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Synthesis, Characterization, and Crystal Structure Analysis of the First Terdentate [C,N,S] Thiosemicarbazone Complex with a Six-Membered Palladacycle: Influence of Steric Effects on Ring Size

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Dedicated to Professor Victor Riera on the occasion of his 70th birthday

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The reaction of the thiosemicarbazone ligands 1-(COMe)-3-[C(H)=NN(H)C(=S)NHR]C_8H_5N, (R = H **a**, Me **b**, Et **c**) with potassium tetrachloropalladate in an ethanol/water mixture led to the new tetranuclear palladium(II) compounds [Pd{1-(COMe)-3-[C(H)=NN=C(S)NHR]C_8H_4N-k^3*C5,N,S*}]$_4$ (R = H **1a**, Me **1b**, Et **1c**) which contain six-membered metallacycles. The thiosemicarbazone ligands in these complexes are terdentate through the C, N, and S atoms and are deprotonated at the NH group. The Pd–S bond formed is sufficiently strong to undergo reactions with nucleophiles without bond cleavage. Reaction of **1a** and **1b** with 1,2-bis(diphenylphosphanyl)ethane (dppe) gave the dinuclear species [{Pd[1-(COMe)-3-{C(H)=NN=C(S)NHR}C_8H_4N]}$_2$(μ-$Ph_2P(CH_2)_2PPh_2$)] (R = H **2a**, Me **2b**). The molecular structure of complex **1b** has been determined by X-ray diffraction analysis.

Introduction

Cyclometalated compounds, which make up a fair portion of species pertaining to the organometallic family, are quite numerous and have been studied to a great degree, among other reasons owing to the great number of organic substrates that can undergo a cyclometalation reaction to form a stable five-membered ring.[1–7] In particular, thiosemicarbazone ligands are prominent in this process in view of the donor atoms they display, which is not only limited to the nitrogen and sulfur atoms of the thiosemicarbazide chain, or to additional donors set on the parent aldehyde or ketone, but also because metal–carbon bonding makes them appropriate terdentate [C,N,S] ligands. This makes them reminiscent of the related terdentate [C,N,N] Schiff bases[8–10] and [C,N,O] semicarbazones[11] in that compounds with two fused rings at the metal center are formed; recently, a further example of [C,N,N] pincer complexes has been reported.[12]

That thiosemicarbazone derivatives exhibit an altogether different chemical behavior is due to the strength of the Pd–$S_{chelate}$ bond, which hinders opening of the metalated and coordination rings at the metal center, thus making the ligands excellent pincer species that powerfully occupy three of the four coordination positions of the metal, thereby allowing only the fourth coordination site to undergo further reaction with nucleophiles.

Another interesting issue related to these ligands is that upon treatment with the corresponding palladium or platinum salt, tetrameric compounds bearing a central Pd_4S_4 or Pt_4S_4 central core are obtained, an outcome which, in the majority of cases, seems to be an inevitable consequence of their chemistry. In view of our previous results, and in efforts to progress further into the chemistry of cyclometalated thiosemicarbazones, we were interested in establishing if tetrameric compounds could also be obtained in the case of six-membered palladacycles, for which purpose we chose ligands derived from condensed systems where five- or six-membered metalated rings may be formed. It has been reported that in ligands with condensed rings, the site and/or the electronic properties of the substituents may force the formation of six-membered metalated rings as opposed to the more stable five-membered ones.[13,14] Furthermore, previous studies have also shown that bulky groups close to the potential metalation site impede metal–carbon bond formation by hindering approach of the metal to the carbon atom.[15] With this in mind we chose the thiosemicarbazones derived from the condensation of 1-acetyl-3-in-

