Functionalized mercaptoacetic and propionic acid amides: synthesis, cyclopalladation features, and catalytic activity of metal complexes*

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Upon treatment with thiophenol or neomenthyl mercaptane, chloroacet- and propionamides with an additional N- or S-donor substituent in the amine part gave new multidentate ligands readily undergoing direct cyclopalladation in the reaction with $PdCl_2(NCPh)_2$. The realization of κ^3-X,N,S-coordination (X = N, S) in the complexes obtained was confirmed by IR and NMR spectroscopy and, in some cases, by single-crystal X-ray crystallography. The evaluation of catalytic activity of the palladocycles in the Suzuki cross-coupling of aryl bromides with $PhB(OH)_2$ allowed us to establish the principal structure—activity correlations.

Key words: palladium(II) complexes, carboxamides, sulfides, sulfoxides, cyclopalladation, catalytic activity, Suzuki cross-coupling.

Progress in coordination chemistry is mainly determined by the development of new types of ligand systems, where directed synthesis of structures with certain geometric and electronic properties remains a key issue. In this respect, multidentate ligands with readily tunable structures are of special interest. Such systems include functionally substituted carboxamides with additional N-, P-, and S-donor centers in both the acid and amine moieties. Among ligands with nitrogen-containing auxiliary donor center pyridine-2-carboxamides (picolinamides) capable of serving as N-monoanionic or neutral ligands[1] are the most popular ones. The introduction of substituents with additional coordination active fragment into the amine part enabled the synthesis of new types of metal chelates with different geometry around the metal center and, as a consequence, different physicochemical properties,[2] for example, complexes with high catalytic activity in different reactions,[3] as well as convenient models for investigation of metal ion binding modes in biochemical systems.[4] Apart from picolinamides, where the nitrogen atom of the heterocycle plays the role of one of the donor centers upon complexation with different metals, there are also described benzoic acid derivatives having *ortho* substituents with the phosphorus atom capable of performing this function. The complexes of such ligands are widely used as catalysts[5] and radiopharmaceuticals.[6]

As to carboxamides with an additional S-donor center, there are literature data on the synthesis and coordinating ability of only mercaptoacetic acid derivatives. These compounds can exhibit mono-[7] or bidentate[8] coordination mode without participation of the amide nitrogen atom. The examples of multidentate analogues of mercaptoacetamides are limited to only several compounds with an additional pyridine fragment.[9] At the same time, recently we have shown that palladium(II) S,N,O-complexes based on (thio)phosphorylacetamides with an additional coordination active P(X) group (X = O, S) feature high catalytic activity in the Suzuki reaction.[10]

In continuation of our studies on the synthesis of multidentate ligands, in the present work we synthesized new functionally substituted mercaptoacetic and propionic acid amides with a flexible aliphatic framework, in which the sulfur or nitrogen atoms of substituents in the amine component serve as the additional coordination sites, as well as studied peculiarities of their direct cyclopalladation and catalytic activity of the resulting metal complexes in the model Suzuki reaction.

* To 90th birthday anniversary of the Corresponding Member of the Russian Academy of Sciences T. A. Mastryukova (1925—2006).

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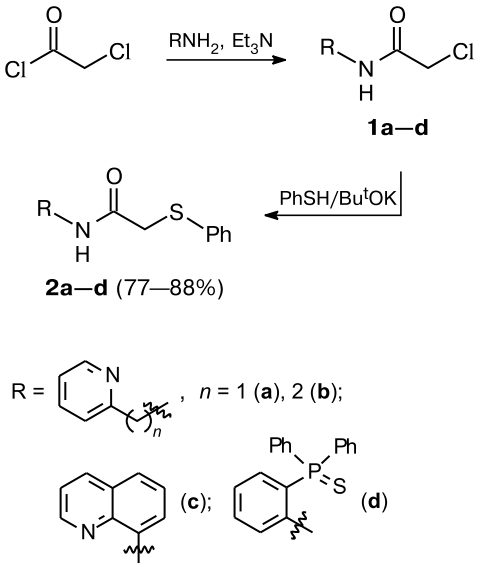
The target ligands (Scheme 1) were synthesized by the reaction of chloroacetyl chloride with functionalized amines, followed by thiophenolysis of the intermediate chloroacetamides **1a**—**d** under action of *in situ* generated PhSK. 2-Aminomethyl- and 2-aminoethylpyridines, 8-aminoquinoline, and 2-(diphenylthiophosphoryl)aniline were chosen as the amine components. This allowed us to obtain ligands **2a**—**d** differing not only in the nature of additional coordination sites (the nitrogen atom of the heterocycles or the sulfur atom of the thiophosphoryl group), but also in the flexibility of spacers between the auxiliary donor group and the amide fragment (a flexible aliphatic spacer in compounds **2a**,**b** or a rigid aromatic spacer in **2c**,**d**).

Scheme 1

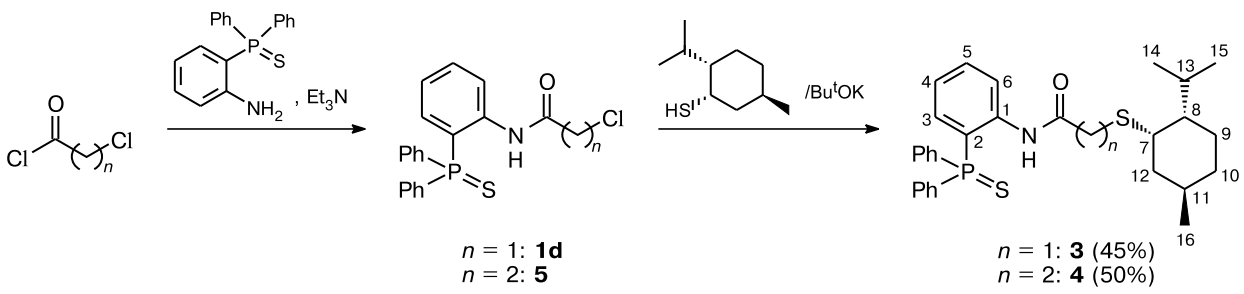


Treatment of chloroacetamide **1d** with potassium derivatives of neomenthylmercaptane led to the formation of functionalized amide **3** with an alicyclic substituent at the sulfur atom of the thioether group (Scheme 2). To compare the complexation abilities, we also synthesized its analogue S,N,S-ligand **4** with an additional methylene unit between the thioether group and the amide fragment (see Scheme 2). The reaction of 3-chloropropionyl chloride with *o*-(diphenylthiophosphoryl)aniline gave, together with the target chloro-substituted amide **5**, also the corresponding acrylanilide. Note that the use of chiral neomenthylmercaptane allowed us to obtain target ligands **3** and **4** in the enantiomerically pure form.

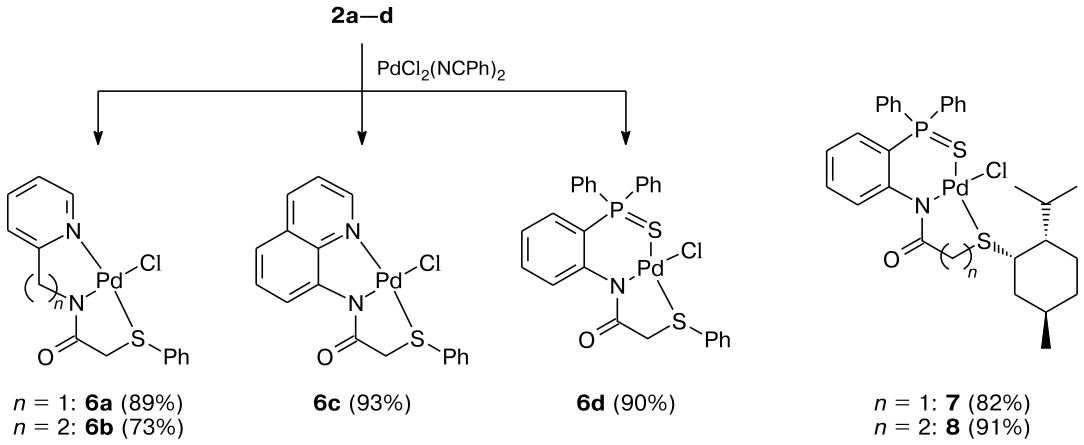
The IR spectra of the crystalline samples of amides **2a**—**d**, **3**, and **4** exhibit, together with the stretching vibrations of the carbonyl group (ν = 1643—1702 cm^{-1}) and the N—H bond (ν = 3201—3330 cm^{-1}), also the absorption bands characteristic for the secondary amide group, which are mainly attributed to the bending vibrations of the NH fragment (ν = 1503—1546 cm^{-1}). The characteristic absorption bands of the thiophosphoryl functional group in compounds **2d**, **3**, and **4** were found in the region of ~635 cm^{-1}. The ^1H NMR spectra of all the amides obtained, apart from the signals of the aliphatic and aromatic protons, also contain the downfeild signals characteristic for the NH protons (δ_H = 7.65—11.12). The ^{13}C NMR spectra can be easily interpreted and also confirm the structure of the compounds obtained. For thiophosphoryl-substituted amides **2d**, **3**, and **4**, the singlets of the phosphorus atoms in the ^{31}P NMR spectra were found in the region characteristic for phosphine sulfides (δ_P = 39.59—40.17).

The reaction of ligands **2a**—**d** with $PdCl_2(NCPh)_2$ in dichloromethane at ~20 °C readily proceeded as the metallation of the amide group with concomitant coordination by the metal atom of the auxiliary N- and S-donor groups, leading to κ^3-*N*,*N*,*S*- and κ^3-*S*,*N*,*S*-palladocycles **6a**—**d** in high yields (Scheme 3). Complexes **7** and **8** with the neomenthyl substituent at the sulfur atom of the thioether group were obtained under similar conditions. The products were obtained in high yields independent from the size of the formed fused metallocycles (from 5,5- to 6,6-membered complexes). Note that in the case of phosphorus-substituted ligands **2d**, **3**, and **4**, the cyclopalladation smoothly proceeded in the absence of a base, whereas for the heterocyclic derivatives **2a**—**c** it was necessary to add Et_3N in order to accelerate the complexation and increase the yields of the target metal complexes.

Scheme 2



Scheme 3



Complexes **6a**—**d**, **7** and **8** are brightly colored, moisture stable compounds with high decomposition points. Their structures and compositions were unambiguously confirmed by elemental analysis, IR and NMR spectroscopy, and, in some cases, by single-crystal X-ray crystallography. The absence of the downfield signals of the hydrogen atom of the amide group in the ^{1}H NMR spectra of all the complexes obtained indicates the occurrence of metallation. The IR spectra of the complexes do not have absorption bands corresponding to the stretching or bending vibrations of the NH fragment, whereas the absorption band of the carbonyl group is considerably shifted to the low-frequency region relative to the IR spectra of the free ligands ($\Delta\nu$ = 29—96 cm^{-1}). The downfield shift of the signals of the protons at the tertiary carbon atoms *ortho* to the N-donor atom in the pyridine ($\Delta\delta_H$ = = 0.36—0.74 ppm) or quinoline ring ($\Delta\delta_H$ = 0.13 ppm), in the ^{1}H NMR spectra of complexes **6a**—**c** relative to the spectra of the corresponding ligands is an indirect evidence of coordination of the palladium atom in these groups. The upfield shift of the signals of the phosphorus atom in the ^{31}P NMR spectra of palladocycles **6d**, **7**, and **8** ($\Delta\delta_P$ = 1.6—3.4 ppm), together with the low-frequency shift of the absorption band characteristic for the P=S group in the IR spectra ($\Delta\nu$ = 27—36 cm^{-1}), indicates the formation of the P(S)—Pd bond. The coordination of the sulfur atom in the thioether group is indicated by the shift of the signals for the carbon atom of the methylene unit in the ^{13}C NMR spectra, with the value and direction of the shift being dependent on the nature of substituent in the RS group (R = Ph or neomenthyl). Note that for phenylmercapto derivatives, the complexation is accompanied by a typical change in the splitting pattern of the signals for the hydrogen atoms of the methylene unit in the acid component in the ^{1}H NMR spectra from one singlet to two doublets or the AB-system. The diastereotopic nature of this fragment is due to the formation of the system of two fused metallocycles, which results in the existence of complexes **6a**—**d** in $CDCl_3$ at ~20 °C as a mixture of stable atropoisomers. The ^{13}C NMR spectrum of complex **6d** based on the thiophosphoryl-substituted ligand also has a double set of signals for the carbon atoms of the phenyl rings in the $Ph_2P(S)$ group. The introduction of a chiral neomenthyl substituent allowed us to obtain κ^3-*S*,*N*,*S*-palladocycles as a mixture of diastereomers, which have different signals for the phosphorus and carbon atoms in the ^{31}P and ^{13}C NMR spectra, respectively, like in the case of 3-mercaptopropionic acid derivative **8**, or differing in the signals for the carbon atoms only in the acid component, like in the case of compound **7** with a shortened aliphatic spacer between the thioether group and the amide fragment. The differences in the ratio of isomers (1 : 2 (**7**), 1 : 3 (**8**)), apparently, is due to the preferable formation of different forms, which requires further detailed investigation.

