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Hybrid *NCS* palladium pincer complexes of thiophosphorylated benzaldimines and their ketimine analogs

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ABSTRACT

A series of novel hybrid pincer ligands bearing thiophosphoryl and imino groups as donating arms was obtained by the condensation of 3-diphenylthiophosphorylbenzaldehyde with RNH_2 (R = Ph, ^{t}Bu) to afford aldimine derivatives **2a**, **b** or by the reaction of lithiated 3-(thiophosphoryl)bromobenzene with an appropriate substituted lactam yielding their ketimine analogs **2c**–**e** with 5–7-membered azacycloalkene moieties. The direct cyclopalladation of the ligands with $(PhCN)_2PdCl_2$ in MeCN under reflux led to κ^3-*NCS* pincer complexes **3b**–**e** with two five-membered fused metallacycles, isolated in low to moderate yields (12–53%); their structures were confirmed by multinuclear NMR and X-ray diffraction study. The palladacycles demonstrated high activity as (pre)catalysts for the Suzuki cross-coupling of phenylboronic acid with aryl bromides, which was found to increase in the series **3e** ~ **3d** <**3c**< **3b**, i.e. passing from ketimine derivatives **3d**, **e** with larger azacycloalkene to their analog with smaller five-membered cyclic imine moiety and further to benzaldimine complex **3b**. The tendency observed was explained by the controlled release of Pd(0) catalytically active species in the case of less sterically hindered complexes.

1. Introduction

Over the last two decades pincer complexes bearing a specific monoanionic terdentate backbone have emerged as a unique class of organometallic compounds mostly owing to their high catalytic activity in various chemical processes. A vast majority of pincer complexes is based on symmetrical derivatives (bis(phosphines), bis(thioethers), bis(amines) etc.), and their structural features as well as physical and chemical properties have been extensively reviewed [1,2]. But recently the interest in this area has been switched to *hybrid* derivatives with two different coordination arms, especially those combining "hard" and "soft" donor atoms [3]. The *unsymmetrical* pincer palladacycles with such *hemilabile* ligands demonstrated high catalytic activity, e.g., for the Suzuki cross-coupling, often surpassing in the efficiency their symmetric analogs [4,5]. However, despite an increasing number of publications devoted to the catalytic performance of hybrid pincer palladium complexes, the systematic investigations in this area are rather scarce and optimal routes for *desymmetrization* are still unclear.

As a part of our ongoing studies on pincer-type palladacycles with organothiophosphorus ligands, we have developed a series of 5,6-membered Pd(II) pincer complexes based on 3-diphenylthiophosphoryloxybenzaldimines **I** (Fig. 1), which were proved to be reasonably good (pre)catalysts for the Suzuki coupling between phenylboronic acid and aryl bromides [6]. Among the related *NCS* palladacycles **II**–**IV** formed by thiophosphorylated benzothiazoles, bearing as coordination arms along with the P=S group the imine moiety of a benzothiazole ring, complexes **II**, **III** with two fused metallacycles of different sizes were much more active than their 5,5-membered counterpart **IV** [7].

According to the kinetic experiments, ^{31}P NMR monitoring of a catalyst destiny after the catalytic cycle, Hg poisoning tests, and observation of palladium black formation, complexes **I**–**III** represented only precatalysts, liberating catalytically active Pd(0) particles. In other words, these data support the Pd(0)/Pd(II) catalytic cycle. At the same time, in the case of 5,5-membered *NCS* palladacycle **IV** and

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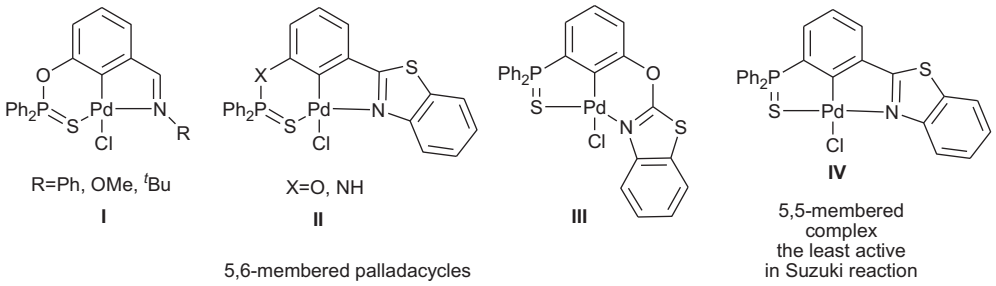


Fig. 1. *NCS* hemilabile pincer complexes with organothiophosphorus ligands.

related 5,5-membered *SCS*' pincer complexes [8] bearing thiophosphoryl and thiocarbamoyl donating arms, which retain their structure over the catalytic process, we cannot disclaim the alternative Pd(II)/Pd(IV) mechanism. Therefore, it seems reasonable to perform the synthesis of *NCS* pincer ligands and corresponding 5,5-membered palladacycles having another type of imine moiety to get more insight into this phenomenon.

Herein, we report on the synthesis of new *NCS* unsymmetrical pincer ligands, namely, thiophosphorylated benzaldimines and their ketimine analogs, bearing as coordination arms along with the phosphine sulfide group either cyclic or acyclic imine moiety, which are capable of forming *NCS* pincer complexes with two five-membered fused metallacycles. Of particular interest is the preparation of ketimine derivatives which could afford hybrid pincer ligands with 5–7-cyclic ketimine fragment, unknown for the symmetric *NCN* bis(imine) pincer prototypes [9]. The introduction of a bulky imine moiety would allow additional estimation of the effect of steric hindrances on the catalytic performance of Pd(II) pincer complexes derived in the model Suzuki reaction.

2. Results and discussion

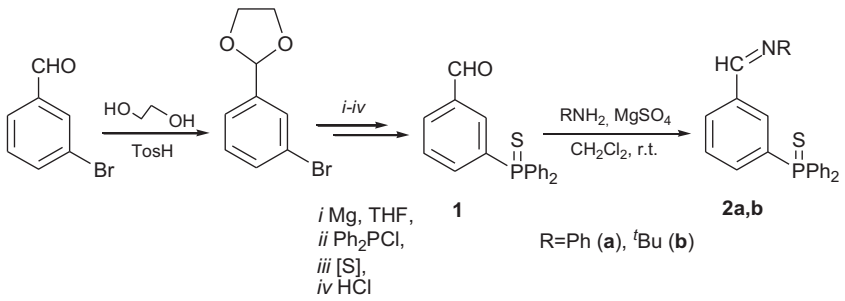
2.1. Synthesis of ligands and complexes

Thiophosphorylated benzaldimines **2a**, **b** with an acyclic imine moiety were readily derived from the condensation of 3-diphenylthiophosphorylbenzaldehyde **1** with aniline or *tert*-butylamine, respectively, as viscous yellowish oils in almost quantitative yields (Scheme 1). The starting thiophosphorylated benzaldehyde **1** was synthesized, in turn, by the reaction of the Grignard reagent of 2-(3-bromophenyl)-1,3-dioxolane with diphenylchlorophosphine followed by the addition of sulfur and acidic deprotection according to the literature procedure [10]. Note that ligands **2a**, **b** were obtained with ~5% admixture of the starting benzaldehyde **1**, which we failed to separate due to the decomposition of the target imines on silica gel, and were used in the subsequent synthesis of palladium complexes without purification.

