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Synthesis of *N*,*P*-, *S*,*P*-, *P*,*P*- and *S*,*P*,*S*-ligands using reactions of cyclopalladated complexes with $KPPh_2$

Nicholas J. Korte, Valeria A. Stepanova, Irina P. Smoliakova*

Chemistry Department, University of North Dakota, 151 Cornell Street, Stop 9024, Grand Forks, ND 58202-9024, USA

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ABSTRACT

Readily available air- and moisture-stable dimeric chloro-bridged *CN*-, *CS*- and *CP*-cyclopalladated complexes with the (sp^2)C–Pd bond react with 4.5 equiv. of $KPPh_2$ in THF to give the corresponding *P*,*N*-, *P*,*S*- and *P*,*P*-bidentate ligands in 35–63% yield. The phosphination method is applicable to five- and six-membered palladacycles derived from (*S*)-*N*,*N*-dimethyl-1-phenylethylamine, (*S*)-4-*tert*-butyl-2-phenyl-2-oxazoline, benzyl methyl sulfide, benzyldiphenylphosphine, 2-benzylpyridine and *N*,*N*-dimethylbiphenyl-2-amine. The reaction of 1.2 equiv. of $KPPh_2$ with the *SCS*-pincer cyclopalladated complex obtained from 1,3-bis(methylthiomethyl)benzene provided the corresponding *S*,*P*,*S*-tridentate ligand in 49% yield.

1. Introduction

Phosphines having an additional donor functionality in their structure, e.g., the amino, imino, or alkylthio group, are common synthetic targets due to high demand for such compounds in catalysis [1–3]. For example, aminophosphines, phosphino-oxazolines, diphosphines, phosphinosulfides and related *N*,*P*-, *P*,*P*- and *P*,*S*-bidentate ligands are common achiral and enantiopure catalysts in a number of important metal-catalyzed transformations including additions to C=C and C=O groups [4], C–C bond formation reactions (e.g., Heck [5] and Suzuki [6] couplings), rearrangements [7] and cyclizations [8]. As a rule, the key step in preparation of such bidentate ligands is the introduction of the phosphino group. Besides metal-catalyzed reactions for creation of a C–P bond [9] there are several general non-catalytic methods for introduction of the PR_2 moiety [1]. For example, the S_N2 reaction of metal phosphides with alkyl halides can be used to prepare phosphines with the (sp^3)C–P bond [10]. When the phosphino group is to be attached to the (sp^2)C atom (e.g., to obtain Ar–PR_2), the most common method used is lithiation of the aryl fragment (either Ar–H or Ar–Hal) followed by treatment with a chlorophosphine, $ClPR_2$ [11]. The use of organomagnesium reagents instead of organolithium intermediates has also been reported [12,13]. In certain cases, $KPPh_2$ can replace F or OTf via nucleophilic aromatic substitution [14–16].

Another possible approach to the synthesis of aminophosphines and related bidentate ligands is the use of air- and moisture-stable cyclopalladated complexes (CPCs) instead of organolithium or other unstable organometallic derivatives. The Sokolov group reported that in the presence of PPh_3, the CPC derived from *N*,*N*-dimethylaminomethylferrocene reacted with lithium phosphides, $LiPR^1R^2$, to yield the corresponding aminophosphines [17]. The Bolm group described the preparation of a planar-chiral phosphino-oxazoline by reacting a paracyclophane-derived mononuclear CPC with $KPPh_2$ [18]. Recently, we investigated the reactions of the dimeric chloro-bridged cyclopalladated complex (CPC) of *N*,*N*-dimethylbenzylamine (**1**) with $LiPPh_2$ [19] and $KPPh_2$ [20] leading to the corresponding aminophosphine (**2**). It was shown that the reactions with $LiPPh_2$ are capricious, and their outcome is affected by many factors, especially the source and age of the phosphide as well as the reagent ratio. Depending on the conditions used in the reactions, different compounds were isolated including the target aminophosphine **2** (Scheme 1). The phosphination of the dimeric CPC **1** with 4.50 equiv. of $KPPh_2$ (the 1:2.25 ratio of Pd:PPh_2) in THF at rt was found to be more consistent and provided the desired compound **2** in 58% yield. Contrary to $LiPPh_2$, commercial samples of $KPPh_2$ and the reagent prepared in our lab from K and $ClPPh_2$, provided the same results. Here we

* Corresponding author. Tel.: +1 701 777 3942; fax: +1 701 777 2331.
E-mail addresses: ismoliakova@chem.und.edu, irina.smoliakova@und.edu (I.P. Smoliakova).