The structures of complexes **6b**—**d** and **8** were confirmed by the data of single-crystal X-ray diffraction studies (Figs 1—4). The main geometric parameters are given in Table 1. In all the complexes, the Pd—Cl bond distance is virtually the same (2.3127(9)—2.3166(15) Å), whereas

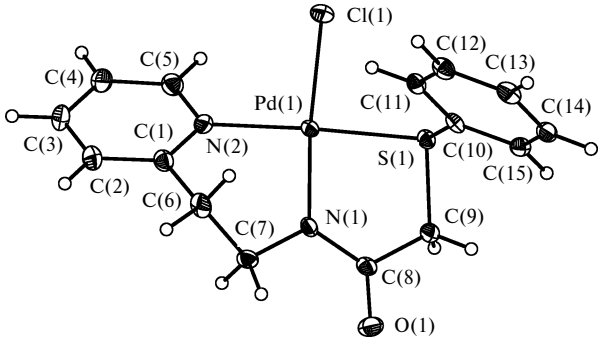


Fig. 1. General view of complex **6b**. Hereinafter, the nonhydrogen atoms are shown as the displacement ellipsoids at a 50% probability level.

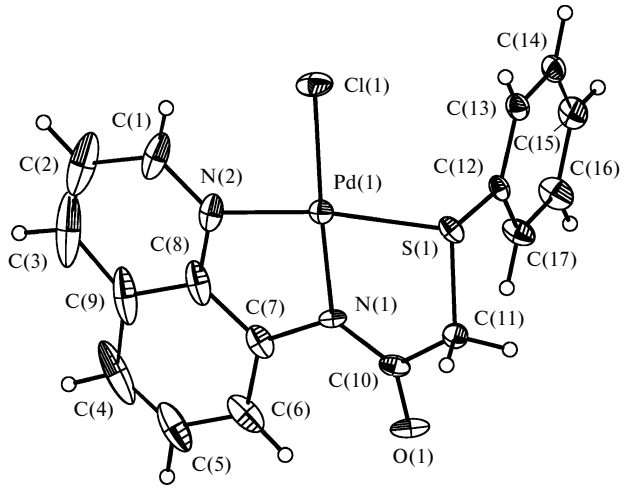


Fig. 2. General view of complex **6c**.

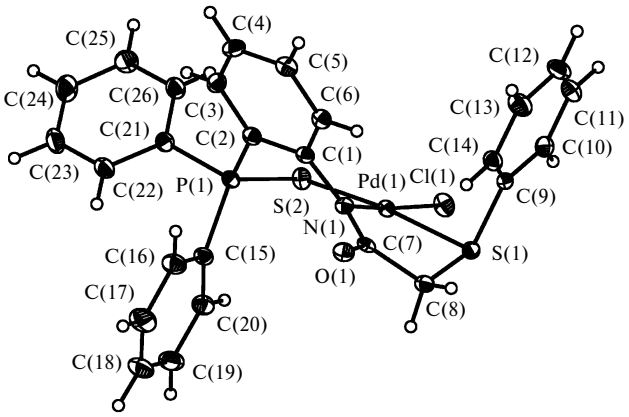


Fig. 3. General view of complex **6d**.

the Pd—N and Pd—S bond distances vary depending on both the nature of the S- and N-donor centers and the sizes of fused metallocycles. In N,N,S-complexes **6b** and **6c**, the Pd—N bond distances with the amide and pyridine or quinoline nitrogen atom (see Figs 1 and 2, Table 1) differ by about 0.07 Å, but synchronously increase on going from 5,5-membered complex **6c** to its analogue with the metallocycles of different sizes (compound **6b**). The N,N-metallocycle in complex **6b** has the *twist* conformation (with the deviation of atoms C(6) and N(2) by 0.79 and 0.44 Å from the plane of the other atoms), whereas the five-membered N,N-palladocycle in compound **6c** is planar. There are no significant variations in the Pd(1)—S(1) bond distances (2.2674(8) Å in **6b** and 2.2662(11) Å in **6c**) or the conformation of the sulfur-containing metallocycle (the *envelop* conformation with the deviation of atoms C(9) in **6b** or C(11) in **6c** by 0.44 and 0.39 Å, respectively). In S,N,S-complexes **6d** and **8** (see Figs 3 and 4, Table 1), the Pd—N and Pd—S bonds are slightly elongated. The last mentioned bonds, depending on the nature of the donor sulfur atom (thiophosphoryl or thioether group) differ by ~0.02 Å and elongate by a similar value on going from 5,6-membered complex **6d** to 6,6-membered analogue **8**. The conformations of the sulfur-containing metallocycles vary from *half-chair* (five-membered metallocycle in complex **8**) to *boat* (in the other cases). Note that N,N,S-complexes **6b**,**c** have nearly ideal square planar geometry around the metal atom, whereas in the case of S,N,S-palladocycles **6d** and **8**, the environment of the palladium atom is noticeably distorted: the S(1)—Pd(1)—S(2) angle varies within 170.66—172.261°, whereas atom S(1) deviates by no more than 0.34—0.40 Å.

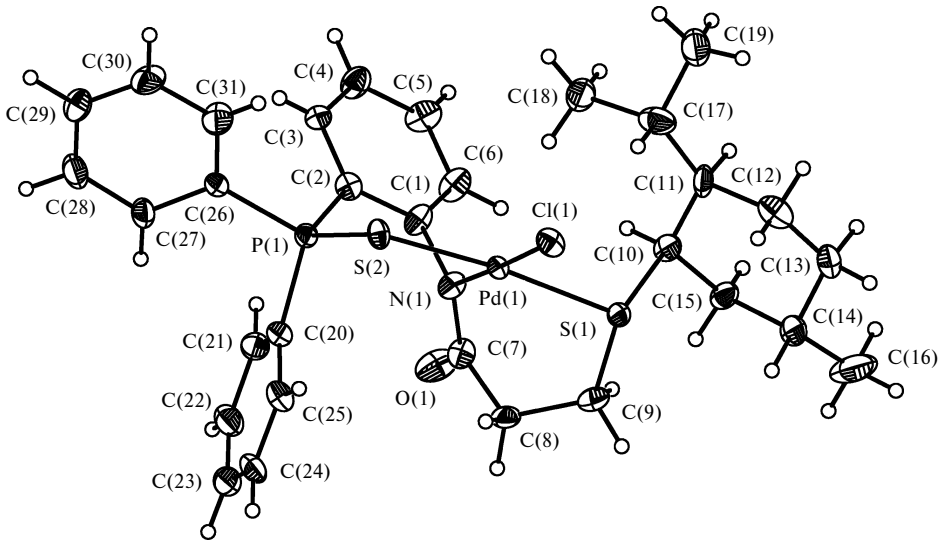


Fig. 4. General view of complex **8**. The second component of the disordered neomenthyl fragment and two solvent molecules of tetrachloromethane are omitted.

Table 1. Principal bond lengths (*d*) and bond angles (ω) in molecules of compounds **6b**—**d**, **8**, and **10**

Parameter	Value
Compound **6b**	
Bond length	*d*/Å
Pd(1)—Cl(1)	2.3153(8)
Pd(1)—N(1)	1.992(2)
Pd(1)—N(2)	2.070(3)
Pd(1)—S(1)	2.2674(8)
N(1)—C(8)	1.350(4)
O(1)—C(8)	1.245(4)
S(1)—C(9)	1.819(3)
Angle	ω/deg
N(1)—Pd(1)—Cl(1)	174.40(7)
N(2)—Pd(1)—Cl(1)	92.93(8)
N(1)—Pd(1)—N(2)	92.48(10)
N(1)—Pd(1)—S(1)	85.36(7)
S(1)—Pd(1)—Cl(1)	89.30(3)
N(2)—Pd(1)—S(1)	176.62(8)
Compound **6c**	
Bond length	*d*/Å
Pd(1)—Cl(1)	2.3162(12)
Pd(1)—N(1)	1.964(3)
Pd(1)—N(2)	2.025(4)
Pd(1)—S(1)	2.2662(11)
N(1)—C(10)	1.297(5)
O(1)—C(10)	1.243(5)
S(1)—C(11)	1.793(4)
Angle	ω/deg
N(1)—Pd(1)—Cl(1)	177.00(10)
N(2)—Pd(1)—Cl(1)	97.72(14)
N(1)—Pd(1)—N(2)	84.42(16)

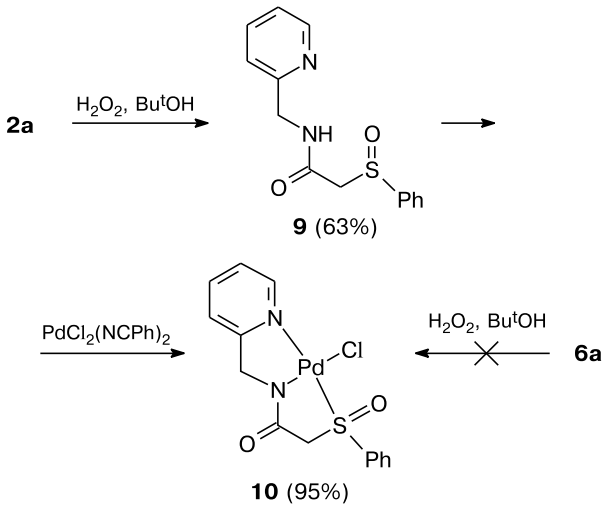
Parameter	Value
Compound **6c**	
Angle	ω/deg
N(1)—Pd(1)—S(1)	84.13(10)
S(1)—Pd(1)—Cl(1)	93.52(5)
N(2)—Pd(1)—S(1)	167.20(13)
Compound **6d**	
Bond length	*d*/Å
Pd(1)—Cl(1)	2.3127(9)
Pd(1)—N(1)	2.0472(16)
Pd(1)—S(1)	2.2938(9)
Pd(1)—S(2)	2.3111(9)
N(1)—C(7)	1.365(2)
O(1)—C(7)	1.233(2)
S(1)—C(8)	1.8116(19)
P(1)—S(2)	2.0176(9)
Angle	ω/deg
S(2)—Pd(1)—Cl(1)	85.963(19)
N(1)—Pd(1)—S(2)	98.81(4)
N(1)—Pd(1)—S(1)	85.37(4)
S(1)—Pd(1)—Cl(1)	90.485(19)
N(1)—Pd(1)—Cl(1)	173.01(4)
S(2)—Pd(1)—S(1)	172.261(18)
Compound **8**	
Bond length	*d*/Å
Pd(1)—Cl(1)	2.3166(15)
Pd(1)—N(1)	2.032(5)
Pd(1)—S(1)	2.3131(15)
Pd(1)—S(2)	2.3338(15)
N(1)—C(7)	1.347(8)

Parameter	Value
Compound **8**	
Bond length	*d*/Å
O(1)—C(7)	1.256(8)
S(1)—C(9)	1.831(7)
P(1)—S(2)	2.010(2)
Angle	ω/deg
S(2)—Pd(1)—Cl(1)	84.29(6)
S(2)—Pd(1)—N(1)	95.32(16)
N(1)—Pd(1)—S(1)	90.76(16)
S(1)—Pd(1)—Cl(1)	89.86(6)
N(1)—Pd(1)—Cl(1)	178.01(16)
S(2)—Pd(1)—S(1)	170.66(6)
Compound **10***	
Bond length	*d*/Å
Pd(1)—Cl(1)	2.3146(5)
Pd(1)—N(1)	1.9629(17)
Pd(1)—N(2)	2.0435(18)
Pd(1)—S(1)	2.2178(5)
N(1)—C(7)	1.330(3)
O(1)—C(7)	1.242(3)
S(1)—C(8)	1.812(2)
S(1)—O(2)	1.4669(16)
Angle	ω/deg
N(1)—Pd(1)—Cl(1)	177.70(5)
N(2)—Pd(1)—Cl(1)	95.87(5)
N(1)—Pd(1)—N(2)	81.97(7)
N(1)—Pd(1)—S(1)	85.36(5)
S(1)—Pd(1)—Cl(1)	96.785(19)
N(2)—Pd(1)—S(1)	167.27(5)

* The data for one of two symmetrically independent molecules.