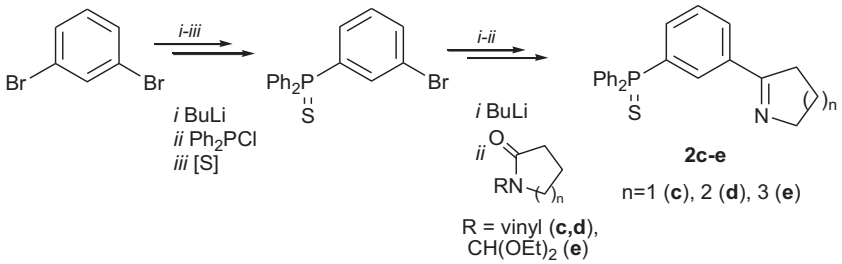
A convenient synthetic route to the thiophosphoryl-ketimino analogs with a cyclic imine moiety was developed *via* metalation of thiophosphorylated bromobenzene with butyllithium followed by the treatment with an equivalent of appropriate substituted lactam according to the earlier developed synthetic strategy [11]. The process was devised starting from commercially available 1,3-dibromobenzene which was converted into the key precursor – 3-(bromophenyl)diphenylphosphine sulfide *via* monophosphorylation with Ph_2PCl followed by *in situ* addition of elemental sulfur to the corresponding phosphine (Scheme 2) [12]. The sequential treatment of monothiophosphorylated bromide with *n*-BuLi and *N*-vinyl pyrrolidone, *N*-(diethoxymethyl)valerolactam or *N*-vinyl caprolactam led to the formation of the target ligands with five-, six-, and seven-membered azacycloalkene moiety, isolated as viscous yellowish oils in moderate yields (38–61%) after chromatography purification.

The structures of ligands **2a**–**e** were confirmed by multinuclear NMR (^{31}P, ^{1}H, and ^{13}C) and IR spectroscopy data. Thus, in the IR spectra the characteristic ν(C=N) band was observed at 1618–1646 cm^{-1}, while the band corresponding to the thiophosphoryl group stretching vibrations appeared at *ca.* 640 cm^{-1}. The singlet signals of the phosphorus atoms in the ^{31}P NMR spectra of **2a**–**e** were detected at 43–44 ppm – the region typical for triarylphosphine sulfides. The signals of aldimine protons in the ^{1}H NMR spectra of acyclic imines **2a** and **2b** appeared as singlets at 8.24 and 8.44 ppm, respectively. The characteristic resonances of $(CH_2)_n$ units in the ^{1}H NMR spectra of their ketimine analogs **2c**–**e** were observed in the expected regions (see Experimental). The ^{13}C NMR spectroscopy data is also consistent with the proposed structures of the final ligands (e.g., $\delta_{C=N}$ in the range of 165–174 ppm, etc.).

The direct cyclopalladation of these ligands at the C2 position of a central phenyl ring to afford the corresponding *NCS* pincer complexes **3a**–**e** was found to proceed most efficiently while



Scheme 1. Synthesis of 3-thiophosphorylbenzaldimines **2a**, **b**.



Scheme 2. Synthesis of thiophosphorylated ketimines **2c**–**e**.

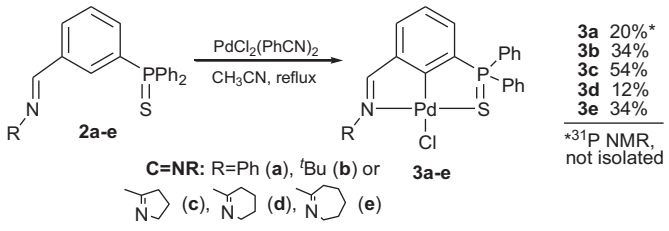
refluxing the equimolar amounts of **2a**–**e** and $(PhCN)_2PdCl_2$ in acetonitrile for 1–8 h depending on the ligand structure (Scheme 3). Although the yields of the complexes isolated in pure form were not high, ranging from 12 to 54%, the harnessing of other conditions was unsuccessful. Thus, the reaction in dichloromethane at room temperature (i.e., under milder conditions) was too sluggish, providing only ~15% of complex **3b** in a month (according to the ^{31}P NMR monitoring data) with the predominance of some coordinatively bonded complexes of $PdCl_2$ [13]. The application of a nonpolar solvent (benzene) under reflux did not afford a pincer product at all. Moreover, elevation of the reaction temperature to 120 °C (replacement of MeCN for benzonitrile) did not result in any significant increase of the yields of the target products. Note that we failed to isolate complex **3a** with a phenyl substituent at the nitrogen atom of the aldimine group due to its decomposition on silica gel.

Complexes **3b**–**e** are pale-yellow or yellow crystalline solids that are air and moisture stable both in the solid state and in solution as well as thermally stable up to $T > 240$ °C.

The structures of the complexes were assigned based on the ^{31}P, ^{1}H NMR and IR spectroscopy data as well as X-ray diffraction analysis. Thus, the bands at *ca.* 600 and 1540 cm^{-1} in the IR spectra of **3b**–**e** are diagnostic of the coordinated P=S and C=N bonds, being shifted to the lower frequencies relative to those of the free ligands by 41–44 and 76–96 cm^{-1}, respectively. The strongly deshielded signals of phosphorus resonances for **3b**–**e** ($\Delta\delta_P$ = 19–25 ppm) unambiguously indicate the coordination of thiophosphoryl group, while the upfiled shift of the imine proton signal in the ^{1}H NMR spectra of **3b** ($\Delta\delta_H$ = 0.17 ppm) evidences the complexation by the aldimine moiety. Moreover, the disappearance of low-field doublets of the H(C2)-protons with an overall reduction of aromatic proton intensity by 1H confirms the occurrence of metalation. Of note is also a general tendency of strong concomitant displacement of the signals of remaining benzene core protons to lower frequencies upon complex formation (see Experimental). The elemental analysis data is also in a good agreement with the suggested compositions of complexes **3b**–**e**. The structures of the palladacycles derived were also confirmed by the X-ray diffraction analysis for complexes **3b**, **3c**, and **3d**, the latter crystallizing with a solvent chloroform molecule (**3d_solv**) and without it (**3d_nosolv**).

According to the X-ray diffraction data for these complexes (Figs. 2–4), the presence of different donor atoms – sulfur atom of P=S group and sp^2-nitrogen atom – causes the distortion of the coordination polyhedron of the palladium atom, the bending along the N…S line. In **3b** and **3**c, the dihedral angles between the CPdSN and ClPdSN planes are as high as ~4° (3.6 and 4.5°, respectively), the angles C(2)Pd(1)Cl(1) are 175.4(1) and 175.6(1)°, and the chlorine atoms deviate by 0.15–0.19 Å from the mean square plane of S(1), N(1), C(2), and Pd(1) atoms. In the case of **3d** with six-membered azacycloalkene moiety, this distortion is much less pronounced. Thus, in the molecules of **3d_nosolv** and **3d_solv** the angles C(2)Pd(1)Cl(1) are 178.0(1) and 176.7(1)°, the angles between the planes C(2)Pd(1)S(1)N(1) and Cl(1)Pd(1)S(1)N(1) are 1.1 and 0.9°, and the deviation of the atom Cl(1) is only 0.01 and 0.03 Å, respectively. Moreover, both 5CN and 5PS metallacycles in complexes **3b**, **3**c, and **3d_nosolv** are planar, while in the case of **3d_solv** the first one is also planar, but the second has a "twist" conformation with the atoms P(1) and S(1) deviating by 0.22 and 0.38 Å, respectively. Note that this study revealed the unexpected crystallization of palladacycle **3b** in a chiral space group $P4_3$ as a result of cross-linking supramolecular aggregation, which is a rare case for pincer complexes that do not include a stereogenic center in their molecule (see, e.g., ref. [14]). This is, apparently, a result of noncenrosymmetric supramolecular assembling formed by rather weak C–H…π contacts; C–H…Cl and C–H…S interactions complete the formation of 3D cross-linked network (Fig. S1 in Supplementary material). The centrosymmetric crystal structures of the other complexes are assembled by numerous but also weak C–H…Cl, C–H…π, C–H…S, and H…H contacts together with π…π interactions in both solvated and non-solvated **3d** complexes as well as C–H…Cl contacts with participation of chloroform molecules and Cl…Cl interactions between them in **3d_solv** only.

It should be mentioned that the yields of the pincer-type complexes obtained via direct cyclopalladation in the case of the



Scheme 3. Direct cyclopalladation of 3-thiophosphorylated benzaldimines **2a**, **b** and their ketimine analogs **2c**–**e**.