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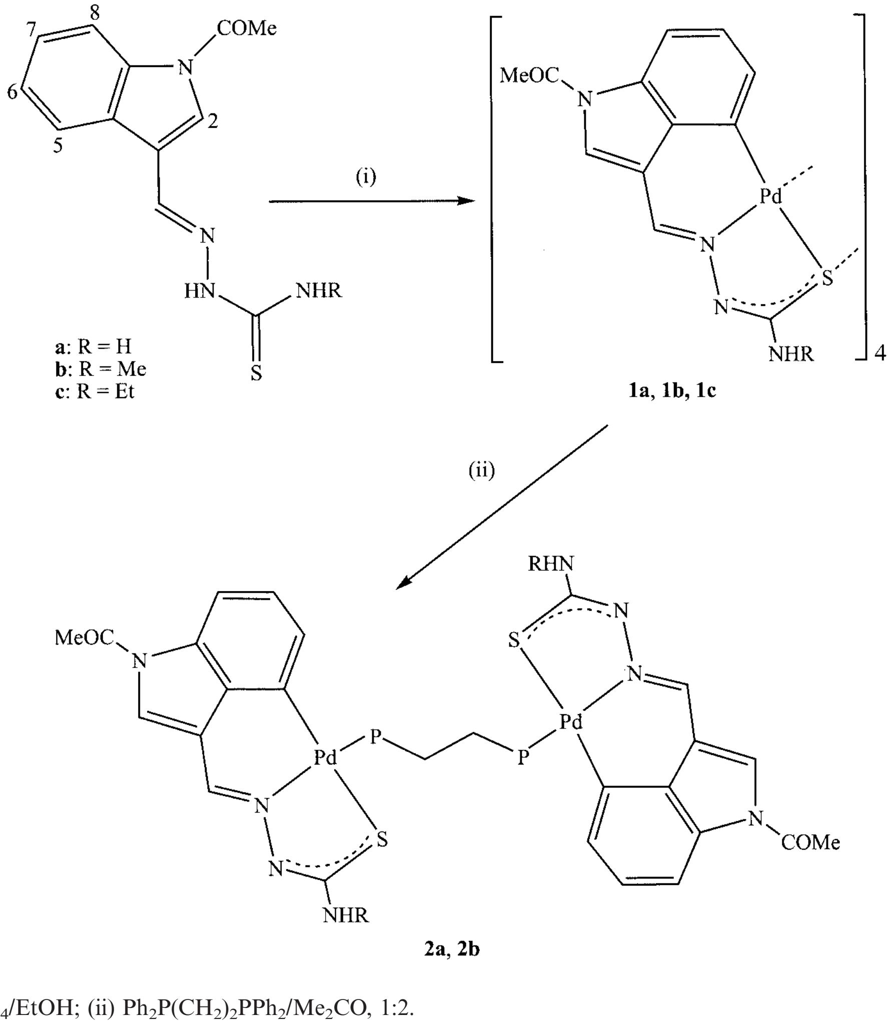
dolecarboxaldehyde and the corresponding thiosemicarbazide, where, although metalation could, in principle, be achieved through the pyrrole (C2) or the phenyl (C5) carbon atoms to give a five- or a six-membered metalated ring, respectively, the acetyl group on the pyrrole nitrogen atom should sufficiently hinder approach of the palladium atom to the C(2) carbon, in which case metalation of the ligand should occur at the C(5) carbon. This paper describes the results of this endeavor.

Results and Discussion

The ligands **a**–**c** were prepared by reaction of 1-acetyl-3-indolecarboxaldehyde with thiosemicarbazide, 4-methylthiosemicarbazide, or 4-ethylthiosemicarbazide, respectively (see Exp. Sect.). The bands at around 3380 and 3140 cm^{-1} in the IR spectra of these compounds are due to ν(N–H) absorption of the NH_2 and NH groups, respectively; the latter is not present in the spectra of the complexes.[15] The ligands also show characteristic ν(C=N) and ν(C=S) stretches in their IR spectra at around 1615 and 830 cm^{-1}, respectively. In the ^{1}H NMR spectra the resonances at around δ = 11.5 and 8.30 ppm were assigned to the NH and HC=N protons, respectively (see Exp. Sect.). New cyclometalated compounds were obtained from the ligands, as shown in Scheme 1. In a typical experiment, a suspension of K_2PdCl_4 in ethanol/water was treated with the corresponding thiosemicarbazone ligand to give complexes [Pd{1-(COMe)-3-[C(H)=NN=C(S)NHR]C_8H_4N-k^3*C5*,*N*,*S*}]$_4$ (R = H **1a**, Me **1b**, Et **1c**) as air-stable solids, which were fully characterized, with the ligand in the (*E*,*Z*) configuration. The mass spectrum (FAB) shows peaks at *m*/*z* 1458 (**1a**), 1515 (**1b**), and 1571 (**1c**) for the molecular ion, and the isotopic composition suggests a tetranuclear complex of formula $C_{48}H_{40}N_{16}O_4Pd_4S_4$ (**1a**), $C_{52}H_{48}N_{16}O_4Pd_4S_4$ (**1b**), and $C_{56}H_{56}N_{16}O_4Pd_4S_4$ (**1c**).

