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Solid-phase cyclopalladation in *S,C,S′*-pincer systems: rising alternative to synthesis in solution

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Abstract: In pursuit of a new simple approach to complex organometallic systems, a possibility of formation of the palladium–carbon bond in the solid state *via* direct cyclopalladation has been studied toward several *S,C,S′*-pincer ligands with thione sulfur donors of different nature. It is found that mixtures of the ligand and $PdCl_2(NCPh)_2$ obtained by manual grinding of reactants in a mortar efficiently undergo solid-phase cyclometalation upon heating in open test tubes without addition of a solvent to afford the desired pincer-type products in high yields. In the case of the most active bis(thiocarbamoyl) ligand, solid-phase cyclopalladation proceeds even at room temperature. For the challenging bis(thiophosphoryl) derivative, the preformed non-metallated complexes can be successfully used as a starting material to essentially enhance the yield of desired pincer complex compared to the conventional synthesis in solution. The solid-phase transformation is followed by IR spectroscopy and SEM analysis. The results obtained show that the suggested solid-phase methodology can serve as a powerful alternative to conventional synthesis of pincer complexes in solution.

Keywords: cyclometalation, solid-phase synthesis, palladium, pincer complexes

Introduction

Pincer complexes having a tridentate monoanionic framework comprise a privileged class of organometallic compounds, finding extensive application as active (pre)catalysts, optoelectronic materials, biomarkers, chemosensors.[1,2] There are several synthetic approaches which give access to pincer metallacycles with almost any type of ligands and metals, but all of them were accomplished only in solution.[2] Nowadays, solid-phase synthesis has emerged as a powerful tool in organic, inorganic and coordination chemistry, affording a great diversity of compounds and functional materials. While numerous transformations involving organometallic species have

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been successfully performed in the solid state,[3] only several reports deal with the direct formation of the metal–carbon bond *via* thermally-induced intramolecular cyclometalation of some preformed coordination complexes leading to monometallacyclic species.[4] Recently we have shown that solid-phase cyclopalladation of coordination predecessors can also be performed in multidentate, pincer-type systems with thiophosphoryl and benzothiazole pendant arms.[5] To our surprise, it was found that mixtures of a ligand and $PdCl_2(NCPh)_2$ obtained simply by manual grinding in a mortar can also be used as starting materials, efficiently undergoing thermally-induced cyclometalation.[5] However, the reactions required high temperatures (200 C) and were accompanied by sample degradation, resulting in reduced yields of the desired pincer products. Therefore, it seemed interesting to investigate whether such a solid-phase strategy is restricted to the particular ligand systems or can become a simple, cheap, efficient, and green alternative to the conventional synthesis of pincer complexes in solution.

Results and discussion

Since cyclopalladation is the most popular type of cyclometalations[6] and palladium derivatives ranks as the most explored and useful transition metal complexes, we focused our attention, first of all, on investigation of the scope of solid-phase cyclopalladation. In pursuit of new objects, we turned to *S,C,S*-pincer ligands with two thione sulfur ancillary donors which would encourage the formation of strong coordinate bonds with the soft, thiophilic Pd^{II} ion. Furthermore, recent studies showed that bis(thiocarbamoyl) and thiophosphoryl-thiocarbamoyl ligands readily form pincer Pd^{II} complexes whereas their bis(thio)phosphoryl analogs undergo cyclopalladation only under forcing conditions and often with low efficiency.[7] Therefore, it would be interesting to compare the reactivity of closely related *S,C,S′*-pincer ligands bearing thione sulfur donors of different nature in solution and in the solid state, especially if take into account the remarkable catalytic activities and luminescence properties of transition metal complexes based on the related derivatives.[8–10] In addition, organosulfur and organothiophosphorus pincer ligands are stable and can be air-handled, which is particularly important for the suggested solid-phase approach.

A convenient synthetic route to a series of novel *S,C,S′*-pincer ligands was devised based on *m*-diphenylphosphorylaniline (Scheme 1). Thus, thiophosphorylation of this aniline with $Ph_2P(S)Cl$ followed by thionation of the resulting *S,O*-derivative with the Lawesson reagent (Scheme 1) afforded unsymmetrical bis(thiophosphoryl) pincer ligand **1**. Application of different carbonyl chlorides instead of $Ph_2P(S)Cl$ at the first stage afforded hybrid thiophosphoryl-thiocarbamoyl ligands having planar secondary (**2**) or sterically hindered tertiary (**3**) thioamide unit (Scheme 1). The key aniline, in turn, was readily available from $Ph_3P{=}O$ *via* nitration and

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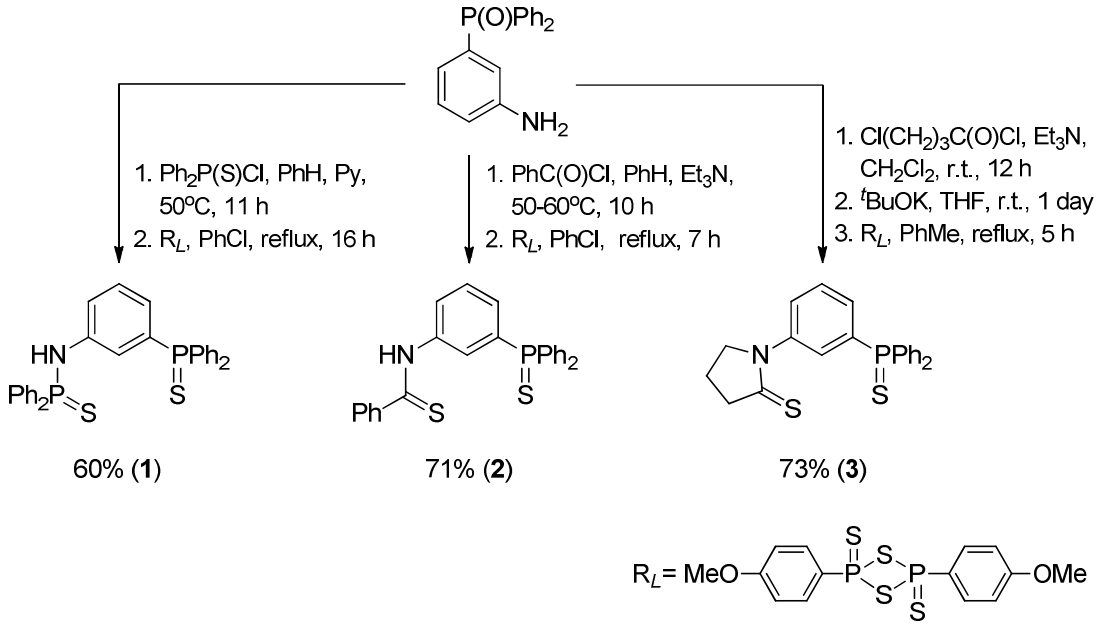
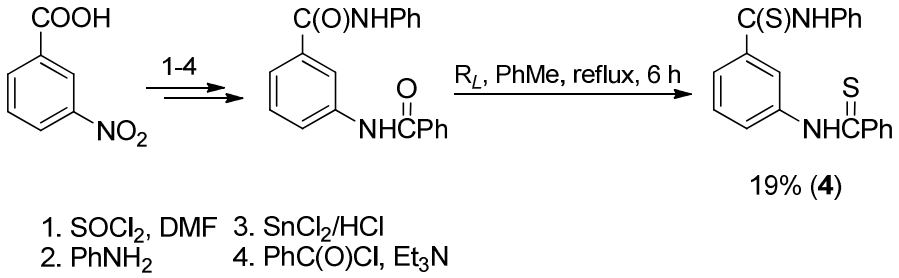
subsequent reduction of the nitro group. Unsymmetrical bis(thiocarbamoyl) pincer ligand (compound **4**) was synthesized from *m*-nitrobenzoic acid (Scheme 2).



Scheme 1 Synthesis of *S,C,S'*-pincer ligands **1**–**3**



Scheme 2 Synthesis of unsymmetrical bis(thiocarbamoyl) pincer ligand **4**

In comparative studies on cyclopalladation of ligands **1**–**4** in solution, it was found that **2**–**4** readily undergo selective cyclopalladation under action of $PdCl_2(NCPh)_2$ at room temperature to form κ^3-*S,C,S'*-pincer complexes **6**–**8** in >80% yields (Table 1, entries 2–4); therewith, the reaction time reduces from 2 days in the case of ligand **4** to 0.5 h in the case of the most sterically hindered ligand **3**. As expected, bis(thiophosphoryl) analog **1** was least active affording palladacycle **5** only in 34% yield even under optimized conditions (Table 1, entry 1). In this case, the reaction mixture filtrate contained several complexes of $[L{\cdot}PdCl_2]$ composition (L – ligand) which we failed to isolate and identify.

