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# Effect of a (hetero)aromatic spacer on the direction of cyclopalladation in ditopic pincer ligands with thione sulfur donors

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#### Abstract

3-Diphenylthiophosphorylaniline and isophthalic or 2,6-pyridinedicarboxylic acids were used as key precursors for the synthesis of ditopic pincer ligands bearing thioamide and thiophosphoryl donor groups. Depending on the nature of a (hetero)aromatic spacer (*meta*functionalized phenylene or pyridine rings), the ligands derived underwent coordination either at the lateral or central pincer units, selectively affording binuclear (in the case of phenylene-based ligand) or mononuclear (in the case of pyridine-based derivative) Pd(II) pincer complexes. The mononuclear pyridine-based palladacycle is prone to deprotonation of the secondary thioamide groups, resulting in sulfide clusters. A structure of the tetramer obtained was elucidated by single-crystal XRD.

Key words: pincer complex, ditopic ligand, palladium, cyclometalation.

#### **1. Introduction**

Among the rich variety of organometallic compounds, pincer complexes comprise one of the most thoroughly studied classes that attract continuous research interest [1, 2]. High stability and tunability provided by specific tridentate ligands promote wide application scope of these complexes—from organic synthesis and catalysis to materials science and medicinal chemistry. Whereas the overwhelming majority of the reported examples represent mononuclear species, there are a limited number of Pd(II), Pt(II), Ru(III), and Re(I) binuclear and trinuclear complexes combining several pincer motifs in their structures (see, for example, Fig. 1) [3]. Besides interesting reactivity patterns and supramolecular structures [3c–f,h–j,m,n], these complexes exhibited remarkable redox properties [3a,g], catalytic activity [3k,l], and photophysical characteristics [3b], sometimes exceeding in the performance their mononuclear prototypes.



Fig. 1. Examples of ditopic pincer complexes.

Most of the known ditopic pincer complexes are appended with nitrogen donors, while their sulfur- and phosphorus-containing analogs remain essentially underexplored. At the same time, mononuclear *S*,*C*,*S*-pincer complexes, in particular, those bearing thione sulfur donors were shown to possess intriguing chemical behavior, valuable luminescence properties, and high catalytic activity in different reactions (Fig. 2) [4]. Therefore, it seemed interesting to develop related ditopic pincer systems. In this communication, we report on the synthesis of potentially dinucleating ligands having thiophosphoryl and thiocarbamoyl coordination arms, where two pincer moieties are bridged by (hetero)aromatic spacers. The peculiarities of their complexation with Pd(II) ions are considered.



Fig. 2. Mononuclear pincer complexes with thione sulfur donors.

#### 2. Results and discussion

A convenient key precursor for the synthesis of novel ligands appeared to be 3diphenylthiophosphorylaniline **1** (Scheme 1). It should be noted that its phosphorylated analog has been used successfully for the creation of hybrid S, C, S'-pincer ligands that led to mononuclear Pd(II) complexes [5]. The synthesis of the P(S)-functionalized aniline was accomplished by analogy with its P(O)-counterpart starting from triphenylphosphine oxide. An additional thionation step was introduced to facilitate the construction of a multidentate ligand

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framework, since the conversion of tertiary phosphine oxides to the corresponding sulfides requires harsh reaction conditions and is more complicated than the thionation of amides [6]. Interestingly, this modification did not affect the overall yield of the target product. In contrast, optimization of the reaction conditions and isolation procedures led even to the more facile and efficient multigram synthesis of the key phosphorus precursor.



Scheme 1. Synthesis of key thiophosphorylated aniline 1.

The reactions of aniline **1** with isophthalic and 2,6-pyridinedicarboxylic acid chlorides under mild conditions smoothly afforded bis(amides) **2** and **3** in high yields (Scheme 2). The latter were transformed to the corresponding bis(thioamides) (compounds **4** and **5**, Scheme 2) upon refluxing with an excess of the Lawesson reagent in chlorobenzene. The structures of the ligands derived were unambiguously confirmed by the multinuclear NMR and IR spectroscopic data. In particular, 2D NMR spectra (COSY, HMQC, and HMBC) allowed for the full assignment of the signals of hydrogen and carbon nuclei (see, for example, Figs. S1–S8 in Supplementary Data (SD)). In the case of bis(thioamide) **4**, most of the signals in the NMR spectra registered at room temperature appeared to be broadened; however, a temperature decrease to 258 K afforded the resolved signals (see Experimental section).

