5,6-Membered palladium pincer complexes of 1-thiophosphoryloxy-3-thiophosphorylbenzenes. Synthesis, X-ray structure, and catalytic activity†

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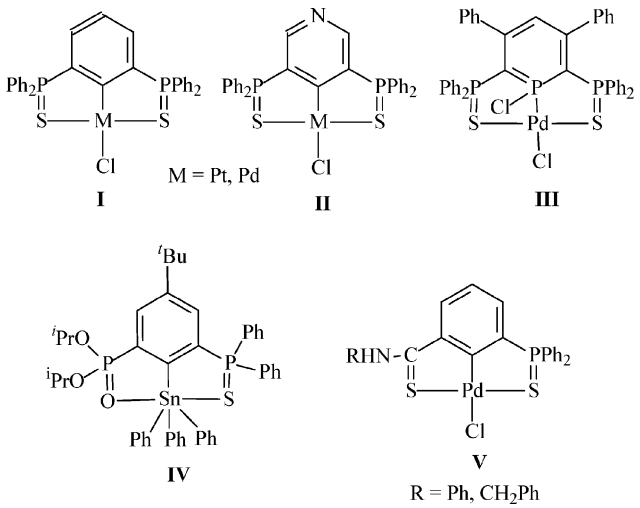
Novel unsymmetrical ligands, 1-thiophosphoryloxy-3-thiophosphorylbenzenes **3a–d**, bearing phosphine sulfide and thiophosphoryloxy moieties as coordinating sites, were found to undergo cyclometalation at the C-2 position of the central benzene ring in a reaction with bis(benzonitrile)palladium dichloride affording rare examples of nonsymmetrical pincer complexes, namely [2-{(thiophosphoryl)oxy}-6-(diphenylthiophosphoryl)phenyl]palladium chlorides **4a–d**, containing 5- and 6-membered fused metallacycles with κ^3-*SCS′*-coordination. Molecular structures of the complexes were characterized by X-ray diffraction. These complexes demonstrated high catalytic activity for the Suzuki cross-coupling reactions of aryl bromides with phenylboronic acid.

Introduction

Pincer complexes containing anionic six-electron donor ligands of the type YCY are of unfailing interest due to their feasible structural modifications with multiple choices of donor atoms and their substituents (Y = NR_2, SR, PR_2, OPR_2, *etc.*), high stability, and remarkable catalytic activities with high TON and TOF values in various processes such as dehydrogenation of alkanes, reduction of ketones, aldol condensation, cross-coupling reactions and so on.[1] However, applications of pincer complexes are not restricted only by catalysis. They may be used as building-blocks for the synthesis of natural compounds[2] and homo- and heterometallic dendrimers,[3,4b–d,g] chemosensors for small molecules (*e.g.* SO_2),[4] biomarkers for peptides,[5] liquid crystal materials,[6] *etc.*

The most common are symmetrical pincer palladium and platinum complexes of PCP, NCN, or SCS types having two identical donor groups and two equivalent five-membered metallacycles. Nevertheless, nonsymmetrical (hybrid) YCY′ pincer complexes possess a wider area of practically important properties as they can combine the properties of a few symmetrical systems and manifest unique reactivity and non-typical features compared with their symmetric analogues. The routes of desymmetrization comprise changes in donor moieties (introduction of different substituents at the same donor atoms or different donor groups), variation of linkers (changing of their length and nature), and central core (shifting of the central aromatic core to give CYY′ system, application of different aromatic rings, and moieties bearing the C(sp^2) vinyl carbon atom). Such alterations allow additional possibilities of controlling steric and electronic properties of the pincer system in total. Among such nonsymmetrical pincer complexes, those bearing metallacycles of different size are rather scarce.[13]

It should be mentioned that even though thiophosphoric acid derivatives and phosphine sulfides are known to form complexes with a variety of metals where the coordination bond is formed *via* the soft sulfur atom of thiophosphoryl group,[7] there are only a few reports dealing with the application of P=S containing compounds in the synthesis of pincer-type complexes.[8–10] For example, 1,3-bis(diphenylthiophosphoryl)benzene,[8] 1,3-bis(diphenylthiophosphoryl)pyridine,[9] and 2,6-bis(diphenylthiophosphoryl)phosphinane[10] form symmetric platinum and palladium pincer complexes **I–III** (Scheme 1). Among hybrid P=S pincer complexes known are only tin complex **IV**[11] of 1-diphenylthiophosphoryl-3-diisopropoxyphosphoryl-5-*tert*-butylbenzene and palladium complexes **V**[12] of 3-diphenylthiophosphorylbenzoic acid thioamides reported by us recently.



Scheme 1 Representatives of thiophosphoryl pincer complexes.

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† Electronic supplementary information (ESI) available: Tables giving complete data collection parameters, atomic coordinates, bond distances and angles, and thermal parameters for **3b**, **4a**, **4c**, as well as the schematic view of complex **4c** with the central fragment shown as a superposition of two isomers. CCDC reference numbers 730242–730244. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b907644a

SCS′-Complexes **V** demonstrated high catalytic activity for the Suzuki cross-coupling of aryl bromides with phenylboronic acid and exhibited the luminescence at 77 and 300 K both in solid state and in solutions.

In this communication we report the convenient synthesis of 1-thiophosphoryloxy-3-thiophosphorylbenzenes suitable as pincer ligands and their nonsymmetrical palladium complexes with fused 5- and 6-membered metallacycles proved to be active catalysts for the Suzuki reaction.

Results and discussion

Synthesis of ligands

The synthetic route of novel SCS′-ligands was elaborated starting from commercially available 3-bromoanisole (Scheme 2). Thus, reaction of the Grignard reagent prepared from this compound with diphenylchlorophosphine afforded (3-methoxyphenyl)diphenylphosphine converted *via* sulfur addition to the corresponding phosphine sulfide **1**. In contrast to the literature data,[14] the synthesis was performed as a one-pot process using the original procedure. Treatment of the phosphine sulfide **1** with pyridine hydrochloride resulted in formation of thiophosphorylated phenol **2** in a reasonably good yield (69%). It should be noted that application of hydrobromic acid typically used for removing of methoxy protective group, yielded 3-diphenylphosphorylphenol, *i.e.* the phosphorylated analogue of **2** bearing the P(O) group instead of the P(S) one. Further thiophosphorylation of 3-diphenylthiophosphorylphenol **2** as a single key precursor allowed a variety of SCS′-pincer-type ligands **3a–d** bearing different substituents at the phosphorus atom of the thiophosphoryloxy moiety to be obtained.

As mentioned above, thiophosphorylation of phenol **2** was carried out by thiophosphorus acid chlorides bearing different substituents at the phosphorus atom, namely thiophosphoric, thiophosphonic and thiophosphinic acid chlorides (Scheme 2). Depending on the nature of this reactant, different reaction conditions were used. To avoid hydrolysis of thiophosphorylating agents, anhydrous conditions were used for the synthesis of tetraalkyldiamido- and (butoxy)methyl-substituted ligands **3a**, **3b** and **3d**. At that, the reaction of more active methylthiophosphonic acid chloride in benzene in the presence of triethylamine as a base resulted in **3d** with a yield of 93%, while thiophosphorylation using tetraalkyldiamido-derivatives did not afford reasonable yields of the desired products **3a,b** under these conditions. The optimized conditions providing the desired **3a,b** in 56–58% yields comprised of using of triethylamine as a solvent and elevated temperature. In the case of the most water-resistant $Ph_2P(S)Cl$, the reaction was performed under phase-transfer catalysis (PTC) conditions using 10% aq. NaOH/benzene system and triethylbenzylammonium chloride (TEBA) as a catalyst.

