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Cyclometallated thiosemicarbazone palladium(II) compounds: The first crystal and molecular structures of mononuclear complexes with a η^1-diphosphine ligand

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Abstract

Treatment of the thiosemicarbazones 2-$XC_6H_4C(Me)$=NN(H)C(=S)NHR (R = Me, X = F, **a**; R = Et, X = F, **b**; R = Me, X = Cl, **c**; R = Et, X = Br, **d**) with potassium tetrachloropalladate(II) in ethanol, lithium tetrachloropalladate(II) in methanol or palladium(II) acetate in acetic acid, as appropriate, gave the tetranuclear cyclometallated complexes $[Pd\{2\text{-}XC_6H_3C(Me)=NN=C(S)NHR\}]_4$ (**1a**–**1d**). Reaction of **1a**–**1d** with the diphosphines $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) or *trans*-Ph_2PCH=$CHPPh_2$ (*trans*-dpe) in 1:2 molar ratio gave the dinuclear cyclometallated complexes $[\{Pd[2\text{-}XC_6H_3C(Me)=NN=C(S)NHR]\}_2(\mu\text{-diphosphine-}P,P)]$ (**2a**–**5a**, **3b**, **3d**, **4c**, **5c**). Reaction of **1a**, **1b** with the short-bite or long-bite diphosphines, dppm or *cis*-dpe, in a 1:4 molar ratio gave the mononuclear cyclometallated complexes $[Pd\{2\text{-}XC_6H_3C(Me)=NN=C(S)NHR\}(diphosphine\text{-}P)]$ (**6a**, **6b**, **7a**). The molecular structure of ligand **a** and of complexes **1a**, **3d**, **5a**, **5c**, **6a**, **6b** and **7a** have been determined by X-ray diffraction analysis. The structure of complex **7a** shows that the long-bite *cis*-bis(diphenylphosphino)ethene phosphine appears as monodentate with an uncoordinated phosphorus donor atom.

Keywords: Thiosemicarbazones; Cyclometallation; Palladium; Diphosphines; Crystal structure

1. Introduction

Cyclometallated complexes are known for a wide range of ligands and extended coverage regarding the aspects of their chemistry is described in various general reviews [1–5]. Cyclometallated compounds are involved in diverse branches of chemistry such as regiospecific organic and organometallic synthesis [6–8], insertion reactions [9,10], asymmetric synthesis with optically active cyclometallated compounds [11,12], catalytic materials [13–15], liquid crystals [16], and species with specific antitumoral activity [17–20].

We have studied thiosemicarbazone CNS donors which yield tetranuclear cyclometallated complexes [21]; for the related compounds with terdentate ligands possessing CNN [22a] or CNO [22b] donor atoms, only mononuclear species were isolated. In the case of the thiosemicarbazones, these produce tetranuclear compounds with two distinct palladium-sulfur bonds, i.e., $Pd–S_{chelating}$ and $Pd–S_{bridging}$, binding tightly to the metal as terdentate [C, N, S], and when treated with tertiary diphosphines, in the resulting compounds each metal atom is bonded to only one phosphorus atom, the strength of the $Pd–S_{chelating}$ bond preventing the chelating bidentate mode of the diphosphine ligand [21a,21c]. Hence, in the resulting complexes, the corresponding diphosphine ligand either bridges two metal centres, yielding dinuclear compounds, or

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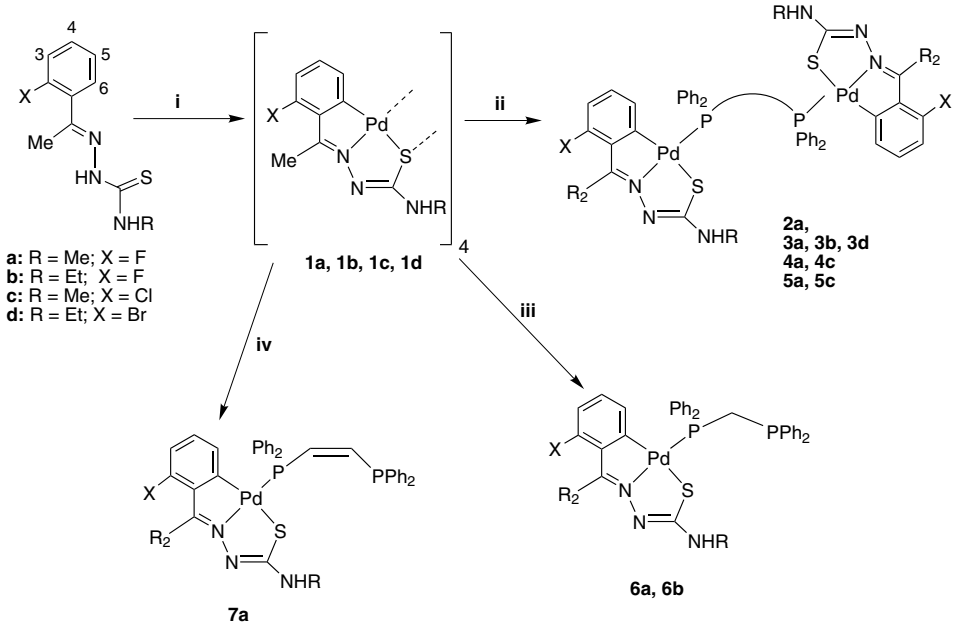
behaves as a η^1-ligand, producing mononuclear species. Whether the diphosphine coordinates through one or the two phosphorus donors is a function of the nature of the ligand and of the reaction conditions, both of which may be modulated appropriately, as we report herein. Therefore, described in the present paper is the account concerning the synthesis and characterization of a new series of mono-, di- and tetranuclear cyclopalladated complexes derived from halogenated thiosemicarbazone ligands, inclusive of the first crystal and molecular structures of the corresponding mononuclear compounds with the pertinent η^1-diphosphine.

2. Results and discussion

The ligands **a**–**d** were prepared by reaction of 4-methyl or 4-ethyl-3-thiosemicarbazide with 2′-fluoro-, 2′-chloro or 2′-bromo acetophenone as appropriate, which were fully characterized (see Section 4). Characteristic ν(N–H) bands for the NHR and NH groups appeared ca. 3300 and 3200 cm^{-1}, respectively, in the IR spectra, the latter disappears in the spectra of the complexes [23]; the typical ν(C=N) and ν(C=S) stretches were situated ca. 1600 and 830 cm^{-1}, respectively. The ^{1}H NMR spectra showed signals ca. δ 8.6 and δ 7.5 for the NHR and NH protons, respectively. From them the cyclometallated complexes shown in Scheme 1 could be prepared by any one of the three alternative methods described, i.e., (a) potassium tetrachloropalladate in ethanol; (b) lithium tetrachloropalladate in methanol; or (c) palladium(II) acetate in glacial acetic acid, leading in all cases to the tetranuclear species **1a**–**1d**, as air-stable solids, with the ligand in the *E*,*Z* configuration, which were fully characterized (preparative details, characterizing microanalytical, mass spectra, IR and ^{1}H and ^{31}P–{^{1}H} NMR data are in Section 4). The mass spectrum (FAB) showed peaks at *m*/*z* 1318 (**1a**), 1375 (**1b**), 1384 (**1c**) and 1620 (**1d**) for the molecular ion whose isotopic composition suggests a tetranuclear complex of formula $C_{40}H_{40}F_4N_{12}Pd_4S_4$ (**1a**), $C_{44}H_{48}F_4N_{12}Pd_4S_4$ (**1b**), $C_{40}H_{40}Cl_4N_{12}Pd_4S_4$ (**1c**) and $C_{44}H_{48}Br_4N_{12}Pd_4S_4$ (**1d**) (see Section 4). This has been confirmed by the crystal structure resolution of complex **1a** (vide infra). The ν(C=N) band was shifted to lower wavenumbers upon complex formation by ca. 30 cm^{-1} [24] in agreement with coordination of the palladium atom to the C=N moiety through the nitrogen lone pair [25,26]. Deprotonation of the –NH– group was clear from the absence of the N*H* resonance in the ^{1}H NMR spectra [27,28], which induces loss of the C=S double bond character as confirmed by the non-existence of the ν(C=S) band. Further proof could be ascertained by comparison of the C–S lengths in the crystal structures of **a**, and of **1a** and **5a**–**7a**, which showed lengthening of this bond in the latter cases.

2.1. Reactivity of the complexes

Prior to describing the reactivity of the aforementioned compounds a brief regarding this issue is mandatory. We have shown that tetranuclear cyclometallated thiosemicarbazone compounds, such as those described above, when reacted with tertiary phosphines only experience cleavage of the Pd–$S_{bridging}$ bond, whereas the Pd–$S_{chelating}$ bond prevails in all cases, even when strong chelating diphosphines are employed, making these ligands excellent terdentate [C,N,S] pincer species. Hence, although one might consider that, under the appropriate conditions, derivatives with the diphosphine bonded to the metal as monodentate leaving



Scheme 1. Reaction conditions: (i) $K_2[PdCl_4]$/EtOH; (ii) PP/acetone, **2**: PP = $Ph_2PCH_2PPh_2$; **3**: PP = $Ph_2P(CH_2)2PPh_2$; **4**: PP = $Ph_2P(CH_2)_3PPh_2$; **5**: PP = *trans*-$Ph_2PCH{=}CHPPh_2$; (iii) $Ph_2PCH2PPh_2$/acetone; and (iv) *cis*-$Ph_2PCH{=}CHPPh_2$/acetone.

