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New thiosemicarbazone palladacycles with chelating bis(diphenylphosphino)methane

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Abstract

Treatment of the thiosemicarbazones 2-$ClC_6H_4C(Me)$=NN(H)C(=S)NHR, (R: Me, **a**; Et, **b**) and 2-$BrC_6H_4C(Me)$=NN(H)C(=S)NHR (R: Me, **c**; Et, **d**) with lithium tetrachloropalladate(II) in methanol or palladium(II) acetate in acetic acid gave the tetranuclear cyclometallated complexes $[Pd\{2\text{-}XC_6H_3C(Me)=NN=C(S)NHR\}]_4$ (X/R: Cl/Me, **1a**; Cl/Et, **1b**; Br/Me, **1c**; Br/Et, **1d**). Reaction of **1a**–**1d** with bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$, in a 1:4 molar ratio and concentrated hydrochloric acid gave the mononuclear complexes $[Pd\{2\text{-}XC_6H_3C(Me)=NN(H)\text{–}C(=S)NHR\}(Ph_2PCH_2PPh_2\text{-}P,P)](Cl)$ (**2a**–**2d**). Reaction of **1a**–**1d** with bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$, in 1:2 and 1:4 molar ratios gave the dinuclear or mononuclear complexes $[\{Pd[2\text{-}XC_6H_3C(Me)=NN=C(S)NHR]\}_2(\mu\text{-}Ph_2PCH_2PPh_2)]$ (**3a**–**3d**), and $[Pd\{2\text{-}XC_6H_3C(Me)=NN=C(S)NHR\}(Ph_2PCH_2PPh_2\text{-}P)]$ (**4a**–**4d**), with bridging and chelating diphosphine, respectively. The molecular structures of complexes **1b**, **1d**, **4c** and **4d** have been determined by X-ray diffraction analysis.

Keywords: Cyclometallation; Thiosemicarbazones; Palladium; C–H activation; Crystal structure

1. Introduction

The diversity of metals and ligands that may be encountered when dealing with cyclometallated compounds is prominent, as well as the usages these species display. Thus, cyclometallation, i.e., the process of intramolecular C–H activation of coordinated ligands by transition metals, has been widely investigated [1–5], and applications reaching from the synthesis of new organic and organometallic compounds to mesogenic species and catalytic materials [6–14] have been studied. Particularly interesting are the multidonor ligands which may bind in a terdentate fashion to the metal center via [C,N,X] (X = N [15–18], O [19,20], S [21,22]) atoms, in view of the structural features they comprise, and also because of the reactivity possibilities they exhibit. Unique to the terdentate [C,N,S] case, the well-known thiosemicarbazone ligands which afford tetranuclear cyclometallated compounds, is the strength of the Pd–$S_{chelating}$ bond, which hinders opening of the metallated and coordination rings at the metal center, thus allowing the ligands to be excellent pincer species which strongly fasten three of the four metal coordination sites, leaving only one for further reaction with nucleophiles. Consequently, treatment of the tetramers with diphosphines did not give in any case species with the phosphine ligand in a chelating mode, and only complexes with bridging or with mono-coordinate diphosphines were obtained [21,22]; in the latter case, the corresponding compounds may behave as bidentate [P,S] metalloligands as we have previously shown [23]. Nevertheless, regeneration of the hydrazinic NH bond was possible by treatment of the corresponding compound with concentrated hydrochloric

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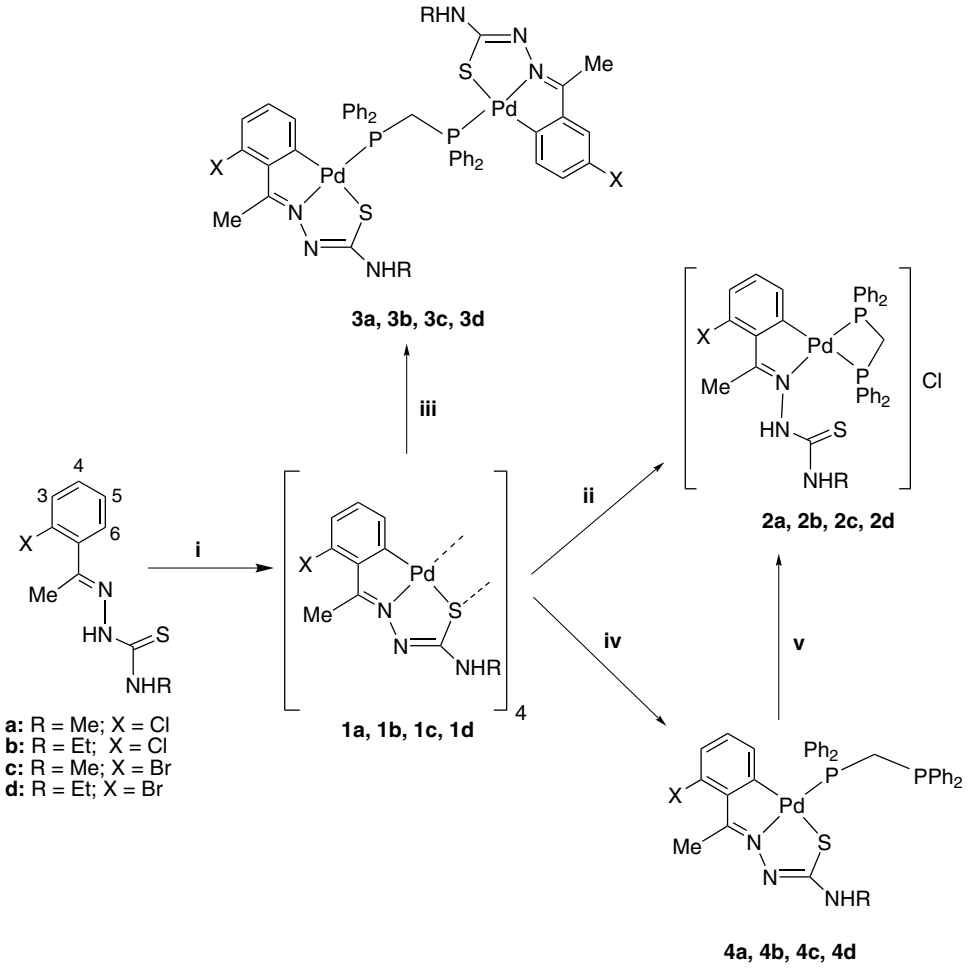
acid, however without cleavage of the Pd–$S_{chelating}$ bond. Therefore, in view of these findings and in our efforts to succeed in devising a route aimed at the preparation of cyclometallated thiosemicarbazone complexes with chelating diphosphines we reasoned that reaction of the tetranuclear palladacycles with a strong chelating diphosphine, plus concentrated hydrochloric acid, should suffice to yield the aforementioned species, and the results of this enterprise are presented herein.

