Polyhedron 51 (2013) 168–179

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Coordination of P(X)-modified (X = O, S) *N*-aryl-carbamoylmethylphosphine oxides and sulfides with Pd(II) and Re(I) ions: Facile formation of 6,6-membered pincer complexes featuring atropisomerism

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ARTICLE INFO

Article history:
Received 25 September 2012
Accepted 21 December 2012
Available online 7 January 2013

Keywords:
Tridentate ligands
Pincer complexes
Rhenium
Palladium

ABSTRACT

Direct acetylation of (thio)phosphorylated anilines **1a**,**b** with *in situ* generated $Ph_2P(O)CH_2C(O)Cl$ or sequential treatment of **1a**,**b** with chloroacetyl chloride and Ph_2PSNa resulted in novel oligodentate ligands, namely, P(X)-modified carbamoylmethylphosphine oxides (CMPO) and sulfides (CMPS) **2a**–**d**. In reactions with $Re(CO)_5Br$ (in the presence of Et_3N) and $(PhCN)_2PdCl_2$ these ligands afforded κ^3-*XNY* (*X*,*Y* = *O*,*S*) Re(I) (**4a**,**d**) and Pd(II) (**6b**–**d**) pincer complexes with two fused six-membered metallocycles, owing to ready metallation at the amide nitrogen atom. In the absence of a base, the interaction of **2a** with the same rhenium precursor yielded ten-membered κ^3-*OO* metallocycle **5** with Re(I) ion coordinated only by phosphoryl groups. According to the NMR spectroscopy data, the complexes obtained form stable atropisomers in solution at room temperature. The solid state structures of compounds **2a**,**b** and resulting metallocycles were characterized by X-ray crystallography.

1. Introduction

Organophosphorus compounds amount to the most important ligands in inorganic and organometallic chemistry, playing an indispensable role both in homogeneous catalysis and different metal separation processes. In particular, various phosphoryl-containing substances found wide application in the recovery of rare-earth elements from acidic radioactive liquid wastes [1]. The main advances in this field over more than semicenturary history pertain to the development of bidentate ligands, namely, carbamoylmethylphosphine oxides (CMPO) of general formula $R^1{}_2P(O)CH_2C(O)NR^2R^3$ [2] which were proved to be the most preferable extractants in terms of availability, cost, and extraction efficiency. While a priority was continuously placed on CMPO and related phosphoryl-containing derivatives, their thiophosphoryl analogs have received far less attention [3].

Carbamoylmethylphoshoryl derivatives usually serve as neutral bidentate ligands bounding to a metal center through the oxygen atoms of amide and phosphoryl groups [4]. It is natural to assume that the introduction of ancillary donating arm(s) may strongly affect the coordination behavior of modified CMPO compounds. Thus, the condensation of *ortho*-phosphorylated aniline and its thioanalog with phosphorylacetic acid derivatives would lead to oligodentate ligands in which the P=X (X = O, S) group of aniline fragment could serve as a useful directing group for metallation at the amide nitrogen atom of carbamoylmethyl(thio)phosphoryl moiety, thereby, resulting in a pincer-type tridentate monoanionic framework. Pincer complexes comprise a unique class of organometallic compounds that receives growing attention in catalysis, materials science and many other fields [5,6]. Unfailing interest to these derivatives stems from the presence of multiple sites for directed structural modifications offering ample opportunities for fine-tuning of their steric and electronic properties. While most of organophosphorus pincer-type ligands relate to trivalent phosphorus derivatives (phosphines, phosphinites, phosphites and so on), recently we have shown that thiophosphoryl-containing ligands bearing the four-coordinated phosphorus center can successfully compete in catalytic performance with their P(III) counterparts [7].

Herein we report on the facile synthesis of novel tridentate ligands by the modular assembling of *ortho*-(thio)phosphorylated anilines with CMPO(S) precursors which provide upon complexation with Re(I) and Pd(II) precursors *ONO*, *SNO*, and *SNS* donor sets due to the N–H bond activation of a CMPO(S) fragment, resulting in 6,6-membered pincer complexes.

2. Results and discussion

2.1. Synthesis of ligands

The key phosphorylated aniline **1a** [8] and its thioanalog **1b** [9] are readily accessible from 2-diphenylphosphinoaniline [10] by

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http://dx.doi.org/10.1016/j.poly.2012.12.025

oxidation with H_2O_2 and addition of elemental sulfur, respectively. To anchor a CMPO(S) fragment on the aniline scaffold, two different synthetic approaches have been developed, depending on the nature of the substituent X in the P=X group of a carbamoylmethyl moiety (Scheme 1). The first route (compounds **2a**,**b**) consisted in the acylation of the starting anilines **1a**,**b** with diphenylphosphorylacetic acid chloride generated *in situ* from the corresponding acid using PCl_3 as a mild chlorinating agent via the general procedure previously developed in our laboratory [11]. The second approach used for the synthesis of CMPS derivatives **2c**,**d** was based on the reaction of starting anilines **1a**,**b** with chloroacetyl chloride followed by the treatment of the resulting chloroacetyl derivatives **3a**,**b** with sodium diphenylthiophosphinite. The methods employed (Scheme 1) afforded the desired ligands **2a**–**d** in moderate to good yields (55–79%).

The structures of ligands **2a**–**d** as well as intermediate derivatives **3a**,**b** were unambiguously confirmed based on the multinuclear NMR (^{31}P, ^{1}H, and ^{13}C) and IR spectral data. The ^{31}P NMR spectra of **2a**–**d** show two singlet signals in the regions typical for these classes of organophosphorus compounds. Thus, the signals of the phosphorus resonances of phosphoryl group in $ArP(O)Ph_2$ (**2a**,**c**) and carbamoylmethyl (**2a**,**b**) fragments were observed at ~37 and 27–28 ppm, respectively, while in the case of thiophosphoryl derivatives (**2b**–**d**) the signals of P=S groups were manifested in a narrow range from 38 to 40 ppm independent from the nature of an additional substituent in the $-P(S)Ph_2$ moiety. The presence of a great number of phenyl rings in the molecules of these acetamides complicates the interpretation of ^{1}H NMR spectra in the region typical for aromatic proton signals, however, the signals of the hydrogen atoms of an amide group and doublet signals of the protons of a methylene unit can be easily identified: δ_{NH} 9.92–11.29, δ_{CH2} 3.04–3.61 ppm ($^{2}J_{HP} \sim 14$–15 Hz). The ^{13}C NMR spectral data of compounds **2a**–**d** are also well consistent with the proposed structures: e.g., δ_{CH2} 41–45 ppm ($^{1}J_{PC} = 47$–63 Hz), $\delta_{C(O)NH2} \sim 163$ ppm ($^{2}J_{PC} \sim 5$ Hz). Moreover, unlike the proton spectra, the signals of the carbon atoms of a central benzene ring, as a rule, do not overlap with those of C_{Ph}-atoms of peripheral phenyl moieties (see Section 4). The IR spectra of crystalline samples of **2a**–**d** demonstrate the characteristic stretching vibrations of the carbonyl group (ν(C=O) 1677–1690 cm^{-1}) and N–H bond (ν(NH) 3200–3300 cm^{-1}), whereas the absorption bands typical for the secondary amides and associated mainly with the deformational vibrations of N–H bond are observed in the range from 1500 to 1540 cm^{-1}. The position of absorption bands corresponding to the phosphoryl and thiophosphoryl group vibrations depends on the nature of an additional substituent at the phosphorus atom (aryl or alkyl). Thus, the absorption bands of phosphoryl group of a CMPO moiety are observed at 1198/1203 (**2a**) and 1202 (**2b**) cm^{-1}, while ν(P=O) of triarylphosphine oxide moiety – at 1160/1167 (**2a**) and 1153/1167 (**2c**) cm^{-1}. Analogously, in the case of thiophosphoryl derivatives: ν(P=S) for $ArP(S)Ph_2$ appears in the lower frequency region than that for $CH_2P(S)Ph_2$ fragment (*cf.* 614/637 and 649 cm^{-1}, respectively, in the case of *SNS* ligand **2d**). Note that the observation of several bands corresponding to stretching of the P=O bond as well as broadening of the amide group characteristic vibrations are likely to be connected with the formation of intra- and intermolecular hydrogen bonds.

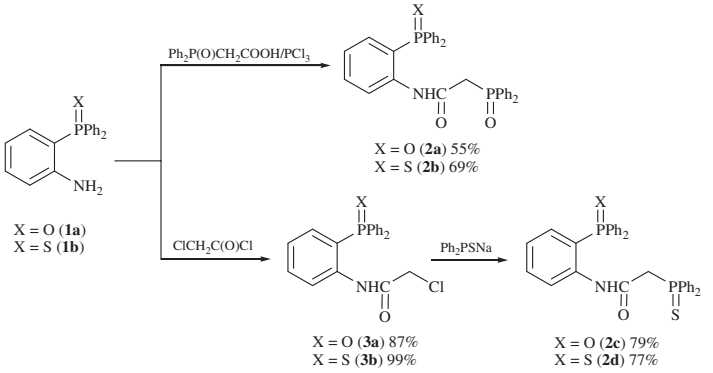
According to the X-ray diffraction data, ligands **2a** (the crystallosolvate with water and ethanol, 0.5 each per one molecule of the product) and **2b** possess quite typical geometrical parameters for the molecules of this type (Fig. 1). Note that the pseudo-torsion angle O(1)P(1)C(2)C(1) in the molecule of **2a** comprises 34.0(1)°. Such a position of the P=O bond respective to the benzene core in the $ArP(O)Ph_2$ fragment is apparently governed by the intramolecular H–bond with the NH group (Fig. 1; N(1)–H(1N) 0.92 Å, H(1N)···O(1) 1.98 Å, N(1)···O(1) 2.782(2) Å, NHO 145(1)°). In **2b**, the same value for the P(1)=S(1) group, which is not such a convenient proton-acceptor as P=O one, is 64.3(1)°.

The CMP-coordination arm in the molecules of **2a** and **2b** is geometrically very similar to that in non-functionalized *N*-arylcarbamoylmethylphosphine oxides, $Ph_2P(O)CH_2C(O)NHAr$ [11], the most pronounced difference being the values of the angle O(2)P(2)C(1)C(2) equal to 57.3(1) and 63.6(1)° in **2a** and **2b**, respectively, and 16–30° in the molecule of $Ph_2P(O)CH_2C(O)NHAr$ or its bis-CMP analog 1,3-$[Ph_2P(O)CH_2C(O)NH]_2C_6H_4$ [11], also due to the differences in the H-bonding patterns. Thus, the P=O group of a CMPO fragment in **2b** is involved in the intramolecular H-bond with the only NH group in a molecule (Fig. 2; N(1)–H(1N) 0.91 Å, H(1N)···O(2) 2.06 Å, N(1)···O(2) 2.7996(17) Å, NHO 138(1)°). In the crystal of **2a**, out of the two symmetry-identical molecules of the ligand in a unit cell, the P=O group of a CMPO moiety forms the H-bond with the hydrate water molecule through the P(2)=O(2) bond (O(1W)···O(2) 2.65(1) Å, OHO ~ 165°), while the other P=O group form hydrogen bond with ethanol molecule (O(1S′)···O(1) 2.80(1) Å, OHO ~ 145°) and the intramolecular H-bond with the amide hydrogen (N(1)–H(1N) 0.92 Å, H(1N)···O(1) 1.98, N(1)···O(1) 2.782(2) Å, NHO 145(1)°). Therefore, the pattern of H-bonds in **2a** and **2b** ensure the cisoid disposition of the P=X groups, which was expected for their complexes only (*vide infra*).

