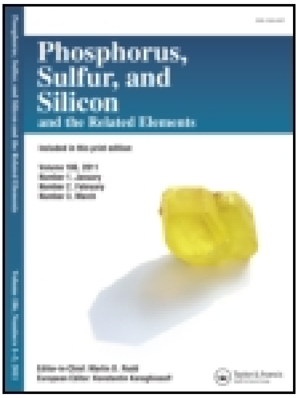

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Thiophosphoryl-, Thiophosphoryloxy-, and Thiophosphorylamino-Benzene Derivatives as Novel Classes of Hybrid Pincer Ligands

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Version of record first published: 25 Apr 2011

To cite this article: Vladimir A. Kozlov, Diana V. Aleksanyan, Andrei A. Vasil'ev & Irina L. Odinets (2011): Thiophosphoryl-, Thiophosphoryloxy-, and Thiophosphorylamino-Benzene Derivatives as Novel Classes of Hybrid Pincer Ligands, Phosphorus, Sulfur, and Silicon and the Related Elements, 186:4, 626-637

To link to this article: http://dx.doi.org/10.1080/10426507.2010.507726

Phosphorus, Sulfur, and Silicon, 186:626–637, 2011
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2010.507726

THIOPHOSPHORYL-, THIOPHOSPHORYLOXY-, AND THIOPHOSPHORYLAMINO-BENZENE DERIVATIVES AS NOVEL CLASSES OF HYBRID PINCER LIGANDS

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Abstract *The synthetic approaches to novel families of SCE ($E = S'$,N,O) hybrid pincer-type ligands bearing thophosphoryl, thiophosphoryloxy, and thiophosphorylamino groups in various combinations with thiophosphoryl-, thiocarbamoyl-, and imine- (including that of benzothiazole ring) donating functions have been developed. All of the ligands readily undergo direct cyclometallation (metal = Pd(II), Pt(II)) to afford 5,5- or 5,6-membered pincer complexes. Palladium complexes displayed from high to excellent catalytic performance in the Suzuki cross-coupling reaction of aryl bromides and phenylboronic acid and the higher asymmetry for a complex served as a factor of its higher catalytic activity.*

Keywords Catalysis; palladium; pincer complexes; pincer ligands; platinum; Suzuki cross-coupling; thiophosphoryl compounds

INTRODUCTION

Pincer complexes containing terdentate anionic six-electron donor ligands of the YEY type (Y presents NR_2, SR, PR_2, OPR_2; E is C or N) are of unfailing interest due to the potential for structural modifications with multiple choices of donor atoms, allowing fine tuning of the reactivity of the metal center. Successful introduction of pincer complexes into homogeneous catalysis as well as their application in organic synthesis or as sensors and switches provided additional impact to this diverse and rapidly developing area and led to the creation and detailed investigation of derivatives bearing a wide range of coordinating groups including optically active ones, fixed on a number of central cores.[1] It should be mentioned that among pincer complexes, independently of the nature of coordination sites, the most common are symmetrical derivatives having two identical donor groups Y and two equivalent five-membered metallacycles. Desymmetrization of a pincer-type structure could improve the chemical and physical properties of the corresponding complexes. Thus,

Received 1 June 2010; accepted 7 July 2010.

The authors are grateful to the Russian Basic Research Foundation (grant 08-03-00508) for financial support.

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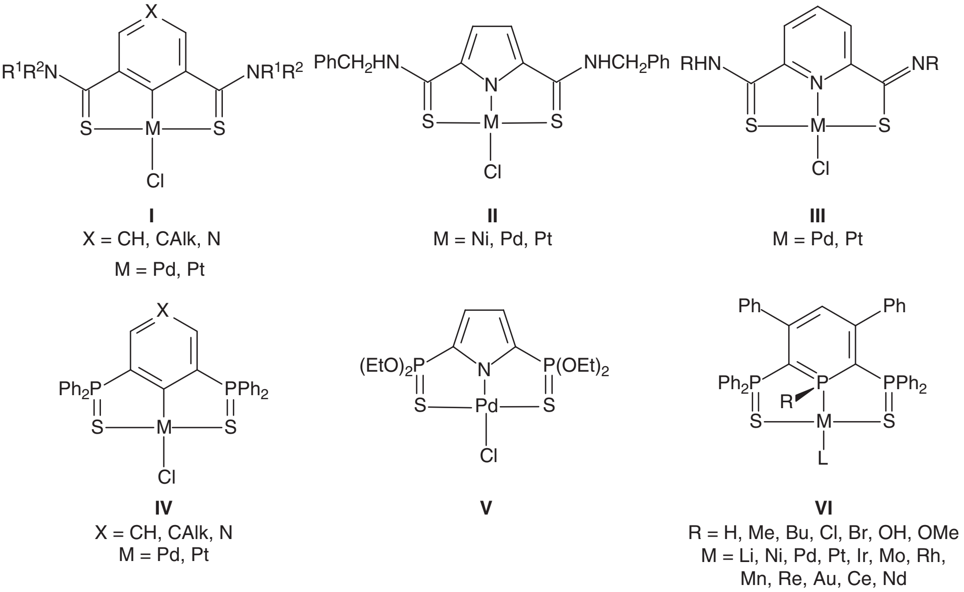
nonsymmetrical (or so-called hybrid) YEY′-pincer complexes can combine the properties of a few symmetrical systems while exhibiting unique reactivity and nontypical features compared with their symmetric analogues. Routes to desymmetrization comprise changes in donor moieties (introducing of different substituents at the same donor atoms or using different donor groups), variation of bridges (changing of their length and nature) the central core (shifting of the central aromatic core to give a CYY′ system, application of different aromatic rings and moieties bearing the C(sp^2) vinyl carbon atom). Such alterations allow the additional possibility of controlling the steric and electronic properties of the pincer system in total and hence catalytic activity or photoluminescence properties compared to their symmetric analogues.[2,3]