2. Results and discussion

The ligands **a**–**d** were synthesized by reaction of 4-methyl or 4-ethyl-3-thiosemicarbazide with 2′-chloro- or 2′-bromoacetophenone as appropriate, in good yields, and were adequately characterized (see Section 6). The most prominent features were the characteristic ν(N–H) bands in the IR spectra ca. 3350 and 3200 cm^{-1}, assigned to the NHR and NH groups, respectively; distinctive ν(C=N) and ν(C=S) stretches appeared in the ranges 1620–1590 and 840–800 cm^{-1}, also, respectively. The NHR and NH proton resonances in the ^{1}H NMR appeared ca. δ 8.6 and 7.5 ppm, respectively. Reaction of the ligands by any one of the two alternative methods described, i.e., (a) lithium tetrachloropalladate and sodium acetate in methanol; or (b) palladium(II) acetate in glacial acetic acid, resulted in all cases in tetranuclear species, $[Pd\{2\text{-}XC_6H_3C(Me)=NN=C(S)NHR\}]_4$ (X/R: Cl/Me, **1a**; Cl/Et, **1b**; Br/Me, **1c**; Br/Et, **1d**) as air-stable solids, with the ligand in the *E*,*Z* configuration, which were fully characterized by microanalytical, mass spectra, IR and ^{1}H NMR determinations (see Section 6). The mass spectrum (FAB) showed peaks at *m*/*z* 1384 (**1a**), 1441 (**1b**), 1563 (**1c**) and 1620 (**1d**) for the molecular ion whose isotopic composition suggests a tetranuclear complex of the formula $C_{40}H_{40}Cl_4N_{12}Pd_4S_4$ (**1a**), $C_{44}H_{48}Cl_4N_{12}Pd_4S_4$ (**1b**), $C_{40}H_{40}Br_4N_{12}Pd_4S_4$ (**1c**) and $C_{44}H_{48}Br_4N_{12}Pd_4S_4$ (**1d**) (see Section 6).

The ν(C=N) band was shifted to lower wavenumbers ca. 30 cm^{-1} [24] indicating palladium coordination to the C=N moiety through the nitrogen lone pair [25,26]. The absence of the N*H* proton resonance in the ^{1}H NMR spectra was in agreement with deprotonation of the hydrazinic nitrogen atom [27,28]; accordingly, the C=S double bond character was minimized as confirmed by the non-existence of the ν(C=S) band [29]. Metallation of the ligands was



Scheme 1. (i) $Li_2[PdCl_4]$/NaAcO/MeOH; $Pd(AcO)_2$/AcOH; (ii) $Ph_2PCH_2PPh_2$/$HCl_{(aq)}$/acetone/1:4; (iii) $Ph_2PCH_2PPh_2$/acetone/1:2; (iv) $Ph_2PCH_2PPh_2$/acetone/1.4; (v) $HCl_{(aq)}$/acetone.

clear from the absence of the four proton ABCD spin system of the *ortho*-substituted phenyl ring; in the spectra of the complexes only three resonances were observed, which were unambiguously assigned to the H3, H4 and H5 protons (see Section 6).

3. Reactivity of the complexes

The reactions of **1a**–**1d** with $Ph_2PCH_2PPh_2$ in a 1:4 molar ratio and concentrated hydrochloric acid gave the hitherto unknown complexes [Pd{2-$XC_6H_3C(Me)$=NN(H)–C(=S)NHR}($Ph_2PCH_2PPh_2$-P,P)](Cl) **2a**–**2d** which were fully characterized (Section 6 and Scheme 1). Conductivity measurements in dry acetonitrile showed they were 1:1 electrolytes, with Λ_m values of ca. 130 ohm^{-1} cm^2 mol^{-1}. The most noticeable feature of these compounds was that protonation occurred at the hydrazinic nitrogen atom as shown by a broad resonance signal at ca. 8.80 ppm in the ^1H NMR spectra, and a band assignable to the ν(C=S) mode at ca. 8.35 cm^{-1} in the IR spectra. The ^{31}P–{^1H} NMR spectra showed two doublets for the two non-equivalent phosphorus nuclei. The resonance at lower frequency was assigned to the phosphorus nucleus *trans* to the phenyl carbon atom in accordance with the higher *trans* influence of the latter with respect to the C=N nitrogen atom [30]. The *H*C=N resonance was only coupled to the ^{31}P nucleus *trans* to nitrogen. This was confirmed by selective decoupling experiments on the ^{31}P atoms. Alternatively, compounds **2a**–**2d** could be prepared by stirring a mixture of **4a**–**4d** and concentrated hydrochloric acid at room temperature. Unfortunately, the yields were rather low in these cases, ca. 25%, and the final product contained unreacted starting material, and so far pure **2a**–**2d** could not be made by this additional route.

Treatment of the tetranuclear species with $Ph_2PCH_2PPh_2$ in the absence of acid gave dinuclear and mononuclear compounds with a bridging or monocoordinate phosphine ligand, respectively. Thus, reaction of **1a**–**1d** and the phosphine in a 1:2 molar ratio produced compounds [{Pd[2-$XC_6H_3C(Me)$=NN=C(S)NHR]}$_2$(μ-$Ph_2PCH_2PPh_2$)] (**3a**–**3d**) as pure air-stable solids, which were completely characterized (see Section 6). The symmetric nature of the complexes was evident from the ^1H NMR data, which showed only one set of signals; and consequently, only one singlet was observed in the ^{31}P–{^1H} spectra showing two equivalent phosphorus nuclei, with a δ value pointing

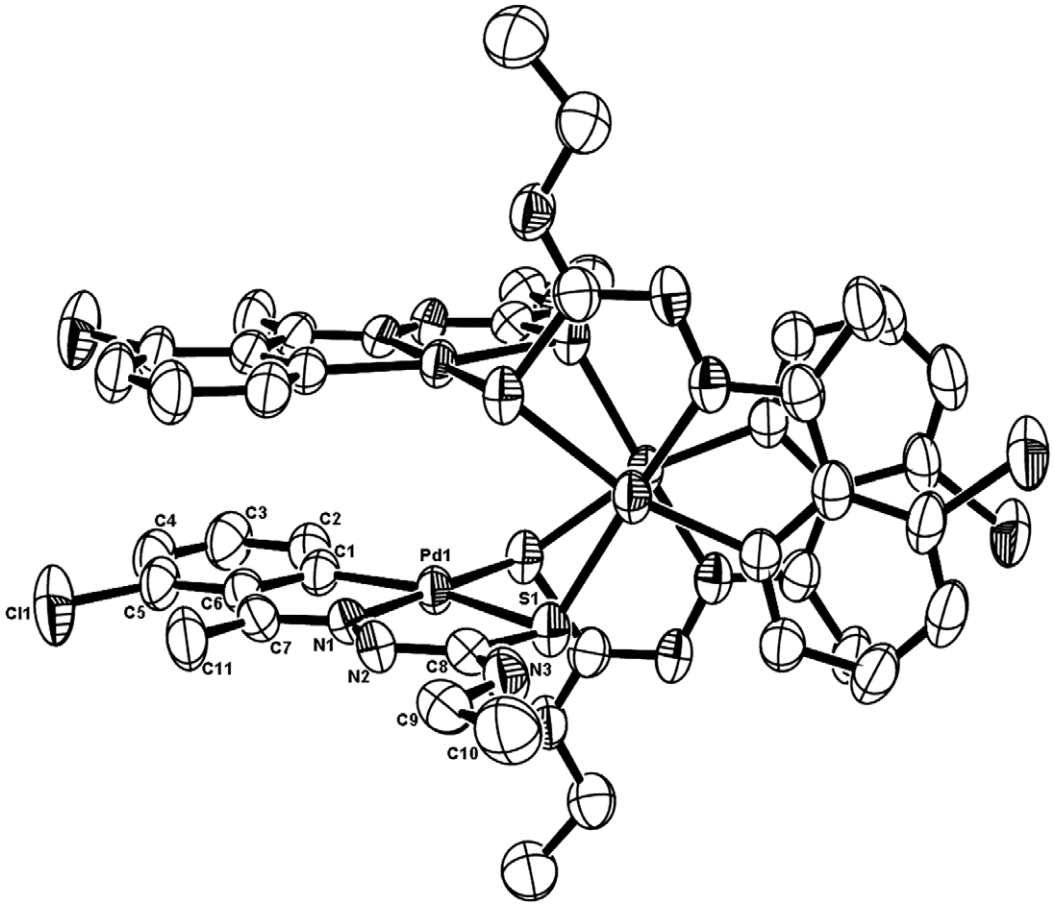


Fig. 1. An ORTEP drawing of the molecular structure for **1b** with the labelling scheme (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.989(4), Pd(1)–C(1) 2.007(5), Pd(1)–S(1)#1 2.3186(16), Pd(1)–S(1) 2.3551(16), S(1)–C(8) 1.792(6), N(1)–C(7) 1.316(6), N(1)–N(2) 1.385(6), N(2)–C(8) 1.308(6), C(6)–C(7) 1.469(8); N(1)–Pd(1)–C(1) 80.9(2), N(1)–Pd(1)–S(1)#1 177.11(13), C(1)–Pd(1)–S(1)#1 96.44(17), N(1)–Pd(1)–S(1) 84.10(13), C(1)–Pd(1)–S(1) 164.66(17), S(1)#1–Pd(1)–S(1) 98.52(4).

towards a phosphorus *trans* to nitrogen geometry [31,32]. The H5 resonance was low frequency shifted by ca. 1.5 ppm, showing coupling to the ^{31}P nucleus, also sustaining a P *trans* to N arrangement [33].