Table 1 Cyclopalladation of pincer ligands **1**–**4** with $PdCl_2(NCPh)_2$: solution *vs* solid-phase studies

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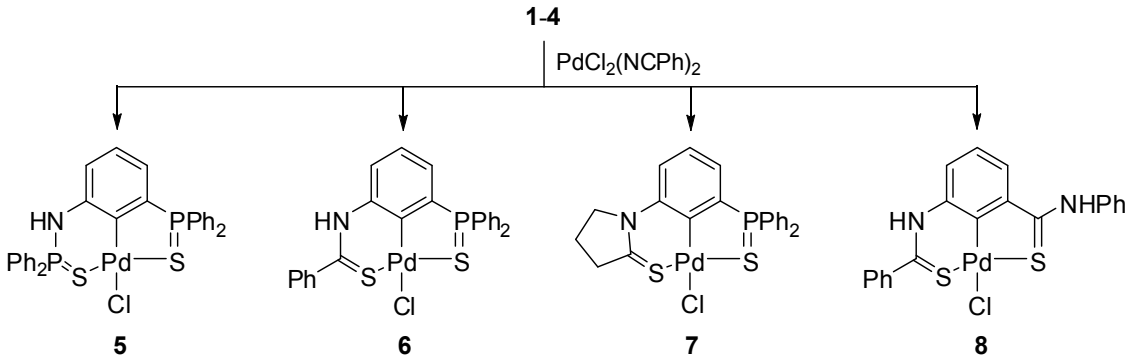

Entry	Ligand	Product	Cyclopalladation in solution		Solid-phase cyclopalladation	
			Conditions	Yield, %[a]	Conditions	Yield, %[a]
1	**1**	**5**	MeCN, reflux, 2 h	34	200°C, 15 min	0
2	**2**	**6**	CH_2Cl_2, r.t., 1 day	92	95–100°C, 5 min	85
3	**3**	**7**	MeCN, r.t., 0.5 h	95	100–110°C, 5 min	100
4	**4**	**8**	CH_2Cl_2/DMSO, r.t., 2 days	80	75–80°C, 5 min r.t., 2 days	75 100[b]

[a]Yields of isolated products; [b]yield estimated by ^{1}H NMR spectroscopy.

Realization of κ^3-*S,C,S'*-coordination in complexes **5**–**8** was unambiguously confirmed by multinuclear NMR and IR spectral data. Their ^{31}P NMR spectra exhibit a noticeable downfield (in the case of compounds **6** and **7**, $\Delta\delta_P$ = 2.6–5.9 ppm) or upfield (in the case of palladacycle **5**, $\Delta\delta_P$ = 0.4–7.8 ppm) shift relative to the signals of the free ligands, indicating the coordination of the thiophosphoryl groups. In the ^{1}H NMR spectra, the intensities of aromatic proton signals are reduced by 1H, proving the occurrence of cyclometalation, and the signals of both thiocarbamoyl ($\Delta\delta_H$ = 0.4–3.7 ppm) and thiophosphorylamine ($\Delta\delta_H$ = 4.1 ppm) NH protons are deshielded upon complexation. In the ^{13}C NMR spectra of palladium complexes **5** and **6**, the signals of the carbon atom (C2) undergoing C–H activation shows a strong downfield shift (up to ~20 ppm) compared to the corresponding ligands; the resonances of the other carbon atoms are also indicative of complex formation. Furthermore, a lower frequency displacement of the P=S bond stretching vibrations (6–15 cm^{-1}) and absorption bands associated with NHCS moiety (e.g., by 9 cm^{-}1 in complex **6**) along with the higher frequency shift of ν(N–H) (up to 38 cm^{-1}) in the IR spectra of palladacycles **5**–**8** compared to the free ligands serve as additional evidence of participation of ancillary donor groups in coordination. The solid-state structure of complex **6** was also elucidated by X-ray crystallography (Figure 1). Note that the complexes obtained efficiently promote the Suzuki cross-coupling of aryl bromides with $PhB(OH)_2$, however, not surpassing in activity some other reported thiophosphoryl-containing hybrid palladacycles (Table S1 in ESI).[10e]

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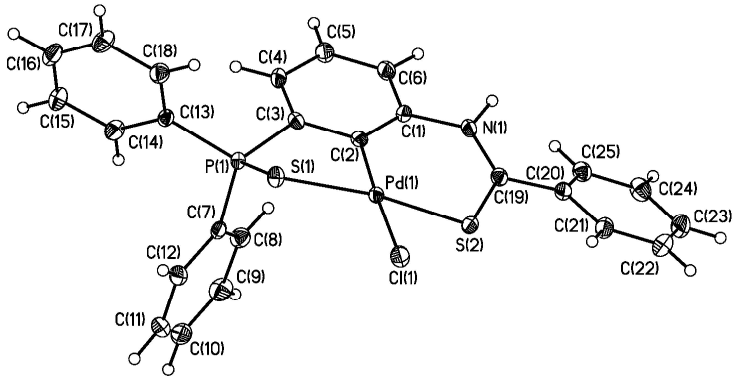
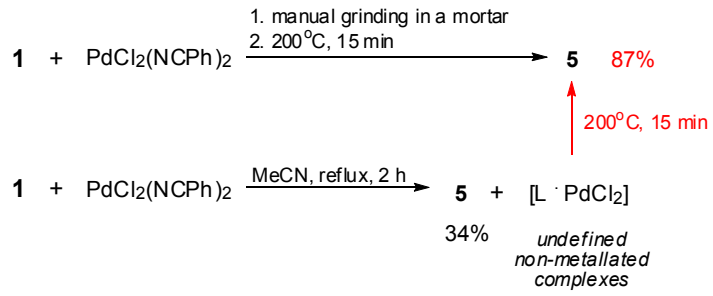


Fig. 1 General view of complex **6** in representation of non-hydrogen atoms *via* thermal ellipsoids at 50% probability level.

To study solid-phase cyclopalladation in *S,C,S′*-pincer systems **1**–**4**, firstly homogeneous mixtures of the corresponding ligand and $PdCl_2(NCPh)_2$ obtained by manual grinding in a mortar were heated in capillaries in a melting point measuring apparatus to define the temperatures corresponding to intensive release of HCl using litmus paper indicators. In the case of ligand **1**, HCl was not detected, and the sample gradually decomposed to give a black thick solid residue. In the other cases, the following temperature ranges of HCl liberation were observed: 71–75 (**2**), 83–85 (**3**), and 55–68 °C (**4**). Further experiments were carried out *via* heating ~50 mg samples in open test tubes on oil bath at slightly higher temperatures for several min (see Table 2). According to the ^{31}P NMR monitoring of the resulting residues dissolved in DMSO immediately before spectrum registration, complexes **6**–**8** were generated in quantitative yields. Simple purification procedures afforded these palladacycles in 75–100% yields (see Table 1). No pincer-type product was observed in the case of bis(thiophosphoryl) derivative **1** even upon heating at 200°C for 15 min. However, when a solid residue obtained by evaporation of the filtrate of a reaction mixture of ligand **1** and $PdCl_2(NCPh)_2$ (presumably representing a mixture of $[L{\cdot}PdCl_2]$ complexes) was heated at 200°C for 15 min, complex **5** was formed in 87% yield (^{31}P NMR monitoring) (Scheme 3). This observation suggests that the preliminary ligand coordination can promote solid-phase cyclopalladation, avoiding undesirable degradation pathways.



Scheme 3 Cyclopalladation of bis(thiophosphoryl) ligand **1**

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Interestingly, the activity series of *S,C,S′*-pincer ligands in the solid state is opposite to that observed in solution (**4** > **2** > **3**), with the least sterically hindered bis(thiocarbamoyl) derivative **4** being the most active. This fact seems to be logical given the crucial role of kinetic factors in the solid-phase reactions but obviously needs further investigations.

To our delight, the solid-phase cyclopalladation of ligand **4** proceeds even at room temperature, coming to completion in 2 days. This observation was supported by IR spectral monitoring (Fig. 2 and Figs S1–S3 in ESI).