The structures of 1-thiophosphoryloxy-3-thiophosphorylbenzenes **3a–d** were unambiguously confirmed by NMR and elemental analysis data. The ^{31}P NMR spectra of **3a–d** show two singlets at *ca.* 43 ppm (region typical for phosphine sulfide group) and in the range of 76.6–94.4 ppm (phosphorus resonances of $OP(S)R^1R^2$ moiety). An interpretation of ^1H NMR spectra in the aromatic proton region is complicated by the presence of signals of several peripheral phenyl rings while the resonances of alkyl protons of NEt_2, Me, OBu and NMe_2 groups can be easily identified. In contrast, the signals of carbon atoms of the central benzene core in the ^{13}C NMR spectra of **3a–d** do not overlap with the resonances of peripheral benzene C_{Ph}-atoms even in the case of compound **3c** containing five phenyl rings.

The structure of **3b** was confirmed by a single crystal X-ray diffraction analysis. In line with the molecular geometry examination, the bond lengths and angles of **3b** (Fig. 1) fall into the range typical for compounds of this type. The mutual disposition of P=S groups is a *transoid* one. Although the torsion angle S(1)P(1)P(2)S(2) is only 47.1(2)°, P(1)–S(1) and P(2)–S(2) lines are directed away from the central phenyl cycle into the different directions. Such a configuration of the **3b** molecule in the crystal is stabilized by a number of relatively weak P=S···H

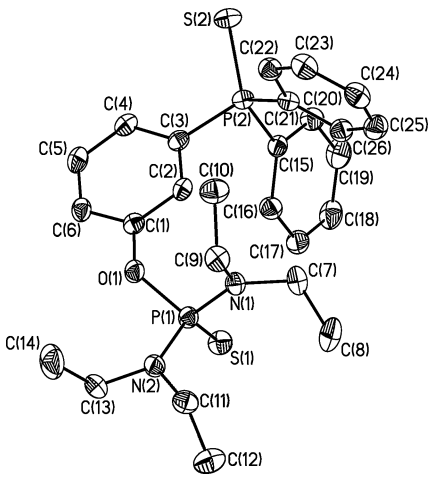
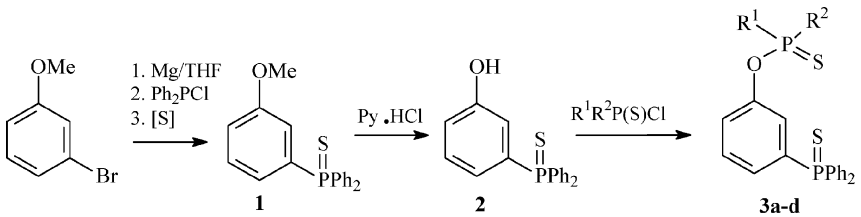
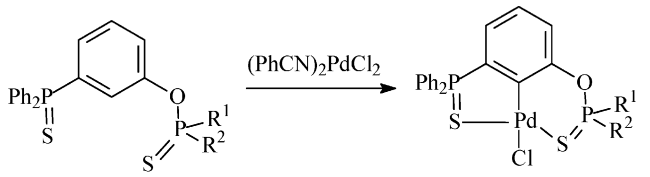


Fig. 1 General view of compound **3b** in representation of atoms *via* thermal ellipsoids ($p = 50\%$). The main bond lengths (Å) and angles (°): P(1)–S(1) 1.9392(9), P(2)–S(2) 1.9555(9), P(1)–O(1) 1.6289(16), O(1)–C(1) 1.389(2), P(2)–C(3) 1.817(2), C(1)–C(2) 1.388(3), C(2)–C(3) 1.395(3); C(1)–C(2)–C(3) 119.11(19), O(1)–P(1)–S(1) 112.49(7), C(3)–P(2)–S(2) 113.61(8).



Scheme 2 Synthesis of 1-thiophosphoryloxy-3-thiophosphorylbenzenes **3a–d**.



3a-d **4a-d**

R^1=R^2= NMe_2 (**a**), NEt_2 (**b**), Ph (**c**); R^1=Me, R^2=OBu (**d**)

Scheme 3 Cyclopalladation of 1-thiophosphoryloxy-3-thiophosphoryl-benzenes.

contacts (S···C 3.656(4)–3.918(4) Å). The latter leads to the formation of corrugated layers, two molecules thick, which are further assembled into 3D framework by stacking interaction between central rings (C···C 3.376(4) Å).

Synthesis of palladium pincer complexes

The reaction of 1-thiophosphoryloxy-3-thiophosphorylbenzenes **3a–d** with $(PhCN)_2PdCl_2$ readily proceeded as cyclopalladation of the central phenyl ring to form the corresponding SCS′-pincer palladium complexes **4a–d** having in the molecule fused 5- and 6-membered palladacycles (Scheme 3). Such direct cyclopalladation of **3a–d** was performed either in benzene solution under reflux for 2 h or in dichloromethane (DCM) or its mixture with methanol (1 : 1) under ambient conditions over a few days.

For the synthesis of dialkylamidophosphoryloxy derivatives **4a,b** the reaction in benzene was found to be more convenient due to the high rate of cyclopalladation comparing with the reaction in CH_2Cl_2. When the diphenylthiophosphoryloxy analogue **3c** was used as a ligand, the yield of the corresponding complex **4c** estimated by ^{31}P NMR spectra of reaction mixtures (C_6H_6, reflux, 2 h or CH_2Cl_2, 20 °C, 7 days), reached only *ca.* 20%. However, addition of methanol to dichloromethane solution allowed not only increasing the yield of pincer-type product **4c**, but accelerating the cyclopalladation too. Thus, the reaction of $(PhCN)_2PdCl_2$ with the ligand **3c** in CH_2Cl_2–MeOH mixed solvent afforded the corresponding complex **4c** in the yield of ~70% over 24 h. The complex **4d** bearing the (butoxy)methylthiophosphoryloxy group was obtained only under mild conditions (dichloromethane solution, 5 days) in the yield of 19% while heating in benzene or addition of methanol to CH_2Cl_2 solution lead to the decomposition of the ligand **3d**. In total, when cyclopalladation was performed in dichloromethane solution the yields of the corresponding complexes decreased in the range **4b** > **4a** > **4c** > **4d** depending on the substituents at the phosphorus atom of the thiophosphoryloxy moiety.

Moreover, the low rate of cyclopalladation in CH_2Cl_2 allowed the process of pincer-type complexes formation to be followed. Thus, initially the ^{31}P NMR spectra of the reaction mixtures display a few pairs of signals corresponding to thiophosphoryloxy and phosphine sulfide groups of the intermediate species (typically 3 pairs) along with the corresponding pair of signals of a ligand. According the distribution of the integral intensities of the signals, two intermediate complexes dominated in reaction mixtures (*e.g.* 30 and 35%, respectively, in the case of **3c** as a starting ligand), the amount of non-coordinated ligand did not exceed 10–15%. For the intermediate complexes the signals in the thiophosphoryloxy group region were either upfield or downfield shifted for 2.5–4 ppm while those for phosphine sulfide groups were downfield shifted for 0.5–2.5 ppm. In time, these signals transform to the single pair of singlets assigned to the final pincer-type complexes. The shifting of phosphorus resonances indicates the coordination by metal center of sulfur atoms of a ligand.[8–10,12]

As for the structure of these intermediate compounds, one can suggest the initial formation of dimeric complexes of 1 : 1 composition with the μ-bridged chlorine atom, which may have different structures. Namely, in these complexes Pd may be coordinated either *via* the same or the different sulfur atoms in the ligand. The signals also may be attributed to complexes $PdCl_2L_2$ of 1 : 2 composition (rather *trans* than *cis* ones) and non-cyclopalladated species with bridged Pd coordination *via* two sulfur atoms of the same ligand being the precursor of final pincer products. Unfortunately, all efforts were futile for the isolation of such intermediate species in an individual form. Note also that during the slow reaction in DCM the precipitation of $PdCl_2$ was observed. In fact, transformation of μ-bridged complexes $[PdCl_2L]_2$ to $PdCl_2L_2$ species with liberation of $PdCl_2$ was reported in literature.[15] Indeed, if 2 equivalents of the ligand were used precipitation of $PdCl_2$ was not observed as was demonstrated using formation of **4c** as a representative example.

