Synthesis and Structural Characterization of Palladium and Platinum Bimetallic Compounds Derived From Bidentate *P*,*S*-Palladacycle Metaloligands

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ABSTRACT: Treatment of 4-MeOC₆H₄C(Me)=NN(H)C(=S)NHMe (1), with potassium tetrachloropalladate gave the tetranuclear compound [Pd{4-MeOC₆H₃C(Me)=NN=C(S)NHMe}]₄ (2), with the ligand as terdendate [C,N,S]. Reaction of 2 with the diphosphines Ph₂PCH₂PPh₂ (dppm), Ph₂PC(=CH₂)PPh₂ (vdpp), and Ph₂PC(CH₂)₂PPh₂ (dpcp) gave the mononuclear complexes [Pd{4-MeOC₆H₃C(Me)=NN=C(S)NHMe}(L)] (L = dppm-P, 3; dpcp-P, 4; vdpp-P, 5) with the diphosphine ligand binding in a monodentate fashion. Compounds 3–5 may bond systematically to a second metal atom, palladium or platinum, through the noncoordinated phosphorus atom and the sulfur atom of the thiosemicarbazone moiety to give the dinuclear compounds 6–10, thus behaving as bidentate *P*,*S*-palladacycle metaloligands. All the compounds have been characterized by elemental analysis, and by IR and NMR spectroscopy; and the crystal and molecular structures of 1, 2, 6–10 have been determined by X-ray crystallography. Inter- and intramolecular hydrogen bonding in the solid results in crystal self-organization leading to chains and/or layers in the molecular array.

Introduction

The chemistry of cyclometalated compounds, and in particular that of palladacycles, has come to be a most interesting part of organometallic chemistry, with many reviews covering this subject.^{1–12} They exhibit a good number of applications that range from the synthesis of new organic and organometallic compounds, to mesogenic species and catalytic materials.¹³⁻¹⁶ In particular, thiosemicarbazones produce tetranuclear compounds with two distinct palladium-sulfur bonds, that is, 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 the metal atom is bonded to only one phosphorus atom; the strength of the Pd-S_{chelating} bond prevents the chelating bidentate mode of the diphosphine ligand.^{17,18} Because the sulfur atom may undergo further coordination, the ensuing moieties behave as bidentate P,S-palladacycle metaloligands. However, coordination through phosphorus alone may be achieved with metals having only one available coordination site, and we have recently reported the first analogous platinacycle metaloligand from a furane thiosemicarbazone, where reaction with an iron pentacarbonyl moiety gives a bimetallic species with the second metal only bonded to the phosphorus atom.¹⁹ Previous bimetallics bearing palladacycle P,S-metaloligands have been limited to the use of only the short-bite diphosphine Ph₂PCH₂PPh₂ (dppm);²⁰ therefore, to widen the scope of our research we have extended the bimetallic systems to include those with 1,1-bis(diphenylphosphine)ethene, Ph2PC-(=CH₂)PPh₂ (vdpp), and 1,1-bis(diphenylphosphine)cyclopropane, Ph₂PC(CH₂)₂PPh₂ (dpcp), as well as including the mixed palladium/platinum species. Furthermore, a salient

feature of thiosemicarbazones, and of their ensuing compounds, is the ability to display intermolecular hydrogen bonding, the latter being important in molecular and crystal organization; also, hydrogen bonding in thiosemicarbazones and their complexes is important given the biologically activity of these materials.²¹⁻²³ In the ligands the C=S and NH groups are capable of forming eight-membered (CSNH)₂ rings, through a pair of N-H···S hydrogen bonds, having two donors and two acceptors. Additional hydrogen bonding may appear between the sulfur atom and a neighboring methyl group, C-H···S, to give seven-membered rings,² as well as intramolecular hydrogen bonds. The eightmembered (CSNH)₂ ring may also be portrayed in the corresponding compounds,²⁴ or it may be absent when other electronegative atoms favor formation of hydrogen bonding with the thioamide NH group, as for example when a methoxy substituent is present, which results in the development of polymeric chains based on N-H···O bonds; analogous situations may arise if halogen atoms from M-X bonds or solvent molecules are present.

Therefore, along with the first palladium—platinum bimetallic compounds derived from bidentate P,S-palladacycle metaloligands, herein we report the structures of the thiosemicarbazone ligand, and of di- and tetranuclear complexes depicting the crystal self-organization which is displayed as a consequence of the differing hydrogen bonds.

Results and Discussion

The sequence of reactions leading to the precursor mononuclear compounds 3-5 can be viewed in Scheme 1 (see Experimental Procedures for characterizing data). The new homo- and heterobimetallic complexes 6-10 were prepared by adding [PdCl₂(NCPh)₂] or [PtCl₂(NCPh)₂], as appropriate, in a 1:1 molar ratio to a solution of the corresponding

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Scheme 1. (i) K₂[PdCl]₄/EtOH/H₂O; (ii) Ph₂PRPPh₂/acetone; (iii) MCl₂(NCPh)₂/acetone



R: **3**, CH₂; **4**, C(CH₂)₂; **5**, C=CH₂ R:

R: **6,9**, CH₂; **7**, C(CH₂)₂;**8**,**10**, C=CH₂ M: **6-8**, Pd; **9**,**10**, Pt; compounds 3-5; they are air-stable solids, with the ligand in the (E,Z) configuration (Experimental Procedures and Scheme 1). The second metal is bonded via the phosphorus and sulfur atoms in a dimetallic six-membered chelate ring. The complexes are soluble in CHCl₃, CH₂Cl₂, DMSO, and acetone, but insoluble in MeOH, EtOH, and water.

Molecular and Crystal Structures of 6-10. Crystals were monoclinic, with space groups 6, $8 \cdot CH_2Cl_2$ ($P12_1/c1$), 7 (C12/c1), 9, $10 \cdot CH_2Cl_2$ ($P2_1/c$). The most significant parameters for these compounds are shown in Tables 1 and 2 (7, 9, $10 \cdot CH_2Cl_2$ Figures 1 and 2; 6, Supporting Information, Figure S1, $8 \cdot CH_2Cl_2$, Supporting Information, Figure S2). The metal atoms show distorted square-planar environments, with the distortion most noticeable in the Pd(2) or Pt atoms, due to the greater rigidity imposed by the thiosemicarbazone ligand on the Pd(1) atom, and to the presence of terminal chloride ligands on the second metal, which enhances vibration during the crystallographic measurement process.