The choice of the mentioned *meta*-functionalized carbonyl derivatives ensured the formation of two lateral pincer motifs. At the same time, the central (hetero)aromatic moiety with two thiocarbamoyl pendant arms can also adopt a tridentate coordination mode, either monoanionic (in the case of phenylene-containing ligand **4**) or neutral (in the case of pyridine-substituted ligand **5**). The realization of the second complexation scenario would afford mononuclear complexes with two equivalent five-membered fused palladacycles, whereas the expected ditopic coordination involving the P=S and C=S donor groups would lead to 5,6-membered unsymmetrical binuclear derivatives. Therefore, it seemed interesting to estimate the possibility of selective cyclopalladation in these systems.



Scheme 2. Synthesis of ditopic pincer ligands with (hetero)aromatic spacers 4 and 5.

Reaction of ligand **4** with two equivalents of PdCl<sub>2</sub>(NCPh)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature smoothly afforded the desired binuclear complex **6** with two pincer fragments in a high yield (Scheme 3). Interestingly, the <sup>31</sup>P NMR spectrum of the reaction mixture at room temperature in 5 days displayed broadened signals in the range of 46.5–48.6 ppm, which were partially resolved upon cooling to 258 K (Fig. S9 in SD). Presumably, the steric congestion of a ditopic pincer system with the bulky Ph<sub>2</sub>P(S) pendant arms resulted in restricted rotation and formation of conformational isomers, which slowly interconverted in chlorinated hydrocarbons (*vide infra*). Thus, for example, addition of DMF led to conversion of these signals to a sole singlet at 48.4 ppm (Fig. S10 in SD). A significant downfield shift of the phosphorus resonances compared to that of the free ligand unambiguously indicated coordination of the P=S donor groups ( $\Delta\delta_P$  up to ~5.5 ppm). Note that a relatively long reaction time (*cf.* 5 days instead of 1 day in the case of a mononuclear analog [5]) was stipulated by the slow conversion of an intermediate complex (or a mixture of complexes) formed immediately after mixing of the reagents, which, in turn, was connected with its (or their) low solubility in CH<sub>2</sub>Cl<sub>2</sub>. The addition of more polar solvents, such as DMF, although accelerated the reaction, but essentially complicated the product isolation.

The <sup>31</sup>P NMR monitoring of the analogous reaction of ligand **5**, having a pyridine spacer, with  $PdCl_2(NCPh)_2$  in  $CH_2Cl_2$  did not reveal coordination of the thiophosphoryl groups. Independent from a relative amount of the metal precursor (1–3 equivalents), the <sup>31</sup>P NMR spectra showed signals in a narrow range of 42–43 ppm—a region typical for the non-coordinated phosphine sulfides. Furthermore, a sole singlet signal (at 42.3 ppm) was detected only in the case of 1:1 metal/ligand ratio. This suggests that the coordination of ligand **5** occurred selectively at the central pincer unit involving the pyridine ring and the thiocarbamoyl donor groups. Optimization of the reaction conditions allowed for the isolation of mononuclear complex **7** in a good yield (Scheme 3).



Scheme 3. Complexation of ditopic pincer ligands 4 and 5 with Pd(II) ions.

The compositions of complexes **6** and **7** were confirmed by the elemental analyses. Their structures were supported by the IR spectroscopic data. Thus, the lower-frequency shift of the P=S bond stretching vibrations was detected only in the case of complex **6**. This is a characteristic feature of pincer complexes involving P=S ancillary donor groups [5, 6]. In the case of complex **7**, the mentioned absorption band was observed in the region typical for free phosphine sulfides (*cf.* 640 cm<sup>-1</sup> for complex **7** and 637 cm<sup>-1</sup> for the corresponding ligand **5**). Furthermore, the IR spectra of the complexes obtained showed N–H stretching vibrations in the range of 3150–3220 cm<sup>-1</sup> instead of 3234–3258 cm<sup>-1</sup> for the free ligands, which confirms the coordination of thioamide groups in both compounds.

Unfortunately, after isolation and drying, complex 6 appeared to be poorly soluble in chlorinated hydrocarbons. Furthermore, as well as in the case of the reaction mixture, the <sup>31</sup>P NMR spectrum of a solution of this palladacycle in CDCl<sub>3</sub> at room temperature showed broadened signals in the region characteristic for the coordinated Ph<sub>2</sub>P(S) groups, which converted to a number of singlet signals in the range of 45.5–48.6 ppm upon cooling to 258 K (Fig. S11 in SD). The existence of several conformers was further supported by the presence of a range of well resolved signals at 11.33–12.51 ppm in the <sup>1</sup>H NMR spectrum registered at the reduced temperature, which were attributed to the NHC(S) protons (Figs. S12 and S13 in SD). Although complex 6 rapidly decomposes in coordinating solvents, the <sup>31</sup>P and <sup>1</sup>H NMR spectra registered in 5 min after its dissolution in (CD<sub>3</sub>)<sub>2</sub>SO eventually confirmed the suggested structure of this complex (Figs. S14 and S15 in SD). Note that the content of undefined decomposition products reached 12% even over such a short period of time. However, a strongly downfieldshifted phosphorus resonance of the main component was indicative of coordination of lateral pincer units ( $\delta_P = 49.09$  ppm). Furthermore, the <sup>1</sup>H NMR spectrum displayed the characteristic singlet of H(C1) proton of the non-metallated central phenylene ring along with the other aromatic and NHC(S) proton signals.

