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Synthesis and characterization of dinuclear complexes of Pd^{II} containing the $(\mu\text{-N–C–S})_2$ skeleton

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Abstract

The reaction of [Pd(C ∧ N)(acac)] [C ∧ N = dmba (2-(dimethylaminomethyl)phenyl-C^1,N), 8-mq (8-quinolylmethyl-C,N); acac = acetylacetonate] with the 2-mercapto derivatives H[N ∧ S] {H[N ∧ S] = pySH (2-mercaptopyridine), bztzSH (2-mercaptobenzothiazole), pymSH (2-mercaptopyrimidine), bzmdSH (2-mercaptobenzimidazole), and tzSH (2-mercaptothiazoline)} in 1:1 molar ratio (CH_2Cl_2, room temperature) results in the protonation of the acetylacetonate ligand, which is eliminated as acetylacetone, and N,S-bridging coordination of the anionic groups $[N \wedge S]^-$, giving the corresponding neutral dinuclear derivatives $[Pd(C \wedge N)(\mu\text{-}N \wedge S)]_2$ (C ∧ N = dmba, N ∧ S = pyS **1**, bztzS **2**, pymS **3**, bzmdS **4**, tzS **5**; C ∧ N = 8-mq, N ∧ S = pyS **6**, bztzS **7**, pymS **8**, bzmdS **9**, tzS **10**). In these complexes, two $[Pd(C \wedge N)]^+$ fragments are bridged by two $[N \wedge S]^-$ ligands in a head-to-tail disposition and with a C-*trans*-to-N ligand arrangement around the palladium(II) centre. On the other hand, the reaction of [Pd(C ∧ N)(acac)] (C ∧ N = dmba, 8-mq) with the same 2-mercapto derivatives, but in 1:2.3 molar ratio (CH_2Cl_2, room temperature), allows the synthesis of the homoleptic dinuclear derivatives $[Pd(\mu\text{-}N \wedge S)_2]_2$ (by protonation of both the acetylacetonate and the *ortho*-metallated ligands) only when N ∧ S = pyS **11**, bztzS **12**, pymS **13**, while for N ∧ S = bzmdS and tzS the corresponding $[Pd(C \wedge N)(\mu\text{-}N \wedge S)]_2$ (**4**, **5**, **9**, **10**) complexes were obtained. Complexes **1**–**13** have been characterized through IR and NMR spectroscopic methods. © 1997 Elsevier Science S.A.

Keywords: *Ortho*-metallated; Palladium; Dinuclear; N,S-bridging ligands; NOESY

1. Introduction

The combination of an exocyclic thione (thioketo) group and a heterocyclic molecule, which may contain nitrogen, oxygen, sulphur or a combination of these, generates a group of compounds with considerable coordination potential. Molecules such as 2-mercaptopyridine (pySH), 2-mercaptobenzothiazole (bztzSH), 2-mercaptopyrimidine (pymSH), 2-mercaptobenzimidazole (bzmdSH), and 2-mercaptothiazoline (tzSH) belong to this class of ligands, and they have shown a rich coordination chemistry [1]. The deprotonation of these molecules could be easily accomplished by a variety of methods, generating the corresponding anions (see Fig. 1) which also display an interesting chemical behaviour and a high versatility as ligands. For instance, several coordination modes have been found for pyridine-2-thiolate (S-coordinated [2–4] N,S-chelated [4–11], N,S-bridging [12–16] and N,S-triply bridging [15]) and benzothiazole-2-thiolate (double and triply bridging [17–21]); and dinuclear Pt (III) compounds containing bridging pyridine-2-thiolate or pyrimidine-2-thiolate ligands have been synthesized [22–24]. However, very few examples of Pd (II) complexes containing this kind of ligands have been reported and, as far as we know, they are restricted to the pyridine-2-thiolate group [14,15].

We have previously shown that acetylacetonate complexes of Pd(II) are useful precursors in synthetic work, since they react with weak protic acids H[L–L] resulting in the displacement of acetylacetone, coordination of the anionic $[L\text{–}L]^-$ group and formation of mononuclear [25–29] or dinuclear [30] complexes depending on

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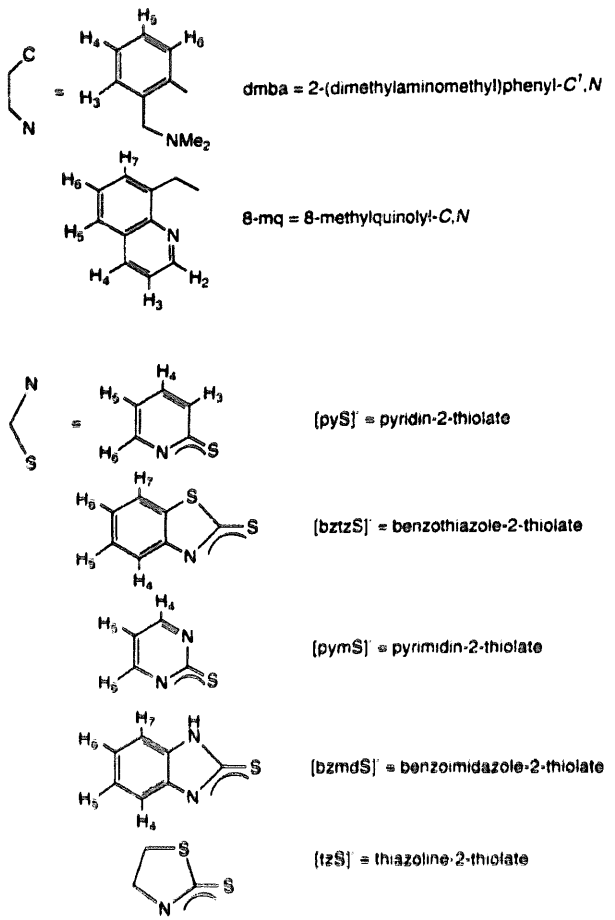


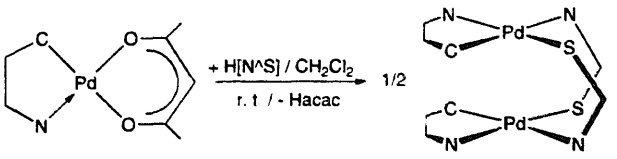
Fig. 1. Schematic representation and proton labelling of the different ligands employed in the synthesis of complexes **1–13**.

whether the deprotonated acid $[L{-}L]^-$ is *endo*- or *exo*-bidentate. Following our study of the reactivity of acetylacetonato complexes towards weak protic acids, we report here the results obtained from the reactions of [Pd(C ∧ N)(acac)] (C ∧ N = dmba, 8-mq) with the 2-mercapto derivatives above specified, which contain acidic H atoms.

