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The Influence of Substituents at C^2 Carbon of Thiosemicarbazones on the Bonding Pattern of Bis(diphenylphopshano)alkanes in Palladium(II) Complexes

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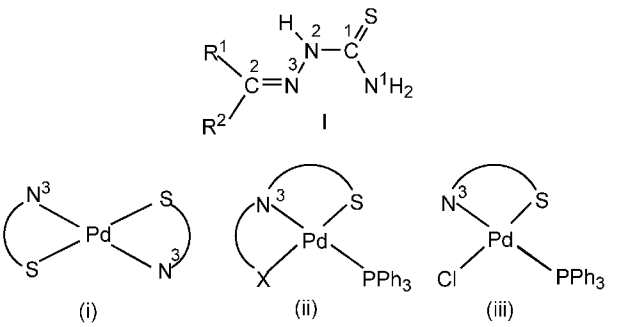
Abstract. Reactions of *trans*-$PdCl_2(PPh_3)_2$ with acetone thiosemicarbazone (Hactsc) and benzaldehyde thiosemicarbazone (Hbtsc) in a 1:1 molar ratio in the presence of Et_3N yielded the neutral complexes [Pd(η^2-N^3,S-actsc)(PPh_3)Cl] (**1**) and [Pd(η^2-N^3,S-btsc)(PPh_3)Cl] (**2**) respectively. In contrast, reactions of *cis*-$PdCl_2$(dppe) (dppe = bis(diphenylphosphanyl)ethane) and *cis*-$PdCl_2$(dppp) (dppp = bis(diphenylphosphanyl)propane) with Hbtsc gave the ionic complexes [Pd(η^2-N^2,S-btsc)(η^2-dppe)]Cl (**3**) and [Pd(η^2-N^3,S-btsc)(η^2-dppp)]Cl (**4**) because of the chelation effect. The reaction of salicylaldehyde thiosemicarbazone (H_2stsc) with *cis*-$PdCl_2$(dppm) (dppm = bis(diphenylphosphanyl)methane)- and *cis*-$PdCl_2$(dppp) yielded the dinuclear complexes [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppm)] (**5**) and [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppp)] (**6**). Complexes **1**−**6** were characterized with spectroscopic techniques [IR, ^{1}H, ^{31}P{^{1}H} NMR], and single-crystal X-ray crystallography. The ligands are negative bidentate in complexes **1**−**4** and di-negative tridentate (O, N^3, S) in complexes **5** and **6**. Diphosphanes exhibited both chelating (η^2; **3**, **4**) as well as bridging (μ; **5**, **6**) modes.

Introduction

Thiosemicarbazones (structure I, Scheme 1) are an important class of organic ligands, and have been explored for their analytical applications, variable bonding modes and biological relevance [1−3]. Palladium(II) and platinum(II) complexes with thiosemicarbazones have been particularly interesting because of their antitumor, antibacterial, antifungal and catalytic activities [4, 5]. In the absence of co-ligands such as tertiary phosphane or bipyridyl compounds, mono-, tri- and tetranuclear complexes of Pd^{II} with thiosemicarbazones have been reported [6].

Our research focused on reactions of thiosemicarbazones with transition metals [7], and a series of mononuclear palldium(II) complexes, namely (i) *trans*- [Pd(η^2-N^3,S-L)$_2$] (L = $ttsc^-$, $ftsc^-$) [8], (ii) [Pd(η^3-X,N^3,S-L)(PPh_3)] (X, L = C, $aptsc^{2-}$; N, $ptsc^{2-}$; O, $stsc^{2-}$) [9, 10], (iii) [Pd(η^2-N^3,S-L)(PPh_3)Cl] (L = $ttsc^-$, $ftsc^-$) [8], have been reported using thiophene-2-carbaldehyde thiosemicarbazone (Httsc), furan-2-carbaldehyde thiosemicarbazone (Hftsc), salicylaldehyde thiosemicarbazone (H_2stsc), acetophenone thiosemicarbazone (H_2aptsc) and pyrrole-2-carbaldehyde thiosemicarbazone (H_2ptsc) (Scheme 1).



Scheme 1.

In continuation of our interest in the chemistry of Pd^{II}-thiosemicarbazones, we used ditertiary phosphanes, which offer a variety of bonding possibilities (see Scheme 1), as co-ligands. In this paper, palladium(II) complexes with a series of thiosemicarbazones (Scheme 2) in presence of mono- and ditertiary phosphanes are reported.

Experimental Section

Materials and Methods

Benzaldehyde, acetone, salicylaldehyde, thiosemicarbazide, Ph_3P, bis(diphenylphosphanyl)methane (dppm), bis(diphenylphosphanyl-)propane (dppp) and $PdCl_2$ were purchased from Aldrich Sigma Ltd. The thiosemicarbazone ligands were prepared by the reported

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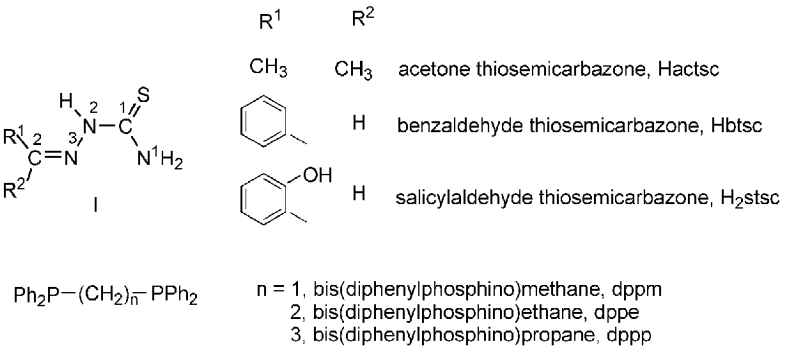

Scheme 2.

methods [11]. The ligand bis(diphenylphosphanyl)ethane (dppe) was prepared by a reported method [12]. The complexes $PdCl_2(PPh_3)_2$ and $PdCl_2L$ (L = dppm, dppe, dppp) were prepared by the reaction of a $PdCl_2$ solution in CH_3CN with PPh_3 or ditertiaryphosphane [13]. C, H and N analyses were carried out with a thermoelectron FLASHEA1112 analyzer. The melting points were determined with a Gallenkamp electrically heated apparatus. IR spectra were recorded as KBr pellets with a Pye−Unicam SP3−300 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as internal reference. The $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz with 85 % phosphoric acid as external reference.