Dissolution of palladacycle 7 even in non-coordinating solvents led to spontaneous deprotonation of the secondary thioamide groups accompanied by oligomerization. This made

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impossible its characterization by single-crystal XRD and NMR spectroscopy. Thus, the <sup>1</sup>H NMR spectra registered directly after dissolution of this complex in CDCl<sub>3</sub> did not reveal the expected signals of the NH protons and contained only broadened patterns in the range of aromatic proton signals. Slow diffusion of Et<sub>2</sub>O into NMP–CHCl<sub>3</sub> solution of complex **7** afforded red prisms suitable for XRD analysis. The latter appeared to be tetramer **8**, resulting from deprotonation of the coordinated NHC(S) moieties (Scheme 4, Fig. 3). This confirmed that coordination of ligand **5** involved the central pincer unit. All the thioamide groups in chloride-free complex **8** converted into iminothiolate ones; and one of the iminothiolate group from each dianionic pincer fragment serves as a bridging ligand.



Scheme 4. Clusterization of complex 7.



**Fig. 3.** General view of complex **8**. For clarity, Ph<sub>2</sub>P(S) groups are shown as thermal ellipsoids of the phosphorous atoms given at 50% probability level. Solvate NMP and CHCl<sub>3</sub> molecules are omitted.

Deprotonation of secondary thioamide groups in *S*,*N*,*S*-pincer systems with central pyridine units has already been described in the literature [7]. Thus, the spontaneous loss of protons in one or both of the NHC(S)Ph coordination arms in symmetrical ligands afforded

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stable mononuclear Pd(II) and Pt(II) complexes with either mono- or dianionic ligands [7e]. In the case of the related Ru(II) complex, the stepwise deprotonation of the thioamide protons led firstly to a mononuclear derivative, which then converted to a dimer with two dianionic S,N,Sligands [7a]. A propensity of a Pt(II) bis(thioamide) pincer complex for reversible deprotonation/protonation enabled its use as a molecular switch for half sulfur mustard [7b]. Finally, treatment of Pd(II) counterparts with organozinc or Grignard reagents afforded bis(thioimide) pincer clusters which efficiently catalyze the Negishi cross-coupling [7c,d]. Thus, the coordination behavior of ligand 5 with a pyridine central ring is in good agreement with the literature data, and the presence of the thiophosphoryl pendant arms does not affect the selectivity upon complexation with Pd(II) ions, although facilitates deprotonation of the thioamide groups. As for the related monotopic pincer systems with phenylene central moieties, a literature survey has revealed only several mononuclear complexes with iminothiolate donor groups (M = Pt, Ru, Ni) which were formed upon addition of strong bases [8]. Spontaneous deprotonation in phenylene-based bis(thioamide) pincer systems was observed only once and afforded a Pt(II) chalcogenide cluster in 4% yield [9]. Therefore, the stability of complex  $\mathbf{6}$  is in line with the previously published data. What is important to note about this system is the selective activation of unsymmetrical lateral pincer units instead of a symmetrical central pocket. Furthermore, the conjugation of two S, C, S-pincer units through a *meta*-phenylene spacer resulted in a sterically congested system with complicated interconversion of conformational isomers.

#### **3.** Conclusions

In this work, new ditopic pincer ligands bearing P=S and C=S donor groups were shown to undergo site-selective cyclopalladation/coordination depending on the nature of (hetero)aromatic spacers. Further studies will shed more light on the reactivity and properties of the related dinucleating systems with thione sulfur donors.

#### 4. Experimental

#### 4.1. General remarks

Unless otherwise mentioned, all manipulations were carried out without taking precautions to exclude air and moisture. Dichloromethane was distilled over P<sub>2</sub>O<sub>5</sub>. Isophthaloyl [10] and 2,6-pyridinedicarbonyl [11] dichlorides were obtained by treatment of the corresponding acids with an excess of SOCl<sub>2</sub> according to the published procedures. All other chemicals and solvents were used as purchased.

