, with a N–Pd–S *trans* geometry. The deviations from the mean plane are as follows: Pd, −0.0233, S(1) 0.2211, S(2) −0.2122, N(1) −0.2356, N(4) 0.2499 Å. The angles between adjacent atoms in

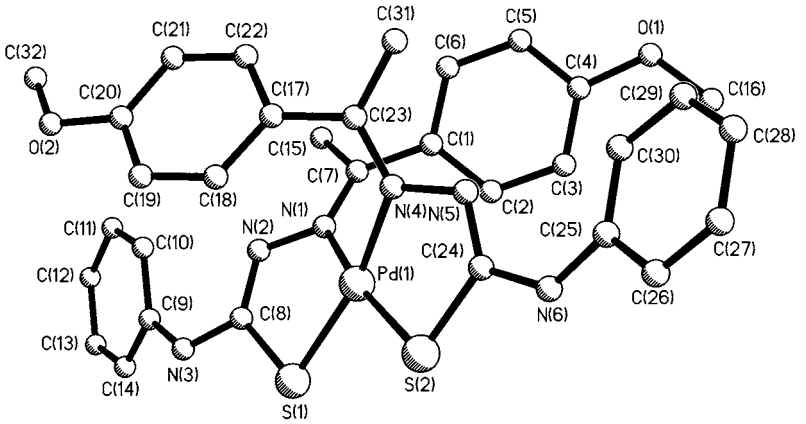


Fig. 1. Crystal structure of compound **3f** with the labelling scheme. Hydrogen atoms have been omitted for clarity.

the coordination sphere are close to the expected value of 90°, in the range 100.06(5)–81.42(11)°, with the distorsions being most noticeable in the thiosemicarbazone ligand. The angles N(1)–Pd(1)–S(1) 82.28(11)° and N(4)–Pd(1)–S(2) 81.42(11)° are less than 90° and S(2)–Pd(1)–S(1) 100.06(5)° and N(1)–Pd(1)–N(4) 98.85(16)° are thus greater than 90°. All bond distances are within the expected range. The S(1)–C(8) and S(2)–C(24) bond lengths, 1.758(6) and 1.777(5) Å, respectively, and the N(2)–C(8) bond lengths, 1.290(7) and 1.286(6) Å, respectively, are consistent with increased single and double bond character, also respectively. The chelate rings Pd(1), S(1), C(8), N(2) and N(1) and Pd(1), S(2), C(24), N(5) and N(4), show mean deviations from the plane of 0.1591 and 0.1512 Å, respectively. The molecular units are stacked in a three-dimensional array held together by intermolecular hydrogen bonding as follows: one thiosemicarbazone ligand is bonded through the amide hydrogen atom and the sulfur atom (see Fig. 2) with N(6)···S(2) 3.468(5) and H(6A)···S(2) 2.55(8) Å, with an N(6)–H(6A)···S(2) angle of 156.6(2)°, whilst the other thiosemicarbazone ligand is bonded through the amide hydrogen and the oxygen atom of the methoxy group (see Fig. 2) with N(3)···O(1) 3.159(7) and H(3A)···O(1) 2.14(7) Å, with an N(3)–H(3A)···O(1) angle of 172.5(3)° (see Fig. 2). All the molecular units joined by hydrogen bonding are nearly parallel.

A further notice to complex **3f** in the solid should be made regarding its potential chirality related to the

Table 2
Crystal data for compound **3f**

Formula	$C_{32.5}H_{32.5}Cl_{1.5}N_6O_2PdS_2$
Formula weight	762.84
Temperature (K)	293 (2)
Wavelength (Å)	0.71073
Crystal color	Yellow
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	12.2861(2)
b (Å)	19.2981(3)
c (Å)	15.4813(3)
β (°)	94.0530(10)
V (Å^3)	3661.41 (11)
Z	4
D_{calc} (mg m^{-3})	1.384
Absorption coefficient (mm^{-1})	0.767
Crystal size (mm)	$0.40 \times 0.30 \times 0.30$
θ Range for data collection (°)	1.66–28.29
Index ranges	$-10<h<16$, $-24<k<25$, $-20<l<20$
Reflections collected	26661
Independent reflections	9048 ($R_{int} = 0.0494$)
Completeness to $2\theta = 28.29°$	99.4%
Absorption correction	Semi-empirical
Refinement method	Full-matrix-block least squares on F^2
Data/restraints/parameters	9048/6/424
GOF on F^2	1.149
Final R indices [$I>2.0\sigma(I)$]	$R_1 = 0.0642$, $wR_2 = 0.1750$
R indices (all data)	$R_1 = 0.1046$, $wR_2 = 0.1971$
Largest difference peak and hole (e Å^{-3})	1.179 and −0.649