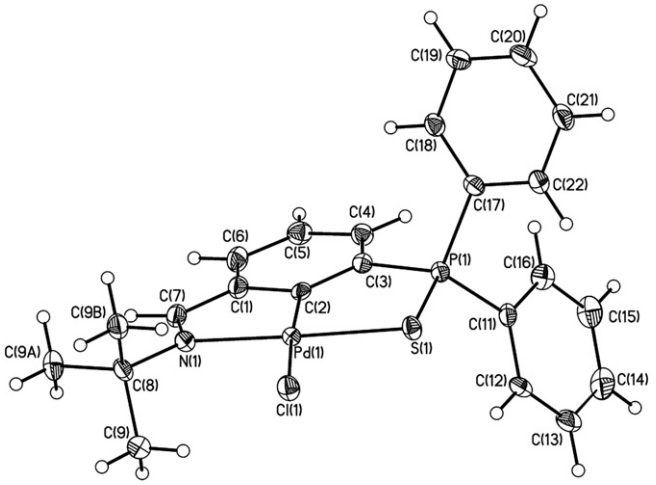


Fig. 2. General view of complex **3b** in representation of atoms by thermal ellipsoids (p = 50%).

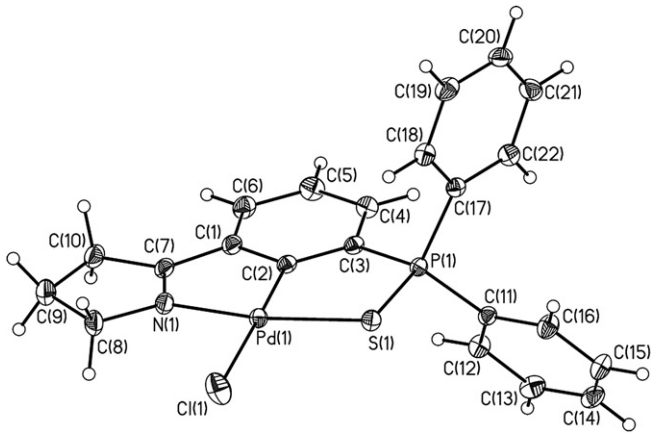


Fig. 3. General view of complex **3c** in representation of atoms by thermal ellipsoids ($p = 50\%$).

other *SCY* (*Y*═*S*′, *N*) hybrid pincer ligands bearing thiophosphoryl function [6–8] are much higher than those observed for thiophosphoryl-imino ligands **2a**–**e**. However, it is well known that the direct cyclopalladation of symmetric bis(imine) derivatives is often failed due to the kinetically preferred metalation at 4,6-positions of the central phenyl ring to give bis(monopalladacyclic) species [15,16]. This was observed for dialdiminobenzenes with Et [15a,b], CH_2Ph, *n*-Bu, Oct [15a], and tetrahydrofurfuryl [15c] substituents at the imine nitrogen atoms upon metalation with $Pd(OAc)_2$ in chloroform [15a] or toluene [15c] or with $Li_2[PdCl_4]$ in methanol [15b]. Only in the case of bis(*N*-cyclohexylimine) derivatives the pincer-type product was obtained in less than 15% yield under reflux with $Pd(OAc)_2$ in glacial acetic acid [9a]. Taking into account the strong dependence of the reaction time on the nature of an imine donating moiety for thiophosphoryl-imino ligands **2a**–**e**, it can be concluded that in our case the formation of pincer complexes **3a**–**e** is also complicated by the processes involving imine group (e.g., metalation at the C6-position of the benzene core, hydrolysis of an aldimine bond under the action of liberating HCl and so on). Although we did not manage to isolate and analyze the side products in any case, the comparison of the results on the direct cyclopalladation of *NCN* bis(imine) derivatives and hybrid pincer ligands with thiophosphoryl(oxy) and imine donating groups allowed to conclude that the yield of pincer complexes increases from <15% in the case of symmetric bis(imine) derivatives [9a] to 12–54% upon the replacement of one of the *N*-donor groups for the soft *S*-donor phosphine sulfide moiety, and further to 53–66% upon elongation of a thiophosphoryl coordination arm [6]. Therefore, *desymmetrization* of a pincer ligand structure via introduction of the second thiophosphoryl coordination arm instead of imine group facilitates the process of direct cyclometallation which may start either from the first coordination of the thiophilic palladium atom with the soft sulfur donor or from the simultaneous coordination of a metal with both donor centers. In other words, the *desymmetrization* of a pincer ligand obviously serves as a factor increasing the efficiency of direct cyclopalladation of the above ligands to produce pincer-type complexes.

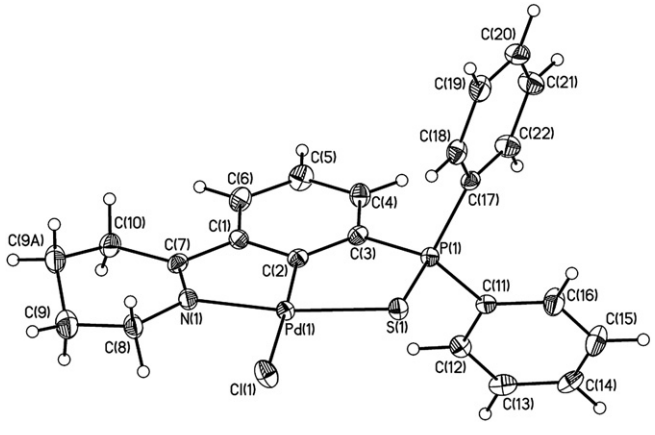


Fig. 4. General view of complex **3d_nosolv** (**3d_solv** is practically the same) in representation of atoms by thermal ellipsoids ($p = 50\%$).

2.2. Catalytic studies

It should be noted that before the beginning of our investigation, the data concerning the catalytic activity of pincer palladacycles with organothiophosphorus ligands were limited to a single publication of Le Floch [17] dealing with the palladium-catalyzed electrophilic allylation of aldehydes with allylstannanes using symmetric *SPS* pincer complex featuring a central λ^4-phosphinine unit and two lateral phosphine sulfide groups. As mentioned above, in our study we used the Suzuki–Miyaura cross-coupling as a model reaction to estimate the catalytic activity of *SCS*′ and *NCS* pincer palladacycles and elucidate if they could serve as true catalysts.

Therefore, complexes **3b**–**e** were tested in the cross-coupling between aryl bromides and phenylboronic acid similar to the study performed for the related complexes. Note that all experiments were carried out under the conditions previously successfully adopted for the other *NCS* pincer complexes: heating in DMF at 120 °C using K_3PO_4 as a base, which allowed us to make a correct comparison between the results both for the present series and complexes **I**–**IV**. Therefore, this test is an appropriate activity evaluation benchmark.

Fig. 5 outlines the results as kinetic evolution of the conversions of two electronically varied substrates, namely, 4-bromoacetophenone and 4-bromoanisole in time at the catalyst loading of 1 mol%. As is obvious, in the reaction of 4-bromoacetophenone (Fig. 5A) complex **3b** based on aldimine derivative appeared to be more active than its ketimino analogs **3c**–**e**, providing almost quantitative conversion of the substrate (97%) in 1 h. Among the ketimino analogs, complex **3c** with a five-membered azacycloalkene moiety was slightly more active than the other ones for the first hour of the reaction, while subsequently palladacycles **3c**–**e** equalized in their activity towards this easy-to-couple substrate. While passing to the electronically deactivated 4-bromoanisole (Fig. 5B), the structure–activity dependences for the complexes of the present series became more pronounced. Again, complex **3b** was the most active one, providing over 90% of the corresponding biaryl product in 2 h, while its ketimino counterpart **3c** with a five-membered azacycloalkene moiety led only to 67% conversion in 5 h. More sterically hindered complexes **3d**, **e** based on six- and seven-membered cyclic imine derivatives were almost inactive in the reaction with 4-bromoanisole at this concentration of a (pre)catalyst.