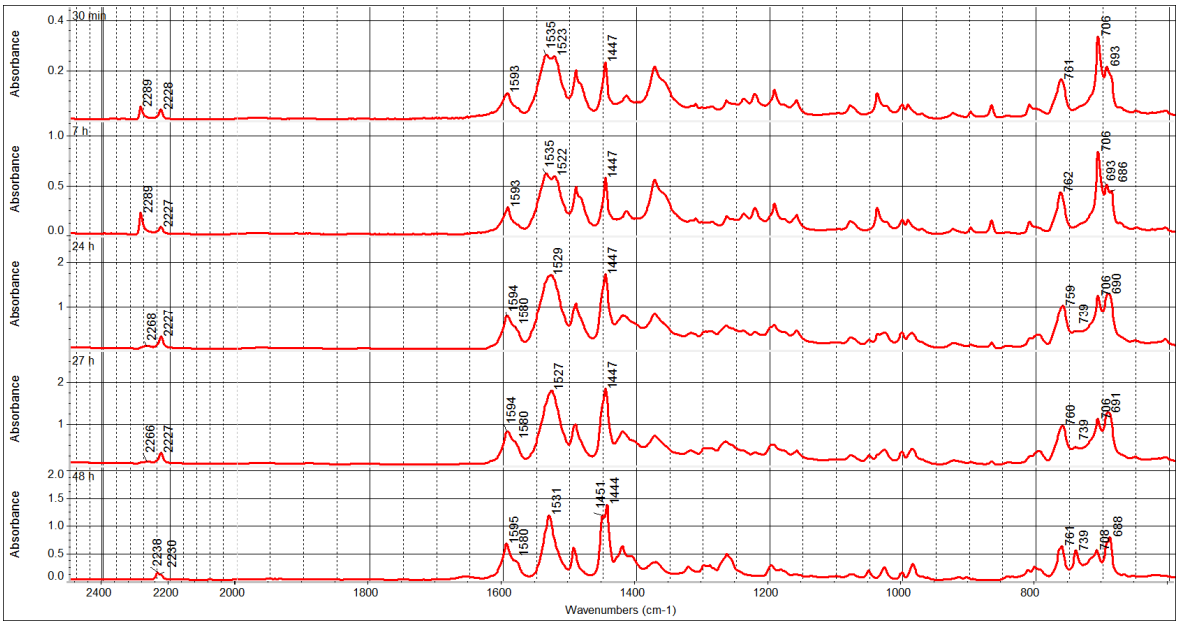

Fig. 2 IR spectral monitoring of room-temperature solid-phase cyclopalladation of ligand **4** with $PdCl_2(NCPh)_2$ (reaction times from top to bottom: 30 min, 7 h, 24 h, 27 h, 48 h).

An intriguing point was the effect of a palladium source. Using ligand **3** as a representative example, we found that monomeric complexes of $PdCl_2$ with loosely bound ligands can be used as efficient cyclometalating agents in the solid state (Table 2, entries 1, 2). Therewith, the temperature required for solid-phase cyclopalladation in the case of cyclooctadiene derivative (Table 2, entry 1) featuring *cis*-arrangement of the auxiliary ligand was higher than in the case of *trans*-$PdCl_2(NCPh)_2$. Presumably, double *S,S*-coordination is a key step in the formation of pincer palladium complex for this particular ligand system, therefore, cyclopalladation proceeds easier with trans-$PdCl_2(NCPh)_2$. A simple salt such as palladium chloride exhibited considerably lower activity, which was attributed to its polymeric structure consisting of infinite chains. Moreover, ionic K_2PdCl_4 requiring upon cyclometalation the liberation of two molecules of potassium chloride also showed very low efficiency. Therefore, solid-phase cyclopalladation strongly depends on the nature of a cyclometalating agent.

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Table 2 Effect of different Pd(II) sources on solid-phase cyclopalladation of ligand **3**

Entry	Pd(II) source	Conditions	Yield of complex 7, %[a]
1	$PdCl_2(NCPh)_2$	100–110°C, 5 min	100
2	$PdCl_2(COD)$	130–140°C, 15 min	100
3	$PdCl_2$	160–165°C, 15 min	30
4	K_2PdCl_4	170–175°C, 15 min	20

[a]Yields estimated by ^{31}P NMR spectroscopy.

Scanning electron microscopy studies performed for the reaction of ligand **3** with $PdCl_2$(COD) revealed considerable restructuring upon solid-phase cyclopalladation (Fig. 3). Thus, two different phases can be clearly distinguished in the initial mixture of the reactants at the magnification degree of 1000 (Fig. 3a): needles were tentatively attributed to ligand **3** and microcrystalline powder was attributed to $PdCl_2$(COD). The residue obtained after solid-phase synthesis was found to be much more homogeneous: it looks like a sponge at the low magnification degree (×30, Fig. 3c) and reveals a microcrystalline structure only upon 20000-fold increase (Fig. 3d) when the initial mixture shows separate crystals (Fig. 3b).

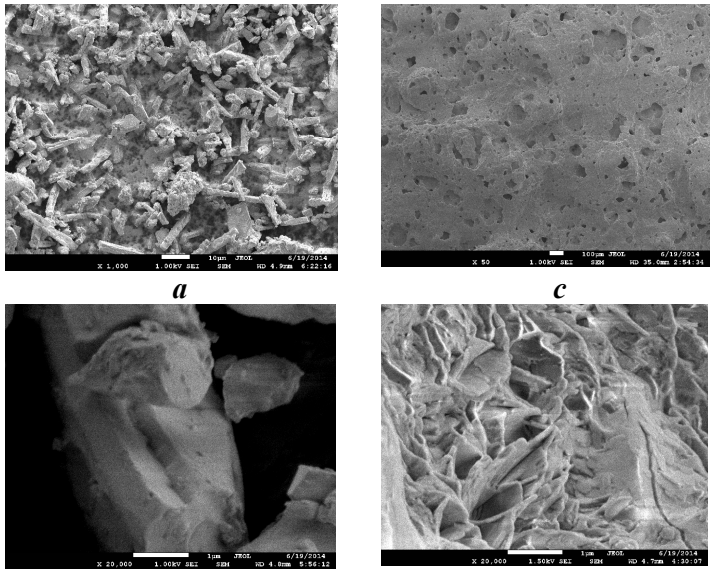

Fig. 3 SEM images of the initial mixture of ligand **3** and $PdCl_2$(COD) (***a***,***b***) and sample obtained after solid-phase synthesis (***c***,***d***).

Although all the ligands and palladium precursors are stable and do not undergo melting under conditions utilized for solid-phase cyclopalladation (Tables 1 and 2), in some cases, the formation of a semi-melt was detected, which may be responsible for the high efficiency of the overall process. Fig. 4 depicts the photographs of the initial mixture of ligand **3** and $PdCl_2$(COD) (Fig. 4a), a semi-melt corresponding to the intensive release of HCl (Fig. 4b), and the resulting solidified sample representing almost neat pincer complex **7** (Fig. 4c).

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DOI: 10.1039/C4DT03477E

a ***b*** ***c***

Fig. 4 Photographs of the initial mixture of ligand **3** and $PdCl_2(COD)$ (***a***, T = 25°C), semi-melt formed during solid-phase reaction (***b***, T = 130–140°C), and the resulting solid sample representing almost neat complex **7** (***c***, T > 140°C).

Conclusions

In summary, we have shown that solid-phase cyclopalladation in *S,C,S′*-pincer-type systems can be efficiently carried out at elevated or even room temperature using homogenized mixtures of the ligand and appropriate Pd^{II} precursor obtained simply by grinding the reactants in a mortar. The application of a mixture of preformed coordination complexes as a starting material in the case of challenging bis(thiophosphoryl) ligand considerably enhanced the overall yield of the palladacycle. The absence of a solvent at least during synthesis, easy performance, and high efficiency allow for considering solid- phase cyclopalladation as a powerful alternative to conventional synthesis of complex organometallic systems in solution. Investigations on the scope of solid-phase cyclometalation using various types of pincer and related multidentate systems and different metals as well as mechanistic studies of this phenomenon are currently under way in our laboratory.

Experimental

If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. Benzene and THF were distilled over sodium/benzophenone ketyl. Dichloromethane and acetonitrile were distilled from P_2O_5. Pyridine was distilled from CaH_2. Unsymmetrical bis(amide) predecessor for ligand **4**, 3-(benzoylamino)-*N*-phenylbenzamide,[11] was synthesized starting from 3-nitrobenzoic acid chloride via condensation with aniline followed by reduction of the nitro group with tin(II) chloride.[10d] $Ph_2P(S)Cl$[12] was obtained according to the literature procedure. All other chemicals and solvents were used as purchased without further purification.