Furthermore, among pincer ligands, highly attractive are those bearing a sulfur atom as pendant arms. They include thioether, thioamide, and phosphine-sulfide derivatives and may form both anionic S-E-S$^-$ or dianionic S-E-S^{2-} ligands. Though the most studied among these species are metallacycles formed by the ligands bearing bis-thioether functions, the complexes with coordination via thioamide and phosphine sulfide moieties[4] with a benzene, pyridine, pyrrole, or indene core have been in focus only over the last decade but already have been found to possess high catalytic activity in cross-coupling reactions[5] and photoluminescent properties[6] (Scheme 1).



I
X = CH, CAlk, N
M = Pd, Pt

II
M = Ni, Pd, Pt

III
M = Pd, Pt

IV
X = CH, CAlk, N
M = Pd, Pt

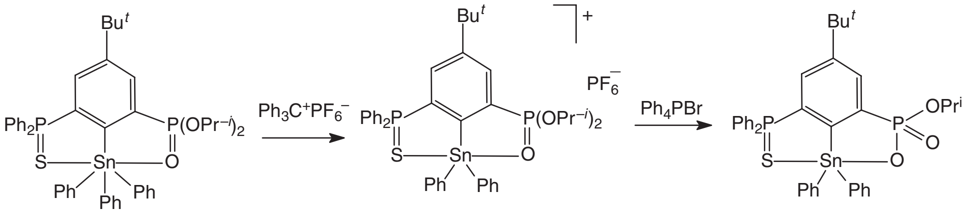
V

VI
R = H, Me, Bu, Cl, Br, OH, OMe
M = Li, Ni, Pd, Pt, Ir, Mo, Rh, Mn, Re, Au, Ce, Nd

Scheme 1 Representative complexes of thione sulfur–based pincer ligands with (hetero)aromatic core.

Nevertheless, before the beginning of our investigations the known representatives of hybrid systems bearing a thione sulfur atom were limited to neutral and cationic tin complexes formed by a SCO-pincer ligand containing the soft sulfur atom of the phosphine sulfide group along with the hard oxygen from P=O coordinating moiety (Scheme 2).[7]

In view of the aforesaid, it seems reasonable to develop the synthetic strategies to other types of hybrid SCE pincer ligands and investigate their ability to undergo cyclometallation as well as catalytic and luminescent properties. Focusing on this problem, we



Scheme 2 First example of tin SCO-pincer complexes.

have developed a few series of hybrid pincer-type ligands bearing thiophosphoryl, thiophosphoryloxy, and thiophosphorylamino groups in various combinations with thiophosphoryl-, thiocarbamoyl-, and imine- (including that of benzothiazole ring) donating functions and obtained the corresponding platinum and palladium pincer complexes. This minireview discusses the synthetic strategies used for the design of these ligands, features of their complexation with noble metals, as well as catalytic performance in the Suzuki reaction. The results have been partially published whereas some are communicated preliminary in this article. All experimental details, including synthetic procedures, spectroscopic characterization of the ligands and their pincer complexes, may be found in the corresponding cited full papers.

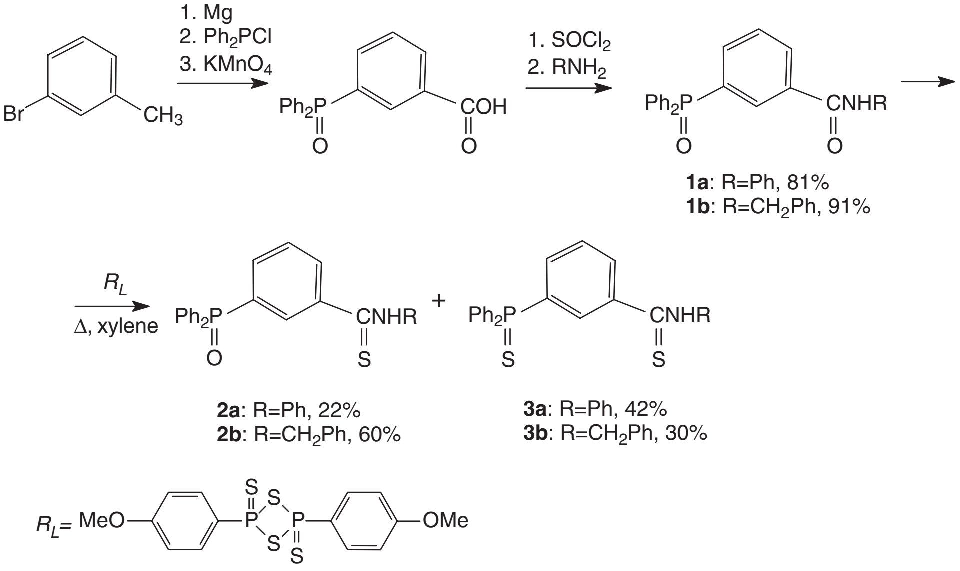
RESULTS AND DISCUSSION

The first elaborated SCE (E = S′) system[8] was designed as the formal combination of two symmetric SCS analogues, namely, isophthalic acid thioamides **I** and (bisthiophosphoryl)benzene **IV**. The multistep synthesis of the ligands, namely, 3-diphenylthiophosphorylbenzoic acid thioamides, started from commercially available 3-bromotoluene and was completed with thionation of the intermediate 3-diphenylphosphoryl benzamides using the Lawesson reagent (Scheme 3). The latter proceeded as a step-by-step process and provided the mixture of the corresponding thioamides **2a**,**b** and **3a**,**b** bearing diphenylphosphoryl and diphenylthiophosphoryl groups, respectively, which were separated by chromatography.