Using the most active complex of this study – aldimine derivative **3b** as a representative example, it was shown that the high conversion level of 4-bromoacetophenone could be reached within 1 h even when the amount of a catalyst precursor was reduced to 0.1 mol%. Although further reduction in the catalyst loading to 0.01 mol% significantly decelerates the coupling, the overall yield of the biaryl product in 5 h still remains rather good (84%) (Fig. 6A). However, further decrease of the catalyst loading up to 0.001 mol% led to a drop in the conversion to several percent only. For the less active substrate, 4-bromoanisole (Fig. 6B), unlike ketimino derivatives **3c**–**e** being inactive already at the 1 mol% concentration, complex **3b** showed rather high activity even at 0.1 mol% loading, although no coupling was observed upon further decrease (to 0.01 mol%) of the complex amount.

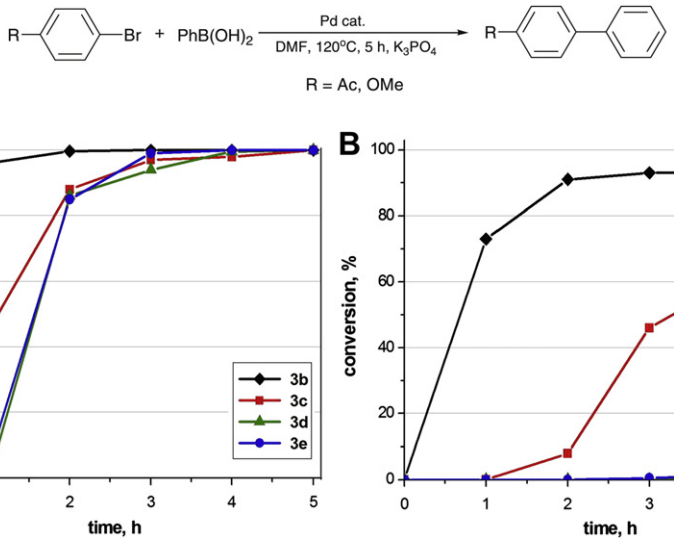


Fig. 5. Plots of conversion vs time for the couplings of 4-bromoacetophenone (A) and 4-bromoanisole (B) with phenylboronic acid catalyzed by 1 mol% of complexes **3b**–**e**.

The ^{31}P NMR monitoring of a complex's destiny after the catalytic cycle (the representative reaction was the coupling of 4-bromoacetophenone and phenylboronic acid at 1 mol% catalyst loading) revealed that the least active palladacycles **3d**, **e** decompose with the formation of only one phosphorus-containing product with δ_P at *ca*. 38 ppm, being situated in the region of free P═S derivatives, thereby, suggesting the rupture of the Pd–S and probably Pd–C bonds. The ^{31}P NMR spectrum for the reaction catalyzed by complex **3c**, having a five-membered azacycloalkene moiety, displayed along with the signal at ~38 ppm two singlets at ~26 and ~30 ppm. These species were tentatively assigned, as before in the case of complex **IV** [7], to the metalated and non-metalated phosphoryl-containing derivatives, presumably resulting from the transformation of the thiophosphoryl group into P═O moiety and thermally induced demetalation of the starting complex under the reaction conditions. At the same time, the ^{31}P NMR spectrum of the reaction mixture catalyzed by the most active complex **3b** showed an intensive signal at 31.2 ppm and a set of resonances in the range of 58.3–62.36 ppm – the region typical for metalated P═S-coordinated species. Thus, none of the pincer complexes **3b**–**e** serves as a catalyst in its starting form.

The mechanism of the cross-coupling reactions catalyzed by pincer complexes is a matter of considerable debate and both Pd(0)/Pd(II) and Pd(II)/Pd(IV) catalytic cycles were proposed [2e,18]. Motivated by conflicting reports, the detailed investigations of the stability and activity in catalysis of symmetrical *SCS* palladium pincer complexes formed by bis(thioether) ligands revealed that these compounds are not actual catalysts in the Heck cross-coupling and leached Pd(0) species following Pd(0)/Pd(II) mechanism [19] similar to 5,6-membered hybrid *SCS′* and *NCS* analogs in the Suzuki reaction [6,7]. At the same time, the stability of hybrid *SCS′* Pd complexes tested in the Suzuki reaction [8] gave evidence of Pd(II)/Pd(IV) mechanism.

The kinetic studies performed for the conversion of 4-bromoacetophenone (see Fig. 5A) revealed the sigmoidal kinetics and distinct induction period required for the generation of catalytically active species at least for ketimino derivatives **3c**–**e**. This fact substantiates our conclusion that these complexes serve only as precatalysts in contrast to the above mentioned 5,5-membered *SCS′* complexes [8] and *NCS* complex **IV** [7]. Moreover, the lack of activity of complexes **3b**–**e** under conditions of the so-called mercury drop test [20] indicates that the true catalysts in these systems have Pd(0) nature. Thus, addition of a few drops of Hg(0) to the reaction mixtures consisting of 4-bromoacetophenone, phenylboronic acid, K_3PO_4, and 0.1 mol% of complex **3b** or 1 mol% of complexes **3c**–**e** prior to heating led only to the trace amounts of a biaryl product in each case. Furthermore, when excess of Hg(0) was added at the reaction time of 30 min (**3b**) or 1.5 h (**3c**–**e**), the coupling terminated at the conversion level of 75–78%, 72%, 51–52%, and 33–35% in the case of complexes **3b**, **3c**, **3d**, and **3e**,

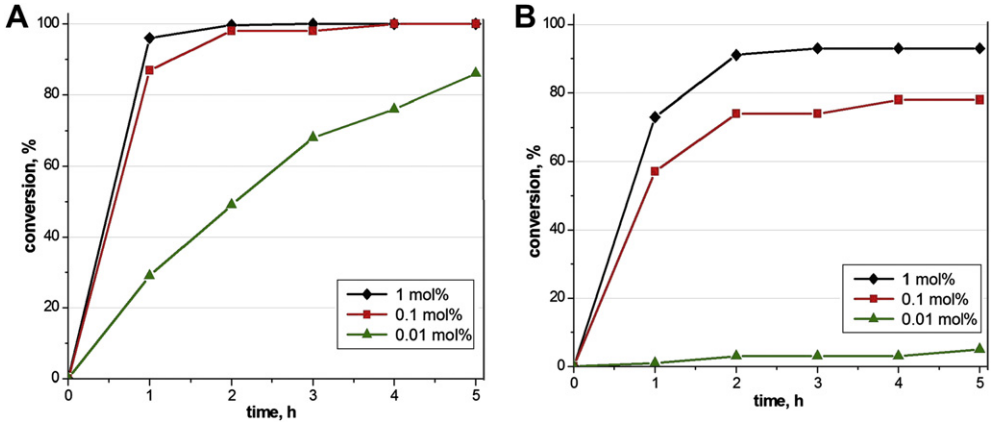


Fig. 6. Plots of conversion vs time for the couplings of 4-bromoacetophenone (A) and 4-bromoanisole (B) with phenylboronic acid catalyzed by different amounts of complex **3b**.

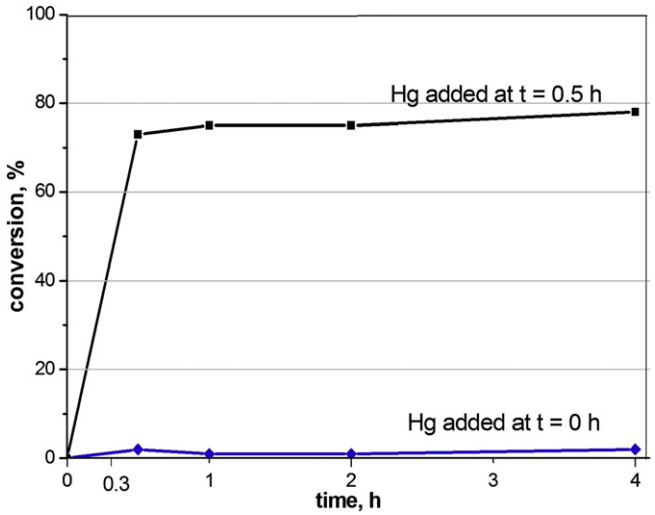


Fig. 7. Conversion of 4-bromoacetophenone as a function of time for the Suzuki coupling with 0.1 mol% of complex **3b** in the presence of Hg(0).

respectively (3–4 points up to $t = 4$ h). Fig. 7 illustrates the representative reaction catalyzed by complex **3b**.