Reaction of **1a**–**1d** with $Ph_2PCH_2PPh_2$ in a 1:4 molar ratio gave the air-stable compounds [Pd{2-XC_6H_3C(Me)=NN=C(S)NHR}($Ph_2PCH_2PPh_2$-P)] (**4a**–**4d**). Characteristic microanalytical and spectroscopic data are given in Section 6. Even when excess diphosphine was used, only cleavage of the Pd–$S_{bridging}$ bonds was produced, therefore yielding species with coordination of the phosphine to the metal atom only through one phosphorus atom. The two doublets in the ^{31}P–{^1H} spectra were assigned to the two non-equivalent phosphorus nuclei with the signal for the phosphorus nucleus bonded to the metal center at higher frequency. The proton part of the *PCH_2P* ABXY spin system appeared as an apparent doublet at ca. 3.2 ppm.

4. Structural studies

4.1. Crystal structures of complexes *1b*, *1d*, *4c* and *4d*

Suitable crystals were grown by slowly evaporating chloroform/*n*-hexane solutions. The crystal structures are shown in Figs. 1–4. Crystal data are given in Table 1.

4.1.1. [Pd{2-XC_6H_3C(Me)=NN=C(S)NHEt}]$_4$ (X = Cl, *1b*; X = Br, *1d*)

The palladium(II) atoms in each structure are in slightly distorted square-planar environments (rms = 0.0132 **1b** and rms = 0.0132 **1d**), with small deviations from the coordination plane (±0.0412 **1b** and ±0.0437 **1d**), and are associated to two fused five-membered chelate rings: the C,N metallacycle and the N,S-chelate moiety, as a consequence of bonding to a terdentate C,N,S ligand. An eight-membered ring of palladium and sulfur atoms, with alternating Pd–$S_{bridging}$ and Pd–$S_{chelating}$ bonds compiles the central part of the molecule; the other two coordination positions at the metal are occupied by a phenyl carbon atom and the nitrogen atom of the C=N group (Figs. 1 and 2).

The angles between adjoining atoms in the coordination sphere are close to the theoretical value of 90°; with the most noteworthy strain in the C(1)–Pd(1)–N(1) values due to chelation of the ligand [22,23] [80.9(2)° **1b**; 81.4(3)° **1d**]. The Pd–C [2.007(5) Å **1b**, 1.990(7) Å **1d**] and Pd–N [1.989(4) Å **1b**, 1.988(6) Å **1d**] bond lengths are shorter than the expected values of 2.081 Å and 2.01 Å [34], respectively, probably induced by partial multiple-bond character [19,35]. The differing *trans* influence of the phenyl carbon and the azomethine nitrogen atoms is

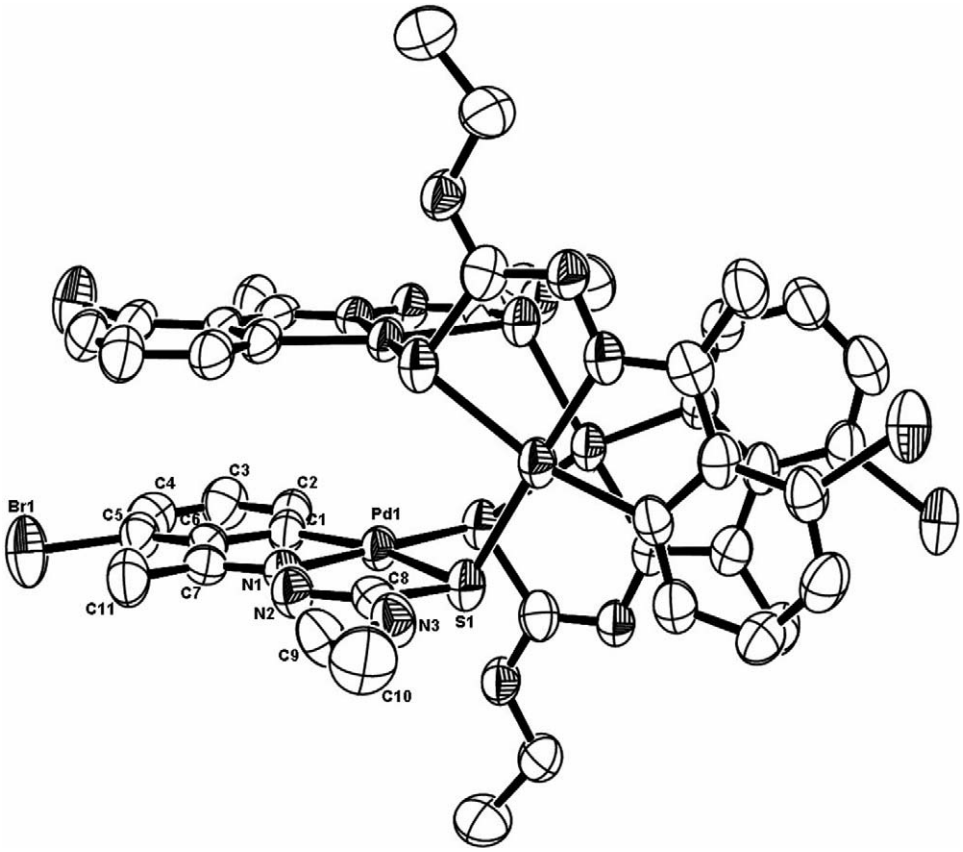


Fig. 2. An ORTEP drawing of the molecular structure for **1d** with the labelling scheme (50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.988(6), Pd(1)–C(1) 1.990(7), Pd(1)–S(1)#1 2.315(2), Pd(1)–S(1) 2.355(2), S(1)–C(8) 1.794(7), N(1)–C(7) 1.330(8), N(1)–N(2) 1.381(8), N(2)–C(8) 1.304(8); N(1)–Pd(1)–C(1) 81.4(3), N(1)–Pd(1)–S(1)#1 177.48(17), C(1)–Pd(1)–S(1) 96.2(2), N(1)–Pd(1)–S(1) 84.01(19), C(1)–Pd(1)–S(1)#1 165.0(2), S(1)#1–Pd(1)–S(1) 98.27(7).