NMR spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were

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registered using the *J*MODECHO mode; the signals for the carbon atoms bearing odd and even numbers of protons have opposite polarities. The numeration for the carbon atoms of the central benzene ring in descriptions of the spectral data is in agreement with IUPAC nomenclature for ligand **1**. The same principle of numbering was used for description of a solid-state molecular structure of complex **6** characterized by X-ray crystallography.

Column chromatography was carried out using Merck silica gel 60 (230-400 mesh ASTM). IR spectra were recorded on a Nicolet Magna-IR750 FT-spectrometer, resolution 2 cm^{-1}, 128 scans. The assignment of absorption bands in the IR spectra was made according to ref.[13] C, H, Cl, Pd, and S elemental analyses for complex **8** were carried out according to the method developed at the A. N. Nesmeyanov Institute of Organoelement Compounds RAS.[14] Melting points were determined with MPA 120 EZ-Melt Automated Melting Point Apparatus and were uncorrected.

The surface morphology of a homogeneous mixture of ligand **3** and $PdCl_2(NCPh)_2$ obtained by manual grinding in a mortar as well as the surface morphology of the sample derived after solid-phase synthesis were analyzed using a JEOL JSM-7001F scanning electron microscope at accelerating voltages of 1–1.5 kV without any treatment of the surface.

Syntheses

3-(Diphenylphosphoryl)aniline. A stirred solution of triphenylphosphine oxide (11.12 g, 0.040 mol) and KNO_3 (4.25 g, 0.042 mol) in conc. H_2SO_4 was heated at 50–60 °C for 6 h. After cooling to room temperature, the reaction mixture was poured onto ice, and the resulting solution was extracted with chloroform. After separation, the organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. To a solution of the resulting residue, bearing a mixture of isomeric (nitrophenyl)(diphenyl)phosphine oxides, in 150 mL of EtOH, $SnCl_2 \cdot 2H_2O$ (54.2 g, 0.240 mol) was added. The stirred reaction mixture was refluxed for 6 h, then the solvent was replaced for EtOAc (150 mL), and the obtained solution was washed with saturated aqueous solution of Na_2CO_3. The organic layer was separated and treated with dilute aqueous hydrochloric acid, then the aqueous phase was made alkaline to pH ~12, and the desired product was extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The resulting residue was purified by column chromatography to give 5.30 g of the target *meta*-isomer along with 1.30 g of *para*-isomer (eluent: $CHCl_3$–EtOH (20:1)). Yield: 41%. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): 29.54 ppm. Mp: 160–162 °C (compare with 166 °C in ref.[15]

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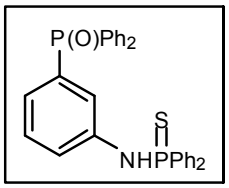
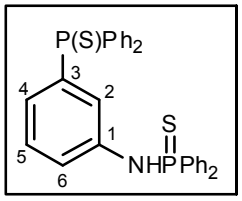


***N*-[3-(Diphenylphosphoryl)phenyl]-*P*,*P*-diphenylthiophosphinic amide.** A solution of $Ph_2P(S)Cl$ (0.86 g, 3.5 mmol) in 2 mL of benzene was slowly dropwise added to a solution of 3-(diphenylphosphoryl)aniline (1.0 g, 3.4 mmol) in 10 mL of dry pyridine at ~10 °C. The resulting reaction mixture was diluted with 20 mL of benzene and heated at 50 °C under stirring for 11 h. The precipitate was filtered off, washed with benzene and Et_2O to give 1.5 g of the target compound as a white crystalline solid. Yield: 86%. Mp: 256–259 °C (dec). $^{31}P\{^1H\}$ NMR (121.49 MHz, $(CD_3)_2SO$): 25.50 ($P(O)Ph_2$), 49.85 ($NHP(S)Ph_2$). ^1H NMR (300.13 MHz, $(CD_3)_2SO$): 7.17–7.65 (m, 20H, H_{Ar}), 7.94 (dd, 4H, *o*-H in $P(S)Ph_2$, $^3J_{HH}$=7.1 Hz, $^3J_{HP}$=13.7 Hz), 8.50 (d, 1H, NH, $^2J_{HP}$=8.7 Hz). IR (KBr, ν/cm^{-1}): 511(m), 531(m), 540(s), 615(w), 636(w) (P=S), 678(w), 691(s), 710(m), 720(s), 748(m), 785(w), 831(w), 961(w), 996(w), 1103(m), 1119(m), 1161(w), 1181(s) (P=O), 1238(m), 1292(m), 1436(m), 1469(m), 1482(w), 1582(sh, w), 1591(m), 2946(w), 3049(w), 3116(w). Anal. Calcd for $C_{30}H_{25}NOP_2S$: C, 70.72; H, 4.95; N, 2.75. Found: C, 70.59; H, 5.05; N, 2.74%.



***N*-[3-(Diphenylthiophosphoryl)phenyl]-*P*,*P*-diphenylthiophosphinic amide, 1.** A mixture of *N*-[3-(diphenylphosphoryl)phenyl]-*P*,*P*-diphenylthiophosphinic amide (1.3 g, 2.6 mmol) and Lawesson reagent (0.8 g, 2.0 mmol) in 40 mL of chlorobenzene was refluxed for 16 h. After cooling to room temperature, the resulting solution was sequentially washed with aqueous solution of Na_2CO_3 and water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was crystallized from EtOAc–hexane mixture (1:1) followed by purification by column chromatography (eluent: CH_2Cl_2–hexane (1:1)) to give 0.8 g of ligand **1** as a white crystalline solid. Yield: 60%. Mp: 200–202 °C (dec.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 43.23 ($P(S)Ph_2$), 52.54 ($NHP(S)Ph_2$) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 5.08 (d, 1H, NH, $^2J_{HP}$=6.6 Hz), 7.09 (d, 1H, H(C6), $^3J_{HH}$=8.2 Hz), 7.18–7.29 (m, 3H, H_{Ar}), 7.35–7.52 (m, 12H, H_{Ar}), 7.61 (dd, 4H, *o*-H in $P(S)Ph_2$, $^3J_{HP}$=13.2 Hz, $^3J_{HH}$=8.01 Hz), 7.91 (dd, 4H, *o*-H in $NHP(S)Ph_2$, $^3J_{HP}$=13.4 Hz, $^3J_{HH}$=7.7 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$/$(CD_3)_2SO$): δ 121.07 (d, C4, $^2J_{CP}$=6.2 Hz), 121.25–121.50 (unresolved m, C2), 123.48 (d, C6, $^3J_{CP}$=10.8 Hz), 127.51 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$=12.1 Hz), 127.59 (d, *m*-C in $NHP(S)Ph_2$, $^3J_{CP}$=12.7 Hz), 128.10 (d, C5, $^3J_{CP}$=14.3 Hz), 130.50 (s, *p*-C in $P(S)Ph_2$), 130.72 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$=11.4 Hz), 130.89 (s, *p*-C in $NHP(S)Ph_2$), 131.07 (d, *o*-C in $NHP(S)Ph_2$, $^2J_{CP}$=10.8 Hz), 131.68 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$=85.1 Hz), 131.88 (d, C3, $^1J_{CP}$=85.1 Hz), 132.53 (d, *ipso*-C in $NHP(S)Ph_2$, $^1J_{CP}$=103.0 Hz), 140.72 (d, C1, $^2J_{CP}$=15.0 Hz). IR (KBr, ν/cm^{-1}): 488(m), 509(m), 514(m), 615(w) and 640(s) (both P=S), 690(s), 695(m), 715(s), 719(sh, s), 758(w),

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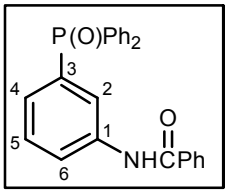
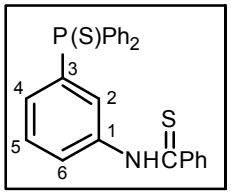
794(w), 852(w), 944(m), 994(w), 1097(sh, m), 1104(m), 1243(w), 1274(w), 1376(m), 1435(m), 1480(sh, m), 1486(m), 1571(sh, w), 1577(sh, w), 1590(m), 3053(w), 3138(w). Anal. Calcd for $C_{30}H_{25}NP_2S_2$: C, 68.55; H, 4.79; N, 2.66. Found: C, 68.71; H, 5.07; N, 2.61%.