Taking into account an important role in transition metal chemistry of such weak donor ligands as sulfoxides[11], we have chosen ligand **2a** as an example to demonstrate a possibility of the oxidation of the thioether group with an excess of hydrogen peroxide in anhydrous *tert*-butyl alcohol (Scheme 4). It is important to note that under these conditions the thioether is oxidized to sulfoxide, and no product of its further oxidation (sulfone) was formed. The IR spectrum of compound **9**, together with the absorption bands of the functional amide group (ν/cm^{-1}: 1551 (NHCO), 1669 (C=O), 3278 (NH)), exhibits also a strong absorption band in the region of 1043 cm^{-1} characteristic for the stretching vibrations of the S=O bond. In the ^{13}C NMR spectrum, the signals of the carbon atoms of the methylene unit and the *ipso*-carbon atom in the phenyl ring directly bonded to the sulfoxide group are downfield shifted relative to the spectrum of the starting sulfide **2a** ($\Delta\delta_C$ = 22.48 and 7.23 ppm, respectively). In the ^{1}H NMR spectrum, the signals for the hydrogen atoms of the prochiral methylene group in the $S(O)CH_2$ fragment are found as two doublets because of the introduction of the center of asymmetry (the sulfur atom of the sulfoxide group).

Scheme 4



The reaction of ligand **9** with $PdCl_2(NCPh)_2$ in dichloromethane at ~20 °C in the presence of Et_3N also proceeded as the metallation of the amide group with concomitant coordination of the nitrogen atom of the pyridine ring and

the sulfur atom of the sulfoxide fragment, leading to κ^3-*N*,*N*,*S*-complex **10** in high yield (see Scheme 4). An attempt to oxidize the sulfanyl group in palladocycle **6a** under conditions similar to those used in the synthesis of ligand **9** did not give sulfoxide complex **10**: the starting complex **6a** was recovered unchanged from the reaction mixture even after 7 days of the reaction contact.

In the ^{1}H NMR spectrum, like in the case of sulfide analogues, the complexation of sulfoxide **9** was accompanied by a characteristic downfield shift of the signal of the proton at the tertiary carbon atom *ortho* to the N-donor center of the pyridine ring ($\Delta\delta_H$ = 0.4 ppm), as well as of the signal of the carbon atom in the $S(O)CH_2$ fragment in the ^{13}C NMR spectrum ($\Delta\delta_C$ = 10.38 ppm). The IR spectrum of complex **10** does not exhibit absorption bands of the stretching or bending vibrations of the NH fragment, which, together with the disappearance of the downfield signal for the amide protons in the ^{1}H NMR spectrum, confirms the occurrence of metallation. Apart from that, the absorption band of the stretching vibrations of the S(O) group is strongly shifted toward higher frequencies relative to the IR spectrum of the free ligand (ν = 1117 cm^{-1}). Complex **10** crystallizes with two symmetrically independent molecules in the unit cell (Fig. 5), which differ in both the Pd(1)—S(1) bond distance (2.2178(5) and 2.2214(6) Å) (see Table 1) and the conformations of the fused metallocycles. Thus, the N,S-metallocycle is a flattened *envelope* with the deviation of Pd(1) atom by 0.20 Å or a *half-chair* with the deviation of Pd(1) and C(8) atoms by 0.50 and 0.30 Å, respectively, with the conformation of the second five-membered metallocycle being changed from a planar to the flattened *envelope* with the deviation of Pd(1) atom by 0.25 Å. This leads to the difference in the geometry of the palladium atom coordination site: the first molecule has nearly ideal square planar geometry, whereas the second has a distorted square planar geometry with a slight folding along the N(1)—Pd(1)—Cl(1) line with the N(2)—Pd(1)—S(1) angle of 163.41(5)°.

The catalytic activity of palladocycles obtained was tested in the model Suzuki reaction, the cross-coupling of aryl bromides with $PhB(OH)_2$ (Scheme 5). For correct comparison of the results, all the experiments were carried out under similar conditions: heating in DMF at 120 °C for 5 h in the presence of K_3PO_4 as a base. Almost all the complexes obtained in this work exhibit a high level of activity in the cross-coupling of 4-bromoacetophenone (**11a**) with $PhB(OH)_2$ at the concentration of 1 mol.% (Table 2). Palladocycles **7** and **8** with the alkyl (neomenthyl) substituent at the sulfur atom of the thioether group were more active than their phenylmercapto-substituted analogue **6d**. It was found that upon a decrease in the concentration of the palladium complexes to 0.1 mol.%, S,N,S-complexes **6d**, **7**, and **8** afforded a higher level of conversion of 4-bromoacetophenone than N,N,S-hemilabile palladocycles **6a**—**c** and **10** (see Table 2). Note that the sulfoxide derivative **10** turned out to be more active (pre)catalyst than its sulfide prototype **6a**. An increase in the catalytic activity was also observed upon elongation of the aliphatic spacer between the auxiliary donor group and the amide fragment. Thus, the yield of biaryl **12a** with a 0.1 mol.% of complex **6b** based on the aminoethylpyridine ligand was 50% *versus* 25% in the case of its aminomethylpyridine analogue **6a**. At the same time, complex **8**, which is a 3-mercaptopropionic acid derivative, exhibited higher catalytic activity than palladocycle **7** based on mercaptoacetamide. In the case of less active 4-bromoanisole (**11b**), most complexes obtained in this work were revealed to be inefficient: the conversion of **11b** was 4—27% at 1 mol.% concentration of the (pre)catalyst. However, S,N,S-palladocycle **8** exhibited a high enough level of activity in the cross-coupling of 4-bromoanisole with $PhB(OH)_2$ not only at the catalyst loading of 1 mol.%, but also upon a ten-fold decrease in the concentration of the palladium (pre)catalyst (75 and 77%, respectively).

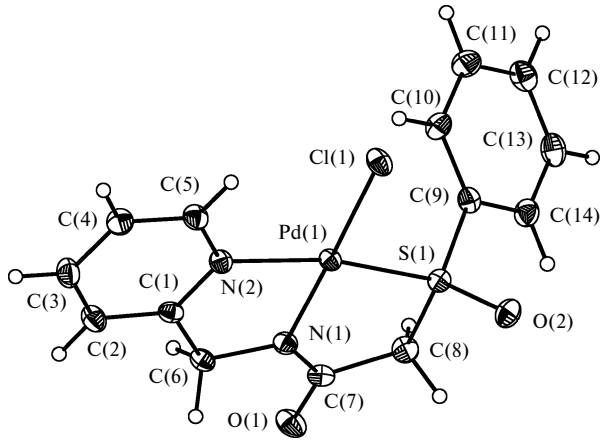
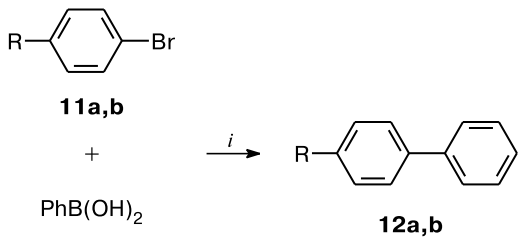


Fig. 5. General view of one of two symmetrically independent molecules of complex **10** in crystal.

Scheme 5



R = C(O)Me (**a**), OMe (**b**)

i. Catalyst [Pd], DMF, 120 °C, 5 h, K_3PO_4.

In conclusion, the functionalized mercaptoacetic and propionic acid amides with an additional N- or S-donor cen-

Table 2. Catalytic activity of Pd^{II} N,N,S- and S,N,S-complexes in the cross-coupling of 4-bromoacetophenone (**11a**) with $PhB(OH)_2$ (Suzuki reaction)

Catalyst loading (mol.%)	Yield of product **12a** (%)						
	6a	**6b**	**6c**	**6d**	**7**	**8**	**10**
1	98	95	96	58	87	100	100
0.1	25	50	37	76	84	100	53

ter in the amine part in the reaction with $PdCl_2(NCPh)_2$ easily form κ^3-X,N,S-complexes (X = N, S) with the tridentate monoanionic coordination mode. The preliminary evaluation of the catalytic activity of the resulting metal complexes allowed us to determine the main tendencies in the structure—activity correlation, which will be used for the modification of the ligand framework in search for new efficient catalysts.

Experimental

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AV-300 (300.13, 75.47, and 121.49 MHz, respectively) and Bruker AMX-400 (400.13, 100.61, and 161.98 MHz, respectively) in $CDCl_3$, using residual signals of the solvent as an internal standard (^1H, ^{13}C) and 85% aqueous H_3PO_4 as an external standard (^{31}P). ^{13}C NMR spectra were registered in the JMODECHO mode: the signals of carbon atoms with odd and even numbers of protons had the opposite polarities. In the description of the NMR spectra of phenylmercapto derivatives, the numbering scheme for carbon atoms of the amine component corresponded to that in the compound names, for neomenthyl analogues the numbering scheme for carbon atoms is given in Scheme 2. The notations M and m in the description of NMR spectra of complexes **7** and **8** refer to the major and minor isomer, respectively.

IR spectra were recorded on a Magna-IR 750 Nicolet Fourier-transform spectrometer, resolution 2 cm^{-1}, number of scans 128 (in KBr pellets). Absorption bands were assigned according to the literature data.[12]

Reaction progress was monitored by TLC on Silufol TLC Plates w/UV254. Chromatographic purification of products was carried out on Macherey—Nagel silica gel (MN Kiselgel 60, 0.063—0.2 mm). Melting points were measured on an EZ Melt apparatus (Stanford Research Systems, USA) and are uncorrected.

Dichloromethane was distilled over P_2O_5, THF was distilled from Na/benzophenone. *N*-Substituted chloroacetamides **1a**,[9a,13] **1c**,[14] and **1d** (see Ref. 15) were obtained by the reaction of $ClCH_2C(O)Cl$ with the corresponding amines according to the known procedures. The synthesis of amide **2b** was described in the patent,[16] however, its physicochemical characteristics were not reported. Neomenthylmercaptane was synthesized according to the procedure published earlier.[17] Other starting compounds were obtained from commercial sources (Acros, Sigma—Aldrich) and used without additional purification.

2-Chloro-*N*-[2-(pyridin-2-yl)ethyl]acetamide (1b). A solution of chloroacetyl chloride (0.61 g, 5.41 mmol) in dichloromethane (5 mL) was slowly added dropwise to a stirred solution of 2-(pyridin-2-yl)ethylamine (0.66 g, 5.41 mmol) and Et_3N (0.55 g, 5.41 mmol) in CH_2Cl_2 (20 mL) at −10 °C under argon atmosphere. The reaction mixture was stirred for 1 h at ~20 °C, then washed with distilled water. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4. The solvent was removed *in vacuo* to give compound **1b** (1.01 g, 94%) as a dark oil, which was used further without purification. ^1H NMR (400.13 MHz), δ: 3.09 (t, 2 H, CH_2Py, $^3J_{H,H}$ = 6.2 Hz); 3.78 (dt, 2 H, CH_2N, $^3J_{H,H}$ = = 6.2 Hz, $^3J_{H,H}$ = 6.0 Hz); 4.08 (s, 2 H, CH_2Cl); 7.24 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = 7.6 Hz); 7.25 (dt, 1 H, H(C(5)), Py, $^3J_{H,H}$ = 3.7 Hz, $^3J_{H,H}$ = 7.6 Hz); 7.68 (dt, 1 H, H(C(4)), Py, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz); 7.81 (br.s, 1 H, NH); 8.60 (d, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 3.7 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 36.16 (s, CH_2Py); 38.78 (s, CH_2N); 42.60 (s, CH_2Cl); 121.71 and 123.44 (both s, C(3) and C(5), Py); 136.86 (s, C(4), Py); 148.90 (s, C(6), Py); 158.97 (s, C(2), Py); 165.85 (s, C=O).