2. Results and discussion

2.1. Synthesis of complexes 1–13

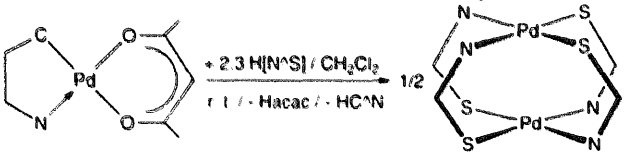
The reaction of [Pd(C ∧ N)(acac)] [C ∧ N = 2-(dimethylaminomethyl)phenyl-C^1,N or dmba, 8-quinolylmethyl-C,N or 8-mq; acac = acetylacetonate] with the 2-mercapto derivatives pySH, bztzSH, pymSH, bzmdSH and tzSH (1:1 molar ratio) in CH_2Cl_2 at room temperature results in the protonation of the acetylacetonate ligand, which is eliminated as acetylacetone, by the acidic H atom of the 2-mercapto derivative and coordination of the resulting anionic heterocyclic 2-thiolate groups (see Fig. 1), to give neutral derivatives of stoichiometry [Pd(C ∧ N)(N ∧ S)] (C ∧ N = dmba, N ∧ S = pyS **1**, bztzS **2**, pymS **3**, bzmdS **4**, tzS **5**; C ∧ N = 8-mq, N ∧ S = pyS **6** bztzS **7**, pymS **8**, bzmdS **9**, tzS **10**) (see Eq. (1)) as determined from their elemental analyses of C, H, N.



(1)

Conductivity measurements performed for the adequately soluble complexes **1–6** in acetone solutions ($c \cong 5 \times 10^{-4}$ M) showed the neutral nature of these compounds since they behave as non-electrolytes. The determination of the molecular weight of **3** and **4**, as representative examples, from their $CHCl_3$ solutions are in good agreement with a dinuclear stoichiometry $[Pd(C \wedge N)(N \wedge S)]_2$. In addition, the mass spectra of **1–6** (see Section 4: complexes **7–10** did not show any peak in these spectra, probably due to their low solubility) show the presence of the molecular peak corresponding to a dinuclear formulation $[Pd(C \wedge N)(N \wedge S)]_2^+$ and, in many cases, an additional peak corresponding to the loss of a $[N \wedge S]^-$ ligand $[Pd_2(C \wedge N)_2(N \wedge S)]^+$. The dinuclear stoichiometry of complexes **1–10** will be confirmed later by NMR spectroscopy (see below).

When the reactions between [Pd(C ∧ N)(acac)] and the same 2-mercapto derivatives are performed under the same experimental conditions (CH_2Cl_2, room temperature) but using an 1:2.3 molar ratio (Pd:N ∧ S), the results vary as a function of both the *ortho*-metallated ligand and the 2-mercapto derivative implied. Thus, the reaction of [Pd(dmba)(acac)] with pySH, bztzSH or pymSH results in the protonation of both the acetylacetonate and the dmba ligands, and formation of very insoluble solids of stoichiometry $[Pd(N \wedge S)_2]$ (N ∧ S = pyS **11**, bztzS **12**, pymS **13**) (see Eq. (2)), as determined from their elemental analyses of C, H, N. In spite of their low solubility, the mass spectra of **12** and **13** could be obtained and showed peaks corresponding to a dinuclear stoichiometry $[Pd(N \wedge S)_2]_2$ (see Section 4) (**13** showed also a peak corresponding to the loss of a $pymS^-$ ligand $[Pd_2(pymS)_3]^+$), suggesting a dinuclear structure for complexes **11–13**. The X-ray determination of the molecular structure of **11**, which have been already reported [14], confirms this hypothesis: and it is sensible to assume a similar nuclearity for complexes **12** and **13**, in which two Pd(II) centres are bridged by four N ∧ S ligands in a S-*trans*-to-N and head-to-head disposition of the ligands, as represented in Eq (2).



(2)