All bond lengths are within the expected range, with allowance for the strong *trans* influence of the phosphorus donor ligand,¹⁸ which is reflected in the Pd(1)–N(1) distance of 2.020(4)-2.036(11) Å [cf. sum of the covalent radii for

| Table 1. | Crystal Data | for 6, 7. | , 8∙CI | 12Cl2, 9, | , and 10. | CH ₂ Cl ₂ |
|----------|--------------|-----------|--------|-----------|-----------|---------------------------------|
| | | | | | | ~ ~ ~ |

| | • | , , | 2 2/ / | 2 | |
|---|---|---|---|---|---|
| | 6 | 7 | $8 \cdot CH_2Cl_2$ | 9 | $10 \ \mathrm{CH_2Cl_2}$ |
| formula | C ₃₆ H ₃₅ Cl ₂ N ₃ O- P ₂ Pd ₂ S | C ₃₈ H ₃₇ Cl ₂ N ₃ O- P ₂ Pd ₂ S | C ₃₈ H ₃₇ Cl ₄ N ₃ O- P ₂ Pd ₂ S | C ₃₆ H ₃₅ Cl ₂ N ₃ O- P ₂ PdPtS | C ₃₈ H ₃₇ Cl ₄ N ₃ O- P ₂ PdPtS |
| M | 903.37 | 929.41 | 1000.31 | 992.06 | 1089.00 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $P12_{1}/c1$ | C12/c1 | $P12_{1}/c1$ | $P2_1/c$ | $P2_1/c$ |
| $a(\text{\AA})$ | 18.112(3) | 47.44(1) | 8.942(2) | 18.163(3) | 8.984(1) |
| b (Å) | 12.157(2) | 9.832(2) | 16.756(3) | 12.247(2) | 16.724(2) |
| c (Å) | 16.295(2) | 18.287(5) | 27.091(5) | 16.669(3) | 27.058(3) |
| β (°) | 105.503(2) | 93.010(5) | 98.452(4) | 105.957(3) | 98.387(2) |
| $V(Å^3)$ | 3457.4(9) | 8518(4) | 4014.9(13) | 3565.0(10) | 4021.6(8) |
| Z | 4 | 8 | 4 | 4 | 4 |
| $\mu (\mathrm{mm}^{-1})$ | 1.383 | 1.125 | 1.329 | 4.757 | 4.354 |
| theta range for collection | 1.17-28.35° | 0.86-18.52° | 1.52-26.44° | 2.03-26.4° | 1.44-28.31° |
| absorption correction | SADABS | SADABS | SADABS | SADABS | SADABS |
| unique reflections, R | 8382 R(int) = 0.0454] | 3182 | 8218 [R(int) = 0.0844] | 7263 [R(int) = 0.0652] | 9694 [R(int) = 0.0443] |
| R(int) | 0.0454 | 0.0995 | 0.0844 | 0.0652 | 0.0443 |
| data/restraints/parameters | 8382/0/431 | 3182/36/433 | 8218/0/460 | 7263/0/427 | 9694/0/463 |
| goodness-of-fit | 1.135 | 0.964 | 1.014 | 1.075 | 1.106 |
| $R\left[F, I > 2\sigma(I)\right]$ | 0.0366 | 0.0545 | 0.0458 | 0.0393 | 0.0343 |
| $wR[F^2, all data]$ | 0.1028 | 0.1512 | 0.1146 | 0.097 | 0.0738 |
| max and min transmission | 0.883 and 0.780 | 1 and 0.549 | 0.887 and 0.866 | 0.717 and 0.509 | 0.647 and 0.512 |
| largest diff peak and hole $(e \cdot Å)^{-3}$ | 1.418 and -0.904 | 0.809 and -0.621 | 0.805 and -0.742 | 0.826 and -1.18 | 0.866 and -1.007 |

Table 2. Selected Bond Lengths (Å) and Angles (°) in 1, 2, 6, 7, 8 · CH₂Cl₂, 9, and 10 · CH₂Cl₂

| | 1 | 2 | (| 7 | | | 10 CU CI |
|---------------------|----------|-----------|------------|-----------|-----------------------------------|-----------|----------------------|
| | I | 2 | 0 | / | 8.CH ₂ Cl ₂ | 9 | $10 \cdot CH_2 Cl_2$ |
| C(6)-Pd(1) | | 2.014(7) | 2.038(4) | 1.955(17) | 2.023(6) | 2.038(7) | 2.023(5) |
| N(1) - Pd(1) | | 1.994(6) | 2.027(3) | 2.036(11) | 2.026(5) | 2.025(6) | 2.020(4) |
| S(1) - Pd(1) | | 2.364(2) | 2.334(1) | 2.255(4) | 2.334(2) | 2.334(2) | 2.334(1) |
| Pd(1) - P(1) | | | 2.258(1) | 2.255(4) | 2.026(5) | 2.264(2) | 2.259(1) |
| S(1) - M(2) | | | 2.303(1) | 2.312(3) | 2.257(2) | 2.296(2) | 2.299(1) |
| P(2) - M(2) | | | 2.248(1) | 2.281(3) | 2.257(2) | 2.228(2) | 2.234(1) |
| M(2) - Cl(1) | | | 2.343(1) | 2.330(4) | 2.340(2) | 2.343(2) | 2.346(1) |
| M(2) - Cl(2) | | | 2.339(1) | 2.321(4) | 2.321(2) | 2.333(2) | 2.327(1) |
| C(7) - N(1) | 1.287(4) | 1.309(8) | 1.292(5) | 1.294(18) | 1.295(8) | 1.308(9) | 1.303(7) |
| N(1) - N(2) | 1.376(3) | 1.381(8) | 1.383(5) | 1.382(16) | 1.381(7) | 1.394(8) | 1.383(6) |
| N(2)-C(8) | 1.365(4) | 1.300(9) | 1.303(5) | 1.258(16) | 1.293(8) | 1.280(9) | 1.296(7) |
| C(8)-S(1) | 1.672(3) | 1.777(8) | 1.809(4) | 1.832(16) | 1.809(6) | 1.808(7) | 1.810(6) |
| C(6)-Pd(1)-N(1) | | 81.5(3) | 80.97(15) | 81.0(7) | 81.1(2) | 80.6(3) | 81.2(2) |
| N(1) - Pd(1) - S(1) | | 82.85(17) | 82.89(10) | 83.5(5) | 83.28(16) | 82.86(18) | 83.34(13) |
| S(1) - Pd(1) - P(1) | | | 95.15(4) | 96.94(13) | 97.09(6) | 94.70(7) | 96.73(5) |
| C(6) - Pd(1) - P(1) | | | 100.98(12) | 98.6(6) | 98.38(17) | 101.8(2) | 98.63(15) |
| S(1)-M(2)-Cl(1) | | | 94.35(4) | 91.26(13) | 93.26(6) | 93.60(7) | 93.02(5) |
| Cl(1)-M(2)-Cl(2) | | | 89.35(4) | 88.38(14) | 89.59(6) | 87.69(8) | 87.74(5) |
| Cl(2)-M(2)-P(2) | | | 91.37(4) | 89.67(13) | 87.86(6) | 91.78(8) | 89.36(5) |
| S(1)-M(2)-P(2) | | | 86.70(4) | 90.08(12) | 88.92(6) | 87.90(7) | 89.57(5) |