[Pd(η²-N³,S-actsc)(PPh₃)Cl] (1)

To *trans*-$PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) suspended in toluene (15 mL) was added solid Hactsc (0.009 g, 0.09 mmol), followed by the addition of Et_3N (0.726 g, 7.175 mmol). The mixture was stirred for 3 h. A clear light orange solution formed and $Et_3NH^+Cl^-$ precipitated at the bottom of the flask. The solution was filtered to remove $Et_3NH^+Cl^-$ and allowed to evaporate at room temperature. After evaporation, a red crystalline product was formed. Yield: 0.021 g, 56 %, m.p. 248 °C. $C_{22}H_{23}ClN_3PPdS$: C, 49.4; H, 4.3; N, 7.9 %. Found: C, 48.9; H, 4.3; N, 7.1 %. **IR** (KBr): ν(N−H) 3526 b, 3338 sh, 3334 w, ν(C=N), δ(N−H) and ν(C=C) 1598 s, 1568 b, ν(P−C_{Ph}) 1090 s, ν(C−S) 842 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 7.71−7.84 (m, *o*-H, 6 H), 7.38−7.51 (m, *m* & *p*-H, 9 H), 4.45 (s, NH_2, 2 H), 2.70 (s, CH_3, 3 H), 2.12 (s, CH_3, 3 H). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 28,3, $\Delta\delta$ ($\delta_{complex}-\delta_{PPh3}$) = 33.0.

[Pd(η²-N³,S-btsc)(PPh₃)Cl] (2)

Compound **2** was prepared similarly using *trans*-$PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) and solid Hbtsc (0.013 g, 0.07 mmol). Yield: 0.023 g, 56 %, m.p. 265 °C. $C_{26}H_{23}ClN_3PPdS$: C, 53.4; H, 4.0; N, 7.2 %. Found: C, 53.5; H, 4.3; N, 7.1 %. **IR** (KBr): ν(N−H) 3467 s, 3461 sh, 3377 s, ν(C=N), δ(N−H) and ν(C=C) 1596 s, 1508 b, ν(P−C_{Ph}) 1095 s, ν(C−S) 840 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.58 (d, C^2H, 1 H), 8.14 (m, $C^{4,8}$H, 2 H), 7.72−7.79 (m, *o* & *p*-PhH, 9 H) 7.38−7.75 (m, *m*-H + C^{5-7}H, 6 H), 4.38 (s, NH_2, 2 H). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 18.0, $\Delta\delta$ ($\delta_{complex}-\delta_{PPh3}$) = 22.7.

[Pd(η²-N²,S-btsc)(η²-P,P-dppe)]Cl (3)

To $PdCl_2$(dppe) (0.05 g, 0.087 mmol) suspended in a 15 mL toluene-acetonitrile mixture (3:1 v/v) was added solid Hbtsc (0.016 g, 0.089 mmol), followed by the addition of Et_3N (0.726 g, 7.175 mmol). Afterwards, the mixture was stirred for 3 h. A clear orange solution formed. The solution was allowed to evaporate and after a few days, additionally formed $Et_3NH^+Cl^-$ was separated by filtration. After further evaporation, the filtrate gave a yellow solid, which was recrystallized from an acetonitrile-ethanol mixture. Yield: 0.037 g, 60 %, m.p. 180 °C. $C_{34}H_{32}ClN_3P_2PdS$: C, 56.8; H, 4.5; N, 5.8 %. Found: C, 57.1; H, 4.7; N, 6.1 %. **IR** (KBr): ν(N−H) 3426 b, 3348 sh, ν(C=N), δ(N−H) and ν(C=C) 1608 s, 1528 b, ν(P−C_{Ph}) 1095 s, ν(C−S) 842 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.51 (d, C^2H, 1 H), 8.14−8.18 (m, C^4H, 8 H, 2 H) 7.30−7.82 (m, *o*, *m* & *p*-H + C^{5-7}H, 23 H), 4.88 (s, NH_2, 2 H), 2.85 {m, $(CH_2)_2$, 4H}.

[Pd(η²-N³,S-btsc)(η²-P,P-dppp)]Cl·C₂H₅OH (4)

Compound **4** was prepared by the same method used for complex **3** with $PdCl_2$(dppp) (0.05 g, 0.084 mmol) and solid Hbtsc (0.015 g, 0.084 mmol). Yield: 0.034 g, 52 %, m.p. 205 °C. $C_{37}H_{40}ClN_3OP_2PdS$: C, 57.0; H, 4.1; N, 5.4 %. Found: C, 56.8; H, 4.4; N, 5.2 %. **^{1}H NMR** ($CDCl_3$): δ = 8.52 (d, C^2H, 1 H), 7.71−7.78 (m, *o*, *p* & *m*-H + C^{5-7}H, 23 H), 4.98 (s, NH_2, 2 H), 3.20 {m, $(CH_2)_3$, 6H}. **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 8.3, 4.1.