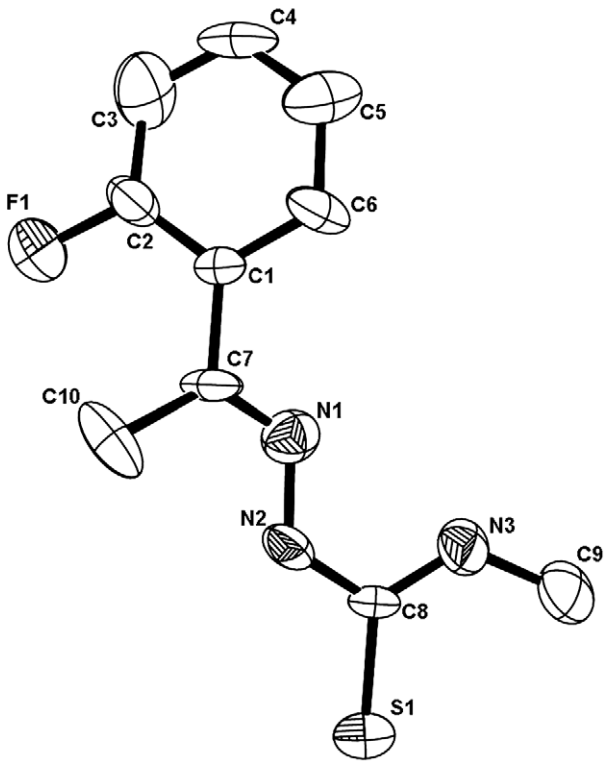


Fig. 1. An ORTEP drawing of the molecular structure for a with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–C(7) 1.489(4); N(1)–C(7) 1.279(4); N(1)–N(2) 1.386(3); N(2)–C(8) 1.348(4); S(1)–C(8) 1.694(3); C(8)–N(3) 1.325(4); C(6)–C(1)–C(7) 121.0(3); N(1)–C(7)–C(1) 115.1(3); C(7)–N(1)–N(2) 117.1(3); C(8)–N(2)–N(1) 118.9(3); N(3)–C(8)–N(2) 116.9(3); N(3)–C(8)–S(1) 124.1(2); N(2)–C(8)–N(1) 119.0(2).

one uncoordinated phosphorus atom could be obtained, long-chain diphosphines failed to do so, yielding dinuclear compounds with the phosphine bridging the two metal centers; regrettably, only in the case of short bite diphosphines such as $Ph_2PCH_2PPh_2$, dppm, and $Ph_2PC(=CH_2)PPh_2$, vdpp, could the desired compounds be attained, of which no crystal structures had yet been reported. However, even in the latter cases the phosphine may bridge two metals and mixtures of the mono- and dinuclear compounds have been found by us [21a]. These compounds may behave as bidentate [*P*,*S*] metalloligands as we have previously shown [21d]. We then reasoned that although diphosphines bearing a carbon chain of two or more atoms are not prone to behave as monodentate, should there be steric hindrance between the corresponding cyclometallated moieties, phosphine linkage would be limited to only one phosphorus donor. In order to prove our assertion, we sought out to develop the chemistry related to the case with *cis*-$Ph_2PCH{=}CHPPh_2$ as is described below, which typifies the first example where a long-bite diphosphine coordinates as monodentate in cyclometallated thiosemicarbazones compounds.

Thus, when **1a**–**1d** were treated with the corresponding diphosphine in 1:2 molar ratio, the compounds **2a**, **3a**, **3b**, **3d**, **4a**, **4c**, **5a** and **5c** were obtained as pure air-stable solids, which were fully characterized (see Section 4). The ^{1}H NMR spectra showed the H5 resonance was coupled to the ^{31}P nucleus and shifted to lower frequency by ca. 1–1.5 ppm, suggesting a P *trans* to N arrangement [29]. The ^{31}P resonance was a singlet signal in accordance with two equivalent phosphorus nuclei in each case; the chemi-

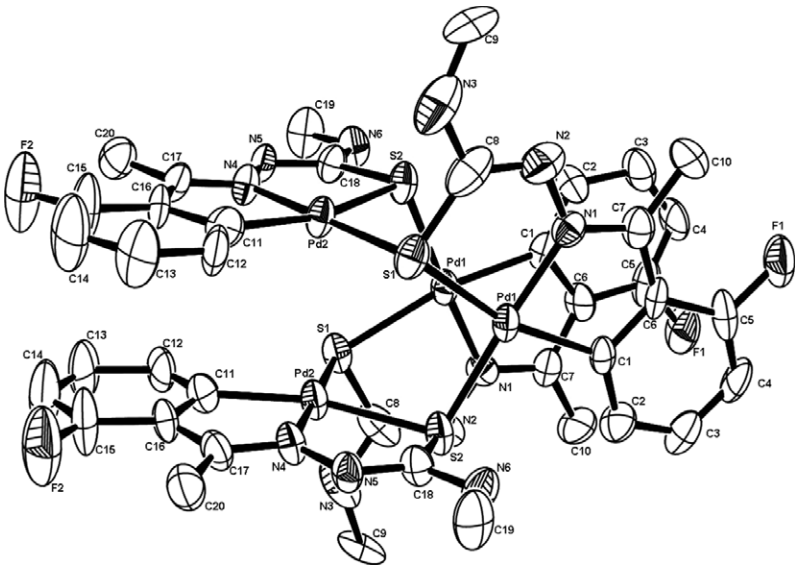


Fig. 2. An ORTEP drawing of the molecular structure for **1a** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–C(1) 2.023(11); Pd(1)–N(1) 1.985(10); Pd(1)–S(2) 2.325(4); Pd(1)–S(1) 2.369(3); S(1)–C(8) 1.747(17); N(2)–C(8) 1.338(17); N(1)–N(2) 1.377(13); N(1)–C(7) 1.321(13); C(1)–C(7) 1.440(17); Pd(2)–C(11) 2.000; (12); Pd(2)–N(4) 2-010(10); Pd(2)–S(1)#1 2.332(4); Pd(2)–S(2) 2.366(3); S(2)–C(18) 1.783(12); N(5)–C(18) 1.298(13); N(4)–N(5) 1.382(13); N(4)–C(17) 1.304(14); C(16)–C(17) 1.448(17); C(1)–Pd(1)–N(1) 80.6(5); C(1)–Pd(1)–S(2) 96.6(4); S(1)–Pd(1)–S(2) 95.85(14); N(1)–Pd(1)–S(1) 83.9(3); N(1)–Pd(1)–S(2) 177.0(3); C(1)–Pd(1)–S(1) 163.6(4); C(11)–Pd(2)–N(4) 81.8(5); C(11)–Pd(2)–S(1)#1 97.4(4); S(1)#1–Pd(2)–S(2) 98.44(13); N(4)–Pd(2)–S(2) 82.3(3); N(4)–Pd(2)–S(1)#1 179.2(3); C(11)–Pd(2)–S(2) 163.1(4).

cal shift values also supported a phosphorus *trans* to nitrogen geometry [30,31,11].

Treatment of **1a**–**1d** with the short-bite and long-bite diphosphines, dppm or *cis*-dpe, respectively, in 1:4 molar ratio produced the compounds **6a**, **6b** and **7a**, as pure air-stable solids. Characteristic microanalytical and spectroscopic data are given in Section 4. The mononuclear compounds showed cleavage of only the Pd–$S_{bridging}$ bonds giving coordination of the phosphine to the metal atom only through one phosphorus atom. The ^{31}P NMR spectra showed two doublets assigned to the two non-equivalent phosphorus nuclei; the ^{31}P resonance of the phosphorus nucleus bonded to the metal center appeared at higher frequency. For **6a** and **6b** the resonance for the CH_2 protons of the phosphine, which are part of an ABXY spin system, appeared as an apparent doublet ca. 3.2 ppm; for compound **7a** the ethylene phosphine protons belong to an AA′XX′ spin system and appear as an apparent triplet at 5.81 ppm, with an *N* value of 28 Hz.

2.2. Structural studies: crystal structures of ligand ***a*** and of complexes ***1a, 3d, 5a, 5c, 6a, 6b*** and ***7a***

Suitable crystals were grown by slowly evaporating a chloroform/*n*-hexane solutions. The crystal structures of

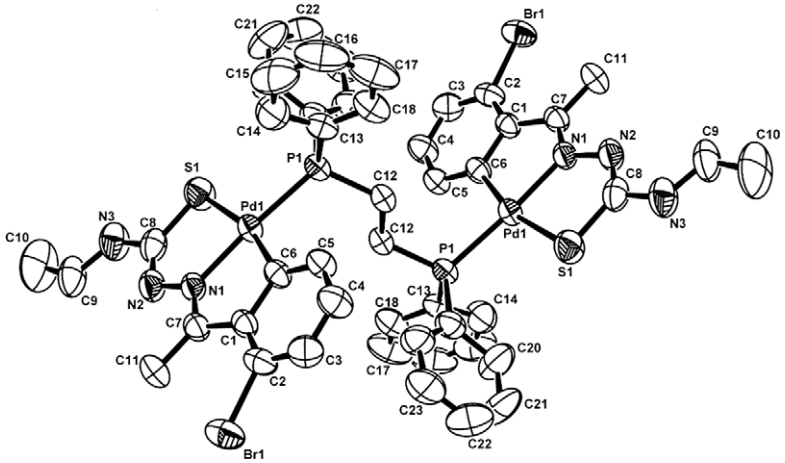


Fig. 3. An ORTEP drawing of the molecular structure for **3d** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.025(5); Pd(1)–C(1) 2.042(6); Pd(1)–P(1) 2.2544(16); Pd(1)–S(1) 2.3225(19); S(1)–C(8)1.766(8); N(2)–C(8)1.286(10); N(3)–C(8) 1.356(6);N(1)–N(2) 1.371(7); N(1)–C(7) 1.286(8); C(1)–C(7)1.496(8); P(1)–C(12) 1.829(6); P(1)–C(13) 1.807(7); P(1)–C(19) 1.834(7); N(1)–Pd(1)–C(6) 80.4(2); C(6)–Pd(1)–P(1) 96.47(17); P(1)–Pd(1)–S(1) 99.53(7); N(1)–Pd(1)–S(1) 83.69(16); N(1)–Pd(1)–P(1) 176.03(16); C(1)–Pd(1)–S(1) 163.78(17).