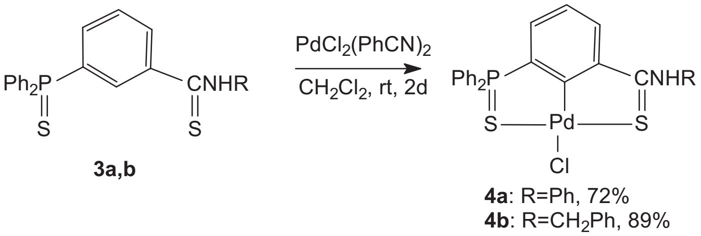
In contrast to both symmetric prototypes **I**, **IV**, their hybrid analogues **2a**,**b** readily underwent direct cyclopalladation at the C-2 position of the central benzene ring reacting with $PdCl_2(PhCN)_2$ in CH_2Cl_2 under ambient conditions to yield the corresponding pincer-type complexes **4a**,**b** with κ^3-SCS′ coordination (Scheme 4). It should be noted that the related O,S-thioamides **2a**,**b** did not react with $PdCl_2(PhCN)_2$, suggesting that double S,S-coordination was a crucial factor for cyclopalladation.[8]

Furthermore, we exploited the combination of phosphine sulfide and thiophosphoryloxy moieties as coordinating sites in the hybrid SCS′-pincer systems. The desired ligands **6a–d** were obtained via thiophosphorylation of 3-diphenylthiophosphorylphenol **5** as a single key precursor. Similar to compounds **2**, the direct cyclopalladation of the ligands **6a–d** easily proceeded at the C-2 position of the central benzene ring in a reaction with bis(benzonitrile)palladium dichloride and afforded the rare example of pincer complexes **7a–d**, containing fused 5- and 6-membered metallacycles with κ^3-SCS′-coordination (Scheme 5).[9]

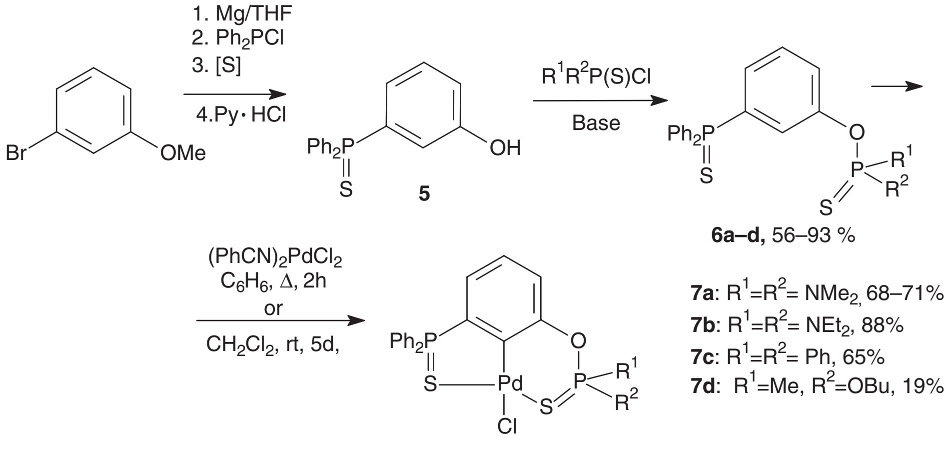
Unlike the 5,5-membered palladium complexes **I-V** having either two C=S or two P=S groups or the hybrid complexes **4a**,**b** bearing one P=S and one C=S group bound



Scheme 3 Synthesis of 3-diphenylthiophosphorylbenzoic acid thioamides.



Scheme 4 Synthesis of 5,5-membered hybrid κ^3-SCS′ palladium pincer complexes.



Scheme 5 Synthesis of 1-thiophosphoryloxy-3-thiophosphorylbenzenes and 5,6-membered palladacycles.

