Novel Cyclometallated Complexes Derived From a Halogenated Thiosemicarbazone. Crystal and Molecular Structures of 2-$FC_6H_4C(Me)=NN(H)C(=S)NHPh$ and $[(Pd\{2\text{-}FC_6H_3C(Me)=NN=C(S)NHPh\})_2(\mu\text{-}PPh_2(CH_2)_2PPh_2)]$

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Abstract. Treatment of the thiosemicarbazone 2-$FC_6H_4C(Me)=NN(H)C(=S)NHPh$, **a**, with palladium(II) acetate in acetic acid, or with lithium tetrachloropalladate(II) in methanol, gave the tetranuclear cyclometallated complex $[Pd\{2\text{-}FC_6H_3C(Me)=NN=C(S)NHPh\}]_4$ **(1a)**. Reaction of **1a** with the diphosphines $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2PCH=CHPPh_2$ (*trans*-dpe) $Ph_2P(CH_2)_3Ph_2$ (dppp) or $Ph_2P(CH_2)_4Ph_2$ (dppb) in a 1:2 molar ratio gave the dinuclear cyclometallated complexes $[(Pd\{2\text{-}FC_6H_3C(Me)=NN=C(S)NHPh\})_2(\mu\text{-}Ph_2P(CH_2)_nPPh_2)]$, (n = 2, **2a**; 3, **4a**; 4, **5a**) and $[(Pd\{2\text{-}FC_6H_3C(Me)=NN=C(S)NHPh\})_2(\mu\text{-}Ph_2PCH=CHPPh_2)]$, (**3a**). The X-ray crystal structure of ligand **a** and of complex **2a** are described. The structure of complex **2a** shows the palladium atom is bonded to four different donor atoms: C, N, S and P.

Keywords: Cyclometallation; C-H activation; Palladium; Thiosemicarbazones

1 Introduction

The last two decades have seen a growing interest in cyclometallated palladium(II) complexes [1] in view of their novel and outstanding applications, for instance their use as intermediates in organic and organometallic synthesis [2], the design of liquid crystals [3], or their pharmacological properties [4] which include antiparasital [5], antibacterial [6], and antitumoral activities [7–10]. Some thiosemicarbazones increase their antitumoral activity upon chelate formation with specific metal ions [11]. These ligands are produced by the condensation of a thiosemicarbazide and an aldehyde or ketone, and although they usually coordinate to the metal through the imine nitrogen and the sulphur atoms [12, 13], additional coordination sites, pertaining to the aldehyde and/or ketone, may also be present, enhancing their coordination capability [14], which is, as well, dependent on the thiol-thione tautomeric equilibrium [15, 16], although the most common coordinate mode is in the anionic thiolate form [12–17]. Consequently, a tremendous amount of transition metal chemistry has been published involving these ligands, which in some cases show terdentate coordination [18–20]. We have studied the tetranuclear *ortho*-metallated complexes with thiosemicarbazones as terdentate [C, N, S] donors [21], and although other terdentate *ortho*-metallated complexes have reported earlier [22], in those cases, the terdentate ligand, [C, N, N] [23] or [C, N, O] [24] showed no sulfur donor atoms, and only mononuclear complexes were isolated.

In the present work we report the novel cyclometallated compounds derived from a halogenated thiosemicarbazone, 2-$FC_6H_4C(Me)=NN(H)C(=S)NHPh$, which are tetranuclear species, and the reactivity of the latter with tertiary phosphines where the strength of the Pd-$S_{chelating}$ bond allows only cleavage of the Pd-$S_{bridging}$ bond.

2 Experimental Section

General procedures

Solvents were purified by standard methods [25]. Chemicals were reagent grade. Lithium tetrachloropalladate was prepared *in situ* by treatment of palladium(II) chloride with lithium chloride in methanol. Palladium(II) acetate and palladium(II) chloride were purchased from Alfa Products. The phosphines $Ph_2P(CH_2)_2PPh_2$ (dppe), and *trans*- $Ph_2PCH=CHPPh_2$ (t-dpe), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) were purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the Universidad of Santiago de Compostela using a Carlo Erba Elemental Analyzer Model EA1108. IR spectra were recorded as Nujol mulls or KBr discs with a Perkin-Elmer 1330, with a IR-FT Mattson Model Cygnus-100 and with a Bruker Model IFS-66V 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.