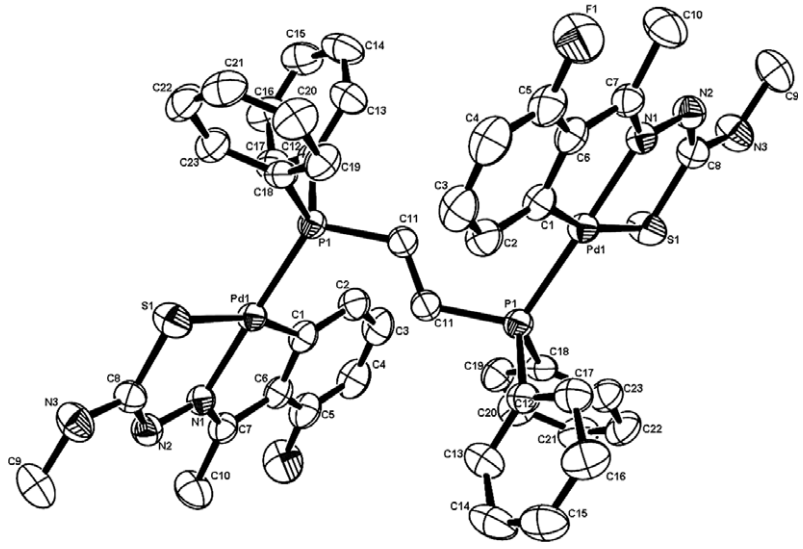


Fig. 4. An ORTEP drawing of the molecular structure for **5a** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.022(2); Pd(1)–C(1) 2.036(2); Pd(1)–P(1) 2.2421(7); Pd(1)–S(1) 2.3208(8); S(1)–C(8) 1.759(3); N(2)–C(8) 1.309(3); N(3)–C(8) 1.342(3); N(1)–N(2) 1.381(3); N(1)–C(7) 1.297(3); C(6)–C(7) 1.478(4); P(1)–C(11) 1.818(3); P(1)–C(12) 1.821(3); P(1)–C(18) 1.824(2); N(1)–Pd(1)–C(1) 81.26(9); C(1)–Pd(1)–P(1) 97.97(8); P(1)–Pd(1)–S(1) 97.51(3); N(1)–Pd(1)–S(1) 83.25(6); N(1)–Pd(1)–P(1) 178.77(6); C(1)–Pd(1)–S(1) 164.51(8).

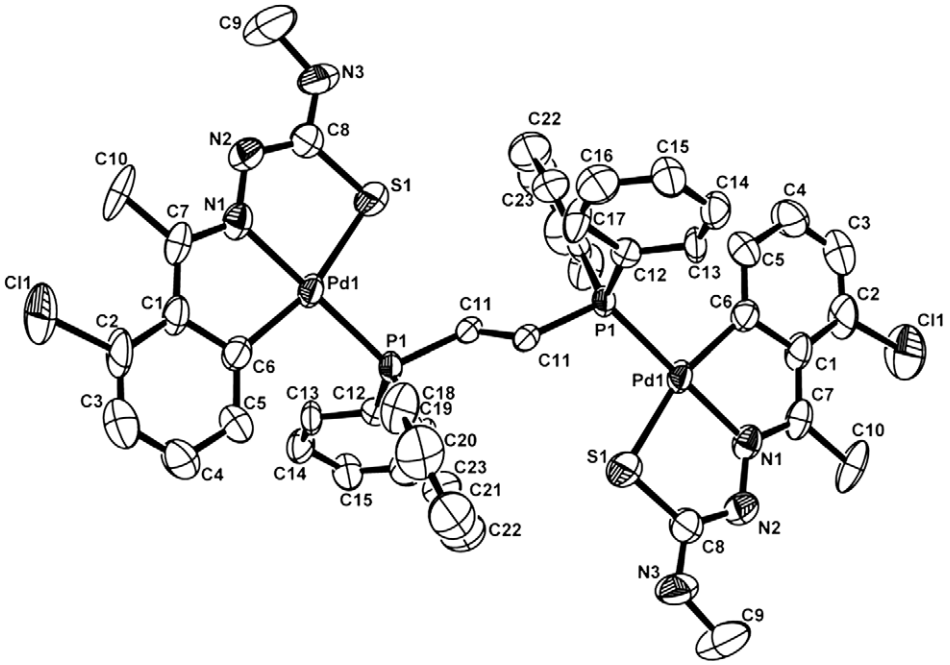


Fig. 5. An ORTEP drawing of the molecular structure for **5c** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.012(9); Pd(1)–C(6) 2.023(12); Pd(1)–P(1) 2.259(3); Pd(1)–S(1) 2.327(4); S(1)–C(8) 1.764(12); N(2)–C(8) 1.323(14); N(3)–C(8) 1.313(13); N(1)–N(2) 1.380(12); N(1)–C(7) 1.314(14); C(1)–C(7) 1.427(15); P(1)–C(11) 1.795(10); P(1)–C(12) 1.799(10); P(1)–C(18) 1.807(11); N(1)–Pd(1)–C(6) 81.0(4); C(6)–Pd(1)–P(1) 99.1(3); P(1)–Pd(1)–S(1) 96.18(12); N(1)–Pd(1)–S(1) 83.6(3); N(1)–Pd(1)–P(1) 178.7(3); C(6)–Pd(1)–S(1) 164.7 (3).

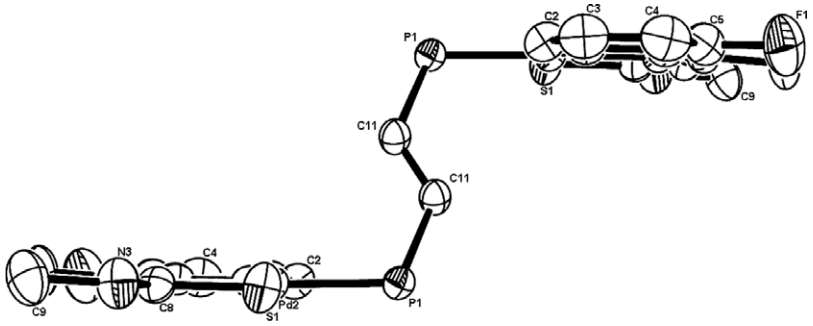


Fig. 6. An ORTEP drawing of the molecular structure for **5a** depicting the parallel arrangement of the cyclometallated moieties.

the complexes are shown in Figs. 1–8, respectively. Crystal data are given in Tables 1 and 2.

2.2.1. 2-$FC_6H_4C(Me)$=NN(H)C(=S)NHMe (**a**)

Ligand **a** crystallizes in the orthorhombic $C2cb$ space group as the *E*,*Z*-isomer with relation to the N(1)–C(7) and N(8)–C(3) bonds, respectively, Fig. 1.

This arrangement is often found in thiosemicarbazones with at least one hydrogen attached to N(3) due to weak N(3)–H(3)···N(1) hydrogen bonding. The C(8)–S(1), 1.747(17) Å, and the N(1)–C(7) bond distances, 1.321(13) Å, are consistent with a formal double bond character. The C(1)–C(7)–N(1) 111.7(12)° and C(7)–N(1)–N(2) 118.1(12)° bond angles, are in agreement with sp^2 hybridization of the carbon and nitrogen atoms of the C=N moiety. The thioamide chain C(7)–N(1)–N(2)–C(8)–[S(1)]–N(3) is planar (rms = 0.0367) and at an angle of 39.4(4)° with the fluorinated phenyl ring (rms = 0.0015). The parameters for the hydrogen bonding interaction in ligand **a** are as follows: H(3)···O(1) 2.55 Å, N(3)···O(1) 3.224(3) Å, N(3)–H(3)···O(1) 136.4°, H(3)···N(1) 2.23 Å, N(3)···N(1) 2.624(4) Å, N(3)–H(3)···N(1) 107.7°, H(1S)···S(1)#1 2.57(6) Å, O(1)···S(1)#1 3.364(5) Å, O(1)–H(1S)···S(1)#1 158(5) °, H(2)···S(1)#2 2.98 Å, N(2)···S(1)#2 3.736(3) Å, N(2)–H(2)···S(1)#2 147.9°, with the symmetry transformations #1: $x - 1/2, -y + 2, z + 1/2$; #2: $x, -y + 2, -z$.

2.2.2. [Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHMe}]$_4$ (**1a**)

The core of the molecule consists of an eight-membered ring of alternating palladium and sulfur atoms, Fig. 2.

The remaining two coordination sites of each palladium atom are occupied by the phenyl carbon atom and the

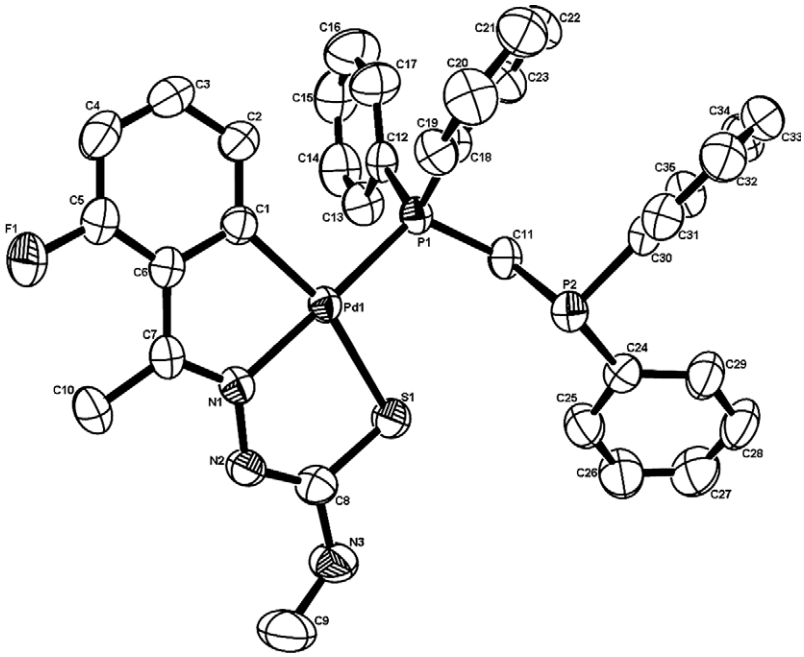


Fig. 7. An ORTEP drawing of the molecular structure for **6a** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.034(3); Pd(1)–C(1) 2.035(3); Pd(1)–P(1) 2.2592(8); Pd(1)–S(1) 2.3204(10); S(1)–C(8) 1.753(4); N(2)–C(8)1.307(5); N(3)–C(8) 1.352(5); N(1)–N(2) 1.387(4); N(1)–C(7) 1.292(4); C(6)–C(7) 1.467(5); P(1)–C(11) 1.839(3); P(2)–C(11) 1.862(3); N(1)–Pd(1)–C(1) 81.21(12); C(1)–Pd(1)–P(1) 97.44(10); P(1)–Pd(1)–S(1) 98.52(3); N(1)–Pd(1)–S(1) 82.75(8); N(1)–Pd(1)–P(1) 177.75(8); C(1)–Pd(1)–S(1) 163.81(10).