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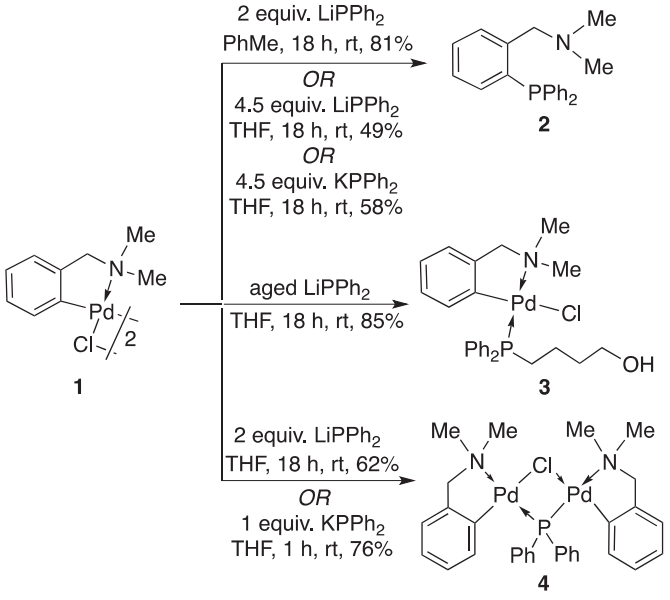


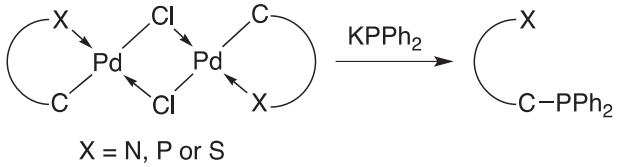
Scheme 1. Reactions of metal phosphides with CPC **1** [19,20].

report the synthesis of aminophosphines, iminophosphines, diphosphines, sulfidophosphines and related compounds using reactions of $KPPh_2$ with known chloro-bridged dimeric *CN*-, *CP*- and *CS*-CPCs containing either a five- or six-membered palladacycle (Scheme 2).

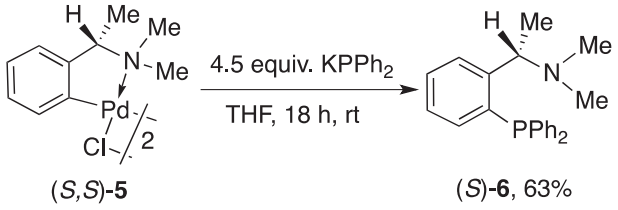
2. Results and discussion

First, the closest analog of CPC **1**, complex (*S*,*S*)-**5**, was used in the reaction with a 0.5 M solution of $KPPh_2$ in THF. The reaction provided aminophosphine (*S*)-**6** in 63% (Scheme 3). Interestingly, in the reaction with a higher concentration of the complex, 10 mg/mL instead of 5 mg/mL, the aminophosphine yield dropped to 24%. A 1 M solution of $LiPPh_2$ (synthesized from $ClPPh_2$ and Li [21]) was also tested in reactions with CPC (*S*,*S*)-**5**. The best yield of (*S*)-**6** was 46% (the Pd:PPh_2 ratio of 1:2.25, THF, rt, 18 h). For comparison, aminophosphine (*S*)-**6** (or its salt with HCl [22]) was prepared from (*S*)-*N*,*N*-dimethyl-1-phenylethylamine via lithiation with *n*-BuLi followed by treatment with Ph_2PCl in 35 [23] and 60% [22] yield.