palladium and nitrogen, 2.01 Å²⁵]. The C(8)-S(1) (1.808(7)-1.832(16) Å) and N(2)-C(8) (1.258(16)-1.303(5) Å) bond lengths show increased single and double bond character, respectively, consequent upon deprotonation of the hydrazynic NH group (Table 2). As for the second metal the differing trans influences of the phosphorus, P(2), and sulfur atoms, S(1), is put forward in the slightly longer M(2)-Cl(1) bond distance as compared to M(2)-Cl(2). The Cremer-Pople parameters²⁶ (Supporting Information Table T1) show the six-membered bimetallic ring in a boat conformation, except in 9 where the situation is intermediate between boat and twist-boat. The metal coordination planes (C6, N1, S1, P1) and (P2, S1, Cl1, Cl2) are essentially planar, and at an angle of 71.64(6)-75.47(7)°. The $M \cdots M$ distance within the ring is greater than the sum of the van der Waals radii²⁷ in all cases, precluding any metal-metal interaction.

In compound 7, the cyclopropane ring and phosphine planes, C(24)-C(25)-C(26) and P(1)-C(24)-P(2), respectively, are at an angle of 86.41°.



Figure 1. Crystal structure for complex 7. Ellipsoids are shown at the 30% probability level.

Compounds 6 and 9, are isostructural, hence displaying nearly identical cell parameters; the asymmetric units contain one molecule of the dinuclear compound. The N-H···O parameters for the interactions between molecules for **6** $[N(3)-H(3N)\cdots O(1)\#: 0.780, 2.483, 3.247 Å,$ 166.54°; #: x, y - 1, z] and for **9** [N(3)-H(3)···O(1)#: 0.859, 2.417 3.247 Å, 162.64°; #: x, 1 + y, z] suggest close contacts²⁸ between the methoxy group and the amide group, which contribute to formation of chains along the b axis (Figure 3a). Furthermore, besides the N-H···O interactions, and other minor intramolecular contacts involving the hydrazinic nitrogen atom [6: $C(11)-H(11A)\cdots N(2)$: 0.960, 2.344, 2.776 Å, 106.65°; **9**: C(11)−H(11C)····N(2): 0.960, 2.348, 2.777 Å, 106.44°], interactions between a chlorine atom with CH groups from the phosphine phenyl rings produce interweaving of the b axis chains along the c axis (Figure 3b), leading to a two-dimensional network of molecules on the *bc* plane [6: $C(23)-H(23)\cdots Cl(1)\#: 0.930$, 2.599, 3.461 Å, 154.30°, #: x, 1/2 - y, -1/2 + z; 9: C(13) - $H(13) \cdots Cl(1) #: 0.931, 2.667, 3.497 \text{ Å}, 148.92^\circ; #: x, 1/2 - y,$ 1/2 + z]. Additional C-H···Cl interactions produce pairs of sheets along the *ac* plane [6: $C(2)-H(2)\cdots Cl(1)\#$: 0.931, 2.746, 3.657 Å, 166.23°; #: 1 - x, 1 - y, 2 - z; 9: C(2)- $H(2) \cdots Cl(1) #: 0.929, 2.823, 3.721 \text{ Å}, 162.78^{\circ}; #: -x, -y, -z]$ (Figure 4); in each pair the phosphine phenyls are orientated toward the outer part of the structure. Furthermore, there are C-H··· π contacts^{29,30} between the a phosphine phenyl and C-H atoms of neighboring molecules from adjacent sheet pairs, at a H···centroid distance of about 2.6 Å, that give rise to the environment for the structure that is represented in Figure 5.

As for compounds $8 \cdot CH_2Cl_2$ and $10 \cdot CH_2Cl_2$, they are also isostructural and the asymmetric unit contains one molecule of the dinuclear compound and dichloromethane molecule; the presence of dichloromethane solvent molecules in the crystal lattice produces an altogether different picture for these two compounds as compared to compounds 6 and 9 that merits further comment. Thus, hydrogen bonding interactions involving the solvent molecules, as well as the methoxy and the amide groups $[8 \cdot CH_2Cl_2: N(3) H(3A) \cdot \cdot \cdot Cl(1S)\#: 0.860, 2.771, 3.582 Å, 157.80^\circ; \#: 2 - x,$



Figure 2. Crystal structure for 9 and 10. Ellipsoids are shown at the 30% probability level.



Figure 3. View of 6 showing the formation of chains along the (a) b axis; (b) c axis.



Figure 4. View of **6** showing the formation of antiparallel chains along the *bc* plane.