The IR data are in agreement with deprotonation of the ligand at the hydrazine nitrogen upon complex formation[16–19] (vide supra). The ν(C=N) band is shifted to lower wavenumbers,[20] contrary to the trend observed for other thiosemicarbazone complexes, which show a shift to higher wavenumbers.[15] The ν(C=S) band disappears, in agreement with loss of double-bond character upon deprotonation of the NH group. Although these data are in good accordance with metalation of the thiosemicarbazone, they give little insight as to the metalated carbon atom, for which definite proof was obtained from the ^{1}H NMR spectra, whose data are fully consistent with metalation of the C(1)



Scheme 1. (i) K_2PdCl_4/EtOH; (ii) $Ph_2P(CH_2)_2PPh_2/Me_2CO$, 1:2.

carbon atom. Thus, a singlet at δ = 7.41 (**1a**), 7.41 (**1b**) and 7.68 ppm (**1c**) was assigned to the pyrrole C(2)H proton resonance, which is shifted to lower frequency with respect to its position in the spectra of the free ligands ($\delta \approx$ 8.3 ppm). The complex ABCD spin system due to the H(5)–H(8) protons that is seen for the ligands is absent in the spectra of the complexes, where it gives way to a simple three-proton first-order spectrum that can be unambiguously assigned and clearly indicates loss of the H5 proton upon metalation. Thus, two doublets at around δ = 8.6 and 8.4–8.0 ppm were ascribed to the H6 and H8 protons, respectively, whereas a triplet at around δ = 7.1 ppm was assigned to the H7 resonance (see Exp. Sect.). Also relevant is the absence of the signal for the NH group and the high-field shift of the HC=N resonance by about 0.4–0.9 ppm.[21,22] Only one set of signals was detected in the ^{1}H NMR spectra, thereby precluding mixtures of compounds bearing different metalated carbons and confirming the strong steric hindrance exerted by the C(O)Me group, which selectively directs the palladium atom towards the phenyl C5 atom.

Crystal and Molecular Structure of 1b

Suitable crystals of complex **1b** were grown by slowly evaporating a DMSO solution. Crystal data are given in the Exp. Sect. An ORTEP illustration of the structure, with selected interatomic distances and angles, is shown in Figure 1.

The asymmetric unit of **1b** consists of two molecules of compound **1b** and eight DMSO solvent molecules. Although the overall structure for each molecule is only approximately S_4-symmetric, the four cyclometalated moieties are not symmetry-related. Nevertheless, discussion shall be limited to the data pertaining to one fourth of the molecule, i.e., the one involving Pd(1A); the structural data for the other three molecular units are very similar. The palladium atom exhibits a slightly distorted square-planar geometry with a central nucleus comprised of an eight-membered ring of alternating palladium and sulfur atoms, which adopts a boat conformation. Each palladium atom is bonded to four different donor atoms: three pertaining to a terdentate thiosemicarbazone, namely the aryl C(1) carbon, the imine N(2) nitrogen, and the thioamide S(1) sulfur atom, with a fourth donor being a sulfur atom S(1B) from a neighboring ligand. The plane formed by the ligating atoms at palladium [C(1A), N(2A), S(1A), S(1B): plane 1] is essentially planar (rms = 0.0132), with slight displacement of the metal atom by ±0.0395 Å. The remaining planes at palladium: the metallacycle [Pd(1A), C(1A), C(6A), C(10A), C(11A), N(2A): plane 2], the coordination ring [Pd(1A), N(2A), N(3A), C(12A), S(1A): plane 3], and the metalated phenyl ring [C(1A), C(2A), C(3A), C(4A), C(5A), C(6A): plane 4] are nearly coplanar [angles between planes 1 and 2 = 1.60(0.08)°, 1 and 3 = 1.13(0.08)°, 1 and 4 = 1.35(0.10)°, 2 and 3 = 2.70(0.08)°, 2 and 4 = 2.80(0.12)°, and 3 and 4 = 1.23(0.11)°]. All bond lengths are in their typical ranges, and the S(1A)–C(12A) [1.765(8) Å] and N(3A)–C(12A) bond lengths [1.299(7) Å] are consistent with increased single- and double-bond character, respectively. The Pd(1A)–S(1A) bond [2.3380(14) Å] is longer than the Pd(1A)–S(1B) bond [2.3208(13) Å], thus confirming the greater *trans* influence of the phenyl carbon as compared to the imine nitrogen atom. The Pd(1A)–C(1A) bond [2.021(5) Å] is shorter than the expected value of 2.081 Å,[23] probably due to partial multiple-bond character.[11,24] The Pd(1)–N(1) bond [2.064(4) Å] is longer than previous values found in related complexes (sum of the covalent radii for palladium and nitrogen: 2.01 Å[10]), due not only to the *trans* influence of the sulfur atom but also to the greater size of the met-