Enantiopure phosphino-oxazolines are common ligands in various metal-catalyzed asymmetric transformations [3,24]. Practically all known methods for introduction of the PPh_2 group have been used for synthesis of these compounds [11–15,18,25–27]. The yields of phosphination products usually range from 30 to 50%; notable exceptions are the reactions of $KPPh_2$ with 2-(2-fluorophenyl)-2-oxazolines and the corresponding triflates, in which the reported yields were above 76% [13,14]. To learn whether phosphino-oxazolines can be obtained by reacting chloro-bridged CPCs with metal phosphides without PPh_3 [18], dimer (*S*,*S*)-**7** was reacted with $KPPh_2$ under the conditions used for complex **5**



Scheme 2. Preparation of *N*,*P*-, *P*,*P*- and *S*,*P*-bidentate ligands by reacting dimeric μ-Cl-CPCs with $KPPh_2$.



Scheme 3. Preparation of aminophosphine **6**.

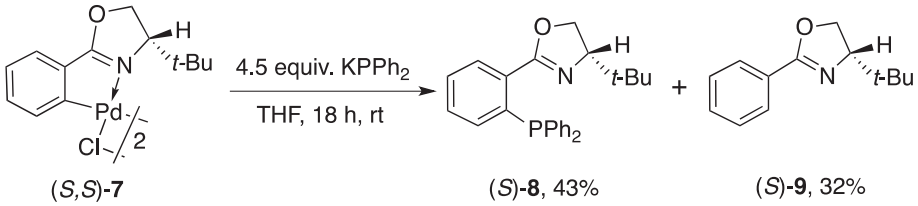
(Scheme 4). The major product was phosphino-oxazoline (*S*)-**8**, which was isolated in 43% after chromatography. Surprisingly, in this reaction a significant amount, 32%, of oxazoline (*S*)-**9** was isolated. Analogous protonated ligands were also detected in some other reactions of CPCs with $KPPh_2$ (*vide infra*). Noteworthy that the formation of similar products, Ar–H, was reported in the Pd-catalyzed phosphination reactions of aryl triflates, Ar–OTf, with PPh_3 [28]. One can suggest that the C–H coupling can occur as a result of the following events: (i) adventitious cleavage of the C–O bond in THF by $KPPh_2$, (ii) coordination of the resulting alkoxide to the Pd(II) center, (iii) β-hydride elimination of the resulting Pd(II) alkoxide to form a Pd(II) aryl hydride and (iv) subsequent C–H coupling of this intermediate.

The studied phosphination method can also be applied to *CS*-palladacycles. The *S*-containing CPC **10** reacted with 4.5 equiv. of $KPPh_2$ in THF to give 51% yield of sulfidophosphine **11** (Scheme 5), which was rather quickly oxidized to the corresponding phosphine oxide **11a**. The only preparation method described for this compound is based on the consecutive treatment of 2-bromobenzyl methyl sulfide with *n*-BuLi and $ClPPh_2$; the reported yield of **11** was 40% [29].

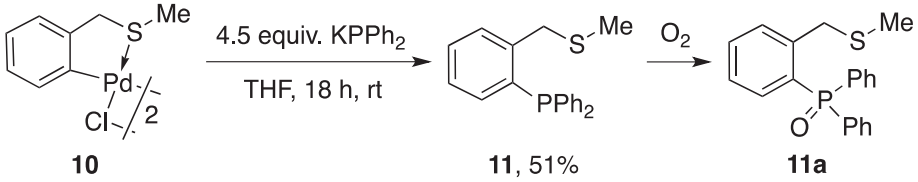
Besides *CN*- and *CS*-palladacycles, the dimeric *CP*-complex **12** derived from benzyldiphenylphosphine was also used. Initial experiments showed that the target diphosphine **13** was produced in the reaction, but it was quickly oxidized to the corresponding dioxide **14** and two monoxides. To avoid separation of too many products, air was bubbled into the mixture in the end of the reaction. Three compounds were isolated after preparative TLC: dioxide **14** in 35%, phosphine oxide **15** (12%) and the mononuclear complex **16** in 13% (Scheme 6). Oxide **15** must be formed via the same pathway as compound **9**. As for complex **16**, the formation of its analog was reported in some reactions of complex **1** with $LiPPh_2$ [19]. Apparently, this complex is formed as a result of a P–P coupling of PPh_2-containing intermediates as proposed in our previous papers [19,20]. Varying the reaction time and reagent ratio led to a decreased yield of the target diphosphine oxide **14**. Increasing the reaction temperature from 20 to 40 °C resulted in the formation of only traces of dioxide **14** and 22% yield of **15** along with 9% of complex **16**.