[Pd₂(η³-O,N³,S-stsc)₂(μ-dppm)] (5)

To $PdCl_2$(dppm) (0.05, 0.09 mmol) suspended in toluene (15 mL) was added H_2stsc (0.017 g, 0.09 mmol). Afterwards, Et_3N (1.452 g, 14.350 mmol) was added and the mixture was stirred for 4 h. Solid $Et_3NH^+Cl^-$ settled at the bottom of the flask was separated. Slow evaporation of the yellow solution at room temperature yielded yellow crystals of the product. Yield: 0.067 g, 65 %, m.p. 277 °C. $C_{41}H_{36}N_6O_2P_2Pd_2S_2$: C, 50.1; H, 3.6; N, 8.5 %. Found: C, 49.9; H, 3.8; N, 8.5 %. **IR** (KBr): ν(N−H) 3548 b, 3365 sh, 3280 w, ν(C=N), δ(N−H) and ν(C=C) 1600 s, 1587 b, ν(P−C_{Ph}) 1097 s, ν(C−S) 795 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.06 (d, C^2H, 2 H), 7.75 (m, *o*-H, 8 H), 7.16−7.37 (m, C^5H + *m* & *p*-H, 14 H), 6.59 (m, C^{6-8}H, 6 H), 4.78 (s, NH_2, 4H), 4.39 (t, CH_2, 2H). **$^{31}P\{^1H\}$ NMR** ($CDCl_3$): δ = 21.2, $\Delta\delta$ ($\delta_{complex}-\delta_{dppm}$) = 42.8.

[Pd₂(η³-O,N³,S-stsc)₂(μ-dppp)] (6)

Compound **6** was prepared by the same method used for compound **5** with $PdCl_2$(dppp) (0.05 g, 0.084 mmol) and solid H_2stsc (0.017 g, 0.084 mmol). Yield: 0.048 g, 56 %, m.p. 245 °C. $C_{43}H_{40}N_6O_2P_2Pd_2S_2$: C, 51.0; H, 4.00; N, 8.3 %. Found: C, 50.7;

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H, 4.3; N, 8.5 %. **IR** (KBr): ν(N−H) 3548 b, 3365 sh, 3280 w, ν(C=N), δ(N−H) and ν(C=C) 1600 s, 1587 b; ν(P−C_{Ph}) 1097 s, ν(C−S) 810 s cm^{-1}. **^{1}H NMR** ($CDCl_3$): δ = 8.20 (m, C^2H, 2 H), 7.2−7.75 (m, *o*-H, 8 H), 7.16−7.37 (m, C^5H + *m* & *p*-H, 14 H), 6.59 (m, C^{6-8}H, 6 H), 4.70 (s, NH_2, 4H), 1.96−2.25 {m, $(CH_2)_3$, 6H}.

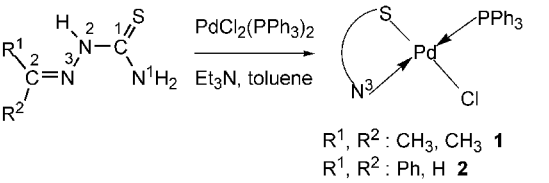
X-ray Crystallography

Single crystal of compounds **1**−**6** were mounted on Bruker AXS SMART APEX CCD (**1**, **2**), Bruker Smart CCD-1000 (**3**), Siemens P4 (**4**), Oxford Diffraction Gemini (**5**) and Bruker X8 Kappa Apex II (**6**) diffractometers each equipped with a graphite monochromator and Mo-K_α radiaton (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 298(2) (**1**), 100(2) (**2**, **6**), 293(2) (**3**), 295(2) (**4**) and 200(2) (**5**) K respectively. The data for complexes **1** and **2** were processed with SAINT and corrected for absorption using SADABS or multiscan. The structure was solved by direct methods and refined by full-matrix least-squares techniques using the program SHELXS-97 (**3**, **5**, **6**) and SHELXTL 6.14 (**1**, **2**) [14]. Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms. The data for **4** was collected using the θ−2θ technique. 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 full-matrix least-squares methods based on F^2. All hydrogen atoms were refined isotropically, fixed geometrically, and were not refined. 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]. 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-691196, 691197, 691198, 666764, 691199, and 691200 for **1**−**6** respectively.

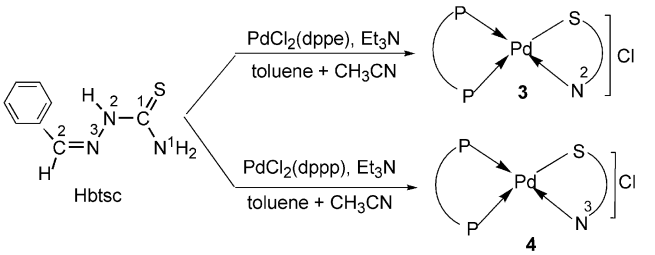
Results and Discussion

Synthesis

Reaction of $PdCl_2(PPh_3)_2$ with acetone thiosemicarbazone (Hactsc) in 1:1 molar ratio yielded orange complex [Pd(actsc)(PPh_3)Cl] (**1**); similar reaction with benzaldehyde thiosemicarbazone (Hbtsc) gave [Pd(btsc)(PPh_3)Cl] (**2**) (Scheme 3). Reactions of $PdCl_2$(dppe) and $PdCl_2$(dppp) with Hbtsc in 1:1 molar ratio yielded crystals of ionic complexes [Pd(btsc)(dppe)]Cl (**3**) and [Pd(btsc)(dppp)]Cl (**4**) respectively (Scheme 4). The behavior of salicylaldehyde thiosemicarbazone (H_2stsc) is different and on reaction with $PdCl_2$(dppm) and $PdCl_2$(dppp), it has formed



Scheme 3.



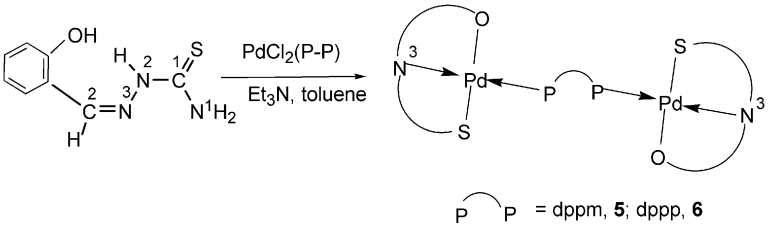
Scheme 4.

dinuclear complexes [Pd_2(stsc)$_2$(dppm)] (**5**) and [Pd_2(stsc)$_2$(dppp)] (**6**) respectively with bridging dppm and dppp ligands (Scheme 5). The deprotonation of N^2H group occurs in all the complexes and in **6**, additionally OH group also deprotonates. The thio-ligands are N^3, S-chelating in **1**, **2** and **4**; N^2,S-chelating in **3** and coordination is through O, N^3, S donor atoms in **5** and **6**.