1 − y, 1 − z; C(25)-H(25B)···O(1)#: 0.933, 2.583, 2.362 Å, 141.44°; #: 1 + x, y, z; C(38)−H(38A)···Cl(1)#: 0.970, 2.678, 3.421 Å, 133.77°; #: 1 − x, 1 − y, 1 − z; **10**·CH₂Cl₂: N(3)− H(3N)···Cl(1S)#: 0.860, 2.769, 3.589 Å, 159.79°; #: −x, 2 + y, −z; C(1S)−H(1S)···Cl(1)#: 0.971, 2.708, 3.456 Å, 134.27°; #: 1 − x, 2 + y, −z; C(25)−H(25B)···O(1)#: 0.931, 2.581, 3.350 Å, 140.31°; #: −1 + x, y, z] (Figure 6) produce sets of antiparallel chains along the *a* axis, with channels running through the face-to-face solvent molecules (Figure 7). Furthermore, π−π and CH···π interactions (Figure 8a) produce additional short contacts^{29,30} between the phosphine phenyls (light blue and red lines in Figure 8b), of the C−H···π



Figure 5. Structure of 6 along the *ac* plane.

 $(H \cdots centroid < 3.0 \text{ Å})$ type, to give parallel zigzagging planes (light blue and red lines), perpendicular to the *bc* plane, with the chains on the edges and the separation between planes lodging the aforementioned channels.

The asymmetric unit of 7 also contains solvent molecules, although in this case the quality of the diffraction data did not allow the position of this molecule to be resolved clearly. As a result in this case the solvent was removed from the structure using SQUEEZE program³¹ implemented in PLATON.^{32,33}



Figure 6. View of $10 \cdot CH_2Cl_2$ along the *a* axis.



Figure 7. Structure of 10 · CH₂Cl₂ along the *ab* plane, showing the arrangement of the antiparallel chains.

Molecular and Crystal Structures of 1 and 2. The most significant parameters for these compounds are shown in Tables 2 and 3. Compound 1 crystallizes in the monoclinic P21/n space group as the *E*,*Z* isomer relative to the N(1)–C(7) and N(3)–C(8) bonds, respectively, typical of thiosemicarbazones where hydrogen bonding is present. For 1, a supramolecular structure based on dimers linked by a (CSNH)₂ ring and by N–H···O bonding was found. The two monomers in each dimer are linked by a nonplanar (CSNH)₂ ring through N–H···S bonds [1: N(2)–H(2)···S(1)#: 0.860, 2.825, 3.429 Å, 128.70°; #: 2 – x, -y, -z] (Figure 9).

The molecule seems to be essentially planar with the phenyl ring and the C(7)–N(1)–N(2)–C(8)–N(3) group making an angle of 11.62°. The dimers are linked end-to-end by N–H···O bonds involving the methoxy group [1: N(3)–H(3)···O(1)#: 0.861, 2.465, 3.141 Å, 136.04°; #1: 5/2 - x, 1/2 + y, -2 - 1/2 - z]; this results in two mutually perpendicular layouts of parallel dimers running along the c axis in opposite directions (Supporting Information, Figure S3 for the structure of 1). Any resemblance to the ligand arrangement in the solid is lost in the ensuing compounds because the sulfur atom is involved in bonding to the metal.

The tetranuclear compound **2** crystallizes in the tetragonal $P4_2/n$ space group; the asymmetric unit comprises a metalated thiosemicarbazone ligand. Within each molecule, the metalated moieties are displayed as two perpendicular sets of nearly coplanar antiparallel pairs separated by about 3.6 Å (Figure 10). Compound **2** shows intramolecular $\pi - \pi$ interactions between the parallel metalacycles [$d_{centroids} = 3.435$ Å, $\alpha = 2.65^{\circ}; \beta = \gamma = 11.82^{\circ}$, sym code: 1/2 - x, 1/2 - y, z]; there are intermolecular hydrogen bonds between the methoxy and the amide groups [N(3)-H(3N)···O(1)#, 0.861, 2.117, 2.954 Å, 163.93°, #: 1/2 + x, -y, 1/2 + z] that produce the tridimensional growth of the crystal lattice (Figure 11). When viewed along the *ab* plane, this produces a strikingly beautiful crystal array with alternating square and cross-shaped cavities (Figure 12; Supporting Information, Figure S4, view along the *a* axis).

IR Spectroscopy. The IR spectrum of the ligand showed the typical $v(N-H)_{amide}$, $v(N-H)_{hydrazinic}$, v(C=N), and v(C=S) stretches at 3367, 3191, 1608, and 836 cm⁻¹, respectively. Comparison of the spectra of the compounds with that of the free ligand shows the disappearance of the $v(N-H)_{hydrazinic}$ and v(C=S) bands. Both these observations are consistent with deprotonation of the NH group and with loss of the double bond character of the C=S group; the latter feature is confirmed in the crystal structures by the lengthening of the C-S bond. The position of the $v(N-H)_{amide}$ stretch in the complexes shows that this group is uncoordinated to the metal atom. The v(C=N) stretch shifts to lower wavenumbers upon complex formation ca. 30 cm⁻¹, suggesting coordination of the metal through the nitrogen lone pair.^{34–36} The IR spectra of complexes 6-10 also include two v(Pd-Cl) or v(Pt-Cl) bands, with the one trans to the phosphorus atom appearing at lower wavelengths ca. 295 cm⁻¹, in agreement with the greater trans influence of the phosphorus atom, and the M-Cl stretch trans to sulfur ca. 310 cm^{-1} .