The structure of the complexes **4a–d** was assigned by NMR (^1H, ^{31}P and ^{13}C), IR spectra and elemental analysis data. As compared with the corresponding free ligands, in the ^{31}P NMR spectra of complexes the signals of thiophosphoryloxy moieties were shifted upfield to 8.7–13.1 ppm in contrast with the downfield shifted (to 1.2–4.4 ppm) signals of the phosphine sulfide groups. As mentioned above, the shifting of phosphorus resonances unambiguously indicates the coordination by metal center of both sulfur atoms of phosphine sulfide groups.[8–10,12] The ^1H and ^{13}C NMR spectra of complexes **4a–d** confirmed the occurrence of C-metalation: the resonance of the C(2)-*H* proton was absent, and the signal of the C(2)-carbon atom in the ^{13}C NMR spectra was strongly shifted downfield compared to the signal in the corresponding free ligand. It should be mentioned that signals of C(1)- and C(3)-carbon atoms in palladacycles were also downfield shifted by ~14 and ~5 ppm, respectively, with regard to their resonances in the parent ligands. Moreover, the ^{13}C NMR data for complexes **4a,b** show clearly that metalation changes not only the chemical shifts of C(1), C(2), and C(3) but also J_{PC} coupling constants which increase significantly. Thus, the $^1J_{PC(3)}$ coupling constant averaged *ca.* 85 Hz for the starting ligands **3a,b** increases to approximately 105.5 Hz for the corresponding complexes; a $^3J_{PC(2)}$ coupling constant between the C2-carbon and the phosphorus atom of the thiophosphoryloxy moiety being equal to 11.8 Hz in **3b** increases up to 22.5 Hz in **4b**. The coupling constants between the C(1) atom and both phosphorus nucleus also changed from 5.3–5.9 Hz to 7.2–8.1 Hz in the case of $^2J_{PC(1)}$ and from 15.8–16.1 Hz to 21.3–22.0 Hz for $^3J_{PC(1)}$. Also, it should be noted that the signals of protons of central benzene ring in the ^1H NMR spectra of pincer complexes **4a–d** can be easily interpreted even in the case of compound **4c**, which contains four additional peripheral phenyl rings, as they are significantly shifted upfield and do not overlapped with the signals of the other aromatic protons.

X-Ray diffraction analysis performed for **4a** and **4c** unambiguously confirmed formation of palladium pincer complexes. According to the X-ray data the bond lengths and angles in **4a**

(Fig. 2) and **4c** (Fig. 3) are close to those for the known palladated SCS and SCS′-ligands. It should be mentioned that due to strong disorder at two positions of the central core of the complex **4c** in the crystal (Fig. 1S), the details of palladium-to-ligand binding will be mainly discussed for **4a**. The P=S groups in both **4a** and **4c** become longer by 0.04 Å upon the complex formation, while the C–C(2) bonds change only in a minor way. However, the value of C(1)–C(2)–C(3) varies from 119.11(19)° in free **3b** ligand to *ca.* 114° in the complexes. The analogous tendency was also observed for the C(3)P(2)S(2) angle, which decreases to 105.65(8) in **4a** and 101.6(2)° in **4c** as compared with 113.61(8)° for **3b**. On the other hand, the binding of metal to the second sulfur atom does not lead to such a distortion of the SPO angle.

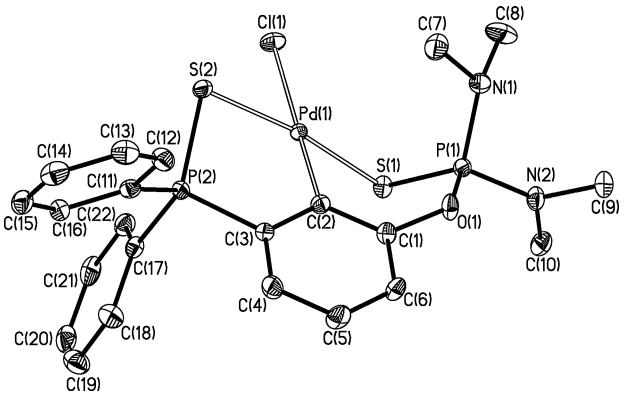


Fig. 2 General view of compound **4a** in representation of atoms *via* thermal ellipsoids (p = 50%). The main bond lengths (Å) and angles (°) are: Pd(1)–Cl(1) 2.4013(6), Pd(1)–S(1) 2.3376(6), Pd(1)–S(2) 2.3393(6), Pd(1)–C(2) 2.008(2), P(1)–S(1) 1.9782(8), P(2)–S(2) 2.0065(8), C(1)–C(2) 1.399(3), C(2)–C(3) 1.406(3); C(1)–C(2)–C(3) 114.0(2), O(1)–P(1)–S(1) 111.21(7), C(3)–P(2)–S(2) 105.65(8).

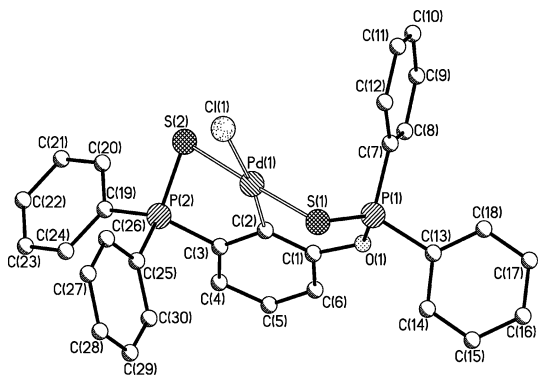


Fig. 3 General view of compound **4c**. The disordering is omitted for clarity (see Fig. S1) The main bond lengths (Å) and angles (°) are: Pd(1)–Cl(1) 2.3742(10), Pd(1)–S(1) 2.3298(10), Pd(1)–S(2) 2.3428(10), Pd(1)–C(2) 2.055(7), P(1)–S(1) 1.9914(13), P(2)–S(2) 1.9738(14), C(1)–C(2) 1.386(9), C(2)–C(3) 1.410(9); C(1)–C(2)–C(3) 114.1(6), O(1)–P(1)–S(1) 115.99(15), C(3)–P(2)–S(2) 101.6(2).

Unlike the 5,5-membered palladium complexes **I–V** having two P=S groups[8,9] or P=S and C=S groups[12] bonded directly with the central phenyl ring, the P=S bonds in **4a,c** significantly deviate from the plane of the central core. The latter is reflected in significant puckering of both 5- and 6-membered metallacycles. Indeed, in **4a** the 5-membered cycle is characterized by an envelope conformation with the deviation of S(2) atom from the plane of Pd(1), P(2), C(2) and C(3) atoms by as much as 1.02 Å, and the 6-membered cycle by a conformation that can be described as highly distorted chair with the deviation of S(1) atom from the plane of Pd(1), P(1), O(1), C(1), C(2) by 1.32 Å. The nonplanarity of Pd-containing cycles in comparison with those, for example, in **V**,[12] lead in turn to the distortion of the palladium square-planar configuration with the dihedral angle between S(2)Pd(1)C(2)Cl(2) and S(1)Pd(1)C(2)Cl(2) planes equal to 9.4°. In other words, the PdSSClC square is characterized by folding along Cl(1)Pd(1)C(2) line with the deviation of S(2) and S(1) atoms from the corresponding Pd(1)S(1)Cl(1)C(2) and Pd(1)S(2)Cl(1)C(2) planes equal to 0.38 Å. Furthermore, the significant puckering of the above palladacycles leads to the rather high value (33.9°) of the dihedral angle between PdSSClC square and the central aromatic cycle. Despite this fact, the Pd(1)–C(2) bond lengths are equal in **4a** and known symmetrical 5,5-membered complex **II**[8] (2.008(2) and 2.006 Å, respectively). It should be mentioned that in hybrid 5,5-membered complexes **V** the corresponding Pd(1)–C(2) bond lengths were slightly shorter (1.973(1) Å).[12]

Analysis of supramolecular organization in crystals of these complexes revealed that molecules **4a** and **4c** exhibit the similar binding pattern despite the difference in the nature of substituents at the phosphorus atom of the O–P=S moiety. In both cases there are bifurcated H–C···Cl bond (C···Cl 3.573–3.676 Å) and one C–H···S (C···S 3.638 in **4a** Å and 3.583 Å in **4c**) contact of comparable strength. In addition, the presence of aromatic fragments in two complexes allows the occurrence of weaker π···π and C–H···π contacts.

