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Rotation of a double C=N bond driven by palladium†

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Abstract: Thiosemicarbazones are used as ligands forming many examples of compounds. Chemistry of these molecules with palladium often includes cyclopalladated but in some cases coordination compounds were reported. Structure of these complexes has not been widely described; different studies show wide structures variety. The treatment of these ligands with palladium salts lead the formation of these kind of complexes which structure and reactivity is more similar to organometallic cyclopalladated compounds than expected.

Keywords: Thiosemicarbazone, palladium, isomerization, coordination chemistry

1. Introduction

Palladium plays an important role in organometallic chemistry [1]; it also has interesting coordination compounds with biological [2] and catalytic applications [3]. Thiosemicarbazones are an important and versatile type of ligands due to the number and variety of donor atoms they 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 [4]. Furthermore, there has been considerable interest in these ligands because of their potentially biological activity of their metal complexes; they have been screened for potential antitumor and antiviral activity [5].

Deprotonation of the hydrazine group in thiosemicarbazones opens new possibilities by the conformational species. Depending on what species is more stable it is possible to form organometallic [*C*,*N*,*S*] or other coordination compounds [*N*,*S*].

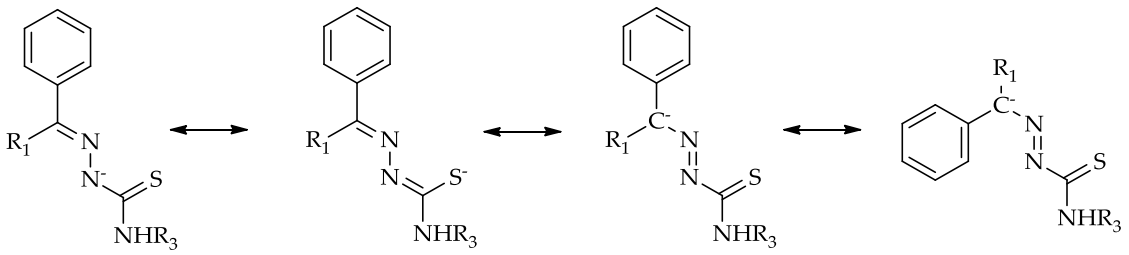


Figure 1.

Many studies about cyclopalladation of thiosemicarbazones [*C*,*N*,*S*] have been previously reported [6], most frequently tetranuclear sulfur bridge complexes are produced [7]; trinuclear complexes have also been reported [8]. These examples show the tendency to form links between

palladium centers, when the ligand acts is in the thiolate form due to deprotonation of the thiol form in semicarbazone group [9]. By avoiding this deprotonation is possible to form mononuclear complexes [10].

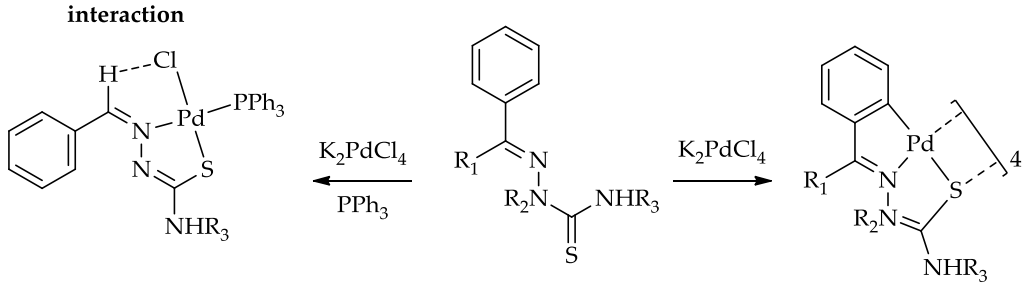


Figure 2.

Ligand structure factors conditioning the coordination modes *[C,N,S]* and *[N,S]* were previously described [11]. These chemical behaviors were conditioned by the R_1 substituent. For R_1 = H *[N,S]* coordination is preferred while for R_1 = Me, Et or Ph cyclopalladated complexes are obtained. Previous reports state that this trend follows two factors; first of all H shows fewer steric hindrance than Me, Et or Ph. To understand the importance of this, it is necessary to take into consideration the structure formed in coordination complexes (Figure 1). For *[N,S]* complexes the geometry of the C=N bond has changed from *E* on ligand to *Z* in complex. It is in this new conformation where steric hindrance influence of R_1 group is important.

As a consequence of C=N isomerization to *Z* geometry, the C-Pd bond has been moved away from metallic atom hindering metallation. Second factor was reported by some studies which consider write about possible interactions between chlorine and hydrogen R_1 atom where this structure is supported.

Despite these two factors is possible to synthesize organometallic compounds for R_1 = H (Figure 2). An option is to use a thiosemicarbazone with a R_2 group other than H, this stops isomerization of C=N bond, and coordination *[N,S]* complexes are not formed because proximity between the aromatic ring and palladium promotes C-Pd bond formation. A second option to form organometallic complexes is to add a base in the reaction medium. The role of the base is believed to be deprotonation of the aromatic ring, but it is also possible that the base promotes exchange of the chlorine ligand for the acetate ligand, increasing steric hindrance which does not allow formation of the *[N,S]* complex when the C=N bond is in *Z* conformation; for this reason formation of *[C,N,S]* complex from the C=N *E* conformation is more favored.

