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Palladium(II) Cyclometalated Thiosemicarbazone Compounds: A New Class of Bidentate P,S Metallo Ligands

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*Summary: Reaction of the tetranuclear compounds **1−4** with bis(diphenylphosphino)methane gave the mononuclear complexes **5−8**, with the diphosphine ligand binding in a monodentate fashion. Compounds **5−8** are capable of bonding systematically to a second palladium atom through the noncoordinated phosphorus atom and the sulfur atom of the thiosemicarbazone moiety to give the dinuclear compounds **9−12**, thus behaving as new bidentate P,S-metallo ligands. All of the compounds have been characterized by IR and NMR spectroscopy, and the molecular structure of **9** has been determined by X-ray crystallography.*

Introduction

Cyclometalated compounds[1−6] are a well-researched group of organometallic species. The M−C and M−Y (Y = donor atom) bonds may undergo a considerable number of conversions enhancing their reactivity, as in insertion reactions[7] and reactions with nucleophiles.[8] Thiosemicarbazones 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.[9,10] It seemed likely that these complexes would bind to a second metal through the uncoordinated phosphorus atom to give bridging diphosphine compounds, similar to the thiosemicarbazone dinuclear species[9] where coordination of the sulfur atom to a second metal center is lost. However, our preliminary results presented here show this not to be the outcome, the sulfur atom also exhibiting coordinative capacity by behaving as terdentate, thus giving rise to an *unprecedented class of bidentate P,S metallo ligands*, and in this work we present definitive proof of the behavior of these new cyclometalated palladium(II) compounds. Numerous examples of metallo ligands with P[11,12] or S[13,14] donor atoms are known, and among the latter, sulfur-containing macrocycles have been reported,[15,16] as well as thiolate metallo ligands[17,18] with tertiary diphosphines, whose role is limited to that of alternative terminal ligands, the donor abilities of the corresponding metallo ligand being restricted to the thiolate core. Furthermore, P,S-donor metallo ligands have also been described which comprise, among others, pendant phosphine−thiolate species[19−21] and combined thiolate−cyclopen-

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tadienylphosphine metallo ligands.[22] In the compounds communicated here the diphosphine plays a paramount role in the coordination of the metallo ligand, for two reasons: first, it splits the tetranuclear structure of the starting material, making it possible to obtain a great variety of new metallo ligands as a function of the initial tetramer and of the diphosphine, and second, it firmly binds the two metals, making these species altogether different from the known thiolate and the phosphine−thiolate metallo ligands.

Experimental Section

General Comments. Chemicals were used as supplied from commercial sources. Elemental analyses were carried out by the Unidade de Analise Elemental de la Universidad de Santiago de Compostela using a Carlo-Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene disks on Perkin-Elmer 1330, Mattson Model Cygnus-100, and Bruker Model IFS-66V spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$ (^1H, ^{13}C) or 85% H_3PO_4 ($^{31}P\{^1H\}$) and were recorded on Bruker AMX 300, AMX 500, and WM 250 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.

Preparation of [$PdCl_2$\{Pd[2-FC_6H_3C(Me)=NN=C(S)-NHMe](Ph$_2$PCH$_2$PPh$_2$)-*P,S*\}] (9). To a suspension of complex **5** (50 mg, 0.070 mmol) in acetone (15 cm^3) was added [$PdCl_2$-($PhCN)_2$] (27 mg, 0.070 mmol), and the mixture was stirred for 4 h. The resulting yellow solid was filtered off and dried. Yield: 54.3 mg, 87%. Anal. Found: C, 47.1; H, 3.5; N, 4.7; S, 3.4. Calcd for $C_{35}H_{32}N_3Cl_2FP_2SPd_2$: C, 47.2; H, 3.6; N, 4.7; S, 3.6. IR (cm^{-1}): ν(N−H) 3430 m; ν(C=N) 1572 m; ν(Pd−Cl) 327, 284 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.58 (2H, m, H3, H4); 6.07 (1H, t, H5, ^3J(H4H5) = 6.1 Hz; ^3J(PH) = 5.1 Hz); 5.20 (1H, m, N*H*Me); 3.20 (1H, t, PC*H*$_2$P, *N* = 23.1 Hz); 3.08 (3H, d, NMe, ^3J(HH) = 5.1 Hz); 2.67 (3H, d, MeC=N, ^5J(HF) = 4.4 Hz). ^{31}P NMR (δ, $CDCl_3$): 22.7 (1P, d, ^2J(PP) = 26.7 Hz); 16.8 (1P, d).