***N*-[3-(Diphenylphosphoryl)phenyl]benzamide.** A stirred mixture of 3-(diphenylphosphoryl)aniline (1.4 g, 4.8 mmol), benzoyl chloride (0.7 g, 5.0 mmol), and triethylamine (0.7 mL, 5.0 mmol) in 25 mL of benzene was heated at 50–60 °C for 10 h. The resulting precipitate was filtered off, washed with water, recrystallized from acetone, and dried under vacuum to give 1.5 g of *N*-[3-(diphenylphosphoryl)phenyl]benzamide as a white crystalline solid. Yield: 69%. Mp: 226–228 °C (acetone). $^{31}P\{^1H\}$ NMR (161.98 MHz, $(CD_3)_2SO$): δ 25.65 ppm. ^1H NMR (400.13 MHz, $(CD_3)_2SO$): δ 7.31 (dd, 1H, H(C4), $^3J_{HP}$=11.4 Hz, $^3J_{HH}$=7.6 Hz), 7.51–7.60 and 7.63–7.67 (both m, 8H+6H, H_{Ar}), 7.94 (d, 2H, *o*-H in C(O)Ph, $^3J_{HH}$=7.2 Hz), 8.10 (d, 1H, H(C6), $^3J_{HH}$=7.9 Hz), 8.15 (d, 1H, H(C2), $^3J_{HP}$=13.4 Hz), 10.48 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$/$(CD_3)_2SO$ (1:1)): δ 121.27 (d, C2, $^2J_{CP}$ = 11.3 Hz), 121.85 (s, C6), 124.65 (d, C4, $^2J_{CP}$ = 9.1 Hz), 125.80 (s, *m*-C in C(O)Ph), 126.33 (s, *o*-C in C(O)Ph), 126.72 (d, *m*-C in $P(O)Ph_2$, $^3J_{CP}$ = 11.7 Hz), 127.06 (d, C5, $^3J_{CP}$ = 14.1 Hz), 129.65 (d, *o*-C in $P(O)Ph_2$, $^2J_{CP}$ = 9.3 Hz), 129.71 (s, *p*-C in C(O)Ph), 130.12 (s, *p*-C in $P(O)Ph_2$), 130.52 (d, *ipso*-C in $P(O)Ph_2$, $^1J_{CP}$ = 100.9 Hz), 130.82 (d, C3, $^1J_{CP}$ = 105.1 Hz), 132.69 (s, *ipso*-C in C(O)Ph), 137.74 (d, C1, $^3J_{CP}$ = 14.5 Hz), 164.00 (s, C=O). IR (KBr, ν/cm^{-1}): 524(m), 541(s), 693(s), 705(m), 713(m), 723(s), 753(w), 791(w), 893(w), 1100(w), 1121(m), 1182(s) (P=O), 1239(m), 1246(sh, w), 1264(w), 1310(s), 1394(m), 1413(w), 1436(m), 1477(s), 1542(s), 1580(sh, w), 1594(m), 1668(s) (C(O)NH), 3054(w), 3177(w), 3230(w). Anal. Calcd for $C_{25}H_{20}NO_2P{\cdot}H_3CC(O)CH_3$: C, 73.83; H, 5.75; N, 3.08. Found: C, 73.91; H, 5.29; N, 3.20%.



***N*-[3-(Diphenylthiophosphoryl)phenyl]benzenecarbothioamide, 2.** A mixture of *N*-[3-(diphenylphosphoryl)phenyl]benzamide (1.3 g, 3.3 mmol) and Lawesson reagent (1.7 g, 4.2 mmol) in 15 mL of chlorobenzene was refluxed for 7 h. After cooling to room temperature, the resulting solution was diluted with benzene (35 mL) and washed with water, aqueous solution of Na_2CO_3, and again with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was crystallized from Et_2O and recrystallized from benzene to give 1.0 g of ligand **2** as a yellow crystalline solid. Yield: 71%. Mp: 190–193 °C (C_6H_6). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 43.04 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 7.40–7.60 (m, 11H, H_{Ar}), 7.73–7.78 (m, 6H, H_{Ar}), 8.06 (d, 1H, H(C2), $^3J_{HP}$=13.7 Hz), 8.14 (br s, 1H, H(C6)), 9.09 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $(CD_3)_2SO$): 127.56 (d, C5,

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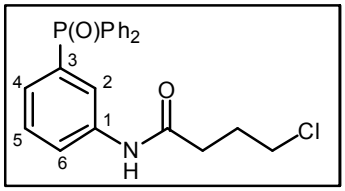
$^{3}J_{CP}$=13.1 Hz), 127.63 (s, C6), 127.98 (s, *m*-C in C(S)Ph), 128.51 (s, *o*-C in C(S)Ph), 129.32 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$=12.0 Hz), 129.62 (d, C4, $^{2}J_{CP}$=13.4 Hz), 129.66 (d, C2, $^{2}J_{CP}$=10.6 Hz), 131.44 (s, *p*-C in C(S)Ph), 132.26 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$=10.6 Hz), 132.42 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$=2.5 Hz), 132.68 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$=74.5 Hz), 133.30 (d, C3, $^{1}J_{CP}$=84.1 Hz), 140.72 (d, C1, $^{3}J_{CP}$=15.2 Hz), 142.90 (s, *ipso*-C in C(S)Ph), 198.62 (s, C=S). IR (KBr, ν/cm^{-1}): 503(m), 517(s), 614(w), 635(s) (P=S), 692(s), 712(s), 717(s), 742(w), 774(w), 789(w), 998(w), 1103(s), 1212(m), 1305(w), 1345(sh, m), 1360(s), 1414(m), 1436(s), 1448(m), 1474(m), 1478(m), 1489(w), 1536(m) (NHCS), 1583(m), 3050(w), 3072(w), 3213(w). Anal. Calcd for $C_{25}H_{20}NPS_2$: C, 69.90; H, 4.69; N, 3.26. Found: C, 69.77; H, 4.73; N, 3.21%.

4-Chloro-*N*-[3-(diphenylphosphoryl)phenyl]butanamide. A solution of 4-chlorobutyryl chloride (0.9 g, 6.4 mmol) in 15 mL of dichloromethane was slowly dropwise added to a stirred mixture of 3-(diphenylphosphoryl)aniline (1.9 g, 6.5 mmol) and Et_3N (0.9 mL, 6.5 mmol) in 25 mL of CH_2Cl_2 at 10 °C. The resulting reaction mixture was stirred at r.t. for 12 h and then washed with water, 5% aqueous solution of Na_2CO_3, and again with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was crystallized from EtOAc to give 2.5 g of the desired compound as a white crystalline solid. Yield: 96%. Mp: 189–192 °C (EtOAc). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, $CDCl_3$): δ 29.83 ppm. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.01–2.10 (m, 2H, CH_2), 2.44 (t, 2H, $CH_2C(O)$, $^{3}J_{HH}$=7.3 Hz), 3.42 (t, 2H, CH_2Cl, $^{3}J_{HH}$=6.4 Hz), 6.99 (dd, 1H, H(C4), $^{3}J_{HP}$=11.5 Hz, $^{3}J_{HH}$=7.7 Hz), 7.37 (dt, 1H, H(C5), $^{3}J_{HH}$=7.9 Hz, $^{4}J_{HP}$=4.1 Hz), 7.43–7.48 and 7.54–7.58 (both m, 4H+2H, H_{Ar}), 7.64 (dd, 4H, *o*-H in $P(O)Ph_2$, $^{3}J_{HP}$=12.1 Hz, $^{3}J_{HH}$=7.1 Hz), 8.18 (d, 1H, H(C2), $^{3}J_{HP}$=13.2 Hz), 8.51 (d, 1H, H(C6), $^{3}J_{HH}$=8.0 Hz), 10.60 (br s, 1H, NH). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$): δ 28.07 (s, CH_2), 34.05 (s, $CH_2C(O)$), 44.51 (s, CH_2Cl), 123.24 (d, C2, $^{2}J_{CP}$ = 9.2 Hz), 123.35 (br s, C6), 125.99 (d, C4, $^{2}J_{CP}$ = 11.2 Hz), 128.68 (d, *m*-C in $P(O)Ph_2$, $^{3}J_{CP}$ = 12.2 Hz), 128.98 (d, C5, $^{3}J_{CP}$ = 14.0 Hz), 131.61 (d, C3, $^{1}J_{CP}$ = 105.8 Hz), 131.99 (d, *o*-C in $P(O)Ph_2$, $^{2}J_{CP}$ = 10.1 Hz), 132.00 (d, *ipso*-C in $P(O)Ph_2$, $^{1}J_{CP}$ = 104.4 Hz), 132.24 (d, *p*-C in $P(O)Ph_2$, $^{4}J_{CP}$ = 2.0 Hz), 140.49 (d, C1, $^{3}J_{CP}$ = 13.6 Hz), 171.42 (s, C=O). IR (KBr, ν/cm^{-1}): 501(w), 516(m), 541(s), 697(m), 708(w), 729(m), 752(m), 760(sh, w), 791(w), 974(w), 1080(w), 1098(w), 1122(m), 1176(s) (P=O), 1220(w), 1243(m), 1297(w), 1308(w), 1332(m), 1381(w), 1399(w), 1416(w), 1437(m), 1477(m), 1553(s) (C(O)NH), 1593(m), 1605(m), 1688(s) (C=O), 3051(m), 3124(w), 3181(w), 3249(w). Anal. Calcd for $C_{22}H_{21}ClNO_2P$: C, 66.42; H, 5.32; N, 3.52. Found: C, 66.70; H, 5.25; N, 3.38%.