The NMR spectra were recorded on Bruker Avance 400 and Avance 500 spectrometers, and the chemical shifts ( $\delta$ ) were referenced internally by the residual solvent signals relative to

tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or externally to  $H_3PO_4$  (<sup>31</sup>P). In most cases, <sup>13</sup>C{<sup>1</sup>H} NMR spectra were registered using the *J*MODECHO mode; the signals for the *C* nuclei bearing odd and even numbers of protons have opposite polarities. The assignment of the NMR spectra of ligands 4 and 5 was carried out based on the  ${}^{1}H{-}^{1}H{-}COSY$ , HMOC, and HMBC experiments. The results obtained were used for interpretation of the NMR spectra of the other compounds from this study.

The IR spectra were recorded on a Nicolet Magna-IR750 FT-spectrometer, resolution 2 cm<sup>-1</sup>, 128 scans. The assignment of absorption bands in the IR spectra was made according to ref. [12]. Column chromatography was carried out using Macherey-Nagel silica gel 60 (MN Kieselgel 60, 70-230 mesh). Melting points were determined with an MPA 120 EZ-Melt automated melting point apparatus (Stanford Research Systems).

#### 4.2. Syntheses

#### **3-Diphenylthiophosphorylaniline**, 1.

A mixture of triphenylphosphine oxide (10.40 g, 0.037 mol) and conc. H<sub>2</sub>SO<sub>4</sub> (50 mL) was stirred at room temperature until complete dissolution of Ph<sub>3</sub>P(O). Then KNO<sub>3</sub> (4.25 g, 0.042 mol) was added portionwise, and the mixture was heated at 50–60 °C for 3 h. After cooling to room temperature, it was poured onto ice, and the resulting solution and resin-like precipitate were extracted with chloroform. The organic layer was separated, sequentially washed with saturated aq. NaHCO<sub>3</sub> and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness. A stirred mixture of the resulting residue, the Lawesson reagent (8.08 g, 0.020 mol), and chlorobenzene (60 mL) was refluxed for 3 h. The solution obtained was diluted with chloroform, washed with saturated aq. NaHCO<sub>3</sub> and water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness. The resulting residue was purified by column chromatography on silica gel (eluent: CHCl<sub>3</sub>) give viscous brown oil bearing mixture of isomeric to a a (nitrophenyl)diphenylphosphine sulfides. A stirred mixture of this residue, SnCl<sub>2</sub>·2H<sub>2</sub>O (50.7 g, 0.225 mol), and ethanol (150 mL) was refluxed for 9.5 h. After cooling to room temperature, it was poured onto ice. Then NaOH was added portionwise to pH  $\sim 10$ , and the resulting solution was extracted with chloroform. The aqueous phase was separated, filtered (using filter paper), and additionally extracted with chloroform. The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue obtained was purified by column chromatography (eluent: CHCl<sub>3</sub>). The crude product was additionally purified by column chromatography using EtOAc-hexane (1:1) mixture to give 5.11 g of meta-thiophosphorylated aniline as a white crystalline solid. Yield: 44%. <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, CDCl<sub>3</sub>): 43.73 ppm. Mp: 182–184 °C (compare with 182–183 °C in ref. [13]).

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### General procedure for the synthesis of bis(amides) 2 and 3.

A solution of the corresponding acid dichloride (0.65 mmol) in  $CH_2Cl_2$  (10 mL) was added to a stirred solution of aniline **1** (402 mg, 1.30 mmol) and  $Et_3N$  (135 mg, 1.33 mmol) in  $CH_2Cl_2$ (10 mL). The reaction mixture was stirred at room temperature for 2 h and left under ambient conditions for 1 day. The solvent was removed under vacuum. The resulting residue was purified by column chromatography (eluent: hexane–acetone (2:1) (**2**) or  $CH_2Cl_2$ –EtOH (100:1) (**3**)) to give the target compounds as white crystalline solids. Note that bis(amide) **3** was additionally rinsed with  $Et_2O$  to remove traces of the unreacted aniline.

*N*,*N*'-bis[3-(diphenylthiophosphoryl)phenyl]benzene-1,3-dicarboxamide, 2.