Crystal Structures

Complexes **1**, **2**, **3** and **6** crystallize in the monoclinic space group whereas complexes **4** and **5** crystallize in the triclinic space group. The crystallographic data for complexes **1**−**6** are given in Table 1 and selected bond parameters are presented in Table 2.

In [Pd(η^2-N^3,S-actsc)(PPh_3)Cl] (**1**) (Figure 1), acetone thiosemicarbazonate (btsc$^-$) binds through nitrogen (N2 for **1**, N1 for **2**) and sulfur donor atoms to the Pd^{II} atom. The other two sites are occupied by the chlorido and PPh_3 ligands. The Pd−S, Pd−N and Pd−P bond lengths [2.2552(5), 2.118(2) and 2.2565(5) Å] of complex **1** are comparable with those of similar complexes reported in literature [8]. The S−Pd−Cl and N−Pd−P bond angles of complex **1** [170.32(2), 172.81(5)°] are close to linearity. The structure of [Pd(η^2-N^3, S-btsc)(PPh_3)Cl] (**2**) (Figure 2) is similar to **1**, its bond angles are somewhat closer to linearity [N−Pd−P, 175.34(10); S−Pd−Cl, 174.02(4)°]. Addition-



Scheme 5.

Table 1. Crystallographic data for Complexes **1**−**6**.

	1	**2**	**3**
Empirical formula	$C_{22}H_{23}ClN_3PPdS$	$C_{26}H_{23}ClN_3PPdS$	$C_{34}H_{32}ClN_3P_2PdS$
M	534.31	582.35	718.48
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$ (No. 14)
a /Å	9.4915(5)	10.3584(7)	15.103(6)
b /Å	25.0846(13)	14.4039(10)	15.964(6)
c /Å	9.6424(5)	17.0380(12)	16.437(6)
β /°	99.6990(10)	101.8400(10)	117.201(6)
V /Å^3	2262.9(2)	2488.0(3)	3525(2)
Z	4	4	4
Unique reflections/ R_{int}	5613, 0.0230	6108, 0.0249	6454, 0.0377
GOF	1.047[a)]	1.032[b)]	1.028[c)]
R indices (all data)	*R*1 = 0.0309, *wR*2 = 0.0737	*R*1 = 0.0593, *wR*2 = 0.1309	*R*1 = 0.0662, *wR*2 = 0.0937
	4	**5**	**6**
Empirical formula	$C_{37}H_{40}ClN_3OP_2PdS$	$C_{49}H_{48}N_{10}O_2P_2Pd_2S_2$	$C_{43}H_{40}N_6O_2P_2Pd_2S_2$
M	778.57	1147.83	1011.67
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$ (No. 14)
a /Å	9.832(1)	16.3294(4)	10.740(3)
b /Å	9.872(1)	18.4736(5)	45.015(10)
c /Å	18.491(2)	20.0836(5)	8.772(3)
α /°	79.40(1)	76.701(2)	−
β /°	80.70(1)	67.081(2)	105.647(5)
γ /°	78.03(1)	73.554(2)	−
V /Å^3	1711.5(3)	5302.5(2)	4084(2)
Z	2	4	4
Unique reflections/ R_{int}	6348, 0.0377	34450, 0.0429	8654, 0.0369
GOF	1.028[d)]	0.671[e)]	1.302[f)]
R indices (all data)	*R*1 = 0.0625, *wR*2 = 0.1308	*R*1 = 0.1634, *wR*2 = 0.0954	*R*1 = 0.0493 and *wR*2 = 0.1137

a) $w = 1/[S^2(F_o^2)+(0.0382P)^2+0.9240P]$; b) $w = 1/[S^2(F_o^2)+(0.0495P)^2+12.6758P]$; c) $w = 1/[S^2(F_o^2)+(0.0438P)^2]$; d) $w = 1/[S^2(F_o^2)+(0.0727P)^2]$; e) $w = 1/[S^2(F_o^2)+(0.0411P)^2]$; f) $w = 1/[S^2(F_o^2)+27.7956P]$ where $P = (F_o^2+2F_c^2)/3$ in each case.

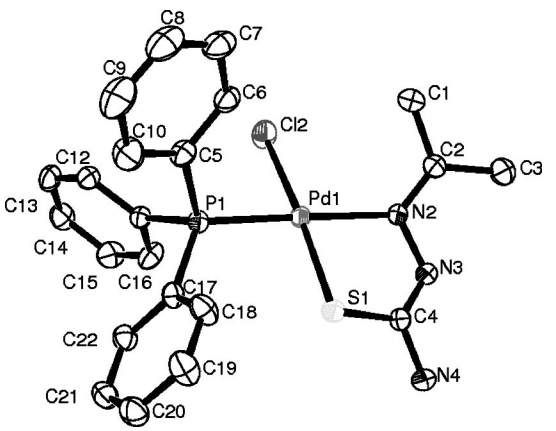


Figure 1. ORTEP diagram of the complex [Pd(η^2-N^3,S-actsc)(PPh$_3$)Cl] (**1**) with atomic numbering scheme. Hydrogens have been removed for clarity.

ally, the Pd−S, Pd−N and Pd−P bond lengths [2.236(2), 2.1024(4) and 2.254(1) Å] are similar to those of complex **1**. Hactsc and Hbtsc are negative chelating bidentate ligands and thus one halogen ion retained in each complex. Recently, we reported that acetophenone thiosemicarbazone (H_2aptsc), pyrrole-2-carbaldehyde thiosemicarbazone (H_2ptsc) and salicylaldehyde thiosemicarbazone (H_2stsc) behave as tridentate ligands, their coordination causes the removal of both halogens bonded to the palladium(II) ion and the formation of complexes with the stoichiometry [Pd(η^3-X,N^3,S-L)(PPh$_3$)] (X, L = C, aptsc^{2-}; N^4, ptsc^{2-}; O, stsc^{2-}) [9, 10].