Table 3
Selected bond lengths (Å) and bond angles (°) for compound **3f**

Bond lengths			
Pd(1)–S(1)	2.2747(14)	Pd(1)–N(1)	2.049(4)
Pd(1)–S(2)	2.2655(13)	Pd(1)–N(4)	2.057(4)
S(1)–C(8)	1.758(6)	N(1)–N(2)	1.399(6)
N(2)–C(8)	1.290(7)	N(1)–C(7)	1.308(6)
S(2)–C(24)	1.777(5)	N(4)–N(5)	1.403(5)
N(5)–C(24)	1.286(6)	N(4)–C(23)	1.304(6)
Bond angles			
N(1)–Pd(1)–N(4)	98.85(16)	N(1)–Pd(1)–S(2)	169.21(13)
N(4)–Pd(1)–S(2)	81.42(11)	N(1)–Pd(1)–S(1)	82.28(12)
N(4)–Pd(1)–S(1)	166.20(12)	S(2)–Pd(1)–S(1)	100.06(5)
C(8)–S(1)–Pd(1)	93.76(19)	N(2)–C(8)–S(1)	125.2(4)
N(2)–N(1)–Pd(1)	117.0(3)	C(8)–N(2)–N(1)	112.8(4)
C(24)–S(2)–Pd(1)	94.98(17)	N(5)–C(24)–S(2)	125.1(4)
C(24)–N(5)–N(4)	111.3(4)	N(5)–N(4)–Pd(1)	118.7(3)

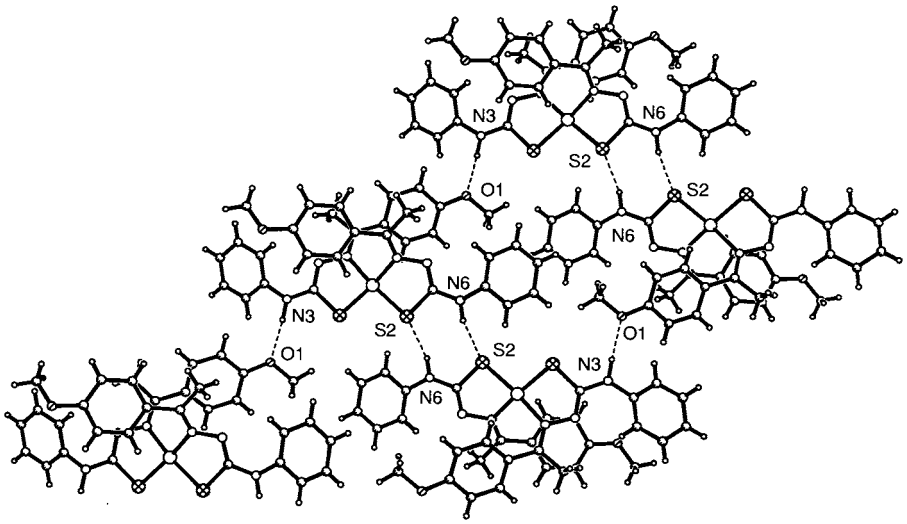


Fig. 2. Hydrogen bond interactions in compound **3f**.

non-planarity of the chelated five-membered rings at palladium. This stems from the differing conformations of the chelate rings as has been described by Bailar et al. [23]. In complex **3f** the two benzylidene groups are overlapping and to avoid steric hindrance between them the chelate rings at palladium must be slightly twisted, which impedes planar geomtery about the metal atom, as the crystallographic data show. The non-planarity of the PdNNCS rings introduces chirality in complex **3f**. The space group of the crystal structure (see Table 2) indicates that both enantiomers are present in the solid state linked via hydrogen bonds (vide supra) (Fig. 2). A more detailed view of both enantiomers is depicted in Fig. 3.