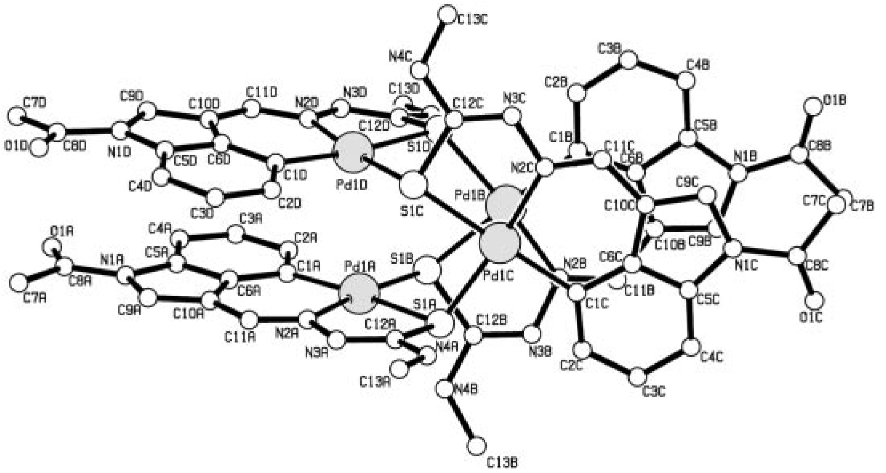


Figure 1. Molecular structure of **1b**, with labelling scheme. Hydrogen atoms have been omitted for clarity. Selected bond lengths and angles: Pd(1A)–C(1A) 2.021(5), Pd(1A)–N(2A) 2.064(4), Pd(1A)–S(1B) 2.3208(13), Pd(1A)–S(1A) 2.3380(14), S(1A)–C(12A) 1.749(6), N(3A)–C(12A) 1.299(7), N(3A)–N(2A) 1.439(5), N(2A)–C(11A) 1.292(6), C(1A)–C(6A) 1.390(6), C(11A)–C(10A) 1.410(7), C(10A)–C(6A) 1.457(6); C(1A)–Pd(1A)–N(2A) 94.27(18), C(1A)–Pd(1A)–N(2A) 94.27(18), N(2A)–Pd(1A)–S(1B) 173.23(12), C(1A)–Pd(1A)–S(1A) 176.29(14), N(2A)–Pd(1A)–S(1A) 83.45(12), S(1B)–Pd(1A)–S(1A) 89.92(5), C(6A)–C(1A)–Pd(1A) 118.7(4), C(1A)–C(6A)–C(10A) 130.4(5), C(11A)–C(10A)–C(6A) 125.2(4), N(2A)–C(11A)–C(10A) 123.5(5), C(11A)–N(2A)–N(3A) 112.1(4), C(11A)–N(2A)–Pd(1A) 128.0(4), N(3A)–N(2A)–Pd(1A) 119.9(3), C(12A)–N(3A)–N(2A) 113.6(4), N(3A)–C(12A)–S(1A) 127.2(4), C(12A)–S(1A)–Pd(1A) 95.4(2).