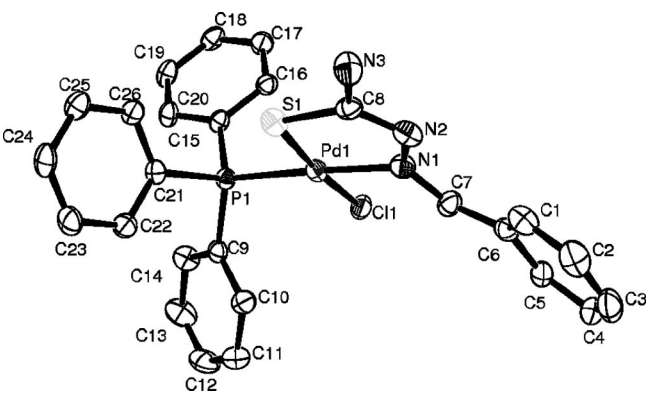


Figure 2. ORTEP diagram of the complex [Pd(η^2-N^3,S-btsc)(PPh$_3$)Cl] (**2**) with numbering scheme. Hydrogens have been removed for clarity.

In the mononuclear complexes [Pd(η^2-N^2,S-btsc)-(dppe)]Cl (**3**) (Figure 3), and [Pd(η^2-N^3,S-btsc)(dppp)]Cl (**4**) (Figure 4), the diphosphane ligands dppe and dppp are coordinated in a chelating manner to Pd^{II} and form five and six membered rings, respectively. Their Pd−P distances

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Table 2. Bond Parameters for Complexes **1**−**6**.

1			
Pd1−N2	2.118(2)	Pd1−Cl2	2.3576(6)
Pd1−P1	2.2565(5)	Pd1−S1	2.2552(5)
N(2)−Pd(1)−S(1)	80.84(4)	S1−Pd1−P1	94.52(2)
N(2)−Pd(1)−P(1)	172.81(5)	N2−Pd1−Cl2	99.26(4)
S(1)−Pd(1)−Cl(2)	170.32(2)	P1−Pd1−Cl2	86.24(2)
2			
Pd(1)−N(1)	2.102(4)	Pd(1)−Cl(1)	2.345(1)
Pd(1)−P(1)	2.254(1)	Pd(1)−S(1)	2.236(2)
N(1)−Pd(1)−S(1)	84.5(1)	N(1)−Pd(1)−Cl(1)	94.1(1)
N(1)−Pd(1)−P(1)	175.3(1)	S(1)−Pd(1)−Cl(1)	174.02(4)
S(1)−Pd(1)−P(1)	92.83(4)	P(1)−Pd(1)−Cl(1)	88.97(4)
3			
Pd1−N2	2.093(3)	Pd1−S1	2.367(2)
Pd1−P2	2.254(2)	Pd1−P1	2.263(2)
N2−Pd1−P2	171.51(8)	N2−Pd1−S1	69.48(8)
N2−Pd1−P1	103.94(8)	P2−Pd1−S1	102.15(4)
P2−Pd1−P1	84.52(4)	P1−Pd1−S1	171.61(4)
4			
Pd−N1	2.127(4)	Pd−P2	2.308(2)
Pd−S	2.294(2)	Pd−P1	2.267(2)
N1−Pd−P1	170.4(2)	N1−Pd−P2	99.3(2)
N1−Pd−S1	82.5(2)	P1−Pd−P2	88.07(5)
P1−Pd−S1	90.57(5)	S1−Pd−P2	175.89(5)
5			
Pd1A−N11A	2.013(2)	Pd1B−N11B	2.028(2)
Pd1A−O1A	2.018(1)	Pd1B−O1B	2.034(2)
Pd1A−S1A	2.2487(5)	Pd1B−S1B	2.2494(5)
Pd1A−P1A	2.2540(4)	Pd1B−P1B	2.2527(4)
Pd2A−N21A	2.017(1)	Pd2B−N21B	2.029(2)
Pd2A−O2A	2.0235(9)	Pd2B−O2B	2.029(1)
Pd2A−S2A	2.2474(4)	Pd2B−S2B	2.2508(4)
Pd2A−P2A	2.2527(4)	Pd2B−P2B	2.2541(4)
N11A−Pd1A−O1A	92.41(5)	N11B−Pd1A−O1B	93.47(5)
N11A−Pd1A−S1A	85.05(4)	N11B−Pd1B−S1B	84.01(4)
O1A−Pd1A−S1A	175.47(3)	O1B−Pd1B−S1B	175.00(3)
N11A−Pd1A−P1A	174.47(3)	N11B−Pd1B−P1B	174.63(3)
O1A−Pd1A−P1A	88.42(3)	O1B−Pd1B−P1B	88.18(3)
S1A−Pd1A−P1A	93.75(2)	S1B−Pd1B−P1B	93.95(2)
N21A−Pd2A−O2A	93.01(4)	N21B−Pd2B−O2B	92.67(5)
N21A−Pd2A−S2A	84.12(3)	N21B−Pd2B−S2B	84.89(4)
O2A−Pd2A−S2A	175.20(4)	O2B−Pd2B−S2B	174.88(4)
S2A−Pd2A−P2A	93.83(2)	S2B−Pd2B−P2B	93.95(2)
N21A−Pd2A−P2A	174.87(4)	N21B−Pd2B−P2B	173.97(4)
O2A−Pd2A−P2A	88.71(3)	O2B−Pd2B−P2B	88.02(3)
6			
Pd1−O11	2.025(3)	Pd2−N22	2.020(4)
Pd1−N12	2.026(4)	Pd2−O21	2.023(4)
Pd1−S1	2.243(2)	Pd2−S2	2.242(2)
Pd1−P1	2.260(2)	Pd2−P2	2.270(2)
O11−Pd1−N12	93.5(2)	N22−Pd2−O21	92.5(2)
O11−Pd1−S1	177.4(1)	N22−Pd2−S2	84.3(2)
N12−Pd1−S1	84.3(1)	O21−Pd2−S2	174.5(1)
O11−Pd1−P1	89.7(1)	N22−Pd2−P2	171.9(2)
N12−Pd1−P1	171.3(2)	O21−Pd2−P2	87.40(1)
S1−Pd1−P1	92.73(5)	S2−Pd2−P2	96.43(5)