Various weak interactions such as C–H···X (X = O in **2a** and X = O, S in **2b**), C–H···π and H···H as well as O···π in **2b** hold the molecules in these crystals.

2.2. Synthesis of complexes

While studying the complexation features of the ligands derived, it was found that the reaction of **2a**,**d** with rhenium pentacarbonyl bromide in toluene solution under reflux in the presence of triethylamine indeed readily proceeds as the metallation at the nitrogen atom of an amide fragment accompanied by



Scheme 1. Synthesis of (thio)phosphoryl-substituted carbamoylmethylphosphine oxides **2a**,**b** and sulfides **2c**,**d**.

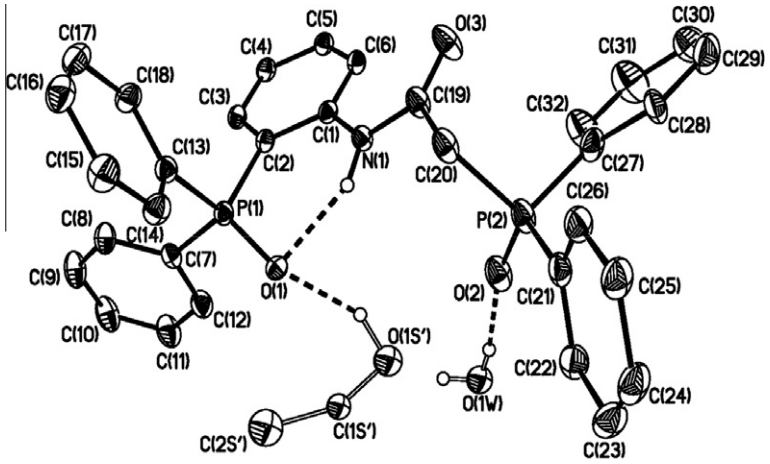


Fig. 1. General view of compound **2a** in representation of atoms by thermal ellipsoids (p = 30%). Either water molecule or ethanol molecule (both disordered by two positions) is present in the asymmetric part of a unit cell. Hereinafter the H(C) atoms are omitted for clarity.

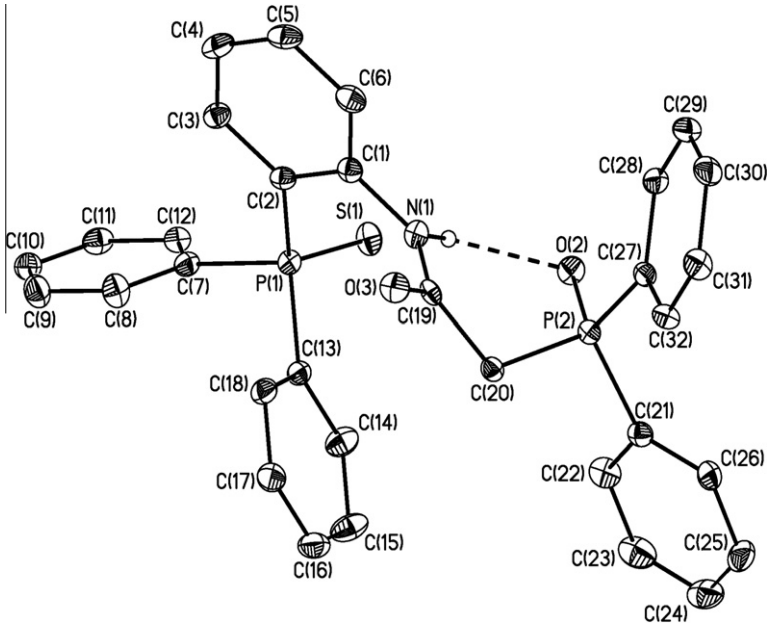
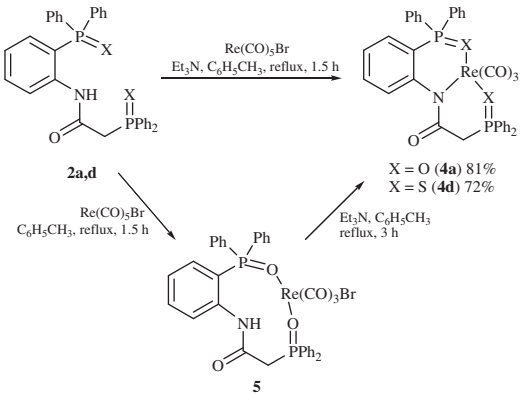


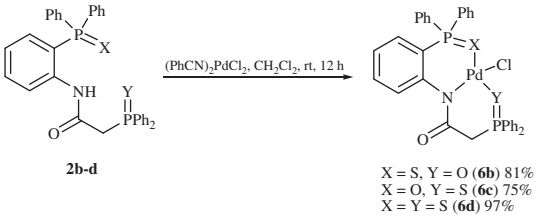
Fig. 2. General view of compound **2b** in representation of atoms by thermal ellipsoids (p = 50%).

the coordination of both of the (thio)phosphoryl donating groups to give κ^3-*ONO* and *SNS* pincer complexes **4a**,**d** in good to high yields (Scheme 2). Thus, unlike the known CMPO derivatives, in these cases the mutual disposition of donating groups facilitates the coordination of a carbamoyl moiety *via* the nitrogen atom rather than the oxygen one. Note that the compounds obtained represent the rare examples of pincer complexes with two six-membered fused metallocycles. Interestingly, in the absence of a base, P(O)-modified CMPO derivative **2a** adopts a neutral κ^2-*OO* bidentate coordination mode without participation of a carbamoyl moiety, bounding to the metal ion *via* oxygen atoms of both phosphoryl groups to give ten-membered metallocycle **5** (Scheme 2). The latter can be readily transformed into the above mentioned complex **4a** under the action of Et_3N (in toluene under reflux for 3 h, ^{31}P NMR monitoring), and, therefore, is likely to be considered as an intermediate in the reaction with the base. It should be noted that the basicity of triethylamine is evidently not enough to abstract proton from the above ligands. Obviously, it facilitates the formation of complexes with the deprotonated ligands, being



Scheme 2. Synthesis of Re(I) complexes **4a**,**d** and **5**.

more thermodynamically stable than those with the neutral ligand form, *via* formation of $Et_3N\cdots H–N$ hydrogen bond and shifting the equilibrium position due to trapping of HBr.



Scheme 3. Synthesis of Pd(II) pincer complexes **6b–d.**

Furthermore, under the action of $(PhCN)_2PdCl_2$ in dichloromethane at room temperature acetamides **2b–d** readily underwent the cyclopalladation (Scheme 3). Note that unlike rhenium derivatives, in these cases the addition of triethylamine promoted the reduction of the palladated species, evident from the liberation of palladium black, rather than facilitated the cyclopalladation itself. The propensity of platinum group metals to the coordination of various organothiophosphorus compounds owing to the presence of the "soft" sulfur atom is well known [12] and explains the ease of formation of bis(phosphine sulfide) derivative **6d**. Moreover, the fact that *ONO* ligand **2a** appeared to be completely inactive in this reaction also could be expected. In this respect, the coordination behavior of hybrid *SNO*-derivatives **2b**,**c**, bearing simultaneously phosphoryl and thiophosphoryl functions, was the most interesting. Both of them were found to form κ^3-*SNO* pincer complexes with two six-membered fused palladocycles. But whereas the cyclopalladation of **2b** proceeds smoothly, affording **6b** in 80% yield, the yield of its counterpart **6c** was less than 50%. It is natural to assume that in the case of hemilabile ligands **2b**,**c**, the metallation is preceded by the formation of κ^1-*S* species, in which the ligand bounds to the palladium atom via sulfur donor center of either $ArP(S)Ph_2$ (**2b**) or CMPS fragment (**2c**), rather than bidentately coordinated intermediate. Therewith, the disposition of the "soft" sulfur center in a flexible carbamoylmethylphosphine sulfide fragment in **2c** affords much more labile κ^1-*S* predecessor than in the case of ligand **2b** featuring a rigid phenylene spacer between the P═S pendant arm and carbamoyl group. Thus, the cyclopalladation of **2c** was complicated by the formation of an inactive monodentately *S*-coordinated complex (^{31}P NMR monitoring) accompanied by the precipitation of $PdCl_2$. Moreover, the starting ligand was partially recovered after chromatographic purification. This can be explained by the transformation of initially formed κ^1-*S* μ-Cl $[LPdCl_2]_2$ species into L_2PdCl_2 complex, as known from the literature [13], or simply decomposition of these intermediates on silica gel. None of such complications was detected in the case of hybrid derivative **2b**. Hence, the coordination of the sulfur atom of P═S group serves as a key factor for further metallation of the N–H bond and disposition of these groups in a ligand backbone indeed dictates the easiness of the formation of κ^2-*SN* anionic intermediates. Note that compounds **6b**,**c** are rare examples of cyclometallated derivatives of platinum group metals with the coordinated P═O moiety.

The complexes obtained are white (rhenium derivatives **4a**,**d**,**5**) and orange (palladium complexes **6b–d**) crystalline solids, thermally stable up to 165 °C as well as air and moisture resistant. The realization of κ^2-*OO* coordination in **5** and κ^3-*XNY* (*X* = *S* and/or *O*) coordination in **4a**,**d**, **6b–d** is supported by the NMR and IR spectral data, as well as X-ray diffraction analysis. Thus, a downfield shift[2] of the phosphorus resonances in the ^{31}P NMR spectra of all the complexes compared to the signals of free ligands **2a–d** unequivocally confirms the coordination of both (thio)phosphoryl

[2] Only in the case of complex **6d**, the signal of the phosphorus atom of carbamoylmethylphosphine sulfide moiety appeared to be upfield shifted relative to the signal of the free ligand by 0.08 ppm.