Yield: 448 mg (92%). Mp: 149–151 °C. <sup>31</sup>P{<sup>1</sup>H} NMR (161.98 MHz, CDCl<sub>3</sub>):  $\delta$  43.19 ppm. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  7.26–7.38 (m, 12H, H<sub>Ar</sub>), 7.42–7.46 (m, 5H, H<sub>Ar</sub>), 7.65 (dd, 8H, *o*-H in P(S)Ph<sub>2</sub>, <sup>3</sup>J<sub>HP</sub> = 13.4 Hz, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.90–7.97 (m, 4H, H<sub>Ar</sub>), 7.99 (d, 2H, H(C8) + H(C8'), <sup>3</sup>J<sub>HP</sub> = 14.8 Hz), 8.28 (s, 1H, H(C1)), 8.88 (br s, 2H, NH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.61 MHz, CDCl<sub>3</sub>):  $\delta$  123.97 (s, C12 + C12'), 124.08 (d, C8 + C8', <sup>2</sup>J<sub>CP</sub> = 13.2 Hz), 125.52 (s, C4), 127.94 (d, C10 + C10', <sup>2</sup>J<sub>CP</sub> = 10.3 Hz), 128.57 (d, *m*-C in P(S)Ph<sub>2</sub>, <sup>3</sup>J<sub>CP</sub> = 12.6 Hz), 129.08 (d, C11 + C11', <sup>3</sup>J<sub>CP</sub> = 13.6 Hz), 129.22 (s, C1), 131.39 (s, C3 + C5), 131.72 (s, *p*-C in P(S)Ph<sub>2</sub>), 132.13 (s, *ipso*-C in P(S)Ph<sub>2</sub>, <sup>1</sup>J<sub>CP</sub> = 82.6 Hz), 132.14 (d, *o*-C in P(S)Ph<sub>2</sub>, <sup>2</sup>J<sub>CP</sub> = 10.8 Hz), 133.31 (d, C9 + C9', <sup>1</sup>J<sub>CP</sub> = 85.0 Hz), 134.49 (s, C2 + C6), 138.34 (d, C7 + C7', <sup>3</sup>J<sub>CP</sub> = 15.4 Hz), 165.51 (s, C=O) ppm. IR (KBr,  $\nu/cm^{-1}$ ): 513(m), 581(vw), 615(w), 640(m) ( $\nu$ P=S), 691(m), 716(s), 747(w), 791(vw), 997(vw), 1027(vw), 1102(m), 1182(vw), 1244(m), 1306(m), 1395(sh, w), 1412(m), 1436(m), 1480(m), 1529(m) (C(O)NH), 1587(m), 1659(sh, m) and 1677(m) (both  $\nu$ C=O), 3053 (vw), 3309 (br, w) ( $\nu$ NH). Anal. Calcd for C<sub>44</sub>H<sub>34</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 70.57; H, 4.58; N, 3.74. Found: C, 70.31; H, 4.83; N, 3.80%.

*N*,*N*'-bis[3-(diphenylthiophosphoryl)phenyl]pyridine-2,6-dicarboxamide, 3.



Yield: 410 mg (84%). Mp: 270–272 °C (dec.).  ${}^{31}P{}^{1}H{}$  NMR (161.98 MHz, CDCl<sub>3</sub>):  $\delta$  43.06 ppm.  ${}^{1}H$  NMR (400.13 MHz, CDCl<sub>3</sub>):  $\delta$  7.38–7.50 (m, 16H, H<sub>Ar</sub>), 7.71 (ddd, 8H, *o*-H in P(S)Ph<sub>2</sub>,  ${}^{3}J_{HP} = 13.4$  Hz,  ${}^{3}J_{HH} = 7.8$  Hz,  ${}^{4}J_{HH} = 1.5$  Hz), 7.97–8.00 (m, 2H, H<sub>Ar</sub>), 8.04–8.10 (m,

ACCEPTED MANUSCRIPT 3H, H<sub>Ar</sub>), 8.42 (d, 2H, H(C3) + H(C5),  ${}^{3}J_{HH} = 7.8$  Hz), 9.82 (br s, 2H, NH) ppm.  ${}^{13}C{}^{1}H{}$  NMR (100.61 MHz, CDCl<sub>3</sub>): δ 124.70–124.92 (m, overlapping signals of C3, C5, C8, and C8'), 125.85 (br s, C12 + C12), 128.47–128.60 (m, overlapping signals of m-C in P(S)Ph<sub>2</sub>, C10, and C10), 128.99–129.15 (unresolved signal of C11 and C11'), 131.63 (s, p-C in P(S)Ph<sub>2</sub>), 132.17 (d, o-C in P(S)Ph<sub>2</sub>,  ${}^{2}J_{CP} = 10.8$  Hz), 132.36 (d, *ipso*-C in P(S)Ph<sub>2</sub>,  ${}^{1}J_{CP} = 85.3$  Hz), 133.65 (d, C9 + C9',  ${}^{1}J_{CP} = 84.9$  Hz), 137.41 (d, C7 + C7',  ${}^{3}J_{CP} = 15.4$  Hz), 139.23–139.32 (unresolved signal of C4), 148.76 (s, C2 + C6), 161.95 (s, C=O) ppm. IR (KBr,  $v/cm^{-1}$ ): 494(w), 512(m), 615(w), 640(m) (vP=S), 693(m), 716(s), 748(w), 793(vw), 837(vw), 897(vw), 998(w), 1027(vw), 1072(w), 1102(m), 1243(vw), 1312(w), 1421(m), 1436(m), 1450(w), 1481(m), 1530(br, m) (C(O)NH), 1550(m), 1583(m), 1672(m) and 1685(m) (both vC=O), 2922(w), 3054(w), 3286(br, w) (vNH). Anal. Calcd for C<sub>43</sub>H<sub>33</sub>N<sub>3</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: C, 68.88; H, 4.44; N, 5.60. Found: C, 68.77; H, 4.58; N, 5.66%.