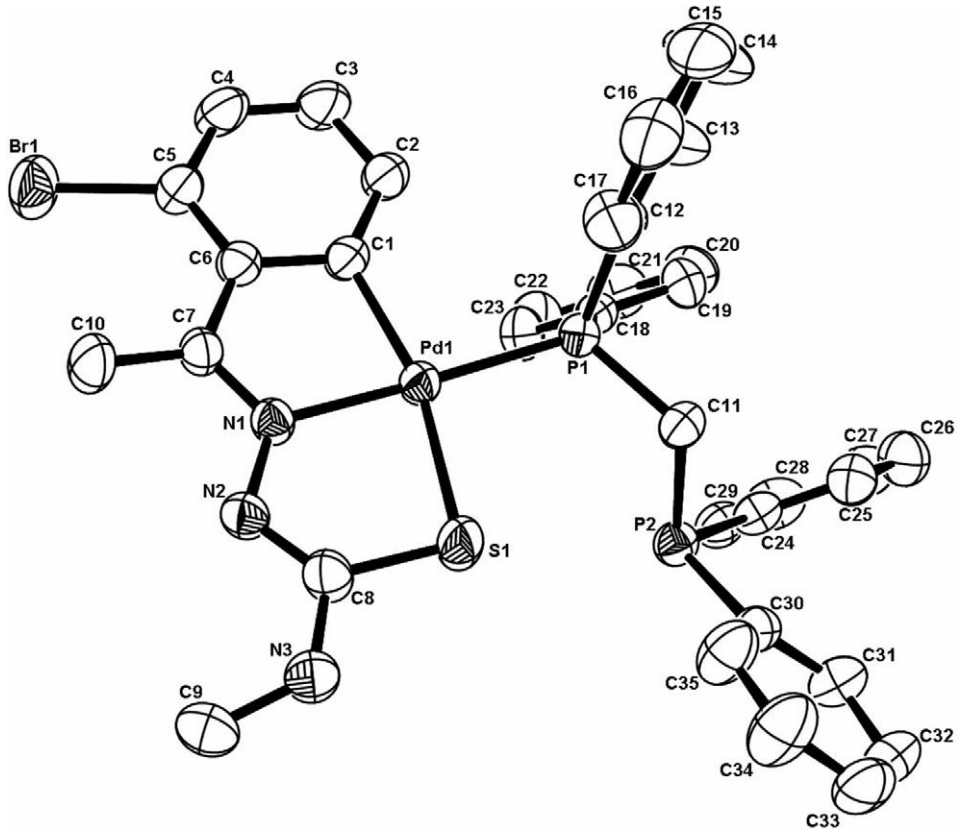


Fig. 3. An ORTEP drawing of the molecular structure for **4c** with the labelling scheme (50% probability). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.018(2), Pd(1)–C(1) 2.026(3), Pd(1)–P(1) 2.2626(8), Pd(1)–S(1) 2.3192(9), P(1)–C(18) 1.823(3), P(1)–C(12) 1.828(3), P(1)–C(11) 1.838(3), S(1)–C(8) 1.754(3), N(1)–C(7) 1.303(4), N(1)–N(2) 1.388(3), N(2)–C(8) 1.307(4), C(6)–C(7) 1.472(4); N(1)–Pd(1)–C(1) 80.77(7), N(1)–Pd(1)–P(1) 177.29(8), C(1)–Pd(1)–P(1) 97.94(2), N(1)–Pd(1)–S(1) 83.23(7), C(1)–Pd(1)–S(1) 163.95(9), P(1)–Pd(1)–S(1) 97.99(3).

put forward in the distinct values of the Pd–$S_{bridging}$ and Pd–$S_{chelating}$ distances [Pd(1)–S(1) 2.3551(16) Å, Pd(1)–S(1)#1 2.3186(16) Å **1b**; Pd(1)–S(1) 2.355(2) Å, Pd(1)–S(1)#1 2.315(2) Å **1d**]. The S(1)–C(8) [1.792(6) Å **1b**; 1.794(7) Å **1d**] and N(2)–C(8) [1.308(6) Å **1b**; 1.304(8) Å **1d**] distances, are consistent with increased single- and double-bond character, respectively, in the deprotonated form. The Pd–Pd lengths of 3.3725(7) Å **1b**, and 3.3596(16) Å **1d**, preclude any Pd–Pd interactions.

*4.1.2. [Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHR}-(Ph$_2$PCH$_2$PPh$_2$-P)] (R: Me **4c**; Et **4d**)*

The crystals consist of discrete molecules and $CHCl_3$, separated by normal van der Waals distances. The palladium coordination sphere is defined by an assorted set of four atoms arising from a terdentate C,N,S thiosemicarbazone and a η^1-diphosphine: the aryl C(1) carbon, the imine N(1) nitrogen, the thioamide S(1) sulfur and the phosphorus P(1) atoms, in a slightly distorted square-planar coordination, [N(1), S(1), C(1), P(1), plane 1] (r.m.s. = 0.0064 Å) **4c**, (Fig. 3), [N(1), S(1), C(1), P(1), plane 1] (r.m.s. = 0.0153 Å) **4d**, (Fig. 4), from which the palladium atom deviates by ±0.0382 Å **4c** and ±0.0328 Å **4d**.

As for the bond distances and the angles at palladium, the data observed for both structures show analogous values that are in accordance with the known theoretical data, with the most noticeable difference being in the Pd–N bond, which displays a marked lengthening due to the *trans* influence of the phosphine ligand [Pd(1)–N(1), 2.018(2) Å **4c**, 2.015(3) Å, **4d**], and the somewhat diminished C(1)–Pd(1)–N(1) angle, 80.77(7)° **4c**, 80.54(14)° **4d** (vide supra). The palladium coordination plane [Pd(1), C(1), N(1), S(1)], and the P(1)C(11)P(2), **4c**, and P(1)C(12)P(2), **4d**, planes are at angles of 68.72° and 69.70°, respectively.

5. Conclusions

We have shown that thiosemicarbazone ligands may yield tetranuclear palladacycles with two distinct Pd–$S_{bridging}$ and Pd–$S_{chelating}$ bonds; the strength of the latter hinders opening of the coordination ring, PdNNCS, bearing the Pd–$S_{chelating}$ bond, and upon reaction with $Ph_2PCH_2PPh_2$, in the absence of acid, only dinuclear and mononuclear compounds were obtained with bridging or monodentate phosphine ligands, respectively, and with the thiosemicarbazone ligand as a terdentate ligand [C,N,S]. However, when concentrated hydrochloric acid