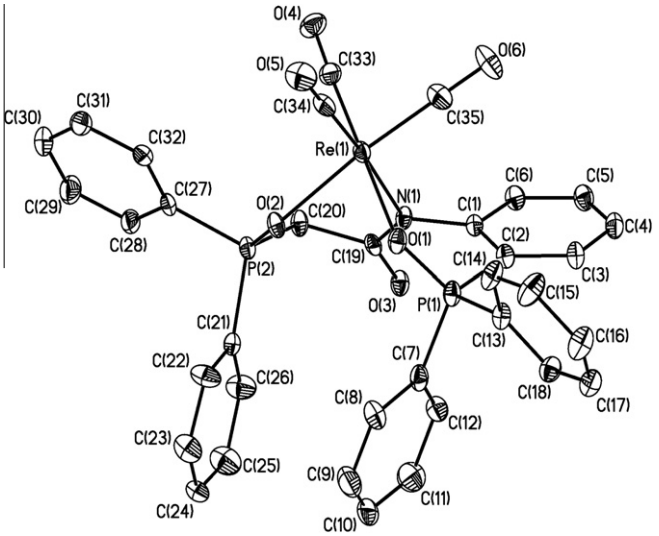


Fig. 3. General view of complex **4a** in representation of atoms by thermal ellipsoids (*p* = 30%).

groups by the Re and Pd atoms. The value of $\Delta\delta_P$ for the P═O group, as a rule, is higher than that for the P═S moiety, varying within the ranges 6.5–17.8 and 1.0–8.3 ppm, respectively. Therewith, the smallest coordination shift was observed for bis(thiophosphorylated) derivatives **4d** and **6d**. Further evidence for the coordination of both of these donor centers can be derived from the bathochromic shift of the absorption bands corresponding to the stretching vibrations of the P═O and P═S groups in the IR spectra of the complexes obtained by 13–53 and ~50 cm^{-1} in the case of rhenium derivatives **4a**,**d**, **5** and ~44–65 and 36–84 cm^{-1} for palladocycles **6b–d**, respectively. The lack of coordination of an amide fragment in the case of complex **5** is confirmed by the presence of NH proton signal in the ^1H NMR spectrum (δ_H = 10.59 ppm) and characteristic vibrations of a free amide group in the IR spectrum (at 1529 and 3287 cm^{-1}). In contrast, the absence of both NH proton signals in the ^1H NMR spectra and absorption bands at 1500–1540 and 3200–3300 cm^{-1} in the IR spectra of **4a**,**d**, **6b–d** give strong evidence of the occurrence of metallation at the amide nitrogen atom. This is accompanied by a strong concomitant shift of the C═O group stretching vibrations to the region of lower frequencies ($\Delta \sim 70–90$ cm^{-1}). Note that the position of C≡O carbonyl absorption bands in the IR spectra of **4a** and its predecessor **5** indicates their stronger bonding in the case of **4a** with the deprotonated form of the ligand compared to molecular complex **5** (see Section 4). Several features of the ^{13}C NMR spectra of the complexes obtained merit discussion. Thus, the signals of carbamoyl carbon atoms in the ^{13}C NMR spectra of **4a**,**b** and **5b–d** are deshielded upon complexation by 1.9–6.4 ppm with almost 1.5-fold increase of the $^2J_{PC}$ value. A strong downfield shift is observed for the C1 carbon atom of the central phenyl ring, being directly bound to the carbamoyl moiety ($\Delta\delta_{C1}$ = 7.2–13.7 ppm). The signals of other carbon atoms are also indicative of complex formation (e.g., $\Delta\delta_{C6}$ = 4.0–6.5 ppm). Note that each peripheral phenyl ring at both of the phosphorus atoms was found to be distinguishable, giving rise to four sets of *ipso*-, *ortho*-, *meta*-, and *para*-C atom signals instead of two sets in the case of starting ligands **2a–d**. The proton signals of a methylene unit, as another prochiral grouping, also appeared nonequivalently in the ^1H NMR spectra of κ^3-*XNY* complexes **4a**,**d**, **6b–d**. Moreover, the same was observed even in the case of ten-membered metallocycle **5**. The dissymmetrization process that renders these prochiral groups diastereotopic consists in the stabilization of twisted conformations of fused six-membered metallocycles, resulting in atropisomers that do not interconvert at room

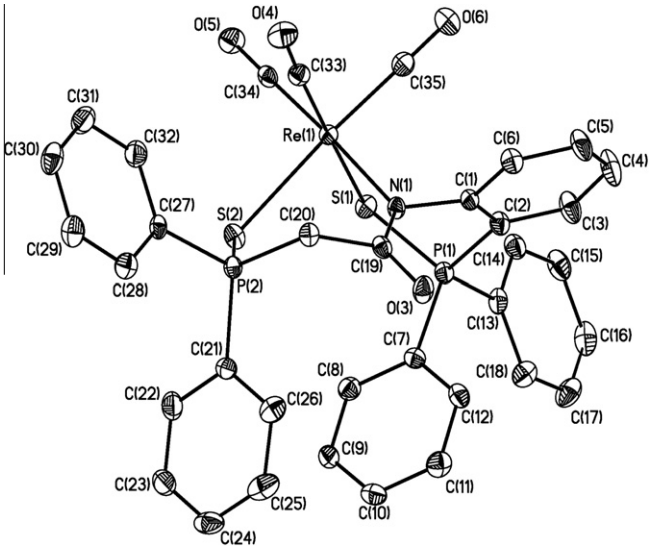


Fig. 4. General view of complex **4d** in representation of atoms by thermal ellipsoids (p = 50%).

temperature, as was observed for other 6,6-membered pincer complexes (*vide infra*).

The solid-state structures of complexes **4a**,**d** (Figs. 3 and 4), **5** (Fig. 5), and **6b**–**d** (Figs. 6–8) were studied by X-ray diffraction analysis. According to its results, in all cases the metal (rhenium or palladium) ion is bonded with both P═O(S) groups and in the case of complexes **4a**,**d**, **6b**–**d** (with the deprotonated ligands) also with the nitrogen atom of an amide fragment.

In **4a** (Fig. 3), which is a crystallosolvate with three chloroform species per two independent molecules of the complex (those having nearly the same geometrical parameters), and **4d** (Fig. 4), the coordination caused only slight elongation of the P═O bonds to ~1.51 Å [4,14] and P═S ones to ~2.00 Å [15], with the values of the above torsion angles X(1)P(1)C(2)C(1) and X(2)P(2)C(1)C(2) here being 50.1(1)° and 43.7(1)° in **4a** and 64.2(3)° and 43.0(3)° in **4d**. In both cases the rhenium atom has nearly ideal octahedral environment.

The conformation of the resulting six-membered metallocycles in **4a** is a half-chair with the deviation of the atoms N(1) and C(2) by 0.88(1) and −0.57(1) Å and a boat with the atoms Re(1) and C(20) deviated by 0.89(1) and 0.64(1) Å. In **4d**, their conformations are the same, although somewhat distorted; the deviations of the above atoms are 0.86(3) and −0.59(1) Å for the metallocycle with the P(1)═S(1) bond and 1.16(3) and 0.59(3) Å for that with P(2)═S(2) bond.

In the crystals of **4a** and **4d**, the molecules of the complexes are assembled into the 3D framework by means of C–H···π, C–H···O, and H···H contacts as well as C–H···S ones in **4d** and interactions C–H···π and Cl···π with the solvate dichloromethane species in **4a**.

As for complex **5** (Fig. 5) with two independent molecules in a crystal, the coordination of the rhenium atom by bromine instead of the ligand nitrogen atom only slightly affects its octahedral environment. In this case, however, the presence of NH group allows for the formation of intramolecular H-bonds that are different in two independent molecules of the complex. Thus, the first one is additionally stabilized by two N–H···O hydrogen bonds (N(1)–H(1N) 0.88 Å, H(1N)···O(1) 2.08 Å, N(1)···O(1) 2.846(8) Å, NHO(1) 145(1)° and N(1)–H(1N) 0.88 Å, H(1N)···O(2) 2.49 Å, N(1)···O(2) 3.049(8) Å, NHO 122(1)°), while in the second molecule (see Fig. S1 in Supplementary material) there are one N–H···O (N(1A)–H(1NA) 0.89 Å, H(1NA)···O(1A) 2.05 Å, N(1A)···O(1A) 2.784(9) Å, NHO 139(1)°) and one N–H···Br (N(1A)–H(1NA) 0.89 Å, H(1NA)···Br(1A) 2.83 Å, N(1A)···Br(1A) 3.576(7) Å, NHBr 142(1)°) H-bond. This is accompanied by the differences in the disposition of the phenyl moieties, so that the above O(1)P(1)C(2)C(1) and O(2)P(2)C(1)C(2) torsion angles are 26.9(8)° and 19.9(8)° in the molecule shown on Fig. 5 and 39.6(7)° and 25.9(7)° in the second one.

In a crystal, the molecules of complex **5** are assembled into the 3D framework by means of numerous C–H···π, C–H···O, C–H···Br and H···H contacts.

In **6b**–**d** (Figs. 6–8), the geometrical parameters of the palladocyclic moiety are rather expected for the fused 6,6-membered pincer complexes [16]. In all cases, the Pd(1) atom is characterized by a square-planar configuration (within 0.03(1)–0.06(1) Å) [17]. The metallocycles in these complexes all have a boat conformation (Figs. 6–8); the atoms Pd(1) and C(20) in one deviating by 1.08(1) and 0.67(1) Å (**6b**), 1.20(1) and 0.67(1) Å (**6c**), 1.39(1) and

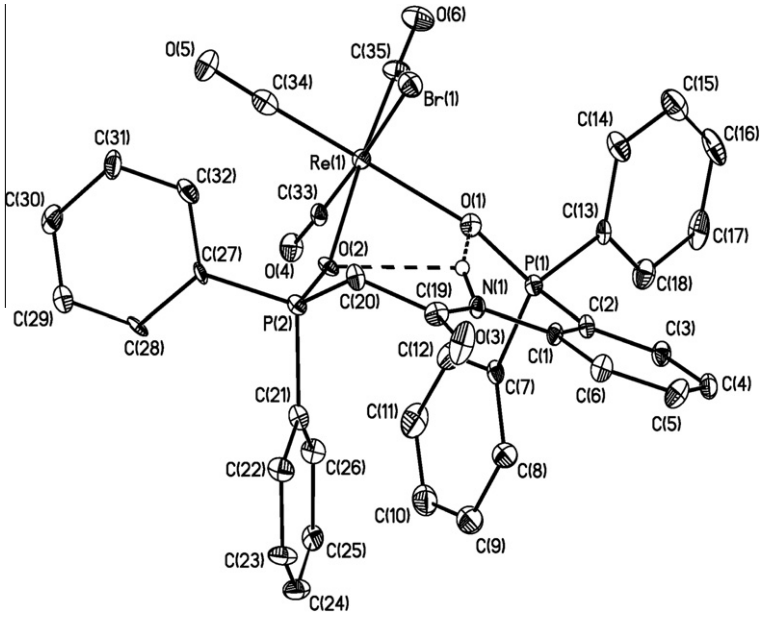


Fig. 5. General view of complex **5** in representation of atoms by thermal ellipsoids (p = 30%). Only one independent molecule of the complex is shown.