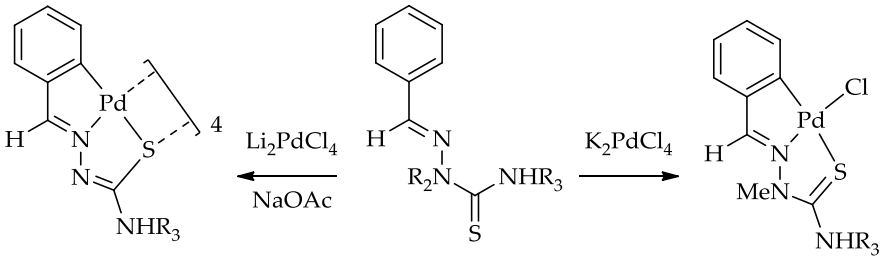


Figure 3.

Cyclopalladated thiosemicarbazones have been widely studied for their biological properties [12] and their probable catalytic activity. The situation is different for palladium complexes; there are few examples of *[N,S]* complexes. This work is a study about [*N*,*S*] thiosemicarbazone complexes and their reactivity with phosphines.

2. Materials and Methods

2.1. General comments

Solvents were purified by standard methods. Reagents were purchased from Sigma–Aldrich. Elemental. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a FISONS elemental analyzer, Model 1108. IR spectra were recorded as KBr pellets or polythene discs on BRUKER Model IFS-66v and IR-FT MATTSON Model CYGNUS-100 spectrophotometers. NMR spectra were obtained as $CDCl_3$ solution and referenced to $SiMe_4$ (^1H) or 85 % H_3PO_4 (^{31}P-{^1H}) and were recorded on BRUKER DPX 250 and Varian Inova 400 spectrometers. X-ray data were collected on a BRUKER SMART 1000 CCD diffractometer. The structures were solved by direct methods and refined by full matrix least squares on F^2. The structure solutions and refinements were carried out with the SHELX-97 program package.

2.2. Preparation of ligands 1-3

Ligands were synthetized preparing a 20 cm^3 water solution of 2.5 mmol of thiosemcarbazone with 0.3 cm^3 of HCl 0.1 M and adding the corresponding aldehyde. Resultant solution was stirred for 4 hour allowing the formation of a white solid product.

2.2.1. 2, 3, 4-OMe-$C_6H_2C(H)$=N-N(H)-C(=S)-N(H)-Me (1)

Yield 92 % FTIR: 3182, 3332 [m, νN-H], 1623 [s, νC=N], 804 [m, νC=S] cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 8.97 (s, 1H, NNH), 7.98 (s, 1H, Hi), 7.52 (d, $^3J_{H^5H^6}$ = 8.9 Hz, 1H, H5), 7.39 (c, $^3J_{HH}$ = 4.8 Hz, 1H, NHMe), 6.68 (d, $^3J_{H^6H^5}$ = 8.9 Hz, 1H, H6), 3.89 (s, 3H, OMe), 3.88 (s, 3H, OMe), 3.84 (s, 3H, OMe), 3.23 (d, $^3J_{HH}$ = 4.8 Hz, 2H, NHMe). $C_{12}H_{17}N_3O_3S$ (283.35) calcd. C, 50.9, H, 6.1, N, 14.9, S, 11.3; found C, 50.8, H, 6.0, N, 14.9, S 11.3.

2.2.2. 2, 3, 4-OMe-$C_6H_2C(H)$=N-N(H)-C(=S)-N(H)-Et (2)

Yield 95 % FTIR: 3165, 3327 [m, νN-H], 1613 [s, νC=N], 838 [m, νC=S] cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 9.02 (s, 1H, NNH), 8.02 (s, 1H, Hi), 7.53 (d, $^3J_{H^5H^6}$ = 8.8 Hz, 1H , H5), 7.36 (t, $^3J_{HH}$ =4.9 Hz, 1H NHEt), 6.71 (d, $^3J_{H^6H^5}$ = 8.8 Hz, 1H, H6), 3.91-3.87 (s, 9H, OMe), 3.76 (dc, $^3J_{HH}$ =4.9 Hz; 7.3 Hz, 2H, $NHCH_2CH_3$), 1.31 (t, $^3J_{HH}$ =7.3 Hz, 3H, $NHCH_2CH_3$). $C_{13}H_{19}N_3O_3S$ (297.37) calcd. C, 52.8, H, 6.4, N, 14.1, S 10.3; found C, 52.5, H, 6.4, N, 14.1, S, 10.8.

2.2.3. 4-OMe-$C_6H_2C(H)$=N-N(H)-C(=S)-N(H)-Me (3)

Yield 87 % FTIR: 3219, 3299 [m, νN-H], 1611 [s, νC=N], 812 [m, νC=S] cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 9.49 (s, 1H, NNH), 7.75 (s, 1H, Hi), 7.56 (d, $^3J_{H^5H^6}$ = 8.8 Hz, 1H, H3/H5), 7.42 (c, $^3J_{HH}$ = 4.9 Hz, 1H, NHMe), 6.89 (d, $^3J_{H^6H^5}$ = 8.8 Hz, 1H,H2/H6), 3.22 (d, $^3J_{HH}$ = 4.9 Hz 3H, $NHCH_3$). $C_{10}H_{13}N_3OS$ (223.29) calcd. C, 53.8, H, 5.9, N, 18.8, S, 14.4; found. C, 53.9, H, 5.9, N, 18.9, S 14.9.

2.3. Preparation of the complex 1a-3a

Complexes were obtained preparing a solution of 15 cm^3 of 0.5 mmol of ligand and mixing that with a solution of 1 equivalent of $K_2[PdCl_4]$ in 5 cm^3 of water. After 24 hours of stirring the formation of an orange solid is observed.