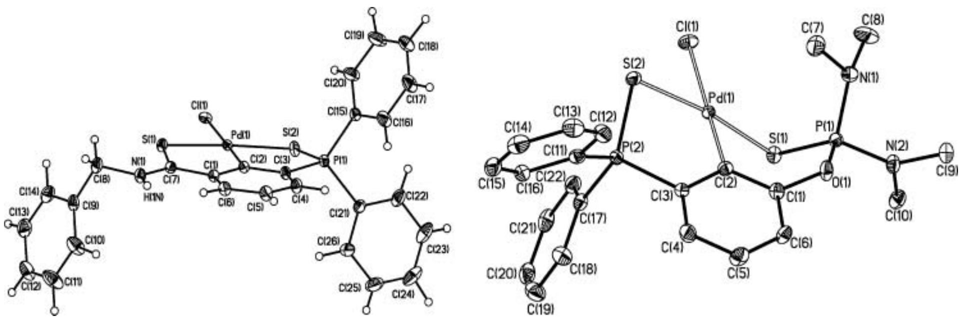
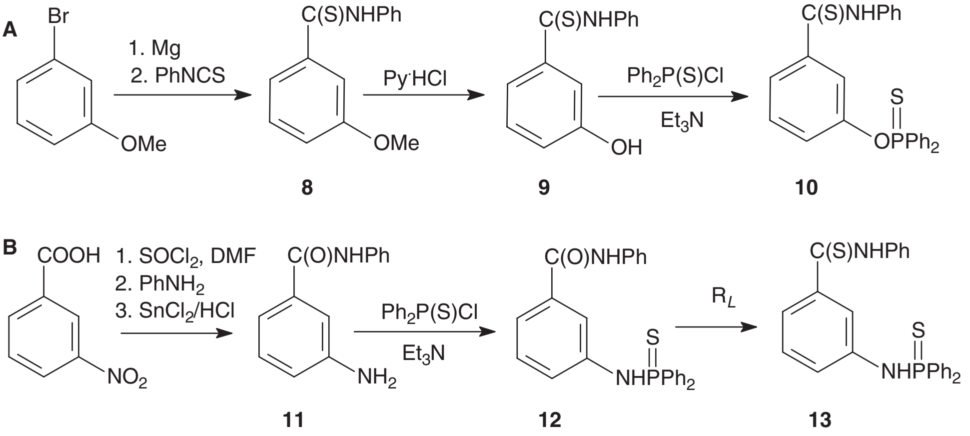


Figure 1 General view of hybrid 5,5-membered palladacycle **4b** (left) and 5,6-membered pincer Pd(II) complex **7c** (right) in representation of atoms via thermal ellipsoids (p = 50%).

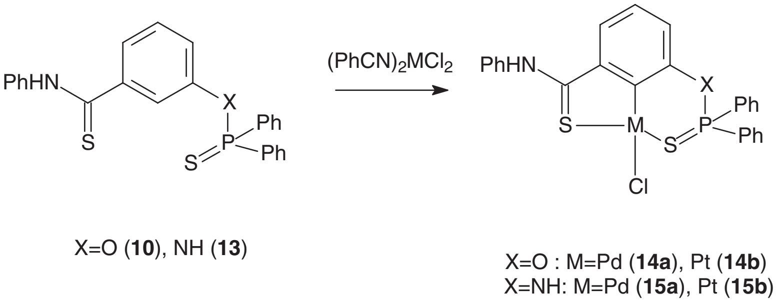
directly to the central phenyl ring, the P=S bonds in complexes **7** significantly deviate from the plane of the central core. The latter is reflected in significant puckering of both 5- and 6-membered metallacycles and further distortion of the palladium configuration. Figure 1 demonstrates the general structure of representative 5,5-membered and 5,6-membered palladacycles.

In continuation of this study, we combined thioamide functionality with thiophosphoryloxy (or thiophosphorylamino) coordinating moieties in the third type of hybrid SCS′-pincer systems, which should also provide distorted 5,6-membered pincer complexes. A convenient synthetic approach for the desired SCS′-pincer ligands was based on the thiophosphorylation of 3-hydroxy- or 3-aminobenzoic acid (thio)anilides as suitable precursors. In the case of thiocarbamoyl-thiophosphoryloxy-based pincer ligand **10**, the intermediate thioamido-phenol **9** was prepared by demethylation of 3-methoxybenzoic acid thioamide **8**, readily available via the reaction of the Grignard reagent of 3-bromoanisole with phenylisothiocyanate (Scheme 6A). The related ligand with an NH-bridge was synthesized by thiophosphorylation of 3-aminobenzamide **11** followed by transformation of the carbonyl group in the compound **12** into thiocarbonyl one by treatment with the Lawesson reagent (Scheme 6B).



Scheme 6 Synthesis of (A) thiocarbamoyl-thiophosphoryloxy- and (B) thiocarbamoyl-thiophosphorylamino-based pincer ligands **10** and **13**.

The reaction of both SCS′ ligands **10**,**13** with $(PhCN)_2PdCl_2$ also proceeded readily as the C2-cyclometallation of the central phenyl ring to afford the corresponding pincer palladium (II) complexes **14a**,**15a** with 5- and 6-membered fused metallacycles in good to high yields (79–95%, Scheme 7). Furthermore, applying more severe conditions (refluxing in acetonitrile or benzonitrile) we succeeded to perform direct cycloplatination of these ligands (Scheme 7).[10] Note that the related OCS ligand **12** bearing carbamoyl moiety did not undergo such direct cyclopalladation.