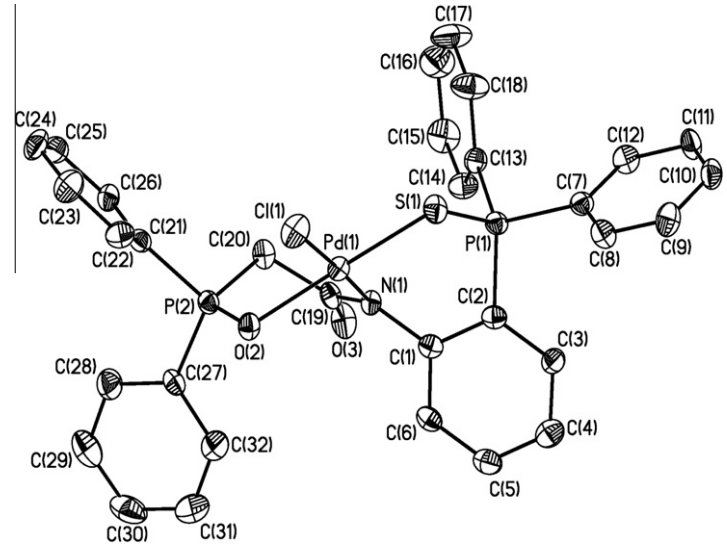


Fig. 6. General view of complex **6b** in representation of atoms by thermal ellipsoids (p = 50%).

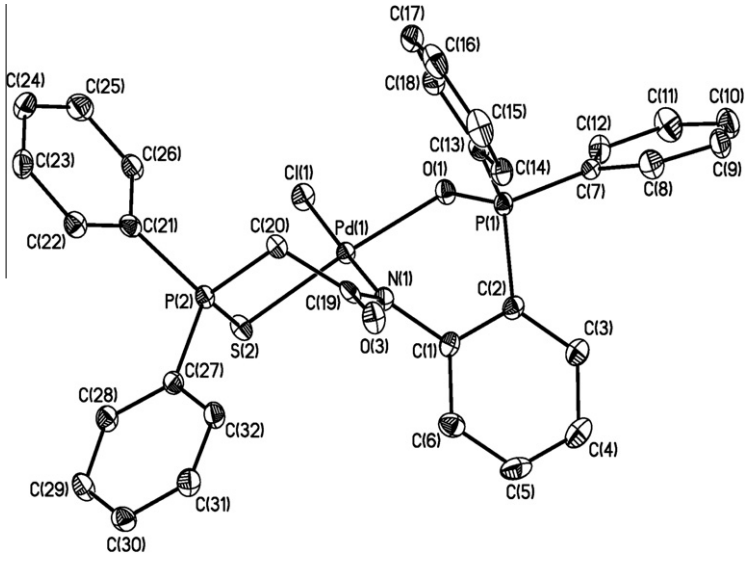


Fig. 7. General view of complex **6c** in representation of atoms by thermal ellipsoids (p = 50%).

0.59(1) Å (**6d**) and the atoms N(1) and P(2) in the other by 0.69(1) and 0.76(1) (**6b**), 0.75(1) and 0.63(1) Å (**6c**), 0.82(1) and 0.78(1) Å (**6d**).

In the palladium derivatives, the values of the above torsion angles S(1)P(1)C(2)C(1) and S(2)P(2)C(1)C(2) are nearly the same for complexes **6b** and **6c** with κ^3-*SNO* coordination (58.5(1) and 69.7(1)° in the former and 59.4(1) and 74.3(1)° in the latter), being slightly different from those in κ^3-*SNS* complex **6d** (60.3(1) and 98.0(1)°, respectively).

In the crystals **6b–d**, the molecules are held together only by weak but numerous contacts C–H···O, C–H···π and C–H···Cl as well as H···H in **6c** and **6d**.

Note that the individual molecules of complexes **4a**,**d** and **6b–d** are virtually chiral due to the fully unsymmetrical surrounding of the metal center, although all the crystals are comprised of both enantiomers. As for the nature of chirality generated, in palladium derivatives **6b–d** highly constrained system of two fused six-membered rings gives rise to left- and right-handed twisted atropisomeric forms (see Fig. S2 in Supplementary material for a representative example of complex **6c**). In the related octahedral rhenium complexes **4a**,**d** with the deprotonated forms of ligands **2a**,**d** bound in a facial manner, the metal center serves as a stereogenic center (see Fig. S3 in Supplementary material for a representative example of complex **4d**). In general, pincer complexes with two six-membered fused metallacycles are quite uncommon compared to their 5,5-membered counterparts and, unlike the complexes from the present, are based on symmetrical ligands [5,6]. Atropisomerism is an intrinsic feature of such systems owing to a possibility of the existence of left- and right-handed twisted forms. Depending on the structure of complexes, the interconversion between two atropisomers can be either rapid on the NMR time scale at room temperature [18] or complicated, as in our case, due to a high rotational barrier, resulting in metallacycles conformationally stable up to 110 °C [19]. Furthermore, most of the solid samples submitted to X-ray diffraction analysis were also racemates, with only one example of *PCP* rhodium complex spontaneously crystallized in a single enantiomeric form [18c]. Note that the synthesis of 6,6-membered metallacycles comprises

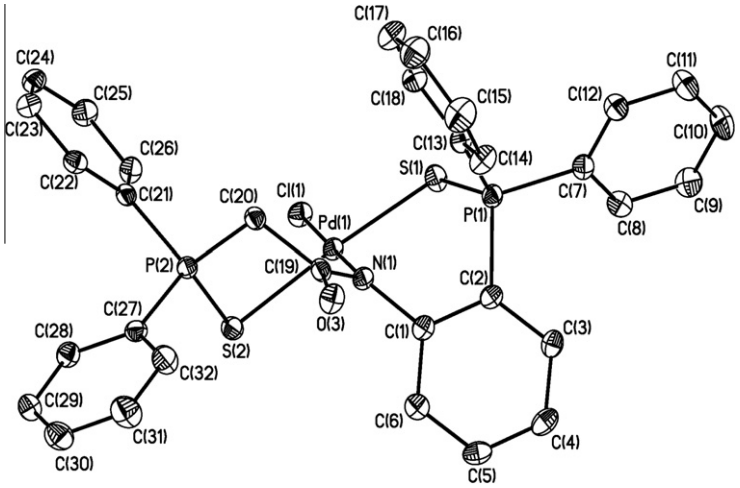


Fig. 8. General view of complex **6d** in representation of atoms by thermal ellipsoids (p = 50%).

the transmetallation, e.g., of (COD)$PdCl_2$ with the corresponding non-metallated silver or mercury complexes [18b,19a,19c,19d,19f], oxidative addition of low-valent metal precursors to C2-halogentaed ligands [19b], and direct cyclopalladation under rather severe conditions (prolonged heating at elevated temperatures) [18a,18d,18e,19e]. Taking into account the ease of formation of complexes **4a**,**d** and **6b**–**d** (in the case of palladium derivatives, direct cyclopalladation smoothly proceeds at room temperature) and stability of atropisomers in solution at room temperature, there is a realistic possibility of resolving the racemic mixtures, which in case of rhenium derivatives could give rise to chiral-at-metal compounds.

3. Conclusions

To summarize the results presented, simple modular assembling procedures of the available building-blocks, *ortho*-(thio)phosphorylated anilines and diphenyl(thio)phosphorylacetic acid derivatives, afford a series of oligondentate ligands **2a**–**d** with donor centers of variable nature, therewith, offering ample opportunities for fine-tuning of their electronic and steric properties. The ligands derived readily underwent N–H bond activation in the reactions with Re(I) and Pd(II) precursors to give κ^3-*XNY* pincer complexes with two fused six-membered metallocycles. In solution at room temperature the complexes obtained exist in stable atropisomeric forms, and now the investigations are ongoing to resolve enantiomers.

4. Experimental

4.1. General remarks

If not noted otherwise, all manipulations were carried out without taking precautions to exclude air and moisture. THF was distilled over sodium/beznophenone ketyl and dichloromethane was distilled from P_2O_5. 2-(Diphenylthiophosphoryl)aniline **1b** [9] and $Ph_2P(S)H$ [20] were obtained according to the literature procedures. All other chemicals and solvents were used as purchased.

NMR spectra were recorded on Bruker Avance-300 and Bruker Avance-400 spectrometers, and the chemical shifts (δ) were internally referenced by the residual solvent signals relative to tetramethylsilane (^1H and ^{13}C) or externally to H_3PO_4 (^{31}P). The ^{13}C NMR spectra were registered using the *J*MODECHO mode; the signals for the C atoms bearing odd and even numbers of protons have opposite polarities. The numeration for carbon atoms of the central benzene ring in the descriptions of the ^{13}C NMR spectral data of all the compounds is in agreement with IUPAC nomenclature used for ligands **2a**–**d**. The same principle of numbering was used for description of the solid-state molecular structures characterized by X-ray crystallography.

Column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM). IR spectra were recorded on a Magna-IR750 Fourier spectrometer (Nicolet), resolution 2 cm^{-1}, 128 scans. The assignment of absorption bands in the IR spectra was made according to Ref. [21] Melting points were determined with MPA 120 EZ-Melt Automated Melting Point Apparatus and were uncorrected.

4.2. 2-(Diphenylphosphoryl)aniline ***1a***

A 35% aq. solution of hydrogen peroxide (10 mL) was slowly dropwise added to a solution of 2-phosphinylaniline (20 g, mol) in 100 mL of chloroform. The resulting reaction mixture was stirred for 1.5 h at room temperature and 1 h at 50 °C, and after cooling to room temperature washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was crystallized upon addition of hexane and dried in *vacuo* to give 19.0 g (90%) **1a** as a white crystalline solid. Mp: 228–230 °C (*cf.* 227–228 °C).[1] $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 35.57.

4.3. General procedure for the synthesis of chloroacetamides ***3a***,***b***

A solution of triethylamine (0.6 mL, 4.3 mmol) and the corresponding *ortho*-(thio)phosphorylated aniline (**1a** or **1b**) (3.4 mmol) in 10 mL of chloroform was slowly dropwise added under an argon atmosphere to a stirred solution of chloroacetyl chloride (0.45 g, 4.0 mmol) in 7 mL of $CHCl_3$, cooled with an ice-salt bath to 0 °C. The reaction mixture was stirred at 0–5 °C for 30 min and left under ambient conditions overnight. The resulting mixture was washed with water (2 × 10 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue obtained was purified by column chromatography on silica gel (eleunt: CH_2Cl_2 (**3a**), hexane–acetone (7:3) (**3b**)) to give **3a**,**b** as white crystalline solids.