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Syntheses

Preparation of 2-$FC_6H_4C(Me)=NN(H)C(=S)NHPh$ (a): 2′-Fluoroacetophenone (82.6 mg, 5.98 mmol) and hydrochloric acid (35 %, 0.65 mL) were added to a suspension of 4-phenyl-3-thiosemicarbazide (100 mg, 5.98 mmol) in water (25 mL) 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: 158 mg, 92 %. Anal. found: C 62.5; H 4.9; N 14.7; S 11.4; $C_{15}H_{14}N_3SF$ (287.4 g/mol) requires C 62.7; H 4.9; N 14.6; S 11.2 %.

IR (cm^{-1}): ν(N-H) 3301m, 3232w; ν(C=N) 1616w; ν(C=S) 833w. **^{1}H NMR** ($CDCl_3$): δ = 9.38 (s, 1 H, NH), 8.80 (s, 1 H, N*H*Ph), 7.67 (d, 2 H, H2′, H6′, $^3J_{HH}$ = 7.9 Hz), 7.56 (td, 1 H, H6, $^3J_{H6H5}$ = 7.9 Hz, $^4J_{H6F}$ = 7.9, $^4J_{H6H4}$ = 1.9 Hz), 7.39 (m, 3 H, H3′, H5′, H4), 7.23 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 7.20 (td, 1 H, H5, $^3J_{H5H4}$ = 7.9 Hz, $^3J_{H5H6}$ = 7.9 Hz, $^4J_{H5H3}$ = 0.9 Hz), 7.14 (ddd, 1 H, H3, $^3J_{H3F}$ = 11.1 Hz, $^3J_{H3H4}$ = 8.3 Hz, $^4J_{H3H5}$ = 0.9 Hz), 2.36 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 2.8 Hz). **FAB-MS**: *m/z* 288 $[MH]^+$.

Preparation of [Pd{2-$FC_6H_3C(Me)=NN=C(S)NHPh$}]$_4$ (1a).
Method 1: Ligand **a** (269 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 this had cooled to room temperature, the yellow precipitate was filtered off, washed with ethanol, and dried. Yield: 231 mg, 66 %. Anal. found: C 45.9; H 3.1; N 10.8; S 8.3; $C_{60}H_{48}N_{12}S_4Pd_4F_4$ (1567.0 g/mol) requires C 46.0; H 3.1; N 10.7; S 8.2 %.

IR (cm^{-1}): ν(N-H) 3407m, ν(C=N) 1586s. **^{1}H NMR** ($CDCl_3$): δ = 7.50 (d, 2 H, H2′, H6′, $^3J_{HH}$ = 7.9 Hz), 7.33 (t, 2 H, H3′, H5′, $^3J_{HH}$ = 7.9 Hz), 7.18 (d, 1 H, H5, $^3J_{H5H4}$ = 6.9 Hz), 7.06 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 6.89 (s, 1 H, N*H*Ph), 6.84 (td, 1 H, H4, $^3J_{H4H3}$ = 8.3 Hz, $^4J_{H4F}$ = 5.1 Hz), 6.71 (ddd, 1 H, H3, $^3J_{H3F}$ = 12.0 Hz, $^3J_{H3H4}$ = 8.3 Hz, $^4J_{H3H5}$ = 0.9 Hz), 2.09 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 3.7 Hz). **FAB-MS**: *m/z* 1567 $[M]^+$.

Method 2: Ligand **a** (340 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 mL). The mixture was stirred for 48 h at room temperature under nitrogen. The yellow precipitate was filtered off, washed with methanol, and dried. Yield: 402 mg, 91 %.