2.3.1. [Pd {2, 3, 4-OMe-$C_6H_2C(H)$=N-N=C(S)-N(H)-Me-N,S}]$_4$ (1a)

Yield 70 % FTIR: 3403 [m, νN-H] 1577 [s, νC=N], 280 [m, νPd-Cl] cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$) δ = 9.02 (s, 4H, Hi), 8.53 (d, $^3J_{H^5H^6}$ = 9.1 Hz, 4H, H5), 6.68 (d, $^3J_{H^6H^5}$ = 9.2 Hz, 4H, H6), 6.11 (c, $^3J_{HH}$ = 4.3 Hz, 4H, NHMe), 4.09 (s, 12H, OMe), 3.89 (s, 12H, OMe), 3.86 (s, 12H, OMe), 3.02 (d, $^3J_{HH}$ =

4.8 Hz, 12H, NHMe). $C_{48}H_{64}Cl_4N_{12}O_{12}Pd_4S_4$ (1696.85) calcd. C, 34.0, H, 3.8, N, 9.9, S, 7.6; found C, 31.7, H, 4.3, N, 9.3, S, 7.0.

2.3.2. [Pd {2, 3, 4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Et-N,S }]$_4$ (2a)

Yield 78 % FTIR: 3477 [m, νN-H] 1579 [s, νC=N], 279 [m, νPd-Cl] cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 9.06 (s, 1H, *Hi*), 8.55 (d, $^3J_{H^5H^6}$ = 9.1 Hz, 4H, *H5*), 7.36 (t, $^3J_{HH}$ = 4.6 Hz, 4H, N*H*Et), 6.70 (d, $^3J_{H^6H^5}$ = 9.1 Hz, 4H, *H6*), 3.92 (s, 12H, O*Me*), 3.88 (s, 12H, O*Me*), 3.85 (s, 12H, O*Me*), 3.76 (dc, $^3J_{HH}$ = 7.3; 4.8 Hz, 8H, NHC$H_2$$CH_3$), 1.31 (t, $^3J_{HH}$ = 7.3 Hz, 12H, NHCH_2CH_3). $C_{52}H_{72}Cl_4N_{12}O_{12}Pd_4S_4$ (1752.95) calcd. C, 35.6; H, 4.1; N, 9.6; S, 7.3; found C, 33.2; H, 4.0; N, 8.9, S, 9.1. X-ray: triclinic; $\overline{P1}$; a (Å) = 11.462(2); b = 16.167(3); c= 20.565(4); α (°) = 91.819(3); β = 91.962(3); γ = 104.556(3); 3683.1(12) A^3; Z = 5; R_1 = 0.0392; *w*R_2 = 0.0993.

2.3.3. [Pd {4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Me-N,S }]$_4$ (3a)

Yield 67 % FTIR: 3383 [m, νN-H] 1587 [s, νC=N], 254 [m, νPd-Cl] cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.56 (s, 4H, Hi), 8.20 (d, $^3J_{H^5H^6}$ = 8.6 Hz, 8H, H3/H5), 6.92 (d, $^3J_{H^6H^5}$ = 8.6 Hz, 8H, H2/H6), 5.98 (c, 4H, NHMe), 3.84 (s, 12H, OMe), 3.03 (d, $^3J_{HH}$ = 4.9 Hz, 12H, NHMe). $C_{40}H_{48}Cl_4N_{12}O_4Pd_4S_4$ (1456.64) calcd. C, 33.0, H, 3.3, N, 11.5, S, 8.8, found C, C, 35.8, H, 3.6, N, 12.5, S, 9.6.

2.4. Preparation of the complex 1b-3b

Complexes were obtained preparing a suspension of 20 cm^3 of 0.5 mmol of complex **1a-3a** and mixing that with a solution of 1 equivalent of $K_2[PdCl_4]$ in 5 cm^3 of water. After 24 hours of stirring the formation of an orange solid is observed.

2.4.1. [Pd {2, 3, 4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Me-N,S} (PPh_3)] (1b)

Yield 78 % FTIR: 3409 [m, νN-H] 1564 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 (d, $^4J_{PH}$ = 8.5 Hz, 1H, Hi) 7.69-7.33 (m 15H, PPh_3), 7.81 (d, $^3J_{H^5H^6}$= 8.7 Hz, 1H, H5) , 6.88(d, $^3J_{H^6H^5}$ = 8.7 Hz, 1H, H6), 4.65 (c, $^3J_{HH}$ = 4.4 Hz, 1H, NHMe), 4.00 (s, 3H, OMe), 3.97 (s, 3H, OMe), 3.85 (s, 3H, OMe), 2.84(c, $^3J_{HH}$ = 4.4Hz, 3H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 20.11 (s). $C_{30}H_{31}ClN_3O_3PPdS$ (686,50) calcd. C, 52.4, H, 4.7, N, 6.1, S, 4.7; found C, 53.7, H, 4.4, N, 6.3, S, 7.2.