#### General procedure for the synthesis of bis(thioamides) 4 and 5.

A mixture of the corresponding bis(amide) (0.35 mmol) and the Lawesson reagent (162 mg, 0.40 mmol) in chlorobenzene (15 mL) was refluxed for 5 h (4) or 9 h (5). After cooling to room temperature, the reaction mixture was diluted with chloroform and sequentially washed with saturated aq. NaHCO<sub>3</sub> (2×50 mL) and water (50 mL). The organic layer was separated, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated to dryness. In the case of compound 4, the resulting residue was purified by column chromatography (eluent: acetone-hexane (1:2)) to give the target bis(thioamide) as a yellow crystalline solid. In the case of compound 5, the resulting residue was recrystallized from EtOAc-hexane and then purified by column chromatography (eluent: CH<sub>2</sub>Cl<sub>2</sub>) to give the target bis(thioamide) as an orange crystalline solid.

#### N,N'-bis[3-(diphenylthiophosphoryl)phenyl]benzene-1,3-dicarbothioamide, 4.



Yield: 188 mg (69%). Mp: >172 °C (dec.).  ${}^{31}P{}^{1}H{}$  NMR (202.47 MHz, CDCl<sub>3</sub>, 258 K):  $\delta$ 43.09 ppm. <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>, 258 K): δ 7.35–7.38 (m, 3H, H(C4) + H(C11) + H(C11'), 7.40–7.45 (m, 10H, *m*-H in  $P(S)Ph_2 + H(C10) + H(C10')$ ), 7.49–7.53 (m, 4H, *p*-H in P(S)Ph<sub>2</sub>), 7.64–7.68 (m, 8H, o-H in P(S)Ph<sub>2</sub>), 7.86 (d, 2H, H(C12),  ${}^{3}J_{HH} = 7.8$  Hz), 7.98 (s, 1H, H(C1)), 7.99 (d, 2H, H(C3) + H(C5),  ${}^{3}J_{HH} = 7.3$  Hz), 8.05 (d, 2H, H(C8) + H(C8'),  ${}^{3}J_{HP} = 14.2$ Hz), 10.14 (br s, 2H, NH) ppm.  ${}^{13}C{}^{1}H$  NMR (125.76 MHz, CDCl<sub>3</sub>, 258 K):  $\delta$  123.66 (s, C4), 127.24 (s, C12 + C12'), 127.77 (d, C8 + C8',  ${}^{2}J_{CP} = 12.5$  Hz), 128.86 (d, *m*-C in P(S)Ph<sub>2</sub>,  ${}^{3}J_{CP} =$ 12.6 Hz), 129.05 (s, C1), 129.38 (d, C11 + C11',  ${}^{3}J_{CP} = 13.2$  Hz), 130.20 (d, C10 + C10',  ${}^{2}J_{CP} =$ 

10.7 Hz), 131.37 (d, *ipso*-C in P(S)Ph<sub>2</sub>,  ${}^{1}J_{CP} = 85.9$  Hz), 131.51 (s, C3 + C5), 132.11 (d, *p*-C in P(S)Ph<sub>2</sub>,  ${}^{4}J_{CP} = 3.0$  Hz), 132.25 (d, *o*-C in P(S)Ph<sub>2</sub>,  ${}^{2}J_{CP} = 11.0$  Hz), 133.08 (d, C9 + C9',  ${}^{1}J_{CP} = 85.4$  Hz), 139.01 (d, C7 + C7',  ${}^{3}J_{CP} = 15.2$  Hz), 141.80 (s, C2 + C6), 197.33 (s, C=S) ppm. IR (KBr,  $\nu/cm^{-1}$ ): 514(m), 614(w), 639(m) ( $\nu$ P=S), 692(s), 715(s), 749(w), 798(vw), 921(vw), 998(w), 1027(vw), 1103(s), 1185(w), 1308(w), 1344(br, m), 1413(m), 1436(s), 1479(m), 1517(br, m), 1585(m), 2924(w), 3053(w), 3234(br, m) ( $\nu$ NH). Anal. Calcd for C<sub>44</sub>H<sub>34</sub>N<sub>2</sub>P<sub>2</sub>S<sub>4</sub>: C, 67.67; H, 4.39; N, 3.59. Found: C, 67.45; H, 4.77; N, 3.41%.