Synthesis of 2-phenylsulfanylacetamides 2a—d (general procedure). A solution of thiophenol (0.55 g, 5.00 mmol) in THF (5 mL) was slowly added dropwise to a stirred suspension of $KOBu^t$ (0.56 g, 5.00 mmol) in THF (20 mL) under argon atmosphere. In 30 min, a solution of the corresponding chloroacetamide **1a—d** (5.00 mmol) in THF (10 mL) was added dropwise to the mixture obtained. Then, the reaction mixture was left under ambient conditions for 12 h and diluted with water, the product was extracted with chloroform. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4. The solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent chloroform—methanol (100 : 1)) to give compound **2a** (1.14 g, 88%) as a light yellow oil and compounds **2b** (1.05 g, 77%), **2c** (1.19 g, 81%), and **2d** (1.78 g, 77%) as light yellow (**2b**) or beige (**2c,d**) crystalline solids.

2-(Phenylsulfanyl)-*N*-(pyridin-2-ylmethyl)acetamide (2a). ^1H NMR (300.13 MHz), δ: 3.74 (s, 2 H, CH_2S); 4.58 (d, 2 H, CH_2Py, $^3J_{H,H}$ = 5.2 Hz); 7.12 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = 7.8 Hz); 7.17—7.39 (m, 6 H, 1 H, Py + 5 H, Ph); 7.61 (dt, 1 H, H(C(4)), Py, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.7 Hz); 7.95 (br.s, 1 H, NH); 8.53 (d, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz), δ: 37.62 (s, CH_2S); 44.61 (s, CH_2Py); 121.64 and 122.22 (both s, C(3) and C(5), Py); 126.58 (s, *p*-C, Ph); 128.64 and 129.06 (both s, *o*-C and *m*-C, Ph); 134.62 (s, *ipso*-C, Ph); 136.60 (s, C(4), Py); 148.92 (s, C(6), Py); 156.07 (s, C(2), Py); 167.99 (s, C=O). IR, ν/cm^{-1}: 451 w, 475 w, 494 w, 562 w, 613 w, 618 w, 639 w, 690 m, 738 m, 758 m, 993 w, 1024 w, 1047 w, 1088 w, 1149 w, 1162 w, 1227 w, 1319 w, 1354 w, 1418 m, 1438 m, 1475 m, 1482 m, 1546 br, m (NHCO), 1570 m, 1583 m, 1593 m, 1643 s (C=O), 2856 v.w, 2929 w, 2978 w, 3051 w, 3312 br, m (NH). Found (%): C, 64.95; H, 5.47; N, 10.69. $C_{14}H_{14}N_2OS$. Calculated (%): C, 65.09; H, 5.46; N, 10.84.

2-(Phenylsulfanyl)-*N*-[2-(pyridin-2-yl)ethyl]acetamide (2b). M.p. 75—77 °C (EtOAc). ^1H NMR (400.13 MHz), δ: 2.89 (t, 2 H, CH_2Py, $^3J_{H,H}$ = 6.2 Hz); 3.58 (s, 2 H, CH_2S); 3.65 (dt, 2 H, CH_2N, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 6.0 Hz); 6.99 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = 7.7 Hz); 7.06—7.09 (m, 1 H, H(C(5)), Py); 7.12—7.22 (m, 5 H, Ph); 7.51 (dt, 1 H, H(C(4)), Py, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.7 Hz); 7.65 (br.s, 1 H, NH); 8.43 (d, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 4.7 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 36.54 (s, CH_2Py); 37.34 (s, CH_2S); 38.67 (s, CH_2N); 121.38 and 123.21 (both s, C(3) and C(5), Py); 126.32 (s, *p*-C, Ph); 126.54 and 128.02 (both s, *o*-C and *m*-C, Ph); 134.73 (s, *ipso*-C, Ph); 136.37

(s, C(4), Py); 149.02 (s, C(6), Py); 158.95 (s, C(2), Py); 167.63 (s, C=O). IR, ν/cm^{-1}: 448 w, 473 w, 502 w, 558 w, 595 w, 629 w, 690 m, 739 s, 752 w, 775 m, 992 w, 1025 w, 1150 w, 1192 w, 1255 w, 1286 m, 1365 w, 1393 m, 1433 m, 1472 m, 1482 m, 1527 s (NHCO), 1568 w, 1584 m, 1650 s (C=O), 2865 v.w, 2918 w, 2956 w, 3015 v.w, 3079 v.w, 3330 m (NH). Found (%): N, 10.28; S, 11.50. $C_{15}H_{16}N_2OS$. Calculated (%): N, 10.29; S, 11.77.

2-Phenylsulfanyl-*N*-(quinolin-8-yl)acetamide (2c). M.p. 98—100 °C (EtOH). ^{1}H NMR (400.13 MHz), δ: 3.94 (s, 2 H, CH_2S); 7.22 (t, 1 H, *p*-H, Ph, $^3J_{H,H}$ = 7.2 Hz); 7.29 (t, 2 H, *m*-H, Ph, $^3J_{H,H}$ = 7.2 Hz); 7.48 (dd, 1 H, H(C(3)), Qu (Qu is the quinoline substituent), $^3J_{H,H}$ = 8.3 Hz, $^3J_{H,H}$ = 4.3 Hz); 7.54—7.58 (m, 2 H, Ph + 2 H, Qu); 8.17 (dd, 1 H, H(C(4)), Qu, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.5 Hz); 8.77 (dd, 1 H, Qu, $^3J_{H,H}$ = 5.2 Hz, $^4J_{H,H}$ = 1.5 Hz); 8.87 (dd, 1 H, H(C(2)), Qu, $^3J_{H,H}$ = 4.3 Hz, $^4J_{H,H}$ = 1.5 Hz); 11.12 (br.s, 1 H, NH). ^{13}C{^{1}H} NMR (100.61 MHz), δ: 39.87 (s, CH_2S); 116.39 (s, C(7), Qu); 121.56 and 121.91 (both s, C(3) and C(5), Qu); 127.05 and 127.12 (both s, C(6), Qu and *p*-C, Ph); 127.86 (s, C(4a), Qu); 129.11 and 129.84 (both s, *m*-C and *o*-C, Ph); 134.02 and 134.44 (both s, C(8), Qu and *ipso*-C, Ph); 136.10 (s, C(4), Qu); 138.68 (s, C(8a), Qu); 148.36 (s, C(2), Qu); 166.68 (s, C=O). IR, ν/cm^{-1}: 484 m, 539 w, 593 w, 635 w, 688 m, 737 m, 743 m, 760 m, 785 m, 824 m, 881 w, 893 w, 946 w, 1029 w, 1073 w, 1156 m, 1235 w, 1254 w, 1329 m, 1391 m, 1423 m, 1437 m, 1482 m, 1489 m, 1521 and 1530 s (NHCO), 1578 w, 1684 s (C=O), 2910 v.w, 2968 v.w, 3051 v.w, 3079 v.w, 3296 m (NH). Found (%): C, 69.41; H, 4.82; N, 9.38. $C_{17}H_{14}N_2OS$. Calculated (%): C, 69.36; H, 4.79; N, 9.52.

***N*-[2-(Diphenylthiophosphoryl)phenyl]-2-(phenylsulfanyl)-acetamide (2d).** M.p. 118—119 °C. ^{31}P{^{1}H} NMR (161.98 MHz), δ: 39.59. ^{1}H NMR (400.13 MHz), δ: 3.25 (s, 2 H, CH_2S); 6.79 (ddd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.5 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = = 1.4 Hz); 7.03—7.07 (m, 1 H, Ar); 7.15—7.28 (m, 5 H, Ar); 7.43—7.54 (m, 7 H, Ar); 7.73 (ddd, 4 H, *o*-H, P(S)Ph_2, $^3J_{P,H}$ = = 13.6 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz); 7.93 (dd, 1 H, H(C(6)), $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,P}$ = 5.2 Hz); 10.30 (br.s, 1 H, NH). ^{13}C{^{1}H} NMR (100.61 MHz), δ: 38.44 (s, CH_2S); 123.28 (d, C(2), $^1J_{C,P}$ = 85.5 Hz); 124.31 (d, C(4), $^3J_{C,P}$ = 12.0 Hz); 125.55 (d, C(6), $^3J_{C,P}$ = 7.1 Hz); 126.51 (s, *p*-C, SPh); 128.60 (d, *m*-C, P(S)Ph_2, $^3J_{C,P}$ = 12.7 Hz); 128.88 and 129.13 (both s, *m*-C and *o*-C, SPh); 130.54 (d, *ipso*-C, P(S)Ph_2, $^1J_{C,P}$ = 86.2 Hz); 131.95 (s, *p*-C, P(S)Ph_2); 132.00 (d, C(3), $^2J_{CP}$ = 9.4 Hz); 132.10 (d, *o*-C, P(S)Ph_2, $^2J_{C,P}$ = 11.1 Hz); 132.67 (d, C(5), $^4J_{C,P}$ = 2.0 Hz); 134.80 (s, *ipso*-C, SPh); 140.44 (d, C(1), $^2J_{C,P}$ = 3.8 Hz); 166.85 (s, C=O). IR, ν/cm^{-1}: 509 m, 522 m, 535 w, 613 w, 631 m (P=S), 653 w, 693 m, 714 s, 740 m, 754 m, 765 w, 898 w, 999 w, 1025 w, 1072 w, 1101 m, 1130 w, 1184 w, 1223 w, 1248 w, 1292 m, 1312 w, 1403 w, 1438 s, 1482 m, 1504 s (NHCO), 1572 m, 1588 w, 1683 s (C=O), 2975 w, 3059 w, 3201 w (NH). Found (%): C, 67.09; H, 4.40; N, 2.94. $C_{26}H_{22}NOPS_2 \cdot 0.2\ H_2O$. Calculated (%): C, 67.42; H, 4.87; N, 3.02.

Synthesis of 2-neomenthylsulfanylacetamides 3 and 4 (general procedure). A solution of (1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexanethiol (neomenthylmercaptane) (0.40 g, 2.33 mmol) in THF (5 mL) was slowly added dropwise to a stirred suspension of KOBu^t (0.26 g, 2.33 mmol) in THF (15 mL) under argon atmosphere. In 30 min, a solution of chloroacetamide **1d** or **5** (2.33 mmol) in THF (10 mL) was added dropwise to the mixture obtained. Then, the reaction mixture was left under ambient conditions for 12 h and diluted with water, the product was extracted with chloroform. The organic layer was separated, washed with saturated aqueous $NaHCO_3$ and water, dried over Na_2SO_4. The solvent was removed *in vacuo*, the resulting residue was purified by column chromatography on silica gel (eluent EtOAc—hexane (1 : 5) (**3**), CH_2Cl_2—hexane (1 : 1) (**4**)) to give compounds **3** (0.55 g, 45%) and **4** (0.62 g, 50%) as white crystalline solids.