[2.254(2) and 2.263(2) Å for **3**; 2.267(2) and 2.308(2) Å for **4**] are slightly different. The thiosemicarbazone ligand, in its deprotonated form btsc$^-$, coordinates through nitrogen (N2) and sulfur donor atoms in complex **3** whereas coordination in **4** happens through nitrogen (N1) and sulfur donor atoms. The Pd−N distance in complex **3** [2.093(3) Å] is shorter than in complex **4** [2.127(4) Å], whereas the Pd−S distance is longer [2.367(2) in **3**, 2.294(2) Å in **4**]. The bite angle is quite different in both complexes because of the binding mode. The difference in bonding may be attributed to the greater flexibility offered by dppp in comparison to dppe, which allows the formation of a five membered chelate ring by the thiosemicarbazone (N^3,S) rather than a four membered chelate ring (N^2,S). The N−Pd−P bond angle is comparable in both complexes [171.61(4)° for **3**; 170.4(2)° for **4**], whereas the other bond angle S−Pd−P in complex **4** [175.89(5)°] is closer to linearity than in complex **3** [171.51(8)°]. The chloride ions are outside the coordination sphere in both complexes to maintain charge neutrality and are stabilized by hydrogen bonding with amino protons [H···Cl = 3.089(3) and 3.465(3) Å for **3**]. The lattice is completed by ethanol, its −OH group is hydrogen bonded to Cl and amino groups. Complex **3** represents the first

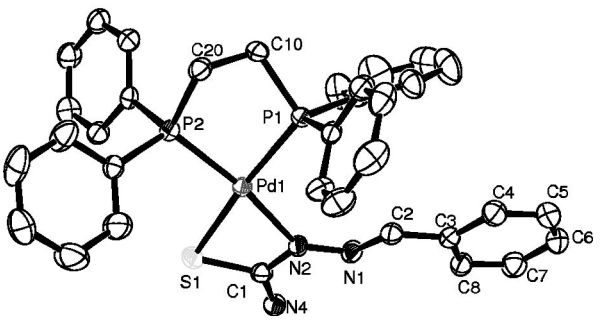

Figure 3. ORTEP diagram of the complex [Pd(η^2-N^2,S-btsc)(η^2-P,P-dppe)]Cl (**3**) with partial atomic numbering scheme. Hydrogens have been removed for clarity.

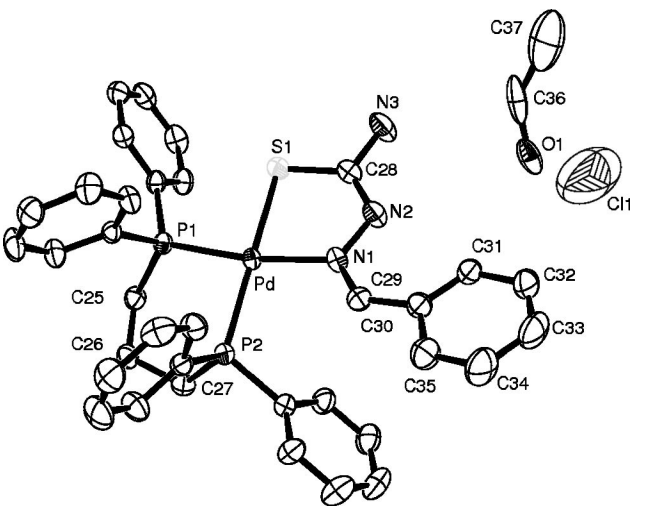

Figure 4. ORTEP diagram of the complex [Pd(η^2-N^3,S-btsc)(η^2-P,P-dppp)]Cl·C_2H_5OH (**4**) with partial atomic numbering scheme. Hydrogens have been removed for clarity.

Pd^{II}−thiosemicarbazone in which N^2,S-chelation takes place. N^2,S chelation has been reported earlier for Ru^{II}, Tl^{III} and Pb^{IV} complexes [19, 20]. Interestingly, depending on the nature of the thiosemicarbazone, dppe has shown bridging behavior in the dinucelar complex, [{Pd[1-(COMe)-3-{C(H)=N^3−N=C(-S)-NHR}C_8H_4N-κ$^3C^5N^3S$]}$_2$(μ-Ph_2P-$(CH_2)_2$−PPh_2)] (R = H, Me) [21]. The thio-ligand is negative tridentate in this complex binding through ring carbon (C^5), nitrogen (N^3) and sulfur donor atoms.

In the dimeric complexes [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppm)] (**5**) (Figure 5) and [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppp)] (**6**) (Figure 6), each Pd^{II} atom is coordinated by $stsc^{2-}$ through oxygen, nitrogen (N^3) and sulfur donors. Two of these units are bridged through dppm and dppp ligands, respectively. The unit cell of complex **5** is made up by two independent molecules with slightly different bond parameters (Table 2). This may be attributed to the different inter- and intramolecular hydrogen bondings. The crystal lattice is completed by acetonitrile, which is hydrogen bonded to pendant amino hydrogen atoms. In [Pd_2(stsc)$_2$dppm] (**5**) (only one molecule will be discussed), the Pd−O [2.0180(11), 2.0235(9) Å], Pd−N [2.0134(13), 2.01739(11) Å], Pd−S [2.2487(5), 2.2474(4) Å] and Pd−P [2.2527(4), 2.2540(4) Å] bond lengths of the two Pd^{II} atoms differ only slightly from one another as the bonding is similar. These parameters are comparable to those of the monomeric complex [Pd(η^3-O,N^3,S-stsc)(PPh_3)] [10] reported earlier. The O−Pd−N bite angle is ≈ 92.5° and the N−Pd−S bite angle is ≈ 85.0°. The *trans* O−Pd−S bond angles [175.47(3), 175.20(4)°] and N−Pd−P [174.47(3), 174.87(4)°] are quite close to linearity.