*N*,*N*'-bis[3-(diphenylthiophosphoryl)phenyl]pyridine-2,6-dicarbothioamide, 5.



Yield: 238 mg (87%). Mp: 277–280 °C (dec.).  ${}^{31}P{}^{1}H{}$  NMR (161.98 MHz, CDCl<sub>3</sub>):  $\delta$ 43.04 ppm. <sup>1</sup>H NMR (500.13 MHz, CDCl<sub>3</sub>): δ 7.44–7.48 (m, 8H, m-H in P(S)Ph<sub>2</sub>), 7.51–7.54 (m, 4H, p-H in P(S)Ph<sub>2</sub>), 7.59 (dt, 2H, H(C11) + H(C11'),  ${}^{3}J_{HH} = 7.8$  Hz,  ${}^{4}J_{HP} = 3.6$  Hz), 7.66 (dd, 2H, H(C10) + HC(10'),  ${}^{3}J_{HP} = 12.5$  Hz,  ${}^{3}J_{HH} = 7.8$  Hz), 7.77 (dd, 8H, *o*-H in P(S)Ph<sub>2</sub>,  ${}^{3}J_{HP} =$ 13.4 Hz,  ${}^{3}J_{HH} = 7.8$  Hz), 8.03 (t, 1H, H(C4),  ${}^{3}J_{HH} = 7.9$  Hz), 8.17–8.19 (m, 2H, H(C12) + H(C12')), 8.45 (d, 2H, H(C8) + H(C8'),  ${}^{3}J_{HP} = 14.3$  Hz), 8.88 (d, 2H, H(C3) + H(C5),  ${}^{3}J_{HH} = 7.9$ Hz), 11.29 (br s, 2H, NH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (125.76 MHz, CDCl<sub>3</sub>): δ 126.44 (d, C12 + C12',  ${}^{4}J_{CP} = 2.8$  Hz), 127.25 (d, C8 + C8',  ${}^{2}J_{CP} = 12.6$  Hz), 127.91 (s, C3 + C5), 128.68 (d, m-C in  $P(S)Ph_2$ ,  ${}^{3}J_{CP} = 12.6 \text{ Hz}$ ), 129.52 (d, C11 + C11',  ${}^{3}J_{CP} = 13.3 \text{ Hz}$ ), 130.48 (d, C10 + C10',  ${}^{2}J_{CP} = 13.3 \text{ Hz}$ ) 10.1 Hz), 131.80 (d, p-C in P(S)Ph<sub>2</sub>,  ${}^{4}J_{CP} = 3.1$  Hz), 132.30 (d, o-C in P(S)Ph<sub>2</sub>,  ${}^{2}J_{CP} = 10.7$  Hz), 132.34 (d, *ipso*-C in P(S)Ph<sub>2</sub>,  ${}^{1}J_{CP} = 85.8$  Hz), 134.15 (d, C9 + C9',  ${}^{1}J_{CP} = 84.5$  Hz), 138.53 (d, C7 + C7',  ${}^{3}J_{CP} = 15.3$  Hz), 138.73 (s, C4), 149.71 (s, C2 + C6), 188.54 (s, C=S) ppm. IR (KBr, v/cm<sup>-1</sup>): 515(s), 561(w), 584(w), 615(m), 637(s) (vP=S), 693(s), 717(s), 733(m), 750(m), 771(vw), 790(w), 823(vw), 873(vw), 904(vw), 998(w), 1028(vw), 1077(m), 1104(s), 1158(vw), 1187(w), 1309(m), 1364(m), 1417(m), 1437(s), 1478(m), 1526(m), 1542(m), 1584(m), 2924(vw), 3053(w), 3074(vw), 3258(m) (vNH). Anal. Calcd for C<sub>43</sub>H<sub>33</sub>N<sub>3</sub>P<sub>2</sub>S<sub>4</sub>: C, 66.05; H, 4.25; N, 5.37. Found: C, 65.91; H, 4.28; N, 5.41%.

Binuclear complex 6 [14].