Figure 8. Compound **10·CH₂Cl₂**. (a) Chain formation through $\pi - \pi$ and CH··· π interactions. (b) View of one layer of the parallel zig-zaging environment, on the *bc* plane. (c) View down the *a* axis.

| Fable 3. | Structural | Data | for | 1 | and 2 | |
|----------|------------|------|-----|---|-------|---|
| able 5. | Suucuia | Data | 101 | | anu 🗕 | · |

| | 1 | 2 |
|-----------------------------|---|------------------|
| formula | C ₁₁ H ₁₅ N ₃ OS | C44H52N12O4Pd4S4 |
| M | 237.32 | 1366.82 |
| crystal system | monoclinic | tetragonal |
| space group | $P2_1/n$ | $P4_2/n$ |
| a (Å) | 7.971(2) | 13.078(1) |
| $b(\mathbf{A})$ | 5.468(2) | 13.078(1) |
| c (Å) | 27.726(8) | 14.998(3) |
| β (°) | 94.583(6) | 90 |
| $V(Å^3)$ | 1204.6(6) | 2565.1(5) |
| Z | 4 | 2 |
| $\mu ({\rm mm}^{-1})$ | 0.252 | 1.596 |
| theta range for collection | 2.72-26.4° | 2.07-24.74° |
| absorption correction | SADABS | SADABS |
| unique reflections | 2437 | 2203 |
| R _{int} | 0.0517 | 0.0619 |
| data/restraints/ parameters | 2437/0/145 | 2203/0/154 |
| GOF | 0.95 | 1.145 |
| $R[F, I > 2\sigma(I)]$ | 0.0508 | 0.0372 |
| $wR[F^2, all data]$ | 0.1496 | 0.1068 |
| max and min transmission | 0.987 and 0.924 | 0.852 and 0.780 |
| largest diff peak and | 0.262 and -0.288 | 0.716 and -0.506 |
| hole $(e \cdot Å^{-3})$ | | |

NMR Spectroscopy. The main modifications in the ¹H NMR spectra of the ligand upon formation of the complexes are the disappearance of the NH (8.58 ppm) and of the C(6)H (7.63 ppm) resonances, the latter being part of the phenyl



Figure 9. Structure of the ligand showing hydrogen bonding interactions.



Figure 10. View of 2 along the *b* axis.



Figure 11. Crystal structure of **2**. Hydrogen atoms are omitted for clarity [expect N3–H3]. Ellipsoids are shown at the 30% probability level.

protons AA'XX' spin system absent in the spectra of the complexes. This is consistent with deprotonation $^{37-40}$ of both groups, and confirms metalation of the C6 carbon atom. The three remaining phenyl proton resonances were unequivocally assigned. The H5 resonance is coupled to the metalated phenyl ring protons and also to the ³¹P nucleus in 3-10, and is shifted toward lower frequency with respect to the spectrum of the ligand. In the bimetallic compounds the PCH_2P signal (in 6 and 9) is an apparent triplet for the proton part of the approximately AA'XX' system, with an N value of about 22 Hz, and the vinylidene proton resonances of vdpp (in 8 and 10) are two doublets of doublets ca. 6.5-6.1 by coupling to both 31 P nuclei. Also, in complexes 3–10 the MeO signal is upfield shifted by influence of the phosphine phenyl ring currents, and the NHMe is strongly shifted to higher field by about 2.4 ppm.

The ${}^{31}P$ NMR spectra consist of two doublets for the two inequivalent phosphorus nuclei, for compounds 3-5 as well



Figure 12. Structure of 2 viewed along the *ab* plane.

as for compounds 6-10. In the former case, the signal that appears at higher field is assigned to the noncoordinated phosphorus nucleus at -25.02, 3, -9.54, 4, -10.40, 5, ppm, however, in compounds 6-10 this signal is displaced to lower field ca. 40 ppm in 6-8, and it is less strongly shifted in the mixed palladium/platinum compounds 9, 23 ppm, and 10, 20 ppm, reflecting coordination of the free phosphorus atom to the second metal center; this is even more evident for the platinum complexes 9 and 10 which show satellites by coupling of the shifted phosphorus to the ¹⁹⁵Pt nucleus.

Conclusions

The synthesis and structural study of bimetallic systems of the type $[MCl_2{Pd[4-MeOC_6H_3C(Me)=NN=C(S)NHMe]}-(Ph_2PRPPh_2)-P,S]$ [where R = CH₂, (CH₂)₂, C = CH₂ and M = Pd, Pt] enabled the identification of new homo- and heterobimetallics from palladacycle thiosemicarbazone-P,Smetaloligands with diphosphines other than Ph_2PCH_2PPh_2.

The presence of short contacts involving hydrogen bonding and $C-H\cdots\pi$ interactions determines the structural motifs present in the crystal structures, where antiparallel chains of molecules arranged in sheets are stacked together face-to-face or in a zigzag fashion. The latter is mainly determined by the presence of solvent molecules that give different environments in the compounds with Ph₂PCH₂PPh₂ and Ph₂PC-(=CH₂)PPh₂. The intermolecular interactions also allow visualization of the remarkable disposition displayed by the tetranuclear palladacycle.

Experimental Procedures

General Comments. Solvents were purified by standard methods.⁴¹ 4-Methoxiacetophenone, 4-methyl-3-thiosemicarbazide, potassium tetrachloropalladate, palladium chloride, and platinum chloride (all from Aldrich) were used as supplied; bis(benzonitrile)dichloropalladium and bis(benzonitrile)dichloroplatinum were synthesized in our laboratory by refluxing palladium or platinum chloride in benzonitrile. 1,1-Bis(diphenylphosphine)cyclopropane, Ph₂PC(CH₂₎₂PPh₂, was synthesized using the Schmidbaur method.⁴² Elemental analyses were performed with a Fisons elemental analyzer, model 1108. IR espectra were recorded as Nujol mulls or polythene discs on Perkin-Elmer 1330, Mattson model Cygnus-100, and Bruker model IFS-66 V spectrophotometers. ¹H NMR spectra in solution were recorded in CDCl₃ at room temperature on Varian Mercury 300 spectrometer operating at 300.14 MHz using 5 mm o.d. tubes; chemical shifts, in ppm, are reported downfield relative to TMS using the solvent signal (CDCl₃, $\delta^{-1}H = 7.26$ ppm) as reference. ³¹P NMR spectra were recorded at 202.46 MHz on a Bruker AMX 500 spectrometer using 5 mm o.d. tubes and are reported in ppm relative to external H₃PO₄ (85%). Coupling constants are reported in Hz. Mass spectra were recorded on a Katros MS50TC spectrometer connected to a DS90 system and operating in the FAB mode (*m*-nitrobenzyl alcohol, Xe, 8 eV; ca. 1.28 × 1015 J); ions were identified by DS90 software, and the data characterizing peaks for the metalated species were calculated using the ¹⁰⁶Pd and ¹⁹⁶Pt isotopes. The physical measurements were carried out by the RIAIDT services of the Universidad de Santiago de Compostela.