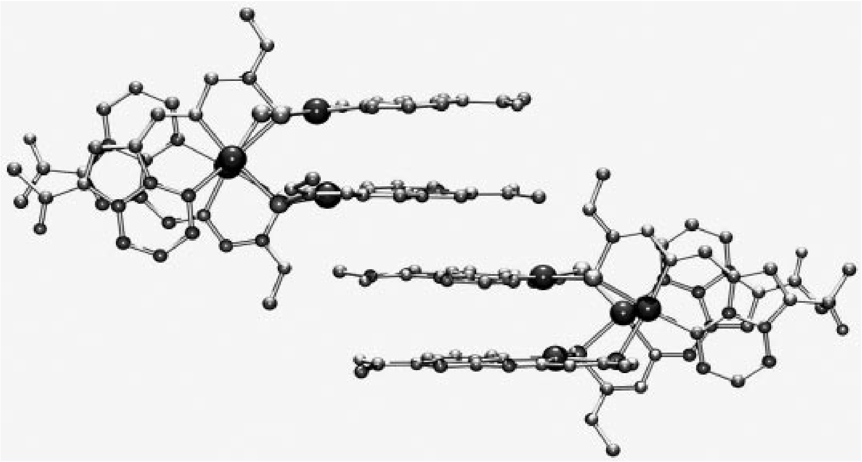


Figure 2. Packing diagram of compound **1b** showing the parallel arrangement of the cyclometalated units.

alated ring in the present compound. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°. However, as opposed to previous results where the C–Pd–N bite angle was less than 90°, due to formation of a five-membered metallacycle,[25,26] the six-membered ring in the present case allows a larger bite of the *C*,*N* chelate, thereby relieving strain on the angle at the metal; consequently, the C(1A)–Pd(1A)–N(1A) angle is 94.27°. On the other hand, inspection of the N(2A)–Pd(1A)–S(1A) bite angle of the five-membered Pd–N–N–C–S ring shows a similar value to that observed earlier in related complexes, with a value of 83.45°. The Pd–Pd bond lengths across parallel sets of cyclometalated moieties, which are in the range 3.8–4.1 Å, preclude any interaction between the metal atoms.

Two noteworthy observations regarding the structure are that pairs of metalated units are fixed in a nearly co-planar parallel mode (angle between planes of about 3.2°, with groups of parallel units separated by about 3.6 Å), and at an angle of 43° to the *a* axis (see Figure 2), thus indicating a possible weak π-stacking with the pyrrole rings set in an alternating disposition (see Figure 2).

Reactivity of the Complexes

Reactions of **1a** and **1b** with $Ph_2P(CH_2)_2PPh_2$ (dppe) were tested in order to corroborate the behavior observed by us in related compounds. Thus, treatment of **1a** and **1b** with $Ph_2P(CH_2)_2PPh_2$ in a 1:2 molar ratio gave compounds $[\{Pd[1\text{-}(COMe)\text{-}3\text{-}[C(H){=}NN{=}C(S)NHR]C_8H_4N]\}_2(\mu\text{-}Ph_2P(CH_2)_2PPh_2)]$ (R = H **2a**, Me **2b**) as pure, air-stable solids, which were fully characterized (Scheme 1). The ^1H NMR spectra show a signal at $\delta = 8.79$ (**2a**) and 8.32 ppm (**2b**), shifted to higher frequency with respect to the corresponding tetramers, which was assigned to the HC=N resonance. It appears as a doublet owing to coupling to the phosphorus nucleus. The H6 resonance [$\delta = 6.11$ (**2a**) and 6.11 ppm (**2b**)] is shifted to lower frequency by about 1.5 ppm with respect to the parent complexes owing to shielding by the phosphane phenyl rings, in accordance with a phosphorus *trans* to nitrogen. The ^{31}P NMR resonance is a singlet at $\delta = 70.41$ (**2a**) and 70.34 ppm (**2b**), thus showing the equivalence of the two ^{31}P nuclei. The ^{31}P chemical shift values are also consistent with a phosphorus *trans* to nitrogen.[27–30]

Conclusions

We have shown that thiosemicarbazones derived from condensed systems, such as indole, may behave as terdentate [C,N,S] pincer ligands in a cyclometalation reaction with palladium salts to give new tetranuclear species, which have been fully characterized in solution, as has one compound in the solid state. From a structural point of view they are closely related to similar systems reported by us previously, although in the present case the condensed rings seem to favor π stacking of the molecules in the unit cell. An added novelty to these compounds is the formation of a six-membered metallacycle, the first example with thiosemicarbazones, which is induced by the presence of bulky groups that hinder formation of the more common, and stable, five-membered metalated ring.