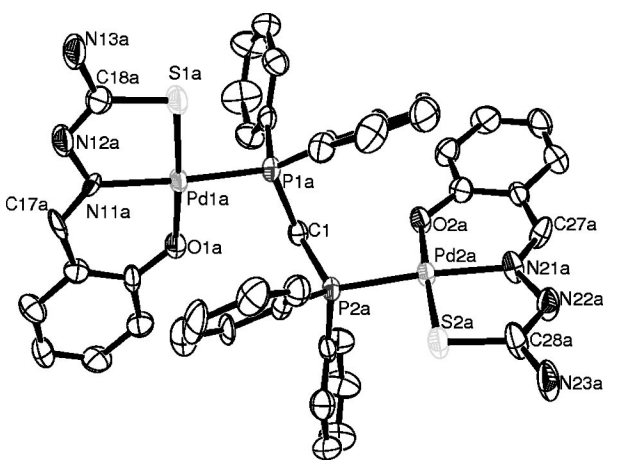

Figure 5. ORTEP diagram of one of the two crystallographically independent units of the complex [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppm)] (**5**) with partial atomic numbering scheme. Hydrogens and solvent molecules have been removed for clarity.

The increase in spacer length of the connecting PPh_2 groups of dppp in **6** vs. dppm in **5** does not affect the Pd−O [2.025(3), 2.023(4) Å] and Pd−S [2.243(2), 2.242(2) Å] bond lengths, however, the Pd−N [2.026(4), 2.020(4) Å] bond lengths, which are trans to Pd−P are longer. Whereas the *trans* bond angles O−Pd−S [177.42(11), 174.45(11)°] are quite close to linearity, the other *trans* angles N−Pd−P deviate significantly from linearity [171.28(12), 171.87(12)°].

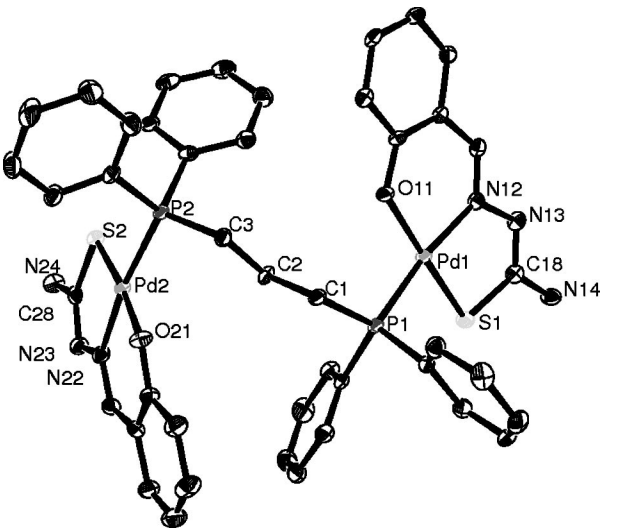

Figure 6. ORTEP diagram of complex [Pd_2(η^3-O,N^3,S-stsc)$_2$(μ-dppp)] (**6**) with partial atomic numbering scheme. Hydrogens have been removed for clarity.

Solution Phase Studies

NMR Spectroscopy

The signals of the −NH protons of the free ligands were absent in all above complexes **1**−**6**, thus supporting deprotonation during complexation. Additional deprotonation of the −OH groups in complexes **5** and **6** was supported by the absence of the corresponding proton signals in their ^{1}H NMR spectra. The $-NH_2$ protons appear as single signal in all complexes because of the free rotation of the $-NH_2$ group along the C^1-N^1 bond axis. In contrast, of two broad signals are observed in the free ligands, because of the restricted rotation of the $-NH_2$ group along the C^1-N^1 bond axis at room temperature [11].

The $^{31}P\{^1H\}$ NMR spectra of complexes **1** and **2** with the ligand PPh_3 show a single signal with a coordination shift of ≈ 32 ppm. In dppm complex **5**, a single signal is observed, demonstrating the equivalence of the phosphorous atoms of the bridging ligand. The $^{31}P\{^1H\}$ NMR spectrum of mononuclear complex **4** shows two signals owing to two different chemical environments of the chelating dppp ligand.

Conclusions

The co-ligand change from monodentate phosphanes to bisphosphanes altered the stoichiometry of the complexes, however, the bonding modes of the thiosemicarbazones remained the same (N^3,S chelation in complexes **1**, **2** and **4**) except for complex **3**, which showed an N^2,S chelation for the first time. The diphosphanes, however, behaved differ-

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ently with a change of the R^1 group at C^2. For R^1 = phenyl, the coordination mode of the diphosphanes is chelating (**3**, **4**), and for R^1 = 2-hydroxyphenyl, the bonding mode is bridging (**5**, **6**). Thus, the bonding mode of the diphosphane co-ligand is influenced by the substituents at the C^2 carbon of the thiosemicarbazone molecule in the mixed ligand complexes.

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References

[1] a) D. X. West, S. Padhye, P. B. Sonawane, *Struct. Bonding (Berlin)* **1991**, *76*, 4; b) J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 197; c) D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yerande, *Coord. Chem. Rev.* **1993**, *123*, 49.