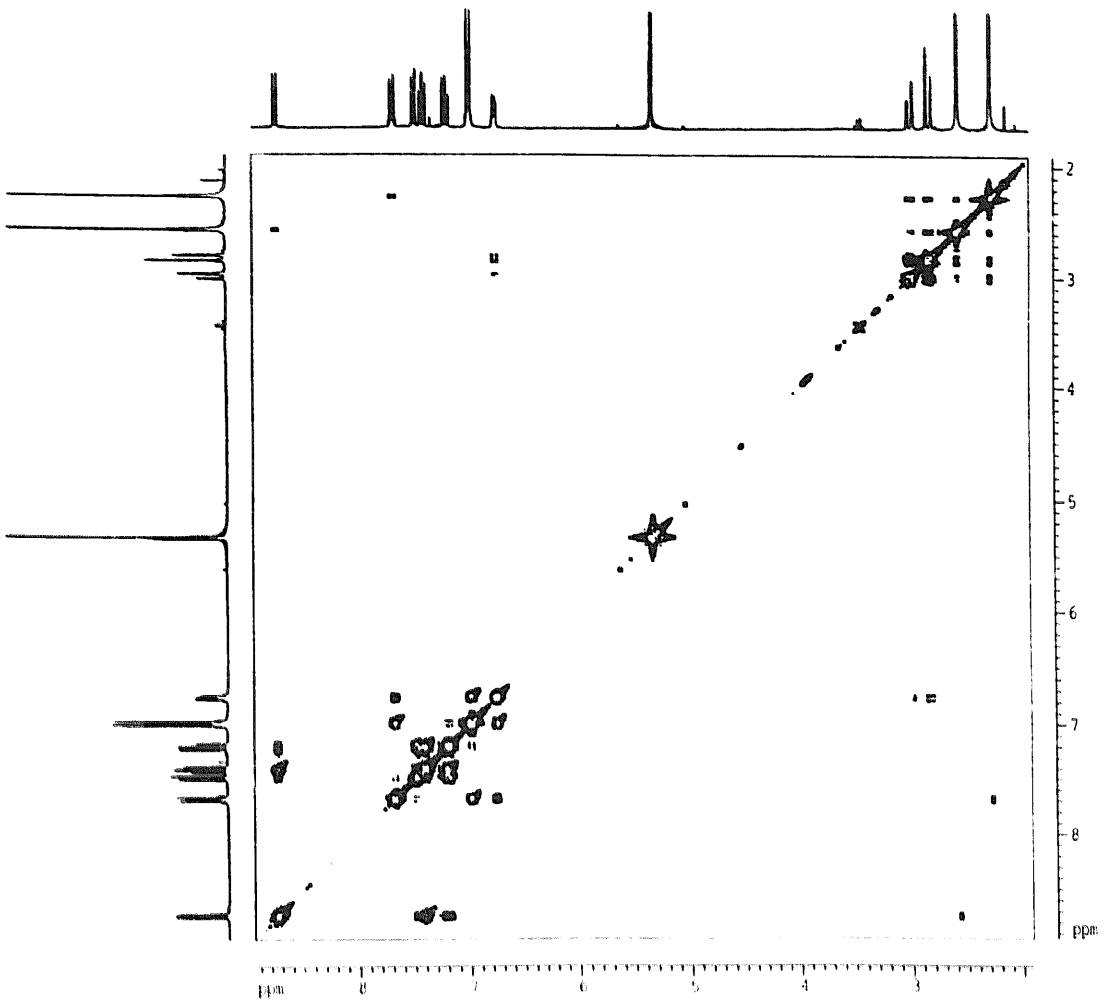


Fig. 2. $^1H-^1H$ NOESY spectrum for complex **2**.

Complexes **11** and **13** could be alternatively obtained from reaction of [Pd(8-mq)(acac)] with pySH and pymSH, respectively (1:2.3 molar ratio, CH_2Cl_2, room temperature). However, the reaction of [Pd(8-mq)(acac)] with bztzSH under the same experimental conditions affords a mixture of **7** and unreacted bztzSH. The same result is obtained even if the reaction is carried out in refluxing benzene. In a similar way, the reaction of [Pd(dmba)(acac)] or [Pd(8-mq)(acac)] with bzmdSH and tzSH (1:2.3 molar ratio, C_6H_6, reflux) affords mixtures of the respective $[Pd(C \wedge N)(N \wedge S)]_2$ complexes (**4**, **5**, **9** and **10**) and the unreacted ligands, the products $[Pd(bzmdS)_2]_2$ or $[Pd(tzS)_2]_2$ were not obtained in these experimental conditions. The lack of reactivity of bztzSH towards the double protonation of [Pd(8-mq)(acac)], when compared with [Pd(dmba)(acac)], could be related with the higher stability of the chelated 8-mq ligand [31,32]. However, it seems that there is not a clear correlation between the lack of reactivity of bztzSH towards the double protonation of [Pd(8-mq)(acac)], when compared with pySH or pymSH, and the pK_a values of the 2-mercapto derivatives. Thus, in spite of the higher acidity of bztzSH ($pK_a = 6.9$ [1]) than that of pySH ($pK_a = 9.97$ [33]), pySH can protonate both the 8-mq and acac ligands to give $[Pd(pyS)_2]_2$, while bztzSH is not able to behave similarly.

2.2. Spectroscopic characterization of complexes 1–13

Further characterization of complexes **1–13** is provided by the analysis of their IR and NMR spectra. The IR spectra of **1–10** (see Section 4) show the disappearance of the absorptions attributed to the $acac^-$ ligand [28], and the presence of characteristic absorptions of the coordinated ligands: two absorptions at about 850 and 740 cm^{-1} indicate the presence of chelated dmba [34], and absorptions at about 1505, 820, and 780 cm^{-1} indicate the presence of chelated 8-mq [34]. The existence of deprotonated ligands $[N \wedge S]^-$ in complexes **1–10** is inferred from the absence of the ν(NH) absorption, except for complexes **4** and **9**, which possess and additional N–H group [35]. Selected internal absorp-

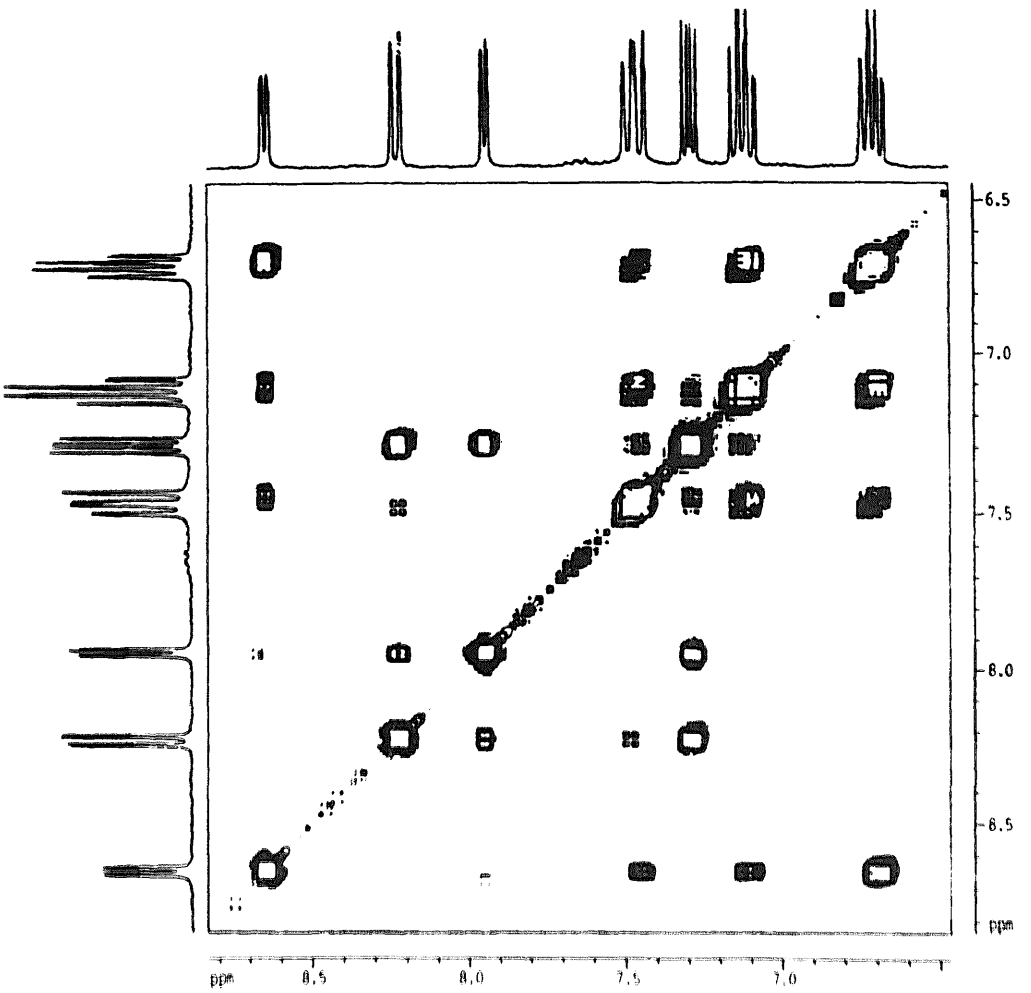


Fig. 3. ^1H–^1H NOESY spectrum for complex **6** (aromatic region).