^{31}P NMR spectroscopy was a very convenient method to confirm the proposed structures **14**–**16**. The spectrum of diphosphine oxide **14** exhibited two doublets at 35.2 and 8.9 ppm and $^4J_{PP} = 6.4$ Hz, while the spectrum of the side product **15** had only one singlet (δ 14.6 ppm) in the region typical for phosphine oxides. Complex **16** provided the spectrum containing three doublets of doublets (δ 49.4, 31.4 and −7.2 ppm). Two signals out of three had a large J_{PP} constant, 449 Hz, suggesting that two different P atoms are connected to each other. The third signal at 31.4 ppm lacked this large constant and was assigned to the metallacycle's P atom. For comparison, the ^{31}P NMR spectrum of the starting chloro-bridged binuclear complex **12** had two signals at 41.40 and 41.43 ppm [30].

To determine if six-membered metallacycles can be used for the phosphination, CPC **17** was selected to react with $KPPh_2$ in THF. The



Scheme 4. Reaction of the oxazoline-derived complex **7** with $KPPh_2$.



Scheme 5. Preparation of the *S*,*P*-bidentate ligand **11** from CPC **10**.

expected *N*,*P*-ligand **18** was isolated in 47% yield (Scheme 7). To the best of our knowledge, this compound has never been reported. It is noteworthy that its closest analog 2-[2-(diphenylphosphino) phenyl]pyridine was recently synthesized in 63% yield via the aromatic nucleophilic substitution reaction of 2-(2-fluorophenyl) pyridine with $KPPh_2$ [31].

Another six-membered palladacycle, **19**, was also subjected to the reaction with $KPPh_2$ (Scheme 8). Aminophosphine **20** was prepared in 47%. In this reaction, 45% of *N*,*N*-dimethyl-2-phenylaniline (**21**) was isolated as well. It is noteworthy that the only reported method for obtaining aminophosphine **20** is a four-step transformation (in the overall 44% yield) with the key step being the Suzuki coupling between (2-bromophenyl)diphenylphosphine oxide and *B*-[2-(dimethylamino)phenyl]boronic acid [32].

It was of interest to test whether pincer complexes can be used in reactions with $KPPh_2$ to produce tridentate ligands, e.g., the never reported *S*,*P*,*S*-derivative **23**. Complex **22** reacted with 2.25 equiv. of $KPPh_2$ (the Pd:PPh_2 ratio of 1:2.25 as in the reactions with the dimeric complexes described above) in THF to yield 19% of *S*,*P*,*S*-ligand **23** and 45% of disulfide **24** (Scheme 9). When the Pd:PPh_2 ratio was changed to 1:1.2, the yields of two isolated products **23** and **24** were practically unchanged: 22 and 44%, respectively. In our previous paper on the reactions of CPC **1** with $LiPPh_2$ [19], we reported a possibility of using a non-coordinating solvent toluene instead of THF. While the use of the non-coordinated solvent did not improve the yield in the reactions with complexes **5**, **7**, **10** and **12**, the yield of *S*,*P*,*S*-ligand **23** was higher in toluene. Moreover, this reaction was sensitive to the concentration of the complex. When the CPC concentration was decreased from the standard 5 mg/mL to 3 mg/mL, the yield of **23** in THF increased from 42% to 49%. In an attempt to further improve the yield, the reaction temperature was increased to 50 °C. As in the case of the reaction with complex **12**, the temperature increase resulted in lowering the yield of **23** to 20% (38% of **22** was isolated as well). Carrying out the phosphination of **22** at 0 °C also provided a lower yield of **23**, 12% (in addition to 24% yield of **24**).