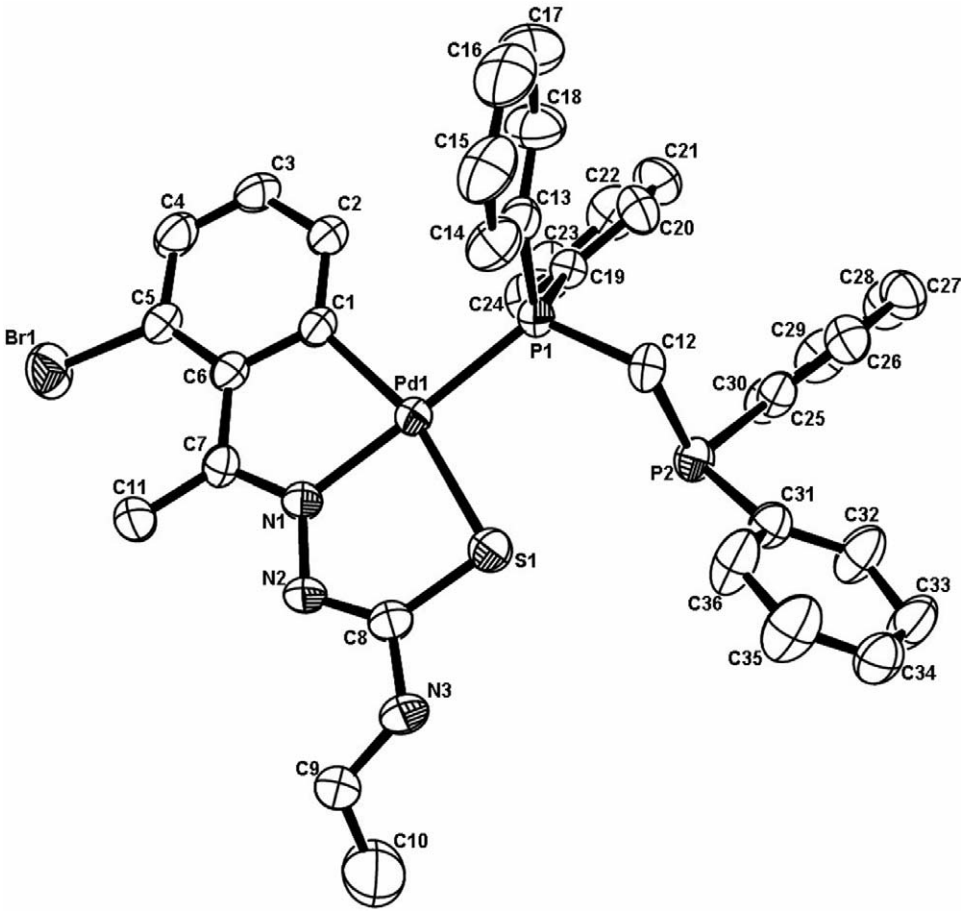


Fig. 4. An ORTEP drawing of the molecular structure for **4d** with the labelling scheme (50% probability). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 2.015(3), Pd(1)–C(1) 2.022(4), Pd(1)–P(1) 2.2659(10), Pd(1)–S(1) 2.3231(11), S(1)–C(8) 1.746(4), P(1)–C(13) 1.833(4), P(1)–C(19) 1.819(4), P(1)–C(12) 1.834(4), N(1)–C(7) 1.302(5), N(1)–N(2) 1.396(4), N(2)–C(8) 1.307(5), C(6)–C(7) 1.467(5); N(1)–Pd(1)–C(1) 80.54(14), N(1)–Pd(1)–P(1) 177.26(9), C(1)–Pd(1)–P(1) 98.33(12), N(1)–Pd(1)–S(1) 83.51(9), C(1)–Pd(1)–S(1) 164.05(12), P(1)–Pd(1)–S(1) 97.59(4).

was added to the reaction mixture, cleavage of the Pd–$S_{chelating}$ bond was produced, with protonation of the thiosemicarbazone and subsequent chelation of the diphosphine ligand, yielding the new thiosemicarbazone palladacycles as 1:1 electrolytes. These could also be made, although impure, by treatment of the compounds with η^1-diphosphine with hydrochloric acid.

6. Experimental

6.1. General procedures

Solvents were purified by standard methods [36]. 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 diphosphine $Ph_2PCH_2PPh_2$ (dppm) was 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 Perkin–Elmer 1330, IR-FT Mattson Model Cygnus-100 and 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. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10^{-3} mol dm^{-3} solutions in dry acetonitrile.

6.2. Syntheses

6.2.1. Preparation of thiosemicarbazone 2-$ClC_6H_4C(Me)$=$NN(H)C(=S)NHMe$ (**a**)

2′-Chloroacetophenone (147 mg, 9.51 mmol) and hydrochloric acid (35%, 0.65 cm^3) 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: 209 mg, 91%. *Anal.* $C_{10}H_{12}ClN_3S$ (241.7 g/mol) requires C, 49.7; H, 5.0; N, 17.4; S, 13.3. Found: C, 49.4; H, 5.0; N, 17.4; S, 13.2%. IR (cm^{-1}): ν(N–H) 3357s, 3239m; ν(C=N) 1591w; ν(C=S) 834m. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 8.62 (s, 1H, NH), 7.53 (br, 1H, N*H*Me), 7.36 (dd, 1H, H6, ^3J(H6H5) = 7.8, ^4J(H6H4) = 1.4), 7.26 (m, 3H, H3, H4, H5), 3.15 (d, 3H, NH*Me*, ^3J(HH) = 4.6), 2.22 (s, 3H, *Me*C=N). FAB-MS: m/z 242 $[M]^+$.

6.2.2. Thiosemicarbazones (**b**–**d**)

These were synthesized following a similar procedure.

6.2.2.1. 2-$ClC_6H_4C(Me)$=NN(H)C(=S)NHEt (**b**).

Yield: 165 mg, 77%. *Anal.* $C_{11}H_{14}ClN_3S$ (255.8 g/mol) requires C, 51.7; H, 5.5; N, 16.4; S, 12.5. Found: C, 51.5; H, 5.5; N, 16.3; S, 12.5%. IR (cm^{-1}): ν(N–H) 3367s, 3201m; ν(C=N) 1592w; ν(C=S) 827m. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 8.59 (s, 1H, NH), 7.53 (br, 1H, N*H*Et), 7.37 (m, 4H, H6, H3, H4, H5), 3.72 (dq, 2H, NH$CH_2$$CH_3$, ^3J(HH) = 7.4 Hz, ^3J(H–NH) = 5.5), 2.27 (s, 3H, *Me*C=N), 1.26 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). FAB-MS: m/z 256 $[M]^+$.

6.2.2.2. 2-$BrC_6H_4C(Me)$=NN(H)C(=S)NHMe (**c**).

Yield: 233 mg, 86%. *Anal.* $C_{10}H_{12}BrN_3S$ (286.2 g/mol) requires C, 42.0; H, 4.2; N, 14.7; S, 11.2. Found: C, 41.8; H, 4.3; N, 14.9; S, 11.0%. IR (cm^{-1}): ν(N–H) 3357s, 3179s; ν(C=N) 1586w; ν(C=S) 833m. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 8.63 (br, 1H, NH), 7.61 (dd, 1H, H6, ^3J(H6H5) = 7.9, ^4J(H4H6) = 1.4), 7.54 (br, 1 H, N*H*Me), 7.36 (dd, 1H, H3, ^3J(H3H4) = 7.9 Hz, ^4J(H3H5) = 1.4), 7.30 (td, 1H, H4, ^3J(H4H3) = 7.9 Hz, ^3J(H4H5) = 7.9 Hz, ^4J(H4H6) = 1.4), 7.25 (ddd, 1H, H5, ^3J(H6H5) = 7.9, ^3J(H5H4) = 7.9, ^4J(H5H3) = 1.4), 3.21 (d, 3H, NH*Me*, ^3J(HH) = 4.6), 2.27 (s, 3H, *Me*C=N). FAB-MS: m/z 287 $[MH]^+$.

6.2.2.3. 2-$BrC_6H_4C(Me)$=NN(H)C(=S)NHEt (**d**).

Yield: 204 mg, 81%. *Anal.* $C_{11}H_{14}BrN_3S$ (300.2 g/mol) requires C, 44.0; H, 4.7; N, 14.0; S, 10.7. Found: C, 43.9; H, 4.7; N, 14.2; S, 10.5%. IR (cm^{-1}): ν(N–H) 3367s, 3208m; ν(C=N) 1588w; ν(C=S) 826m. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 8.60 (br, 1H, NH), 7.61 (dd, 1H, H6, ^3J(H6H5) = 7.9, ^4J(H4H6) = 1.4), 7.54 (br, 1H, N*H*Et), 7.37 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 1.4), 7.31 (td, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9, ^4J(H4H6) = 1.4), 7.25 (ddd, 1H, H5, ^3J(H6H5) = 7.9, ^3J(H5H4) = 7.9, ^4J(H5H3) = 1.4), 3.72 (dq, 2H, NH$CH_2$$CH_3$, ^3J(HH) = 7.4, ^3J(H–NH) = 5.5), 2.26 (s, 3H, *Me*C=N), 1.25 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4 Hz). FAB-MS: m/z 300 $[M]^+$.