2.4.2. [Pd {2, 3, 4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Et-N,S }]$_4$ (2b)

Yield 83 % FTIR: 3387 [m, νN-H] 1583 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92(d, $^4J_{PH}$ = 8.2 Hz, 1H, *Hi*) 7.45-7.24 (m, 15H, P*Ph*$_3$), 7.59 (d, $^3J_{H^5H^6}$ =8.4 Hz, 1H, *H5*), 6.91(d, $^3J_{H^6H^5}$= 8.4 Hz, 1H, *H6*), 5.11 (t, $^3J_{HH}$ = 4.7 Hz, 1H, N*H*Et), 3.95 (s, 3H, O*Me*), 3.89 (s, 3H, O*Me*), 3.76 (s, 3H, O*Me*), 3.17(dc, $^3J_{HH}$ = 7.5 Hz, 4.7 Hz, 2H, NHC$H_2$$CH_3$), 1.79 (t, $^3J_{HH}$ =7.5 Hz, 3H, NHCH_2CH_3). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 20.17 (s). $C_{31}H_{33}ClN_3O_3PPdS$ (700.52)

2.4.3. [Pd {4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Me-N,S }]$_4$ (3b)

Yield 86 % FTIR: 3419 [m, νN-H] 1581 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.18 (d, $^4J_{PH}$ = 8.6 Hz, 1H, Hi) 7.66-7.20 (m 15H, PPh_3), 7.40 (d, $^3J_{H^5H^6}$ = 8.8 Hz, 2H, H2/H6) , 6.87 (d, $^3J_{H^6H^5}$ = 8.8 Hz, 2H, H3/H5), 5.09 (c, $^3J_{HH}$ = 4.7 Hz, 1H, NHMe), 3.79 (s, 3H, OMe), 2.92 (d, $^3J_{HH}$ = 4.7 Hz, 3H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 21.90 (s). $C_{28}H_{27}ClN_3OPPdS$ (626.45) calcd. C, 53.7, H, 4.3, N, 6.7, S, 5.1; found C, 53.0, H, 4.7, N, 6.9, S, 6.2. X-ray: triclinic; $\overline{P1}$; a (Å) = 9.144(3); b = 9.665(1); c= 18.681(4); α (°) = 80.904(1); β = 79.923(2); γ = 71.965(2); 1536.1(11) A^3; Z = 2; R_1 = 0.0268; *w*R_2 = 0.0624.

2.5. Preparation of the complex 1c-3c

Complexes were obtained preparing a solution of 15 cm^3 of 0.5 mmol of ligand and mixing that with a solution of 1 equivalent of $K_2[PdCl_4]$ in 5 cm^3 of water. After 24 hours of stirring the formation of an orange solid is observed.

2.5.1. [Pd {2, 3, 4-OMe-$C_6H_2C(H)$=N-N=C(S)-N(H)-Me-N,S} {$PPh_2CH_2P(=O)Ph_2$-P}] (1c)

Yield 77 % FTIR: 3309 [m, νN-H] 1579 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 (d, $^4J_{PH}$ = 6.8 Hz, 1H, Hi), 8.64 (d, $^3J_{H^5H^6}$ = 9.1 Hz, 1H, H5), 7.95 – 7.28 (m, 20H, PPh_2), 6.70 (d, $^3J_{H^6H^5}$ = 9.2 Hz, 1H, H6), 4.52 (c, $^3J_{HH}$ = 5.0 Hz, 1H, NHMe), 4.01 (s, 3H, OMe), 3.92 (s, 3H, OMe), 3.89 (s, 3H, OMe), 2.92 (d, $^3J_{HH}$ = 5.0 Hz, 3H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 23.25(d, Pd-P), 20.23(d, P=O). $C_{37}H_{38}ClN_3O_4P_2PdS$ (824.60) calcd. C, 53.9, H, 4.6, N, 5.1, S, 3.9; found C, 54.1, H, 5.1, N, 5.3, S, 4.1. X-ray: triclinic; $\overline{P1}$; a (Å) = 13.911(2); b = 14.666(2); c= 20.924(3); α (°) = 106.099(2); β = 90.798(3); γ = 91.960(2); 4099(7) A^3; Z = 2; R_1 = 0.0495; wR_2 = 0.1277.

2.5.2. [Pd {2, 3, 4-OMe-$C_6H_2C(H)$=N-N=C(S)-N(H)-Et-N,S} {$PPh_2CH_2P(=O)Ph_2$-P}] (2c)

Yield 47 % FTIR: 3349 [m, νN-H] 1611 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (d, $^4J_{PH}$ = 6.1 Hz, 1H, *Hi*), 8.32 (d, $^3J_{H^5H^6}$ = 8.1Hz, 1H, *H5*), 7.79 – 7.28 (m, 20H, P*Ph*$_2$), 6.70 (d, $^3J_{H^6H^5}$ = 8.2 Hz, 1H, *H6*), 4.94 (t, 1H $^3J_{HH}$ = 5.1 Hz, N*H*Et), 3.89 (s, 3H, O*Me*), 3.75 (s, 3H, O*Me*), 3.62 (s, 3H, O*Me*), 3.42 (d, $^3J_{HH}$ =7.6; 5.1 Hz, 2H, NHC$H_2$$CH_3$), 1.64 (t, $^3J_{HH}$ =7.6Hz, 3H, $NHCH_2CH_3$). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 23.11(d, Pd-P),19.78(d, P=O). $C_{38}H_{40}ClN_3O_4P_2PdS$ (838.63) calcd. C, 54.4, H, 4.8, N, 5.0, S, 3.8; found C, 57.9, H, 5.2, N, 5.7, S, 4.3.