4.3.1. 2-Chloro-N-[2-(Diphenylphosphoryl)phenyl]acetamide ***3a***

Yield: 1.1 g (87%). Mp: 92–93 °C. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 36.05. ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 4.02 (s, 2 H, CH_2), 7.01 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.6, $^3J_{PH}$ = 13.8),

7.08 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.4, $^4J_{PH}$ = 2.4), 7.48–7.60 (m, 7 H, H_{Ar}), 7.64 (dd, 4 H, *o*-H in $P(O)(C_6H_5)_2$, $^3J_{HH}$ = 7.6, $^3J_{PH}$ = 12.3), 8.47 (dd, 1 H, H–C6, $^3J_{HH}$ = 8.4, $^4J_{PH}$ = 4.3), 11.51 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 42.96 (s, CH_2), 118.94 (d, C2, $^1J_{PC}$ = 100.6), 122.39 (d, C6, $^3J_{PC}$ = 12.1), 123.53 (d, C4, $^3J_{PC}$ = 12.2), 128.64 (d, *m*-C in $P(O)C_6H_5$, $^3J_{PC}$ = 12.2), 130.97 (d, *ipso*-C in $P(O)(C_6H_5)_2$, $^1J_{PC}$ = 105.3), 131.91 (d, *o*-C in $P(O)(C_6H_5)_2$, $^2J_{PC}$ = 8.8), 132.44 (s, *p*-C in $P(O)(C_6H_5)_2$), 132.60 (d, C3, $^2J_{PC}$ = 10.1), 133.23 (d, C5, $^4J_{PC}$ = 1.3), 142.88 (d, C1, $^2J_{PC}$ = 2.7), 165.16 (s, C=O). IR (KBr, ν/cm^{-1}): 513(m), 546(vs), 692(m), 719(m), 726(m), 737(m), 752(w), 763(m), 775(m), 804(w), 1071(w), 1079(w), 1099(w), 1119(m), 1133(w), 1137(w), 1156(m), 1160(sh, m) (P=O), 1166(m) (P=O), 1252(w), 1271(w), 1307(s), 1400(w), 1408(w), 1438(s), 1452(m), 1485(w), 1535(br, s) (NHCO), 1582(s), 1605(br, m), 1678(br, s) (C=O), 3025(w), 3153(br, w) (NH). *Anal.* Calc. for $C_{20}H_{17}ClNO_2P$: C, 64.96; H, 4.63; N, 3.79. Found: C, 65.04; H, 4.57; N, 3.74%.

4.3.2. 2-Chloro-N-[2-(diphenylthiophosphoryl)phenyl]acetamide **3b**

Yield: 1.3 g (99%). Mp: 192–193 °C (EtOAc). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 39.51. ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 3.70 (s, 2 H, CH_2), 6.86 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.9, $^3J_{PH}$ = 14.3), 7.14 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.6, $^4J_{PH}$ = 2.2), 7.48–7.53 (m, 4 H, H_{Ar}), 7.58–7.63 (m, 3 H, H_{Ar}), 7.78 (dd, 4 H, *o*-H in $P(S)(C_6H_5)_2$, $^3J_{HH}$ = 7.9, $^3J_{PH}$ = 13.7), 7.98 (dd, 1 H, H–C6, $^3J_{HH}$ = 7.9, $^4J_{PH}$ = 4.8), 10.22 (br. s, 1 H, NH). IR (KBr, ν/cm^{-1}): 515(m), 523(m), 613(w) (P=S), 634(m) (P=S), 692(m), 714(s), 733(w), 749(w), 757(m), 761(w), 776(m), 1101(m), 1129(w), 1272(w), 1293(w), 1309(w), 1408(w), 1436(s), 1456(w), 1481(w), 1506(br, s) (NHCO), 1570(m), 1573(m), 1682(br, m) (C=O), 2941(w), 2993(w), 3053(w), 3079(w), 3289(br, w) (NH). Analytically pure sample was obtained by recrystallization from EtOAc. *Anal.* Calc. for $C_{20}H_{17}ClNOPS$: C, 62.26; H, 4.44; N, 3.63. Found: C, 62.28; H, 4.51; N, 3.63%.

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

A solution of PCl_3 (0.33 g, 2.4 mmol) in 4 mL of dichloromethane was slowly dropwise added to a stirred solution of diphenylphosphorylacetic acid (1.56 g, 6.0 mmol) in 10 mL of CH_2Cl_2 at 0–5 °C under an argon atmosphere. After stirring for 5 h at room temperature, the resulting solution was cooled again to 0 °C with an ice-salt bath, and then a solution of the corresponding aniline (**1a** or **1b**) (4.8 mmol) and triethylamine (0.17 mL, 1.2 mmol) in 5 mL of CH_2Cl_2 was added. The resulting reaction mixture was stirred for 0.5 h at 0 °C and left overnight. The solution obtained was sequentially washed with 20 mL of diluted hydrochloric acid (1 mL conc. HCl/10 mL H_2O), water (2 × 15 mL), saturated aqueous solution of NaOH (15 mL), and again with water (2 × 15 mL). The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was purified by column chromatography on silica gel (eluent in both cases CH_2Cl_2/MeOH (10:1)) to give **2a**,**b** as white crystalline solids.

4.4.1. 2-(Diphenylphosphoryl)-N-[2-(diphenylphosphoryl)phenyl]-acetamide **2a**

Yield: 1.4 g (55%). Mp: 168–169 °C. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 27.83 ($CH_2P(O)(C_6H_5)_2$), 36.96 ($ArP(O)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 3.46 (d, 2 H, CH_2, $^2J_{PH}$ = 14.5), 6.92–7.00 (m, 2 H, H_{Ar}), 7.37–7.49 and 7.56–7.61 (both m, 11 H + 6 H, H_{Ar}), 7.81 (dd, 4 H, *o*-H in $P(O)(C_6H_5)_2$, $^3J_{PH}$ = 12.1, $^3J_{HH}$ = 8.2), 8.30 (dd, 1 H, H–C6, $^3J_{HH}$ = 8.4, $^4J_{PH}$ = 4.4), 11.29 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, δ/ppm, J/Hz): 41.68 (d, CH_2, $^1J_{PC}$ = 62.9), 116.77 (d, C2, $^1J_{PC}$ = 100.6), 122.18 (d, C6, $^3J_{PC}$ = 7.2), 122.94 (d, C4, $^3J_{PC}$ = 12.6), 128.37 (d, *m*-C in $P(O)(C_6H_5)_2$, $^3J_{PC}$ = 12.4), 128.61 (d, *m*-C in $P(O)(C_6H_5)_2$, $^3J_{PC}$ = 12.6), 131.10 (d, *o*-C in $P(O)(C_6H_5)_2$, $^2J_{PC}$ = 9.8), 131.30 (d, *ipso*-C in $CH_2P(O)(C_6H_5)_2$, $^1J_{PC}$ = 100.3), 131.76 (d, *ipso*-C in $ArP(O)(C_6H_5)_2$, $^1J_{PC}$ = 108.9), 131.85 (d, *p*-C in $P(O)(C_6H_5)_2$, $^4J_{PC}$ = 2.9), 132.03 (d, *o*-C in $P(O)(C_6H_5)_2$, $^2J_{PC}$ = 10.1), 132.45 (d, *p*-C in $P(O)(C_6H_5)_2$, $^4J_{PC}$ = 3.0), 132.55 (d, C3, $^2J_{PC}$ = 10.9), 133.11 (d, C5, $^4J_{PC}$ = 2.0), 143.68 (s, C1), 163.28 (d, C=O, $^2J_{P,C}$ = 4.9). IR (KBr, ν/cm^{-1}): 513(m), 522(m), 548(s), 694(s), 709(m), 718(m), 746(m), 830(w), 961(w), 997(w), 1027(w), 1071(w), 1102(m), 1120(s), 1133(m), 1160(m) and 1167(m) (both P=O in $ArP(O)Ph_2$), 1198(m) and 1203(m) (both P=O in $CH_2P(O)Ph_2$), 1263(w), 1309(br, m), 1438(vs), 1458(w), 1484(w), 1533(br, m) (NHCO), 1583(m), 1608(br, m), 1690(br, m) (C=O), 2922(w), 3054(w), 3174(w), 3239(br, w) (NH). *Anal.* Calc. for $C_{32}H_{27}NO_3P_2$: C, 71.77; H, 5.08; N, 2.62. Found: C, 71.64; H, 5.04; N, 2.64%.

4.4.2. 2-(Diphenylphosphoryl)-N-[2-(diphenylthiophosphoryl)phenyl]-acetamide **2b**

Yield: 1.9 g (69%). Mp: 215–216 °C. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 27.45 ($CH_2P(O)(C_6H_5)_2$), 39.82 ($ArP(S)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 3.04 (d, 2 H, CH_2, $^2J_{PH}$ = 14.6), 6.75 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 14.4), 7.02 (t, 1 H, H–C4, $^3J_{HH}$ = 7.6), 7.39–7.55 (m, 13 H, H_{Ar}), 7.61 (dd, 1 H, H–C6, $^3J_{HH}$ = 8.0, $^4J_{PH}$ = 5.0), 7.68 (dd, 4 H, *o*-H in $ArP(S)(C_6H_5)_2$, $^3J_{PH}$ = 13.8, $^3J_{HH}$ = 7.7), 7.77 (dd, 4 H, *o*-H in $CH_2P(O)(C_6H_5)_2$, $^3J_{PH}$ = 12.1, $^3J_{HH}$ = 7.6), 9.94 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 40.63 (d, CH_2, $^1J_{PC}$ = 61.6), 123.13 (d, C2, $^1J_{PC}$ = 85.5), 124.48 (d, C4, $^3J_{PC}$ = 12.1), 126.03 (d, C6, $^3J_{PC}$ = 7.0), 128.48 (d, *m*-C in $P(X)(C_6H_5)_2$, $^3J_{PC}$ = 12.5), 128.66 (d, *m*-C in $P(X)(C_6H_5)_2$, $^3J_{PC}$ = 12.8), 130.70 (d, *ipso*-C in $ArP(S)(C_6H_5)_2$, $^1J_{PC}$ = 86.2), 131.12 (d, *o*-C in $P(X)(C_6H_5)_2$, $^1J_{PC}$ = 9.9), 131.66 (d, *ipso*-C in $CH_2P(O)(C_6H_5)_2$, $^1J_{PC}$ = 108.0), 132.01 (d, overlapping signals of *p*-C in $P(O)(C_6H_5)_2$ and $P(S)(C_6H_5)_2$, $^4J_{PC}$ = 2.9), 132.03 (d, C3, $^2J_{PC}$ = 7.7), 132.13 (d, *o*-C in $P(X)(C_6H_5)_2$, $^2J_{PC}$ = 11.0), 132.60 (d, C5, $^4J_{PC}$ = 2.6), 140.36 (d, C1, $^2J_{PC}$ = 4.4), 162.85 (d, C=O, $^2J_{PC}$ = 4.8). IR (KBr, ν/cm^{-1}): 516(m), 519(sh, m), 539(w), 545(w), 614(w) and 636(m) (both P=S), 690(m), 694(m), 707(m), 719(s), 725(m), 746(m), 752(m), 844(w), 999(w), 1026(w), 1072(w), 1101(m), 1121(m), 1128(w), 1172(m), 1182(w), 1202(m) (P=O), 1226(w), 1245(w), 1290(w), 1309(w), 1390(w), 1437(s), 1481(w), 1505(s) (NHCO), 1566(w), 1573(w), 1590(w), 1688(s) (C=O), 3023(w), 3051(w), 3208(br, w) (NH). *Anal.* Calc. for $C_{32}H_{27}NO_2P_2S{\cdot}0.25\ CH_2Cl_2$: C, 67.62; H, 4.84; N, 2.45. Found: C, 67.50; H, 4.76; N, 2.33%.