Compounds **10**−**12** were synthesized similarly.

[$PdCl_2$\{Pd[2-FC_6H_3C(Me)=NN=C(S)NHEt]-(Ph$_2$PCH$_2$PPh$_2$)-*P,S*\}] (10). Yield: 56.6 mg, 91%. Anal. Found: C, 47.6; H, 3.7; N, 4.5; S, 3.4. Calcd for $C_{36}H_{34}N_3Cl_2FP_2SPd_2$: C, 47.8; H, 3.8; N, 4.6; S, 3.5. IR (cm^{-1}): ν(N−H) 3425 m; ν(C=N) 1579 m; ν(Pd−Cl) 323, 295 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.55 (2H, m, H3, H4); 6.08 (1H, t, H5, ^3J(H4H5) = 6.8 Hz; ^3J(PH) = 5.6 Hz); 5.20 (1H, m, N*H*Me); 3.54 (2H, m, NC*H*$_2$CH$_3$); 3.19 (1H, t, PC*H*$_2$P, *N* = 23.1 Hz); 2.66 (3H, d, *Me*C=N, ^5J(HF) = 4.3 Hz); 1.27 (2H, m, NCH$_2$*CH*$_3$, ^3J(HH) = 7.2 Hz). ^{31}P NMR (δ, $CDCl_3$): 22.9 (1P, d, ^2J(PP) = 28.5 Hz); 16.8 (1P, d).

[$PdCl_2$\{Pd[2-ClC_6H_3C(Me)=NN=C(S)NHMe]-(Ph$_2$PCH$_2$PPh$_2$)-*P,S*\}] (11). Yield: 52.8 mg, 85%. Anal. Found: C, 46.4; H, 3.7; N, 4.7; S, 3.4. Calcd for $C_{35}H_{32}N_3Cl_3P_2SPd_2$: C, 46.3; H, 3.6; N, 4.6; S, 3.5. IR (cm^{-1}): ν(N−H) 3428 m; ν(C=N) 1570 m; ν(Pd−Cl) 325, 286 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.93 (1H, dd, H3, ^3J(H3H4) = 8.0 Hz, ^5J(H3H5) = 1.1 Hz); 6.45 (1H, t, H4, ^3J(H4H5) = 8.0 Hz); 6.22 (1H, ddd, H5, ^3J(PH) = 6.4 Hz); 5.48 (1H, m, N*H*Me); 3.21 (1H, t, PC*H*$_2$P, *N* = 23.1 Hz); 3.09 (3H, d, NMe, ^3J(HH) = 4.8 Hz); 2.67 (3H, s, *Me*C=N). ^{31}P NMR (δ, $CDCl_3$): 22.5 (1P, d, ^2J(PP) = 26.0 Hz); 16.7 (1P, d).

[$PdCl_2$\{Pd[2-ClC_6H_3C(Me)=NN=C(S)NHEt]-(Ph$_2$PCH$_2$PPh$_2$)-*P,S*\}] (12). Yield: 50.1 mg, 81%. Anal. Found: C, 47.0; H, 3.6; N, 4.5; S, 3.4. Calcd for $C_{36}H_{34}N_3Cl_3P_2SPd_2$: C, 46.9; H, 3.7; N, 4.6; S, 3.5. IR (cm^{-1}): ν(N−H) 3436 m; ν(C=N) 1579 m; ν(Pd−Cl) 328, 288 cm^{-1}. ^1H NMR (δ, $CDCl_3$): 6.92 (1H, d, H3, ^3J(H3H4) = 8.0 Hz); 6.45 (1H, t, H4); 6.22 (1H, dd, H5, ^3J(PH) = 6.5 Hz); 5.45 (1H, m, N*H*Me); 3.54 (2H, m, NC*H*$_2$CH$_3$); 3.20 (1H, t, PC*H*$_2$P, *N* = 22.8 Hz); 2.83 (3H, s, MeC=N); 1.28 (2H, m, NCH$_2$*CH*$_3$, ^3J(HH) = 7.4 Hz). ^{31}P NMR (δ, $CDCl_3$): 22.9 (1P, d, ^2J(PP) = 26.0 Hz); 16.8 (1P, d).