2.5.3. [Pd {4-OMe-$C_6H_2C(H)$=N-N=C(S)-N(H)-Me-N,S} {$PPh_2CH_2P(=O)Ph_2$-P}] (3c)

Yield 62 % FTIR: 3431 [m, νN-H] 1591 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, $^4J_{PH}$ = 7.2Hz, 1H, Hi), 7.80 (d, $^3J_{H^5H^6}$ = 8.1Hz, 2H, H3/H5), 7.75– 7.25(m, 20H, PPh_2), 6.87(d, $^3J_{H^6H^5}$ = 8.2 Hz, 2H, H2/H6), 4.71(c, 1H, $^3J_{HH}$ = 5.1 Hz, NHMe), 3.79 (s, 3H, OMe), 2.95 (d, $^3J_{HH}$ = 5.1 Hz, 3H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 22.15 (d, Pd-P),20.56 (d, P=O). $C_{35}H_{34}ClN_3O_2P_2PdS$ (764.55) calcd. C, 54.9, H, 4.5, N, 5.5, S, 4.2; found C, 56.2, H, 4.9, N, 5.9, S, 5.2.

2.6. Preparation of the complex 1e-3e

Complexes were obtained preparing a solution of 15 cm^3 of 0.5 mmol of ligand and mixing that with a solution of 1 equivalent of $K_2[PdCl_4]$ in 5 cm^3 of water. After 24 hours of stirring the formation of an orange solid is observed.

2.6.1. [Pd {2, 3, 4-OMe-$C_6H_2C(H)$=N-N=C(S)-N(H)-Me-N,S} {μ-$PPh_2(CH_2)_4PPh_2$-P,P}]$_2$ (1e)

Yield 63 % FTIR: 3351 [m, νN-H] 1590 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.84 (d, $^4J_{PH}$ = 4.4 Hz, 2H, Hi), 8.64 (d, $^3J_{H^5H^6}$ = 9.1 Hz, 2H, H5), 7.67 – 7.28 (m, 20H, PPh_2), 6.64 (d, $^3J_{H^6H^5}$ = 9.2 Hz, 2H, H6), 4.77 (c, $^3J_{HH}$ = 5.0 Hz, 2H, NHMe), 3.92 (s, 6H, OMe), 3.85 (s, 6H, OMe), 3.81 (s, 6H, OMe), 2.91 (d, $^3J_{HH}$ = 5.0 Hz, 6H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 21.96(s). $C_{52}H_{60}Cl_2N_6O_6P_2Pd_2S_2$ (1274.89) calcd. C, 49.0, H, 4.7, N, 6.6, S, 5.0; found C, 47.9, H, 5.1, N, 6.3, S, 5.3.

2.6.2. [Pd {2, 3, 4-OMe-$C_6H_2C(H)$=N=C(S)-N(H)-Et-N,S} {μ-$PPh_2(CH_2)_4PPh_2$-P,P}]$_2$ (2e)

Yield 71 % FTIR: 3393 [m, νN-H] 1585 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (d, $^4J_{PH}$ = 4.5 Hz, 2H, *Hi*), 8.32 (d, $^3J_{H^5H^6}$ = 9.0 Hz, 2H, *H5*), 7.67-7.30(m, 20H, P*Ph*$_2$), 6.82 (d, $^3J_{H^6H^5}$ = 9.0 Hz, 2H,

H6), 4.58 (t, $^{3}J_{HH}$ = 5.1 Hz, 2H, N*H*Et), 3.93 (s, 6H, O*Me*), 3.86(s, 6H, O*Me*), 3.71(s, 6H, O*Me*), 3.49 (dc, $^{3}J_{HH}$ = 7.6; 5.1 Hz, 4H, NHC*H*$_2$CH$_3$), 1.53 (t, $^{3}J_{HH}$ = 7.6Hz, 6H, NHCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 22.45 (s). $C_{54}H_{66}Cl_2N_6O_6P_2Pd_2S_2$ (1302.95) calcd. C, 49.7, H, 5.1, N, 6.4, S, 4.9; found C, 49.9, H, 5.0, N, 6.7, S, 4.7.

2.6.3. [Pd {4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Me-N,S} {μ-$PPh_2(CH_2)_4PPh_2$-P,P}]$_2$ (3e)

Yield 74 % FTIR: 3311 [m, νN-H] 1579 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (d, $^{4}J_{PH}$ = 4.3 Hz, 2H, Hi), 8.21 (d, $^{3}J_{H^5H^6}$ = 9.0 Hz, 4H, H3/H5), 7.81 – 7.28 (m, 20H, PPh_2), 6.89 (d, $^{3}J_{H^6H^5}$ = 9.0 Hz, 4H, H2/H6), 4.60 (c, $^{3}J_{HH}$ = 5.1 Hz, 2H, NHMe), 3.81 (s, 6H, OMe), 2.93 (d, $^{3}J_{HH}$ = 5.0 Hz, 6H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 24.59 (s). $C_{48}H_{52}Cl_2N_6O_2P_2Pd_2S_2$ (1154.79) calcd. C, 49.9, H, 4.5, N, 7.3, S, 5.6; found C, 51.1, H, 4.7, N, 7.9, S, 5.9.

2.7. Preparation of the complex 1g-3g

Complexes were obtained preparing a solution of 15 cm^3 of 0.5 mmol of ligand and mixing that with a solution of 1 equivalent of $K_2[PdCl_4]$ in 5 cm^3 of water. After 24 hours of stirring the formation of an orange solid is observed.