Thus, summarizing the results of XRD data, we can mention that the presence of the six-membered CCOPSPd cycle leads to an increase of strain that is reflected in distortion of the palladium configuration.

Catalytic studies

While the catalytic application of symmetrical pincer complexes is well studied and actually presents the most important sphere of their usage, there is far less information about the catalytic activity of their unsymmetrical analogues. Palladacycles in general and pincer palladium complexes in particular are known to be quite efficient catalyst precursors in the palladium catalyzed Suzuki cross-coupling of arylhalides with phenylboronic acids,[1g] being one of the most powerful methods for C_{Ar}–C_{Ar} bond formation. Because of the commercial availability of the starting materials, the relatively mild reaction conditions required, the tolerance of a broad range of functionalities, easy handling and removal of the nontoxic boron-containing by-products, as well as the possibility of using water as a solvent (or co-solvent) and solid-support materials, this cross-coupling reaction has gained prominence in recent years at an industrial level, mainly in the synthesis of pharmaceuticals and fine chemicals. Recent advances also involving non-conventional methodologies that have been applied to the Suzuki reaction are well documented in the literature.[16] In fact, the Suzuki coupling involving bromo- and iodo-arenes substituted with electron-withdrawing groups is promoted by almost any palladium salt or complex (*e.g.* palladium acetate[17]). The main challenges in this cross-coupling pertain to the use of less reactive chloro- and bromo-arenes bearing electron donating

groups and in these cases only a few pincer complexes displayed catalytic activity. It is noteworthy that the best results for coupling of chloro-arenes were obtained just with phosphorus containing pincer complexes or with palladacycles modified by carbenes. That was related to the extra stability provided by these ligands towards the low-ligated catalytically active Pd(0) species involved in catalytic cycle.[1g]

Therefore, the complexes obtained were examined as the catalytic precursors in a standard Suzuki reaction. This selection gives us the possibility for comparison to other above mentioned *SCS*-pincer complexes. All experiments were carried out in DMF solution at 120 °C for 5 h similar to the procedure suggested for testing of pincer palladium complexes formed by 1,3-bis[(*tert*-butylthio)methyl]benzene.[18] In all cases the normal dependence on the electronic properties of the substituent X at the aryl bromide was observed and the complete conversions were reached for activated substrates using 1 mol% of **4a–d**. In the range of complexes tested, complexes **4a,b** bearing dialkylaminothiophosphoryloxy group demonstrated higher activity, with **4b** being the best one. This fact may be explained by the difference in electronic factors of the ligands. However, as electronic factors in **4a**,**b** are almost identical, the higher activity of **4b** should be attributed to steric factors, namely more bulky substituents on the nitrogen atoms in **4b** compared with **4a**.

It should be noted that preformed palladacycles **4** demonstrated higher catalytic activity comparing with catalysts formed *in situ* from the corresponding free ligand and $(PhCN)_2PdCl_2$. Thus, **4b** afforded 93% yield of 4-methoxy-1,1′-biphenyl (see Table 1) while catalysts formed *in situ* in DCM or DMF over 30 min provided 68% and 56% yield of the product respectively. This fact can be easily explained by slow rate of pincer-type complex formation.

Using the best catalyst (**4b**) in this series as a representative example, it was demonstrated that for the most active substrate, bromoacetophenone, the catalyst loading might be lowered to 0.01% and still result in practically quantitative conversion. High TON values were observed even at very low catalyst loading of 0.001 mol%. At the same time, for less active 4-bromoanisole, the amount of a catalyst was crucial for effective cross-coupling (Table 2), apparently due to catalyst destruction during the process of intermediates formation at decreased reaction rate.

Complexes **4a–d** are stable and do not undergo any transformation during 40 days in DMF solution under ambient conditions. However, the ^{31}P NMR monitoring of the reaction mixtures obtained after catalysis revealed the decomposition of initial palladacycles **4** proceeding in different ways depending on the nature of the substituents at the phosphorus atom of thiophosphoryloxy group. Thus, in the ^{31}P NMR spectra of the mixtures obtained after the reactions catalyzed by diaminothiophosphoryloxy-substituted complexes **4a**,**b** two singlets in 1 : 1 ratio were observed: the first one situated in the region typical for non-coordinated thiophosphoryloxy group of the free ligand (80 ppm and 73 ppm for **4a** and **4b** correspondingly) and the second one at 57–58 ppm characteristic for coordinated $C_{Ar}P(S)$ moiety.[12] Therefore, in this particular case we can suggest the 'opening' of the coordinated bond formed by thiohophoryloxy-group resulting in formation of monopalladacycle species **5a**,**b**.

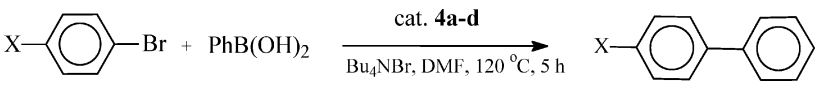
The ^{31}P NMR spectra for the mixtures obtained after catalysis using complexes **4c,d** having $Ph_2P(S)O$- and $Me(BuO)P(S)O$-groups respectively, demonstrated 3 signals in 2 : 1 : 1 ratio. In both cases one signal (at 42.8 ppm and 41.6 ppm for **4c** and **4d**, respectively) is close to that of the coordinated phosphine sulfide group in the starting complexes. In the case of **4c** two other signals were observed at 26 ppm and 15 ppm while for **4d** at 43 ppm and 21 ppm. Based on the NMR data, we may suppose a cleavage of the 6-membered metallacycle with subsequent rupture of P–OAr bond leading to a monopalladacycle complex **6** formed by thiophosphorylated phenol **2** along with non-coordinated species (Scheme 4). Naturally, one should take into account the possible changing of the Cl anion for the bromide one in the presence of Bu_4NBr and bromo-arenes being the components of a reaction mixture. However, such anion exchange should not significantly influence on the chemical shift of the complexes in the ^{31}P NMR spectra due to the distant location of both phosphorus atoms from the Pd-centre.