In general, the formation of Pd(0) particles can occur via two pathways: homolytic cleavage (of the compound itself) or by intervention of one of the aryl reagents in the catalytic reaction via biaryl coupling. Previously, we have shown that *NCS* pincer complexes **II**–**IV** based on thiophosphorylated benzothiazoles can produce Pd(0) catalytically active species just by the reductive elimination of *ortho*-metalated species with an aryl group introduced by phenylboronic acid [21]. So we decided to check if a similar mechanism of formation of catalytically active Pd(0) particles is operative in the case of complexes **3b**–**e** (Scheme 4). Indeed, the heating of complex **3e** with 10 eq. of phenylboronic acid and 15 eq. of K_3PO_4 in DMF at 120 °C for 30 min led to the formation of Pd black and two phosphorus-containing compounds with δ_P at 71 ppm, diagnostic of the starting pincer complex, and 38 ppm - the signal characteristic of the free P=S derivatives which can be tentatively assigned to the biaryl product **6**. Note that the latter signal has already been detected in the ^{31}P NMR spectra of the reaction mixture after catalytic cycle (*vide supra*) confirming the formation of biaryl product over the Suzuki reaction. Note that for the related L–Pd–Ph species of type **5** derived from bis(phosphine) *PCP* pincer complexes [18a,b] no reductive elimination with the liberation of Pd(0) and formation of biaryls was detected, and therefore, the Pd(II)/Pd(IV) catalytic cycle was suggested. However, in the case of *NCS* pincer complexes **3b**–**e**, the hemilabile coordination may facilitate such a reductive elimination by decoordination of one of the ancillary arms in order to achieve the *ortho*-mutual disposition of two leaving phenyl fragments. In this respect, apparently the increase of steric hindrances in the series **3b** < **3c** < **3d** < **3e**, i.e., while passing from the aldimine-based derivative to its ketimine analogs arranged in order of increasing azacycloalkene ring sizes, corresponds to the increase of readiness of the reductive elimination of L–Pd–Ph species **5** to generate Pd(0) particles and biaryls **6**. If that is the case, the more efficient generation of Pd(0) particles by sterically crowded complexes **3d**, **e** can explain the lower activity of these precatalysts in the Suzuki reaction, since higher concentrations of the released Pd(0) particles would facilitate their agglomeration which, in turn, would lead to the formation of inactive species. Therewith, the generation of these catalytically active species in the systems with five-membered azacycloalkene complex **3c** and especially aldimine derivative **3b** occurs in a controlled manner, which is responsible for their higher activity. The controlled (constant and reluctant) *in situ* release of Pd(0) catalytically active species from their inactive precursors is a new concept in Pd(0)/Pd(II)-catalysis [22], which may become a powerful alternative to the conventional approaches that imply addition of various stabilizers for Pd(0) species (phosphine or carbene ligands, tetrabutylammonium bromide [23] and so on).

Table 1
NCS Pd(II) pincer complexes with organothiophosphorus ligands catalyzing the Suzuki cross-coupling of 4-bromoanisole and phenylboronic acid. Reaction conditions: DMF, 120 °C, 5 h, K_3PO_4.

Cat. load (mol%)	Yield of 4-methoxybiphenyl, %*									
	I		II		III	IV	3b	3c	3d	3e
	R = OMe	R = ^{t}Bu	X = O	X = NH						
1	86	91	98.5	99	61	97	93	67	3	2
0.1	99	84	100	99.5	81	92	78	–	–	–
0.01	0	3	92	98	92	77	5	–	–	–

*Estimated by GC.

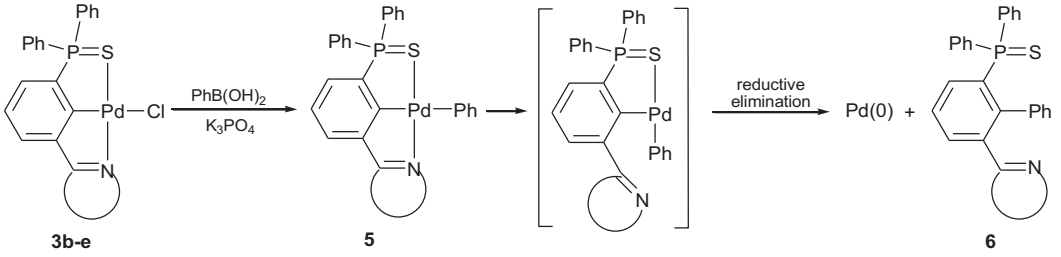
Finally, to compare the catalytic activity of *NCS* pincer Pd(II) complexes with organothiophoshorus ligands of different nature, Table 1 outlines the results obtained for the coupling of a representative substrate – 4-bromoanisole.

Independently of the nature of the true catalyst, a general tendency is obvious: the catalytic activity of *NCS* pincer-type palladacycles based on hemilabile thiophosphoryl-imino ligands increases while passing from the complexes with two fused five-membered metallacycles **IV**, **3b**–**e** to 5,6-membered complexes **I**–**III**, and from ketimine derivatives to their aldimine analogs, and further to the complexes having as a coordination arm the flexible heterocyclic imine moiety.

Finally, efforts in application of hybrid pincer-type palladacycles with organothiophosphorus ligands, including those of *NCS*-type, in different catalytic reactions where they could serve as true catalysts [24] are ongoing in our laboratory.

3. Conclusions

To summarize the results presented, we have devised the original synthetic approaches to novel hybrid pincer ligands bearing as



Scheme 4. Suppositional way of generation of Pd(0) species.

coordination arms either cyclic or acyclic imine moiety along with the thiophosphoryl group. The direct cyclopalladation of these ligands afforded *NCS* pincer palladium complexes with two five-membered fused metallacycles. The catalytic activity of the complexes obtained in the Suzuki coupling of phenylboronic acid with aryl bromides was shown to increase while passing from the ketimine derivatives **3d**, **e** to their analog **3c** with a smaller five-membered cyclic imine moiety, and further to complex **3b** formed by thiophosphorylated benzaldimine. This tendency was explained by the reduction of steric hindrances with reducing azacycloalkene ring sizes and, more profoundly, upon a transition to the aldimine derivative that led to the controlled release of Pd(0) particles.

4. Experimental

4.1. General remarks

All manipulations with organolithium compounds were carried out using flame-dried glass equipment and anhydrous solvents under argon, otherwise no precautions were taken to exclude air and moisture. Tetrahydrofuran was distilled from sodium/benzophenone, dichloromethane and acetonitrile were distilled over P_2O_5. 2-(3-Bromophenyl)-1,3-dioxolane [25] and 3-(diphenylthiophosphoryl)benzaldehyde **1** [10] were obtained according to the literature procedures. All other chemicals and solvents were used as purchased.

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 (^{1}H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were registered using the *J*MODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. The numeration for carbon atoms of the central benzene ring in the descriptions of the ^{1}H and ^{13}C NMR spectral data of ligands **2a**–**e** and complexes **3b**–**e** is in agreement with IUPAC nomenclature used for ligands **2a**–**e**. The same principle of numbering was used to describe the solid-state molecular structures 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 Magna-IR750 Fourier spectrometer (Nicolet) in KBr pellets, resolution 2 cm^{-1}, 128 scans. The assignment of absorption bands in the IR spectra was made according to ref. [26]. HRMS were obtained on a Varian MAT CH7A instrument with an ESI source at 70 eV. Melting points were determined with a MPA 120 EZ-Melt Automated Melting Point Apparatus and were uncorrected.

4.2. General procedure for the synthesis of benzaldimine ligands **2a, b**

A mixture of 3-(diphenylthiophosphoryl)benzaldehyde **1** (0.85 g, 2.6 mmol), the corresponding amine (2.6 mmol), and $MgSO_4$ (3.20 g, 2.7 mmol) in 9 mL of CH_2Cl_2 was refluxed for 5 h and left under ambient conditions for 3 days. The resulting mixture was filtered and evaporated to dryness to give quantitatively the desired ligands **2a**, **b** as viscous yellowish oils (95% pure according to the ^{31}P and ^{1}H NMR data), which were used in the synthesis of metal complexes without further purification.