2.7.1. [Pd {2, 3, 4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Me-N,S} {$PPh_2(CH_2)_4PPh_2$-P,P}]PF_6 (1g)

Yield 87 % FTIR: 3291 [m, νN-H] 1602 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.40 (d, $^{4}J_{PH}$ = 9.2 Hz, 1H, *Hi*), 7.85 – 7.20 (m, 21H, P*Ph*$_2$, *H5*), 6.53 (d, $^{3}J_{H^6H^5}$ = 9.3 Hz, 1H, *H6*), 4.77 (c, $^{3}J_{HH}$ = 5.4 Hz, 1H, N*H*Me), 3.81 (s, 3H, O*Me*), 3.63 (s, 3H, O*Me*), 3.13 (s, 3H, O*Me*), 2.88 (d, $^{3}J_{HH}$ = 4.9 Hz, 3H, NH*Me*). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 24.41 (d, $^{2}J_{PP}$ = 42.55 Hz, 1P), 21.40 (d, $^{2}J_{PP}$ = 42.55 Hz, 1P), -145.79 (sept, $^{1}J_{PF}$ = 721.44 Hz). $C_{40}H_{44}F_6N_3O_3P_3PdS$ (960.19) calcd. C, 50.0, H, 4.6, N, 4.4, S, 3.3; found C, 51.2, H, 4.9, N, 4.6, S, 3.7.

2.7.2. [Pd {2, 3, 4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Et-N,S} {$PPh_2(CH_2)_4PPh_2$-P,P}]PF_6 (2g)

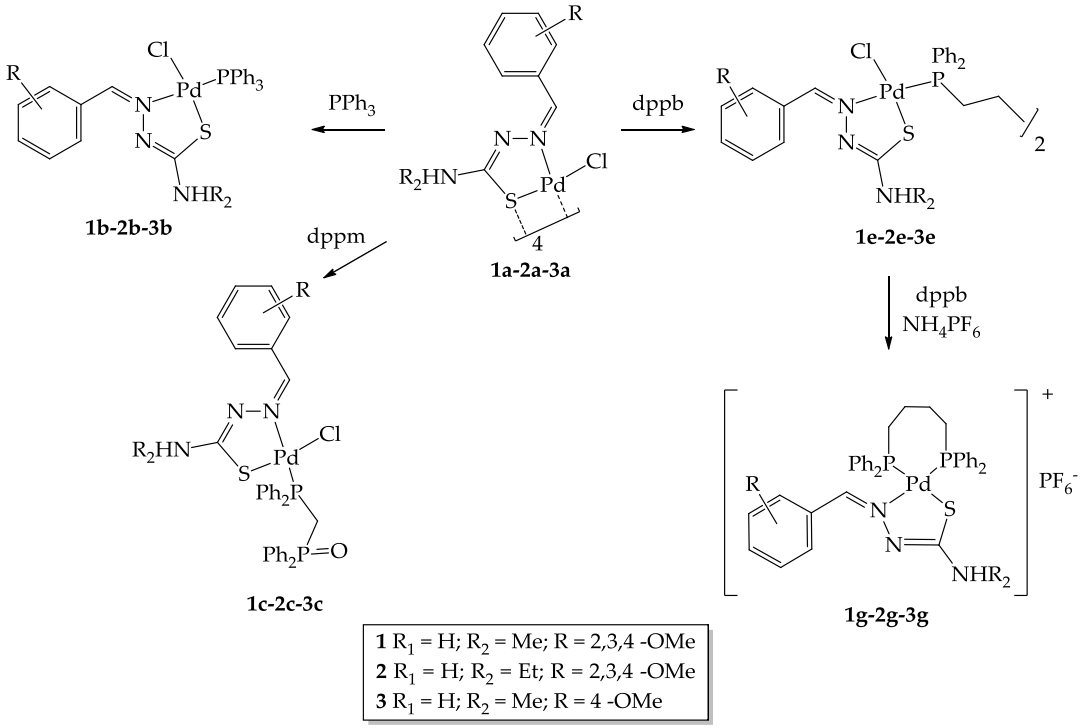
Yield 79 % FTIR: 3411 [m, νN-H] 1605 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, $^{4}J_{PH}$ = 8.9 Hz, 1H, *Hi*), 7.82 (d, $^{3}J_{H^5H^6}$ = 8.5 Hz, *H5*) 7.84 – 7.28 (m, 20H, P*Ph*$_2$), 6.78 (d, $^{3}J_{H^6H^5}$ = 8.5 Hz, 1H, *H6*), 4.74 (t, $^{3}J_{HH}$ = 5.1 Hz, 1H, N*H*Et), 3.92(s, 3H, O*Me*), 3.86 (s, 3H, O*Me*), 3.42 (dc, $^{3}J_{HH}$ = 7.2 Hz; 5.1 Hz, NHC*H*$_2$CH$_3$), 3.15 (s, 3H, O*Me*), 1.65 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H, NHCH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 25.67 (d, $^{2}J_{PP}$ = 47.88 Hz, 1P), 21.92 (d, $^{2}J_{PP}$ = 47.88 Hz, 1P), -146.27 (sept, $^{1}J_{PF}$ = 691.58). $C_{41}H_{46}F_6N_3O_3P_3PdS$ (974.22) calcd. C, 50.6, H, 4.8, N, 4.3, S, 3.3; found C, 50.7, H, 4.9, N, 4.5, S, 4.2.