Preparation of [(Pd{2-$FC_6H_3C(Me)=NN=C(S)NHPh$}$_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (2a). The diphosphine $Ph_2P(CH_2)_2PPh_2$ (26 mg, 0.065 mmol) was added to a suspension of complex **1a** (50 mg, 0.032 mmol) in acetone (15 mL). The mixture was stirred for 4 h and the resulting yellow solid was filtered off and dried. Yield: 30.4 mg, 40 %. Anal. found: C 56.9; H 4.2; N 6.8; S 5.2; $C_{56}H_{48}N_6S_2P_2Pd_2F_2$ (1181.9 g/mol) requires C 56.9; H 4.1; N 7.1; S 5.4 %.

IR (cm^{-1}): ν(N-H) 3423m; ν(C=N) 1585m. **^{1}H NMR** ($CDCl_3$): δ = 7.50 (d, 2 H, H2′, H6′, $^3J_{HH}$ = 7.9 Hz), 7.41 (t, 2 H, H3′, H5′, $^3J_{HH}$ = 7.4 Hz), 6.99 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 6.66 (s, 1 H, N*H*Ph), 6.55 (m, 2 H, H3, H4), 6.13 (m, 1 H, H5), 2.87 (br, 2 H, P(CH_2)$_2$P), 2.67 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 4.6 Hz). **^{31}P-{^{1}H} NMR** ($CDCl_3$): δ = 31.6 (s).

Compounds **3a-5a** were obtained following a similar procedure and obtained as yellow solids.

[(Pd{2-$FC_6H_3C(Me)=NN=C(S)NHPh$}$_2$(μ-$Ph_2PCH=CHPPh_2$)] (3a). Yield: 44.7 mg, 59 %. Anal. found: C 56.8; H 3.8; N 6.9; S 5.2; $C_{56}H_{46}N_6S_2P_2Pd_2F_2$ (1179.9 g/mol) requires C 57.0; H 3.9; N 7.1; S 5.4 %.

IR (cm^{-1}): ν(N-H) 3412m; ν(C=N) 1583m. **^{1}H NMR** ($CDCl_3$): δ = H2′, H6′ (signals hidden by the phosphane resonances), 7.26 (t, 2 H, H3′, H5′, $^3J_{HH}$ = 7.4 Hz), 6.97 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 6.62 (s, 1 H, N*H*Ph), 6.51 (dd, 1 H, H3, $^3J_{H3F}$ = 12.0 Hz, $^3J_{H3H4}$ = 8.3 Hz), 6.40 (td, 1 H, H4, $^3J_{H4H3}$ = 8.3 Hz, $^4J_{H4F}$ = 5.5 Hz), 6.19 (m, 1 H, H5), 2.65 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 4.2 Hz). **^{31}P-{^{1}H} NMR** ($CDCl_3$): δ = 32.3 (s).

[(Pd{2-$FC_6H_3C(Me)=NN=C(S)NHPh$}$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (4a). Yield: 48.6 mg, 64 %. Anal. found: C 57.4; H 4.4; N 6.7; S 5.3; $C_{57}H_{50}N_6S_2P_2Pd_2F_2$ (1196.0 g/mol) requires C 57.2; H 4.2; N 7.0; S 5.4 %.

IR (cm^{-1}): ν(N-H) 3420s; ν(C=N) 1584m. **^{1}H NMR** ($CDCl_3$): δ = 7.42 (d, 2 H, H2′, H6′, $^3J_{HH}$ = 7.9 Hz), H3′, H5′ (signals hidden by the phosphane resonances), 6.90 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 6.68 (s, 1 H, N*H*Ph), 6.46 (m, 2 H, H3, H4), 6.08 (m, 1 H, H5), 2.55 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 4.2 Hz), 2.42 (br, 2 H, P$CH_2CH_2CH_2$P), 2.01 (br, 1 H, PCH$_2CH_2$CH$_2$P). **^{31}P-{^{1}H} NMR** ($CDCl_3$): δ = 26.9 (s).

[(Pd{2-$FC_6H_3C(Me)=NN=C(S)NHPh$}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)] (5a). Yield: 50.0 mg, 65 %. Anal. found: C 57.3; H 4.5; N 6.6; S 5.2; $C_{58}H_{52}N_6S_2P_2Pd_2F_2$ (1210.0 g/mol) requires C 57.6; H 4.3; N 6.9; S 5.3 %.