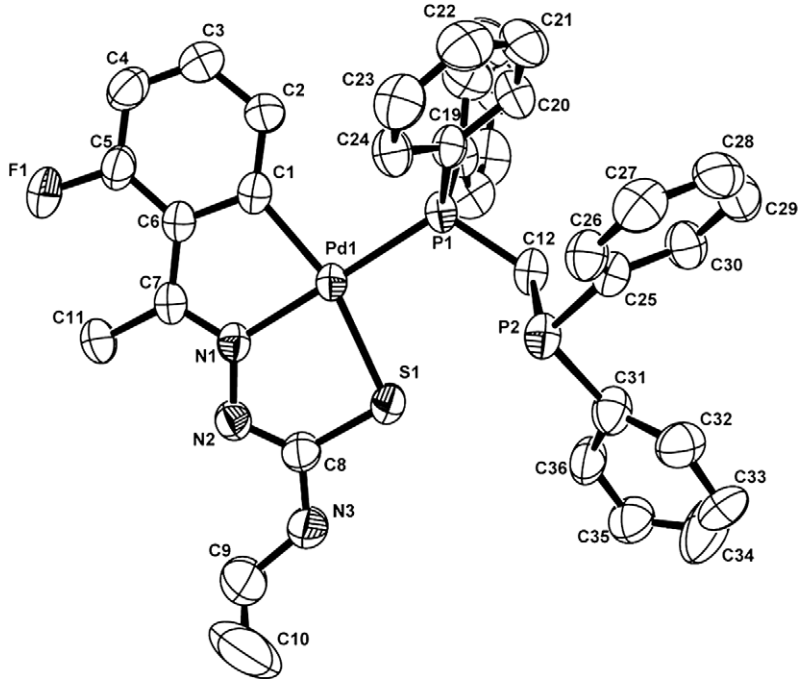


Fig. 8. An ORTEP drawing of the molecular structure for **6b** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.031(4); Pd(1)–C(1) 2.038(5); Pd(1)–P(1) 2.2616(13); Pd(1)–S(1) 2.3323(15); S(1)–C(8) 1.758(6); N(2)–C(8) 1.313(7); N(3)–C(8) 1.343(7); N(1)–N(2) 1.379(6); N(1)–C(7) 1.300(6); C(6)–C(7) 1.457(8); P(1)–C(12) 1.858(5); P(2)–C(12) 1.855(5); N(1)–Pd(1)–C(1) 81.30(19); C(1)–Pd(1)–P(1) 97.74(15); P(1)–Pd(1)–S(1) 98.34(5); N(1)–Pd(1)–S(1) 82.56(12); N(1)–Pd(1)–P(1) 177.45(12); C(1)–Pd(1)–S(1) 163.80(15).

nitrogen atom of the C=N group in a square-planar environment. Each of the four palladium atoms belongs to two fused five-membered chelate rings: the *C,N* metalacycle and the *N,S*-chelate moiety, as a result of bonding to a tridentate *C,N,S* ligand. The C(8)–S(1) and S(2)–C(18) distances, 1.747(17) and 1.783(12) Å, respectively, are consistent with

Table 1
Crystal data and structure refinement data for **a**, **1a**, **3d** and **5a**

Compound	**a**	**1a**	**3d**	**5a**
Empirical formula	$C_{10}H_{13}FN_3O_{0.50}S$	$C_{40}H_{40}F_4N_{12}Pd_4S_4$	$C_{48}H_{48}Br_2N_6P_2Pd_2S_2$	$C_{48}H_{44}C_{l6}F_2N_6P_2Pd_2S_2$
Formula weight	234.29	1318.68	1207.60	1294.45
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	1.54184	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Prism	Monoclinic	Triclinic
Space group	$C2cb$	$I41/a$	$C2/c$	$P\bar{1}$
Unit cell dimensions				
a (Å)	7.4210(7)	13.688(5)	29.709(5)	10.5849(15)
b (Å)	23.1470(17)	13.688(5)	18.535(3)	11.2957(16)
c (Å)	13.6180(8)	52.59(2)	10.0522(17)	12.4969(17)
α (°)				86.684(5)
β (°)			99.005(3)	66.445(4)
γ (°)				76.396(5)
V (Å^3)	2339.2(3)	9854(6)	5467.1(16)	1330.2(3)
Z	8	8	4	1
D_{calc} (Mg/m^3)	1.331	1.778	1.467	1.616
Absorption coefficient (mm^{-1})	2.410	1.664	2.290	1.163
F(000)	984	5184	2408	648
Crystal size (mm^3)	$0.40 \times 0.28 \times 0.08$	$0.44 \times 0.24 \times 0.16$	$0.30 \times 0.20 \times 0.13$	$0.38 \times 0.16 \times 0.13$
θ Range for data collection (°)	3.82–57.52	2.61–28.02	1.30–26.40	1.78–30.62
Index ranges	$-8/h/8$, $-25/k/0$, $-14/l/0$	$-18/h/0$, $-18/k/0$, $0/l/69$	$-37/h/36$, $0/k/23$, $0/l/12$	$-15/h/15$, $-15/k/16$, $-16/l/17$
Reflections collected	1598	6429	5613	20765
Independent reflections (R_{int})	1598 (0.0000)	5951 (0.0846)	5613 (0.0000)	8021 (0.0380)
Completeness to θ	99.8% (57.52°)	99.8% (28.02°)	99.9% (26.40°)	97.9% (30.62°)
Absorption correction	Semi-empiric	Semi-empiric	Semi-empiric	Semi-empiric
Maximum and minimum transmission	0.8306 and 0.4457	0.7767 and 0.5280	0.7550 and 0.5466	0.8635 and 0.6662
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1598/1/148	5951/13/299	5613/6/329	8021/0/322
Goodness-of-fit on F^2	1.071	0.902	1.004	0.949
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0433$, $wR_2 = 0.1169$	$R_1 = 0.0599$, $wR_2 = 0.1189$	$R_1 = 0.0523$, $wR_2 = 0.1574$	$R_1 = 0.0353$, $wR_2 = 0.0774$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.1212$	$R_1 = 0.3078$, $wR_2 = 0.1757$	$R_1 = 0.0920$, $wR_2 = 0.1853$	$R_1 = 0.0657$, $wR_2 = 0.0874$
Largest difference in peak and hole (e Å^{-3})	0.255 and −0.292	1.085 and −0.793	1.673 and −1.080	0.662 and −0.633

increased single-bond character, and the C(8)–N(2) and N(5)–C(18) distance, 1.338(17) and 1.298(13) Å, respectively, with increased double-bond character in the deprotonated form. The Pd–$S_{chelating}$ distances [Pd(1)–S(2) 2.325(4) and Pd(2)–S(1)#1 2.332(4)] are shorter than the Pd–$S_{bridging}$ ones [Pd(1)–S(1) 2.369(3) and Pd(2)–S(2) 2.366(3)] putting forward the greater *trans* influence of the phenyl carbon as compared to the imine nitrogen atom. The Pd(1)–Pd(1)# and Pd(2)–Pd(2)# lengths of 3.3001(10) and 3.3262(12) Å, respectively, preclude any Pd–Pd interactions.

2.2.3. [{Pd[2-$BrC_6H_3C(Me)$=NN=C(S)NHEt]}$_2$(μ-$Ph_2P(CH_2)_2PPh_2$–P,P)] (**3d**), [{Pd[2-$FC_6H_3C(Me)$=NN=C(S)NHMe]}$_2$(μ-Ph_2PCH=CHPPh_2–P,P)] (**5a**), [{Pd[2-ClC_6H_3-C(Me)=NN=C(S)NHMe]}$_2$(μ-Ph_2PCH=CHPPh_2–P,P)] (**5c**)

The crystals consist of discrete molecules, separated by normal van der Waals distances. The palladium(II) atom in each case is bonded to four different donor atoms, a tridentate *C*,*N*,*S* thiosemicarbazone through the aryl C(1) or C(6) carbon, the imine N(1) nitrogen, and the thioamide S(1) sulfur atom, and to a phosphorus atom P(1) of the bridging diphosphine ligand, in a slightly distorted square-planar coordination, [Pd(1), N(1), S(1), C(6), P(1), plane 1] (rms = 0.0495 Å) **3d**, [Pd(1), N(1), S(1), C(1), P(1), plane 1] (rms = 0.0060 Å) **5a**, [Pd(1), N(1), S(1), C(6), P(1), plane 1] (rms = 0.0049 Å) **5c** (see Figs. 3–5).