tions of the anionic $[N \wedge S]^-$ ligands are given in the Section 4. The IR spectra of **11–13** show the disappearance of the absorptions attributed to both acac$^-$ and $[C \wedge N]^-$ ligands, and the presence of bands assigned to the $[N \wedge S]^-$ groups at similar wavelenghts to those observed in complexes **1–3** or **6–8**.

The ^1H NMR spectra of complexes **1–5** (Table 1) show the presence of a single isomer in solution, since only one set of signals is observed. The benzylic methylene group appears as an AB quartet, and the N-methyl groups as two sharp singlets. This fact rules out immediately a mononuclear structure with chelating $[N \wedge S]^-$ ligands or a symmetrical dimer bridged by the $[N \wedge S]^-$ ligands though sulphur atoms alone. Thus, only the possibility of an asymmetric NCS-bridging mode remains, and by analogy with certain acetate-bridged complexes [36,37], this might be expected to generate a dimeric 'open-book' structure. Previously, it has been proposed for complex $[Pd(dmba)(\mu\text{-pyS})]_2$ **1** [15] a head-to-tail structure, with the pyridine ring *trans* to the carbon atom of the dmba chelate, on the basis of the absence of anisotropic shielding of H_6 (dmba) by a *cis*-pyridine ring [38], and assuming that the relative disposition of the ligands is preserved in subsequent reactions.

In order to obtain a direct information about the stereochemistry of these dinuclear derivatives **1–10**, we have performed ^1H–^1H NOESY measurements for complexes **1–6**; the nuclear Overhauser effect measurement can be used to determine the pattern of relative interatomic interactions in molecules of fixed geometry, with some degree of internal molecular motion tolerated [39,40]. All these complexes **1–10** are good candidates for NOESY purposes, since they show a temperature independent ^1H NMR spectra, but only complexes **1–6** show an adequate solubility. As a representative example, Fig. 2 shows the NOESY spectrum of complex $[Pd(dmba)(\mu\text{-bztzS})]_2$ **2**. Proton labelling (Figs. 1, 2 and 4) was obtained unambiguously from ^1H–^1H homodecoupling and COSY experiments. As can be seen, there is not interactions between H_6 (dmba) and the aromatic protons (H_4–H_7) of the bztzS ligand, this fact