IR (cm^{-1}): ν(N-H) 3402m; ν(C=N) 1584m. **^{1}H NMR** ($CDCl_3$): δ = 7.48 (d, 2 H, H2′, H6′, $^3J_{HH}$ = 7.4 Hz), 7.27 (t, 2 H, H3′, H5′, $^3J_{HH}$ = 7.4 Hz), 6.97 (t, 1 H, H4′, $^3J_{HH}$ = 7.4 Hz), 6.71 (s, 1 H, N*H*Ph), 6.54 (m, 2 H, H3, H4), 6.18 (m, 1 H, H5), 2.65 (d, 3 H, CH_3C=N, $^5J_{HF}$ = 4.2 Hz), 2.34 (br, 2 H, P$CH_2CH_2CH_2CH_2$P), 1.82 (br, 2 H, PCH$_2CH_2$CH$_2$CH$_2$P). **^{31}P-{^{1}H} NMR** ($CDCl_3$): δ = 28.7 (s).

Crystal structures

Crystals of ligand **a** and complex **2a·2CHCl$_3$** were mounted on a glass fiber and transferred to the diffractometer.

For **a** room temperature X-ray data was collected on a MACH3 Enraf Nonius diffractometer using graphite monochromated Cu-K_α radiation by the omega/2-theta method.

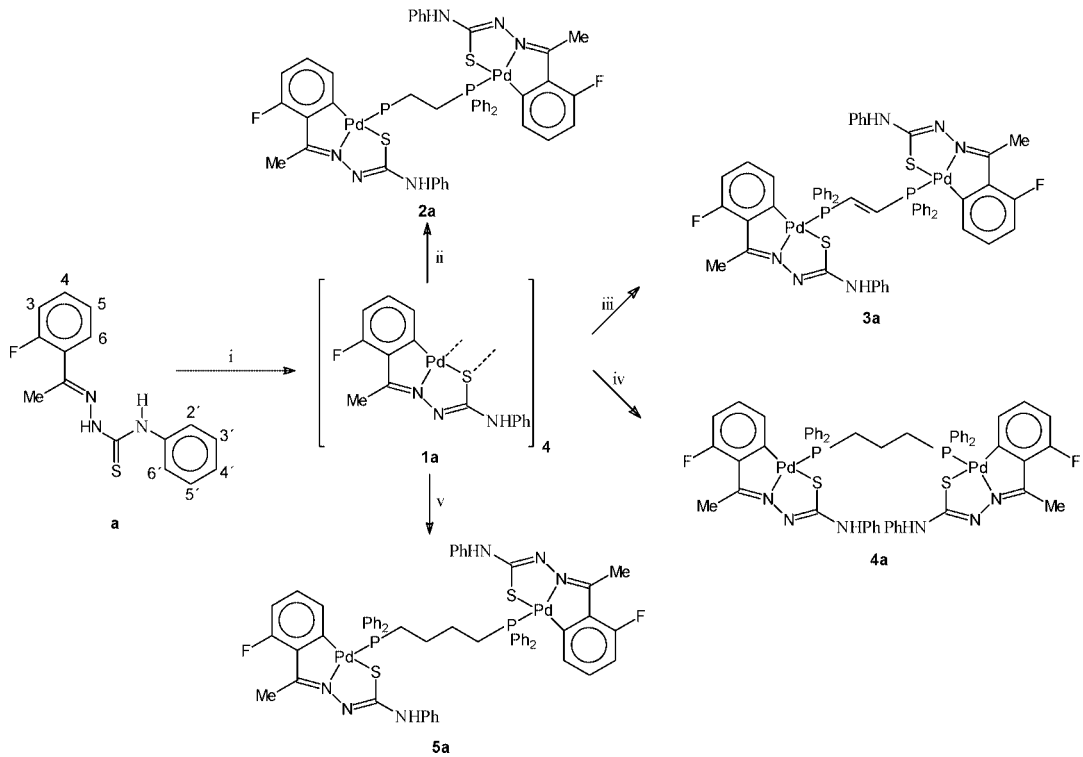
Three dimensional, room temperature X-ray data was collected with Siemens (**2a**) by the omega scan method, using monochromated Mo-K_α radiation.