The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, in the range 99.1(3)–80.4(2)°; angles N(1)–Pd(1)–C(6), N(1)–Pd(1)–C(1) for **5c**, and N(1)–Pd(1)–S(1) on the one hand, and angles C(6)–Pd(1)–P(1), C(1)–Pd(1)–P(1) for **5c**, and P(1)–Pd(1)–S(1), on the other, are diminished and increased by ca. 7–9 Å, respectively, consequent upon formation of the two five-membered rings. All bond distances are in their typical ranges, with allowance for Pd–N bond lengthening due to the *trans* influence of the phosphine ligand, which is reflected in the Pd(1)–N(1) distance of 2.025(5) Å for **3d**, 2.034(3) Å for **5a**, 2.012(9) Å for **5c** (cf. sum of the covalent radii for palladium and nitrogen, 2.01 Å [32]), also, the Pd–C of 2.042(6) Å for **3d**, 2.035(3) Å for **5a**, 2.023(12) Å for **5c**, bond length is shorter than the expected value of 2.081 Å probably induced by partial multiple-bond character [33,34]. The

Table 2
Crystal data and structure refinement data for **5c**, **6a**, **6b** and **7a**

Compound	**5c**	**6a**	**6b**	**7a**
Empirical formula	$C_{23}H_{21}ClN_3PPdS$	$C_{36}H_{33}Cl_3FN_3P_2PdS$	$C_{37}H_{34}Cl_3FN_3P_2PdS$	$C_{36}H_{32}FN_3P_2PdS$
Formula weight	544.31	833.40	846.42	726.05
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71073	0.71073	0.71069
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P21/n$
Unit cell dimensions				
a (Å)	9.191(5)	10.7745(2)	10.84840(10)	10.276(5)
b (Å)	11.331(5)	11.92770(10)	11.9862(2)	15.983(5)
c (Å)	12.229(5)	15.6328(2)	15.8380(2)	21.088(5) Å
α (°)	80.900(5)	86.9720(10)	86.7630(10)	
β (°)	69.200(5)	78.4630(10)	78.7630(10)	101.354(5)
γ (°)	81.631(5)	68.6900(10)	68.4240(10)	
Volume (Å^3)	1170.1(9)	1833.44(4)	1878.16(4)	3396(2)
Z	2	2	2	4
D_{calc} (Mg/m^3)	1.545	1.510	1.497	1.420
Absorption coefficient (mm^{-1})	1.080	0.904	0.884	0.737
$F(000)$	548	844	858	1480
Crystal size (mm^3)	$0.22 \times 0.09 \times 0.06$	$0.50 \times 0.30 \times 0.20$	$0.30 \times 0.25 \times 0.20$	$0.37 \times 0.21 \times 0.09$
θ Range for data collection (°)	1.83–24.79	1.33–28.27	1.31–28.26	1.61–26.45
Index ranges	$-9/h/10$, $-13/k/13$, $0/l/14$	$-9/h/14$, $-15/k/15$, $-15/l/20$	$-12/h/14$, $-8/k/15$, $-21/l/20$	$-12/h/12$, $0/k/20$, $0/l/26$
Reflections collected	3869	11572	12898	6985
Independent reflections (R_{int})	3869 (0.0000)	8553 (0.0193)	8910 (0.0238)	6985 (0.0000)
Completeness to θ	96.1% (24.79°)	94.1% (28.27°)	95.7% (28.26°)	99.8% (26.45°)
Absorption correction	Semi-empiric	Semi-empiric	Semi-empiric	Semi-empiric
Maximum and minimum transmission	0.9380 and 0.7971	0.8398 and 0.6605	0.8430 and 0.7773	0.9366 and 0.7722
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	3869/0/273	8553/12/491	8910/70/472	6985/0/399
Goodness-of-fit on F^2	1.020	1.012	1.028	0.948
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0674$, $wR_2 = 0.1086$	$R_1 = 0.0441$, $wR_2 = 0.1061$	$R_1 = 0.0622$, $wR_2 = 0.1555$	$R_1 = 0.0329$, $wR_2 = 0.0682$
R indices (all data)	$R_1 = 0.1936$, $wR_2 = 0.1507$	$R_1 = 0.0597$, $wR_2 = 0.1158$	$R_1 = 0.0904$, $wR_2 = 0.1756$	$R_1 = 0.0753$, $wR_2 = 0.0806$
Largest difference in peak and hole (e Å^{-3})	1.033 and −1.165	0.988 and −0.958	1.214 and −1.151	0.353 and −0.505

S(1)–C(8) bond length, 1.766(8) Å for **3d**, 1.753(4) Å for **5a**, 1.764(12) Å for **5c**, and the N(2)–C(8) length, 1.286(10) Å for **3d**, 1.307(5) Å for **5a**, 1.323(14) Å for **5c**, are consistent with increased single and double bond character, respectively, as a result of deprotonation. The planes at palladium: the coordination plane [Pd(1), N(1), S(1), C(6) or C(1), P(1), plane 1], the metallacycle [Pd(1), C(1), C(6), C(7), N(1), plane 2], the coordination ring [Pd(1), N(1), N(2), C(8), S(1), plane 3] and the metallated phenyl ring [C(1), C(2), C(3), C(4), C(5), C(6), plane 4], are nearly coplanar (angles between planes: 1/2 = 3.38(0.12), 1/3 = 2.31(0.10), 1/4 = 8.17(0.15), 2/3 = 2.42(0.13), 2/4 = 4.86(0.20), 3/4 = 6.47(0.14)° for **3d**; 1/2 = 1.45(0.05), 1/3 = 1.35(0.04), 1/4 = 1.87(0.08), 2/3 = 0.53(0.06), 2/4 = 0.88(0.10), 3/4 = 0.54(0.08)° for **5a**; 1/2 = 1.76(0.15), 1/3 = 1.36(0.17), 1/4 = 2.65(0.28), 2/3 = 0.40(0.20), 2/4 = 3.25(0.35), 3/4 = 3.47(0.31)° for **5c**). Therefore, the two cyclometallated moieties in each of the three structures are essentially planar with overall rms values for the deviations from the least-square planes of **3d**, **5a**, and **5c**, and it is also noteworthy to remark the mutually parallel alignment of the mentioned groups in a totally symmetric emplacement across the phosphine carbon–carbon bond, as depicted, e.g., for compound **5a** in Fig. 6.

*2.2.4. [Pd{2-FC$_6$H$_3$C(Me)=NN=C(S)NHMe}-(Ph$_2$PCH$_2$ PPh$_2$–P)] (**6a**), [Pd{2-FC$_6$H$_3$C–(Me)=NN=C(S)NHEt}(Ph$_2$PCH$_2$PPh$_2$–P)] (**6b**), [Pd{2-FC$_6$H$_3$C-(Me)=NN=C(S)–NHMe}(Ph$_2$PCH=CHPPh$_2$–P)] (**7a**)*

As for the crystal structures of **6a**, **6b** and **7a**, these exemplify the first accounts of crystal structures pertaining to cyclopalladated thiosemicarbazone compounds with mono-coordinated η^1-diphosphines (see Figs. 7–9).

The asymmetric unit of each crystal structure comprises a mononuclear palladium(II) complex, which reveals the palladium atom is in a square-planar environment with the thiosemicarbazone ligand behaving as terdentate, and the phosphine ligand bonded *trans* to the iminic nitrogen atom. All bond distances are within the expected values, with the Pd–N bond displaying marked lengthening due to the *trans* influence of the phosphine ligand. The angles in the environment of the metal atom show deviations from the ideal 90° similar to those described above for compounds **3d**, **5a**,

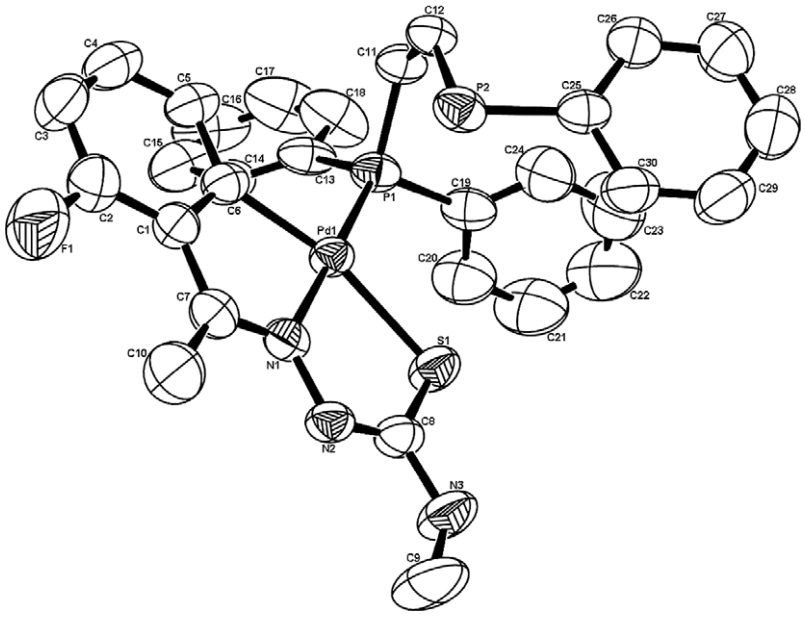


Fig. 9. An ORTEP drawing of the molecular structure for **7a** with labeling scheme (30% probability). Hydrogen atoms, as well as one phosphine phenyl ring, have been omitted for clarity. Selected bond lengths (Å) and angles (°) (at the metal): Pd(1)–N(1) 2.019(2); Pd(1)–C(1) 2.088(2); Pd(1)–P(1) 2.2536(10); Pd(1)–S(1) 2.3430(13); S(1)–C(8) 1.742(3); N(2)–C(8) 1.302(4); N(3)–C(8) 1.355(4); N(1)–N(2) 1.380(3); N(1)–C(7) 1.294(4); C(1)–C(7) 1.463(4); P(1)–C(11) 1.804(3); P(2)–C(12) 1.823(3); C(11)–C(12) 1.310(4); N(1)–Pd(1)–C(6) 80.88(12); C(6)–Pd(1)–P(1) 98.48(9); P(1)–Pd(1)–S(1) 97.84(3); N(1)–Pd(1)–S(1) 82.78(8); N(1)–Pd(1)–P(1) 179.07(8); C(6)–Pd(1)–S(1) 163.47(9).

and **5c**. The palladium coordination plane [Pd(1), C(1), N(1), S(1)], **6a**, **6b**, and the P(1)C(11)P(2), **6a**, P(1)C(12) P(2), **6b**, planes are at 69.15° and 69.70°, respectively; for compound **7a** the coordination [Pd(1), C(6), N(1), S(1)] and [P(1)C(11)C(12)P(2)] planes are at an angle of 71.29°. The Pd(1)–P(2) bond distances, 4.1147(0.0001) **6a**, 4.1062(0.0001) **6b** and 3.1772(0.0013) **7a**, preclude any interaction between palladium and the non-coordinated phosphorus atom.