The products **5a**,**b**, and **6** of the decomposition also showed the catalytic activity and catalyzed the reaction of a new portion of aryl bromide and phenylboronic acid added to the same reaction

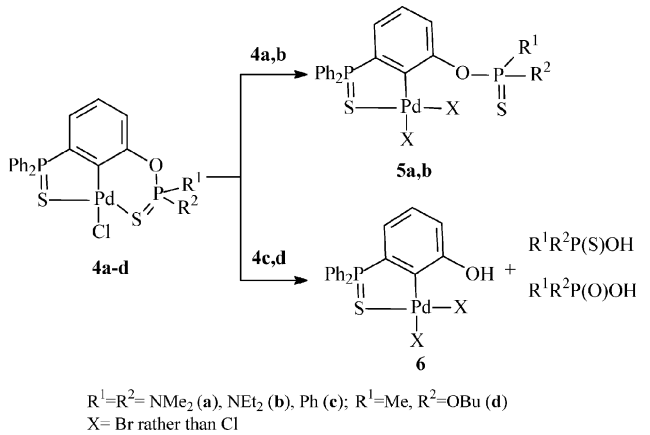
Table 2 Influence of catalyst **4b** amount on the conversion in the Suzuki cross-coupling

X	Cat. mol%	Yield (%)	TON
Ac	1	100	100
	0.3	100	333
	0.1	99.8	998
	0.03	99.1	3303
	0.01	93	9300
	0.003	47	15 667
	0.001	38	38 000
OMe	1	93	93
	0.3	65	217
	0.1	68	680
	0.03	51	1700
	0.01	7	700

Table 1 Palladacycles **4** catalyzed the Suzuki cross-coupling



Catalyst (1 mol%)	R^1, R^2	Yield (%) C(O)Me	F	OMe	NMe_2
4a	$R^1 = R^2 = NMe_2$	100	91	85	54
4b	$R^1 = R^2 = NEt_2$	100	98	93	60
4c	$R^1 = R^2 = Ph$	100	96	70	6
4d	$R^1 = Me$, $R^2 = OBu$	100	89	80	20



Scheme 4 Possible way of decomposition of the complexes **4a–d** over the catalytic cycle.

mixture (a biaryl derivative obtained at the first catalytic cycle was considered as an inert component). However, the catalytic activity of the monopalladacycle species was lower comparing with that for pincer-type complexes **4**. Thus, using the most active **4b** as a catalyst, the reaction of 4-bromoacetophenone was performed at the first catalytic cycle to afford quantitative yield of the biphenyl product. To the liquid phase obtained after separation of solids 4-bromoanisole as a substrate was added along with fresh portions of phenylboronic acid and K_3PO_4, and the reaction resulted in the corresponding biaryl in 69% yield (for comparison, complex **4b** gave 93% of the same product, see Table 1). In the second experiment, the reaction of 4-bromoanisole was carried out at the first catalytic cycle under the catalytic action of **4b** (93% yield of the product, Table 1) and followed by the second catalytic cycle where 4-bromoacetophenone was used as a substrate. In this case, the arylation at the second cycle proceeded in the quantitative yield confirming rather high catalytic activity of monopalladacycle formed over the catalytic reaction.

In the absence of tetrabutylammonium bromide—a salt known to stabilize palladium nanoparticles[19]—approximately 15% decrease of the yield of the final product was observed for the reaction mixtures catalyzed by **4b**. Therefore we cannot exclude the competitive mechanism including the cleavage of the palladium–carbon bond and/or formation of palladium nanoparticles as the active form of the catalysts. To elucidate the detailed the peculiarities of the catalytic cycle in this particular case further investigation exceeding the bounds of the above study will be performed in future and published elsewhere.

In general, the catalytic activity in the Suzuki cross-coupling of the new 5,6-membered complexes **4a–d** is higher comparing with the activity for other pincer complexes with *SCS*-coordination reported in the literature. Thus, the above mentioned 5,5-membered nonsymmetrical complexes **V** (there being more active catalyst precursors in this reaction that symmetric *SCS*-complexes formed by 1,3-bis[(*tert*-butylthio)methyl]benzene[12]) provided up to 83% of 4-methoxy-1,1′-biphenyl at the typical catalyst loading of 3 mol% while complexes **4** gave up to 90% of the same product being used in 1 mol%. Note also that the data concerning the catalytic activity for palladium *SCS* complexes **I–IV** are absent in the literature.

Taking into account that the pincer conformation of compounds **4a–d** does not survive the conditions of catalytic reaction, these 5,6-membered catalytic precursors are less stable than 5,5-membered *SCS*-pincer complexes and though they provided higher reactivity it might be that it is not the pincer compound that does the catalysis.

Conclusion

To summarize the results presented, we developed the synthetic route to novel *SCS′*-pincer ligands, namely 1-thiophosphoryloxy-3-thiophosphorylbenzenes. Direct cyclopalladation of these ligands at the C-2 position of the central benzene ring resulted in nonsymmetrical pincer complexes having fused 5- and 6-membered palladacycles. These compounds possess a very distorted geometry of both the palladium 'square' and even the ligand. Despite these 5,6-membered palladium *SCS*-pincer complexes demonstrated higher catalytic activity in the Suzuki cross-coupling reaction than 5,5-membered *SCS*-pincer compounds their pincer conformation is unstable under severe catalytic conditions.

Experimental

General remarks

If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. THF was distilled from sodium benzophenone ketyl under argon atmosphere. The starting diphenylchlorophosphine sulfide $Ph_2P(S)Cl$,[20] *N*,*N*,*N′*,*N′*-tetramethyl-phosphorodiamidothioic chloride $(Me_2N)_2P(S)Cl$,[21] its tetraethyl analogue $(Et_2N)_2P(S)Cl$[22] and $(BuO)MeP(S)Cl$[23] were obtained according to the literature procedures. All other solvents and chemicals 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 registered using the JMODECHO 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 ^1H and ^{13}C spectral data is in agreement with IUPAC nomenclature used for the ligands. The same principle of numbering was used for description of solid-state molecular structures characterized by X-ray crystallography.

IR spectra were recorded in KBr on a Fourier-spectrometer "Magna-IR750"(Nicolet), resolution 2 cm^{-1}, 128 scans. The assignment of the absorption bands in IR spectra was made according to ref. 24. Flash chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). Melting points were determined with an Electrothermal IA9100 Digital Melting Point Apparatus and were uncorrected.

Synthesis of ligands

(3-Methoxyphenyl)diphenylphosphine sulfide 1. A solution of diphenylchlorophosphine (27.6 g, 125 mmol) in THF (30 mL) was slowly added dropwise to the Grignard reagent, prepared from magnesium (3.0 g, 125 mmol), 3-bromoanisole (24.3 g, 130 mmol) and THF (300 mL), in an argon atmosphere at 0–5 °C. The reaction mixture was heated at 50–55 °C for 2 h, cooled down and

stirred overnight at ambient temperature. Then, the mixture was treated successively with a saturated aqueous solution of NH_4Cl and diluted hydrochloric acid (15 mL of conc. HCl/90 mL of water). The desired product was extracted with benzene (150 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and filtered. Then, finely powdered sulfur (4.0 g, 125 mmol) was added to benzene filtrate and the obtained mixture was stirred under ambient conditions for 3 days. The solvent was removed under reduced pressure and the resulting residue was twice crystallized from hexane (2 × 70 mL) to give **1** (26.9 g, 66%) as a white solid. M.p.: 110–111 °C (hexane). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 43.88 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 3.81 (s, 3H, CH_3), 7.04–7.06 (m, 1H, H_{Ar}), 7.16–7.22 (m, 1H, H_{Ar}), 7.32–7.39 (m, 2H, H_{Ar}), 7.43–7.55 (m, 6H, H_{Ar}), 7.69–7.77 (m, 4H, H_{Ar}) (*cf.*[25]). Anal. Calcd. for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28; S, 9.89%. Found: C, 70.37; H, 5.29; S, 9.67%.