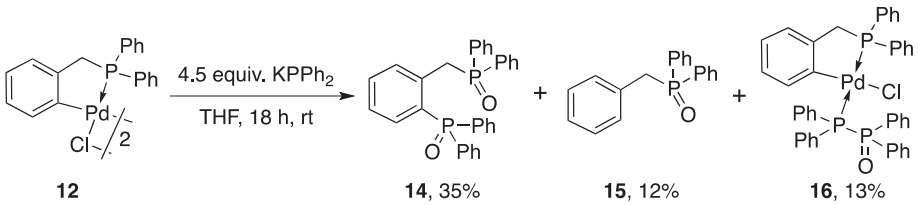
3. Conclusion

We have shown that structurally different μ-Cl-CPCs with five- and six-membered palladacycles containing an N, S or P donor heteroatom can be successfully converted to the corresponding aminophosphines, phosphino-oxazolines, phosphinosulfides, diphosphines and related phosphines containing another donor functionality. This method is complimentary to other known methods of phosphination. The yields of the isolated products are comparable with those reported for the most common method of the (sp^2)C–P bond formation via ortho-lithiation of benzylamines and related substrates possessing ligand properties followed by treatment with a chlorophosphine, $ClPR_2$ [1]. The use of pincer CPCs and complexes with six-membered palladacycles allows preparation of new bi- and tridentate ligands, which are difficult to obtain using other methods. Compared to the lithiated intermediates, air- and moisture-stable CPCs can be prepared in advance and in high yield. Currently, we are studying the possibility of asymmetric phosphination of CPCs using prochiral phosphides as well as the (sp^3)C–P bond formation using reactions of $KPPh_2$ with CPCs having the (sp^3)C–Pd bond.

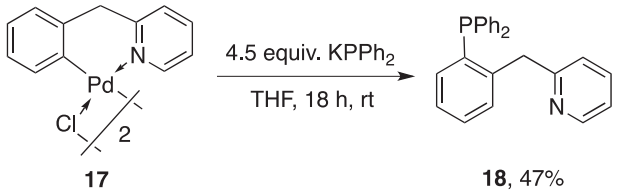
4. Experimental

4.1. General methods and materials

All reactions with either $KPPh_2$ or $LiPPh_2$ were carried out under a positive pressure of Ar using Schlenk techniques. Column chromatography was performed by using Natland silica gel 60 (230–400 mesh). Preparative thin-layer chromatography (TLC) was



Scheme 6. Reaction of *C*,*P*-CPC **12** with $KPPh_2$.



17 **18**, 47%

Scheme 7. Preparation of *P,N*-ligand **18** from the six-membered CPC **17**.

carried out on 200 × 250 mm glass plates with an unfixed layer of Natland silica gel 60 (230–400 mesh) that was premixed with ca. 10% of Sigma–Aldrich TLC standard grade silica gel with a fluorescent indicator. Analytical TLC was performed on Merck silica gel 60 (F_{254}) 250 μm pre-coated aluminum plates. Compounds were visualized on TLC plates using UV light (254 nm) and/or iodine stain. Routine ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (126 MHz), and $^{31}P\{^{1}H\}$ (202 MHz) as well as DEPT, COSY, and HETCOR/HMQC NMR spectra were recorded on a Bruker AVANCE 500 NMR spectrometer. Chemical shifts are reported in ppm with $SiMe_4$ as an internal standard (^{1}H and ^{13}C) or $P(OEt)_3$ as an external standard (^{31}P). Spin–spin coupling constants are given in Hz. Spectra of products obtained in the reactions of CPCs with either $LiPPh_2$ or $KPPh_2$ were recorded in $CDCl_3$ unless stated otherwise. Benzene and toluene were dried by refluxing over K/benzophenone ketyl, distilled under N_2, and kept over potassium. THF was first distilled over CaH_2, then over K/benzophenone under Ar right before the reaction. Hexane and dichloromethane were distilled over CaH_2. Acetone was distilled over $KMnO_4$ before use. The 0.5 M solution of $KPPh_2$ in THF was purchased from Sigma–Aldrich. Preligands (*S*)-*N*,*N*-dimethyl-1-phenylethylamine, benzyl methyl sulfide, benzyldiphenylphosphine, 2-phenylaniline and 2-benzylpyridine were purchased from Sigma–Aldrich and used as received.