Table 1
^{1}H NMR data (δ, ppm; J, Hz) for complexes **1–11**

No.	C∧N resonances	N∧S resonances
1	7.62 (m, 1H, H_6), 6.91 (m, 2H, H_4, H_5), 6.68 (m, 1H, H_3) 3.12, 2.93 (AB spin system, 2H, CH_2N, $^2J_{HH}$ = 13.4) 2.53 (s, 3H, NMe_2), 2.38 (s, 3H, NMe_2)	8.58 (ddd, 1H, H_6, $^3J_{6-5}$ = 5.6, $^4J_{6-4}$ = 1.8, $^5J_{6-3}$ = 0.75) 7.28 (ddd, 1H, H_3, $^3J_{3-4}$ = 8.1, $^4J_{3-5}$ = 1) 7.02 (ddd, 1H, H_4, $^3J_{4-5}$ = 7.2), 6.70 (ddd, 1H, H_5)
2	7.68 (m, 1H, H_6), 6.99 (m, 2H, H_4, H_5), 6.76 (m, 1H, H_3) 3.00, 2.83 (AB spin system, 2H, CH_2N, $^2J_{HH}$ = 13.7) 2.57 (s, 3H, NMe_2), 2.28 (s, 3H, NMe_2)	8.73 (dt, 1H, H_4, $^3J_{4-5}$ = 8.3, $^4J_{4-6} \cong {}^5J_{4-7}$ = 0.4) 7.48 (ddd, 1H, H_7, $^3J_{7-6}$ = 8.0, $^4J_{7-5}$ = 1.2) 7.41 (ddd, 1H, H_5, $^3J_{5-6}$ = 7.4), 7.20 (ddd, 1H, H_6)
3	7.67 (m, 1H, H_6), 6.93 (m, 2H, H_4, H_5), 6.70 (m, 1H, H_3) 2.98, 2.83 (AB spin system, 2H, CH_2N, $^2J_{HH}$ = 13.6) 2.53 (s, 3H, NMe_2), 2.34 (s, 3H, NMe_2)	8.71 (s, broad, 1H, H_6), 8.20 (s, broad, 1H, H_4) 6.75 (t, 1H, H_5, $^3J_{5-4} \cong {}^3J_{5-6}$ = 5.0)
4	7.70 (m, 1H, H_6), 6.98 (m, 2H, H_4, H_5), 6.82 (m, 1H, H_3) 3.22, 2.97 (AB spin system, 2H, CH_2N, $^2J_{HH}$ = 13.6) 2.60 (s, 3H, NMe_2), 2.32 (s, 3H, NMe_2)	8.78 (s, broad, 1H, NH), 8.10 (dd, 1H, H_4, $^3J_{4-5}$ = 7.9, $^4J_{4-6}$ = 0.7), 7.14 (ddd, 1H, H_5, $^3J_{5-6}$ = 4.6, $^4J_{5-7}$ = 3.8), 7.03 (m, 2H, H_6, H_7)
5	7.45 (m, 1H, H_6), 6.91 (m, 2H, H_4, H_5), 6.72 (m, 1H, H_3) 2.98, 2.81 (AB spin system, 2H, CH_2N, $^2J_{HH}$ = 13.6) 2.60 (s, 3H, NMe_2), 2.48 (s, 3H, NMe_2)	4.17 (m, 2H, CH_2N), 3.35 (m, 2H, CH_2S)
6	8.23 (dd, 1H, H_4 $^3J_{4-3}$ = 8.3, $^4J_{2-4}$ = 1.5), 7.95 (dd, 1H, H_2, $^3J_{3-2}$ = 4.9), 7.48 (dd, 1H, H_5, $^3J_{5-6}$ = 8.1, $^4J_{5-7}$ = 0.9), 7.29 (dd, 1H, H_3), 7.13 (pt, 1H, H_6, $^3J_{5-6} \cong {}^3J_{6-7}$ = 8.1), 6.73 (dd, 1H, H_7), 2.90, 2.30 (AB spin system, 2H, CH_2, $^2J_{HH}$ = 14.4)	8.65 (ddd, 1H, H_6 $^3J_{6-5}$ = 5.6, $^4J_{6-4}$ = 1.8, $^5J_{6-3}$ = 0.7) 7.45 (dt, 1H, H_3 $^3J_{3-4}$ = 8.3, $^4J_{3-5} \cong {}^5J_{3-6}$ = 0.7) 7.10 (ddd, 1H, H_4, $^3J_{4-5}$ = 7.0), 6.69 (ddd, 1H, H_5)
7	8.13 (dd, 1H, H_4, $^3J_{4-3}$ = 8.4, $^4J_{2-4}$ = 1.5), 7.96 (dd, 1H, H_2, $^3J_{3-2}$ = 4.9), 7.69–7.20 (m, 2H, H_3, H_5), 6.99 (pt, 1H, H_6, $^3J_{5-6} \cong {}^3J_{6-7}$ = 7.2), 6.58 (dd, 1H, H_7, $^4J_{7-5}$ = 1.2), 3.19, 2.22 (AB spin system, 2H, CH_2, $^2J_{HH}$ = 15)	8.72 (ddd, 1H, H_4, $^3J_{4-5}$ = 8.1, $^4J_{4-6}$ = 1.2, $^5J_{4-7}$ = 0.6) 7.69–7.20 (m, 3H, H_5, H_6, H_7)
8	8.27 (dd, 1H, H_4 $^3J_{4-3}$ = 8.2, $^4J_{2-4}$ = 1.3), 8.01 (dd, 1H, H_2, $^3J_{3-2}$ = 4.8), 7.47 (dd, 1H, H_5, $^3J_{5-6}$ = 7.2, $^4J_{5-7}$ = 1.2), 7.35 (dd, 1H, H_3), 7.09 (pt, 1H, H_6, $^3J_{5-6} \cong {}^3J_{6-7}$ = 7.2), 6.62 (dd, 1H, H_7), 2.99, 2.15 (AB spin system, 2H, CH_2, $^2J_{HH}$ = 13.9)	8.30 (s, broad, 2H, H_6, H_4) 6.74 (t, 1H, H_5, $^3J_{5-4} \cong {}^3J_{5-6}$ = 5.0)
9	8.15 (dd, 1H, H_4 $^3J_{4-3}$ = 8.4, $^4J_{2-4}$ = 1.6), 8.07 (dd, 1H, H_2, $^3J_{3-2}$ = 4.9), 7.31 (dd, 1H, H_5, $^3J_{5-6}$ = 7.2, $^4J_{5-7}$ = 1.2), 7.25 (dd 1H, H_3), 6.98 (pt, 1H, H_6, $^3J_{5-6} \cong {}^3J_{6-7}$ = 7.2), 6.60 (dd, 1H, H_7), 3.05, 2.12 (AB spin system, 2H, CH_2, $^2J_{HH}$ = 15.4)	8.94 (s, broad, 1H, NH), 8.05 (dd, 1H, H_4, $^3J_{4-5}$ = 8.0, $^4J_{4-6}$ = 1.1), 7.15–7.02 (m, 3H, H_5, H_6, H_7)
10	8.42 (dd, 1H, H_2, $^3J_{3-2}$ = 4.9, $^4J_{2-4}$ = 1.5), 8.21 (dd, 1H, H_4, $^3J_{3-4}$ = 8.3), 7.46 (dd, 1H, H_3), 7.32 (dd, 1H, H_5, $^3J_{5-6}$ = 8.1, $^4J_{5-7}$ = 1.0), 6.94 (pt, 1H, H_6, $^3J_{5-6} \cong {}^3J_{6-7}$ = 8.1), 6.49 (dd, 1H, H_7), 2.75, 1.73 (AB spin system, 2H, CH_2, $^2J_{HH}$ = 14.9)	4.39 (m, 2H, CH_2N), 3.46 (m, 2H, CH_2S)
11	8.35 (ddd, 1H, H_6, $^3J_{6-5}$ = 5.7, $^4J_{6-4}$ = 1.7, $^5J_{6-3}$ = 0.7), 7.24 (ddd, 1H, H_3, $^3J_{3-4}$ = 7.8, $^4J_{3-5}$ = 0.9), 7.09 (ddd, 1H, H_4, $^3J_{4-5}$ = 7.2), 6.78 (ddd, 1H, H_5)	

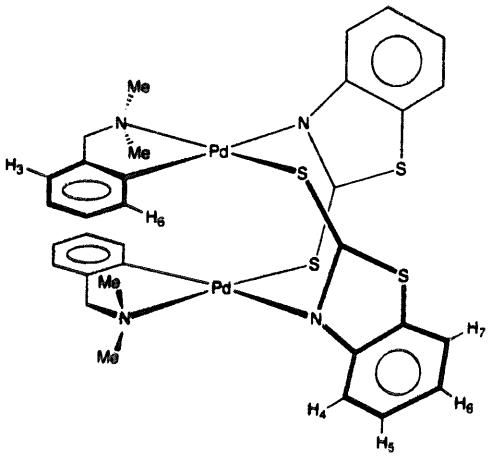


Fig. 4. Schematic representation and proton labelling for compound **2**.