4-MeOC₆H₄C(Me)=NN(H)C(=S)NHMe (1). 4-Methoxiacetophenone (714 mg, 4.75 mmol) and hydrocloric acid (35%, 0.65 cm³) were added to a suspension of 4-methyl-3-thiosemicarbazide (500 mg, 4.75 mmol) in water (40 cm³) to give a clear solution, which was stirred at room temperature for 4 h. The white solid formed was filtered off, washed with cold water, and dried in vacuo.

Yield: 1046 mg, 93%. Anal. Found: C: 55.6, H: 6.5, N: 17.5, S: 13.4; C₁₁H₁₅N₃OS (237.32 g/mol) requires C: 55.7, H: 6.4, N: 17.7, S: 13.5%. IR(cm⁻¹): ν (N–H) 3191, 3367; ν (C=N) 1608; ν (C=S) 836. ¹H NMR (CDCl₃): 8.58 (s, 1H, NN*H*), 7.63 (m, 2H, *H2/H6*, N = 8.8), 7.62 (br, 1H, N*H*Me), 6.85 (m, 2H, *H3/H5*, N = 8.8), 3.85 (s, 3H, OMe), 3.27 (d, 3H, NHMe, ³J_{NHMe} = 4.4), 2.24 (s, 3H, MeC=N). Single crystals of **1** were grown by slow evaporation from ethanol solution.

 $[Pd{4-MeOC_6H_3C(Me)=NN=C(S)NHMe}]_4$ (2). To a stirred solution of potassium tetrachloropalladate (200 mg, 0.61 mmol) in water (6 cm³) was added ethanol (40 cm³). The fine yellow suspension of potassiun tetrachloropalladate obtained was treated with ligand 1 (1.1 equiv, 160 mg, 0.67 mmol). The mixture was stirred for 24 h at room temperature. The yellow precipitate was filtered off, washed with ethanol, and dried.

Yield: 185 mg, 89%. anal. found: C: 38.6, H: 3.9, N: 12.0, S: 9.2; $C_{44}H_{52}N_{12}O_4S_4Pd_4$ (1366.90 g/mol) requires C: 38.7, H: 3.8, N: 12.3, S: 9.4%. IR(cm⁻¹): ν (N–H) 3358; ν (C=N) 1573. ¹H NMR (CDCl₃): 7.13 (d, 1H, H5, ⁴J(H3H5) = 2.7), 6.50 (d, 1H, H2, ³J(H2H3) = 8.6), 6.40 (dd, 1H, H3, ³J(H2H3) = 8.6, ⁴J(H3H5) = 2.7), 4.99 (q, 1H, NHMe, ³J_{NHMe} = 5.1), 3.87 (s, 3H, OMe), 2.98 (d, 3H, NHMe, ³J_{NHMe} = 5.1), 1.84 (s, 3H, MeC=N). FAB-MS: m/z 1366 [M]⁺. Single crystals of **2** were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

 $[Pd\{4-MeOC_6H_3C(Me)=NN=C(S)NHMe\}(Ph_2PCH_2PPh_2-P)]$ (3). The diphosphine Ph_2PCH_2PPh_2 (112.5 mg, 0.29 mmol) was added to a solution of complex 2 (100 mg, 0.07 mmol) in acetone (20 cm³). The mixture was stirred for 24 h. The resulting yellow solid was filtered off and dried.

Yield: 149.1 mg, 70%. Anal. Found: C: 59.9, H: 5.0, N: 5.9, S: 4.5; C₃₆H₃₅N₃OP₂SPd (726.12 g/mol) requires C: 59.6, H: 4.9, N: 5.8, S: 4.4%. IR(cm⁻¹): ν (N–H) 3357; ν (C=N) 1577. ¹H NMR (CDCl₃): 8.0–7.1 (m, 20H, 4×*Ph*), 6.92 (d, 1H, *H2*, ³*J*(H2H3) = 8.2), 6.30 (dd, 1H, *H3*, ³*J*(H2H3) = 8.2, ⁴*J*(H3H5) = 2.7), 5.85 (m, 1H, *H5*), 4.70 (q, 1H, N*H*Me, ³*J*_{NHMe} = 4.9), 3,26 (d, 2H, PC*H*₂P, ²*J*(HP) = 8.9), 3.14 (s, 3H, O*Me*), 2.97 (d, 3H, NH*Me*, ³*J*_{NHMe} = 4.9), 2.32 (s, 3H, *Me*C=N). ³¹P-{¹H} NMR (CDCl₃): 26.60 (d, P_A, ²*J*_{AB} = 72.0), -25.02 (d, P_B, ²*J*_{AB} = 72.0).

Compounds 4 and 5 were obtained similarly as yellow solids from the diphosphines $Ph_2PC(CH_2)_2PPh_2$ and $Ph_2PC(=CH_2)PPh_2$, respectively.

[Pd{4·MeOC₆H₃C(Me)=NN=C(S)NHMe}(Ph₂PC(CH₂)₂PPh₂-P)] (4). Yield: 192.3 mg, 87%. Anal. Found: C: 60.9, H: 5.1, N: 5.6, S: 4.2; C₃₈H₃₇N₃OP₂SPd (752.15 g/mol) requires C: 60.7, H: 5.0, N: 5.6, S: 4.3%. IR(cm⁻¹): ν (N-H) 3434; ν (C=N) 1577. ¹H NMR (CDCl₃): 8.0–7.2 (m, 4×Ph), 7.04 (d, 1H, H2, ³J(H2H3) = 8.2), 6.53 (dd, 1H, H5, ³J(H5P) = 4.5, ⁴J(H3H5) = 2.3), 6.45 (dd, 1H, H3, ³J(H2H3) = 8.2, ⁴J(H3H5) = 2.3), 4.56 (br, 1H, NHMe), 3.51 (s, 3H, OMe), 2.89 (d, 3H, NHMe, ³J_{NHMe} = 5.2), 2.32 (s, 3H, MeC=N). ³¹P-{¹H} NMR (CD₂Cl₂): 61.32 (d, P_A, ²J_{AB} = 28.0), -9.54 (d, P_B, ²J_{AB} = 28.0).