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} = 0.8112/0.5898 (**a**), and 1.0000/0.7925 (**2a**)]. 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 = 0.0524 (**a**) and 0.0411 (**2a**) (observed data, F), and wR_2 = 0.1585 (**a**) and 0.1200 (**2a**) (all unique data, F^2), with allowance for thermal anisotropy of all non-hidrogen atoms. Minimum and maximum final electron densities: −0.414 and 0.384 (**a**), −0.987 and 0.926 (**2a**). The structure solutions and refinements were carried out with the SHELX-97 [26] program package.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 257436 (**a**) and no. 257437 (**2a**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

3 Results and Discussion

Ligand **a** was prepared by reaction of 4-phenythiosemicarbazide with 2′-fluoroacetophenone (see Experimental section). The bands at 3301 and 3232 cm^{-1} were due to ν(N-H) of the NH_2 and NH groups, respectively, the latter disappears in the spectra of the complexes [27]. The NH_2 protons gave rise to two characteristic broad resonances in the



Scheme 1 (i) $Pd(AcO)_2$ / AcOH or LiCl + $PdCl_2$ / MeOH; (ii) $Ph_2P(CH_2)_2PPh_2$ / acetone (1:2); (iii) $Ph_2PCH{=}CHPPh_2$ / acetone (1:2); (iv) $Ph_2P(CH_2)_3PPh_2$ / acetone (1:2); (v) $Ph_2P(CH_2)_4PPh_2$ / acetone (1:2).

^{1}H NMR spectra which were attributed to the restricted rotation of the NH_2 group about the C(=S)NH_2 bond axis. The NH proton showed a broad signal at δ8.80. The new cyclometallated complexes obtained from **a** are shown in Scheme 1.

Preparative details, characterizing microanalytical, mass spectra, IR and ^{1}H and ^{31}P-{^{1}H} data are in the Experimental section. Treatment of **a** with palladium(II) acetate in glacial acetic acid a gave clear solution from which [Pd{2-FC_6H_3C(Me)=NN=C(S)NHPh}]$_4$ (**1a**), was isolated as a yellow air-stable solid, with the ligand in the *E*,*Z* configuration. Alternatively, compound **1a** could be obtained by reaction of ligand **a** with lithium tetrachloropallate in methanol. The product was characterized by elemental analysis (C, H, N and S) and the mass spectrum (FAB) showed a peak at m/z 1567 for the molecular ion whose isotopic composition suggests a tetranuclear complex of formula $C_{60}H_{48}N_{12}S_4Pd_4F_4$. The position of the NH_2 bands in the spectra of the complexes shows this group is un-coordinated to the palladium atom. The ν(C=N) band was shifted to lower wavenumbers upon complex formation [28], a trend that is opposed to the one observed in other thiosemicarbazone complexes where the shift is towards higher wavenumbers [27]. We suggest this should be attributed to the C=N moiety being part of a five-membered metalacycle, as has been found by us and others [29, 30]. The ν(C=S) band disappears in the complexes, in accordance with loss of the double bond character upon deprotonation of the NH group; this is shown in the lengthening of the C-S bond in the structures of **2a** (vide infra).The absence of the signal for the NH group in the ^{1}H NMR spectra reveals deprotonation as observed in coordination compounds of these ligands [31, 32].

Reactivity of the complexes

The reaction of the complexes **1a** with nucleophiles such as amines, thallium(I) acetylacetonate, thallium(I) cyclopentadienyl or tertiary phosphines is difficult when compared to the analogous palladium(II) semicarbazone compounds; this is due to thepresence of the stronger Pd-S bond as compared to the Pd-O bond in terms of Pearson's concept [33], and to the tetranuclear nature of the Pd_4 cluster. Only in the case of tertiary phosphines was the reaction successful as we report here. Thus, treatment of **1a** with tertiary diphosphines gave dinuclear species, where only the bond at palladium to the $S_{bridging}$ atom was cleaved. The Pd-$S_{chelating}$ bond of the tridentate thiosemicarbazone ligands remains, even when a large excess of diphosphine was used; furthermore, the chelate effect of the bidentate phosphine did not promote Pd-Schelating bond cleavage. This behavior is in contrast with that shown by semicarbazone ligands, in related cyclometalated palladium(II) complexes, where the Pd-O bond was easily cleaved by the phosphine [34]. Some examples are given here with $Ph_2P(CH_2)_nPPh_2$ (n = 2, dppe; n = 3, dppp; n = 4dppb) and $Ph_2PCH{=}CHPPh_2$ (*trans*-dppe). Thus, when **1a** and **1b** were treated with the corresponding phosphine in 1:2 molar ratio, the com-