3. Conclusions

We have shown that thiosemicarbazone ligands readily undergo the cyclometallation reaction to give tetranuclear compounds with a central core consisting of an eight-memberd ring of alternating palladium and sulfur atoms, whose subsequent reaction with tertiary diphosphines may be modulated to give dinuclear or mononuclear species as a function of (1) the molar ratio and of (2) the length of the carbon chain, P–$(C)_n$–P, connecting both phosphorus atoms. Although, in principle, for $n = 1$ mono- or dinuclear compounds may be obtained as a function of the molar ratio used, as is the case with bis(diphenylphosphino)methane, whereas for $n = 2$, dinuclear species with bridging phosphine are always obtained, as we have observed earlier, a third issue to be considered is the nature of the carbon chain, which may likewise modify the final product in relation to its mono- or dinuclear essence. Hence, with the diphospine *cis*-bis(diphenylphosphino)ethene the spatial arrangement of the donor atoms, imposed by the *cis* geometry of the C=C double bond, hinders bonding of a metallated moiety to a second phosphorus atom of the phosphine ligand, in view of the resulting steric impediment, rendering a compound with a η^1-diphosphine ligand.

4. Experimental

4.1. General procedures

Solvents were purified by standard methods [35]. Chemicals were reagent grade. Lithium tetrachloropalladate was prepared in situ by treatment of palladium(II) chloride with lithium chloride in methanol. Palladium(II) acetate, potassium tetrachloropalladate, and palladium(II) chloride were purchased from Alfa Products. The phosphines $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp), *trans*-$Ph_2P(CH{=}CH)PPh_2$ (*trans*-dpe) and *cis*-$Ph_2P(CH{=}CH)PPh_2$ (*cis*-dpe) were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the Universidad of Santiago using a Carlo Erba Elemental Analyzer Model EA1108. IR spectra were recorded as Nujol mulls or KBr discs with a Perkin–Elmer 1330, with an IR-FT Mattson Model Cygnus-100 and with a Bruker Model IFS-66 V spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H) or H_3PO_4 (^{31}P–{^1H}) and were recorded with Bruker AMX 300, AMX 500 and WM250 spectrometers. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

4.2. Synthesis

4.2.1. Preparation of 2-$FC_6H_4C(Me)$=NN(H)C(=S)-NHMe (**a**)

2′-Fluoroacetophenone (131 mg, 9.51 mmol) and hydrochloric acid (35%, 0.65 mL) were added to a suspension of 4-methyl-3-thiosemicarbazide (100 mg, 9.51 mmol) in water (25 cm^3) 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: 178 mg, 83%. Anal. Found: C, 53.1; H, 5.4; N, 18.5; S, 14.2%; $C_{10}H_{12}FN_3S$ (225.3 g/mol) requires: C, 53.3; H, 5.4; N, 18.6; S, 14.2%. IR (cm^{-1}): *ν*(N–H) 3317m, 3182m; *ν*(C=N) 1616w; *ν*(C=S) 839w. ^{1}H NMR (*δ* ppm, *J* Hz): 8.68 (s, 1H, NH), 7.61 (br, 1H, N*H*Me), 7.50 (td, 1H, H6, ^3JH6H5 = 7.9, ^4JH6F = 7.9, ^4JH6H4 = 1.9), 7.38 (dddd, 1H, H4, ^3JH4H3 = 8.3, ^4JH4H6 = 1.9), 7.17 (td, 1H, H5, ^3JH5H4 = 7.9, ^3JH5H6 = 7.9, ^4JH5H3 = 0.9), 7.10 (ddd, 1H, H3, ^3JH3F = 11.1, ^3JH3H4 = 8.3, ^4JH3H5 = 0.9), 3.24 (d, 3H, NH*Me*, ^3JHH = 4.6), 2.28 (d, 3H, MeC=N, ^5JHF = 2.3). FAB-MS: *m*/*z* 226 $[MH]^+$.

Ligands **b** and **c** were prepared analogously.

4.2.2. 2-$FC_6H_4C(Me)$=NN(H)C(=S)NHEt (**b**)

Yield: 188 mg, 93%. Anal. Found: C, 55.0; H, 5.8; N, 17.6; S, 13.6%; $C_{11}H_{14}FN_3S$ (239.3 g/mol) requires: C, 55.2; H, 5.9; N, 17.6; S, 13.4%. IR (cm^{-1}): *ν*(N–H) 3358m, 3235w; *ν*(C=N) 1614w; *ν*(C=S) 837w. ^{1}H NMR (*δ* ppm, *J* Hz): 8.63 (s, 1H, NH), 7.56 (br, 1H, N*H*Et), 7.49 (td, 1H, H6, ^3JH6H5 = 7.9 Hz, ^4JH6F = 7.9, ^4JH6H4 = 1.9), 7.38 (dddd, 1H, H4, ^3JH4H3 = 8.3, ^4JH4H6 = 1.9), 7.18 (td, 1H, H5, ^3JH5H4 = 7.9 Hz, ^3JH5H6 = 7.9 Hz, ^4JH5H3 = 0.9), 7.10 (ddd, 1H, H3, ^3JH3F = 11.1, ^3JH3H4 = 8.3, ^4JH3H5 = 0.9), 3.75 (dq, 2H, NH$CH_2$$CH_3$, ^3JHH = 6.9 Hz, ^3JH–NH = 5.6), 2.28 (d, 3H, MeC=N, ^5JHF = 2.3), 1.30 (t, 3H, NHCH$_2$$CH_3$, ^3JHH = 6.9). FAB-MS: *m*/*z* 240 $[MH]^+$.

4.2.3. 2-$ClC_6H_4C(Me)$=NN(H)C(=S)NHMe (**c**)

Yield: 209 mg, 91%. Anal. Found: C, 49.4; H, 5.0; N, 17.4; S, 13.2%; $C_{10}H_{12}ClN_3S$ (241.7 g/mol) requires: C, 49.7; H, 5.0; N, 17.4; S, 13.3%. IR (cm^{-1}): *ν*(N–H) 3357s, 3239m; *ν*(C=N) 1591w; *ν*(C=S) 834m. ^{1}H NMR (*δ* ppm, *J* Hz): 8.62 (s, 1H, NH), 7.53 (br, 1H, N*H*Me), 7.36 (dd, 1H, H6), 7.26 (m, 3H, H3, H4, H5), 3.15 (d, 3H, NH*Me*, ^3JHH = 4.6), 2.22 (s, 3H, MeC=N). FAB-MS: *m*/*z* 242 $[M]^+$.

4.2.4. 2-$BrC_6H_4C(Me)$=NN(H)C(=S)NHEt (**d**)

Yield: 204 mg, 81%. Anal. Found: C, 43.9; H, 4.7; N, 14.2; S, 10.5%; $C_{11}H_{14}BrN_3S$ (300.2 g/mol) requires: C, 44.0; H, 4.7; N, 14.0; S, 10.7%. IR (cm^{-1}): *ν*(N–H) 3367s, 3208m; *ν*(C=N) 1588w; *ν*(C=S) 826m. ^{1}H NMR (*δ* ppm, *J* Hz): 8.60 (br, 1H, NH), 7.61 (dd, 1H, H6, ^3JH6H5 = 7.9), 7.54 (br, 1H, N*H*Et), 7.37 (dd, 1H, H3, ^3JH3H4 = 7.9, ^4JH3H5 = 1.4), 7.31 (td, 1H, H4, ^3JH4H3 = 7.9, ^3JH4H5 = 7.9, ^4JH4H6 = 1.4), 7.25 (ddd, 1H, H5, ^3JH5H4 = 7.9, ^4JH5H3 = 1.4), 3.72 (dq, 2H, NH$CH_2$$CH_3$, ^3JHH = 7.4, ^3JH–NH = 5.5), 2.26 (s, 3H, MeC=N), 1.25 (t, 3H, NHCH$_2$$CH_3$, ^3JHH = 7.4). FAB-MS: *m*/*z* 300 $[M]^+$.

4.2.5. Preparation of [Pd{2-$FC_6H_3C(Me)$=NN=C(S)-NHMe}]$_4$ (**1a**)

Method 1: To a stirred solution of potassium tetrachloropalladate (200 mg, 0.61 mmol) in water (6 cm^3) was added ethanol (40 cm^3). The fine yellow suspension of potassium tetrachloropalladate obtained was treated with 2-FC_6H_4C(Me)=NN(H)C(=S)NHMe (**a**) (152 mg, 0.67 mmol, 10% excess). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with ethanol and dried. Yield: 172 mg, 85%. Anal. Found: C, 36.5; H, 3.0; N, 12.6; S, 9.7%; $C_{40}H_{40}F_4N_{12}Pd_4S_4$ (1318.8 g/mol) requires: C, 36.4; H, 3.1; N, 12.7; S, 9.7%. IR (cm^{-1}): *ν*(N–H) 3437m; *ν*(C=N) 1584s. ^{1}H NMR (*δ* ppm, *J* Hz): 7.27 (d, 1H, H5, ^3JH5H4 = 6.9), 6.94 (td, 1H, H4, ^3JH4H3 = 8.3, ^4JH4F = 5.1), 6.61 (ddd, 1H, H3, ^3JH3F = 12.5, ^3JH3H4 = 8.3, ^4JH3H5 = 0.9), 5.03 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 2.98 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.08 (d, 3H, MeC=N, ^5JHF = 3.7). FAB-MS: *m*/*z* 1318 $[M]^+$.