4.2.1. N-{[3-(Diphenylthiophosphoryl)phenyl]methylidene}aniline, **2a**

^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$): δ 43.14 ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.70–7.80 (m, 4H, H_{Ar}), 7.47–7.62 (m, 13H, H_{Ar}), 8.17 (d, 1H, H(C6), $^3J_{HH}$ = 7.6 Hz), 8.20 (d, 1H, H(C2), $^3J_{HP}$ = 14.2 Hz), 8.44 (s, 1H, CH=N). IR (KBr, ν/cm^{-1}): 512(m), 614(w), 639(m) (P=S), 691(s), 715(s), 750(m), 1101(m), 1173(w), 1278(w), 1310(w), 1436(m), 1481(m), 1499(m), 1513(w), 1601(m), 1621(m) (C=N), 3050(w).

4.2.2. N-{[3-Diphenylthiophosphoryl]phenyl]methylidene}-tert-butylamine, **2b**

^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$): δ 43.25 ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.25 (s, 9H, $C(CH_3)_3$), 7.42–7.53 (m, 7H, H_{Ar}), 7.60 (dd, 1H, H(C4), $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 12.6 Hz), 7.72 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 13.4 Hz), 8.06 (d, 1H, H(C2), $^3J_{HP}$ = 13.7 Hz), 8.07 (d, 1H, H(C6), $^3J_{HH}$ = 6.9 Hz), 8.24 (s, 1H, CH=N). ^{13}C{^{1}H} NMR (100.61 MHz, $CDCl_3$): δ 29.33 (s, CH_3), 57.34 (s, $C(CH_3)_3$), 128.30 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.3 Hz), 128.37 (d, C5, $^3J_{CP}$ = 12.6 Hz), 129.51 (d, C6, $^4J_{CP}$ = 2.8 Hz), 131.39 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.8 Hz), 131.94 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 10.8 Hz), 132.17 (d, C3, $^1J_{CP}$ = 68.3 Hz), 132.37 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 87.4 Hz), 132.62 (d, C2, $^2J_{CP}$ = 11.4 Hz), 133.32 (d, C4, $^2J_{CP}$ = 10.5 Hz), 137.36 (d, C1, $^3J_{CP}$ = 12.0 Hz), 153.81 (s, C=N). IR (KBr, ν/cm^{-1}): 500(w), 517(m), 615(w), 642(s) (P=S), 691(s), 716(s), 750(w), 1103(m), 1203(w), 1367(w), 1436(m), 1480(w), 1573(vw), 1587(vw), 1642(m) (C=N), 2867(w), 2901(w), 2928(w), 2966(m), 3053(w).

4.3. Synthesis of (3-bromophenyl)(diphenyl)phosphine sulfide

To a solution of (3-bromophenyl)diphenylphosphine, prepared according to the literature procedure [12] from 1,3-dibromobenzene (5.4 g, 23 mmol), *n*-BuLi (1.6 M in hexane, 15 mL, 24 mmol), and Ph_2PCl (4.8 g, 22 mmol), in 30 mL of THF at −50 °C, sulfur (0.8 g, 25 mmol) was added portionwise. Then the reaction mixture was allowed to warm to room temperature under stirring and left overnight. The resulting solution was quenched with water and diluted with Et_2O. The organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness. The resulting brown semisolid residue was crystallized from EtOH followed by additional purification by silica gel column chromatography (EtOAc) to give the desired product as a white crystalline solid. Yield: 2.5 g (30%). Mp: 92–94 °C (benzene-hexane (1:3)). ^{31}P{^{1}H} NMR (161.97 MHz, $CDCl_3$): δ 42.76 ppm. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.30 (dt, 1H, H(C5), $^3J_{HH}$ = 7.8 Hz, $^4J_{HP}$ = 3.3 Hz), 7.44–7.48 (m, 4H, H_{Ar}), 7.51–7.57 (m, 2H, H_{Ar}), 7.59–7.64 (m, 2H, H_{Ar}), 7.70 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 13.5 Hz), 7.86 (d, 1H, H(C2), $^3J_{HP}$ = 13.2 Hz). Anal. Calcd. for $C_{18}H_{14}BrPS$: C, 57.92; H, 3.78; P, 8.30. Found: C, 57.74; H, 3.68; N, 8.23%.

4.4. General procedure for the synthesis of ketimine ligands **2c**–**e**

A solution of (3-bromophenyl)(diphenyl)phosphine sulfide (500 mg, 1.34 mmol) in 5 mL of THF was added dropwise to a stirred mixture of 2.5 M solution of *n*-butyllithium in hexane (0.59 mL, 1.47 mmol) and tetrahydrofuran (20 mL), keeping the temperature in the range from −80 to −90 °C. After stirring for 30 min at −80 °C, the reaction mixture was cooled to −90 °C and then a solution of the corresponding *N*-protected lactam (1.34 mmol: 149 mg of *N*-vinyl pyrrolidone, 270 mg of *N*-(diethoxymethyl)valerolactam or 187 mg of *N*-vinyl caprolactam) in 5 mL of THF was added dropwise. The cooling bath was removed and the temperature was allowed to rise to r.t. The resulting reaction mixture was quenched with saturated aqueous solution of NH_4Cl (5 mL), the organic phase was separated and slowly added (over 15 min) to aq. 3 M HCl (20 mL) under stirring at 40 °C. During the addition, the organic solvent was collected under reduced pressure (120 torr) using a short-path distilling head. Then the reaction mixture was stirred for 20 min at 40 °C and carefully made alkaline with aq. 10 M NaOH (15 mL) under cooling (ice bath). The water solution obtained was extracted with CH_2Cl_2 (2 × 15 mL), the combined organic layers were dried over K_2CO_3 and concentrated under reduced pressure. The

resulting residue was purified by column chromatography to give **2c**–**e** as viscous yellowish oils (eluent: hexane–EtOAc (from 5/1 to 1/1)).

4.4.1. 5-[3-(Diphenylthiophosphoryl)phenyl]-3,4-dihydro-2H-pyrrole, **2c**

Yield: 300 mg (61%). $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$): δ 43.43 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.98–2.06 (m, 2H, NCH_2CH_2), 2.89 (*t*, 2H, N=C–CH_2, $^3J_{HH}$ = 7.0 Hz), 4.05 (*t*, 2H, NCH_2, $^3J_{HH}$ = 7.3 Hz), 7.40–7.55 (m, 7H, H_{Ar}), 7.58–7.81 (m, 5H, *o*-H in P(S)Ph_2 + H_{Ar}), 8.08 (d, 1H, H(C6), $^3J_{HH}$ = 7.8 Hz), 8.19 (d, 1H, H(C2), $^3J_{HP}$ = 13.9 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 22.75 (NCH_2CH_2), 35.09 (N=C–CH_2), 61.76 (CH_2N), 128.69 (d, C5+*m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.1 Hz), 130.61 (d, C6, $^4J_{CP}$ = 2.9 Hz), 131.53 (d, C2, $^2J_{CP}$ = 11.1 Hz), 131.80 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.9 Hz), 132.3 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 10.5 Hz), 133.45 (d, C3, $^1J_{CP}$ = 85.0 Hz), 132.76 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 83.4 Hz), 133.91 (d, C4, $^2J_{CP}$ = 11.1 Hz), 135.15 (d, C1, $^3J_{CP}$ = 13.1 Hz), 172.53 (s, C=N). IR (KBr, ν/cm^{-1}): 511(m), 519(s), 613(w), 640(s) (P=S), 691(m), 698(m), 716(vs), 746(m), 753(m), 996(w), 1088(sh,w), 1100(s), 1174(w), 1325(m), 1416(w), 1436(s), 1479(w), 1568(vw), 1618(m) (C=N), 2856(w), 2921(w), 2968(w), 3051(vw). HRMS (ESI): calcd. for $C_{22}H_{20}NNaPS$ (M + Na) 384.0946, found 384.0953.