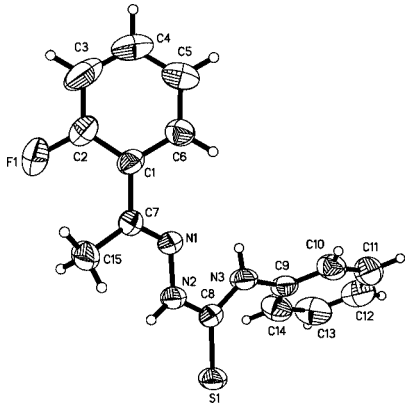


Figure 1 Molecular structure of ligand **a** with labelling scheme.

C(1)-C(7) 1.485(3), C(7)-N(1) 1.278(3), N(1)-N(2) 1.382(3), N(2)-C(8) 1.355(3), C(8)-S(1) 1.674(2), C(8)-N(3) 1.345(3), N(3)-C(9) 1.421(3), C(1)-C(7)-N(1) 113.9(2), C(7)-N(1)-N(2) 119.0(2), N(2)-C(8)-N(3) 114.4(2), C(8)-N(3)-C(9) 127.6(2).

pounds [(Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHPh})$_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (**2a**), [(Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHPh})$_2$(μ-Ph_2PCH=$CHPPh_2$)] (**3a**), [(Pd{2-$FC_6H_3C(Me)$=NN=C(S)-NHPh})$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**4a**), [(Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHPh})$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)] (**5b**), were obtained as pure air-stable solids, which were fully characterised (see Experimental). The ^{1}H NMR spectra showed the H5 resonance was shifted to lower frequency by ca. 1 ppm, appearing as a multiplet due to additional coupling to the ^{31}P nucleus. The ^{31}P resonance was a singlet signal in accordance with centrosymmetric compounds [35]; the chemical shift values are in agreement with a phosphorus *trans* to nitrogen [36−39].

Crystal Structure of 2-$FC_6H_4C(Me)$=NN(H)C(=S)NHPh

Ligand a crystallizes in the monoclinic P$\bar{1}$ space group as the *E*-isomer with respect to the N(1)-C(7) bond and *Z* with respect to the N(8)-C(3) bond, Figure 1.

This arrangement is often found in thiosemicarbazones with at least one hydrogen attached to N(3) [40, 41] due to weak N(3)-H(3)...N(1) hydrogen bonding. The C(8)-S(1) bond distance, 1.674(2) Å,the N(1)-C(7) distance, 1.278(3) Å, are consistent with a formal double bond character. Furthermore, the C(8)-N(3) distance, 1.345(3) Å, is also consistent with partial double bond character. The C(1)-C(7)-N(1) 113.9(2)° and C(7)-N(1)-N(2) 119.0(2)°, 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 = 0.0384) and at an angle of 37.06° with the fluorinated phenyl ring (rms = 0.0016). The parameters for the hydrogen bonding interaction in ligand **a**, which may be seen in Figure 2, are as follows:

N(3)···N(1) 2.564(3) Å, H(3)···N(1) 2.13 Å, N(3)-H(3)···N(1) 110.8 Å, N(2)···S(1)#1 3.684 Å, H(2)···S(1)# 2.83 Å, N(2)-H(2)···S(1)#1 169.8°; S(1)···C(15)#1 3.470(3) Å, H(15)#1···S(1) 2.91 Å, C(15)#1-H(15C)#1···S(1) 118.7°, S(1)···N(2)#1 3.684(2) Å, H(2)#1···S(1) 2.83 Å, N(2)#1-H(2)#1···S(1) 169.8°, C(15)···S(1)# 3.470(3) Å, H(15C)···S(1)#1 2.91 Å, C(15)-H(15)···S(1)#1 118.7°, with the symmetry operation #1[−x+2, −y, −z+2].