Crystal Structure Determination. Three-dimensional X-ray data were collected at 150(2) K in the range $1.60 < 2\theta < 28.34°$ on a Bruker Smart CCD diffractometer by the ω-scan method using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Of the 9940 reflections measured, 9940 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 5.0$. The structure was solved by direct methods (SHELXS-86) and refined anisotropically (SHELXL-97) by full-matrix blocked least squares on F^2 with allowance for the thermal anisotropy of all non-hydrogen atoms. Refinement converged at a final *R* = 0.0435 (R_w = 0.1015). The structure solution and refinement were carried out using the program package SHELX-97.[23]

Crystal data and details on data collection and refinement for compound **9**: $C_{35}H_{32}N_3Cl_2FP_2SPd_2\cdot 2Me_2CO$, fw = 1007.54, monoclinic, $P2_1/c$, *a* = 25.500(5) Å, *b* = 8.8668(18) Å, *c* = 18.404(4) Å, β = 90.792(4)°, *V* = 4160.8(15) Å^3, *Z* = 4. A total of 9940 reflections were measured, with 7746 having $I > 2\sigma(I)$. The θ range was 1.60−28.34° with *hkl* indices of −33 to 34, 0−11, and 0−24. An absorption correction was applied (μ = 1.163 mm^{-1}, 0.422−1.0 transmission). *R* values ($I > 2\sigma(I)$): R1 = 0.0435, wR2 = 0.1015. *R* values (all reflections): R1 = 0.0636, wR2 = 0.1122. GOF = 1.059. The residual electron density was between −0.969 and 1.675 e/Å^3.

Results and Discussion

The thiosemicarbazones **a**−**d** were prepared by treatment of 4-(methylthio)semicarbazide or 4-(ethylthio)-semicarbazide with 2-fluoroacetophenone or 2-chloroacetophenone as appropriate, which were fully characterized. In particular, the IR spectra showed the typical ν(C=N) and ν(C=S) stretches and the ^1H NMR spectra revealed the NH resonances at ca. 8.60 ppm. Treatment of the ligands with potassium tetrachloropalladate in ethanol/water yielded the tetranuclear compounds **1**−**4** as air-stable solids, with the ligand in the *E,Z* configuration (Scheme 1). They were characterized by elemental analyses (C, H, N) and by IR and ^1H NMR spectroscopy. The mass spectra (FAB) showed peaks at *m/z* 1318, 1375, 1384, and 1440, respectively, in agreement with tetranuclear complexes, analogous to others reported by us[9,10] and by others.[24−26] The most noticeable feature in the IR spectra was the absence of the ν(C=S) band, in accordance with loss of the double-bond character after deprotonation of the NH moiety, and the shift of the ν(C=N) band to lower wavenumbers on formation of the compounds.[10,27] No signal was observed for the NH group in the ^1H NMR spectra, which confirmed deprotonation as observed earlier.[24,25,28,29] Metalation of the ligand was evident

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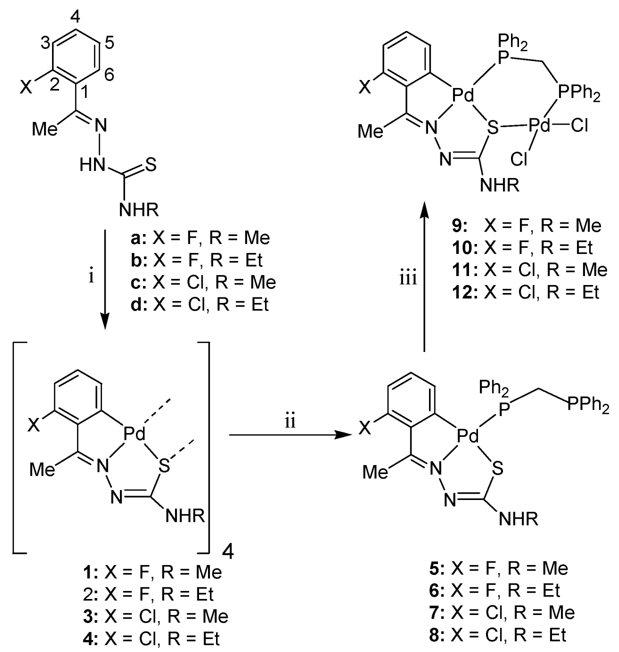
Scheme 1[a]