***N*-[2-(Diphenylthiophosphoryl)phenyl]-2-(neomenthylsulfanyl)acetamide (3).** M.p. 142—144 °C, $[\alpha]_D^{20}$ +72.6° (*c* 0.45, $CHCl_3$). ^{31}P{^{1}H} NMR (121.49 MHz), δ: 39.71. ^{1}H NMR (400.13 MHz), δ: 0.81—0.86 (m, 1 H, Alk (Alk is the neomenthyl substituent)); 0.86 (d, 3 H, H(C(16)), $^3J_{H,H}$ = 6.4 Hz); 0.89 (d, 3 H, H(C(14)) or H(C(15)), $^3J_{H,H}$ = 6.6 Hz); 0.90 (d, 3 H, H(C(15)) or H(C(14)), $^3J_{H,H}$ = 6.5 Hz); 1.03—1.21 (m, 3 H, Alk); 1.64—1.76 (m, 3 H, Alk); 1.88—1.95 (m, 2 H, Alk); 2.80, 2.82 (ABq, 2 H, CH_2S, $J_{A,B}$ = 15.3 Hz); 3.18 (br.s, H(C(7))); 6.85 (ddd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.4 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz); 7.08—7.12 (m, 1 H, Ar); 7.49—7.60 (m, 7 H, Ar); 7.78 (ddd, 4 H, *o*-H, P(S)Ph_2, $^3J_{H,P}$ = 13.7 Hz, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.4 Hz); 8.00 (dd, 1 H, H(C(6)), $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,P}$ = 5.0 Hz); 10.24 (br.s, 1 H, NH). ^{13}C{^{1}H} NMR (100.61 MHz), δ: 20.74, 20.97 (both s, C(14) and C(15)); 22.05 (s, C(16)); 25.71 (s, C(9)); 26.25, 29.69 (both s, C(11) and C(13)); 35.23, 35.91 (both s, C(10) and CH_2S); 39.89 (s, C(12)); 45.58, 48.79 (both s, C(7) and C(8)); 123.36 (d, C(2), $^1J_{C,P}$ = 85.5 Hz); 124.21 (d, C(4), $^3J_{C,P}$ = 12.1 Hz); 125.63 (d, C(6), $^2J_{C,P}$ = 7.3 Hz); 128.63 (d, *m*-C, P(S)Ph_2, $^3J_{C,P}$ = 12.8 Hz); 130.65 (d, *ipso*-C, P(S)Ph, $^1J_{P,C}$ = = 85.8 Hz); 130.80 (d, *ipso*-C, P(S)Ph, $^1J_{C,P}$ = 85.8 Hz); 131.96 (d, *p*-C, P(S)Ph_2, $^4J_{C,P}$ = 2.9 Hz); 132.07 (d, C(3), $^2J_{C,P}$ = 10.3 Hz); 132.12 (d, *o*-C, P(S)Ph, $^2J_{C,P}$ = 11.0 Hz); 132.17 (d, *o*-C, P(S)Ph, $^2J_{C,P}$ = 11.0 Hz); 132.72 (d, C(5), $^4J_{C,P}$ = 2.2 Hz); 140.73 (d, C(1), $^2J_{C,P}$ = 4.4 Hz); 168.29 (s, C=O). IR, ν/cm^{-1}: 514 m, 525 m, 537 w, 613 w, 636 m (P=S), 694 m, 717 s, 753 m, 766 w, 1000 w, 1100 m, 1132 w, 1183 w, 1238 w, 1296 m, 1309 w, 1386 w, 1405 w, 1437 s, 1480 w, 1503 s (NHCO), 1575 m, 1689 s (C=O), 2847 w, 2867 w, 2914 m, 2945 m, 3057 w, 3268 br, w (NH). Found (%): C, 68.95; H, 6.68; N, 2.66. $C_{30}H_{36}NOPS_2$. Calculated (%): C, 69.06; H, 6.96; N, 2.68.

***N*-[2-(Diphenylthiophosphoryl)phenyl]-2-(neomenthylsulfanyl)propionamide (4).** M.p. 136—137 °C, $[\alpha]_D^{20}$ +142.54° (*c* 0.41, $CHCl_3$). ^{31}P{^{1}H} NMR (121.49 MHz), δ: 40.17. ^{1}H NMR (400.13 MHz), δ: 0.82—0.98 (m, 10 H, Alk); 1.06—1.22 (m, 3 H, Alk); 1.56—1.74 (m, 3 H, Alk); 1.87—1.92 (m, 2 H, Alk); 2.21—2.34 (m, 2 H, Alk); 2.39—2.52 (m, 2 H, Alk); 3.08 (br.s, 1 H, H(C(7))); 6.83 (ddd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.5 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.4 Hz); 7.09—7.14 (m, 1 H, Ar); 7.51—7.65 (m, 7 H, Ar); 7.77 (ddd, 4 H, *o*-H, P(S)Ph_2, $^3J_{H,P}$ = 13.7 Hz, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.6 Hz); 8.13 (dd, 1 H, H(C(6)), $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = = 4.9 Hz); 10.00 (br.s, 1 H, NH). ^{13}C{^{1}H} NMR (100.61 MHz), δ: 20.74, 20.99 (both s, C(14) and C(15)); 22.13 (s, C(16)); 25.87 (s, C(9)); 26.22 (s, C(11) or C(13)); 26.59 (s, CH_2S); 29.83 (s, C(13) or C(11)); 35.29 (s, C(10)); 37.91 (s, CH_2); 40.50 (s, C(12)); 46.81, 48.74 (both s, C(7) and C(8)); 121.93 (d, C(2), $^1J_{C,P}$ =85.5 Hz); 123.98 (d, C(4), $^3J_{C,P}$ = 12.5 Hz); 125.24 (d, C(6), $^3J_{P,C}$ = 7.0 Hz); 128.72 (d, *m*-C, P(S)Ph_2, $^3J_{C,P}$ = = 12.8 Hz); 130.63 (d, *ipso*-C, P(S)Ph, $^1J_{C,P}$ = 85.8 Hz); 130.64 (d, *ipso*-C, P(S)Ph, $^1J_{C,P}$ = 86.2 Hz); 132.03—132.23 (m, overlapped signals of *o*-C and *p*-C, P(S)Ph_2 and C(3)); 132.86 (d, C(5), $^4J_{C,P}$ = 2.2 Hz); 140.95 (d, C(1), $^2J_{C,P}$ = 4.4 Hz); 169.35 (s, C=O). IR, ν/cm^{-1}: 504 w, 516 m, 531 w, 614 w, 635 m (P=S), 693 m, 716 s, 757 m, 999 w, 1101 m, 1130 w, 1161 w, 1183 w, 1234 w, 1293 m, 1365 w, 1436 s, 1456 w, 1480 w, 1503 m (NHCO), 1573 m, 1594 w, 1691 and 1702 m (C=O), 2837 w,

2867 w, 2913 m, 2949 m, 3053 w, 3283 br, w (NH). Found (%): C, 69.74; H, 7.26; N, 2.62. $C_{31}H_{38}NOPS_2$. Calculated (%): C, 69.50; H, 7.15; N, 2.61.

3-Chloro-*N*-[2-(diphenylthiophosphoryl)phenyl]propionamide (5). A solution of 3-chloropropionyl chloride (0.51 g, 4.01 mmol) in dichloromethane (5 mL) was slowly added dropwise to a mixture of 2-diphenylthiophosphorylaniline (1.24 g, 4.01 mmol) and Et_3N (0.41 g, 4.06 mmol) in CH_2Cl_2 (40 mL) at 5—10 °C. The reaction mixture was stirred for 4 h at ~20 °C, then washed with water. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent EtOAc—hexane (1 : 3)) to give compound **5** (1.00 g, 63%) as a white crystalline solid, m.p. 159—160 °C. $^{31}P\{^1H\}$ NMR (121.49 MHz), δ: 40.28. ^1H NMR (300.13 MHz), δ: 2.49 (t, 2 H, CH_2, $^3J_{H,H}$ = 6.9 Hz); 3.54 (t, 2 H, CH_2Cl, $^3J_{H,H}$ = 6.9 Hz); 6.81 (dd, 1 H, H(C(3)), Ar, $^3J_{H,P}$ = 14.5 Hz, $^3J_{H,H}$ = 7.8 Hz); 7.06—7.11, 7.47—7.61 (both m, 1 H + 7 H, Ar); 7.72 (dd, 4 H, *o*-H, Ph, $^3J_{H,P}$ = 13.9 Hz, $^3J_{H,H}$ = 7.1 Hz); 8.14 (dd, 1 H, H(C(6)), Ar, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,P}$ = 5.1 Hz); 10.21 (s, 1 H, NH). IR, ν/cm^{-1}: 503 w, 516 s, 527 w, 551 w, 614 w, 637 m (P=S), 672 w, 696 s, 714 s, 757 s, 997 w, 1073 w, 1098 m, 1132 w, 1189 w, 1236 w, 1300 m, 1438 s, 1481 w, 1508 s (NHCO), 1571 m, 1593 w, 1687 s (C=O), 3049 w, 3274 m (NH). Found (%): C, 63.09; H, 4.94; N, 3.44. $C_{21}H_{19}ClNOPS$. Calculated (%): C, 63.08; H, 4.79; N 3.50. The side product ***N*-[2-(diphenylthiophosphoryl)phenyl]-prop-2-enamide** (0.30 g, 21%) was isolated as a white crystalline compound, m.p. 156—157 °C. $^{31}P\{^1H\}$ NMR (121.49 MHz), δ: 40.28. ^1H NMR (300.13 MHz), δ: 5.60 (X, ABX, 1 H, CH_2, $J_{B,X}$ =10.6 Hz, $J_{A,X}$ = 0.7 Hz); 6.02 (B, ABX, 1 H, CH, $J_{A,B}$ = = 17.1 Hz, $J_{B,X}$ = 10.6 Hz); 6.20 (A, ABX, 1 H, CH_2, $J_{A,B}$ = 17.1 Hz, $J_{A,X}$ = 0.7 Hz); 6.81 (ddd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.5 Hz, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.4 Hz); 7.05—7.10 (m, 1 H, Ar); 7.46—7.60 (m, 8 H, Ar); 7.72 (ddd, 4 H, *o*-H, $P(S)Ph_2$, $^3J_{H,P}$ = 13.7 Hz, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.5 Hz); 8.28 (dd, 1 H, H(C(6)), $^3J_{H,H}$ = = 8.2 Hz, $^4J_{H,P}$ = 5.2 Hz); 10.28 (s, 1 H, NH). IR, ν/cm^{-1}: 505 w, 518 m, 614 w, 635 m (P=S), 676 w, 693 m, 712 s, 753 m, 775 w, 798 w, 976 m, 998 w, 1077 w, 1100 m, 1131 w, 1178 m, 1283 m, 1311 w, 1402 w, 1435 s, 1480 w, 1505 s (NHCO), 1575 m, 1595 w, 1629 w, 1685 s (C=O), 3055 w, 3284 w (NH). Found (%): C, 69.41; H, 5.06; N, 3.69. $C_{21}H_{18}NOPS$. Calculated (%): C, 69.40; H, 4.99; N, 3.85.

Synthesis of palladium κ^3-*N*,*N*,*S*-complexes 6a—c (general procedure). A solution of $PdCl_2(NCPh)_2$ (76 mg, 0.198 mmol) in dichloromethane (5 mL) was slowly added dropwise to a solution of the corresponding ligand **2a—c** (0.198 mmol) and Et_3N (28 μL, 0.200 mmol) in CH_2Cl_2 (10 mL). In 12 h, the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2—MeOH (50 : 1)) to give complexes **6a** (70 mg, 89%), **6b** (60 mg, 73%), and **6c** (80 mg, 93%) as yellow (**6a**,**b**) or dark orange (**6c**) crystalline solids.

κ^3-*N*,*N*,*S*-Chloro[*N*-(2-phenylsulfanylacetyl)-*N*-(pyridin-2-ylmethyl)amido]palladium(II) (6a). M.p. 225—227 °C (decomp.). ^1H NMR (400.13 MHz), δ: 3.72 (d, 1 H, CH_2S, $^2J_{H,H}$ = 16.8 Hz); 4.16 (d, 1 H, CH_2S, $^2J_{H,H}$ = 16.8 Hz); 4.88 (s, 2 H, CH_2Py); 7.32 (m, 1 H, H(C(5)), Py); 7.37 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = = 8.0 Hz); 7.43—7.47 (m, 3 H, Ar); 7.86 (dt, 1 H, *p*-H, Ph, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz); 7.93—7.95 (m, 2 H, Ar); 8.89 (dd, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 5.8 Hz, $^4J_{H,H}$ = 0.9 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz), δ: 45.19 (s, CH_2S); 56.02 (s, CH_2Py); 121.55 and 122.89 (both s, C(3) and C(5), Py); 129.97 (s, *o*-C or *m*-C, Ph); 130.44 (s, *p*-C, Ph); 130.81 (s, *ipso*-C, Ph); 130.94 (s, *o*-C or *m*-C, Ph); 139.07 (s, C(4), Py); 148.60 (s, C(6), Py); 167.53 (s, C(2), Py); 175.98 (s, C=O). IR, ν/cm^{-1}: 439 w, 476 w, 687 w, 711 w, 749 m, 763 m, 889 w, 1000 w, 1052 w, 1095 w, 1159 w, 1212 w, 1281 w, 1384 m, 1442 m, 1483 m, 1563 m, 1596 s, 1614 sh, s, 1618 s (C=O), 2093 w, 3075 w. Found (%): N, 6.84; S, 7.72. $C_{14}H_{13}ClN_2OPdS$. Calculated (%): N, 7.02; S, 8.03.