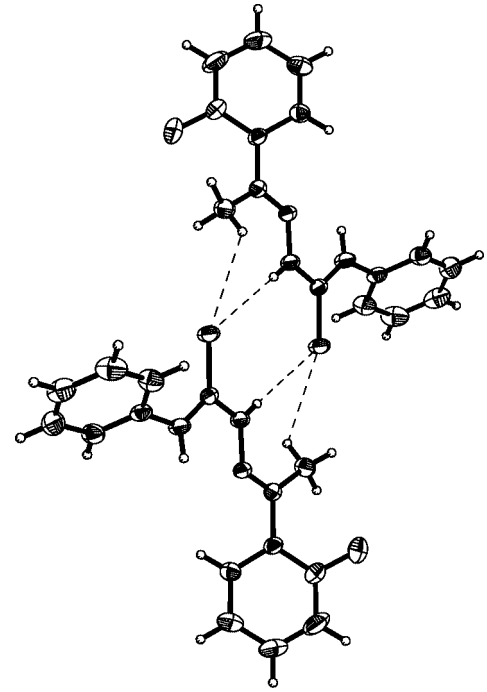


Figure 2 Hydrogen bonding in ligand **a**.

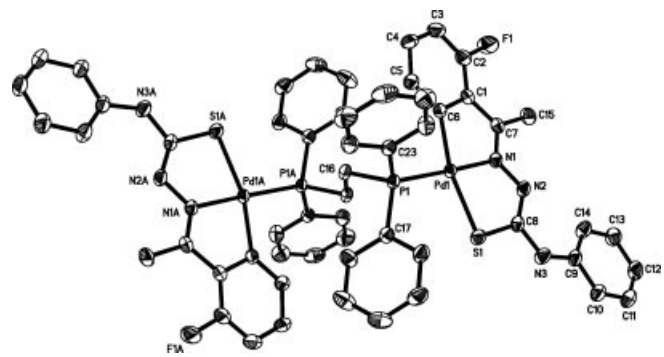


Figure 3 Molecular structure of complex **2a** with labelling scheme. Ellipsoids drawn at 30 %. Hydrogen atoms and solvent have been omitted for clarity.

Crystal Structure of [(Pd{2-$FC_6H_3C(Me)$=NN=C(S)NHPh})$_2$(μ-$Ph_2P(CH_2)_2P$-Ph_2)]

Suitable crystals were grown by slowly evaporating a chloroform/n-hexane solution of the complex. The labeling scheme for the compound is shown in Figure 3.

The crystals consist of discrete molecules, separated by normal van der Waals distances. Crystallographic data and

Table 1 Crystallographic data for complexes **a** and **2a**.

	a	**2a**
Empirical formula	C_{15} H_{14} F N_3 S	C_{58} H_{50} C_{16} F_2 N_6 P_2 Pd_2 S_2
Formula mass	287.35	1420.60
T /K	293(2)	293(2)
λ /Å	1.54184 Å	1.54184 Å
Crystal system	triclinic	triclinic
Space group	P$\bar{1}$	P$\bar{1}$
a /Å	6.1685(12)	9.8353(2)
b /Å	10.8190(11)	12.7847(3)
c /Å	11.2038(8)	12.9406(3)
α /°	99.954(9)	111.1160(10)
β /°	91.746(11)	97.8950(10)
γ /°	98.229(7)	96.2960(10)
V /Å^3	727.70(17)	1481.05(6)
Z	2	1
μ /mm^{-1}	2.019	1.053
max., min. transmissions	0.8112, 0.5898	0.9492, 0.7788
$\rho_{calc.}$ /gcm^{-3}	1.311	1.593
θ range /°	4.01 to 74.79	1.57 to 23.34
reflections collected	3124	10158
independent reflections	2959 [R(int) = 0.0267]	7014 [R(int) = 0.1169]
R_1 [$I>2\sigma(I)$]	0.0524	0.0411
R_1 [all data]	0.0958	0.1095
wR_2	0.1379	0.0532
wR_2 [all data]	0.1585	0.1186

Table 2 Selected bond lengths/Å and angles/° for complex **2a**.