Experimental Section

General Remarks: Solvents were purified by standard methods.[31] All chemicals were reagent grade. K_2PdCl_4 was purchased from Alfa Products and 1,2-bis(diphenylphosphanyl)ethane (dppe) from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the Universidad de Santiago using a Carlo Erba Elemental Analyzer (model 1108). IR spectra were recorded as Nujol mulls or KBr discs with a Perkin–Elmer 1330 or a Mattson spectrophotometer. NMR spectra were obtained for solutions in [D$_6$]DMSO with Bruker WM-250 and AMX-300 spectrometers and are referenced to $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$). 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.

Synthesis of 1-(COMe)-3-[C(H)=NN(H)C(=S)NH$_2$]C$_8$H$_5$N (a): 1-Acetyl-3-indolecarboxaldehyde (411 mg, 0.002 mol) and hydrochloric acid (35%, 0.6 mL) were added to a suspension of thiosemicarbazide (200 mg, 0.002 mol) 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 vacuo. Yield: 497 mg (87%). $C_{12}H_{12}N_4OS$ (260.32): calcd. C 55.4, H 4.7, N 21.5, S 12.3; found C 55.5, H 4.7, N 21.6, S 12.4. IR: ν(N–H) 3388 m, 3132 m cm^{-1}; ν(C=O) 1709 s; ν(C=N) 1617 s; ν(C=S) 838 m. ^1H NMR ([D_6]DMSO): δ = 11.48 (s, 1 H, NH), 8.35 (s, 1 H, H2), 8.34 (m, 2 H, H5,H8), 8.30 (s, 1 H, *H*C=N), 8.24, 7.61 (br., 2 H, N*H₂*), 7.36 (m, 2 H, H6, H7), 2.68 ppm (s, 3 H, COMe).

Thiosemicarbazones **b** and **c** were prepared following a similar procedure.

1-(COMe)-3-[C(H)=NN(H)C(=S)NHMe]C_8H_5N (b): Yield: 480 mg (92%). $C_{13}H_{14}N_4OS$ (274.35): calcd. C 56.9, H 5.1, N 20.4, S 11.7; found C 56.7, H 5.0, N 20.6, S 11.8. IR: ν(N–H) 3289 m, 3129 m cm^{-1}; ν(C=O) 1715 s; ν(C=N) 1612 s; ν(C=S) 823 m. ^1H NMR ([D_6]DMSO): δ = 11.50 (s, 1 H, NH), 8.37 (m, 2 H, H5,H8), 8.33 (s, 1 H, H2), 8.30 (s, 1 H, *H*C=N), 8.06 (br., 1 H, N*H*Me), 7.39 (m, 2 H, H6, H7), 3.08 (d, $^3J_{H,H}$ = 4.4 Hz, 3 H, NH*Me*), 2.68 ppm (s, 3 H, COMe).

1-(COMe)-3-[C(H)=NN(H)C(=S)NHEt]C_8H_5N (c): Yield: 431 mg (89%). $C_{14}H_{16}N_4OS$ (288.37): calcd. C 55.8, H 5.6, N 19.4, S 11.1; found C 55.6, H 5.5, N 19.3, S 11.0. IR: ν(N–H) 3372 m, 3140 m cm^{-1}; ν(C=O) 1719 s; ν(C=N) 1615 s; ν(C=S) 831 m. ^1H NMR ([D_6]DMSO): δ = 11.45 (s, 1 H, NH), 8.36 (m, 2 H, H5, H8), 8.33 (s, 1 H, H2), 8.30 (s, 1 H, *H*C=N), 8.10 (br., 1 H, N*H*Et), 7.40 (m, 2 H, H6, H7), 3.65 (m, 2 H, NH$CH_2$$CH_3$), 2.67 (s, 3 H, COMe), 1.19 ppm (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, NH $CH_2$$CH_3$).