κ^3-*N*,*N*,*S*-Chloro[*N*-(2-phenylsulfanylacetyl)-*N*-(2-pyridin-2-ylethyl)amido]palladium(II) (6b). M.p. 230—232 °C (decomp.). ^1H NMR (400.13 MHz), δ: 2.86—2.93 (m, 1 H, CH_2Py); 3.10—3.13 (m, 2 H, CH_2N); 3.50—3.55 (m, 1 H, CH_2Py); 3.60 (d, 1 H, CH_2S, $^2J_{H,H}$ = 16.7 Hz); 3.94 (d, 1 H, CH_2S, $^2J_{H,H}$ = 16.7 Hz); 7.30 (m, 1 H, H(C(5)), Py); 7.35 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = = 7.7 Hz); 7.42—7.47 (m, 3 H, *m*-C, Ph and H(C(4)), Py); 7.82 (dt, 1 H, *p*-H, Ph, $^3J_{H,H}$ = 7.7 Hz, $^4J_{H,H}$ = 1.5 Hz); 7.88 (dd, 2 H, *o*-H, Ph, $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,H}$ = 1.5 Hz); 9.17 (dd, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 5.9 Hz, $^4J_{H,H}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz), δ: 41.09, 41.15, and 42.40 (three s, CH_2S, CH_2Py and CH_2N); 122.80 and 124.62 (both s, C(3) and C(5), Py); 129.92 (s, *o*-C or *m*-C, Ph); 130.37 (s, *p*-C, Ph); 130.41 (s, *o*-C or *m*-C, Ph); 130.57 (s, *ipso*-C, Ph); 139.75 (s, C(4), Py); 152.92 (s, C(6), Py); 159.07 (s, C(2), Py); 178.10 (s, C=O). IR, ν/cm^{-1}: 433 w, 501 w, 527 w, 587 w, 658 w, 697 w, 759 m, 768 m, 788 w, 898 w, 938 w, 1023 w, 1112 w, 1156 m, 1228 w, 1239 w, 1252 w, 1306 w, 1333 w, 1386 m, 1438 m, 1480 m, 1572 m, 1595 s (C=O), 2856 w, 2921 w, 2998 w. Found (%): C, 43.69; H, 3.77; N, 6.65. $C_{15}H_{15}ClN_2OPdS$. Calculated (%): C, 43.60; H, 3.66; N, 6.78.

κ^3-*N*,*N*,*S*-Chloro[*N*-(2-phenylsulfanylacetyl)-*N*-(quinolin-8-yl)amido]palladium(II) (6c). M.p. 215—217 °C (decomp.). ^1H NMR (400.13 MHz), δ: 3.93 (d, 1 H, CH_2S, $^2J_{H,H}$ = 17.1 Hz); 4.54 (d, 1 H, CH_2S, $^2J_{H,H}$ = 17.1 Hz); 7.37—7.52 (m, 6 H, Ar); 7.98—8.01 (m, 2 H, Ar), 8.25 (dd, 1 H, H(C(4)), Qu, $^3J_{H,H}$ = 8.3 Hz, $^4J_{H,H}$ = 1.5 Hz); 8.90 (dd, 1 H, Qu, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 1.0 Hz); 9.00 (dd, 1 H, H(C(2)), Qu, $^3J_{H,H}$ = 5.2 Hz, $^4J_{H,H}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 46.58 (s, CH_2S); 120.93, 121.09 and 122.06 (three s, C(3), C(5) and C(7), Qu); 129.29 (s, *p*-C, Ph or C(6), Qu); 129.76 (s, C(4a), Qu); 130.04 (s, *m*-C or *o*-C, Ph); 130.45 (s, C(6), Qu *or p*-C, Ph); 130.92 (s, *o*-C or *m*-C, Ph); 139.23 (s, C(4), Qu); 145.80, 146.80 (both s, C(8) and C(8a), Qu); 148.63(s, C(2), Qu); 175.81 (s, C=O).* IR spectrum, ν/cm^{-1}: 469 w, 499 w, 540 w, 688 w, 746 m, 755 w, 766 w, 780 w, 826 m, 895 w, 984 w, 999 w, 1100 w, 1173 w, 1233 w, 1339 m, 1385 m, 1443 w, 1464 m, 1483 w, 1505 m, 1571 w, 1618 s (C=O), 2899 w, 2998 v.w, 3057 v.w. Found (%): C, 46.83; H, 3.03; N, 6.59. $C_{17}H_{13}ClN_2OPdS$. Calculated (%): C, 46.91; H, 3.01; N, 6.44.

Synthesis of palladium κ^3-*S*,*N*,*S*-complexes 6d, 7, and 8 (general procedure). A solution of $PdCl_2(NCPh)_2$ (64 mg, 0.167 mmol) in dichloromethane (5 mL) was slowly added dropwise to a solution of ligand **2d**, **3**, or **4** (0.167 mmol) in CH_2Cl_2 (5 mL). In 12 h, the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2—MeOH (50 : 1)) to give complexes **6d** (90 mg, 90%), **7** (93 mg, 82%), and **8** (101 mg, 89%) as red (**6d**) or orange (**7**, **8**) crystalline solids.

κ^3-*S*,*N*,*S*-Chloro{*N*-[2-(diphenylthiophosphoryl)phenyl]-*N*-(2-phenylsulfanylacetyl)amido}palladium(II) (6d). M.p. >253 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz), δ: 37.98. ^1H NMR

* The signal of the *ipso*-C quaternary carbon atom of the phenyl group was not observed.

(400.13 MHz), δ: 3.51, 3,56 (ABq, 2 H, CH_2S, $J_{A,B}$ = 16.2 Hz); 6.77 (dd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.8 Hz, $^3J_{H,H}$ = 7.6 Hz); 7.01 (dt, 1 H, H(C(4)), $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 2.7 Hz); 7.16 (dd, 1 H, H(C(6)), $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 5.9 Hz); 7.43—7.49 (m, 4 H, Ar); 7.57—7.62 (m, 4 H, Ar); 7.66—7.71 (m, 4 H, Ar); 7.85—7.94 (m, 4 H, Ar). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 42.88 (s, CH_2S); 122.60 (d, C(2), $^1J_{C,P}$ = 86.2 Hz); 123.70 (d, C(4), $^3J_{C,P}$ = 13.2 Hz); 124.54 (d, *ipso*-C, Ph, $^1J_{C,P}$ = 86.2 Hz); 128.13 (d, *ipso*-C, Ph, $^1J_{C,P}$ = 88.8 Hz); 129.11 (d, *m*-C, P(S)Ph, $^3J_{C,P}$ = 13.6 Hz); 129.22 (d, *m*-C, P(S)Ph, $^3J_{C,P}$ = 12.8 Hz); 129.68 (s, *ipso*-C, SPh); 129.80 (s, *m*-C or *o*-C, SPh); 129.84 (d, C(6), $^3J_{C,P}$ = 8.0 Hz); 130.09 (s, *p*-C, SPh); 130.64 (s, *o*-C or *m*-C, SPh); 130.89 (d, C(3), $^2J_{C,P}$ = 9.2 Hz); 132.08 (d, *o*-C, P(S)Ph, $^2J_{C,P}$ = 11.7 Hz); 132.92 (d, *p*-C, P(S)Ph or C(5), $^4J_{C,P}$ = 2.9 Hz); 133.22 (d, *o*-C, P(S)Ph, $^2J_{C,P}$ = 10.6 Hz); 133.41 (d, *p*-C, P(S)Ph or C(5), $^4J_{P,C}$=2.6 Hz); 133.51 (d, *p*-C, P(S)Ph or C(5), $^4J_{C,P}$ = 2.2 Hz); 150.47 (d, C(1), $^2J_{C,P}$ = 3.3 Hz); 176.70 (s, C=O). IR, ν/cm^{-1}: 494 w, 523 m, 532 m, 604 m (P=S), 621 w, 659 w, 690 m, 704 m, 723 w, 740 m, 753 m, 906 w, 999 w, 1025 w, 1070 w, 1105 m, 1136 w, 1162 w, 1186 w, 1266 w, 1309 m, 1436 m, 1463 m, 1481 w, 1565 w, 1578 m, 1624 s (C=O), 2919 w, 2973 w, 3055 w. Found (%): C, 52.30; H, 3.53; N, 2.30. $C_{26}H_{21}ClNOPPdS_2$. Calculated (%): C, 52.01; H, 3.53; N, 2.33.

κ^3-*S*,*N*,*S*-Chloro{*N*-[2-(diphenylthiophosphoryl)phenyl]-*N*-(2-neomenthylsulfanylacetyl)amido}palladium(II) (7). The ratio of M and m isomers was 2 : 1. M.p. >270 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz), δ: 37.89. ^1H NMR (400.13 MHz), δ: 0.90—0.92 (m, 3 H (M) + 3 H (m), H(C(16))); 0.95 (d, 3 H, H(C(14)) or H(C(15)) (M), $^3J_{H,H}$ = 6.4 Hz); 0.96 (d, 3 H, H(C(14)) or H(C(15)) (m), $^3J_{H,H}$ = 6.2 Hz); 0.99 (d, 3 H, H(C(15)) or H(C(14)) (M), $^3J_{H,H}$ = 6.5 Hz); 1.28 (d, 3 H, H(C(15)) or H(C(14)) (m), $^3J_{H,H}$ = 6.4 Hz); 1.52—1.64, 1.79—1.88 (both m, 7 H (M) + 7 H (m), Alk); 2.19—2.22 (m, 1 H (m), Alk); 2.55—2.66 (m, 1 H (M) + 1 H (m), Alk); 2.88—2.91 (m, 1 H (M), Alk); 3.04 (d, 1 H, CH_2S (m), $^2J_{H,H}$ = 16.0 Hz); 3.06 (d, 1 H, CH_2S (M), $^2J_{H,H}$ = 16.0 Hz); 3.32 (d, 1 H, CH_2S (m), $^2J_{H,H}$ = 16.0 Hz); 3.34 (d, 1 H, CH_2S (M), $^2J_{H,H}$ = 16.0 Hz); 3.62 (br.s, 1 H, H(C(7)) (M)); 3.86 (br.s, 1 H, H(C(7)) (m)); 6.81 (dd, 1 H, H(C(3)), $^3J_{H,P}$ = 14.7 Hz, $^3J_{H,H}$ = 7.9 Hz); 7.04—7.08, 7.45—7.72 (both m, 1 H + 10 H, Ar); 7.87 (dd, 2 H, *o*-H, P(S)Ph, $^3J_{H,P}$ = = 14.7 Hz, $^3J_{H,H}$ = 7.3 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz), δ: 20.67 (s, C(14) or C(15) (M)); 21.35 (s, C(16) (M + m)); 21.79 (s, C(14) or C(15) (m)); 22.04 (s, C(15) or C(14) (M + m)); 25.22 (s, C(9) (M + m)); 26.30 (s, C(11) or C(13) (m)); 27.22 (s, C(11) or C(13) (M)); 28.91 (s, C(13) or C(11) (m)); 29.84 (s, C(11) or C(13) (M)); 34.80 (s, CH_2S (M)); 35.19 (s, CH_2S (m)); 38.04, 38.18 (both s, C(10) and C(12) (m)); 42.58, 42.91 (both s, C(10) and C(12) (M)); 49.14 (s, C(7) or C(8) (M)); 49.46, 51.86 (both s, C(8) and C(7) (m)); 55.65 (s, C(7) or C(8) (M)); 123.71 (d, C(4), $^3J_{C,P}$ = 13.2 Hz); 129.04 (d, *m*-C, P(S)Ph, $^3J_{C,P}$ = = 13.2 Hz); 129.21 (d, *m*-C, P(S)Ph, $^3J_{C,P}$ = 12.1 Hz); 129.73 (d, C(6), $^3J_{C,P}$ = 7.7 Hz); 131.11 (d, C(3), $^2J_{C,P}$ = 9.3 Hz); 131.98 (d, *o*-C, P(S)Ph, $^2J_{C,P}$ = 11.0 Hz); 132.77 (s, *p*-C, P(S)Ph); 132.28—133.53 (overlapped signals of C(5), *o*-C, and *p*-C, P(S)Ph); 150.47 (s, C(1)); 176.88 (s, C=O (m)); 177.40 (s, C=O (M)).* IR, ν/cm^{-1}: 524 m, 536 m, 601 m (P=S), 622 w, 691 m, 705 m, 720 w, 741 m, 756 m, 999 w, 1107 m, 1139 w, 1187 w, 1267 w, 1330 m, 1388 w, 1438 m, 1462 m, 1482 w, 1561 w, 1580 m, 1624 s (C=O), 2866 m, 2921 m, 2949 m, 3057 w. Found (%): C, 53.46; H, 5.24; N, 2.03. $C_{30}H_{35}ClNOPPdS_2 \cdot 0.2CH_2Cl_2$. Calculated (%): C, 53.38; H, 5.25; N, 2.06.