4.2. Synthesis of the starting compounds

4.2.1. $LiPPh_2$ [21]

Lithium pieces (37.9 mg, 0.00546 mol) were placed into an Ar-filled Schlenk flask, then 5.4 mL of freshly distilled THF were added, and finally $ClPPh_2$ (0.5 mL, 0.003 mol) was introduced dropwise for 12 min. The reaction mixture was stirred for 21 h. The reaction mixture changed in appearance from colorless to dark red. The NMR sample was prepared under air-free conditions using 10 μL of d_8-THF and 0.25 mL of the $LiPPh_2$ reaction mixture. $^{31}P\{^{1}H\}$ NMR (d_8-THF, δ, ppm): −30.6 (broad), −31.3 (sharp), and −35.4 (broad).

4.3. Preligand preparation

4.3.1. 2-tert-Butyl-4,4-dimethyl-2-oxazoline (**25**)

The oxazoline was prepared using the reported procedure [33,34] in 64% yield. Spectral data of the synthesized product were identical to those reported previously [34].

4.3.2. (S)-4-tert-Butyl-2-phenyl-2-oxazoline (**9**)

The oxazoline was prepared in 70% yield by refluxing benzonitrile and (*S*)-*tert*-leucinol in abs. chlorobenzene for 40 h in a Schlenk flask that contained sublimed $ZnCl_2$ as described for other oxazolines [14]. R_f 0.63 (1:3 ether–hexane). Spectral data of the synthesized product were identical to those reported previo usly [35].

4.3.3. N,N-Dimethylbiphenyl-2-amine (**21**)

The compound was prepared using the reported procedure for the methylation of similar aromatic amines [36] in 47% yield. R_f 0.35 (hexane). Spectral data of the synthesized product were identical to those reported previously [37].

4.3.4. 1,3-Bis(methylthiomethyl)benzene (**24**)

The compound was obtained from 1,3-bis(bromomethyl)benzene and MeSNa using the procedure described by Dupont et al. [38] in 92% yield. R_f 0.48 (benzene). ^{1}H NMR (δ, ppm): 2.00 (s, 6H, 2 CH_3), 3.67 (s, 4H, 2 CH_2), 7.23 (m, 4H, H arom.). $^{13}C\{^{1}H\}$ NMR (δ, ppm): 15.0 (2 CH_3), 38.3 (2 SCH_2), 127.5 (C(4) and C(6) arom.), 128.6 (C(5) arom.), 129.3 (C(2) arom.), 138.5 (C(1) and C(3) arom.).

4.4. Preparation of cyclopalladated complexes

4.4.1. (S,S)-Di-μ-chlorobis-{2-[1-(N,N-dimethylamino)ethyl] phenyl-C,N}dipalladium(II) [(S,S)-5]

Complex **5** was synthesized from (*S*)-*N*,*N*-dimethyl-1-phenylethylamine as a yellow powder using a known procedure [39] with a yield of 97%. R_f 0.83 (5:1 benzene–acetone); m.p. 193–196 °C (dec.) [lit. m.p. [39] 195–200 °C (dec.)]. The ^{1}H NMR data for the synthesized compound matched those reported in the literature [39].