2.7.3. [Pd {4-OMe-C_6H_2C(H)=N-N=C(S)-N(H)-Et-N,S} {$PPh_2(CH_2)_4PPh_2$-P,P}]PF_6 (3g)

Yield 76 % FTIR: 3299 [m, νN-H] 1595 [s, νC=N] cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.59 (d, $^{4}J_{PH}$ = 9.2 Hz, 1H, Hi), 7.91 – 7.20 (m, 22H, PPh_2, H3/H5), 6.65 (d, $^{3}J_{H^6H^5}$ = 9.2 Hz, 2H, H2/H6), 4.89 (c, $^{3}J_{HH}$ = 5.1 Hz, 1H, NHMe), 3.10 (s, 3H, OMe), 2.85 (d, $^{3}J_{HH}$ = 5.1 Hz, 3H, NHMe). ^{31}P{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 23.10 (d, $^{2}J_{PP}$ = 40.32 Hz, 1P), 20.24 (d, $^{2}J_{PP}$ = 40.32 Hz, 1P), -145.51 (sept, $^{1}J_{PF}$ = 758.27 Hz). $C_{38}H_{40}F_6N_3OP_3PdS$ (900.14) calcd. C, 50.7, H, 4.5, N, 4.7, S, 3.6; found C, 50.1, H, 4.2, N, 5.7, S, 4.1.

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, IR spectroscopy (data in the experimental section), and by ^{1}H, ^{31}P-{^{1}H}.



Scheme 1.

Synthesis of ligands **1, 2, 3** was performed mixing both reagents in water solution [13]. Formation of compounds **1-3a** was achieved trying to synthesize cyclopalladated products using $K_2[PdCl_4]$ under the same conditions which were described in previous papers [14]. The ^1H NMR show signals for all aromatic protons, this means that the C-Pd bond has not been formed, absence of the hydrazine proton signal in accordance with thiolate formation and in the IR spectra the ν(C=N) band is shifted *ca.* 15 cm^{-1} in relation to the ligand spectra, in agreement with N-Pd coordination. Also, the ν(C=S) stretch disappears on going to the complexes from the ligands. The structure of the complexes where could be better understood through molecular structure of compound **2a**.

Reactivity of compounds **1**-**3a** with different phosphine ligands was studied. When complexes **1**-**3a** react with triphenylphosphine, mononuclear complexes **1**-**3b** were obtained. The ^1H NMR of all phosphine complexes show ^{31}P-^1H; coupling when the reaction occurs through sulfur bridging position. Bis(diphenylphosphino)methane (dppm) reacts with these compounds in a monodentate mode **1**-**3c**, this behavior is common in cyclopalladated thiosemicarbazones [15]. Crystal structur of **1c** was obtained.

Bis(diphenylphosphine)butane (dppb) leads to the formation of dinuclear complexes **1**-**3e** where this ligand is bridging. The long carbon chain in this case allows bridge formation; this behavior is different from dppm which due to the short carbon chain cannot bridge two metal centers probably because of steric hindrance.

From compounds **1**-**3e** is possible to form chelate-phosphine complexes adding ammonium hexafluorophosphate which allows Pd-Cl bond cleavage.

3.1. Crystal structure of 2a

Suitable crystals for X-ray diffraction of compound **2a** have been obtained by the slow evaporation of chloroform solution. The molecular structure is showed in Figure 4, selected interatomic distances and angles are showed in Table 1. The crystal structure show tetranuclear nature of this molecule, a structure similar to tetranuclear cyclopalladated compounds. The main difference between **2a** and cyclopalladated compounds is the presence of terminal Pd-Cl bond instead of Pd-C bond. There were many coordination compounds of this type where other structures where supposed for example dinuclear compounds with bridge chlorine ligands. This structure

shows that perhaps these suppositions were wrong. Thiosemicarbazones prefer a coordination mode where the sulfur acts as a bridge between palladium atoms. The reason why this kind of structure was not previously found probably is because insolubility of the complexes. This example is an exceptional case, probably compound **2a** shows a higher solubility because of the R_3 substituent, in this case an ethyl group.

Table 1. Selected bond lengths (Å) and angles (º) for **2a**

Bond lengths (Å)					
Pd1-N1	2.058(3)	S1-Pd2	2.2932(10)	S4-Pd3	2.3171(10)
Pd1-S1	2.2402(11)	Pd2-S3	2.2468(10)	Pd3-S2	2.2337(10)
Pd1-S2	2.2969(10)	S3-Pd4	2.3016(11)	C12-S1	1.792(4)
Pd1-Cl1	2.3361(11)	Pd4-S4	2.2367(10)	S1-C28	1.832(4)
Angles (º)					
N1-Pd1-S1	83.86(9)	S2-Pd1-Cl1	85.92(4)	Pd1-S1-Pd2	119.82(4)
S1-Pd1-S2	94.40(4)	Cl1-Pd1-N1	96.26(9)	S1-Pd2-S3	90.79(4)

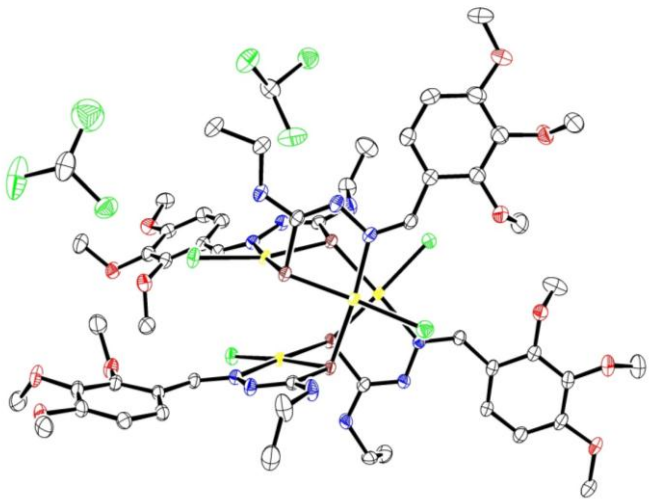


Figure 4. Molecular structure of complex **2a**.