κ^3-*S*,*N*,*S*-Chloro{*N*-[2-(diphenylthiophosphoryl)phenyl]-*N*-(2-neomenthylsulfanylpropyl)amido}palladium(II) (8). The ratio of m and M isomers was 1 : 3. M.p. >220 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz), δ: 36.81 (m), 36.96 (M). ^1H NMR (400.13 MHz), δ: 0.80 (d, 3 H, H(C(16)) (M), $^3J_{H,H}$ = 6.4 Hz); 0.83—0.88 (m, 1 H (M) + 1 H (m), Alk); 0.89 (d, 3 H, H(C(16)) (m), $^3J_{H,H}$ = 6.9 Hz); 0.91 (d, 3 H, H(C(14)) or H(C(15)) (m), $^3J_{H,H}$ = 7.1 Hz); 0.94 (d, 3 H, H(C(14)) or H(C(15)) (M), $^3J_{H,H}$ = 6.5 Hz); 1.00 (d, 3 H, H(C(15)) or H(C(14)) (M), $^3J_{H,H}$ = 6.2 Hz); 1.06 (d, 3 H, H(C(15)) or H(C(14)) (m), $^3J_{H,H}$ = 6.6 Hz); 1.26—1.87 (m, 7 H (M) + 7 H (m), Alk); 2.10—2.19 (m, 1 H (M) + 1 H (m), Alk); 2.29—2.43 (m, 1 H (M) + 1 H (m), Alk); 2.62—3.04 (m, 3 H (M) + 3 H (m), Alk); 3.58 (br.s, 1 H, H(C(7)) (M)); 3.80 (br.s, 1 H, H(C(7)) (m)); 6.87 (dd, 1 H, H(C(3)) (m), $^3J_{H,P}$ = 14.7 Hz, $^3J_{H,H}$ = 7.6 Hz); 6.89 (dd, 1 H, H(C(3)) (M), $^3J_{H,P}$ = 14.8 Hz, $^3J_{H,H}$ = 7.6 Hz); 7.09 (dt, 1 H, H(C(4)) (m), $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 3.0 Hz); 7.10 (dt, 1 H, H(C(4)) (M), $^3J_{H,H}$ = 7.6 Hz, $^4J_{H,P}$ = 3.2 Hz); 7.27 (dd, 1 H, H(C(6)) (m), $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,P}$ = 5.4 Hz); 7.32 (dd, 1 H, H(C(6)) (M), $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,P}$ = 5.5 Hz); 7.50—7.62 (m, 6 H (M) + 6 H (m), Ar); 7.67—7.74 (m, 3 H (M) + 3 H (m), Ar); 7.79 (dd, 2 H, *o*-H, P(S)Ph (m), $^3J_{H,P}$ = 14.3 Hz, $^3J_{H,H}$ = 7.2 Hz); 7.81 (dd, 2 H, *o*-H, P(S)Ph (M), $^3J_{H,P}$ = 14.5 Hz, $^3J_{H,H}$ = = 7.4 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 20.30 (s, C(16) (M)); 21.25 (s, C(16) (m)); 21.96 (s, C(14) or C(15) (M + m)); 22.10 (s, C(15) or C(14) (M)); 22.12 (s, C(15) or C(14) (m)); 24.41 (s, C(9) (M)); 24.58 (s, C(9) (m)); 26.50 (s, C(11) or C(13) (m)); 27.13 (s, CH_2S (m)); 27.22 (s, C(11) or C(13) (M)); 28.73 (s, C(13) or C(11) (m)); 29.79 (s, C(11) or C(13) (M)); 33.17 (s, CH_2S (M)); 34.91 (s, C(10) (M)); 35.10 (s, C(10) (m)); 38.88 (s, CH_2 (m)); 41.83 (s, C(12) (m)); 42.12 (s, CH_2 (M)); 43.04 (s, C(12) (M)); 49.15 (s, C(7) or C(8) (M)); 49.89 (s, C(8) or C(7) (m)); 52.57 (s, C(7) or C(8) (m)); 57.23 (s, C(8) or C(7) (M)); 123.62 (d, C(4) (m), $^3J_{C,P}$ = 11.7 Hz); 123.75 (d, C(4) (M), $^3J_{C,P}$ = 13.2 Hz); 124.24 (d, C(2) (M), $^1J_{C,P}$ = 85.8 Hz); 124.30 (d, C(2) (m), $^1J_{C,P}$ = 85.1 Hz); 125.83 (d, *ipso*-C, P(S)Ph (m), $^1J_{C,P}$ = 87.3 Hz); 125.93 (d, *ipso*-C, P(S)Ph (M), $^1J_{C,P}$ = 86.9 Hz); 126.99 (d, *ipso*-C, P(S)Ph (M), $^1J_{C,P}$ = 89.5 Hz); 127.11 (d, *ipso*-C, P(S)Ph (m), $^1J_{C,P}$ = 89.5 Hz); 128.77 (d, *m*-C, P(S)Ph (M + m), $^3J_{C,P}$ = 13.6 Hz); 129.13 (d, *m*-C, P(S)Ph (M + m), $^3J_{C,P}$ = = 12.5 Hz); 130.56 (d, C(6) (M), $^3J_{C,P}$ = 8.1 Hz); 130.90 (d, C(6) (m), $^3J_{C,P}$ = 8.1 Hz); 131.50 (d, C(3) (M), $^2J_{C,P}$ = 9.5 Hz); 131.60 (d, C(3) (m), $^2J_{C,P}$ = 11.0 Hz); 131.82 (d, *o*-C, P(S)Ph (m), $^2J_{C,P}$ = 11.4 Hz); 131.85 (d, *o*-C, P(S)Ph (M), $^2J_{C,P}$ = 11.7 Hz); 132.70 (d, *p*-C, P(S)Ph (M + m), $^4J_{C,P}$ = 3.3 Hz); 133.30 (d, *p*-C, P(S)Ph (M + m), $^4J_{C,P}$ = 2.6 Hz); 133.46 (d, *o*-C, P(S)Ph (m), $^2J_{C,P}$ = 10.3 Hz); 133.47 (d, C(5) (m), $^4J_{C,P}$ = 2.6 Hz); 133.49 (d, *o*-C, P(S)Ph (M), $^2J_{C,P}$ = 10.3 Hz); 133.57 (d, C(5) (M), $^4J_{C,P}$ = 2.2 Hz); 150.45 (d, C(1) (m), $^2J_{C,P}$ = 4.8 Hz); 150.49 (d, C(1) (M), $^2J_{C,P}$ = 3.7 Hz); 172.13 (s, C=O (M)); 172.18 (s, C=O (m)). IR, ν/cm^{-1}: 499 w, 525 m, 541 w, 599 m (P=S), 620 w, 691 m, 702 m, 719 m, 752 w, 998 w, 1106 m, 1135 w, 1185 w, 1265 w, 1301 w, 1369 m, 1437 s, 1461 m, 1579 m, 1606 s (C=O), 2864 m, 2920 m, 2947 m, 3054 w. Found (%): C, 55.19; H, 5.51; N, 2.06. $C_{31}H_{37}ClNOPPdS_2$. Calculated (%): C, 55.03; H, 5.51; N. 2.07.

2-Phenylsulfinyl-*N*-(pyridin-2-ylmethyl)acetamide (9). A 7% solution of hydrogen peroxide (5.67 g) in *tert*-butyl alcohol was

* The signals of the C(2) and *ipso*-C quaternary carbon atoms of the diphenylthiophosphotyl group were not observed.

slowly added dropwise to a solution of compound **2a** (0.43 g, 1.67 mmol) in methanol (15 mL). The reaction mixture was stirred for 12 h at ~20 °C and then diluted with distilled water (30 mL), the product was extracted with chloroform. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (eluent $CHCl_3$—MeOH (50 : 1)) to give compound **9** (0.29 g, 63%) as a yellow oil. ^{1}H NMR (400.13 MHz), δ: 3.67 (d, 1 H, $CH_2S(O)$, $^2J_{H,H}$ = 13.9 Hz); 3.77 (d, 1 H, $CH_2S(O)$, $^2J_{H,H}$ = 13.9 Hz); 4.52 (d, 2 H, CH_2Py, $^3J_{H,H}$ = 5.4 Hz); 7.17—7.20 (m, 2 H, Py); 7.45—7.48 (m, 3 H, Ph); 7.60—7.65 (m, 1 H, Py + 2 H, Ph); 7.93 (br.s, 1 H, NH); 8.52 (d, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 4.5 Hz). $^{13}C\{^1H\}$ NMR (75.47 MHz), δ: 44.67 (s, CH_2Py); 60.10 (s, $CH_2S(O)$); 121.73 and 122.20 (both s, C(3) and C(5), Py); 123.84 and 129.15 (both s, *o*-C and *m*-C, Ph); 131.27 (s, *p*-C, Ph); 136.64 (s, C(4), Py); 141.85 (s, *ipso*-C, Ph); 148.85 (s, C(6), Py); 155.90 (s, C(2), Py); 163.57 (s, C=O). IR, ν/cm^{-1}: 490 w, 612 w, 632 w, 691 m, 749 m, 892 w, 998 w, 1021 m, 1043 m (S=O), 1072 w, 1087 m, 1149 w, 1201 w, 1254 w, 1310 m, 1443 m, 1476 m, 1551 br, m (NHCO), 1571 m, 1592 m, 1664 sh, s, 1669 s (C=O), 2924 w, 3057 m, 3278 br, m (NH). Found (%): C, 60.98; H, 5.33; N, 9.79. $C_{14}H_{14}N_2O_2S$. Calculated (%): C, 61.29; H, 5.14; N, 10.21.

κ^3-*N*,*N*,*S*-Chloro[*N*-(pyridin-2-ylmethyl)-*N*-(2-phenylsulfinylacetyl)amido]palladium(II) (10). A solution of $PdCl_2(NCPh)_2$ (98 mg, 0.255 mmol) in dichloromethane (5 mL) was slowly added dropwise to a solution of ligand **9** (70 mg, 0.255 mmol) and Et_3N (36 μL, 0.258 mmol) in CH_2Cl_2 (10 mL). In 12 h, the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (eluent CH_2Cl_2—MeOH (50 : 1)) to give complex **10** (101 mg, 95%) as a light yellow crystalline solid. M.p. 215—220 °C (decomp.). ^{1}H NMR (400.13 MHz), δ: 4.48 (d, 1 H, $CH_2S(O)$, $^2J_{H,H}$ = 16.7 Hz); 4.71 (d, 1 H, $CH_2S(O)$, $^2J_{H,H}$ = 16.7 Hz); 5.01, 5.11 (ABq, 2 H, CH_2Py, $J_{A,B}$ = 20.3 Hz); 7.41 (t, 1 H, H(C(5)), Py, $^3J_{H,H}$ = 6.5 Hz); 7.49 (d, 1 H, H(C(3)), Py, $^3J_{H,H}$ = 8.0 Hz); 7.65—7.74 (m, 3 H, *m*-H, Ph and H(C(4)), Py); 7.96 (dt, 1 H, *p*-H, Ph, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.6 Hz); 8.22 (dd, 2 H, *o*-H, Ph, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = = 1.6 Hz); 8.92 (dd, 1 H, H(C(6)), Py, $^3J_{H,H}$ = 5.3 Hz, $^4J_{H,H}$ = 0.7 Hz). $^{13}C\{^1H\}$ NMR (100.61 MHz), δ: 56.92 (s, CH_2Py); 70.48 (s, $CH_2S(O)$); 121.79 and 123.29 (both s, C(3) and C(5), Py); 125.43 and 129.98 (both s, *o*-C and *m*-C, Ph); 133.84 (s, *p*-C, Ph); 139.88 (s, C(4), Py); 141.20 (s, *ipso*-C, Ph); 148.96 (s, C(6), Py); 167.31 (s, C(2), Py); 169.34 (s, C=O). IR, ν/cm^{-1}: 420 w, 470 w, 508 m, 531 m, 683 m, 713 w, 750 m, 765 m, 879 w, 998 w, 1033 w, 1080 m, 1096 m, 1117 m (S=O), 1153 m, 1218 m, 1286 w, 1369 m, 1392 m, 1445 m, 1486 m, 1566 m, 1600 sh, s, 1626 s (C=O), 2914 w, 2981 w, 3051 w. Found (%): C, 40.54; H, 3.37; N, 6.77. $C_{14}H_{13}ClN_2O_2PdS$. Calculated (%): C, 40.50; H, 3.16; N, 6.75.