 $[Pd{4-MeOC_{6}H_{3}C(Me)=NN=C(S)NHMe}(Ph_{2}PC=CH_{2}PPh_{2}-P)]$ (5). Yield: 176.7 mg, 82%. Anal. Found: C: 60.3, H: 5.0, N: 5.6, S: 4.3; C₃₇H₃₅N₃OP₂SPd (738.13 g/mol) requires C: 60.2, H: 4.8, N: 5.7,

S: 4.3%. IR(cm⁻¹): ν (N–H) 3357; ν (C=N) 1579. ¹H NMR (CDCl₃): 8.2–7.1 (m, 4x*Ph*), (d, 1H, *H2*, ³*J*(H2H3) = 8.2), 7.0 (d, 1H, *H2*, ³*J*(H2H3) = 8.8), 6.71 (br, 1H, PC = CH), 6.38 (dd, 1H, *H3*, (dd, 1H, *H3*, ³*J*(H2H3) = 8.8, ⁴*J*(H3H5) = 2.9), 6,00 (m, 1H, *H5*), 5.88 (br, 1H, PC = CH), 4.71 (q, 1H, NHMe, ³*J*_{NHMe} = 4.9), 3.19 (s, 3H, OMe), 2.99 (d, 3H, NHMe, ³*J*_{NHMe} = 4.9), 2.39 (s, 3H, MeC=N). ³¹P-{¹H} NMR (CDCl₃): 46.23 (d, P_A, ²*J*_{AB} = 83.0), -10.40 (d, P_B, ²*J*_{AB} = 83.0).

[PdCl₂{Pd[4-MeOC₆H₃C(Me) = NN = C(S)NHMe](Ph₂PCH₂-PPh₂)-*P*,*S*}] (6). To a solution of complex 3 (50 mg, 0.07 mmol) in acetone (12 cm³) was added [PdCl₂(NCPh)₂] (26.4 mg, 0.07 mmol) and the mixture was stirred for 24 h. The resulting orange solid was filtered off and dried. Yield: 38.9 mg, 64%. Anal. Found: C: 47.9, H: 3.8, N: 4.6, S: 3.5; C₃₆H₃₅Cl₂N₃OP₂SPd₂ (903.44 g/mol) requires C: 47.9, H: 3.9, N: 4.7, S: 3.6%. IR(cm⁻¹): ν (N–H) 3417; ν (C=N) 1577, ν (Pd–Cl) 305, 297. ¹H NMR (CDCl₃): 7.9–7.2 (m, 20H, 4×*Ph*), 7.20 (d, 1H, *H2*, ³*J*(H2H3) = 8.7), 6.49 (dd, 1H, H3, ³*J*(H2H3) = 8.7, ⁴*J*(H3H5) = 2.7), 5.92 (m, 1H, *H5*), 5.29 (q, 1H, N*H*Me, ³*J*_{NHMe} = 5.2), 3.24 (t, 2H, PCH₂P, *N* = 22.6), 3.23 (s, 3H, *OMe*), 3.10 (d, 3H, NH*Me*, ³*J*_{NHMe} = 5.2), 2.50 (s, 3H, *Me*C=N). ³¹P-{¹H} NMR (CDCl₃): 23.15 (d, P_A, ²*J*_{AB} = 30.2), 17.12 (d, P_B, ²*J*_{AB} = 30.2). Single crystals of 6 were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

Compounds 7 and 8 were obtained as orange solids following a similar procedure, from 4 and 5, respectively.

[PdCl₂{Pd[4-MeOC₆H₃C(Me)=NN=C(S)NHMe](Ph₂PC(CH₂)₂-PPh₂)-*P*,*S*}] (7). Yield: 35.1 mg, 57%. Anal. Found: C: 49.0, H: 4.1, N: 4.6, S: 3.4; C₃₈H₃₇Cl₂N₃OP₂SPd₂ (929.48 g/mol) requires C: 49.1, H: 4.0, N: 4.5, S: 3.4%. IR(cm⁻¹): ν (N−H) 3434; ν (C=N) 1574, ν (Pd−Cl) 319, 293. ¹H NMR (CDCl₃): 8.0−7.2 (m, 20H, 4x*Ph*), 7.12 (d, 1H, *H2*, ³*J*(H2H3) = 8.2), 6.38 (dd, 1H, *H3*, ³*J*(H2H3) = 8.2, ⁴*J*(H3H5) = 2.3), 5.58 (q, 1H, N*H*Me, ³*J*_{NHMe} = 5.3), 5.43 (dd, 1H, *H5*, ³*J*(H5P) = 4.7, ⁴*J*(H3H5) = 2.3), 3.12 (d, 3H, NH*Me*, ³*J*_{NHMe} = 5.3), 2.94 (s, 3H, O*Me*), 2.46 (s, 3H, *Me*C=N), 1.3−1.0 (m, 4H, PC(C*H*₂)₂). ³¹P-{¹H} NMR (CDCl₃): 46.52 (d, P_A, ²*J*_{AB} = 65.2), 34.30 (d, P_B, ²*J*_{AB} = 65.2). Single crystals of 7 were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