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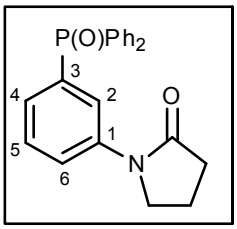
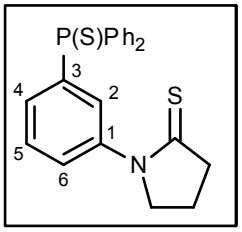


1-[3-(Diphenylphosphoryl)phenyl]pyrrolidin-2-one. Potassium *tert*-butoxide (0.6 g, 5.4 mmol) was added to a suspension of 4-chloro-*N*-[3-(diphenylphosphoryl)phenyl]butanamide (2.1 g, 5.3 mmol) in 15 mL of abs. THF at 5 °C. The reaction mixture was stirred at r.t. for 1 day. The solvent was removed under reduced pressure. A solution of the resulting residue in dichloromethane was washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was crystallized from EtOAc to give 1.5 g of 1-[3-(diphenylphosphoryl)phenyl]pyrrolidin-2-one as a white crystalline solid. Yield: 79%. Mp: 173–175 °C (EtOAc). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 29.00 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 2.12–2.19 (m, 2H, CH_2), 2.61 (t, 2H, $CH_2C(O)$, $^3J_{HH}$=8.1 Hz), 3.86 (t, 2H, CH_2N, $^3J_{HH}$=7.0 Hz), 7.38 (dd, 1H, H(C4), $^3J_{HP}$=11.8 Hz, $^3J_{HH}$=7.6 Hz), 7.45–7.51 and 7.55–7.59 (both m, 5H+2H, H_{Ar}), 7.69 (dd, 4H, *o*-H in $P(O)Ph_2$, $^3J_{HP}$=12.0 Hz, $^3J_{HH}$=7.6 Hz), 7.82 (dt, 1H, H(C2), $^3J_{HP}$=13.3 Hz, $^4J_{HH}$=1.3 Hz), 8.10 (dt, 1H, H(C6), $^3J_{HH}$=8.0 Hz, $^4J_{HH}$=1.3 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 17.86 (s, CH_2), 32.66 (s, $CH_2C(O)$), 48.45 (s, CH_2N), 122.31 (d, C2, $^2J_{CP}$ = 11.4 Hz), 123.49 (d, C6, $^4J_{CP}$ = 2.6 Hz), 127.69 (d, C4, $^2J_{CP}$ = 9.6 Hz), 128.53 (d, *m*-C in $P(O)Ph_2$, $^3J_{CP}$ = 12.3 Hz), 129.04 (d, C5, $^3J_{CP}$ = 13.3 Hz), 132.03 (d, *o*-C in $P(O)Ph_2$, $^2J_{CP}$ = 10.0 Hz), 132.04 (d, *p*-C in $P(O)Ph_2$, $^4J_{CP}$ = 2.8 Hz), 132.31 (d, *ipso*-C in $P(O)Ph_2$, $^1J_{CP}$ = 104.5 Hz), 133.17 (d, C3, $^1J_{CP}$ = 103.7 Hz), 139.72 (d, C1, $^3J_{CP}$ = 14.2 Hz), 174.45 (s, C=O). IR (KBr, ν/cm^{-1}): 497(m), 510(m), 541(s), 591(w), 691(m), 700(m), 707(w), 724(s), 754(m), 759(m), 797(w), 1084(w), 1108(m), 1119(m), 1195(s) (P=O), 1221(w), 1275(w), 1290(w), 1326(m), 1388(s), 1426(w), 1434(m), 1443(w), 1476(m), 1485(m), 1570(w), 1592(m), 1694(s) (C=O), 2883(w), 2947(w), 2981(w), 3076(w). Anal. Calcd for $C_{22}H_{20}NO_2P$: C, 73.12; H, 5.58; N, 3.88. Found: C, 73.09; H, 5.64; N, 3.78%.



1-[3-(Diphenylthiophosphoryl)phenyl]pyrrolidine-2-thione, 3. A mixture of 1-[3-(diphenylphosphoryl)phenyl]pyrrolidin-2-one (1.0 g, 2.8 mmol) and Lawesson reagent (1.2 g, 3.0 mmol) in 20 mL of toluene was refluxed for 5 h. After cooling to room temperature, the resulting solution was poured into water. The organic layer was separated, and the aqueous phase was extracted additionally with chloroform. The combined organic fraction was washed with 5% aqueous solution of Na_2CO_3 and water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting crystalline residue was recrystallized from benzene–diethyl ether to give 0.8 g of ligand **3** as a pale yellow crystalline solid. Yield: 73%. Mp: 157–159 °C (C_6H_6/Et_2O (1:2)). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 42.99 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 2.15–2.22 (m, 2H, CH_2), 3.18 (t, 2H, $CH_2C(S)$,

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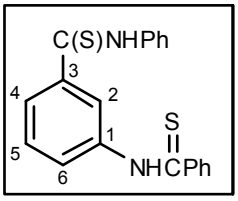
$^{3}J_{HH}$=7.8 Hz), 4.10 (t, 2H, CH_2N, $^{3}J_{HH}$=7.2 Hz), 7.42–7.54 (m, 7H, H_{Ar}), 7.63 (dt, 1H, H(C4), $^{3}J_{HP}$=12.7 Hz, $^{3}J_{HH}$=7.8 Hz), 7.73–7.80 (m, 5H, H_{Ar}), 7.96 (dt, 1H, H(C2), $^{3}J_{HP}$=14.0 Hz, $^{4}J_{HH}$=1.8 Hz). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $CDCl_3$): δ 20.57 (s, CH_2), 46.48 (s, $CH_2C(S)$), 58.12 (s, CH_2N), 127.55 (d, C6, $^{4}J_{CP}$ = 2.7 Hz), 128.63 (d, C2, $^{2}J_{CP}$ = 12.2 Hz), 128.66 (d, *m*-C in $P(S)Ph_2$, $^{3}J_{CP}$ = 12.7 Hz), 129.24 (d, C5, $^{3}J_{CP}$ = 13.6 Hz), 130.94 (d, C4, $^{2}J_{CP}$ = 10.3 Hz), 131.78 (d, *p*-C in $P(S)Ph_2$, $^{4}J_{CP}$ = 2.8 Hz), 132.28 (d, *ipso*-C in $P(S)Ph_2$, $^{1}J_{CP}$ = 85.7 Hz), 132.32 (d, *o*-C in $P(S)Ph_2$, $^{2}J_{CP}$ = 10.8 Hz), 134.22 (d, C3, $^{1}J_{CP}$ = 84.5 Hz), 140.56 (d, C1, $^{3}J_{CP}$ = 14.8 Hz), 203.32 (s, C=S). IR (KBr, ν/cm^{-1}): 509(m), 517(s), 592(w), 615(w), 642(m) (P=S), 670(w), 692(s), 716(s), 744(w), 753(m), 797(w), 997(w), 1073(w), 1102(m), 1144(m), 1257(m), 1296(s), 1311(m), 1415(s), 1436(s), 1455(w), 1478(m), 1487(s), 1571(w), 1592(w), 2920(w), 2985(w), 3044(w). Anal. Calcd for $C_{22}H_{20}NPS_2$: C, 67.15; H, 5.12; N, 3.56. Found: C, 67.19; H, 5.08; N, 3.42%.