[a] Legend: (i) $K_2[PdCl_4]$/EtOH/H_2O; (ii) $Ph_2PCH_2PPh_2$/acetone/H_2O; (iii) $[PdCl_2(PhCN)_2]$/acetone.

from the absence of the H6 signal, the three remaining proton resonances being unequivocally assigned.

The reaction of complexes **1**−**4** with bis(diphenylphosphino)methane in a 1:4 molar ratio gave the mononuclear compounds **5**−**8**, respectively, as air-stable solids. The ^{1}H NMR spectra showed the H5 resonance as a multiplet owing to coupling to the phenyl ring protons and to the ^{31}P nucleus; this signal was strongly shifted to lower frequency, ca. 1.2 ppm, with respect to the corresponding tetranuclear compound. An apparent doublet at ca. 3.25 ppm was assigned to the ABXY system for the PCH_2P protons. The ^{31}P NMR spectra exhibited two doublets assigned to the two inequivalent phosphorus nuclei: ca. 25 ppm for the phosphorus atom bonded to the metal atom and ca. −25 ppm for the noncoordinated phosphorus.

Treatment of **5**−**8** with an equimolar amount of $[PdCl_2(PhCN)_2]$ gave the dinuclear compounds $[PdCl_2\{Pd[2\text{-}XC_6H_3C(Me){=}NN{=}C(S)NHR](Ph_2PCH_2PPh_2)\text{-}P,S\}]$ (**9**, X = F, R = Me; **10**, X = F, R = Et; **11**, X = Cl, R = Me; **12**, X = Cl, R = Et), as air-stable solids which were fully characterized (see the Experimental Section). The analytical and spectroscopic data showed that the second metal is bonded via the phosphorus and sulfur atoms in a dimetallic six-membered chelate ring. Important spectroscopic features of **9**−**12** include two ν(Pd−Cl) bands in the IR spectra, with that trans to the phosphorus atom appearing at lower wavelengths, ca. 285 cm^{-1}, in agreement with the greater trans influence of the phosphorus atom, and the Pd−Cl stretch trans to sulfur at ca. 325 cm^{-1}. The ^{31}P NMR spectra showed the low-field shift of the terminal ^{31}P resonance upon coordination to the metal, which is displaced by approximately 42 ppm, appearing at ca. 17 ppm, while the signal of the initially coordinated phosphorus atom shows a negligible shift. An apparent triplet was assigned to the two PCH_2P resonances in the ^{1}H NMR spectra, for the proton part of the approximately AA′XX′ system, with an *N* value of 23 Hz (see the Experimental Section).