3-(Diphenylthiophosphoryl)phenol 2. A mixture of compound **1** (6.3 g, 20 mmol) and pyridine hydrochloride (6.8 g, 60 mmol) was heated under stirring at 180–190 °C (oil bath) for 5 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, washed with water, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The obtained residue was purified by silica gel column chromatography (eluent: ethyl acetate–hexane (1 : 3)) followed by recrystallization from ethyl acetate–hexane mixture (1 : 1, 25 mL) to yield **2** (4.3 g, 69%) as a white solid. M.p.: 132–134 °C (ethyl acetate–hexane (1 : 1)).$^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 43.59 ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.02 (d, $^3J_{HH}$ = 7.98 Hz, 1H, H_{Ar}), 7.18 (dd, $^3J_{HH}$ = 7.93 Hz, $^3J_{PH}$ = 11.91 Hz, 1H, H_{Ar}),7.38 (t, $^3J_{HH}$ = 7.93 Hz, 1H, H_{Ar}), 7.46–7.60 (m, 7H, H_{Ar}+*o*-H, *p*-H in C_6H_5P), 7.77 (dd, $^3J_{HH}$ = 7.32 Hz, $^3J_{PH}$ = 12.78 Hz, 4H, *m*-H in C_6H_5P), 7.69–7.77 (m, 4H, H_{Ar}) (*cf.* m.p. 132–133 °C[14]).

(*N*,*N*,*N*′,*N*′-Tetraethyl)diamidothiophophosphoric acid *O*-(3-diphenylthiophosphoryl)phenyl ester 3b. A mixture of phenol **2** (1.45 g, 4.7 mmol) and $(Et_2N)_2P(S)Cl$ (1.15 g, 4.7 mmol) in triethylamine (2 mL) was heated at 115–120 °C in an oil bath for 3 h. After cooling to room temperature, the reaction mixture was dissolved in dichloromethane (25 mL) and washed with diluted hydrochloric acid (3 mL conc. HCl/50 mL of water). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography (eluent: hexane–acetone (5 : 1)) followed by recrystallization from hexane to give **3b** as white crystals (1.40 g, 58%). M.p.: 81–82 °C (hexane). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 43.16 ($P(S)Ph_2$), 76.61 ($OP(S)(NEt_2)_2$) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.04 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH_3), 2.99–3.20 (m, 8H, CH_2), 7.25–7.27 (m, 1H, H_{Ar}), 7.34–7.57 (m, 9H, H_{Ar}), 7.70–7.75 (m, 4H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 13.57 (d, $^4J_{PC}$ = 2.9 Hz, CH_3), 39.89 (d, $^3J_{PC}$ = 5.1 Hz, CH_2), 124.64 (dd, $^3J_{PC}$ = 5.5 Hz, $^4J_{PC}$ = 2.6 Hz, C5), 124.86 (dd, $^2J_{PC}$ = 5.1 Hz, $^3J_{PC}$ = 11.8 Hz, C2), 127.72 (d, $^2J_{PC}$ = 9.5 Hz, C4), 128.31 (d, $^3J_{PC}$ = 12.5 Hz, *m*-C in PC_6H_5), 129.41 (d, $^3J_{PC}$ = 14.7 Hz, C6), 131. 34 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C in PC_6H_5), 132.08 (d, $^2J_{PC}$ = 11.0 Hz, *O*-C in PC_6H_5), 132.40 (d, $^1J_{PC}$ = 85.8 Hz, *ipso*-C in PC_6H_5), 133.88 (d, $^1J_{PC}$ = 85.1 Hz, C3), 150.81 (dd, $^2J_{PC}$ = 5.9 Hz, $^3J_{PC}$ = 16.1 Hz, C1). Anal. Calcd. for $C_{26}H_{34}NO_2P_2S_2$: C, 60.44; H, 6.63; N, 5.42%. Found: C, 60.51; H, 6.59; N, 5.44%.

(*N*,*N*,*N*′,*N*′-Tetramethyl)diamidothiophophosphoric acid *O*-(3-diphenylthiophosphoryl)phenyl ester 3a. **3a** was obtained by analogous procedure excluding using of *N*,*N*,*N*′,*N*′-tetramethylphosphorodiamidothioic chloride (0.88 g, 4.7 mmol) instead of $(Et_2N)_2P(S)Cl$. Yield: 1.0 g, 56%, white solid. M.p.: 95–97 °C (hexane). $^{31}P\{^1H\}$ NMR (167.98 MHz, $CDCl_3$): δ 43.07 ($P(S)Ph_2$), 81.24 ($OP(S)(NMe_2)_2$) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 2.62 (d, $^3J_{PH}$ = 12.3 Hz, 12H, CH_3), 7.22–7.25 (m, 1H, H_{Ar}), 7.31–7.35 (m, 1H, H_{Ar}), 7.38–7.55 (m, 8H, H_{Ar}), 7.70–7.75 (m, 4H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$): δ 36.82 (d, $^2J_{PC}$ = 3.5 Hz, CH_3), 124.62, 124.68, 124.77 (overlapped C2+C5), 128.00 (d, $^3J_{PC}$ = 10.4 Hz, C6), 128.45 (d, $^3J_{PC}$ = 12.5 Hz, *m*-C in PC_6H_5), 129.66 (d, $^2J_{PC}$ = 14.5 Hz, C4), 131.58 (s, *p*-C in PC_6H_5), 132.07 (d,$^2J_{PC}$ = 11.1 Hz, *O*-C in PC_6H_5), 132.35 (d, $^1J_{PC}$ = 85.1 Hz, *ipso*-C in PC_6H_5), 134.24 (d, $^1J_{PC}$ = 84.4 Hz, C3), 150.60 (dd, $^2J_{PC}$ = 5.3 Hz, $^3J_{PC}$ = 15.8 Hz, C1). Anal. Calcd. for $C_{22}H_{26}ON_2P_2S_2$: C, 57.38; H, 5.69; N, 6.08%. Found: C, 57.42; H, 5.88; N, 5.61%.

Diphenylthiophosphinic acid *O*-(3-diphenylthiophosphoryl)-phenyl ester 3c. 3-Diphenylthiophosphorylphenol **2** (2.00 g, 6.5 mmol) was added portion-wise to a stirred mixture of 10% aq. NaOH (0.26 g, 6.5 mmol), TEBA-Cl (0.07 g, 0.325 mmol, 5 mol%) and benzene (6 mL). Then a solution of $Ph_2P(S)Cl$ (1.63 g, 6.65 mmol) in benzene (10 mL) was slowly added dropwise to the obtained suspension. The reaction mixture was stirred for 30 min at room temperature and 2 h at 55–60 °C. After that, it was poured into separating funnel and diluted with water (50 mL). The mixture was extracted with benzene (2 × 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting residue was crystallized from ether (40 mL) and recrystallized from ethyl acetate (20 mL) to give **3c** (3.00 g, 89%) as a white solid. M.p.: 128–130 °C. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 42.83 ($P(S)Ph_2$), 83.59 ($OP(S)Ph_2$) ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.29–7.72 (m, 20H), 7.91–7.99 (m, 4H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 124.88 (dd, $^4J_{PC}$ = 2.6 Hz, $^3J_{PC}$ = 4.4 Hz, C6), 125.37 (dd, $^2J_{PC}$ = 10.9 Hz, $^3J_{PC}$ = 5.2 Hz, C2), 128.34, 128.47, 128.48, 128.55 (overlapped signals of C5, *m*-C in $OP(S)C_6H_5$ and *m*-C in $P(S)C_6H_5$), 129.63 (d, $^2J_{PC}$ = 14.3 Hz, C4), 131.20 (d, $^2J_{PC}$ = 11.7 Hz, *o*-C in $P(S)C_6H_5$), 131.44 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C in $P(S)C_6H_5$), 132.05 (d, $^2J_{PC}$ = 10.6 Hz, *o*-C in $OP(S)C_6H_5$), 132.10 (s, *p*-C in $OP(S)C_6H_5$), 132.22 (d, $^1J_{PC}$ = 85.8 Hz, *ipso*-C in $P(S)C_6H_5$), 133.46 (d, $^1J_{PC}$ = 111.1 Hz, *ipso*-C in $OP(S)C_6H_5$), 134.43 (d, $^1J_{PC}$ = 84.0 Hz, C3), 150.19 (dd, $^2J_{PC}$ = 8.4 Hz, $^3J_{PC}$ = 16.1 Hz, C1). IR (KBr, ν/cm^{-1}: 508, 641,645 (P=S), 689, 719, 733, 807, 927,1103, 1207(C_{Ph}–O), 1408, 1434, 1438 ($P–C_{Ph}$), 1467, 1479, 1570, 1586, 3048. Anal. Calcd. for $C_{30}H_{24}OP_2S_2$: C, 68.43; H, 4.59; S, 12.18%. Found: C, 68.21; H, 4.62; S, 12.29%.