4.5. General procedure for the synthesis of ligands **2c**,**d**

A 60% dispersion of NaH in mineral oil (0.1 g, 2.5 mmol) was portionwise added to a solution of $Ph_2P(S)H$ (0.5 g, 2.3 mmol) in 5 mL of THF under vigorous stirring and argon atmosphere. The reaction mixture was stirred for 15 min, then a solution of the corresponding chloroacetamide (**3a** or **3b**) (2.3 mmol) in 10 mL of THF was added. The resulting mixture was stirred for 2 h at 40 °C and left overnight. The solvent was removed *in vacuo*, the residue was dissolved in $CHCl_3$ and washed with water. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The resulting residue was purified by column chromatography on silica gel (eluent: hexane–acetone (7:3) (**2c**), CH_2Cl_2–MeOH (10:1) (**2d**)) to give **2c**,**d** as white crystalline solids.

4.5.1. N-[2-(Diphenylphosphoryl)phenyl]-2-(diphenylthiophosphoryl)-acetamide **2c**

Yield: 1.0 g (79%). Mp: 184–185 °C. $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 36.84 ($ArP(O)(C_6H_5)_2$), 38.65 ($CH_2P(S)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, *J*/Hz): 3.61 (d, 2 H, CH_2, $^2J_{PH}$ = 14.1), 6.94–7.02 (m, 2 H, H_{Ar}), 7.38–7.50 (m, 11 H, H_{Ar}) 7.56–7.63 (m, 6 H, H_{Ar}), 7.88 (dd, 4 H, *o*-H in $P(X)(C_6H_5)_2$,

$^3J_{PH}$ = 13.5, $^3J_{HH}$ = 7.5), 8.35 (dd, 1 H, H–C6, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 4.4), 11.29 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, δ/ppm, J/Hz): 44.78 (d, CH_2, $^1J_{PC}$ = 48.9), 117.12 (d, C2, $^1J_{PC}$ = 100.3), 122.39 (d, C6, $^3J_{PC}$ = 8.0), 123.02 (d, C4, $^3J_{PC}$ = 12.9), 128.40 (d, *m*-C in $P(X)(C_6H_5)_2$, $^3J_{PC}$ = 12.6), 128.63 (d, *m*-C in $P(X)(C_6H_5)_2$, $^3J_{PC}$ = 12.6), 131.30 (d, *ipso*-C in $ArP(O)(C_6H_5)_2$, $^1J_{PC}$ = 106.0), 131.37 (d, *o*-C in $P(X)(C_6H_5)_2$, $^2J_{PC}$ = 10.9), 131.49 (d, *p*-C in $P(X)(C_6H_5)_2$, $^4J_{PC}$ = 3.2), 132.02 (d, *o*-C in $P(X)(C_6H_5)_2$, $^2J_{PC}$ = 10.1), 132.18 (d, *ipso*-C in $CH_2P(S)(C_6H_5)_2$, $^1J_{PC}$ = 83.6), 132.40 (d, *p*-C in $P(X)(C_6H_5)_2$, $^4J_{PC}$ = 2.9), 132.61 (d, C3, $^2J_{PC}$ = 10.6), 133.15 (d, C5, $^4J_{PC}$ = 2.0), 143.57 (d, C1, $^2J_{PC}$ = 2.9), 163.04 (d, C=O, $^2J_{PC}$ = 4.9). IR (KBr, ν/cm^{-1}): 519(m), 547(s), 598(w), 648(w) (P=S), 692(s), 711(s), 739(m), 747(m), 769(sh, w), 791(w), 961(w), 998(w), 1027(w), 1070(w), 1076(w), 1102(m), 1120(m), 1134(m), 1153(m) and 1167(m) (both P=O), 1268(w), 1311(br, s), 1410(w), 1437(vs), 1457(w), 1483(w), 1507(w), 1540(br, m) (NHCO), 1583(s), 1609(br, m), 1684(br, m) (C=O), 2918(w), 3055(w), 3180(br, w) (NH), 3250(br, w) (NH). *Anal.* Calc. for $C_{32}H_{27}NO_2P_2S$: C, 69.68; H, 4.93; N, 2.54. Found: C, 69.49; H, 5.01; N, 2.44%.

4.5.2. 2-(Diphenylthiophosphoryl)-N-[2-(diphenylthiophosphoryl)-phenyl]acetamide **2d**

Yield: 1.0 g (77%). Mp: 215–216 °C. $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 38.25 ($CH_2P(S)(C_6H_5)_2$), 40.07 ($ArP(S)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.24 (d, 2 H, CH_2, $^2J_{PH}$ = 14.0), 6.78 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 14.3), 7.03 (t, 1 H, H–C4, $^3J_{HH}$ = 7.7), 7.44–7.55 (m, 13 H, H_{Ar}), 7.64–7.69 (m, 5 H, H_{Ar}), 7.84 (dd, 4 H, *o*-H in $P(S)(C_6H_5)_2$, $^3J_{PH}$ = 13.6, $^3J_{HH}$ = 8.2), 9.92 (br. s, 1 H, NH). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, J/Hz): 43.71 (d, CH_2, $^1J_{PC}$ = 47.4), 122.91 (d, C2, $^1J_{PC}$ = 85.2), 124.39 (d, C4, $^3J_{PC}$ = 12.0), 125.91 (d, C6, $^3J_{PC}$ = 6.8), 128.29 (d, *m*-C in $P(S)(C_6H_5)_2$, $^3J_{PC}$ = 12.6), 128.47 (d, *m*-C in $P(S)(C_6H_5)_2$, $^3J_{PC}$ = 12.9), 130.59 (d, *ipso*-C in $ArP(S)(C_6H_5)_2$, $^1J_{PC}$ = 85.8), 131.15 (d, *o*-C in $P(S)(C_6H_5)_2$, $^2J_{PC}$ = 10.8), 131.45 (d, *p*-C in $P(S)(C_6H_5)_2$, $^4J_{PC}$ = 3.1), 131.71 (d, *ipso*-C in $CH_2P(S)(C_6H_5)_2$, $^1J_{PC}$ = 83.4), 131.80 (d, *p*-C in $P(S)(C_6H_5)_2$, $^4J_{PC}$ = 3.1), 131.94 (d, C3, $^2J_{PC}$ = 9.2), 131.98 (d, *o*-C in $P(S)(C_6H_5)_2$, $^2J_{PC}$ = 11.1), 132.43 (d, C5, $^4J_{PC}$ = 2.2), 140.19 (d, C1, $^2J_{PC}$ = 4.3), 162.29 (d, C=O, $^2J_{PC}$ = 5.2). IR (KBr, ν/cm^{-1}): 515(m), 530(w), 535(w), 614(w) and 637(m) (both P=S in $ArP(S)Ph_2$), 649(w) (P=S in $CH_2P(S)Ph_2$), 692(s), 711(s), 721(m), 740(m), 750(m), 758(w), 800(w), 841(w), 998(w), 1025(w), 1071(w), 1102(m), 1130(w), 1247(w), 1290(w), 1310(w), 1392(w), 1436(vs), 1481(w), 1500(m) (NHCO), 1574(w), 1591(w), 1677(s) (C=O), 2852(w), 2922(w), 3055(w), 3250(br, w) (NH). *Anal.* Calc. for $C_{32}H_{27}NOP_2S_2$: C, 67.71; H, 4.79; N, 2.47; S, 11.30. Found: C, 67.71; H, 4.83; N, 2.49; S, 11.37%.

4.6. General procedure for the synthesis of Re(I) complexes **4a**,**d**

A solution of $Re(CO)_5Br$ (51 mg, 0.126 mmol), triethylamine (17.5 μL, 0.126 mmol), and the corresponding ligand (**2a** or **2b**) (0.126 mmol) in 10 mL of toluene was refluxed for 1.5 h. After cooling to room temperature, the solvent was removed *in vacuo* and the resulting residue was purified by column chromatography on silica gel (eluent $CHCl_3$) to give **5a**,**b** as white crystalline solids.

4.6.1. Complex **4a**

Yield: 83 mg (82%). Mp: >264 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 45.59 ($CH_2P(O)(C_6H_5)_2$), 45.94 $Ar(P(O)(C_6H_5)_2)$. ^1H NMR (300.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.43 (dd, 1 H, CH_2, $^2J_{PH}$ = 4.1, $^2J_{HH}$ = 15.1), 4.07 (dd, 1 H, CH_2, $^2J_{PH}$ = 19.3, $^2J_{HH}$ = 15.1), 6.81 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.5, $^3J_{PH}$ = 14.3), 6.99–7.05 (m, 3 H, H_{Ar}), 7.14–7.25 (m, 3 H, H_{Ar}), 7.31–7.46 (m, 5 H, H_{Ar}), 7.51–7.66 (m, 12 H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, J/Hz): 40.84 (d, CH_2, $^1J_{PC}$ = 58.3), 121.34 (d, C2, $^1J_{PC}$ = 101.6), 123.21 (d, C4, $^3J_{PC}$ = 13.6), 127.81 (d, *ipso*-C in $ArP(O)C_6H_5$, $^1J_{PC}$ = 111.1), 128.00 (d, *m*-C in $P(O)C_6H_5$, $^3J_{PC}$ = 13.9), 128.66 (d, *m*-C in $P(O)C_6H_5$, $^3J_{PC}$ = 12.5), 128.74 (d, *m*-C in $P(O)C_6H_5$, $^3J_{PC}$ = 12.8), 128.76 (d, C6, $^3J_{PC}$ = 8.4), 128.94 (d, *ipso*-C in $ArP(O)C_6H_5$, $^1J_{PC}$ = 112.2), 129.03 (d, *ipso*-C in $CH_2P(O)C_6H_5$, $^1J_{PC}$ = 108.9), 129.14 (d, *m*-C in $P(O)C_6H_5$, $^3J_{PC}$ = 12.8), 129.66 (d, *ipso*-C in $CH_2P(O)C_6H_5$, $^1J_{PC}$ = 92.1), 130.58 (d, *o*-C in $P(O)C_6H_5$, $^2J_{PC}$ = 10.6), 131.02 (d, *o*-C in $P(O)C_6H_5$, $^2J_{PC}$ = 11.4), 132.08 (d, *o*-C in $P(O)C_6H_5$, $^2J_{PC}$ = 11.4), 132.42 (d, C3, $^2J_{PC}$ = 11.7), 132.43 (d, *p*-C in $P(O)C_6H_5$, $^4J_{PC}$ = 2.6), 132.58 (d, *p*-C in $P(O)C_6H_5$, $^4J_{PC}$ = 2.9), 132.67 (d, *o*-C in $P(O)C_6H_5$, $^2J_{PC}$ = 10.3), 132.88 (d, *p*-C in $P(O)C_6H_5$, $^4J_{PC}$ = 2.9), 132.95 (d, *p*-C in $P(O)C_6H_5$, $^4J_{PC}$ = 2.9), 133.61 (d, C5, $^4J_{PC}$ = 2.2), 157.42 (s, C1), 167.54 (d, C=O, $^2J_{P,C}$ = 7.3), 193.92 (s, CO), 195.68 (s, CO), 195.74 (s, CO). IR (KBr, ν/cm^{-1}): 523(w), 536(w), 553(s), 569(m), 630(w), 689(m), 695(m), 723(m), 736(w), 747(m), 760(w), 808(w), 820(w), 845(w), 979(w), 998(w), 1027(w), 1068(m), 1093(m), 1130(s) (P=O in $ArP(O)Ph_2$), 1140(m), 1150(s) (P=O in $CH_2P(O)Ph_2$), 1266(w), 1327(br, m), 1393(w), 1437(s), 1464(w), 1486(w), 1568(sh, w), 1579(m), 1603(s) (C=O), 1856(vs) (CO), 1868(vs) (CO), 1903(vs) (CO), 1910(vs) (CO), 2017(vs) (CO), 2853(w), 2922(w), 2959(w), 3056(w). *Anal.* Calc. for $C_{35}H_{26}NO_6P_2Re$: C, 52.24; H, 3.26; N, 1.74. Found: C, 52.57; H, 3.56; N, 1.68%.