4.4.2. 6-[3-(Diphenylthiophosphoryl)phenyl]-2,3,4,5-tetrahydropyridine, **2d**

Yield: 195 mg (39%). $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$): δ 44.18 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.60–1.66 and 1.75–1.81 (both m, 2H + 2H, CH_2CH_2), 2.55 (*t*, 2H, N=C–CH_2, $^3J_{HH}$ = 6.3 Hz), 3.79 (*t*, 2H, CH_2N, $^3J_{HH}$ = 5.7 Hz), 7.41–7.52 (m, 7H, H_{Ar}), 7.60 (dd, 1H, H(C4), $^3J_{HH}$ = 7.9, $^3J_{HP}$ = 12.6 Hz), 7.70 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.8, $^3J_{HP}$ = 13.1 Hz), 7.97 (d, 1H, H(C6), $^3J_{HH}$ = 7.6 Hz), 8.17 (d, 1H, H(C2), $^3J_{HP}$ = 14.0 Hz). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 19.61 (s, CH_2), 21.74 (s, CH_2), 27.17 (s, CH_2), 50.07 (s, CH_2N), 128.44 (d, C5, $^3J_{CP}$ = 12.5 Hz), 128.74 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.5 Hz), 129.36 (d, C6, $^4J_{CP}$ = 2.9 Hz), 130.08 (d, C2, $^2J_{CP}$ = 11.5 Hz), 131.72 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.9 Hz), 132.34 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 10.5 Hz), 132.72 (d, C3, $^1J_{CP}$ = 83.4 Hz), 132.93 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 85.3 Hz), 133.25 (d, C4, $^2J_{CP}$ = 10.6 Hz), 140.66 (d, C1, $^3J_{CP}$ = 12.5 Hz), 165.34 (s, C=N). IR (KBr, ν/cm^{-1}): 507(m), 517(s), 615(w), 643(s) (P=S), 692(s), 697(s), 716(vs), 748(m), 756(w), 997(w), 1026(w), 1074(w), 1100(s), 1352(w), 1400(m), 1437(s), 1480(m), 1572(vw), 1586(vw), 1636(m) and 1646(w) (both C=N), 2857(w), 2939 (m), 3052(w). HRMS (ESI): calcd. for $C_{23}H_{23}NPS$ (M + H) 376.1283, found 376.1270.

4.4.3. 7-[3-(Diphenylthiophosphoryl)phenyl]-3,4,5,6-tertrahydro-2H-azepine, **2e**

Prior to purification by preparative chromatography (according to the general procedure) the residue was dried with toluene using a Dean–Stark trap. Yield: 187 mg (38%). $^{31}P\{^1H\}$ NMR (161.97 MHz, $CDCl_3$): δ 43.54 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.47–1.53 (m, 2H, CH_2), 1.56–1.61 (m, 2H, CH_2), 1.79–1.85 (m, 2H, CH_2), 2.74–2.77 (m, 2H, N=C–CH_2), 3.77–3.79 (m, 2H, CH_2N), 7.39–7.50 (m, 7H, H_{Ar}), 7.57 (dd, 1H, H(C4), $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 12.5 Hz), 7.70 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.3 Hz, $^3J_{HP}$ = 13.3 Hz), 7.88 (d, 1H, H(C6), $^3J_{HH}$ = 7.8 Hz), 8.12 (d, 1H, H(C2), $^3J_{HP}$ = 14.2 Hz). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 23.55 (s, CH_2), 25.99 (s, CH_2), 31.22 (s, CH_2), 31.49 (s, CH_2), 52.71 (s, CH_2N), 128.50 (d, C5, $^3J_{CP}$ = 12.5 Hz), 128.63 (d, *m*-C in P(S)Ph_2, $^3J_{CP}$ = 12.1 Hz), 129.98 (d, C6, $^4J_{CP}$ = 2.9 Hz), 130.47 (d, C2, $^2J_{CP}$ = 11.5 Hz), 131.72 (d, *p*-C in P(S)Ph_2, $^4J_{CP}$ = 2.9 Hz), 132.32 (d, *o*-C in P(S)Ph_2, $^2J_{CP}$ = 11.1 Hz), 132.83 (d, *ipso*-C in P(S)Ph_2, $^1J_{CP}$ = 92.5 Hz), 132.87 (d, C3, $^1J_{CP}$ = 85.5 Hz), 132.91 (d, C4, $^2J_{CP}$ = 10.5 Hz), 142.14 (d, C1, $^3J_{CP}$ = 12.5 Hz), 173.80 (s, C=N). IR (KBr, ν/cm^{-1}): 516(m), 614(w), 640(s) (P=S), 691(s), 717(s), 748(m), 997(w), 1058(w), 1102(s), 1253(w), 1343(w), 1398(w), 1436(s), 1480(w), 1572(vw), 1586(vw), 1630(m) (C=N), 2850(w), 2922(m), 3052(w). HRMS (ESI): calcd. for $C_{24}H_{25}NPS$ (M + H) 390.1440, found 390.1440.

4.5. General procedure for the synthesis of pincer complexes **3a**–**e**

A solution of $(PhCN)_2PdCl_2$ (50 mg, 0.130 mmol) and the corresponding ligand (0.137 mmol) in 7 mL of MeCN was refluxed for 1 (in the case of ligand **2e**), 3 (**2a**, **d**), 5 (**2b**) or 8 h (**2c**). To isolate palladacylces **3a**, **b**, **d**, the reaction mixture was evaporated to dryness, the residue was washed with Et_2O and purified by column chromatography (eluent: CH_2Cl_2). Note that due to the decomposition on silica gel, complex **3a** having a phenyl substituent at the nitrogen atom of the imine moiety was not isolated. Analytically pure samples of complexes **3b**, **d** were obtained by recrystallization from $CHCl_3$–EtOH (1:5) mixture. In the case of complexes **3c**, **e**, insoluble in acetonitrile, the resulting precipitate of pincer products were filtered off, washed with CH_3CN and Et_2O (**3c**) or DMSO–Et_2O (1:3) mixture (**3e**) and dried in *vacuo*.

4.5.1. [2-(tert-Butyliminomethyl)-6-(diphenylthiophosphoryl) phenyl]palladium chloride, **3b**

Yellow crystalline solid. Yield 34%. Mp: >240 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 63.58 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.64 (s, 9H, $C(CH_3)_3$), 6.96 (dd, 1H, H(C4), $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 8.9 Hz), 7.12 (dt, 1H, H(C5), $^3J_{HH}$ = 7.7 Hz, $^4J_{HP}$ = 4.3 Hz), 7.43 (d, 1H, H(C6), $^3J_{HH}$ = 7.6 Hz), 7.50 (dt, 4H, *m*-H in P(S)Ph_2, $^3J_{HH}$ = 7.9 Hz, $^4J_{HP}$ = 4.6 Hz), 7.61 (t, 2H, *p*-H in P(S)Ph_2, $^3J_{HH}$ = 7.4 Hz), 7.78 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 13.6 Hz), 8.07 (s, 1H, CH=N). IR (KBr, ν/cm^{-1}): 529(m), 598(s) (P=S), 690(s), 705(s), 721(s), 751(m), 806(w), 969(m), 997(w), 1103(s), 1107(s), 1184(m), 1197(m), 1241(w), 1368(m), 1436(s), 1481(w), 1546(m) (C=N), 1597(m), 2919(w), 2962(w), 3021(w). Anal. Calcd. for $C_{23}H_{23}ClNPPdS \cdot 0.1\ CHCl_3$: C, 52.32; H, 4.39; N, 2.64; S, 6.05. Found: C, 52.39; H, 4.51; N, 2.71; S, 5.88%.