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A solution of PdCl<sub>2</sub>(NCPh)<sub>2</sub> (29 mg, 0.076 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added dropwise to a solution of ligand **4** (30 mg, 0.038 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL). The resulting mixture was left under ambient conditions for 5 days. During this time, a yellow precipitate that was formed immediately after mixing of the reagents gradually dissolved and regenerated in a small amount of unidentified brown crystals, which were filtered off. The filtrate was evaporated to dryness. The resulting residue was rinsed with Et<sub>2</sub>O, collected by filtration and dried in *vacuo* to give complex **6** as a pale-yellow crystalline solid. Yield: 31 mg (76%). Mp: >210 °C (dec.). IR (KBr,  $v/cm^{-1}$ ): 481(w), 517(s), 569(vw), 611(m), 627(m) (vP=S), 690(s), 708(s), 718(m), 747(m), 794(w), 998(w), 1026(vw), 1104(s), 1186(m), 1224(vw), 1280(vw), 1310(vw), 1334(vw), 1382(w), 1406(w), 1437(s), 1481(w), 1527(vw), 1588(br, m), 2928(w), 3053(m), 3148(br, w) and 3220(br, w) (both *v*NH). Anal. Calcd for C<sub>44</sub>H<sub>32</sub>Cl<sub>2</sub>N<sub>2</sub>P<sub>2</sub>Pd<sub>2</sub>S<sub>4</sub>: C, 49.73; H, 3.04; N, 2.64. Found: C, 49.49; H, 3.09; N, 2.71%.

Mononuclear complex 7.



A solution of PdCl<sub>2</sub>(NCPh)<sub>2</sub> (14 mg, 0.036 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added dropwise to a solution of ligand **4** (28 mg, 0.036 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The resulting red solution was left under ambient conditions for 1 day, partially evaporated to initiate precipitation of the target product, and left for another 4 days. The precipitate obtained was collected by filtration, rinsed with Et<sub>2</sub>O and dried in *vacuo* to give complex **7** as a dark-red crystalline solid. Yield: 25 mg (73%). Mp: >200 °C (dec.). IR (KBr,  $v/cm^{-1}$ ): 515(m), 597(vw), 614(w), 640(m) (vP=S), 692(s), 716(s), 749(w), 810(vw), 974(vw), 998(w), 1038(w), 1102(s), 1182(vw), 1214(w), 1276(w), 1308(w), 1424(sh, m), 1436(s), 1468(sh, m), 1479(m), 1538(br, s), 2923(vw), 3053(w), 3200(br, vw) (vNH). Anal. Calcd for C<sub>43</sub>H<sub>33</sub>Cl<sub>2</sub>N<sub>3</sub>P<sub>2</sub>PdS<sub>4</sub>: C, 53.84; H, 3.47; N, 4.38. Found: C, 53.65; H, 3.62; N, 4.60%.

#### 4.3. X-ray diffraction

Crystals of complex **8** (C<sub>172</sub>H<sub>124</sub>N<sub>12</sub>P<sub>8</sub>Pd<sub>4</sub>S<sub>16</sub> · 3.25(C<sub>5</sub>H<sub>9</sub>NO) · CHCl<sub>3</sub>, M = 3986.69) are triclinic, space group P-1: a = 16.2564(16), b = 18.2164(18), c = 34.197(4) Å,  $\alpha$  = 80.008(2),  $\beta$  = 83.310(2),  $\gamma$  = 64.148(2)°, V = 8965.6(16) Å<sup>3</sup>, Z = 2, d<sub>calc</sub> = 1.477 gcm<sup>-3</sup>,  $\mu$ (MoK $\alpha$ ) = 7.57 cm<sup>-1</sup>, F(000) = 4067. Intensities of 139667 reflections were measured at 120 K with a Bruker APEX2 DUO CCD diffractometer [ $\lambda$ (MoK $\alpha$ ) = 0.71072Å,  $\omega$ -scans, 2 $\theta$ <56°], and 43288 independent reflections [R<sub>int</sub> = 0.1457] were used for further refinement. The structure was solved by the

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direct method and refined by the full-matrix least-squares technique against  $F^2$  in the anisotropicisotropic approximation. The positions of hydrogen atoms were calculated, and they were refined in the isotropic approximation within the riding model. Note that the obtained crystals of complex **8** contained solvate *N*-methyl-2-pyrrolidone molecules most of which had partial occupancy or were disordered or even both. However, our attempts to model this disorder did not improve the quality of the structural model. For the best one obtained, the refinement converged to wR2 = 0.1896 and GOF = 0.997 for all the independent reflections (R1 = 0.0682 was calculated against F for 22835 observed reflections with I>2 $\sigma$ (I)). All calculations were performed using SHELXTL PLUS 5.0. CCDC 1882961 contains the supplementary crystallographic information for this paper [15].

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#### Appendix A. Supplementary data

NMR spectra of ligand **5**; NMR monitoring of the reaction of ligand **4** with PdCl<sub>2</sub>(NCPh)<sub>2</sub>;

NMR spectra of complex 6;

Cif file of complex 8

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Two pincer units in the resulting ligands are bridged by (hetero)aromatic spacers

The ligands obtained undergo site-selective cyclopalladation depending on the spacer

Dinculear S, C, S- and mononuclear S, N, S-complexes are readily obtained in high yields

Pyridine-based S,N,S-complex spontaneously converts to a tetrameric sulfide cluster

A ALANCE