Considering only a fragment composed by one palladium atom and a ligand unit (Figure 5) it is important to see that geometry of C=N bond has changed to *Z*. This conversion occurs probably during the deprotonation of the thiosemicarbazone, missing hydrazinic proton. As a result C6 is too far away from palladium atom, this distance avoid the formation of C-Pd bond in this compounds.

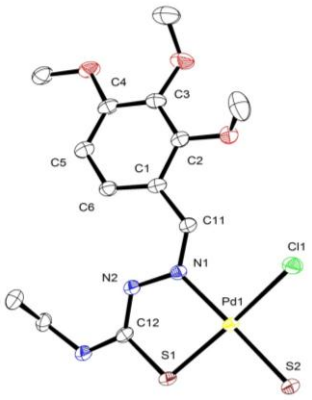


Figure 5. A fragment of complex **2a**.

Between the four palladium atoms sulfur atoms provide bridging. This links form an eight-membered structure which adopt a boat conformation (Figure 6). This type of structure is very close to the structure formed in cyclopalladated compounds. It also justifies similarities between reactivity of these coordination complexes and cyclopalladated compounds reacting with short chain diphosphine ligands which can act as monodentate.

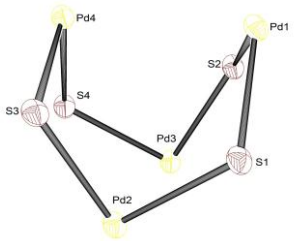


Figure 6. Eight-membered structure which a boat conformation.

3.2. Crystal structure of 3b

Suitable crystals for X-ray diffraction of compound **3b** have been obtained by the slow evaporation of chloroform solution. The molecular structure is showed in Figure 7, selected interatomic distances and angles are showed in Table 2. The crystal structure shows a molecule of **3b** and chloroform. This structure confirm that reaction takes place through the bridging sulfur atom, and that the phosphorous atom is in *trans* position to iminic nitrogen.

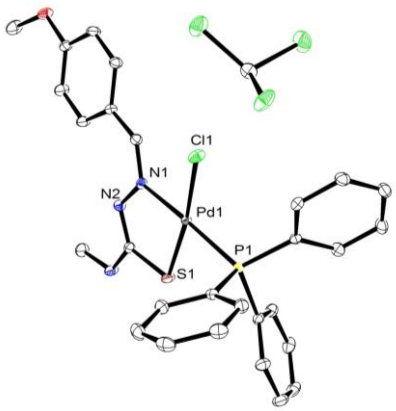


Figure 7. View of the molecular structure of complex **3b**.

Table 2. Selected bond lengths (Å) and angles (º) for **3b**

Bond lengths (Å)		**Angles (º)**	
Pd1-N1	2.0968(14)	N1-Pd1-Cl1	93.75(4)
Pd1-S1	2.2400(8)	S1-Pd1-N1	83.12(5)
Pd1-Cl1	2.3508(9)	S1-Pd1-P1	91.41(4)
Pd1-P1	2.2744(7)	Cl1-Pd1-P1	91.73(3)

3.3 Crystal structure of 1c

Suitable crystals for X-ray diffraction of compound **1c** have been obtained by the slow evaporation of chloroform solution. The molecular structure is showed in Figure 8, selected interatomic distances and angles are showed in Table 3. The crystal structure shows a molecule of **1c**.

Table 3. Selected bond lengths (Å) and angles (º) for **1c**

Bond lengths (Å)		**Angles (º)**	
Pd1-N1	2.094(3)	N1-Pd1-Cl1	94.67(10)
Pd1-S1	2.2407(13)	S1-Pd1-N1	83.38(10)
Pd1-Cl1	2.3450(12)	S1-Pd1-P1	94.66(5)
Pd1-P1	2.2729(12)	Cl1-Pd1-P1	87.15(4)

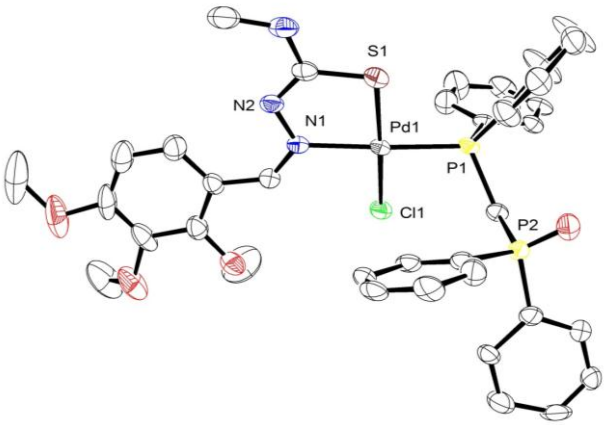


Figure 8. View of the molecular structure of complex **1c**.

4. Conclusions

Thiosemicarbazones form [*N*,*S*] complexes under certain circumstances. It is essential that isomerization of the iminic bond be allowed by R_1 being H. Coordination [*N*,*S*] complexes present a tetranuclear structure similar to cyclopalladated thiosemicarbazones. This is refleted in the similarity of the reactivity of the complexes. A further advantage with respect to cyclopalladated is that they present two reactive positions.

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Conflicts of Interest: The authors declare no conflict of interest.

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