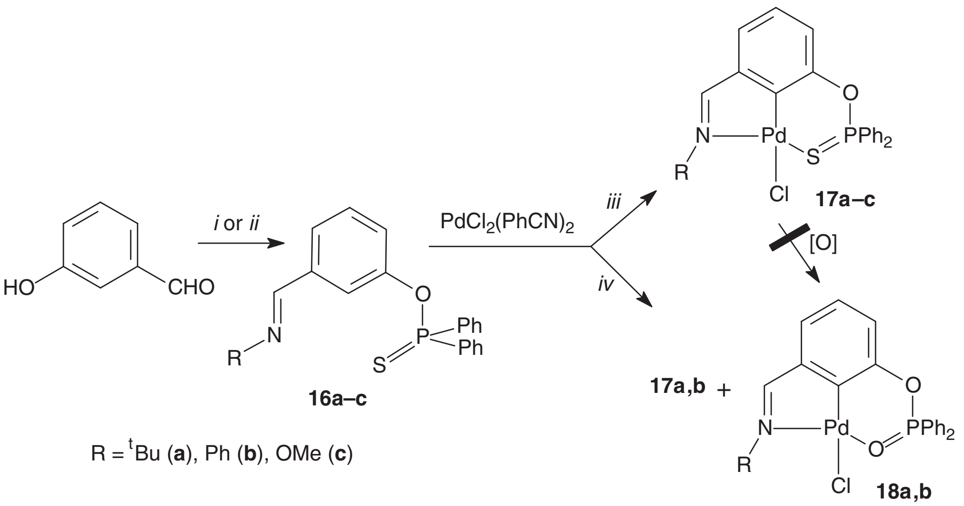


Scheme 7 Cyclometallation of thiophosphoryl-thiocarbamoyl pincer ligands **10**,**13**.

This successful study prompted us to develop a pincer system having fused 5- and 6-membered palladacycles that would contain a thiophosphoryloxy group along with a donor moiety of completely different nature. The imine functionality was a donating group of choice because azomethines represent one of the most popular types of ligands in organometallic and coordination chemistry.[11] The desired SCN pincer-type ligands **16a–c** were synthesized, starting from commercially available 3-hydroxybenzaldehyde, by two reciprocal routes differing in the sequence of thiophosphorylation and condensation with amino component depending on the nature of the latter (Scheme 8).[11] The typical cyclopalladation reaction with $PdCl_2(PhCN)_2$ proceeded readily in benzene or benzene–methanol solutions to afford the corresponding hybrid SCN-pincer complexes **17a–c** with 5- and 6-membered fused metallacycles in moderate to good yields. Performing the same reaction of ligands **16a**,**b** ($R = {}^tBu$, Ph) in dichloromethane followed by treatment with alcohol (either methanol or ethanol) resulted in unexpected formation of the related OCN palladacycles **18a**,**b** as minor products, along with the above SCN complexes **17a**,**b**.

Figure 2 illustrates the structure of SCN pincer complex **17b** and its NCO counterpartner **18b** (separated by chromatography) according to the X-ray diffraction analysis data. In general, the principal bond lengths in these complexes and the conformation of 5- and 6-membered palladacycles along with distortions of the coordinated palladium polyhedron are almost the same and independent from the coordination pattern. In other words, according to the X-ray data, the complex **18b** is almost isostructural to the related **17b**.

Complexes **18a**,**b** represent the products of formal oxidation of the P=S group in the starting ligand, which was suggested to proceed in the metal ion coordination sphere. However, the detailed mechanism of such an oxidation is still unclear. It should be emphasized that the complexes **18a**,**b** present only the second example of the noble metal pincer compounds bearing a coordinated phosphoryl group. The first one, an unsymmetrical platinum NCO-pincer complex, resulting from insertion of the terminal oxo-ligand into



Reaction conditions. i: $Ph_2P(S)Cl$, TEBA, 10%aq.$NaOH/C_6H_6$ then $RNH_2/MgSO_4$ (R=Ph,tBu)
ii: $MeONH_2 \cdot HCl/Na_2CO_3$ then $Ph_2P(S)Cl$, TEBA, 10%aq.$NaOH/C_6H_6$
iii: C_6H_6 or $C_6H_6/MeOH$; iv: $CH_2Cl_2/MeOH$

Scheme 8 Influence of the reaction conditions on the result of cyclopalladation of *meta*-(diphenylthiophosphoryloxy)benzaldimines.

the Pt—P bond of the Pt(IV) PCN-pincer complex containing the phosphine moiety, was recently reported by Milstein's group.[12]

Finally, we designed SCN ligands bearing thiophosphoryl, thiophosphoryloxy, or thiophosphorylamino pendant arms in combination with a heterocyclic imine function of benzothiazole ring. The latter may be either directly bonded with the central phenyl core or via an oxygen linker. Such variations of the SCN pincer ligand system allowed the creation of 5,5-membered or 5,6-membered fused metallacycles. Moreover, adjusting the linker nature, we could provide the corresponding 6-membered cycle with coordination of a metal both via the S-atom of P=S group or via the N-atom of the thiazole ring. The first ligand **19** of this series was obtained by the known oxidative cyclization[13] of secondary N-arylthioamides **2a** or **3a** with $K_3[Fe(CN)_6]$ similar to the transformation of 1,3-bis(secondary thioamide)benzene. Naturally, starting from compound **2a** an additional thionation step was required (Scheme 9). Both routes afforded the final compound in ca. 60% yield.