3. Conclusions

The results presented here are further examples which show that cyclometallated palladium(II) compounds with thiosemicarbazones are of tetranuclear nature regardless of the starting palladium precursor, as we have shown earlier. This stems from the strength of the Pd–S bond, which endures attack of nucleophiles such as tertiary phosphines. Mononuclear palladium(II) complexes may also be obtained from thiosemicarbazones, which lack the σ palladium–carbon bond. The strength of the palladium–sulfur bond is made clear in that it prevails even in the decomposition processes cyclometallated compounds suffer in solution, so that the organic moiety is firmly held to the metal center to give coordination compounds bearing the thiosemicarbazone ligand as opposed to the compounds formed with other organic ligands where the sulfur atom is absent. Furthermore, the spatial disposition of the benzylidene groups leads to a chiral complex with both enantiomers present in the solid state.

4. Experimental

4.1. Materials and instrumentation

Solvents were purified by standard methods [24]. Chemicals were reagent grade. Lithium tetrachloropalladate was made in situ by treating palladium(II) chloride with lithium chloride in methanol or ethanol. Palladium(II) acetate and potassium tetrachloropalladate were purchased from Alfa Products; dppm from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometer. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 ($^{31}P-\{^1H\}$) and were recorded on Bruker WM250 and AMX-300 spectrometers. All chemical shifts were reported downfield from standards.

4.2. Preparations

4.2.1. Preparation of 4-$MeOC_6H_4C(H)=NN(H)C(=S)NHMe$ (**a**)

To a suspension of thiosemicarbazide (0.5 g, 4.76 mmol) in water (25 cm^3) 4-methoxybenzaldehyde (0.65 g, 4.76 mmol) and hydrochloric acid (35%, 0.65 cm^3) were added to give a clear solution, which was stirred at room temperature for 4 h. The white solid that precipitated was filtered off, washed with cold water and dried in air. Yield 80%. Anal. Found: C, 53.5; H, 6.0; N,

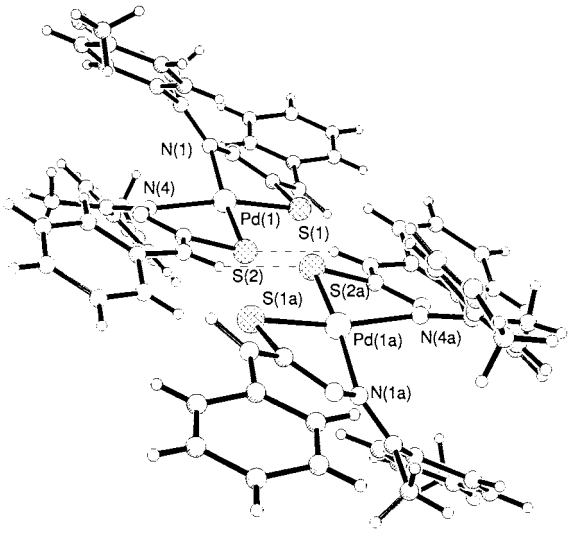


Fig. 3. The enantiomers of compound **3f** showing hydrogen bonding.

18.6. Anal. Calc.: C, 53.8; H, 5.9; N, 18.8%. IR: ν(C=N) 1603s, br cm^{-1}; ν(C=S) 849m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 177.9 (C=S); 142.0 (C=N); 161.0 (C4); 129.2 (C2, C6); 127.2 (C1); 114.5 (C3, C5); 55.6 (MeO); 31.1 (NHMe).

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

4.2.2. 4-$MeOC_6H_4C(H)$=NN(H)C(=S)NHEt ***(b)***

Yield 87%. Anal. Found: C, 55.5; H, 6.8; N, 17.7. Anal. Calc.: C, 53.7; H, 6.4; N, 17.7%. IR: ν(C=N) 1604s, br cm^{-1}; ν(C=S) 832m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 177.1 (C=S); 143.1 (C=N); 161.9 (C4); 129.3 (C2, C6); 127.2 (C1); 114.7 (C3, C5); 55.8 (MeO); 39.7 (CH_2CH_3); 15.0 (CH_2CH_3).

4.2.3. 4-$MeOC_6H_4C(H)$=NN(H)C(=S)NHPh ***(c)***

Yield 92%. Anal. Found: C, 63.0; H, 5.5; N, 14.8. Anal. Calc.: C, 63.0; H, 5.3; N, 14.7%. IR: ν(C=N) 1611s, br cm^{-1}; ν(C=S) 828m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 175.8 (C=S); 143.8 (C=N); 162.1 (C4); 138.3 (C7); 129.6 (C2, C6); 129.2 (C8, C12); 126.6 (C10); 126.2 (C1); 125.1 (C9, C11); 114.8 (C3, C5); 55.9 (MeO).