Pd(1)-N(1)	2.024(3)	N(1)-Pd(1)-S(1)	82.88(8)
Pd(1)-S(1)	2.3333(9)	N(1)-Pd(1)-C(6)	80.55(8)
Pd(1)-P(1)	2.2663(8)	S(1)-Pd(1)-P(1)	99.24(3)
Pd(1)-C(6)	2.0324	P(1)-Pd(1)-C(6)	97.34(3)
N(1)-C(7)	1.293(3)	N(1)-Pd(1)-P(1)	176.18(8)
C(7)-C(1)	1.4650	S(1)-Pd(1)-C(6)	163.42(3)
C(1)-C(6)	1.4356	Pd(1)-P(1)-C(16)	111.74(4)
N(1)-N(2)	1.391(4)	Pd(1)-N(1)-C(7)	118.46(17)
N(2)-C(8)	1.294(3)	N(1)-C(7)-C(1)	113.34(12)
C(8)-S(1)	1.7704(11)	C(7)-C(1)-C(6)	116.6
N(1)-Pd(1)-S(1)	82.8(3)	C(1)-C(6)-Pd(1)	110.8
N(1)-Pd(1)-C(6)	96.2(4)		

selected interatomic distances and angles are listed in Tables 1 and 2.

In complex **2a** each palladium atom belongs to two fused five-membered chelate rings: the *C*,*N* metalacycle and *N*,*S*-chelate moiety, as a result of bonding to a tridentate *C*,*N*,*S* ligand. The palladium(II) atom is to four different donor atoms, a tridentate thiosemicarbazone through the aryl C(6) carbon, the imine N(1) nitrogen, and the thioamide S(1) sulfur atom, and to a phosphorus atom P(1) of the bis(diphenylphosphino)ethane, in a slightly distorted square-planar coordination, [Pd(1), N(1), S(1), C(6), P(1)), plane 1] (r.m.s = 0.0305 Å). The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°, in the range 97.34(3)° to 80.55(8)°, with the distortions being most noticeable in the thiosemicarbazone ligand. The angles N(1)-Pd(1)-C(6), 80.55(8)°,and N(1)-Pd(1)-S(1), 82.88(8)° are less than 90°, and the angles C(6)-Pd(1)-P(1), 97.34(3)°,and S(1)-Pd(1)-P(1), 99.24(3)°, are thus greater than 90°. All bond distances are within the expected range, with allowance for the strong *trans* influence of the phosphorus donor ligand, which is reflected in the Pd(1)-N(1) distance of 2.024(3) Å (cf. sum of the covalent radii for palladium and nitrogen, 2.01 Å [40]). The Pd(1)-C(6) bond length [2.0324 Å] is shorter than the expected value of 2.081 Å [40]; partial multiple-bond character has been invoked as reasoning [41,42]. The S(1)-C(8) bond length, 1.7704(11) Å, and the N(2)-C(8) length, 1.294(3) Å, are consistent with increased single and double bond character, respectively, in the deprotonated form. The palladium coordination plane [Pd(1), N(1), S(1), C(6), P(1)), plane 1] is coplanar with the metalacycle [Pd(1), C(1), C(6), C(7), N(1), plane 2], and with the coordination ring [Pd(1), N(1), N(2), C(8), S(1), plane 3] (angles between planes: 1/2 = 1.35, 1/3= 3.64°). Furthermore, the metalacycle [Pd(1), C(1), C(6), C(7), N(1), plane 2], is also co-planar with the coordination ring [Pd(1), N(1), N(2), C(8), S(1), plane 3] and with the metallated phenyl ring [C(1), C(2), C(3), C(4), C(5), C(6), plane 4] (angles between planes: 2/3 = 2.34, 2/4 = 3.65°).

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