Preparation of 1a: Ethanol (40 mL) was added to a stirred solution of K_2PdCl_4 (100 mg, 0.306 mmol) in water (6 mL) and the fine yellow suspension obtained was treated with **a** (80 mg, 0.306 mmol). The mixture was stirred for 24 h at room temperature. The brown precipitate was filtered off, washed with ethanol, and dried in vacuo. Yield: 264 mg (59%). $C_{48}H_{40}N_{16}O_4Pd_4S_4$ (1458.9): calcd. C 39.5, H 2.8, N 15.4, S 8.8; found C 39.8, H 2.8, N 15.2, S 8.7. IR: ν(N–H) 3331 m cm^{-1}; ν(C=O) 1709 s; ν(C=N) 1604 m. ^1H NMR ([D_6]DMSO): δ = 8.66 (br., 1 H, H6), 8.41 (s, 1 H, H2), 8.24 and 7.61 (br., 2 H, N*H₂*), 7.98 (br., 1 H, H8), 7.44 (s, 1 H, *H*C=N), 7.13 (t, $^3J_{H7,H6}$ = $^3J_{H7,H8}$ = 7.8 Hz, 1 H, H7), 2.72 ppm (s, 3 H, COMe). FAB-MS: *m/z* 1458 $[M]^+$.

Compounds **1b** and **1c** were synthesized following a similar procedure.

1b: Yield: 342 mg (62%). $C_{52}H_{48}N_{16}O_4Pd_4S_4$ (1515.0): calcd. C 41.2, H 3.2, N 15.0, S 8.5; found C 40.9, H 3.2, N 15.2, S 8.6. IR: ν(N–H) 3394 m cm^{-1}; ν(C=O) 1710 s; ν(C=N) 1600 m. ^1H NMR ([D_6]DMSO): δ = 8.58 (d, $^3J_{H7,H6}$ = 8.0 Hz, 1 H, H6), 7.98 (d, $^3J_{H7,H8}$ = 8.0 Hz, 1 H, H8), 7.86 (s, 1 H, *H*C=N); 7.41 (s, 1 H, H2), 7.05 (t, $^3J_{H7,H6}$ = $^3J_{H7,H8}$ = 8.0 Hz, 1 H, H7), 6.20 (br., 2 H, N*H*Me), 2.85 (d, $^3J_{H,H}$ = 4.4 Hz, 3 H, NH*Me*), 2.55 ppm (s, 3 H, COMe). FAB-MS: *m/z* 1515 $[M]^+$.

1c: Yield: 300 mg (55%). $C_{56}H_{56}N_{16}O_4Pd_4S_4$ (1571.10): calcd. C 42.8, H 3.6, N 14.3, S 8.2; found C 43.0, H 3.6, N 14.2, S 8.1. IR: ν(N–H) 3359 m cm^{-1}; ν(C=O) 1716 s; ν(C=N) 1603 m. ^1H NMR ($CDCl_3$): δ = 8.63 (d, $^3J_{H7,H6}$ = 8.1 Hz, 1 H, H6), 8.41 (d, $^3J_{H7,H8}$ = 8.1 Hz, 1 H, H8), 7.68 (s, 1 H, H2), 6.79 (t, $^3J_{H7,H6}$ = $^3J_{H7,H8}$ = 8.1 Hz, 1 H, H7), 6.33 (s, 1 H, *H*C=N), 4.83 (br., 2 H, N*H*Et), 3.39 (m, 2 H, NH$CH_2$$CH_3$), 2.76 (s, 3 H, COMe), 0.88 ppm (t, $^3J_{H,H}$ = 6.7 Hz, 3 H, NH $CH_2$$CH_3$). FAB-MS: *m/z* 1571 $[M]^+$.