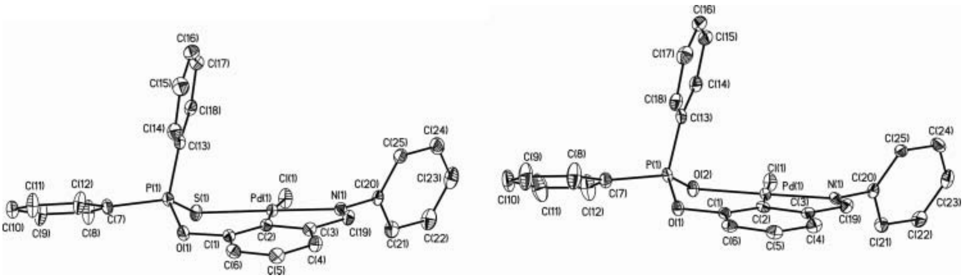
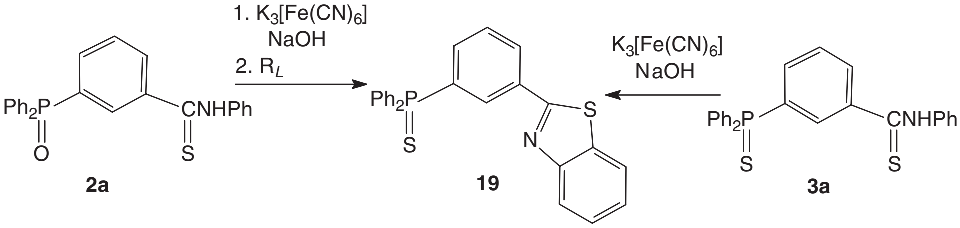
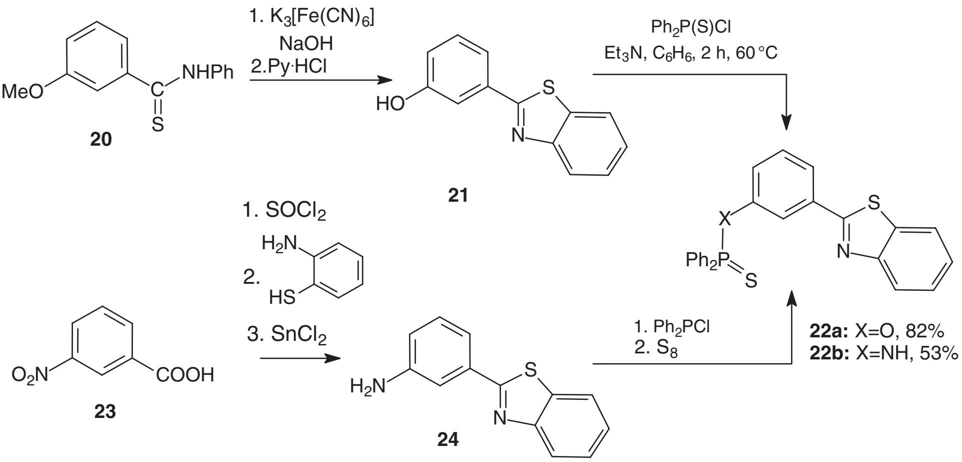


Figure 2 General view of hybrid 5,6-membered SCN **17b** (left) and OCN **18b** (right) palladacycles.



Scheme 9 Synthesis of 2-[3-(diphenylthiophosphoryl)phenyl]-1,3-benzothiazole **19**.

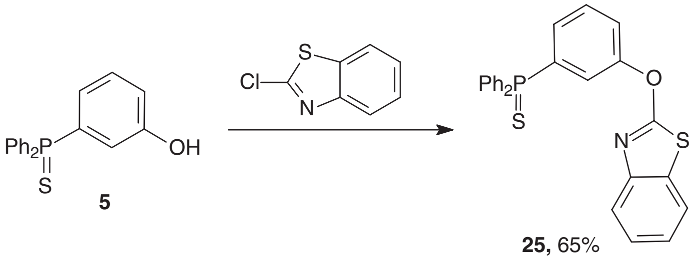
It seems reasonable to choose (thio)phosphorylation of *meta*-benzothiazole-substituted phenol or aniline as a suitable precursor for design of SCN ligands bearing thiophosphoryloxy or thiophosphorylamino groups, similar to the above-described synthesis of thiophosphoryl-thiocarbamoyl pincer ligands **10**,**13**. Hence, the oxidative cyclization of 3-methoxybenzothioamide **20** with $K_3[Fe(CN)_6]$ followed by demethylation afforded benzothiazole substituted phenol **21**, and one-pot condensation of 3-nitrobenzoic acid with aminothiophenol followed by reduction of nitro group with tin(II) chloride provided the corresponding heterocyclic amine **24**. Further (thio)phosphorylations under appropriate conditions depending on the substrate nature gave the final ligands **22a**,**b** in good yields (Scheme 10).



Scheme 10 Synthesis of thiophosphoryloxy- and thiophosphorylamino-based SCN pincer ligands **22a**,**b**-bearing benzothiazole moiety.