Method 2: Ligand **a** (267 mg, 1.18 mmol, 5% excess) and sodium acetate (185 mg, 2.26 mmol) were added to a stirred solution of palladium(II) chloride (200 mg, 1.13 mmol) and lithium chloride (96 mg, 2.26 mmol) in methanol (40 cm^3). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with methanol, and dried. Yield: 360 mg, 97%.

Method 3: Ligand **a** (210 mg, 0.94 mmol, 5% excess) and palladium(II) acetate (200 mg, 0.89 mmol) were added to glacial acetic acid (45 mL) to give a clear solution, which was heated to 60 °C under nitrogen for 24 h. After cooling to room temperature, the yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 289 mg, 98%.

Compounds **1b**–**1d** were prepared similarly by the appropriate methods, as described above.

4.2.6. [Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHEt}]$_4$ (**1b**)

Method 1: Yield: 335 mg, 86%. Anal. Found: C, 38.4; H, 3.3; N, 12.0; S, 9.3%; $C_{44}H_{48}F_4N_{12}Pd_4S_4$ (1374.9 g/mol) requires: C, 38.4; H, 3.5; N, 12.2; S, 9.3%. IR (cm^{-1}): *ν*(N–H) 3425m, *ν*(C=N) 1585s. ^{1}H NMR (*δ* ppm, *J* Hz): 7.28 (d, 1H, H5, ^3JH5H4 = 6.9), 6.94 (td, 1H, H4, ^3JH4H3 = 8.3, ^4JH4F = 5.1), 6.62 (ddd, 1H, H3, ^3JH3F = 12.5, ^3JH3H4 = 8.3, ^4JH3H5 = 0.9), 5.05 (t, 1H, N*H*Et, ^3JNH–H = 5.5), 3.40 (m, 2H, NHC$H_2$$CH_3$), 2.03 (d, 3H, MeC=N, ^5JHF = 4.2), 1.23 (t, 3H, NHCH$_2$CH_3, ^3JHH = 6.9). FAB-MS: *m*/*z* 1375 $[M]^+$.

4.2.7. [Pd{2-$ClC_6H_3C(Me)$=NN=C(S)NHMe}]$_4$ (**1c**)

Method 2: Yield: 346 mg, 89%. Anal. Found: C, 34.6; H, 2.9; N, 11.9; S, 9.2%; $C_{40}H_{40}Cl_4N_{12}Pd_4S_4$ (1384.6 g/mol) requires: C, 34.7; H, 2.9; N, 12.1; S, 9.3%. IR (cm^{-1}): *ν*(N–H) 3425s, *ν*(C=N) 1558s. ^{1}H NMR (*δ* ppm, *J* Hz): 7.44 (dd, 1H, H5, ^3JH5H4 = 7.9, ^4J H5H3 = 0.9), 6.96 (dd, 1H, H3, ^3JH3H4 = 7.9, ^4JH3H5 = 0.9), 6.84 (t, 1H, H4, ^3JH4H3 = 7.9 Hz, ^3JH4H5 = 7.9), 5.07 (q, 1H, N*H*Me,

^3JNH–H = 4.6), 2.98 (d, 3H, NH*Me*, ^3JH–NH = 4.6), 2.22 (s, 3H, MeC=N). FAB-MS: *m/z* 1384 $[M]^+$.

Method 3: Yield: 294 mg, 95%.

4.2.8. [Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHEt}]$_4$ (**1d**)

Method 1: Yield: 353 mg, 77%. Anal. Found: C, 32.5; H, 2.9; N, 10.3; S, 8.0%; $C_{44}H_{48}Br_4N_{12}Pd_4S_4$ (1618.5 g/mol) requires: C, 32.7; H, 3.0; N, 10.4; S, 7.9%. IR (cm^{-1}): *ν*(N–H) 3425m, *ν*(C=N) 1557s. ^{1}H NMR (*δ* ppm, *J* Hz): 7.50 (dd, 1H, H5, ^3JH5H4 = 7.9 Hz, ^4JH5H3 = 0.9), 7.22 (dd, 1H, H3, ^3JH3H4 = 7.9, ^4JH3H5 = 0.9), 6.75 (t, 1H, H4, ^3JH4H3 = 7.9, ^3JH4H5 = 7.9), 5.09 (t, 1H, N*H*Et, ^3JNH–H = 5.5), 3.40 (dq, 2H, NHCH_2CH$_3$, ^3JHH = 7.4, ^3JH–NH = 5.5), 2.21 (s, 3H, MeC=N), 1.24 (t, 3H, NHCH$_2$CH_3, ^3JHH = 7.4). FAB-MS: *m/z* 1620 $[MH]^+$.

Method 2: Yield: 302 mg, 84%.

4.2.9. Preparation of [{Pd[2-FC$_6$H$_3$C(Me)=NN=C(S)-NHMe]}$_2$(*μ*-Ph$_2$PCH$_2$PPh$_2$–P,P)] (**2a**)

The diphosphine $Ph_2PCH_2PPh_2$ (17.8 mg, 0.046 mmol) was added to a suspension of complex **1a** (30 mg, 0.023 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h. and the resulting yellow solid was filtered off and dried. Yield: 35.5 mg, 75%. Anal. Found: C, 51.6; H, 4.1; N, 8.2; S, 6.1%; $C_{45}H_{42}F_2N_6P_2Pd_2S_2$ (1043.8 g/mol) requires: C, 51.8; H, 4.1; N, 8.1; S, 6.1%. IR (cm^{-1}): *ν*(N–H) 3464m; *ν*(C=N) 1581m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.33 (m, 2H, H3, H4), 5.87 (m, 1H, H5), 4.77 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 3.76 (t, 1H, PCH_2P, ^2JHP = 10.2), 3.01 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.51 (d, 3H, MeC=N, ^5JHF = 3.7). ^{31}P–{^{1}H} NMR (*δ* ppm): 23.8s.

Compounds **3a**–**3d**, **4a**, **4c**, **5a** and **5c**, were synthesized following a similar procedure.

4.2.10. [{Pd[2-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(*μ*-Ph$_2$P(CH$_2$)$_2$PPh$_2$–P,P)] (**3a**)

Yield: 44.2 mg, 92%. Anal. Found: C, 52.4; H, 4.3; N, 7.8; S, 6.0%; $C_{46}H_{44}F_2N_6P_2Pd_2S_2$ (1057.8 g/mol) requires: C, 52.2; H, 4.2; N, 7.9; S, 6.1%. IR (cm^{-1}): *ν*(N–H) 3447m; *ν*(C=N) 1579m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.49 (m, 2H, H3, H4), 6.05 (m, 1H, H5), 4.72 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 2.97 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.82 (br, 2H, P(CH_2)$_2$P), 2.57 (d, 3H, MeC=N, ^5JHF = 4.6 Hz). ^{31}P–{^{1}H} NMR (*δ* ppm): 32.0s.

4.2.11. [{Pd[2-FC$_6$H$_3$C(Me)=NN=C(S)NHEt]}$_2$(*μ*-Ph$_2$P(CH$_2$)$_2$PPh$_2$–P,P)] (**3b**)

Yield: 17.6 mg, 37%. Anal. Found: C, 52.9; H, 4.3; N, 7.5; S, 5.7%; $C_{48}H_{48}F_2N_6P_2Pd_2S_2$ (1085.8 g/mol) requires: C, 53.1; H, 4.5; N, 7.7; S, 5.9%. IR (cm^{-1}): *ν*(N–H) 3432m; *ν*(C=N) 1578m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.49 (m, 2H, H3, H4), 6.07 (m, 1H, H5), 4.72 (t, 1H, N*H*Et, ^3JNH–H = 5.1), 3.40 (dq, 2H, NHCH_2CH$_3$, ^3JHH = 7.4, ^3JH–NH = 5.1), 2.83 (br, 2H, P(CH_2)$_2$P), 2.56 (d, 3H, MeC=N, ^5JHF = 4.2), 1.19 (t, 3H, NHCH$_2$CH_3, ^3JHH = 7.4). ^{31}P–{^{1}H} NMR (*δ* ppm): 31.4s.

4.2.12. [{Pd[2-BrC$_6$H$_3$C(Me)=NN=C(S)NHEt]}$_2$(*μ*-Ph$_2$P(CH$_2$)$_2$PPh$_2$–P,P)] (**3d**)

Yield: 30.6 mg, 68%. Anal. Found: C, 47.8; H, 4.1; N, 6.9; S, 5.1%; $C_{48}H_{48}Br_2N_6P_2Pd_2S_2$ (1207.7 g/mol) requires: C, 47.7; H, 4.0; N, 7.0; S, 5.3%. IR (cm^{-1}): *ν*(N–H) 3426m; *ν*(C=N) 1555m. ^{1}H NMR (*δ* ppm, *J* Hz): 7.07 (dd, 1H, H3, ^3JH3H4 = 7.4, ^4JH3H5 = 1.8), 6.26 (m, 1H, H5), 6.23 (t, 1H, H4, ^3JH4H3 = 7.4, ^3JH4H5 = 7.4), 4.78 (br, 1H, N*H*Et), 3.40 (dq, 2H, NHCH_2CH$_3$, ^3JHH = 7.4, ^3JH–NH = 5.5), 2.79 (br, 2H, P(CH_2)$_2$P), 2.74 (s, 3H, MeC=N), 1.19 (t, 3H, NHCH$_2$CH_3, ^3JHH = 7.4). ^{31}P–{^{1}H} NMR (*δ* ppm): 31.8s.

4.2.13. [{Pd[2-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(*μ*-Ph$_2$P(CH$_2$)$_3$PPh$_2$–P,P)] (**4a**)

Yield: 69.5 mg, 85%. Anal. Found: C, 52.8; H, 4.4; N, 7.8; S, 5.9%; $C_{47}H_{46}F_2N_6P_2Pd_2S_2$ (1071.8 g/mol) requires: C, 52.7; H, 4.3; N, 7.8; S, 6.0%. IR (cm^{-1}): *ν*(N–H) 3428m; *ν*(C=N) 1574m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.42 (m, 2H, H3, H4), 6.05 (m, 1H, H5), 4.76 (q, 1H, N*H*Me, ^3JNH–H = 5.0), 2.90 (d, 3H, NH*Me*, ^3JH–NH = 5.0), 2.47 (d, 3H, MeC=N, ^5JHF = 4.7), 2.40 (br, 2H, PCH_2CH$_2$CH_2P), 1.94 (br, 1H, PCH$_2$CH_2CH$_2$P). ^{31}P–{^{1}H} NMR (*δ* ppm): 26.9s.