Methylthiophosphonic acid *O*-butyl-*O*-(3-diphenylthiophosphoryl)phenyl ester 3d. A solution of Me(BuO)P(S)Cl (0.75 g, 4.0 mmol) in benzene (5 mL) was slowly added dropwise to a stirred solution of 3-diphenylthiophosphorylphenol **2** (1.2 g, 3.9 mmol) and triethylamine (0.45 g, 4.5 mmol) in C_6H_6 (35 mL). The reaction mixture was refluxed for 12 h. After cooling to room temperature the precipitate of triethylamine chlorohydrate was filtered off. The filtrate was washed with H_2O (50 mL), the separated water phase was additionally extracted with benzene (30 mL). The combined organic layer was dried over anhydrous

Na_2SO_4, filtered and evaporated to dryness. The resulting residue was purified by silica gel column chromatography (eluent hexane–ethyl acetate (8 : 1)) to give **3d** as viscous white oil. Yield: 1.65 g (93%). $^{31}P\{^1H\}$ (161.98 MHz, $CDCl_3$): δ 42.86 ($P(S)Ph_2$), 94.38 (OP(S)(OBu)Me) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.88 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3), 1.26–1.36 (m, 2H, CH_2CH_3), 1.51–1.60 (m, 2H, OCH_2CH_2), 1.93 (d, $^2J_{PH}$ = 15.5 Hz, 3H, PCH_3), 3.82–3.90 (m, 1H, OCH_2), 4.05–4.13 (m, 1H, OCH_2), 7.27–7.30 (m, 1H, H_{Ar}), 7.39–7.58 (m, 9H, H_{Ar}), 7.69–7.74 (m, 4H, H_{Ar}). Anal Calcd. for $C_{23}H_{26}O_2P_2S_2$: C, 59.98; H, 5.70; S, 13.92%. Found: C, 60.01; H, 5.77; S, 13.98%.

Preparation of Pd(L)Cl complexes

Complexes 4a,b. Method A (general procedure). A benzene solution (7 mL) of $(PhCN)_2PdCl_2$ (54.1 mg, 0.141 mmol) was slowly added dropwise to a solution of **3a** or **3b** (0.141 mmol) in 8 mL of C_6H_6. A reaction mixture was refluxed for 2 h under stirring, filtered and evaporated to dryness. The resulting oily residue was washed with ether (10 mL) to give solid which was filtered off and recrystallized from CH_2Cl_2–Et_2O mixture (1 : 3, 12 mL) to give the corresponding complexes.

Method B (general procedure). A dichloromethane solution (4 mL) of $(PhCN)_2PdCl_2$ (98.0 mg, 0.255 mmol) was slowly added dropwise to a solution of **3a** or **3b** (0.255 mmol) in 3 mL of CH_2Cl_2. The resulting mixture was left under ambient conditions for 5 days and evaporated to a volume of ~1 mL. Addition of ether (15 mL) to the reaction solution afforded precipitation of the corresponding complexes which were filtered off, washed with 15 mL of Et_2O and dried in vacuum.

[2-{[Bis(dimethylamino)thiophosphoryl]oxy}-6-(diphenylthiophosphoryl)phenyl]-palladium chloride 4a. Yield: 60.2 mg (method A, 71%), 104.6 mg (method B, 68%), yellow crystalline solid. M.p.: >175 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$): δ 44.58 ($P(S)PPh_2$), 68.15 ($OP(S)(NMe_2)_2$) ppm. ^1H NMR (300.13 MHz, $CDCl_3$): δ 2.86 (d, $^2J_{PH}$ = 12.5 Hz, 12H, CH_3), 6.69 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 10.4 Hz, 1H, H-C4), 6.79 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H-C6), 6.96 (m, 1H, H-C5), 7.49–7.62 (m, 6H, H_{Ar}), 7.77–7.84 (m, 4H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 37.07 (d, $^2J_{CP}$ = 4.3 Hz, CH_3), 120.75 (dd, $^4J_{PC}$ = 3.2 Hz, $^3J_{PC}$ = 8.6 Hz, C5), 125.12 (d, $^2J_{PC}$ = 15.5 Hz, C4), 126.85 (d, $^3J_{PC}$ = 15.5 Hz, C6), 128.82 (d, $^3J_{PC}$ = 12.6 Hz, *m*-C in $P(S)C_6H_5$), 129.70 (d, $^1J_{PC}$ = 80.2 Hz, *ipso*-C in $P(S)C_6H_5$), 132.36 (d, $^2J_{PC}$ = 11.2 Hz, *O*-C in $P(S)C_6H_5$), 132.64 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C in $P(S)C_6H_5$), 144.38 (dd, $^4J_{PC}$ = 5.0 Hz, $^3J_{PC}$ = 23.4 Hz, C2), 147.89 (d, $^1J_{CP}$ = 105.4 Hz, C3), 155.77 (dd, $^2J_{PC}$ = 7.2 Hz, $^3J_{PC}$ = 22.0 Hz, C1). Anal Calcd. for $C_{22}H_{25}ClN_2OP_2PdS_2$: C, 43.94; H, 4.19; N, 4.66%. Found: C, 43.89; H, 4.19; N, 4.51%.

[2-{[Bis(diethylamino)thiophosphoryl]oxy}-6-(diphenylthiophosphoryl)phenyl]-palladium chloride 4b. Yield: 60.0 mg (method A, 65%), 147.8 mg (method B, 88%), yellow crystalline solid. M.p.: >185 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 44.33 ($P(S)Ph_2$), 64.88 ($OP(S)(NEt_2)_2$) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.20 (t, $^3J_{PH}$ = 7.1 Hz, 12H, CH_3), 3.24–3.41 (m, 8H, CH_2), 6.72 (dd, $^3J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 7.2 Hz, 1H, H–C4), 6.79 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H–C6), 7.00 (m, 1H, H–C5), 7.51–7.56 (m, 4H, H_{Ar}), 7.61–7.64 (m, 2H, H_{Ar}), 7.81–7.86 (m, 4H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$): δ 13.52 (s, CH_3), 40.15 (d, $^2J_{PC}$ = 5.1 Hz, CH_2), 120.91 (dd, C5, $^3J_{PC}$ = 8.1 Hz, $^4J_{PC}$ = 2.9 Hz), 124.90 (d, C4, $^2J_{PC}$ = 15.4 Hz), 126.66 (d, C6, $^3J_{PC}$ = 15.4 Hz), 128.62 (d, $^3J_{PC}$ = 12.5 Hz, *m*-C in $P(S)C_6H_5$), 129.56 (d, $^1J_{PC}$ = 80.0 Hz, *ipso*-C in $P(S)C_6H_5$), 132.20 (d, $^2J_{PC}$ = 11.0 Hz, *O*-C in $P(S)C_6H_5$), 132.43 (d, $^4J_{PC}$ = 2.2 Hz, *p*-C in $P(S)C_6H_5$), 144.90 (dd, $^2J_{PC}$ = 5.8 Hz, $^3J_{PC}$ = 22.5 Hz, C2), 147.98 (d, $^1J_{PC}$ = 105.6 Hz, C3), 155.06 (dd, $^2J_{PC}$ = 8.1 Hz, $^3J_{PC}$ = 21.3 Hz, C1). Anal Calcd for $C_{26}H_{33}ClN_2OP_2PdS_2$: C, 47.49; H, 5.06; N, 4.26%. Found: C, 47.54; H, 5.06; N, 4.22%.