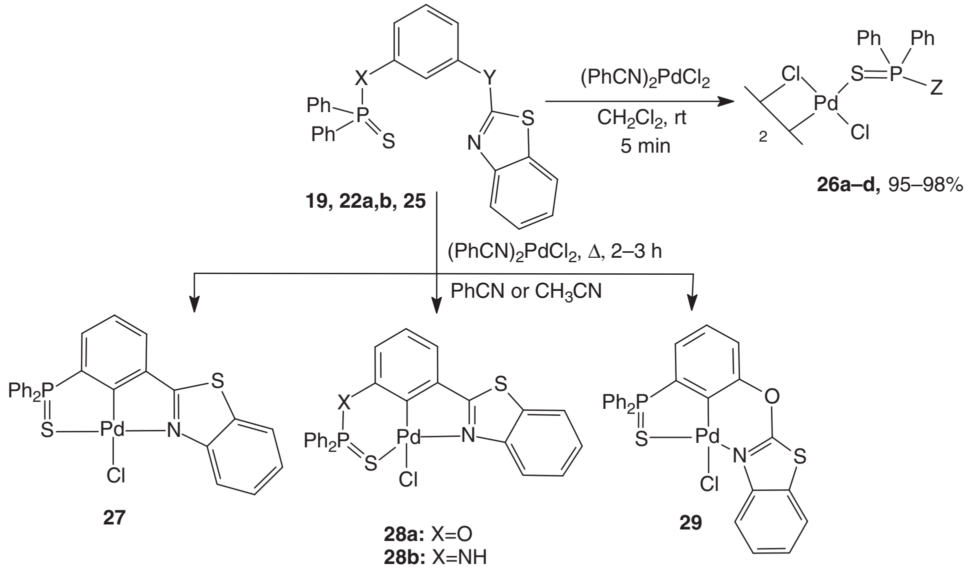
Finally, to introduce an oxygen bridge between the benzothiazole heterocycle and phenyl core (as in the ligand **25**), the reaction of sodium salt of thiophosphorylated phenol **5** with chlorobenzothiazole was used (Scheme 11).

The reaction of ligands **19**, **22a**,**b**, and **25** with $(PhCN)_2MCl_2$ (M = Pd, Pt) as a metal source in CH_2Cl_2 under ambient conditions leads to the μ-Cl bridged complexes **26a–d** with coordinated P=S group, which immediately precipitated from the above solutions. Meanwhile, performing the same reaction at heating in benzonitrile solutions (for more reactive ligand **22b** in acetonitrile) afforded the formation of the corresponding 5,5- and



Scheme 11 Synthesis of 2-[3-(diphenylthiophosphoryl)phenoxy]-1,3-benzothiazole **25**.

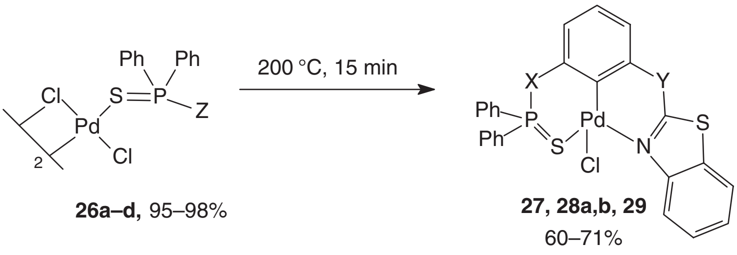
5,6-membered SCN pincer complexes in ca. 60–89% yield depending on the nature of a ligand (Scheme 12).



Scheme 12 Synthesis of of SCN pincer complexes **27–29**-bearing benzothiazole moieties.

A noteworthy observation is that μ-Cl bridged complexes **26a–d** transform into the corresponding pincer products **27–29** under the conditions of solid-phase synthesis, namely, upon heating at 200°C for ca. 15 min, presenting an alternative access for the synthesis of pincer complexes (Scheme 13).

Both 5,5- and 5,6-membered palladium pincer complexes under investigation were tested as (pre)catalysts for the Suzuki-Miyaura cross-coupling of aryl bromides and phenylboronic acid, which is one of the most popular and thoroughly investigated palladium catalyzed reactions. The main challenges in this cross-coupling pertain to the use of less reactive chloro- and bromoarenes bearing electron-donating groups and in these cases only a few pincer complexes displayed catalytic activity. The best results for coupling of chloroarenes were obtained with PCP pincer complexes with diaminophosphonite phosphorus atoms or with palladacycles modified by carbenes. That was related to the extra



Scheme 13 Solid-phase synthesis of SCN pincer complexes **27–29**-bearing benzothiazole moieties.

stability provided by these ligands toward the low-ligated catalytically active Pd(0) species involved in a catalytic cycle.[1a]

This study allowed the direct estimation of the influence of the desymmetrization nature on the catalytic properties. To draw the structure–activity relationship correctly, all experiments were performed under the same conditions: heating in dimethylformamide (DMF) at 120°C using K_3PO_4 as a base for 5 h, similar to the procedure suggested for testing of the best catalyst in this reaction among SCS pincer palladium complexes, that is the complex formed by 1,3-bis[(*tert*-butylthio)methyl]benzene.[14] The experiments were primarily performed in the presence of Bu_4NBr as an additive, a salt known to stabilize palladium nanoparticles.[15] In all cases the normal dependence on the electronic properties of the *para*-substituent X (X = C(O)CH_3, F, OCH_3, CH_3, Et_2N) at the aryl bromide was observed and the complete conversions were reached for activated substrate, that is, 4-bromoacetophenone, using very low catalyst loading (up to 0.01 mol%). Figure 3 outlines the results obtained for the representative reaction of less active 4-bromoanizole.