[2] a) R. K. Mahajan, T. P. S. Walia, Sumanjit, T. S. Lobana, *Talanta* **2005**, *67*, 755; b) R. K. Mahajan, T. P. S. Walia, Sumanjit, T. S. Lobana, *Anal. Sci.* **2006**, *22*, 389; c) R. K. Mahajan, R. Kaur, T. S. Lobana, *Ind. J. Chem.* **2006**, *45A*, 639; d) R. K. Mahajan, I. Kaur, T. S. Lobana, *Talanta* **2003**, *59*, 101.

[3] a) L. J. Ashfield, A. R. Cowley, J. R. Dilworth, P. S. Donnelly, *Inorg. Chem.* **2004**, *43*, 4121; b) J. S. Casas, M. V. Castano, M. C. Cituenyes, A. Sanchez, J. Sordo, *Polyhedron* **2002**, *21*, 1651; c) J. S. Casas, E. E. Castellano, M. Macias, M. C. Rodriguez-Arguelles, A. Sanchez, J. Sordo, *J. Chem. Soc., Dalton Trans.* **1993**, 353.

[4] a) P. Pelagatti, A. Venturini, A. Leporati, M. Carcelli, M. Costa, A. Bacchi, G. Pelizzi, C. Pellizi, *J. Chem. Soc., Dalton Trans.* **1998**, 2715; b) D. Kovala-Demertzi, P. N. Yadav, M. A. Demertzis, J. P. Jasiski, F. J. Andreadaki, I. D. Kostas, *Tetrahedron Lett.* **2004**, *45*, 2923.

[5] E. Bermejo, R. Carballo, A. Castineiras, R. Dominguez, A. E. Liberta, C. Maichle-Moessmer, M. M. Salberg, D. X. West, *Eur. J. Inorg. Chem.* **1999**, 965.

[6] a) J. M. Vila, M. T. Pereira, J. M. Ortigueira, M. Grana, D. Lata, A. Suarez, J. J. Fernandez, A. Fernandez, M. Lopez-Torres, H. Adams, *J. Chem. Soc., Dalton Trans.* **1999**, 4193; b) A. Amoeda, M. Grana, J. Martinez, M. Teresa-Pereira, M. Lopez-Torres, A. Fernandez, J. J. Fernandez, J. M. Vila, *Eur. J. Inorg. Chem.* **2002**, 613; c) J. Martinez, L. A. Adiro, J. M. Antelo, M. Teresa-Pereira, J. J. Fernandez, J. M. Vila, *Polyhedron* **2006**, *25*, 2848.

[7] a) T. S. Lobana, Rekha, R. J. Butcher, A. Castineiras, E. Bermejo, P. V. Bharatam, *Inorg. Chem.* **2006**, *45*, 1535; b) T. S. Lobana, P. Kumari, R. J. Butcher, *Inorg. Chem. Commun.* **2008**, *11*, 11; c) T. S. Lobana, S. Khanna, Rekha, G. Hundal, R. Sultana, Manisha, R. J. Butcher, A. Castineiras, *Cryst. Growth Des.* **2008**, *8*, 1203; d) T. S. Lobana, S. Khanna, R. J. Butcher, A. D. Hunter, M. Zeller, *Inorg. Chem.* **2007**, *46*, 5826.

[8] T. S. Lobana, G. Bawa, G. Hundal, A. P. S. Pannu, R. J. Butcher, B.-J. Liau, C. W. Liu, *Polyhedron* **2007**, *26*, 4993.

[9] T. S. Lobana, G. Bawa, G. Hundal, M. Zeller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 931.

[10] T. S. Lobana, G. Bawa, A. Castineiras, R. J. Butcher, *Inorg. Chem. Commun.* **2007**, *10*, 506.

[11] T. S. Lobana, A. Sanchez, J. S. Casas, A. Castineiras, J. Sordo, M. S. Garcia-Tasenda, E. M. Vazquez-Lopez, *J. Chem. Soc., Dalton Trans.* **1997**, 4289.

[12] a) A. M. Aguion, *J. Org. Chem.* **1964**, *29*, 1660; b) T. S. Lobana, R. Singh, *Polyhedron* **1995**, *14*, 907.

[13] W. L. Steffen, G. J. Palenik, *Inorg. Chem.* **1976**, *15*, 2432.

[14] G. M. Sheldrick, *SHELXL-97*, Program for the Refinement Of Crystal Structures; University of Göttingen; Göttingen, Germany, **1997**.

[15] *XSCANS*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1994**.

[16] *International Tables for X-ray Crystallography*, Kluwer, Dordrecht, The Netherlands, **1995**, vol. C.

[17] G. M. Sheldrick, *SHELXTL-PC*, release 5.03, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1995**.

[18] G. X. Win, L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[19] a) F. Basuli, M. Ruf, C. G. Pierpont, S. Bhattacharya, *Inorg. Chem.* **1998**, *37*, 6113; b) F. Basuli, S.- M. Peng, S. Bhattacharya, *Inorg. Chem.* **1997**, *36*, 5645; c) D. Mishra, S. Naskar, M. G. B. Drew, S. K. Chattopadhyay, *Polyhedron* **2005**, *24*, 1861; d) F. Basuli, S. M. Peng, S. Bhattacharya, *Inorg. Chem.* **2000**, *39*, 1120; e) T. S. Lobana, G. Bawa, R. J. Butcher, B.-J. Liaw, C. W. Liu, *Polyhedron* **2006**, *25*, 2897.

[20] a) J. S. Casas, E. E. Castellano, M. Macias, M. C. Rodriguez-Arguelles, A. Sanchez, J. Sordo, *J. Chem. Soc., Dalton Trans.* **1993**, 353; b) J. S. Casas, E. E. Castellano, J. Ellena, M. S. Garcia-Tasende, A. Sanchez, J. Sordo, A. Touceda-Varela, *Inorg. Chem. Commun.* **2004**, *7*, 1109.

[21] A. Amoedo, L. A. Adrio, J. M. Antelo, J. Martinez, M. T. Pereira, A. Fernandez, J. M. Vila, *Eur. J. Inorg. Chem.* **2006**, *15*, 3016.

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