Catalytic studies. A Schlenk test-tube was charged with aryl bromide **11a,b** (0.125 mmol), $PhB(OH)_2$ (23 mg, 0.188 mmol), DMF (0.5 mL), and freshly powdered K_3PO_4 (53 mg, 0.25 mmol), then a calculated amount of the catalyst as a 0.1 *M* solution in

Table 3. Basic crystallographic data and structure refinement parameters for compounds **6b—d**, **8**, and **10**

Parameter	**6b**	**6c**	**6d**	**8**	**10**
Molecular formula	$C_{15}H_{15}ClN_2OPdS$	$C_{17}H_{13}ClN_2OPdS$	$C_{26}H_{21}ClNOPPdS_2$	$C_{33}H_{37}Cl_9NOPPdS_2$	$C_{14}H_{13}ClN_2O_2PdS$
Molecular weight	413.20	435.20	600.38	984.18	415.17
T/K	120	120	100	120	120
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*Pna*2$_1$	*Pbcn*	*P*2$_1$/*c*	*P*2$_1$/*n*	*P*-1
Z	4	8	4	4	4
a/Å	9.0597(8)	18.8499(12)	9.107(3)	16.0079(4)	10.2663(5)
b/Å	19.0784(17)	10.3731(7)	21.107(8)	15.8962(4)	11.5916(6)
c/Å	8.7568(8)	16.1984(10)	13.158(5)	16.4646(4)	12.6465(7)
α/deg	—	—	—	—	104.1130(10)
β/deg	—	—	103.545(9)	102.2730(10)	90.6280(10)
γ/deg	—	—	—	—	91.5550(10)
V/Å^3	1513.6(2)	3167.3(4)	2458.8(15)	4093.91(18)	1458.77(13)
d_{calc}/g cm^{-3}	1.813	1.825	1.622	1.597	1.890
μ/cm^{-1}	15.39	14.76	11.19	12.11	16.02
F(000)	824	1728	1208	1984	824
$2\theta_{max}$/deg	58	58	58	52	58
Reflection collected	14654	17931	19869	30516	17662
Number of independent reflections	3989	4210	6544	7979	7748
Number of reflections with $I > 2\sigma(I)$	3750	3405	5601	7492	6834
Number of refined parameters	190	208	298	451	379
R_1	0.0269	0.0467	0.0257	0.0659	0.0248
wR_2	0.0618	0.1486	0.0595	0.2435	0.0588
GOF	1.007	1.084	1.001	2.027	1.007
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	1.136/−0.817	0.890/−1.122	0.510/−0.592	1.361/−1.752	0.707/−0.850

DMF was added *via* a syringe.[10b,18] The tube was filled with argon, the reaction mixture was stirred for 5 h at 120 °C. An aliquot of the reaction mixture was diluted with water, extracted with benzene, and analyzed by GC (a 25-m capillary column, SE-30, 150—250 °C at the rate of heating 15 °C min^{-1}). The chromatographic patterns contained peaks of the starting compounds **11a**,**b** and the cross-coupling products **12a**,**b** (the retention times were the same as those of the authentic samples). Sometimes we observed the formation of an insignificant amount of biphenyl (the product of homocoupling of phenylboronic acid taken in the excess), which was not taked into account in the calculation of the chromatographic patterns. We assumed that chemically stable compounds **11a**,**b** and **12a**,**b** in the course of the process do not undergo resinification, and the yields of the products **12** were considered to be equal to the conversions of the starting compounds **11**.

X-ray diffraction study. Single crystals of compounds **6b—d**, **8**, and **10** were obtained by crystallization from CH_2Cl_2—hexane (**6b**), $CHCl_3$—Et_2O (**6c**, **10**), $CHCl_3$—hexane (**6d**), and CH_2Cl_2—CCl_4 (**8**). X-ray diffraction studies of complexes **6b**, **10** and **6c**, **6d**, **8** were carried out on Bruker APEX2 CCD and Bruker APEX2 DUO CCD diffractometers, respectively (Mo-Kα radiation, graphite monochromator, ω-scan mode). The structures were solved by direct method and refined by the full-matrix least squares method against F^2_{hkl} in anisotropic approximation. Positions of hydrogen atoms were calculated geometrically in isotropic approximation, using a riding model. The main crystallographic data and parameters of refinement are given in Table 3. All the calculations were carried out using the SHELXTL PLUS program package.[19]

References

1. (a) O. Belda, C. Moberg, *Coord. Chem. Rev.*, 2005, **249**, 727; (b) A. Rajput, R. Mukherjee, *Coord. Chem. Rev.*, 2013, **257**, 350.
2. (a) A. K. Singh, R. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 2005, 2886; (b) S. Nag, R. J. Butcher, S. Bhattacharya, *Eur. J. Inorg. Chem.*, 2007, 1251; (c) A. K. Singh, R. Mukherjee, *Dalton Trans.*, 2008, 260; (d) A. K. Sharma, S. Biswas, S. K. Barman, R. Mukherjee, *Inorg. Chim. Acta*, 2010, **363**, 2720; (e) D. V. Aleksanyan, Yu. V. Nelyubina, Z. S. Klemenkova, V. A. Kozlov, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2014, **189**, 1028.
3. A. Decken, R. A. Gossage, P. N. Yadav, *Can. J. Chem.*, 2005, **83**, 1185.
4. (a) S. J. Brown, X. Tao, D. W. Stephan, P. K. Mascharak, *Inorg. Chem.*, 1986, **25**, 3377; (b) L. A. Tyler, J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.*, 2000, **39**, 357.
5. (a) S. Ongeri, U. Piarulli, M. Roux, C. Monti, C. Gennari, *Helv. Chim. Acta*, 2002, **82**, 3388; (b) Ch. M. Tomas, R. Mafua, Br. Therrien, E. Rusanov, H. Stoeckli-Evans, G. Süss-Fink, *Chem. Eur. J.*, 2002, **8**, 3343; (c) H. Y. Kwon, S. Y. Lee, B. Y. Lee, D. M. Shin, Y. K. Chung, *Dalton Trans.*, 2004, 921; (d) S. Burger, B. Therrien, G. Süss-Fink, *Helv. Chim. Acta*, 2005, **88**, 478; (e) V. R. Marinho, A. I. Rodrigues, A. J. Burke, *Tetrahedron: Asymmetry*, 2008, **19**, 454; (f) S. Mahadik, S. A. Knott, L. F. Szczepura, S. R. Hitchcock, *Tetrahedron: Asymmetry*, 2009, **20**, 1132.
6. (a) J. D. G. Correia, A. Domingos, I. Santos, H. Spies, *J. Chem. Soc., Dalton Trans.*, 2001, 2245; (b) E. Palma, J. D. G. Correia, A. Domingos, I. Santos, R. Alberto, H. Spies, *J. Organomet. Chem.*, 2004, **689**, 4811.
7. (a) H. Sakurai, H. Uchikubo, K. Ishizu, K. Tajima, Y. Aoyama, H. Ogoshi, *Inorg. Chem.*, 1988, **27**, 2691; (b) M. M. Morlok, K. E. Janak, G. Zhu, D. A. Quarless, G. Parkin, *J. Am. Chem. Soc.*, 2005, **127**, 14039; (c) J. G. Melnick, K. Yurkerwich, G, Parkin, *J. Am. Chem. Soc.*, 2010, **132**, 647.
8. (a) Y. Singh, R. Sharan, R. N. Kapoor, *Ind. J. Chem., Sect. A: Inorg., Phys., Theor. Anal.*, 1986, **25A**, 771; (b) Y. Singh, R. Sharan, R. N. Kapoor, *Synth. React. Inorg. Met.-Org. Chem.*, 1986, **16**, 1225; (c) S. C. Dixit, R. Sharan, R. N. Kapoor, *J. Organomet. Chem.*, 1987, **332**, 135; (d) A. K. Narula, P. Lukose, *J. Organomet. Chem.*, 1990, **393**, 365.
9. (a) P. J. Toscano, L. G. Marzilli, *Inorg. Chem.*, 1983, **22**, 3342; (b) P. J. Toscano, K. J. Fordon, D. Macherone, S. Liu, J. Zubieta, *Polyhedron*, 1990, **9**, 2375; (c) E. L. Klein, M. A. Khan, R. P. Houser, *Inorg. Chem.*, 2004, **43**, 7272; (d) M. J. Al-Jeboori, H. H. Al-Tawel, R. M. Ahmad, *Inorg. Chim. Acta*, 2010, **363**, 1301.
10. A. A. Vasil´ev, V. Yu. Aleksenko, D. V. Aleksanyan, V. A. Kozlov, *Mendeleev Commun.*, 2013, **23**, 344.
11. J. A. Davies, F. R. Hartley, *Chem. Rev.*, 1981, **81**, 79.
12. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1975.
13. Y. Zhang, Z. Li, X. Cao, J. Zhao, *J. Mol. Catal. A: Chem.*, 2013, **366**, 149.
14. A. Shockravi, M. Chaloosi, E. Rostami, D. Heidaryan, A. Shirzadmehr, H. Fattahi, H. Khoshsafar, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2007, **182**, 2115.
15. V. Yu. Aleksenko, E. V. Sharova, O. I. Artyushin, D. V. Aleksanyan, Z. S. Klemenkova, Yu. V. Nelyubina, P. V. Petrovskii, V. A. Kozlov, I. L. Odinets, *Polyhedron*, 2013, **51**, 168.
16. US Pat. 2005/0169863; http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=US&NR=2005169863A1&KC=A1&FT=D&ND=3&date=20050804&DB=worldwide.espacenet.com&locale=en_EP.
17. E. S. Izmest´ev, D. V. Sudarikov, S. A. Rubtsova, P. A. Slepukhin, A. V. Kuchin, *Russ. J. Org. Chem.* (*Engl. Transl.*), 2012, **48**, 184 [*Zh. Org. Khim.*, 2012, **48**, 197].
18. (a) D. V. Aleksanyan, V. Yu. Aleksenko, Yu. V. Nelyubina, A. A. Vasil´ev, R. R. Aysin, Z. S. Klemenkova, V. A. Kozlov, P. V. Petrovskii, I. L. Odinets, *Inorg. Chim. Acta*, 2013, **404**, 167; (b) D. V. Aleksanyan, O. I. Artyushin, G. K. Genkina, A. A. Vasil´ev, Yu. V. Nelyubina, N. E. Shepel´, Z. S. Klemenkova, L. V. Gumileva, V. A. Kozlov, *Russ. Chem. Bull.* (*Int. Ed.*), 2014, **63**, 2309 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2014, 2309]; (c) I. M. Aladzheva, O. V. Bykhovskaya, A. A. Vasil´ev, Yu. V. Nelyubina, Z. S. Klemenkova, *Russ. Chem. Bull.* (*Int. Ed.*), 2015, **64**, 909 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2015, 909].
19. G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112.

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