4.5.2. [2-(3,4-Dihydro-2H-pyrrol-5-yl)-6-(diphenylthiophosphoryl) phenyl]palladium chloride, **3c**

Pale-yellow crystalline solid. Yield 54%. Mp: >270 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, DMSO-d_6): δ 64.39 ppm. ^1H NMR (400.13 MHz, DMSO-d_6): δ 2.13–2.20 (m, 2H, NCH_2CH_2), 2.97 (*t*, 2H, N=C–CH_2, $^3J_{HH}$ = 8.0 Hz), 4.11 (m, 2H, NCH_2), 7.04–7.25 (m, 6H, H_{Ar}), 7.32–7.56 (m, 3H, H_{Ar}), 7.70 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 8.1 Hz, $^3J_{HP}$ = 13.5 Hz). IR (KBr, ν/cm^{-1}): 516(m), 533(s), 597(s) (P=S), 620(w), 689(m), 704(m), 721(m), 751(m), 793(w), 998(w), 1103(vs), 1199(w), 1303(w), 1357(m), 1436(s), 1482(w), 1542(m) (C=N), 1568(w), 1602(w), 2864(w), 2925(w), 3052(w). Anal. Calcd. for $C_{22}H_{19}ClNPPdS$: C, 52.61; H, 3.81; N, 2.79. Found: C, 52.63; H, 3.71; N, 2.88%.

4.5.3. [2-(Diphenylthiophosphoryl)-6-(3,4,5,6-tetrahydro-2-pyridinyl)phenyl]palladium chloride, **3d**

Yellow crystalline solid. Yield 12%. Mp: >265 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 63.37 ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.78–1.87 (m, 4H, CH_2CH_2), 2.69–2.72 (m, 2H, N=C–CH_2), 4.18–4.21 (m, 2H, CH_2N), 6.96–7.00 (m, 1H, H(C4)), 7.09 (dt, 1H, H(C5), $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 4.5 Hz), 7.26 (d, 1H, H(C6), $^3J_{HH}$ = 7.6 Hz), 7.50 (dt, 4H, *m*-H in P(S)Ph_2, $^3J_{HH}$ = 7.7 Hz, $^4J_{HP}$ = 3.2 Hz), 7.60 (d, 2H, *p*-H in P(S)Ph_2, $^3J_{HH}$ = 7.4 Hz), 7.77 (dd, 4H, *o*-H in P(S)Ph_2, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 13.5 Hz). IR (KBr, ν/cm^{-1}): 514(m), 527(s), 554(w), 600(s) (P=S), 620(w), 691(s), 705(s), 721(m), 742(m), 753(m), 781(w), 997(w), 1111(s), 1158(w), 1185(w), 1261(w), 1329(w), 1365(m), 1399(m), 1436(s), 1480(w), 1546(m) (C=N), 1568(w), 1600(w), 2857(w), 2942 (m), 3051(w). Anal. Calcd. for

Table 2
Crystal data and structure refinement parameters for **3b**, **3c**, **3d_nosolv**, and **3d_solv**.

	3b	**3c**	**3d_nosolv**	**3d_solv**
Empirical formula	$C_{23}H_{23}ClNPPdS$	$C_{22}H_{19}ClNPPdS$	$C_{23}H_{21}ClNPPdS$	$C_{24}H_{22}Cl_4NPPdS$
Formula weight	518.30	502.26	516.29	635.66
T, K	100	100	100	100
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	$P4_3$	P-1	$P2_1/c$	P-1
Z	4	2	4	2
a, Å	9.0862(5)	8.4842(5)	9.012(5)	9.9915(4)
b, Å	9.0862(5)	9.1409(5)	27.864(16)	11.1299(4)
c, Å	26.6352(12)	14.0838(11)	8.944(5)	11.9419(5)
α, °	90.00	96.903(1)	90.00	78.3312(6)
β, °	90.00	98.314(1)	110.215(9)	76.9215(6)
γ, °	90.00	111.679(1)	90.00	89.4350(6)
V, Å^3	2199.0(2)	986.26(11)	2108(2)	1265.91(9)
D_{calc} (g cm^{-1})	1.566	1.691	1.627	1.668
Linear absorption, μ (cm^{-1})	11.42	12.7	11.91	13.15
F(000)	1048	504	1040	636
$2\theta_{max}$, °	57	58	58	58
Reflections measured	12807	11807	16628	15295
Independent reflections	4995	5235	5600	6727
Observed reflections [with $I > 2\sigma(I)$]	4829	4908	4691	6014
Parameters	253	244	253	289
R1	0.0291	0.0197	0.0364	0.0279
wR2	0.0666	0.0508	0.0803	0.0660
GOF	1.009	1.009	1.009	1.009
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.729/−0.480	0.566/−0.506	1.167/−0.803	1.041/−0.576

$C_{23}H_{21}ClNPPdS \cdot 0.5\ CHCl_3$: C, 49.00; H, 3.76; N, 2.43. Found: C, 48.81; H, 3.67; N, 2.34%.

4.5.4. [2-(Diphenylthiophosphoryl)-6-(3,4,5,6-tetrahydro-2H-azepin-7-yl)phenyl]palladium chloride, ***3e***

Pale-yellow crystalline solid. Yield: 34%. Mp: >305 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 68.53 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): 1.60–1.70 (m, 4H, CH_2CH_2), 1.87–1.89 (m, 2H, CH_2), 2.83–2.87 (m, 2H, N=C–CH_2), 4.26–4.29 (m, 2H, CH_2N), 7.03 (dd, 1H, H(C4), $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 8.5 Hz), 7.14 (dt, 1H, H(C5), $^3J_{HH}$ = 7.4 Hz, $^4J_{HP}$ = 4.8 Hz), 7.33 (d, 1H, H(C6), $^3J_{HH}$ = 7.5 Hz), 7.49–7.54 (m, 4H, *m*-H in $P(S)Ph_2$), 7.60–7.65 (m, 2H, *p*-H in $P(S)Ph_2$), 7.73 (dd, 4H, *o*-H in $P(S)Ph_2$, $^3J_{HH}$ = 7.2 Hz, $^3J_{HP}$ = 13.6 Hz). IR (KBr, ν/cm^{-1}): 527(s), 547(w), 599(s) (P=S), 619(w), 691(s), 704(m), 720(m), 751(m), 790(w), 998(w), 1076(w), 1108(vs), 1197(w), 1276(w), 1354(m), 1390(m), 1436(vs), 1482(w), 1543(m) (C=N), 1588(m), 2857(w), 2931(m), 2983(w), 3048(w). Anal. Calcd. for $C_{24}H_{13}ClNPPdS \cdot 0.25$ DMSO: C, 53.51; H, 4.49; N, 2.55. Found: C, 53.60; H, 4.28; N, 2.55%.

4.6. Crystal structure determination and data collection

Crystals of complexes **3b**–**d** suitable for X-ray diffraction study were grown by recrystallization from CH_2Cl_2–Et_2O (1:4) (**3b**), CH_2Cl_2–CH_3CN (1:1) (**3c**), and $CHCl_3$–EtOH (1:5) (**3d**). The X-ray diffraction experiments were carried out with a SMART APEX2 CCD diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 100 K. The structures were solved by direct methods and refined by the fullmatrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation within the riding model with the Uiso(H) parameters equal to 1.2 Ueq(*C*i), where U(*C*i) are the equivalent thermal parameters of the carbon atoms to which the corresponding H atoms are bonded. Crystal data and structure refinement parameters for **3b**, **3c**, **3d_nosolv**, and **3d_solv** are given in Table 2. All calculations were performed using the SHELXTL software [27].

4.7. Catalytic studies

In a typical experiment a solution of 0.25 mmol of aryl bromide, 0.375 mmol of $PhB(OH)_2$, 0.5 mmol of K_3PO_4, and the mentioned amount of the corresponding palladium complex (used as titrated solutions in DMF) in 1 mL of DMF was heated at 120 °C from 30 min up to 5 h. To determine the conversion of aryl bromide, aliquots of the reaction mixture, taken after the specified time of heating, were treated with water (3–4 ml), extracted with benzene, and analyzed by GC. Hg(0) poisoning experiments were performed according to ref. [28] with 300 eq. of Hg relative to the metal complex. Hg was added either at t = 0 min or 30 min to the reaction mixture.

Appendix A. Supplementary material

Complete crystallographic data for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre CCDC 862466 (**3b**), 862467 (**3c**), 862468 (**3d_nosolv**), and 862469 (**3d_solv**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.03.029.

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