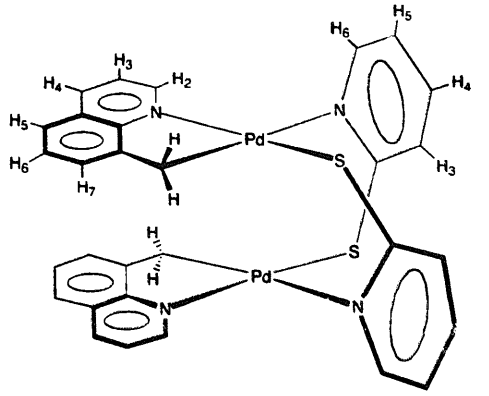


Fig. 5. Schematic representation and proton labelling for compound **6**.

confirming the C(dmba)-*trans*-to-N(bztzS) ligand arrangement [therefore, N(dmba)-*trans*-to-S(bztzS)], and the head-to-tail disposition of the bztzS ligands, as depicted in Eq. (1) and Fig. 4. In such structure, one methyl of the NMe_2 group (dmba) is directed inwards and is close to the zone of aromatic shielding of the other dmba ligand. This fact is clearly seen in the NOE interaction between H_6 (dmba) and the upfield resonance of the NMe_2 group (2.28 ppm). The other methyl of the NMe_2 group (2.57 ppm) is directed outwards and shows a strong NOE interaction with H_4 (bztzS) in keeping with the N-*cis*-to-N disposition. The obvious H_3 (dmba)-CH_2N (dmba) NOE interaction is also observed. Similar results can be inferred from the NOESY spectra of **1**, **3**, **4** and **5**, showing that all these complexes present the same disposition of the ligands. Thus, NOESY measurements allows the unambiguous establishment of the stereochemistry of these complexes (**1–5**).

The ^{1}H NMR spectra of **6–10** (Table 1) show a closely related situation to that described for complexes **1–5**. In all cases only one set of signals is observed, in which the CH_2 protons of the 8-mq ligand appear as an AB quartet, excluding a mononuclear or a dinuclear S-bridging stereochemistry, and suggesting an analogous structure to that proposed for **1–5**. We have also measured the ^{1}H–^{1}H NOESY spectrum of **6** (the most soluble representant of the series) in order to confirm the N-*cis*-to-N geometry. Fig. 3 shows the aromatic region of this spectrum, in which it is possible to observe a weak NOE interaction between H_6 (pyS) and H_2 (8-mq) (see Fig. 5) and a strong NOE interaction between H_3 (pyS) and H_3 (8-mq), in keeping with the N-*cis*-to-N geometry. This geometry could also be inferred from the unusually low chemical shift of H_2 (8-mq), which appears at higher fields than H_4. Due to the presence of the *cis*-pyridine ring, H_2 undergoes the influence of its anisotropic shielding [38] and is shifted to high field. This fact is also observed in complexes **7–9**, having aromatic heterocyclic thiolates, but not in **10** in which H_2 appears at low field than H_4, as expected.

The ^{13}C{^{1}H} NMR spectra of **1–6** (Table 2; complexes **7–10** were insufficiently soluble for ^{13}C mea-

Table 2
^{13}C{^{1}H} NMR data (δ, ppm) for complexes **1–6**

No.	C ∧ N resonances	N ∧ S resonances
1	149.84, 147.82, 135.33, 124.86, 123.97, 122.22 (C_6H_4), 70.89 (CH_2N), 51.76, 50.82 (NMe_2)	173.45 (C_2), 150.03, 133.87, 127.83, 117.03
2	150.03, 147.54, 135.23, 124.77, 123.60, 122.48 (C_6H_4), 70.88 (CH_2N), 52.47, 50.82 (NMe_2)	181.87 (C_2), 152.29, 135.57, 125.92, 125.21, 120.85, 119.66
3	149.70, 146.48, 135.68, 125.21, 124.53, 122.51 (C_6H_4), 70.51 (CH_2N), 51.97, 50.67 (NMe_2)	183.14 (C_2), 158.23 (C_6), 156.04 (C_4), 114.18 (C_5)
4	150.19, 148.92, 135.78, 125.06, 124.33, 122.18 (C_6H_4), 71.31 (CH_2N), 52.19, 51.22 (NMe_2)	162.94 (C_2), 142.92, 134.46, 121.72, 121.52, 116.06, 109.31
5	149.89, 148.18, 135.74, 125.10, 124.32, 122.19 (C_6H_4), 70.84 (CH_2N), 52.28, 51.36 (NMe_2)	180.59 (C_2), 65.11 (CH_2N), 36.25 (CH_2S)
6	152.90, 150.71, 148.97, 137.02, 128.52 (2C), 127.92, 123.10, 121.69 (C_6H_6N), 21.48 (CH_2Pd)	174.02 (C_2), 151.71, 133.77, 129.35, 116.69

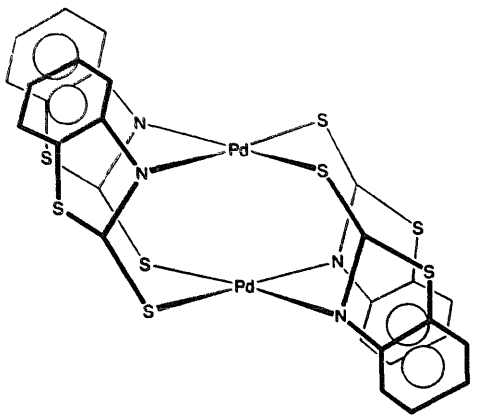


Fig. 6. Schematic representation and proton labelling for compound **12**.

surements) showed the presence of all the expected resonances and did not show remarkable features. On the other hand, complexes **12** (see Fig. 6) and **13** were also insufficiently soluble even for ^{1}H measurements. Only the ^{1}H NMR spectrum of complex **11** could be measured, showing the expected presence of the [pyS]$^-$ resonances alone.

It is also noteworthy the stereoselectivity in the coordination of the [N ∧ S]$^-$ bridging ligands. From the five expected isomers for a dinuclear [Pd(C ∧ N)(μ-N ∧ S)]$_2$ structure, only one is observed. A sensible explanation for this fact lies in the comparison of the different hardness and softness of the donor atoms bonded to palladium [41] and the antisymbiotic behaviour of the Pd(II) centre [42–44]. Thus, the soft carbon atom of the *ortho*-metallated ligand will be particularly stabilized when coordinated *trans* to the hardest donor atom of the heterocyclic thiolate ligand, that is, the N atom. And, in the same way, the position *trans* to the hard N atom of the *ortho*-metallated ligand would be occupied by the soft sulphur atom of the thiolate group.