4.4.2. (S,S)-Di-μ-chlorobis-{2-[2-(4-tert-butyl)oxazolin-2-yl] phenyl-C,N}dipalladium(II) [(S,S)-9]

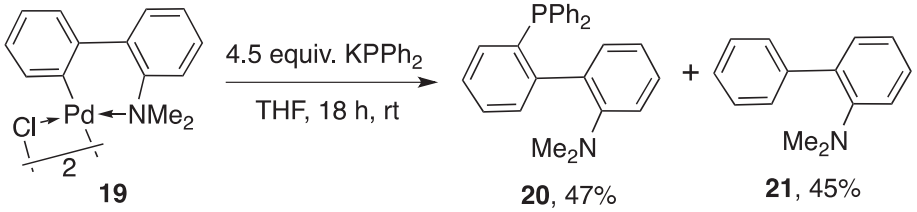
The compound was prepared from 2-*tert*-butyl-4,4-dimethyl-2-oxazoline (**25**) as a pale yellow powder in 69% yield using the reported procedure [35]. R_f 0.47 (1:1 CH_2Cl_2–hexane); m.p. 210–211 °C (dec.) [lit. m.p. [35] 212–212.5 °C (dec.)]. The ^{1}H NMR data for the synthesized complex matched those reported in the literature [35].

4.4.3. Di-μ-chlorobis-[2-(methylthiomethyl)phenyl-C,S] dipalladium(II) (**10**)

The complex was prepared using a modified reported procedure [40]. The precipitate formed during the reaction was placed on a fritted glass filter and washed with acetone (30 mL), then CH_2Cl_2 (25 mL). The filtrate containing the complex was evaporated and the formed yellow solid was recrystallized from CH_2Cl_2 and hexane. Yield 0.2718 g (90%). R_f 0.42 (10:1 benzene–acetone); m.p. 185–186 °C (dec.). The ^{1}H NMR data for the synthesized complex **112** matched those reported in the literature [40].

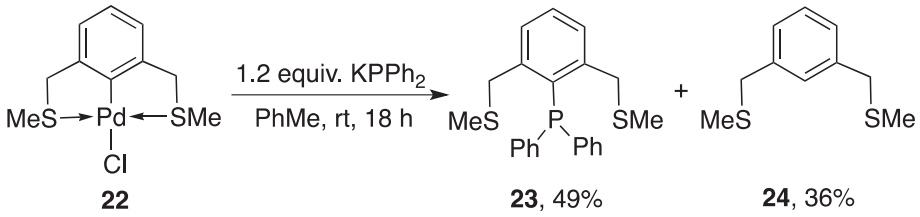
4.4.4. Di-μ-chlorobis-{2-[(diphenylphosphino)methyl]phenyl-C,P} dipalladium(II) (**12**)

The complex was obtained from benzyldiphenylphosphine in 54% yield by using a reported procedure [41]. M.p. 196–199 °C



19 **20**, 47% **21**, 45%

Scheme 8. Synthesis of aminophosphine **20** from CPC **19**.



Scheme 9. Preparation of the *S,P,S*-tridentate ligand **23** from the pincer complex **22**.

(dec.) [lit. [42] 198 °C (dec.)]. The ^{1}H and ^{31}P{^{1}H} NMR data for the synthesized complex were consistent with the literature data [30].

4.4.5. Di-μ-chlorobis-[2-(pyridin-2-ylmethyl)phenyl-C,N] dipalladium(II) (**17**)

Complex **17** was synthesized using a slightly modified reported procedure [43]. In a round-bottomed flask equipped with a stir bar, 2-benzylpyridine (0.0610 g, 0.361 mmol) and $Pd(OAc)_2$ (0.0810 g, 0.361 mmol) were added along with glacial acetic acid (5 mL); the reaction mixture was allowed to stir at rt for 18 h. The solvent was removed on a rotary evaporator. To the beige solid residue LiCl (0.0381 g, 0.899 mmol) was added along with acetone (10 mL), and the reaction was allowed to stir at rt for 18 h. The color of the reaction mixture changed from pink/orange to white. The suspension formed was then transferred onto a fine glass fritted filter and rinsed with acetone (20 mL) and distilled water (10 mL) to remove excess LiCl and residual acetic acid. Yield 0.0833 g (75%); m.p. 249–252 °C (dec.) [lit. [43] 248 °C (dec.)].