6.2.3. Preparation of [Pd{2-$ClC_6H_3C(Me)$=NN=C(S)-NHMe}]$_4$ (**1a**)

Method 1. Ligand **a** (286 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 which formed was filtered off, washed with methanol and dried in vacuo. Yield: 346 mg, 89%. *Anal.* $C_{40}H_{40}Cl_4N_{12}Pd_4S_4$ (1384.6 g/mol) requires C, 34.7; H, 2.9; N, 12.1; S, 9.3. Found: C, 34.6; H, 2.9; N, 11.9; S, 9.2%. IR (cm^{-1}): ν(N–H) 3425s, ν(C=N) 1558s. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 7.44 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 6.96 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.84 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 5.07 (q, 1H, N*H*Me, ^3J(NH–H) = 4.6), 2.98 (d, 3H, N*Me*, ^3J(H–NH) = 4.6), 2.22 (s, 3H, *Me*C=N). FAB-MS: m/z 1384 $[M]^+$.

Method 2. Ligand **a** (226 mg, 0.94 mmol, 5% excess) and palladium(II) acetate (200 mg, 0.89 mmol) were added to glacial acetic acid (45 cm^3) to give a clear solution, which was heated to 60 ° C under nitrogen for 24 h. After cooling to room temperature, the yellow precipitate which formed was filtered off, washed with ethanol and dried in vacuo. Yield: 294 mg, 95%.

6.2.4. Compounds **1b**–**1d**

These were synthesized following a similar procedure.

6.2.4.1. [Pd{2-$ClC_6H_3C(Me)$=NN=C(S)NHEt}]$_4$ (**1b**).

Method 1. Yield: 347 mg, 85%. *Anal.* $C_{44}H_{48}Cl_4N_{12}Pd_4S_4$ (1440.7 g/mol) requires C, 36.7; H, 3.4; N, 11.7; S, 8.9. Found: C, 36.6; H, 3.3; N, 11.8; S, 9.1%. IR (cm^{-1}): ν(N–H) 3429m, ν(C=N) 1559s. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 7.45 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 6.97 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.84 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 5.08 (t, 1H, N*H*Et, ^3J(NH–H) = 5.5), 3.40 (m, 2H, NH$CH_2$$CH_3$), 2.19 (s, 3H, *Me*C=N), 1.24 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). FAB-MS: m/z 1441 $[M]^+$.

Method 2. Yield: 284 mg, 89%.

6.2.4.2. [Pd{2-$BrC_6H_3C(Me)$=NN=C(S)NHMe}]$_4$ (**1c**).

Method 1. Yield: 365 mg, 83%. *Anal.* $C_{40}H_{40}Br_4N_{12}Pd_4S_4$ (1562.4 g/mol) requires C, 30.8; H, 2.6; N, 10.8; S, 8.2. Found: C, 30.7; H, 2.4; N, 10.6; S, 8.1%. IR (cm^{-1}): ν(N–H) 3417m, ν(C=N) 1561s. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 7.49 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 7.22 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.75 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 5.08 (q, 1H, N*H*Me, ^3J(NH–H) = 4.6), 2.98 (d, 3H, NH*Me*, ^3J(H–NH) = 4.6), 2.24 (s, 3H, *Me*C=N). FAB-MS: m/z 1563 $[MH]^+$.

Method 2. Yield: 283 mg, 81%.

6.2.4.3. [Pd{2-$BrC_6H_3C(Me)$=NN=C(S)NHEt}]$_4$ (**1d**).

Method 1. Yield: 353 mg, 77%. *Anal.* $C_{44}H_{48}Br_4N_{12}Pd_4S_4$ (1618.5 g/mol) requires C, 32.7; H, 3.0; N, 10.4; S, 7.9. Found: C, 32.5; H, 2.9; N, 10.3; S, 8.0%. IR (cm^{-1}):

Table 1
Crystal data and structure refinement data for **1b**, **1d**, **4c** and **4d**

Compound	**1b**	**1d**	**4c**	**4d**
Empirical formula	$C_{44}H_{48}Cl_4N_{12}Pd_4S_4$	$C_{11}H_{12}BrN_3PdS$	$C_{36}H_{33}BrCl_3N_3P_2PdS$	$C_{36}H_{34}BrN_3P_2PdS$
Formula weight	1440.58	404.61	894.31	788.97
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	tetragonal	tetragonal	triclinic	triclinic
Space group	$I4_1/a$	$I4_1/a$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions				
a (Å)	17.196(4)	17.249(10)	10.5638(1)	10.7529(5)
b (Å)	17.196(4)	17.249(10)	11.8823(1)	11.9801(6)
c (Å)	16.917(5)	17.228(11)	15.9816(1)	15.9998(8)
α (°)			88.569(1)	89.3630(10)
β (°)			80.760(1)	80.5180(10)
γ (°)			69.257(1)	69.6490(10)
Volume (Å^3)	5002(2)	5126(5)	1850.56(3)	1903.67(16)
Z	4	16	2	2
Density (calculated) (Mg/m^3)	1.913	2.097	1.605	1.376
Absorption coefficient (mm^{-1})	1.843	4.709	1.971	1.703
$F(000)$	2848	3136	896	796
Crystal size (mm^3)	$0.28\times0.24\times0.24$	$0.36\times0.32\times0.20$	$0.60\times0.50\times0.50$	$0.40\times0.30\times0.20$
θ Range for data collection (°)	2.37–29.96	2.36–25.82	1.29–28.28	1.29–28.29
Index ranges	$0/h/24$, $-24/k/0$, $0/l/23$	$-8/h/21$, $-14/k/17$, $-21/l/17$	$-8/h/14$, $-8/k/15$, $-19/l/21$	$-10/h/14$, $-13/k/15$, $-18/l/21$
Reflections collected	3849	5194	12 634	13 248
Independent reflections [R_{int}]	3626 [0.0633]	2484 [0.1207]	8738 [0.0148]	9102 [0.0240]
Completeness to θ (%)	99.8	100.0	95.3	96.1
Absorption correction	multi-scan	multi-scan	multi-scan	multi-scan
Maximum and minimum transmission	0.643 and 0.603	0.309 and 0.200	0.373 and 0.319	0.711 and 0.547
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	3626/0/157	2484/0/156	8738/0/434	9102/12/400
Goodness-of-fit on F^2	0.935	0.956	1.026	1.038
Final R indices [$I>2\sigma(I)$]	$R_1=0.0424$, $wR_2=0.0755$	$R_1=0.0358$, $wR_2=0.0690$	$R_1=0.0394$, $wR_2=0.0898$	$R_1=0.0506$, $wR_2=0.1024$
R indices (all data)	$R_1=0.2227$, $wR_2=0.1026$	$R_1=0.1615$, $wR_2=0.0926$	$R_1=0.0534$, $wR_2=0.0982$	$R_1=0.0823$, $wR_2=0.1148$
Largest differential peak and hole (e Å^{-3})	0.543 and −0.790	0.557 and −0.660	0.757 and −0.642	0.595 and −0.530

ν(N–H) 3425m, ν(C=N) 1557s. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.50 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 7.22 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.75 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 5.09 (t, 1H, N*H*Et, ^3J(NH–H) = 5.5), 3.40 (dq, 2H, NHCH_2CH$_3$, ^3J(HH) = 7.4, ^3J(H–NH) = 5.5), 2.21 (s, 3H, *Me*C=N), 1.24 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). FAB-MS: m/z 1620 [MH]$^+$.

Method 2. Yield: 302 mg, 84%.