4.2.4. 3-$MeOC_6H_4C(H)$=NN(H)C(=S)NHMe ***(d)***

Yield 80%. Anal. Found: C, 54.3; H, 6.4; N, 18.8. Anal. Calc.: C, 53.8; H, 5.9; N, 18.8%. IR: ν(C=N) 1679s, br cm^{-1}; ν(C=S) 813m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 178.6 (C=S); 143.0 (C=N); 160.3 (C3); 135.1 (C1); 130.3 (C2); 120.8, 116.8, 112.4 (C4, C5, C6); 55.9 (MeO); 31.5 (NHMe).

4.2.5. 3-$MeOC_6H_4C(H)$=NN(H)C(=S)NHEt ***(e)***

Yield 86%. Anal. Found: C, 54.9; H, 6.4; N, 17.4. Anal. Calc.: C, 55.7; H, 6.4; N, 17.7%. IR: ν(C=N) 1609s, br cm^{-1}; ν(C=S) 811m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 177.4 (C=S); 143.0 (C=N); 160.3 (C3); 135.2 (C1); 130.3 (C2); 120.7, 116.6, 112.5 (C4, C5, C6); 55.8 (MeO); 39.7 (CH_2CH_3); 15.0 (CH_2CH_3).

4.2.6. 4-$MeOC_6H_4C(Me)$=NN(H)C(=S)NHPh ***(f)***

Yield 86%. Anal. Found: C, 65.1; H, 5.0; N, 13.9. Anal. Calc.: C, 64.2; H, 5.7; N, 14.0%. IR: ν(C=N) 1600s, br cm^{-1}; ν(C=S) 836m cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 176.5 (C=S); 147.6 (C=N); 161.6 (C4); 138.4 (C7); 131.0 (C1); 129.2 (C8, C12); 128.3 (C2, C6); 126.4 (C10); 124.6 (C9, C11); 114.5 (C3, C5); 55.8 (MeO); 14.1 (Me).

4.2.7. Preparation of [Pd{4-$MeOC_6H_3C(H)$=NN=C(S)NHMe}]$_4$ ***(1a)***

Method 1: to a stirred solution of palladium(II) chloride (69 mg, 0.39 mmol) and lithium chloride (34 mg, 0.81 mmol) in methanol (40 cm^3) 4-$MeOC_6H_4C(H)$=NN=C(S)NHMe (**a**) (188 mg, 0.84 mmol) and sodium acetate (500 mg, 6.1 mmol) were added. The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with ethanol and dried. Yield 57%. Anal. Found: C, 35.6; H, 3.2; N, 12.3. Calc.: C, 36.7; H, 3.4; N, 12.8%. IR: ν(C=N) 1580s cm^{-1}. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 167.9 (C=S); 156.2 (C=N); 161.5 (C4); 148.0 (C6); 132.1 (C1); 125.2 (C2); 113.2 (C3, C5); 55.7 (MeO); 32.0 (NHMe).

Method 2: ligand **a** (164 mg, 734 mmol) and palladium(II) acetate (164 mg, 736 mmol) were added to 45 cm^3 of glacial acetic acid to give a clear solution, which was heated to 60°C under reflux for 8 h. After cooling to room temperature, the yellow precipitate was filtered off, washed with ethanol and dried. Yield 32%.

4.2.8. [Pd{4-$MeOC_6H_3C(H)$=NN=C(S)NHEt}]$_4$ ***(1b)***

Method 1: analogous to **1a**. Yield 57%. IR: ν(C=N) 1585s cm^{-1}. Anal. Found: C, 38.7; H, 4.5; N, 11.8. Calc.: C, 38.7; H, 3.8; N, 12.3%. $^{13}C-\{^1H\}$-NMR (62.46 MHz $CDCl_3$, δ, ppm): 168.2 (C=S); 158.8 (C=N); 160.2 (C4); 141.9 (C6); 132.6 (C1); 128.5 (C2); 118.6, 114.3 (C3, C5); 55.4 (MeO); 41.3 (CH_2CH_3); 15.2 (CH_2CH_3).