3. Conclusion

New dinuclear complexes of stoichiometry [Pd(C ∧ N)(μ-N ∧ S)]$_2$ or [Pd(μ-N ∧ S)$_2$]$_2$ have been synthesized in high yield by reaction of [Pd(C ∧ N)(acac)] with different 2-mercapto derivatives H[N ∧ S]. The stoichiometry of the final products depends upon the molar ratio employed and the nature of both the C ∧ N ligand and the 2-mercapto derivative. The reaction is highly stereoselective and only one isomer is formed. Further work about these complexes will concentrate on exploring: (i) their reactivity as 'building-blocks' in the synthesis of polynuclear aggregates, and (ii) their red-ox behaviour in the synthesis of complexes of palladium in high oxidation states.

4. Experimental section

4.1. General comments

Elemental analyses of C, H, N were carried out on a Perkin-Elmer 2400 microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^{1}H (300.13 MHz) and ^{13}C{^{1}H} (75.47 MHz) NMR spectra were recorded from CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer using the solvent signal as internal standard. The two dimensional ^{1}H–^{1}H NOESY experiments performed on compounds **1–6** were carried out at a measuring frequency of 300.13 MHz. The data were acquired into a 512 × 1024 matrix, then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms in each case. The two dimensional ^{1}H–^{1}H COSY experiments performed on compounds **2** and **6** were carried out at a measuring frequency of 300.13 MHz. The data were acquired into a 384 × 1024 matrix, then transformed into 1024 × 1024 points using a sine window in each dimension. Mass spectra were registered in a VG-Autospec spectrometer using the standard Cs ion FAB (acceleration voltage 35 kV). Conductivities were measured on ≅ 5×10^{-4} M acetone solutions with a Philips PW-9509 conductometer. Molecular weight determinations were carried out on a Knauer osmometer using chloroform solutions of concentration ≅ 2.5×10^{-2} m. The starting compound [Pd(dmba)(acac)] was prepared according to published methods [28]; the complex [Pd(8-mq)(acac)] was synthesized following the same experimental procedure than that for [Pd(dmba)(acac)]. The 2-mercapto derivatives were commercially available and were used as purchased. Complexes **1** [15] and **11** [14] were previously reported, although they have been obtained by another synthetic method.

4.2. Preparation of [Pd(dmba)(μ-pyS)]$_2$ 1

To a solution of [Pd(dmba)(acac)] (0.301 g, 0.886 mmol) in 20 ml of CH_2Cl_2 was added 2-mercaptopyridine (0.099 g, 0.886 mmol). The original pale-yellow solution was stirred at room temperature for 3 h, resulting in a gradual change of its colour until a red solution was obtained. The solvent was then evaporated to small volume (ca. 2 ml) and Et_2O (20 ml) was added. Subsequent stirring gave **1** as a yellow solid, which was filtered and air dried. Obtained: 0.247 g (79% yield). The spectral parameters of **1** were identical to those reported previously [15].

4.3. Preparation of [Pd(dmba)(μ-bztzS)]$_2$ 2

Complex **2** was obtained following the same procedure than that described for **1**: [Pd(dmba)(acac)] (0.251 g, 0.737 mmol) was reacted with 2-mercaptobenzothiazole (0.123 g, 0.737 mmol) to give **2** as a pale yellow solid. Obtained: 0.259 g (86% yield).

Anal. Calc. for $C_{32}H_{32}N_4Pd_2S_4$ (813.70): C 47.23; H, 3.96; N, 6.88. Found: C, 47.44: H, 4.01; N, 6.59. IR (ν, cm^{-1}): 1243, 1026 1010 (bztzS); 845, 744 (dmba). Mass spectrum (+FAB) [m/z, (%)]: 814 (100%) [M$^+$]; 648 (90%) [(M-bztzS)$^+$].

4.4. Preparation of [Pd(dmba)(μ-pymS)]$_2$ 3

Complex **3** was obtained following the same procedure than that described for **1**: [Pd(dmba)(acac)] (0.251 g, 0.737 mmol) was reacted with 2-mercaptopyrimidine (0.083 g, 0.737 mmol) to give **3** as a yellow solid. Obtained: 0.245 g (94% yield).

Anal. Calc. for $C_{26}H_{30}N_6Pd_2S_2$ (703.50): C, 44.39; H, 4.29: N, 11.94. Found: C, 43.66; H, 4.25; N, 11.42. IR (ν, cm^{-1}): 1574, 1532, 1190, 993 (pymS); 849, 740 (dmba). Mol. weight found (calc.): 715.45 (703.50). Mass spectrum (+FAB) [m/z, (%)]: 704 (70%) [M$^+$]; 593 (100%) [(M-pymS)$^+$].

4.5. Preparation of [Pd(dmba)(μ-bzmdS)]$_2$ 4

Complex **4** was obtained following the same procedure than that described for **1**: [Pd(dmba)(acac)] (0.251 g, 0.737 mmol) was reacted with 2-mercaptobenzimidazole (0.111 g, 0.737 mmol) to give **4** as a pale orange solid. Obtained: 0.260 g (91% yield).

Anal. Calc. for $C_{32}H_{34}N_6Pd_2S_2$ (779.60): C, 49.30; H, 4.39; N, 10.78. Found: C, 49.26; H, 4.68; N, 10.41. IR (ν, cm^{-1}): 3205 (NH), 1276, 996 (bzmdS): 853, 741 (dmba). Mol. weight found (calc.): 790.30 (779.60). Mass spectrum (+FAB) [m/z, (%)]: 780 (65%) [M$^+$]; 631 (100%) [(M-bzmdS)$^+$].

4.6. Preparation of [Pd(dmba)(μ-tzS)]$_2$ 5

Complex **5** was obtained following the same procedure than that described for **1**: [Pd(dmba)(acac)] (0.251 g, 0.737 mmol) was reacted with 2-mercaptothiazoline (0.088 g, 0.737 mmol) to give **5** as a yellow solid. Obtained: 0.211 g (80% yield).

Anal. Calc. for $C_{24}H_{32}N_4Pd_2S_4$ (717.60): C, 40.17; H, 4.49; N, 7.80. Found: C, 40.04; H, 4.67; N, 7.72. IR (ν, cm^{-1}): 1521, 1032, 974, 940 (tzS); 847, 745 (dmba). Mass spectrum (+FAB) [m/z, (%)]: 718 (15%) [M$^+$].