***N*-Phenyl-3-[(phenylthiocarbonyl)amino]benzenecarbothioamide, 4.** A mixture of 3-(benzoylamino)-*N*-phenylbenzamide (1.2 g, 3.8 mmol) and Lawesson reagent (2.0 g, 5 mmol) in 40 mL of toluene was refluxed for 6 h. The resulting precipitate was filtered off, dissolved in EtOAc. The solution obtained was washed with saturated aqueous solution of $NaHCO_3$ and water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was purified by column chromatography (eluent EtOAc–hexane (3:1)) to give 0.25 g of ligand **4** as a lemon yellow crystalline solid. Yield: 19%. Mp: 194–196 °C. ^{1}H NMR (400.13 MHz, $(CD_3)_2SO$): 7.29 (m, 1H, H(C5)), 7.44–7.56 (m, 6H, H_{Ar}), 7.70 (d, 1H, H(C4), $^{3}J_{HH}$=7.5 Hz), 7.82–7.87 (m, 4H, H_{Ar}), 8.03 (d, 1H, H(C6), $^{3}J_{HH}$=7.8 Hz), 8.29 (s, 1H, H(C2)), 11.86 (br s, 1H, NH), 11.92 (br s, 1H NH). $^{13}C\{^{1}H\}$ NMR (100.61 MHz, $(CD_3)_2SO$): 124.33 (s, C2), 124.59 (s, *o*-C in NHPh), 125.08 (s, C3), 126.82 and 126.92 (both s, C6 and *p*-C in NHPh), 127.95 (s, *o*-C in C(S)Ph), 128.56 (s, *m*-C in NHPh or C(S)Ph), 128.63 (s, C5), 129.02 (s, *m*-C in NHPh or C(S)Ph), 131.40 (s, *p*-C in C(S)Ph), 140.18 and 140.44 (both s, C1 and *ipso*-C in NHPh), 142.95 and 143.46 (both s, C3 and *ipso*-C in C(S)Ph), 197.22 and 198.52 (both s, C=S). IR (KBr, ν/cm^{-1}): 693(s), 705(vs), 769(w), 809(w), 866(w), 991(w), 1037(m), 1078(w), 1158(w), 1192(m), 1221(m), 1240(w), 1264(w), 1310(w), 1360(sh, s), 1372(s), 1414(w), 1447(m), 1485(m), 1491(m), 1521(s) and 1536(s) (both NHCS), 1593(sh, w), 1598(w), 2864(w), 2959(m), 3039(m), 3125(br, m) and 3178(br, m) (both NH). Anal. Calcd for $C_{20}H_{16}N_2S_2$: C, 68.93; H, 4.63; N, 8.04; S, 18.40. Found: C, 68.94; H, 4.66; N, 8.01; S, 18.79%.

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{2-(Diphenylthiophosphoryl)-6-[(diphenylthiophosphoryl)amino]phenyl}palladium chloride, 5. A solution of $PdCl_2(NCPh)_2$ (37 mg, 0.096 mmol) and ligand **1** (51 mg, 0.097 mmol) in 7.5 mL of acetonitrile was refluxed for 2 h. The desired product was collected by filtration, washed with MeCN (5 mL) and Et_2O (5 mL), and recrystallized from DMSO–EtOH (1:2) to give 22 mg of complex **5** as a pale yellow crystalline solid. Yield: 34%. Mp: >250 °C (dec.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $(CD_3)_2SO$): δ 42.80 ($P(S)Ph_2$), 44.71 ($NHP(S)Ph_2$) ppm. ^1H NMR (300.13 MHz, $(CD_3)_2SO$): δ 7.09 (ddd, 1H, H(C4), $^3J_{HP}$=11.6 Hz, $^3J_{HH}$=6.5 Hz, $^4J_{HH}$=2.6), 6.95–7.04 (m, 2H, H_{Ar}), 7.64–7.75 (m, 16H, H_{Ar}), 7.89 (dd, 4H, *o*-H in $P(S)Ph_2$, $^3J_{HP}$=14.2 Hz, $^3J_{HH}$=7.1 Hz), 9.13 (d, 1H, NH, $^2J_{HP}$=9.2 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $(CD_3)_2SO$): δ 121.97 (d, C4, $^2J_{CP}$=10.3 Hz), 125.18 (d, C5, $^3J_{CP}$=16.9 Hz), 125.34 (d, C6, $^3J_{CP}$=15.4 Hz), 129.07 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$=13.2 Hz), 129.41 (d, *m*-C in $NHP(S)Ph_2$, $^3J_{CP}$=11.7 Hz), 129.91 (d, C3, $^1J_{CP}$=82.5 Hz), 130.86 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$=101.2 Hz), 131.82 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$=11.7 Hz), 132.24 (d, *o*-C in $NHP(S)Ph_2$, $^2J_{CP}$=11.0 Hz), 133.19 (s, *p*-C both in $P(S)Ph_2$ and $NHP(S)Ph_2$), 141.40–142.13 (unresolved m, C2), 143.44 (d, C1, $^2J_{CP}$=20.5 Hz), 146.87 (d, *ipso*-C in $NHP(S)Ph_2$, $^1J_{CP}$=104.9 Hz). IR (KBr, ν/cm^{-1}): 510(s), 523(w), 609(m) and 626(m) (both P=S), 688(s), 710(s), 721(s), 745(m), 781(w), 966(br, w), 998(w), 1106(s), 1109(sh, m), 1153(w), 1181(w), 1220(w), 1271(w), 1277(w), 1364(m), 1437(s), 1460(w), 1483(w), 1561(w), 1573(w), 1586(w), 2812(w), 2889(w), 2999(w), 3051(m), 3091(m). Anal. Calcd for $C_{30}H_{24}ClNP_2PdS_2$: C, 54.06; H, 3.63; N, 2.10. Found: C, 53.71; H, 3.67; N, 2.11%.

{2-(Diphenylthiophosphoryl)-6-[(phenylthiocarbonyl)amino]phenyl}palladium chloride, 6. A solution of $PdCl_2(NCPh)_2$ (25 mg, 0.065 mmol) in 2 mL of CH_2Cl_2 was slowly dropwise added to a solution of ligand **2** (28 mg, 0.065 mmol) in 3 mL of dichloromethane. The resulting reaction mixture was left under ambient conditions for 24 h. The desired product was collected by filtration, washed with CH_2Cl_2 (10 mL) and Et_2O (5 mL), and dried *in vacuo* to give 34 mg of complex **6** as a yellow crystalline solid. Yield: 92%. Mp: >185 °C (dec.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $(CD_3)_2SO$): δ 48.95 ppm. ^1H NMR (400.13 MHz, $(CD_3)_2SO$): δ 6.98 (dd, 1H, H(C4), $^3J_{HP}$=11.8 Hz, $^3J_{HH}$=7.6 Hz), 7.34 (dt, 1H, H(C5), $^3J_{HH}$=7.8 Hz, $^4J_{HP}$=4.6 Hz), 7.58–7.61 (m, 2H, *m*-H in C(S)Ph), 7.68–7.72 and 7.74–7.78 (both m, 7H+5H, H_{Ar}), 7.87 (d, 2H, *o*-H in C(S)Ph, $^3J_{HH}$=7.9 Hz), 12.83 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $(CD_3)_2SO$): δ 125.74 (d, C5, $^3J_{CP}$=14.8 Hz), 126.10 (s,

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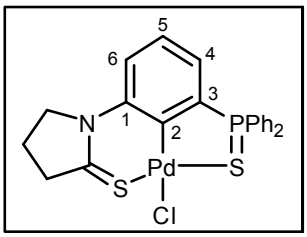
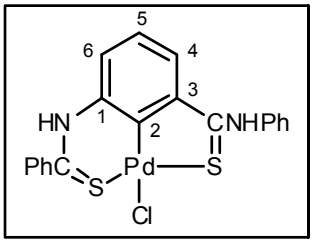
C6), 128.55 (s, *m*-C in C(S)Ph), 129.03 (s, *o*-C in C(S)Ph), 129.76 (d, *m*-C in $P(S)Ph_2$, $^3J_{CP}$=12.6 Hz), 129.88 (d, *ipso*-C in $P(S)Ph_2$, $^1J_{CP}$=80.1 Hz), 130.12 (d, C4, $^2J_{CP}$=16.5 Hz), 132.40 (d, *o*-C in $P(S)Ph_2$, $^2J_{CP}$=11.0 Hz), 132.47 (s, *p*-C in C(S)Ph), 133.55 (d, *p*-C in $P(S)Ph_2$), 136.63 (s, *ipso*-C in C(S)Ph), 138.41 (d, C1, $^3J_{CP}$=20.3 Hz), 144.22 (d, C2, $^2J_{CP}$=26.3 Hz), 150.28 (d, C3, $^1J_{CP}$=108.1 Hz), 176.64 (s, C=S). IR (KBr, ν/cm^{-1}): 515(s), 611(w), 626(m) (P=S), 687(s), 708(s), 719(m), 736(sh, m), 749(m), 793(m), 889(w), 999(m), 1025(w), 1034(w), 1070(w), 1105(s), 1154(w), 1184(m), 1197(w), 1246(w), 1307(w), 1379(m), 1407(m), 1436(s), 1453(m), 1479(w), 1492(w), 1525(m), 1575(sh, m), 1585(m), 3055(m), 3149(w), 3227(m). Anal. Calcd for $C_{25}H_{19}ClNPPdS_2$: C, 52.64; H, 3.36; N, 2.46. Found: C, 52.52; H, 3.25; N, 2.75.