Method 2: ligand **b** (213 mg, 895 mmol) and palladium(II) acetate (215 mg, 898 mmol) were added to 40 cm^3 of glacial acetic acid to give a clear solution, which was heated to 60°C under reflux for 8 h. After cooling to room temperature, the acetic acid was removed under vacuum. The residue was diluted with water and extracted with dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and concentrated in vacuo to give a yellow solid. This was chromatographed on a column packed with silica gel. Elution with dichloromethane/ethanol (1%) afforded product **2b** as a yellow solid after concentration. Yield 26%.

Compounds **1c**–**f** were obtained following a similar procedure to **1a** (method 1) using $Li_2[PdCl_4]$ or $K_2[PdCl_4]$ as appropriate.

*4.2.9. [Pd{4-MeOC$_6$H$_3$C(H)=NN=C(S)NHPh}]$_4$ (**1c**)*

Yield 54%. IR: υ(C=N) 1574s cm^{-1}. Anal. Found: C, 45.8; H, 2.9; N, 9.7. Calc.: C, 46.2; H, 3.4; N, 10.8%.

*4.2.10. [Pd{3-MeOC$_6$H$_4$C(H)=NN=C(S)NHMe}$_2$] (**1d**)*

Yield 61%. IR: ν(C=N) 1576s cm^{-1}. Anal. Found: C, 43.9; H, 4.7; N, 15.5. Calc.: C, 43.6; H, 4.4; N, 15.3%. ^{13}C–{^{1}H}-NMR (62.46 MHz $CDCl_3$, δ, ppm): 173.4 (C=S); 157.4 (C=N); 159.0 (C3); 134.1 (C1); 128.8 (C2); 123.8, 119.1, 114.0 (C4, C5, C6); 55.5 (MeO); 32.6 (NHMe).

*4.2.11. [Pd{3-MeOC$_6$H$_4$C(H)=NN=C(S)NHEt}$_2$] (**1e**)*

Yield 53%. IR: ν(C=N) 1579s cm^{-1}. Anal. Found: C, 45.3; H, 4.1; N, 14.1. Calc.: C, 45.6; H, 4.9; N, 14.5%. ^{13}C–{^{1}H}-NMR (62.46 MHz $CDCl_3$, δ, ppm): 179.4 (C=S); 156.7 (C=N); 159.0 (C3); 134.2 (C1); 128.8 (C2); 123.7, 119.0, 114.0 (C4, C5, C6); 55.5 (MeO); 40.8 (CH_2CH_3); 15.3 (CH_2CH_3).

*4.2.12. [Pd{4-MeOC$_6$H$_3$C(Me)=NN=C(S)NHPh}]$_4$ (**1f**)*

Yield 57%. IR: ν(C=N) 1577s cm^{-1}. Anal. Found: C, 47.5; H, 3.6; N, 10.1. Calc.: C, 47.6; H, 3.7; N, 10.4%. ^{13}C–{^{1}H}-NMR (62.46 MHz $CDCl_3$, δ, ppm): 168.0 (C=S); 160.4 (C4); 159.5 (C=N); 142.2 (C6); 140.8 (C7); 132.0 (C1); 129.1 (C8, C12); 127.9 (C2); 123.3 (C10); 120.2 (C9, C11); 117.8 (C3); 110.1 (C5); 55.4 (MeO); 14.2 (Me).

*4.2.13. [{Pd[4-MeOC$_6$H$_3$C(Me)=NN=C(S)NHPh]}$_2$-(μ-Ph$_2$PCH$_2$PPh$_2$)] (**2f**)*

Bis(diphenylphosphino)methane, dppm, (24 mg, 62 mmol) was added to a stirred suspension of complex **1f** (50 mg, 31 mmol) in acetone (15 cm^3). The mixture was stirred for 3 h, the resulting solid filtered off and dried. Yield 84%. IR: ν(C=N) 1576s cm^{-1}. Anal. Found: C, 57.1; H, 4.8; N, 6.7. Calc.: C, 57.4; H, 4.4; N, 7.1%.

4.3. Single-crystal X-ray diffraction analysis

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° in omega. The 9048 ($R_{int} = 0.05$) independent reflections (of 26661 measured, completeness to $\theta = 28.29$, 99.4%) were corrected for Lorentz and polarisation effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections (minimum and maximun transmission coefficients 0.70 and 0.96). The structure was solved by direct methods and refined by full matrix least squares on F^2 with allowance for thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined in riding mode. The structure solution and refinement were carried out using the program package SHELX-97 [25].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149548 for compound **3f**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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