4.7. Preparation of [Pd(8-mq)(μ-pyS)]$_2$ 6

Complex **6** was obtained following the same procedure than that described for **1**: [Pd(8-mq)(acac)] (0.313 g, 0.900 mmol) was reacted with 2-mercaptopyridine (0.100 g, 0.900 mmol) to give **6** as an orange solid. Obtained: 0.224 g (69% yield).

Anal. Calc. for $C_{30}H_{24}N_4Pd_2S_2$ (717.48): C, 50.22; H, 3.37; N, 7.81. Found: C, 49.80; H, 3.38; N, 7.46. IR (ν, cm^{-1}): 1584, 1542, 1133, 1087 (pyS); 1504, 818, 781 (8-mq). Mass spectrum (+FAB) [m/z, (%)]: 718 (20%) [M$^+$]; 608 (40%) [(M-pyS)$^+$]; 576 (35%) [(M-8mq)$^+$].

4.8. Preparation of [Pd(8-mq)(μ-bztzS)]$_2$ 7

Complex **7** was obtained following the same procedure than that described for **1**: [Pd(8-mq)(acac)] (0.249 g, 0.717 mmol) was reacted with 2-mercaptobenzothiazole (0.120 g, 0.717 mmol) to give **7** as a yellow solid, which precipitated from the CH_2Cl_2 mixture. Obtained: 0.245 g (82% yield).

Anal. Calc. for $C_{34}H_{24}N_4Pd_2S_4$ (829.65): C, 49.22; H, 2.91; N, 6.75. Found: C, 49.29; H, 2.73; N, 6.77. IR (ν, cm^{-1}): 1240, 1023, 1011 (bztzS); 1506, 818, 779 (8-mq).

4.9. Preparation of [Pd(8-mq)(μ-pymS)]$_2$ 8

Complex **8** was obtained following the same procedure than that described for **1**: [Pd(8-mq)(acac)] (0.201 g, 0.578 mmol) was reacted with 2-mercaptopyrimidine (0.065 g, 0.578 mmol) to give **8** as a yellow solid, which precipitated from the CH_2Cl_2 mixture. Obtained: 0.178 g (86% yield).

Anal. Calc. for $C_{28}H_{22}N_6Pd_2S_2$ (719.45): C, 46.74; H, 3.08; N, 11.68. Found: C, 46.67; H, 2.96; N, 11.59. IR (ν, cm^{-1}): 1578, 1533, 1190, 993 (pymS); 1505, 818, 809, 778 (8-mq).

4.10. Preparation of [Pd(8-mq)(μ-bzmdS)]$_2$ 9

Complex **9** was obtained following the same procedure than that described for **1**: [Pd(8-mq)(acac)] (0.250 g, 0.720 mmol) was reacted with 2-mercaptobenzimidazole (0.108 g, 0.720 mmol) to give **9** as a yellow solid, which precipitated from the CH_2Cl_2 mixture. Obtained: 0.220 g (77% yield).

Anal. Calc. for $C_{34}H_{26}N_6Pd_2S_2$ (795.55): C, 51.33; H, 3.29; N, 10.56. Found: C, 50.97; H, 3.31; N, 10.42. IR (ν, cm^{-1}): 3171 (NH), 1275, 993 (bzmdS); 1505, 819, 781 (8-mq).

4.11. Preparation of [Pd(8-mq)(μ-tzS)]$_2$ 10

Complex **10** was obtained following the same procedure than that described for **1**: [Pd(8-mq)(acac)] (0.250 g, 0.720 mmol) was reacted with 2-mercaptothiazoline (0.086 g, 0.720 mmol) to give **10** as a yellow solid, which precipitated from the CH_2Cl_2 mixture. Obtained: 0.134 g (51% yield).

Anal. Calc. for $C_{26}H_{24}N_4Pd_2S_4$ (733.56): C, 42.57; H, 3.30; N, 7.63. Found: C, 42.45; H, 3.35; N, 7.57. IR (ν, cm^{-1}): 1518, 1024, 972, 940 (tzS); 1505, 818, 777 (8-mq).

4.12. Preparation of [Pd(μ-pyS)$_2$]$_2$ 11

To a solution of [Pd(dmba)(acac)] (0.301 g, 0.886 mmol) in 20 ml of CH_2Cl_2 was added 2-mercaptopyridine (0.256 g, 2.306 mmol). The original pale-yellow solution was stirred at room temperature for 4 h. During this time an orange solid precipitated, which was filtered after the reaction time, washed with CH_2Cl_2 (10 ml) and air dried. This solid was identified by analytical and spectroscopic methods as [Pd(μ-pyS)$_2$]$_2$ **11** [14]. Obtained: 0.218 g (76% yield).

Anal. Calc. for $C_{20}H_{16}N_4Pd_2S_4$ (653.43): C, 36.76; H, 2.47; N, 8.57. Found: C, 36.93; H, 2.38; N, 8.44. IR (ν, cm^{-1}): 1543, 1135, 1014, 759, 742 (pyS).

4.13. Preparation of [Pd(μ-bztzS)$_2$]$_2$ 12

Complex **12** was obtained following the same procedure than that described for **11**: [Pd(dmba)(acac)] (0.301 g, 0.886 mmol) was reacted with 2-mercaptobenzothiazole (0.385 g, 2.303 mmol) to give **12** as an orange solid. Obtained: 0.227 g (59% yield).

Anal. Calc. for $C_{28}H_{16}N_4Pd_2S_8$ (877.78): C, 38.31; H, 1.84; N, 6.38. Found: C, 37.92; H, 1.74; N, 6.05. IR (ν, cm^{-1}): 1247, 1026, 1016, 745 (bztzS). Mass spectrum (+FAB) [m/z, (%)]: 878 (10%) [M^+].

4.14. Preparation of [Pd(μ-pymS)$_2$]$_2$ 13

Complex **13** was obtained following the same procedure than that described for **11**: [Pd(dmba)(acac)] (0.246 g, 0.724 mmol) was reacted with 2-mercaptopyrimidine (0.211 g, 1.882 mmol) to give **13** as a brownish solid. Obtained: 0.237 g (99% yield).

Anal. Calc. for $C_{16}H_{12}N_8Pd_2S_4$ (657.38): C, 29.23; H, 1.84; N, 17.04. Found: C, 29.26; H, 1.60; N, 16.85. IR (ν, cm^{-1}): 1573, 1537, 1192, 1005 (pymS). Mass spectrum (+FAB) [m/z, (%)]: 658 (20%) [M^+]; 547 (25%) [(M-pymS)$^+$].

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