[PdCl₂{Pd[4-MeOC₆H₃C(Me)=NN=C(S)NHMe](Ph₂PC = CH₂-PPh₂)-*P*,*S*}] (8). Yield: 44.6 mg, 72%. Anal. Found: C: 48.7, H: 3.8, N: 4.5, S: 3.7; C₃₇H₃₅Cl₂N₃OP₂SPd₂ (915.45 g/mol) requires C: 48.5, H: 3.9, N: 4.6, S: 3.5%. IR(cm⁻¹): ν (N–H) 3413; ν (C=N) 1577, ν (Pd–Cl) 312–299 br. ¹H NMR (CDCl₃): 7.8–7.2 (m, 20H, 4×*Ph*), 7.14 (d, 1H, *H*2, ³*J*(H2H3) = 7.9), 6.54 (dd, 1H, PC=C*H*, ³*J*(HP_{trans}) = 30.6, ³*J*(HP_{cis}) = 18.4), 6.45 (dd, 1H, *H*3, ³*J*(H2H3) = 7.9, ⁴*J*(H3H5) = 2.6), 6.11 (dd, 1H, PC=C*H*, ³*J*(HP_{trans} = 30.6, ³*J*(HP_{cis} = 18.4), 5,80 (m, 1H, *H5*), 5.58 (q, 1H, N*H*Me, ³*J*_{NHMe}= 5.2), 3.20 (s, 3H, OMe), 3.10 (d, 3H, NHMe, ³*J*_{NHMe} = 5.2), 2.48 (s, 3H, MeC=N). ³¹P-{¹H} NMR (CDCl₃): 36.41 (d, P_A, ²*J*_{AB} = 73.8), 27.82 (d, P_B, ²*J*_{AB} = 73.8). Single crystals of **8** were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

Compounds 9 and 10 were obtained analogously as yellow solids from 3 and 5, respectively, and [PtCl₂(NCPh)₂].

[PtCl₂{Pd[4-MeOC₆H₃C(Me) = NN = C(S)NHMe](Ph₂PCH₂-PPh₂)-*P*,*S*}] (9). Yield: 38.6 mg, 57%. Anal. Found: C: 43.6, H: 3.5, N: 4.0, S: 3.1; C₃₆H₃₅Cl₂N₃OP₂SPdPt (992.10 g/mol) requires C: 43.6, H: 3.6, N: 4.2, S: 3.2%. IR(cm⁻¹): ν (N-H) 3414; ν (C=N) 1576, ν (Pd-Cl) 314, 292. ¹H NMR (CDCl₃): 8.0–7.2 (m, 20H, 4×*Ph*), 7.17 (d, 1H, *H2*, ³*J*(H2H3) = 8.6), 6.44 (dd, 1H, *H3*, ³*J*(H2H3) = 8.6, ⁴*J*(H3H5) = 2.4), 5.85 (m, 1H, *H5*), 5.44 (q, 1H, N*H*Me, ³*J*_{NHMe} = 5.2), 3,25 (t, 2H, PCH₂P, *N* = 22.0), 3.20 (s, 3H, OMe), 3.09 (d, 3H, NHMe, ³*J*_{NHMe} = 5.2), 2.43 (s, 3H, MeC=N). ³¹P-{¹H} NMR (CDCl₃): 22.70 (d, P_A, ²*J*_{AB} = 25.1), -2.01 (d, P_B, ²*J*_{AB} = 25.1, ¹*J*(PPt) = 3952). Single crystals of **9** were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

 $[PtCl_2\{Pd[4-MeOC_6H_3C(Me)=NN=C(S)NHMe](Ph_2PC=CH_2-PPh_2)-P,S\}] (10). Yield: 43.3 mg, 64%. Anal. Found: C: 43.9, H: 3.3, N: 4.1, S: 3.0; C_{37}H_{35}Cl_2N_3OP_2SPdPt (1004.11 g/mol) requires C: 44.3, H: 3.5, N: 4.2, S: 3.2%. IR(cm⁻¹): <math>\nu$ (N-H) 3455; ν (C=N) 1575, ν (Pd-Cl) 327-294 br. ¹H NMR (CDCl_3): 7.7-7.2 (m, 20H, 4×Ph), 7.08 (d, 1H, H2, ³J(H2H3) = 8.4), 6.51 (dd, 1H, PC=CH, ³J(HP_trans = 30.6, ³J(HP_{cis} = 17.6), 6.41 (dd, 1H, H3, ³J(H2H3) = 8.4, ⁴J(H3H5) = 2.2), 6.13 (dd, 1H, PC=CH, ³J(HP_trans) = 30.6,

 ${}^{3}J(\text{HP}_{cis}) = 17.6$), 6.03 (q, 1H, NHMe, ${}^{3}J_{\text{NHMe}} = 4.7$), 5,73 (m, 1H, H5), 3.21 (s, 3H, OMe), 3.06 (d, 3H, NHMe, ${}^{3}J_{\text{NHMe}} = 4.7$), 2.37 (s, 3H, MeC=N). ${}^{31}\text{P}-\{^{1}\text{H}\}$ NMR (CDCl₃): 34.14 (d, P_A, ${}^{2}J_{\text{AB}} = 66.1$), 9.61 (d, P_B, ${}^{2}J_{\text{AB}} = 66.1$, ${}^{1}J(\text{PPt}) = 3842$). Single crystals of **10** were grown by slow evaporation from a dichloromethane/hexane (3:1) solution.

X-ray Structure Determination. Single crystals of compounds 1, 2, 6, 7, 8 · CH₂Cl₂, 9, and 10 · CH₂Cl₂ were mounted on glass fibers for data collection in a Siemens Smart-CCD-1000⁴³ Bruker diffractometer equipped with a graphite monochromator at 293 K using Mo K α radiation ($\lambda = 0.71073$ Å). Intensity data were collected as a series of frames, each of ω width 0.3°, integrated⁴⁴ and corrected for absorption⁴⁵ and solved and refined using routine techniques.^{46a} Crystallographic data and selected interatomic distances and angles are listed in Tables 1–3. ORTEP^{46b} and MERCURY⁴⁷ drawings are shown in Figures 1–11 and in the Supporting Information.

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Supporting Information Available: Figures S1, S2, S3, S4, S5 containing crystal structures of 6, $8 \cdot \text{CH}_2\text{Cl}_2$, 1, 2 viewed along the *a* axis, and view of $\pi - \pi$ and CH··· π interactions in 10, respectively; Tables T1–T7. This material is available free of charge via the Internet at http://pubs.acs.org. Also, crystallographic data for this paper can be obtained at the Cambridge Crystallographic Data Centre [CCDC numbers 728243, 728244, 728245, 728246, 728247, 728248, and 728249 for 1, 2, 6, 7, $8 \cdot \text{CH}_2\text{Cl}_2$, 9 and $10 \cdot \text{CH}_2\text{Cl}_2$, respectively].

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