4.6.2. Complex **4d**

Yield: 75 mg (68%). Mp: >240 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 40.40 ($CH_2P(S)(C_6H_5)_2$), 41.45 ($ArP(S)(C_6H_5)_2$). ^1H NMR (300.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.76 (dd, 1 H, CH_2, $^2J_{PH}$ = 10.2, $^2J_{HH}$ = 14.7), 3.92 (dd, 1 H, CH_2, $^2J_{PH}$ = 17.0, $^2J_{HH}$ = 14.7), 6.64 (dd, 1 H, H–C3, $^3J_{HH}$ = 8.0, $^3J_{PH}$ = 15.1), 6.89–7.04 (m, 4 H, H_{Ar}), 7.31–7.39 (m, 5 H, H_{Ar}), 7.47–7.69 (m, 14 H, H_{Ar}). $^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, δ/ppm, J/Hz): 43.30 (d, CH_2, $^1J_{PC}$ = 45.3), 121.81 (d, C2, $^1J_{PC}$ = 85.8), 123.47 (d, C4, $^3J_{PC}$ = 13.1), 126.28 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 88.9), 127.29 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 13.8), 128.19 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 85.1), 128.72 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 12.4), 128.84 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 12.8), 129.04 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 12.8), 129.81 (d, C6, $^3J_{PC}$ = 8.6), 129.92 (d, *ipso*-C in $CH_2P(S)C_6H_5$, $^1J_{PC}$ = 84.8), 130.19 (d, *ipso*-C in $CH_2P(S)C_6H_5$, $^1J_{PC}$ = 78.5), 130.98 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 11.1), 131.02 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 11.1), 131.62 (d, C3, $^2J_{PC}$ = 9.7), 131.86 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 2.8), 132.18 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 3.1), 132.52–132.75 (overlapping signals of two *p*-C + one *o*-C in $P(S)C_6H_5$), 133.28 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 10.0), 133.84 (d, C5, $^4J_{PC}$ = 2.2), 158.08 (s, C1), 168.93 (d, C=O, $^2J_{PC}$ = 7.3), 189.62 (s, CO), 192.44 (d, CO, $^3J_{PC}$ = 2.4), 192.55 (d, CO, $^3J_{PC}$ = 6.9). IR (KBr, ν/cm^{-1}): 525(m), 532(m), 550(w), 588(m) (P=S in $ArP(S)Ph_2$), 604(m) (P=S in $CH_2P(S)Ph_2$), 622(w), 625(w), 647(w), 689(s), 698(m), 709(m), 741(m), 746(m), 759(m), 810(w), 837(w), 885(w), 979(m), 998(w), 1028(w), 1072(w), 1101(s), 1118(m), 1133(w), 1261(w), 1318(br, s), 1387(w), 1438(s), 1462(m), 1481(w), 1559(m), 1580(m), 1604(s) (C=O), 1877(vs) (CO), 1900(vs) (CO), 2014 (vs) (CO), 2962(w), 3062(w). *Anal.* Calc. for $C_{35}H_{26}NO_4P_2ReS_2 \cdot 0.33\ CHCl_3$: C, 48.41; H, 3.03; N, 1.60. Found: C, 48.41; H, 3.13; N, 1.42%.

4.7. Synthesis of complex **5**

A solution of $Re(CO)_5Br$ (52 mg, 0.127 mmol) and ligand **2a** (68 mg, 0.127 mmol) in 10 mL of toluene was refluxed for 1.5 h. After cooling to room temperature, the solvent was removed *in vacuo* and the resulting residue was crystallized from diethyl ether. The desired product was collected by filtration and dried under vacuum (white crystalline solid). Yield: 111 mg (99%). Mp: >165 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 43.35 ($CH_2P(O)(C_6H_5)_2$), 46.18 ($ArP(O)(C_6H_5)_2$). ^1H NMR

(400.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.33 (dd, 1 H, CH_2, $^2J_{PH}$ = 5.4, $^2J_{HH}$ = 14.2), 4.92 (dd, 1 H, CH_2, $^2J_{PH}$ = 22.3, $^2J_{HH}$ = 14.2), 6.99 (dd, 1 H, H–C3, $^3J_{PH}$ = 15.6, $^3J_{HH}$ = 7.8), 7.07 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.8, $^4J_{PH}$ = 3.1), 7.35–7.63 (m, 16 H, H_{Ar}), 7.71 (t, 1 H, H–C5, $^3J_{HH}$ = 7.9), 7.77–7.86 (m, 4 H, H_{Ar}), 8.20 (dd, 1 H, H–C6, $^3J_{HH}$ = 7.9, $^4J_{PH}$ = 4.9), 10.59 (br. s, 1 H, NH). IR (KBr, ν/cm^{-1}): 513(w), 528(m), 550(m), 692(m), 708(w), 722(m), 734(w), 744(m), 750(m), 838(w), 998(w), 1028(w), 1072(w), 1106(m), 1122(m), 1147(m) and 1158(m) (P=O in $ArP(O)Ph_2$), 1171(m) and 1185(m) (P=O in $CH_2P(O)Ph_2$), 1255(w), 1297(m), 1388(w), 1438(s), 1461(w), 1485(w), 1529(m), 1578(m), 1590(w), 1598(w), 1696(m) (C=O), 1877(vs) (CO), 1883(vs) (CO), 1896(vs) (CO), 1902(vs) (CO), 2020(vs) (CO), 2895(w), 2952(w), 3059(w), 3287(w) (NH). *Anal.* Calc. for $C_{35}H_{27}BrNO_6P_2Re$: C, 47.47; H, 3.07; Br, 9.02; N, 1.58; P, 7.10. Found: C, 47.37; H, 2.97; Br, 9.02; N, 1.47; P, 7.14%.

4.8. General procedure for the synthesis of Pd(II) complexes **6b–d**

A solution of $(PhCN)_2PdCl_2$ (66 mg, 0.172 mmol) in 5 mL of dichloromethane was slowly dropwise added to a solution of the corresponding ligand (**2b**, **2c** or **2d**) (0.172 mmol) in 5 mL of CH_2Cl_2. The reaction mixture was left under ambient conditions for 12 h, then the solvent was removed *in vacuo* and the resulting residue was purified by column chromatography on silica gel (eluent $CHCl_3$) to give **6b**–**d** as orange crystalline solids.

4.8.1. Complex **6b**

Yield: 95 mg (80%). Mp: >230 °C (decomp.). $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, δ/ppm): 37.70 ($CH_2P(O)(C_6H_5)_2$), 47.23 ($ArP(S)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.00 (d, 1 H, CH_2, $^2J_{HH}$ = 14.6), 3.84 (dd, 1 H, CH_2, $^2J_{HH}$ = 14.6, $^2J_{PH}$ = 19.7), 6.73–6.78 (m, 2 H, H_{Ar}), 7.00 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.7, $^4J_{PH}$ = 3.2), 7.40 (t, 1 H, H–C5, $^3J_{HH}$ = 7.6), 7.50–7.67 (m, 14 H, H_{Ar}), 7.73–7.76 (dd, 2 H, *o*-H in $P(X)C_6H_5$, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 14.8), 7.80–7.90 (m, 4 H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, J/Hz): 43.73 (d, CH_2, $^1J_{PC}$ = 57.2), 123.11 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 85.1), 123.52 (d, C4, $^3J_{PC}$ = 13.2), 124.24 (d, C2, $^1J_{PC}$ = 86.6), 126.41 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 88.8), 127.55 (d, *ipso*-C in $CH_2P(O)C_6H_5$, $^1J_{PC}$ = 104.7), 127.61 (d, *ipso*-C in $CH_2P(O)C_6H_5$, $^1J_{PC}$ = 104.9), 128.66 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 13.6), 128.82 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 12.4), 129.05 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 13.6), 129.18 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 12.8), 130.05 (d, C6, $^3J_{PC}$ = 8.1), 131.07 (d, C3, $^2J_{PC}$ = 8.8), 131.16 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 10.6), 131.60 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 10.3), 132.03 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 11.7), 132.91 (d, *p*-C in $P(X)C_6H_5$, $^4J_{PC}$ = 2.6), 133.04 (s, *p*-C in $P(X)C_6H_5$), 133.17 (s, *p*-C in $P(X)C_6H_5$), 133.48 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 9.9), 133.53 (s, *p*-C in $P(X)C_6H_5$), 133.94 (d, C5, $^4J_{PC}$ = 2.2), 151.14 (d, C1, $^2J_{PC}$ = 3.7), 165.25 (d, C=O, $^2J_{PC}$ = 6.6). IR (KBr, ν/cm^{-1}): 510(m), 517(s), 552(w), 594(m) (P=S), 619(w), 633(w), 691(m), 712(m), 723(w), 746(m), 752(m), 761(m), 795(w), 841(w), 982(w), 998(w), 1028(w), 1065(w), 1080(w), 1107(m), 1126(m), 1137(s) (P=O), 1163(w), 1189(w), 1264(w), 1329(s), 1378(w), 1437(s), 1462(m), 1483(w), 1560(w), 1576(m), 1590(w), 1616(vs) (C=O), 2852(w), 2922(w), 3057(w). *Anal.* Calc. for $C_{32}H_{26}ClNO_2P_2PdS$: C, 55.51; H, 3.78; N, 2.02. Found: C, 55.06; H, 3.64; N, 1.96%.