Complex 2a: 1,2-Bis(diphenylphosphanyl)ethane (11 mg, 0.028 mmol) was added to a suspension of complex **1a** (20 mg, 0.014 mmol) in acetone (15 mL). The mixture was stirred for 3 h and the resulting orange solid filtered off and dried. Yield: 23.5 mg (76%). $C_{50}H_{44}N_8O_2P_2Pd_2S_2$ (1127.9): calcd. C 53.3, H 3.9, N 9.9, S 5.7; found C 53.1, H 4.0, N 9.8, S 5.8. IR: ν(N–H) 3344 m cm^{-1}; ν(C=O) 1714 s; ν(C=N) 1607 m. ^1H NMR ([D_6]DMSO): δ = 8.96 (s, 1 H, H2), 8.79 (d, $J_{H,P}$ = 2.7 Hz, 1 H, *H*C=N), 8.25 (d, $^3J_{H7,H8}$ = 8.4 Hz, 1 H, H8), 7.09 (t, 1 H, H7), 6.11 (d, $^3J_{H7,H6}$ = 8.4 Hz, 1 H, H6), 2.66 ppm (s, 3 H, COMe). $^{31}P\{^1H\}$ NMR ([D_6]DMSO): δ = 70.41 ppm (s). FAB-MS: *m/z* 1128 $[M]^+$.

Compound **2b** was synthesized following a similar procedure.

2b: Yield: 23.8 mg (78%). $C_{52}H_{48}N_8O_2P_2Pd_2S_2$ (1155.9): calcd. C 54.0, H 4.2, N 9.7, S 5.6; found C 53.8, H 4.1, N 9.8, S 5.5. IR: ν(N–H) 3375 m cm^{-1}; ν(C=O) 1710 s; ν(C=N) 1599 m. ^1H NMR ([D_6]DMSO): δ = 8.90 (s, 1 H, H2), 8.32 (d, $J_{H,P}$ = 2.7 Hz, 1 H, *H*C=N), 8.25 (d, $^3J_{H7,H8}$ = 8.8 Hz, 1 H, H8), 6.83 (t, 1 H, H7), 6.21 (br., 2 H, N*H*Me), 6.11 (d, $^3J_{H7,H6}$ = 8.8 Hz, 1 H, H6), 2.74 (s, 3 H, COMe), 2.50 ppm (d, $^3J_{H,H}$ = 4.4 Hz, 3 H, NH*Me*). $^{31}P\{^1H\}$ NMR ([D_6]DMSO): δ = 70.34 ppm (s). FAB-MS: *m/z* 1156 $[M]^+$.

X-ray Crystallographic Study: A single crystal of complex **1b** was mounted on a glass fiber and transferred to the diffractometer. Three-dimensional, room temperature X-ray data were collected on a Bruker SMART CCD diffractometer by the ω-scan method using graphite-monochromated Mo-K_α radiation (see Table 1 for details). 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 ($T_{max.}/T_{min.}$ = 0.816/0.587). The structure was solved by direct methods and refined by full-matrix least-squares on F^2. Hydrogen atoms were included in calculated positions and refined in a riding mode. The structure contains eight symmetry-related voids of 37 Å^3 containing unresolvable solven; this was treated using the squeeze method, which lowered the R_1 value by about 25%.[32] Refinement converged at a final R = 0.0827 (observed data, F) and wR_2 = 0.1128

Table 1. Crystal data and structure refinement for compound **1b**.

Empirical formula	$C_{208}H_{176}N_{64}O_{16}Pd_{16}S_{16}$
Formula weight	6043.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 13.018(3) Å, α = 86.517(4)° b = 21.501(5) Å, β = 88.051(4)° c = 26.225(6) Å, γ = 86.305(4)°
Volume	7308(3) Å^3
Z	1
Calculated density	1.373 Mg m^{-3}
Absorption coefficient	1.130 mm^{-1}
F(000)	2992
Crystal size	0.65 × 0.40 × 0.18 mm^3
Theta range for data collection	0.95 to 26.43°
Limiting indices	$-16 \le h \le 16$, $-26 \le k \le 26$, $0 \le l \le 32$
Reflections collected/unique	83071/29736 [R(int) = 0.0447]
Completeness to θ	98.9% (26.43°)
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	29736/0/1457
Goodness-of-fit on F^2	1.016
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0404, wR_2 = 0.1005
R indices (all data)	R_1 = 0.0827, wR_2 = 0.1128
Largest diff. peak and hole	0.900 and –0.681 e Å^{-3}

(all unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. Minimum and maximum final electron density –0.681 and 0.900 e Å^{-3}. The structure solution and refinement were carried out using the program package SHELX-97.[33]

CCDC-291523 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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