4.2.14. [{Pd[2-ClC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(*μ*-Ph$_2$P(CH$_2$)$_3$PPh$_2$–P,P)] (**4c**)

Yield: 32.8 mg, 69%. Anal. Found: C, 51.2; H, 4.2; N, 7.6; S, 5.6%; $C_{47}H_{46}Cl_2N_6P_2Pd_2S_2$ (1104.7 g/mol) requires: C, 51.1; H, 4.2; N, 7.6; S, 5.8%. IR (cm^{-1}): *ν*(N–H) 3433m; *ν*(C=N) 1558m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.82 (d, 1H, H3, ^3JH3H4 = 7.9), 6.40 (t, 1H, H4, ^3JH4H3 = 7.9, ^3JH4H5 = 7.9), 6.27 (dd, 1H, H5, ^3JH5H4 = 7.9, ^4JH5P = 5.1), 4.82 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 2.99 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.72 (s, 3H, MeC=N), 2.51 (m, 2H, PCH_2CH$_2$CH_2P), 2.12 (br, 1H, PCH$_2$CH_2CH$_2$P). ^{31}P–{^{1}H} NMR (*δ* ppm): 26.9s.

4.2.15. [{Pd[2-FC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(*μ*-Ph$_2$PCH=CHPPh$_2$–P,P)] (**5a**)

Yield: 69.6 mg, 87%. Anal. Found: C, 52.4; H, 4.0; N, 7.9; S, 6.0%; $C_{46}H_{42}F_2N_6P_2Pd_2S_2$ (1055.8 g/mol) requires: C, 52.3; H, 4.0; N, 8.0; S, 6.1%. IR (cm^{-1}): *ν*(N–H) 3420m; *ν*(C=N) 1577m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.48 (ddd, 1H, H3, ^3JH3F = 12.5, ^3JH3H4 = 8.3, ^4JH3H5 = 0.9), 6.34 (td, 1H, H4, ^3JH4H3 = 8.3, ^4JH4F = 5.1), 6.14 (m, 1H, H5), 4.69 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 2.92 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.56 (d, 3H, MeC=N, ^5JHF = 4.2). ^{31}P–{^{1}H} NMR (*δ* ppm): 32.4s.

4.2.16. [{Pd[2-ClC$_6$H$_3$C(Me)=NN=C(S)NHMe]}$_2$(*μ*-Ph$_2$PCH=CHPPh$_2$–P,P)] (**5c**)

Yield: 24.2 mg, 51%. Anal. Found: C, 50.4; H, 3.7; N, 7.5; S, 5.8%; $C_{46}H_{42}Cl_2N_6P_2Pd_2S_2$ (1088.7 g/mol) requires: C, 50.7; H, 3.9; N, 7.7; S, 5.9%. IR (cm^{-1}): *ν*(N–H) 3446m; *ν*(C=N) 1559m. ^{1}H NMR (*δ* ppm, *J* Hz): 6.77 (dd, 1H, H3, ^3JH3H4 = 7.9, ^4JH3H5 = 1.4), 6.29 (m, 1H, H5), 6.20 (t,

1H, H4, ^3JH4H3 = 7.9, ^3JH4H5 = 7.9), 4.73 (br, 1H, N*H*Me), 2.92 (d, 3H, NH*Me*, ^3JH–NH = 4.6), 2.72 (s, 3H, MeC=N). ^{31}P–{^{1}H} NMR (δ ppm): 32.4s.

4.2.17. Preparation of [Pd{2-FC$_6$H$_3$C(Me)=NN=C(S)-NHMe}(Ph$_2$PCH$_2$PPh$_2$–P)] (6a)

The diphosphine $Ph_2PCH_2PPh_2$ (59.5 mg, 0.155 mmol) was added to a suspension of complex **1a** (50 mg, 0.038 mmol) in acetone (15 cm^3). The mixture was stirred for 4 h. The resulting yellow solid was filtered off and dried. Yield: 93.1 mg, 86%. Anal. Found: C, 58.8; H, 4.6; N, 5.8; S, 4.4%; $C_{35}H_{32}FN_3P_2PdS$ (714.1 g/mol) requires: C, 58.9; H, 4.5; N, 5.9; S, 4.5%. IR (cm^{-1}): ν(N–H) 3435m; ν(C=N) 1577m. ^{1}H NMR (δ ppm, J Hz): 6.44 (m, 2H, H3, H4), 6.00 (m, 1H, H5), 4.77 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 3.25 (d, 2H, P CH_2P, ^2JHP = 9.2), 2.97 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.51 (d, 3H, MeC=N, ^5JHF = 4.6). ^{31}P–{^{1}H} NMR (δ ppm, J Hz): 24.4 (d, 1P, P_A, ^2JPP = 75.1), −26.3 (d, 1P, P_B, ^2JPP = 75.1).

Compounds **6b** and **7a** were obtained as yellow solids following a similar procedure.

4.2.18. [Pd{2-FC$_6$H$_3$C(Me)=NN=C(S)NHEt}(Ph$_2$PCH$_2$PPh$_2$–P)] (6b)

Yield: 100 mg, 95%. Anal. Found: C, 59.6; H, 4.7; N, 5.8; S, 4.3%; $C_{36}H_{34}FN_3P_2PdS$ (728.1 g/mol) requires: C, 59.4; H, 4.7; N, 5.8; S, 4.4%. IR (cm^{-1}): ν(N–H) 3424m; ν(C=N) 1573m. ^{1}H NMR (δ ppm, J Hz): 6.44 (m, 2H, H3, H4), 6.00 (m, 1H, H5), 4.76 (t, 1H, N*H*Et, ^3JNH–H = 5.1), 3.40 (dq, 2H, NHCH_2CH$_3$, ^3JHH = 7.4, ^3JH–NH = 5.1), 3.25 (d, 2H, PCH_2P, ^2JHP = 9.2), 2.50 (d, 3H, MeC=N, ^5JHF = 4.6), 1.18 (t, 3H, NHCH$_2$CH_3, ^3JHH = 7.4). ^{31}P–{^{1}H} NMR (δ ppm, J Hz): 24.4 (d, 1P, P_A, ^2JPP = 75.1), −26.3 (d, 1P, P_B, ^2JPP = 75.1).

4.2.19. [Pd{2-FC$_6$H$_3$C(Me)=NN=C(S)NHMe}(Ph$_2$PCH=CHPPh$_2$–P)] (7a)

Yield: 66.2 mg, 60%. Anal. Found: C, 59.8; H, 4.5; N, 5.8; S, 4.5%; $C_{35}H_{32}FN_3P_2PdS$ (714.1 g/mol) requires: C, 59.6; H, 4.4; N, 5.8; S, 4.4%. IR (cm^{-1}): ν(N–H) 3430m; ν(C=N) 1578m. ^{1}H NMR (δ ppm, J Hz): 6.43 (m, 2H, H3, H4), 6.34 (m, 1H, H5), 5.81 (t, 2H, –HC=CH–, N = 28), 4.69 (q, 1H, N*H*Me, ^3JNH–H = 5.1), 2.94 (d, 3H, NH*Me*, ^3JH–NH = 5.1), 2.50 (d, 3H, MeC=N, ^5JHF = 4.6). ^{31}P–{^{1}H} NMR (δ ppm, J Hz): 22.3 (d, 1P, P_A, ^2JPP = 75.3), −25.2 (d, 1P, P_B, ^2JPP = 75.3).

4.3. Crystal structures

Crystals of ligand **a** and of complexes (**1a**, **3d**, **5a**, **5c**, **6a**, **6b**, **7a**) were mounted on a glass fiber and transferred to the diffractometer.

For **a** and **1a** room temperature X-ray data were collected on a MACH3 Enraf Nonius diffractometer using graphite monochromated Cu Kα radiation by the $\omega/2\theta$ method (**a**), and using monochromated Mo Kα radiation by the omega method (**1a**).

Three dimensional, room temperature X-ray data were collected with Siemens (**6a**, **6b**) and Bruker (**3d**, **5a**, **5c** and **7a**) SMART CCD diffractometers by the omega scan method, using monochromated Mo Kα radiation.

All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections [T_{max}/T_{min} = 0.8306/0.4457 (**a**), 0.7767/0.528 (**1a**), 0.755/0.5466 (**3d**), 0.843/0.7773 (**4b**), 0.8635/0.6662 (**5a**), 0.9380/0.7971 (**5c**), 0.8398/0.6605 (**6a**) and 0.9366/0.7722 (**7a**)]. The structures were solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0433 (**a**), 0.0599 (**1a**), 0.0523 (**3d**), 0.0353 (**5a**), 0.0674 (**5c**), 0.0441 (**6a**), 0.0622 (**6b**) and 0.0329 (**7a**) (observed data, F), and wR_2 = 0.1212 (**a**), 0.1757 (**1a**), 0.1853 (**3d**), 0.0874 (**5a**), 0.1756 (**5b**), 0.1507 (**5c**), 0.1158 (**6a**), and 0.0806 (**7a**) (all unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron densities: −0.292 and 0.255 (**a**), −0.793 and 1.085 (**1a**), −1.08 and 1.673 (**3d**), −0.633 and 0.662 (**5a**), −1.165 and 1.033 (**5c**), −0.958 and 0.988 (**6a**), −1.151 and 1.214 (**6b**), −0.505 and 0.061e Å^{-3} (**7a**). The structure solutions and refinements were carried out with the SHELX-97 [36] program package.

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Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 287850 (**a**), 287855 (**1a**), 287857 (**3d**), 287856 (**5a**), 287851 (**5c**), 287853 (**6a**) and 287852 (**7a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.014.

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