{2-[(Diphenylthiophosphoryl)oxy]-6-(diphenylthiophosphoryl)-phenyl}-palladium chloride 4c. A dichloromethane solution (2 mL) of $PdCl_2(PhCN)_2$ (84.3 mg, 0.22 mmol) was added dropwise to a solution of **3c** (115.8 mg, 0.22 mmol) in 3.5 mL of CH_2Cl_2. In one hour the reaction mixture was slowly poured into methanol (7.5 mL) and left under ambient conditions for 4 days, then filtered and evaporated to dryness. The ether (10 mL) was added to the oily residue to give yellow solid, which was filtered off and recrystallized from CH_2Cl_2–Et_2O mixture (1 : 2, 15 mL) to give **4c** (95.3 mg, 65%) as a yellow crystalline solid. M.p.: >250 °C (decomp). $^{31}P\{^1H\}$ NMR (161.98 MHz, DMSO-d_6): δ 47.24 ($P(S)Ph_2$), 74.92 ($OP(S)Ph_2$) ppm. ^1H NMR (300.13 MHz, $CDCl_3$/DMSO-d_6): δ 6.73 (dd, $^3J_{PH}$ = 10.7 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, H–C4), 7.12 (m, 1H, H–C5), 7.20 (d, $^3J_{HH}$ = 7.8 Hz, 1H, H–C6), 7.57–7.73 (m, 16H, H_{Ar}), 7.95–8.02 (M, 4H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, DMSO-d_6) (due to the low solubility of the compound the signals of carbon atoms of central benzene ring were not observed): δ 129.60, 129.75, 129.90 (overlapped signals of *m*-C in $OP(S)C_6H_5$ and *m*-C in $P(S)C_6H_5$), 131.94 (d, $^2J_{PC}$ = 12.1 Hz, *o*-C in $P(S)C_6H_5$), 132.68 (d, $^2J_{PC}$ = 11.1 Hz, *o*-C in $OP(S)C_6H_5$), 133.80 (s, *p*-C in $P(S)C_6H_5$), 134.34 (s, *p*-C in $OP(S)C_6H_5$). Anal. Calcd for $C_{30}H_{23}ClOP_2PdS_2$: C, 53.98; H, 3.47; S, 9.61%. Found: C, 53.90; H, 3.64; S, 9.51%.

[2-{[Butoxy(methyl)thiophosphoryl]oxy}-6-(diphenylthiophosphoryl)phenyl]-palladium chloride 4d. A dichloromethane solution (4 mL) of $PdCl_2(PhCN)_2$ (109.4 mg, 0.29 mmol) was slowly added dropwise to a solution of **3d** (131.4 mg, 0.29 mmol) in 3 mL of CH_2Cl_2. The reaction mixture was left under ambient conditions for 5 days and poured into hexane (7 mL). In an hour, the resulting mixture was filtered and evaporated to dryness. The obtained residue was washed with Et_2O (10 mL) and dissolved in CH_2Cl_2 (7 mL). Slow evaporation of solvent from this solution under ambient conditions resulted in **4d** as a yellow crystalline solid. Yield: 33.2 mg (19%). M.p.: >168 °C (decomp.) $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$): δ 45.75 ($P(S)Ph_2$), 84.16 (OP(S)(OBu)Me) ppm. ^1H NMR (400.13 MHz, $CDCl_3$): δ 0.91 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH_3), 1.36–1.46 (m, 2H, CH_2CH_3), 1.67–1.76 (m, 2H, OCH_2CH_2), 2.24 (d, $^2J_{PH}$ = 15.3 Hz, 3H, PCH_3), 4.46–4.60 (m, 2H, OCH_2), 6.71–6.76 (m, 1H, H–C4), 6.84 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H–C6) 6.95–7.04 (m, 1H, H–C5), 7.59–7.65 (m, 2H, H_{Ar}), 7.49–7.56 (m, 4H, H_{Ar}), 7.73–7.86 (m, 4H, H_{Ar}). Anal. Calcd for $C_{30}H_{23}ClOP_2PdS_2$: C, 45.93; H, 4.19; S, 10.66%. Found: C, 45.78; H, 4.03; S, 10.37%.

Catalytic experiments

In a typical experiment, a solution of 1 mmol of aryl bromide, 1.5 mmol of $PhB(OH)_2$, 2 mmol of K_3PO_4, 0.2 mmol of Bu_4NBr, and the mentioned amount of the corresponding palladium

complex in 5 mL of DMF was heated at 120 °C over 5 h. After cooling the reaction mixture was immediately filtered, treated with water, extracted with benzene and analyzed by GC and ^{31}P NMR.

Crystal structure determination and data collection

The single crystals suitable for X-ray experiments were obtained by slow evaporation from hexane solution (**3b**, Fig. 1) from CH_2Cl_2 solution (**4a**, Fig. 2) or by slow diffusion of ethanol into DMSO solution (**4c**, Fig. 3). The X-ray diffraction experiments were carried out with a SMART APEX2 CCD diffractometer for **4a** and **4c** and with a SMART 1000 CCD diffractometer for **3b**, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans) at 100 K (**4a** and **4c**) and 120 K (**3b**). The structures were solved by direct methods and refined by the full-matrix least-squares against F^2 in anisotropic approximation for no-hydrogen atoms. The H(C) atom positions were calculated and they were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to 1.2 $U_{eq}(C_i)$, for methyl groups equal to 1.5 $U_{eq}(C_{ii})$, where U(C_i) and U(C_{ii}) are respectively the equivalent thermal parameters of the carbon atoms to which corresponding H atoms are bonded. Crystal data and structure refinement parameters for **3b**, **4a** and **4c** are given in Table 3. All calculations were performed using the SHELXTL software.[26]

Table 3 Crystal data and structure refinement parameters for **3b**, **4a** and **4c**

	3b	4a	4c
CCDC number	730242	730243	730244
Empirical formula	$C_{26}H_{34}N_2OP_2S_2$	$C_{22}H_{25}ClN_2OP_2PdS_2$	$C_{30}H_{23}ClOP_2PdS_2$
Formula weight	516.61	601.35	667.39
T/K	120(1)	100(1)	100(1)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Z	2	2	4
a/Å	9.1250(16)	8.6417(4)	12.2080(13)
b/Å	11.081(3)	10.3955(5)	8.7616(8)
c/Å	14.998(3)	13.6809(7)	26.551(3)
α (°)	83.718(16)	95.103(5)	90.00
β (°)	78.009(16)	98.150(5)	102.341(5)
γ (°)	66.27(2)	95.827(5)	90.00
V/Å^3	1357.4(6)	1203.64(10)	2774.3(5)
D_c (g cm^{-1})	1.264	1.659	1.598
Linear absorption, μ/cm^{-1}	3.35	12.07	10.55
F(000)	548	608	1344
$2\theta_{max}$ (°)	58	54	56
Reflections measured	15045	8467	13205
Independent reflections (Rint)	7182 (0.0507)	5205 (0.0195)	6636 (0.0456)
Observed reflections [with $I > 2\sigma(I)$]	4787	4534	4859
Parameters	302	284	372
R_1 for observed refl.	0.0507	0.0265	0.0426
wR_2 for independent refl.	0.1224	0.0626	0.0936
GOF	1.004	1.004	1.004
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.604/-0.305	0.553/-0.504	0.980/-1.034

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