4.8.2. Complex **6c**

Yield: 55 mg (46%). Mp:>230 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 43.30 ($ArP(O)(C_6H_5)_2$), 46.90 ($CH_2P(S)(C_6H_5)_2$). ^1H NMR (300 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.45 (dd, 1 H, CH_2, $^2J_{PH}$ = 8.5, $^2J_{HH}$ = 14.0), 4.14 (dd, 1 H, CH_2, $^2J_{PH}$ = 17.9, $^2J_{HH}$ = 14.0), 6.77 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.7, $^4J_{PH}$ = 4.2), 6.86 (dd, 1 H, H–C6, $^3J_{HH}$ = 8.0, $^3J_{PH}$ = 13.4), 7.06 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.7, $^4J_{PH}$ = 2.5), 7.41–7.65 (m, 17 H, H_{Ar}), 7.84–7.89 (m, 4 H, H_{Ar}). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, J/Hz): 46.13 (d, CH_2, $^1J_{PC}$ = 43.8), 123.48 (d, C4, $^3J_{PC}$ = 13.2), 126.19 (d, *ipso*-C in $CH_2P(S)C_6H_5$, $^1J_{PC}$ = 80.3), 126.49 (d, C2, $^1J_{PC}$ = 102.3), 126.62 (d, *ipso*-C in $ArP(O)C_6H_5$, $^1J_{PC}$ = 111.5), 126.90 (d, *ipso*-C in $CH_2P(S)$-C_6H_5, $^1J_{PC}$ = 86.2), 128.50 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 13.5), 128.64 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 13.2), 128.87 (d, C6, $^3J_{PC}$ = 7.3), 129.04 (d, *ipso*-C in $ArP(O)C_6H_5$, $^1J_{PC}$ = 108.4), 129.24 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 12.8), 129.35 (d, *m*-C in $P(X)C_6H_5$, $^3J_{PC}$ = 12.8), 131.78 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 11.0), 131.80 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 11.0), 132.04 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 11.0), 132.27 (d, C3, $^2J_{PC}$ = 11.0), 132.59 (d, *p*-C in $P(X)C_6H_5$, $^4J_{PC}$ = 2.9), 133.00 (d, *o*-C in $P(X)C_6H_5$, $^2J_{PC}$ = 10.6), 133.07 (d, *p*-C in $P(X)C_6H_5$, $^4J_{PC}$ = 2.9), 133.25 (d, *p*-C in $P(X)C_6H_5$, $^4J_{PC}$ = 3.3), 133.28 (d, *p*-C in $P(X)C_6H_5$, $^4J_{PC}$ = 2.9), 134.06 (d, C5, $^4J_{PC}$ = 1.8), 150.73 (d, C1, $^2J_{PC}$ = 1.5), 164.92 (d, C=O, $^2J_{PC}$ = 6.2). IR (KBr, ν/cm^{-1}): 516(w), 550(m), 564(s) (P=S), 582(w), 691(m), 717(m), 732(m), 747(m), 751(m), 836(w), 893(w), 988(w), 998(w), 1026(w), 1056(m), 1085(w), 1105(m), 1123(s) (P=O), 1193(w), 1267(w), 1311(w), 1347(m), 1375(w), 1437(s), 1462(m), 1483(w), 1562(w), 1580(m), 1615(vs) (C=O), 2850(w), 3054(w). Analytically pure sample was obtained upon recrsytallization from CH_2Cl_2–hexane (1:2). *Anal.* Calc. for $C_{32}H_{26}$-$ClNO_2P_2PdS$: C, 55.51; H, 3.78; N, 2.02. Found: C, 55.14; H, 3.67; N, 1.93%.

4.8.3. Complex **6d**

Yield: 111 mg (91%). Mp: >285 °C (decomp.). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, δ/ppm): 38.17 ($CH_2P(S)(C_6H_5)_2$), 41.04 ($ArP(S)(C_6H_5)_2$). ^1H NMR (400.13 MHz, $CDCl_3$, δ/ppm, J/Hz): 3.28 (dd, 1 H, CH_2, $^2J_{PH}$ = 9.5, $^2J_{HH}$ = 13.3), 3.73 (dd, 1 H, CH_2, $^2J_{PH}$ = 17.0, $^2J_{HH}$ = 13.3), 6.80 (dd, 1 H, H–C3, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 14.0), 7.02 (dt, 1 H, H–C4, $^3J_{HH}$ = 7.6, $^4J_{PH}$ = 3.6), 7.18 (dd, 1 H, H–C6, $^3J_{HH}$ = 7.5, $^4J_{PH}$ = 5.2), 7.45–7.57 (m, 11 H, H_{Ar}), 7.61–7.67 (m, 4 H, H_{Ar}), 7.74 (dd, 2 H, *o*-H in $P(S)C_6H_5$, $^3J_{HH}$ = 7.8, $^3J_{PH}$ = 14.7), 7.81 (dd, 2 H, *o*-H in $P(S)C_6H_5$, $^3J_{HH}$ = 7.9, $^3J_{PH}$ = 13.7), 7.93 (dd, 2 H, *o*-H in $P(S)C_6H_5$, $^3J_{HH}$ = 7.7, $^3J_{PH}$ = 14.2). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, δ/ppm, J/Hz): 46.61 (d, CH_2, $^1J_{PC}$ = 44.0), 123.52 (d, C4, $^3J_{PC}$ = 13.2), 124.23 (d, C2, $^1J_{PC}$ = 84.7), 126.58 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 87.3), 127.19 (d, *ipso*-C in $ArP(S)C_6H_5$, $^1J_{PC}$ = 88.4), 127.75 (d, *ipso*-C in $CH_2P(S)C_6H_5$, $^1J_{PC}$ = 82.2), 128.26 (d, *ipso*-C in $CH_2P(S)C_6H_5$, $^1J_{PC}$ = 81.4), 128.67 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 13.6), 129.09 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 12.5), 129.14 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 12.8), 129.26 (d, *m*-C in $P(S)C_6H_5$, $^3J_{PC}$ = 13.2), 130.31 (d, C6, $^3J_{PC}$ = 8.1), 131.45 (d, C3, $^2J_{PC}$ = 9.2), 131.75 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 11.00), 131.96 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 11.7), 132.00 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 11.4), 132.64 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 3.3), 132.87 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 3.3), 133.05 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 2.9), 133.28 (d, *p*-C in $P(S)C_6H_5$, $^4J_{PC}$ = 2.9), 133.48 (d, *o*-C in $P(S)C_6H_5$, $^2J_{PC}$ = 10.3), 134.09 (d, C5, $^4J_{PC}$ = 2.2), 151.14 (d, C1, $^2J_{PC}$ = 4.4), 165.56 (d, C=O, $^2J_{PC}$ = 6.6). IR (KBr, ν/cm^{-1}): 525(m), 548(m), 586(s) (P=S in $CH_2P(S)(C_6H_5)_2$, 601(m) (P=S in $ArP(S)(C_6H_5)_2$), 621(w), 633(w), 688(s), 703(m), 716(m), 745(s), 841(w), 892(w), 983(w), 988(w), 1027(w), 1071(w), 1104(s), 1186(w), 1265(w), 1314(w), 1337(br, m), 1379 (w), 1437(s), 1462(m), 1481(w), 1577(m), 1609(s) (C=O), 2910(w), 3054(w). *Anal.* Calc. for $C_{32}H_{26}ClNOP_2PdS_2$: C, 54.25; H, 3.70; N, 1.98. Found: C, 54.35; H, 3.88; N, 1.91%.

4.9. Crystal structure determination and data collection

Single crystals suitable for X-ray experiments were obtained by recrystallization from ethanol (**2a**) or acetonitrile (**2b**) or slow diffusion of hexane into CH_2Cl_2 (**5**, **6d**) or $CHCl_3$ (**4a**, **4d**, **6b**, **6c**) solutions. X-ray diffraction experiments were carried out with a SMART 1000 CCD diffractometer for compound **2a** and with a SMART APEX2 CCD diffractometer for **2b** and complexes **4a**, **4d**, **5**, **6b**, **6c**, and **6d**, using graphite monochromated Mo Kα radiation

Table 1
Crystal data and structure refinement parameters for **2a**, **2b**, **4a**, **4d**, **5**, **6b**, **6c**, and **6d**.

	2a	**2b**	**4a**	**4d**	**5**	**6b**	**6c**	**6d**
Empirical formula	$C_{33}H_{31}NO_4P_2$	$C_{32}H_{27}NO_2P_2S$	$C_{73}H_{55}Cl_9N_2O_{12}P_4Re_2$	$C_{35}H_{26}NO_4P_2ReS_2$	$C_{35}H_{26}BrNO_6P_2Re$	$C_{32}H_{26}ClNO_2P_2PdS$	$C_{32}H_{26}ClNO_2P_2PdS$	$C_{32}H_{26}ClNOP_2PdS_2$
Formula weight	567.53	551.55	1967.52	836.83	884.62	692.39	692.39	708.45
T (K)	100	100	296	100	100	100	100	100
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	Cc	$P\bar{1}$	$P2_1/c$
Z	2	4	4	4	8	4	2	4
a (Å)	11.5340(7)	15.6006(9)	16.6737(10)	13.5079(7)	10.7141(14)	20.989(5)	10.5238(14)	10.3137(4)
b (Å)	11.6240(7)	9.5574(6)	24.8693(14)	12.5963(6)	17.032(2)	10.319(2)	11.8007(16)	13.3546(6)
c (Å)	12.0915(8)	18.4115(11)	18.5059(10)	18.7405(9)	36.494(5)	16.737(6)	13.2223(18)	21.9310(10)
α (°)	62.690(1)	–	–	–	–	–	83.239(3)	–
β (°)	89.856(2)	97.3710(10)	99.2510(10)	98.3320(10)	97.676(2)	124.833(3)	66.574(2)	92.8430(10)
γ (°)	82.338(1)	–	–	–	–	–	70.724(2)	–
V (Å^3)	1424.40(15)	2722.5(3)	7573.9(7)	3155.0(3)	6599.6(15)	2975.4(14)	1422.1(3)	3017.0(2)
D_{calc} (g cm^{-1})	1.323	1.346	1.725	1.762	1.781	1.546	1.617	1.560
Linear absorption μ (cm^{-1})	1.92	2.68	36.57	41.27	50.37	9.22	9.65	9.76
$F(000)$	596	1152	3864	1648	3448	1400	700	1432
$2\theta_{max}$ (°)	58	58	56	58	52	60	58	58
Reflections measured	21150	27954	73889	24651	61306	30322	16911	23507
Independent reflections	7564	7226	18263	8367	12950	8509	7516	7990
Observed reflections [$I > 2\sigma(I)$]	5272	5814	11680	6950	9461	7175	5935	6772
Parameters	403	343	924	406	830	362	361	361
R_1	0.0543	0.0384	0.0641	0.0266	0.0504	0.0469	0.0381	0.0291
wR_2	0.1393	0.1011	0.1902	0.0586	0.1323	0.0953	0.0850	0.0715
Goodness-of-fit (GOF)	0.999	0.999	1.320	1.006	1.014	1.005	1.003	1.007
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.519/−0.586	0.492/−0.372	4.325/−2.666	1.244/−1.079	2.502/−1.887	0.493/−0.912	0.733/−0.800	0.504/−0.426

(λ = 0.71073 Å, ω-scans) at RT (**4a**) and 100 K (others). The structures were solved by direct method and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. Hydrogen atoms of OH groups in **2a** and of NH groups in both **2a** and **2b** were found in difference Fourier synthesis; the H(C) atom positions were calculated. All hydrogen atoms were refined in isotropic approximation in riding model. Crystal data and structure refinement parameters for **2a**, **2b**, **4a**, **4d**, **5**, **6b**, **6c**, and **6d** are given in Table 1. All calculations were performed using the SHELXTL software [22].

Acknowledgement

The authors are grateful to the Russian Foundation for Basic Research (Grant 12-03-00793-a) for the financial support.

Appendix A. Supplementary material

CCDC 883555–883562 contain the supplementary crystallographic data for compounds **2a,b**, **4a,d**, **5**, and **6b–d**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.12.025.

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