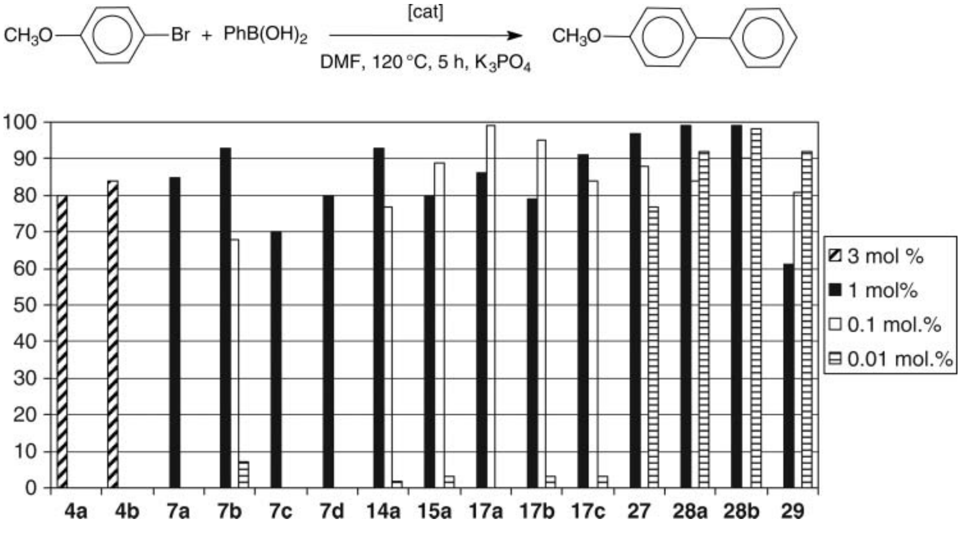


Figure 3 Catalytic activity of SCS′ and SCN pincer palladium complexes for the coupling of 4-bromoanizole and phenylboronic acid.

For this substrate, 5,5-membered SCS′ complexes **4a**,**b** did not provide the quantitative conversion even used in 3 mol%. Their bisphosphorus 5,6-membered SCS′ analogues **7a–d** possess the catalytic activity at the same level used in 1 mol%. Among these compounds the complex **7b** bearing diethylamino groups at the phosphorus atom of the 6-membered metallacycle was the most active. However, its activity decreased up to 68 and 7% as the catalyst loading was reduced to 0.1 and 0.01 mol%, respectively. The corresponding monopalladacycle species formed after the catalytic cycle also possessed catalytic activity in the above reaction but were slightly less active. Furthermore, their 5,6-membered SCS′ analogues with the thiocarbamoyl group instead of phosphine sulfide (compounds **14a**,**15a**), also decomposing over the catalytic process, as well as SCN complexes **17a–c** displayed the same level of activity used both in 0.1 and 0.01 mol%. Moreover, in some cases the activity at lower catalyst loading of 0.01 mol% was even higher than that when 0.1 mol% of a catalyst was used. Nevertheless, in these cases the yield drastically decreased when the catalyst loading was decreased up to 0.001 mol%. Interestingly, in the case of catalysts **4a**,**b**, **7a–d**, and **17a–c** the yields decreased by about 15% if the reaction was performed in the absence of Bu_4NBr, whereas this salt slightly inhibited the reaction with participation of **14a**,**15a**. For example, at the catalyst loading of 0.1 mol% the conversion increased from 77% up to 99% for **14a** and from 89% up to 99% for **15a**, respectively. The same tendency was observed for SCN palladium complexes **27–29** with a benzothiazole ring. In the absence of Bu_4NBr they provided a conversion greater than 90% when used in 0.01 mol% only. However, a further decreased of catalyst loading up to 0.001 mol% resulted in a conversion of a few percentages for this particular substrate. Furthermore, these palladium complexes **27–29** manifested catalytic activity for the Suzuki cross-coupling reaction of 4-chloroacetophenone with phenylboronic acid and complex **28b** provided 93% conversion used in the amount 0.1 mol%.

Monitoring of the reaction mixtures by ^{31}P spectra revealed that the complexes **4a**,**b** remained unchanged after the cross-coupling reaction, excluding the possible changing of the Cl anion for the bromine one in the presence of Bu_4NBr being the component of reaction mixture. On the other hand, other pincer palladium complexes, which are stable in DMF solution under ambient conditions for at least 40 days, underwent decomposition of the initial palladacycles after catalytic reaction, proceeding in different ways depending on the nature of the substituents in the ligand. Therefore, they apparently serve as a reservoir, providing the catalytic cycle with highly catalytically active Pd^0 particles and at high level of catalyst loading these particles may stick together while the activity passes the maximum at 0.1–0.01 mol% loading and later on dramatically decreases.

In general, SCS′ and SCN complexes derived from thiophosphoryl compounds provided the highest catalytic activity in the Suzuki-Miyaura cross-coupling among all tested SCS pincer complexes. The higher catalytic efficiency of 5,6-membered SCS′ and SCN complexes may be attributed to their hemilabile properties, because they contain rather weakly bonded thiophosphoryloxy or thiophosphorylamino groups that may facilitate substrate interaction with the metal center. Regardless of whether hybrid complexes are real catalysts or precatalysts, the general tendency is absolutely clear: the higher asymmetry for a pincer palladium complex with at least one P=S coordinating group may serve as a factor of its higher catalytic activity in the Suzuki-Miyaura cross-coupling.

CONCLUSION

To summarize the results presented, we developed synthetic approaches to a few novel families of organothiophosphorus pincer ligands that undergo direct cyclometallation to afford hybrid SCS′ and NCS palladium pincer complexes having fused 5,5- or 5,6-membered metallacycles. In the course of the study the unexpected oxidation of the thiophosphoryl group in the palladium ion coordination sphere providing the corresponding NCO pincer complexes with coordination via the oxygen atom of the phosphoryl group as well as unusual solid-phase transformation of μ-Cl-bridged complexes to the pincer ones were revealed. In view of the easy synthetic routes, easy handling, and high catalytic activity of the complexes obtained, further development of this area seems to be of interest.

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