6.2.5. *[(Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHMe})-(Ph$_2$PCH$_2$PPh$_2$)-P,P](Cl) (**2a**)*

The diphosphine $Ph_2PCH_2PPh_2$ (17.0 mg, 0.044 mmol) was added to a suspension of complex **1a** (15 mg, 0.011 mmol) in acetone (15 cm^3), and the mixture was treated with two drops of concentrated hydrochloric acid (35%). The resulting solution was stirred for 4 h and the yellow solid formed was filtered off and dried in vacuo. Yield: 19.6 mg, 42%. *Anal*. $C_{35}H_{33}Cl_2N_3P_2PdS$ (767.0 g/mol) requires C, 54.8; H, 4.3; N, 5.5; S, 4.2. Found: C, 54.7; H, 4.2; N, 5.5; S, 4.1%. IR (cm^{-1}): ν(N–H) 3440s, 3210; ν(C=N) 1557m. ^{1}H NMR($CDCl_3$, δ ppm, J Hz): 6.69 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.21 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.05 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 4.82 (q, 1H, N*H*Me, ^3J(NH–H) = 5.1), 3.61 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.57 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.01 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 2.69 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} ($CDCl_3$, δ ppm, J Hz): 24.4 (d, 1P, ^2J(PP) = 13.1), 22.8 (d, 1P, ^2J(PP) = 13.3). Λ_m = 133.1 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

Compounds **2b**–**2d** were synthesized similarly.

6.2.6. *[(Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHEt})-(Ph$_2$PCH$_2$PPh$_2$)-P,P](Cl) (**2b**)*

Yield: 15.4 mg, 34%. *Anal*. $C_{36}H_{35}Cl_2N_3P_2PdS$ (781.0 g/mol) requires C, 55.4; H, 4.5; N, 5.4; S, 4.1. Found: C, 55.4; H, 4.4; N, 5.4; S, 4.0%. IR (cm^{-1}): ν(N–H) 3432s; ν(C=N) 1558m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.77 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 1.4), 6.32 (t, 1H, H4,

^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.02 (ddd, 1H, H5, ^3J(H5H4) = 7.9 Hz, ^4J(H5P) = 5.1, ^4J(H5H3) = 1.4), 4.81 (t, 1H, N*H*Et, ^3J(NH–H) = 5.5), 3.60 (d, 1H, P CH_2P, ^2J(HP) = 9.2), 3.56 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.42 (dq, 2H, NHCH_2CH$_3$, ^3J(HH) = 7.4 Hz, ^3J(H–NH) = 5.5), 2.67 (s, 3H, *Me*C=N), 1.20 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 24.3 (d, 1P, ^2J(PP) = 13.1), 22.7 (d, 1P, ^2J(PP) = 13.1). Λ_m = 132.7 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

6.2.7. [(Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHMe})-(Ph$_2$PCH$_2$PPh$_2$)-P,P](Cl) (**2c**)

Yield: 33.0 mg, 74%. *Anal.* $C_{35}H_{33}BrClN_3P_2PdS$ (811.5 g/mol) requires C, 51.8; H, 4.1; N, 5.2; S, 4.0. Found: C, 51.6; H, 4.0; N, 5.1; S, 3.9%. IR (cm^{-1}): ν(N–H) 3426m; ν(C=N) 1559s. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.01 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.22 (t, 1H, H4, ^3J(H4H3) = 7.9 Hz, ^3J(H4H5) = 7.9), 6.10 (m, 1H, H5), 4.83 (br, 1H, N*H*Me), 3.72 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.68 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 2.98 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 2.70 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 24.1 (d, 1P, ^2J(PP) = 13.1), 22.7 (d, 1P, ^2J(PP) = 13.1). Λ_m = 125.6 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

6.2.8. [(Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHEt})-(Ph$_2$PCH$_2$PPh$_2$)-P,P](Cl) (**2d**)

Yield: 13.2 mg, 30%. *Anal.* $C_{36}H_{35}BrClN_3P_2PdS$ (825.5 g/mol) requires C, 52.4; H, 4.3; N, 5.1; S, 3.9. Found: C, 52.3; H, 4.3; N, 5.0; S, 3.9%. IR (cm^{-1}): ν(N–H) 3428m; ν(C=N) 1557m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.01 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 0.9), 6.22 (t, 1H, H4, ^3J(H4H3) = 7.9 Hz, ^3J(H4H5) = 7.9), 6.10 (m, 1H, H5), 4.82 (br, 1H, N*H*Et), 3.60 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.56 (d, 1H, PCH_2P, ^2J(HP) = 9.2), 3.41 (dq, 2H, NHCH_2CH$_3$, ^3J(HH) = 7.4 Hz, ^3J(H–NH) = 5.5), 2.68 (s, 3H, *Me*C=N), 1.20 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 24.2 (d, 1P, ^2J(PP) = 13.7), 22.8 (d, 1P, ^2J(PP) = 14.5). Λ_m = 130.2 ohm^{-1} cm^2 mol^{-1} (in acetonitrile).

6.2.9. [(Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHMe})$_2$-(μ-Ph$_2$PCH$_2$PPh$_2$)] (**3a**)

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 in vacuo. Yield: 19.6 mg, 42%. *Anal.* $C_{45}H_{42}Cl_2N_6P_2Pd_2S_2$ (1076.7 g/mol) requires C, 50.2; H, 3.9; N, 7.8; S, 6.0. Found: C, 50.1; H, 3.9; N, 7.7; S, 5.8%. IR (cm^{-1}): ν(N–H) 3440s; ν(C=N) 1557m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.69 (dd, 1H, H3, ^3J(H3H4) = 7.9 Hz, ^4J(H3H5) = 0.9), 6.21 (t, 1H, H4, ^3J(H4H3) = 7.9 Hz, ^3J(H4H5) = 7.9), 6.05 (dd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5H3) = 0.9), 4.82 (q, 1H, N*H*Me, ^3J(NH–H) = 5.1), 3.73 (t, 1H, PCH_2P, ^2J(HP) = 10.2), 3.01 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 2.69 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): δ = 23.7s.

Compounds **3b**–**3d** were prepared analogously.

6.2.10. [(Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHEt})$_2$-(μ-Ph$_2$PCH$_2$PPh$_2$)] (**3b**)

Yield: 15.4 mg, 34%. *Anal.* $C_{47}H_{46}Cl_2N_6P_2Pd_2S_2$ (1104.7 g/mol) requires C, 51.1; H, 4.2; N, 7.6; S, 5.8. Found: C, 51.3; H, 4.5; N, 7.5; S, 5.7%. IR (cm^{-1}): ν(N–H) 3432s; ν(C=N) 1558m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.77 (dd, 1H, H3, ^3J(H3H4) = 7.9, ^4J(H3H5) = 1.4), 6.32 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.02 (ddd, 1H, H5, ^3J(H5H4) = 7.9, ^4J(H5P) = 5.1, ^4J(H5H3) = 1.4), 4.81 (t, 1H, N*H*Et, ^3J(NH–H) = 5.5), 3.58 (t, 1H, PCH_2P, ^2J(HP) = 9.2), 3.42 (dq, 2H, NHCH_2CH$_3$, ^3J(HH) = 7.4, ^3J(H–NH) = 5.5), 2.67 (s, 3H, MeC=N), 1.20 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 22.9s.

6.2.11. [(Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHMe})$_2$-(μ-Ph$_2$PCH$_2$PPh$_2$)] (**3c**)

Yield: 33.0 mg, 74%. *Anal.* $C_{45}H_{42}Br_2N_6P_2Pd_2S_2$ (1165.6 g/mol) requires C, 46.4; H, 3.6; N, 7.2; S, 5.5. Found: C, 46.1; H, 3.7; N, 6.9; S, 5.4%. IR (cm^{-1}): ν(N–H) 3426m; ν(C=N) 1559s. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.01 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.22 (t, 1H, H4, ^3J(H4H3) = 7.9 Hz, ^3J(H4H5) = 7.9), 6.10 (m, 1H, H5), 4.83 (br, 1H, N*H*Me), 3.71 (t, 1H, PCH_2P, ^2J(HP) = 10.2), 2.98 (d, 3H, NH*Me*, ^3J(H–NH) = 5.1), 2.70 (s, 3H, MeC=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 23.6s.