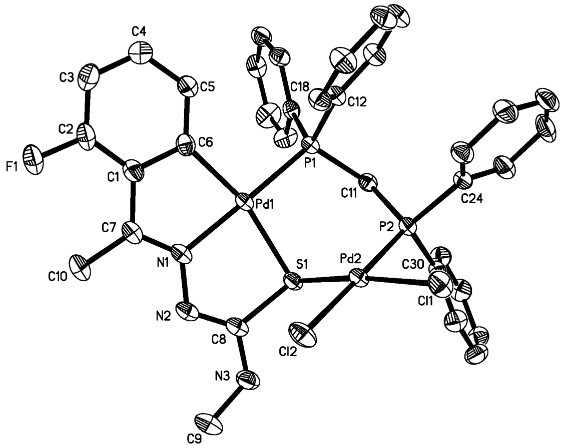


Figure 1. ORTEP drawing of the molecular structure for **9** with labeling scheme (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) at the metal atoms: Pd(1)−N(1), 2.020(3); Pd(1)−C(6), 2.012(4); Pd(1)−S(1), 2.3214(11); Pd(1)−P(1), 2.2465(11); Pd(2)−S(1), 2.3074(11); Pd(2)−P(2), 2.2644(11); Pd(2)−Cl(1), 2.3160(11); Pd(2)−Cl(2), 2.3448(11); N(1)−Pd(1)−C(6), 81.16(16); N(1)−Pd(1)−S(1), 84.00(10); N(1)−Pd(1)−P(1), 176.65(10); C(6)−Pd(1)−S(1), 165.15(12); C(6)−Pd(1)−P(1), 98.38(12); S(1)−Pd(1)−P(1), 96.46(4); S(1)−Pd(2)−P(2), 86.42(4); S(1)−Pd(2)−Cl(2), 93.49(4); S(1)−Pd(2)−Cl(1), 170.41(4); P(2)−Pd(2)−Cl(1), 90.36(4); P(2)−Pd(2)−Cl(2), 179.20(4); Cl(1)−Pd(2)−Cl(2), 89.85(4).

Molecular Structure of Complex 9. Suitable crystals were grown by slow evaporation of an acetone solution of complex **9**. The labeling scheme for the complex is shown in Figure 1. The crystal consists of discrete molecules separated by normal van der Waals distances. Crystallographic data are given in the Experimental Section and the Supporting Information, and selected interatomic distances and angles are listed in the figure caption.

The asymmetric unit of the crystal structure comprises a dinuclear palladium(II) complex, which presents two slightly distorted square-planar palladium(II) centers with different sets of donors. Three sites of the coordination sphere of one metal atom, Pd(1), are occupied by the aryl carbon atom, the nitrogen atom of the C=N moiety, and the sulfur atom, all of which pertain to the thiosemicarbazone ligand, with the remaining site occupied by a phosphorus atom from the diphosphine, P(1). The Pd(1) atom belongs to two fused five-membered chelate rings, the C,N metallacycle and the N,S-chelate ring, as a result of bonding to a terdentate C,N,S ligand. The angles between adjacent atoms in the coordination geometry of the metal are close to 90°, with the most noticeable distortion in the N(1)−Pd(1)−C(6) angle of 81.16(16)°, consequent upon chelation; the sum of angles at the palladium atom is 360°. All bond lengths are within the expected range, with allowance for the strong trans influence of the phosphorus donor ligand,[10] which is reflected in the Pd(1)−N(1) distance of 2.020(3) Å (cf. sum of the covalent

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radii for palladium and nitrogen, 2.01 Å[30]). The S(1)−C(8) bond length, 1.817(4) Å, and the N(2)−C(8) length, 1.297(6) Å, are consistent with increased single- and double-bond character, respectively. The Pd(1)−C(6) bond length of 2.012(4) Å and the Pd(1)−P(1) bond length of 2.2465(11) Å are shorter than the expected values of 2.081 and 2.41 Å,[30] respectively; this suggests some degree of multiple-bond character in the Pd−C_{aryl}[31−33] and Pd−P linkages.[34] The second metal, Pd(2), is coordinated to a sulfur atom, a phosphorus atom, P(2), and two terminal chlorine atoms, Cl(1) and Cl(2). The sum of angles at Pd(2) is 360.12°. The differing trans influences of phosphorus, P(2), and sulfur, S(1), are demonstrated by the slightly longer Pd(2)−Cl(2) bond distance, 2.3448(11) Å, as compared to Pd(2)−Cl(1), 2.3160(11) Å. The Pd(2)−P(2) bond distance, 2.2644(11) Å, is also shorter than the expected value (vide supra). The metallacycle Pd(1), C(6), C(1), C(7), N(1) and the coordination ring Pd(1), N(1), N(2), C(8), S(1) are planar, with mean deviations from the plane of ±0.0163 and ±0.0173 Å, respectively, and are at an angle of 1.38°. The two palladium coordination planes (Pd1, C6, N1, S1, P1) and (Pd2, P2, S2, Cl1, Cl2), which are planar with mean deviations of ±0.0296 and ±0.0942 Å, respectively, form an angle of 76.85(2)°. Four atoms of the six-membered coordination ring (Pd1, P1, C11, S1) are coplanar, with mean deviations from the plane in the range ±0.0204 Å, and this plane forms an angle of 5.71° with the metallacycle (Pd1, C6, C1, C7, N1).

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Supporting Information Available: Text giving experimental details for the synthesis and chracterization of **a**−**d**, **1**−**4**, and **5**−**8** and CIF files giving crystallographic data for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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