[2-(Diphenylthiophosphoryl)-6-(2-thioxopyrrolidin-1-yl)]palladium chloride, 7. A solution of $PdCl_2(NCPh)_2$ (31 mg, 0.081 mmol) in 4 mL of acetonitrile was slowly dropwise added to a solution of ligand **3** (32 mg, 0.081 mmol) in 4 mL of MeCN. In 30 min, the desired product was collected by filtration, washed with MeCN (5 mL) and Et_2O (10 mL), and dried *in vacuo* to give 41 mg of complex **7** as a light yellow crystalline solid. Yield: 95%. Mp: >200 °C (dec.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $(CD_3)_2SO$): δ 45.55 ppm. ^1H NMR (400.13 MHz, $(CD_3)_2SO$): δ 2.25–2.34 (m, 2H, CH_2), 3.26 (t, 2H, $CH_2C(S)$, $^3J_{HH}$=7.6 Hz), 4.50 (t, 2H, CH_2N, $^3J_{HH}$=6.9 Hz), 6.95 (dd, 1H, H(C4), $^3J_{HP}$=11.9 Hz, $^3J_{HH}$=7.3 Hz), 7.30–7.36 (m, 1H, H(C5)), 7.58 (d, 1H, H(C6), $^3J_{HH}$=8.4 Hz), 7.65–7.78 (m, 10H, H_{Ar}). IR (KBr, ν/cm^{-1}): 509(m), 528(w), 551(w), 598(w), 612(m) and 627(s) (both P=S), 690(s), 706(s), 720(m), 746(sh, m), 749(m), 783(w), 998(w), 1106(s), 1162(w), 1188(w), 1266(w), 1311(s), 1385(m), 1417(w), 1436(s), 1460(m), 1484(m), 1490(m), 1557(w), 1562(w), 2987(w), 3051(w). Anal. Calcd for $C_{22}H_{19}ClNPPdS_2$: C, 49.45; H, 3.58; N, 2.62. Found: C, 49.27; H, 3.54; N, 2.73%.



{2-(Anilinothiocarbonyl)-6-[(phenylthiocarbonyl)amino]phenyl}palladium chloride, 8. A solution of $PdCl_2(NCPh)_2$ (46 mg, 0.120 mmol) in 7 mL of CH_2Cl_2 was slowly dropwise added to a solution of ligand **4** (42 mg, 0.121 mmol) in 0.5 mL of DMSO. The resulting reaction mixture was left under ambient conditions for 2 d. The desired product was collected by filtration, washed with CH_2Cl_2 (10 mL) and Et_2O (5 mL), and dried *in vacuo* to give 47 mg of complex **8** as a yellow crystalline solid. Yield: 80%. Mp: >230 °C (dec.) ^1H NMR (400.13 MHz, $(CD_3)_2SO$): 7.42 (t, 1H, H_{Ar}, $^3J_{HH}$=8.0 Hz), 7.45–7.49 (m, 1H, H_{Ar}), 7.56–7.61 (m, 6H, H_{Ar}), 7.68 (t, 1H, *p*-H in C(S)NHPh, $^3J_{HH}$=7.4 Hz), 7.83 (d, 1H, H(C4), $^3J_{HH}$=7.9 Hz), 7.88 (d, 2H, *o*-H in C(S)NHPh,



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$^3J_{HH}$=7.3 Hz), 8.00 (d, 1H, H(C6), $^3J_{HH}$=7.3 Hz), 12.25 and 12.65 (both br s, 1H+1H, NH). IR (KBr, ν/cm^{-1}): 688(m), 690(sh, m), 708(m), 712(sh, m), 739(m), 760(w), 767(w), 802(w), 811(w), 984(w), 1027(w), 1051(w), 1182(w), 1196(w), 1259(m), 1263(m), 1306(w), 1310(w), 1322(w), 1369(w), 1406(m), 1421(m), 1443(s), 1451(s), 1494(m), 1531(s), 1579(m), 1595(m), 3044(m), 3098(w), 3158(w) and 3216(m) (both NH). Anal. Calcd for $C_{20}H_{15}ClN_2PdS_2$: C, 49.09; H, 3.09; Cl, 7.24; N, 5.72; Pd, 21.75; S, 13.11. Found: C, 49.08; H, 3.09; Cl, 7.25; N, 5.64%; Pd, 21.89; S, 13.08%.

General procedure for the solid-phase synthesis of complexes 6–8. A mixture of the corresponding ligand and $PdCl_2(NCPh)_2$ (ca 50 mg), obtained by manual grinding of the reactants in a mortar for several minutes, was heated at specified temperature (see Table 1) (oil bath) for 5 min to give the desired pincer-type products in quantitative yields as it was estimated by ^{31}P or ^1H NMR spectroscopy. In the case of ligand **3**, the resulting light yellow solid residue was rinsed with Et_2O (10 mL) and dried in air to give complex **7** in a quantitative yield. In the case of ligands **2** and **4**, the resulting brown (**2**) or orange (**4**) residue was dissolved in a DMSO–CH_2Cl_2 mixture (1:15, 30 mL) and filtered through a pad of cotton. After removal of dichloromethane, complexes **6** and **8** were precipitated with Et_2O. Note that complex **8** was obtained as a crystallosolvate with DMSO (Anal. Calcd for $C_{20}H_{15}ClN_2PdS_2 \cdot 2DMSO$: C, 44.65; H, 4.22; N, 4.34. Found: C, 44.64; H, 4.32; N, 4.38%).

Crystal structure determination and data collection. Crystals of complex **6** ($C_{25}H_{19}ClNPPdS_2$, M = 570.35), which were obtained by slow diffusion of ethanol into DMSO solution of **6**, are monoclinic, space group $P2_1/c$, at 100K: a = 12.9875(5), b = 13.4110(5), c = 13.5738(5) Å, β = 110.7650(10)°, V = 2210.65(14) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.714 gcm^{-3}, μ(MoKα) = 12.36 cm^{-1}, F(000) = 1144. Intensities of 25908 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoKα) = 0.71072Å, ω-scans, 2θ<58°], and 5867 independent reflections [R_{int} = 0.0385] were used in further refinement. The structure was solved by the direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The hydrogen atom of the NH group was located from the Fourier density synthesis and refined in isotropic approximation. The H(C) atom positions were calculated. All hydrogen atoms were refined in the isotropic approximation in riding model with the Uiso(H) parameters equal to 1.2 Ueq(Xi), where U(Xi) are the equivalent thermal parameters of the parent atoms to which the corresponding H atoms are bonded. For compound **6** the refinement converged to wR2 = 0.0628 and GOF = 1.002 for all independent reflections (R1 = 0.0250 was calculated against F for 5017 observed reflections with I>2σ(I)). All calculations were performed using SHELXTL PLUS 5.0.

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CCDC 971436 contains the supplementary crystallographic data for **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Electronic supplementary information

Electronic supplementary information (ESI) available: IR spectra of ligand **4** and complex **8**; IR spectral monitoring of solid-phase cyclopalladation of ligand **4**; catalytic performance of complexes **5**–**8** in the Suzuki cross-coupling.

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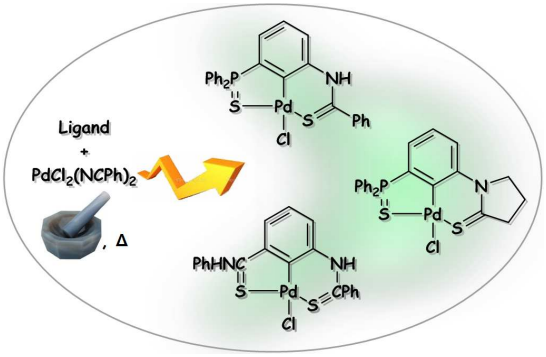

Cyclopalladation of pincer ligands can proceed efficiently in the solid state, serving as a powerful alternative to synthesis in solution.