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

Yield: 13.2 mg, 30%. *Anal.* $C_{47}H_{46}Br_2N_6P_2Pd_2S_2$ (1193.6 g/mol) requires C, 47.3; H, 3.9; N, 7.0; S, 5.4. Found: C, 47.1; H, 3.9; N, 6.7; S, 5.2%. IR (cm^{-1}): ν(N–H) 3428m; ν(C=N) 1557m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 7.01 (dd, 1H, H3, ^3J(H3H4) = 7.9 Hz, ^4J(H3H5) = 0.9), 6.22 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.10 (m, 1H, H5), 4.82 (br, 1H, N*H*Et), 3.58 (t, 1H, PCH_2P, ^2J(HP) = 9.2), 3.41 (dq, 2H, NHCH_2CH$_3$, ^3J(HH) = 7.4, ^3JH–NH = 5.5), 2.68 (s, 3H, *Me*C=N), 1.20 (t, 3H, NHCH$_2$$CH_3$, ^3J(HH) = 7.4). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm): 23.7s.

6.2.13. [Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHMe}-(Ph$_2$PCH$_2$PPh$_2$-P)] (**4a**)

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 in vacuo. Yield: 130 mg, 78%. *Anal.* $C_{35}H_{32}ClN_3P_2PdS$ (730.5 g/mol) requires C, 57.5; H, 4.4; N, 5.8; S, 4.4. Found: C, 57.7; H, 4.5; N, 5.5; S, 4.3%. IR (cm^{-1}): ν(N–H) 3431m; ν(C=N) 1555m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.75 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.31 (t, 1H, H4,

^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.15 (m, 1H, H5), 4.81 (br, 1H, N*H*Me), 3.22 (d, 2H, P*CH*$_2$P, ^2J(HP) = 9.5), 2.97 (d, 3H, NH*CH*$_3$, ^3J(H–NH) = 5.1), 2.67 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 24.1 (d, 1P, P_A, ^2J(PP) = 79.8), −26.7 (d, 1P, P_B, ^2J(PP) = 79.8).

Compounds **4b**–**4d** were prepared analogously.

6.2.14. [Pd{2-ClC$_6$H$_3$C(Me)=NN=C(S)NHEt}-(Ph$_2$PCH$_2$PPh$_2$-P)] (**4b**)

Yield: 127 mg, 70%. *Anal.* $C_{36}H_{34}ClN_3P_2PdS$ (744.6 g/mol) requires C, 58.1; H, 4.6; N, 5.6; S, 4.3. Found: C, 57.9; H, 4.7; N, 5.7; S, 4.2%. IR (cm^{-1}): ν(N–H) 3423s; ν(C=N) 1555m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.74 (d, 1H, H3, ^3J(H3H4) = 7.9), 6.31 (t, 1H, H4, ^3J(H4H3) = 7.9, ^3J(H4H5) = 7.9), 6.15 (m, 1H, H5), 4.81 (br, 1H, N*H*Et), 3.41 (m, 2H, NH*CH*$_2$CH$_3$), 3.24 (d, 2H, P*CH*$_2$P, ^2J(HP) = 9.5), 2.67 (s, 3H, *Me*C=N), 1.18 (t, 3H, NHCH$_2$*CH*$_3$, ^3J(HH) = 7.4). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 23.7 (d, 1P, P_A, ^2J(PP) = 79.8), −26.7 (d, 1P, P_B, ^2J(PP) = 79.8).

6.2.15. [(Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHMe})$_2$-(Ph$_2$PCH$_2$PPh$_2$-P)] (**4c**)

Yield: 64.1 mg, 73%. *Anal.* $C_{35}H_{32}BrN_3P_2PdS$ (775.0 g/mol) requires C, 54.2; H, 4.2; N, 5.4; S, 4.1. Found: C, 54.5; H, 4.4; N, 5.3; S, 4.0%. IR (cm^{-1}): ν(N–H) 3428m; ν(C=N) 1558m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.98 (m, 1H, H3), 6.21 (m, 1H, H4), 6.11 (m, 1H, H5), 4.83 (br, 1H, N*H*Me), 3.23 (d, 2H, P*CH*$_2$P, ^2J(HP) = 9.7), 2.98 (d, 3H, NH*CH*$_3$, ^3J(H–NH) = 5.1), 2.69 (s, 3H, *Me*C=N). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 23.9 (d, 1P, P_A, ^2J(PP) = 79.8), −26.8 (d, 1P, P_B, ^2J(PP) = 79.8).

6.2.16. [Pd{2-BrC$_6$H$_3$C(Me)=NN=C(S)NHEt}-(Ph$_2$PCH$_2$PPh$_2$-P)] (**4d**)

Yield: 149 mg, 86%. *Anal.* $C_{36}H_{34}BrN_3P_2PdS$ (789.0 g/mol) requires C, 54.8; H, 4.3; N, 5.3; S, 4.1. Found: C, 55.0; H, 4.5; N, 5.0; S, 3.9%. IR (cm^{-1}): ν(N–H) 3418m; ν(C=N) 1556m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 6.97 (m, 1H, H3), 6.21 (m, 1H, H4), 6.12 (m, 1H, H5), 4.81 (br, 1H, N*H*Et), 3.42 (m, 2H, NH*CH*$_2$CH$_3$), 3.24 (d, 2H, P*CH*$_2$P, ^2J(HP) = 9.7), 2.68 (s, 3H, *Me*C=N), 1.22 (t, 3H, NHCH$_2$*CH*$_3$, ^3J(HH) = 7.4 Hz). ^{31}P–{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 23.6 (d, 1P, P_A, ^2J(PP) = 75.1), −26.7 (d, 1P, P_B, ^2J(PP) = 75.1).

7. Crystal structures

Crystals of complexes **1b**, **1d**, **4c** and **4d**, were mounted on a glass fibre and transferred to the diffractometer. Three dimensional, room temperature X-ray data were collected with CAD4 Enraf Nonius (**1b** and **1d**) and Siemens (**4c** and **4d**) diffractometers 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 semi-empirical methods based on symmetry-equivalent and repeated reflections [T_{max}/T_{min} = 0.643/0.603 (**1b**), 0.309/0.200 (**1d**), 0.373/0.319 (**4c**) and 0.711/0.547 (**4d**)]. 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 using the riding mode. The structure of **4d** contains 1 symmetry related void of 297.00 Å^3 containing unresolvable solvent, this was treated using the squeeze method lowering the R_1 value by 5.76% [37]. Refinement converged at a final R = 0.0424 (**1b**), 0.0358 (**1d**), 0.0394 (**4c**) and 0.0506 (**4d**) (observed data, F), and wR_2 = 0.1026 (**1b**), 0.0926 (**1d**), 0.0982 (**4c**) and 0.1148 (**4d**) (all unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron densities: −0.790 and 0.543 (**1b**), −0.660 and 0.557 (**1d**), −0.642 and 0.757 (**4c**), −0.530 and 0.595 e Å^{-3} (**4d**). The structure solutions and refinements were carried out with the SHELX-97 [38] 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 292962 (**1b**), 292963 (**1d**), 292965 (**4c**) 29294 (**4d**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 12336033; e-mail: deposit@ccdc.cam.ac.uk, or on the web www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.04.013.

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