4.4.6. Di-μ-chlorobis-[2′-(2-N,N-dimethylamino)biphenyl-C,N] dipalladium(II) (**19**)

Complex **19** was synthesized using the reported procedure [44] in 75% yield as a white powder. R_f 0.63 (1:1 benzene–acetone); m.p. 169–170 °C (dec.). The ^{1}H NMR data for the synthesized complex matched those reported in the literature [44].

4.4.7. [2,6-Bis(methylthiomethyl)phenyl-S,C,S]palladium(II) chloride (**22**)

Disulfide **24** (61.8 mg, 0.312 mmol) and CPC **1**(86.2 mg, 0.156 mmol) were transferred to a 10-mL flask. Benzene (3 mL) and glacial acetic acid (3 mL) were added and the reaction mixture was refluxed for 4 h. After the solvent was removed on a rotary evaporator, the crude product was purified using preparative TLC (silica gel, 7:3 benzene–acetone). Complex **22** was isolated as a pale yellow solid in 94% yield (99.4 mg). R_f 0.53 (7:3 benzene–acetone); m.p. 194–196 °C (dec.). Spectroscopic data for the complex were identical to the literature data [38].

4.5. Reactions of cyclopalladated complexes with metal diphenylphosphides

4.5.1. (S)-ortho-(Diphenylphosphino)-α-methyl-N,N-dimethylbenzylamine [(S)-6]

4.5.1.1. Method 1 using $LiPPh_2$. Complex (*S,S*)-**5** (29.6 mg, 0.0510 mmol) was transferred into an Ar-filled 10-mL Schlenk flask. The flask was placed under vacuum, then filled with Ar followed by the addition of THF (3.0 mL) using a syringe. Then a 0.5 M solution of $LiPPh_2$ in THF (0.46 mL, 0.23 mmol) was introduced dropwise for 5 min. The mixture appeared yellow, dark red, and finally dark yellow. The reaction mixture was stirred under Ar for 18 h at rt. After the solvent was removed on a rotary evaporator, the crude mixture was dissolved in CH_2Cl_2 (0.5 mL) and the concentrated mixture was placed on a preparative TLC (silica gel, 10:1 benzene–acetone). Compound (*S*)-**6** was isolated as a light yellow liquid in 46% yield (15.6 mg).

4.5.1.2. Method 2 using $KPPh_2$. The same procedure was used as in Method 1 except that a 0.5 M solution of $KPPh_2$ in THF was used in lieu of the $LiPPh_2$ solution. Starting with 24.6 mg of complex (*S,S*)-**5**, compound (*S*)-**6** was obtained in 63% yield (17.5 mg). R_f 0.46 (3:1 benzene–acetone); $[\alpha]_D^{21}$ −77° (*c* 0.0057, CH_2Cl_2) [lit. [45] $[\alpha]_D^{25}$ −53.7° (*c* 0.004, CH_2Cl_2)]. ^{1}H NMR (δ, ppm): 1.12 (d, 3H, $^{3}J = 6.7$, CH), 1.94 (s, 6H, $N(CH_3)_2$), 4.05 (m, 1H, α-CH_3), 6.84 (ddd, 1H, ^{3}J = 7.7, $^{3}J_{HP} = 4.1$, $^{4}J = 1.0$, H(6) arom.), 7.04 (td, 1H, $^{3}J = 7.7$, $^{4}J_{HH} = 1.0$, H(5) arom.), 7.14 (br. m, 1H, H(4) arom.), 7.22 (br. m, 10H, PPh_2), 7.44 (dd, 1H, $^{3}J = 8.2$, $^{4}J_{HP} = 4.1$, H(3) arom.). ^{31}P{^{1}H} NMR (δ, ppm): −31.85. ^{13}C{^{1}H} NMR (δ, ppm): 18.6 (s, α-CH_3), 42.5 (s, NCH_3), 61.9 (d, $^{3}J_{CP} = 21.4$, CH), 126.5 (d, $^{3}J_{CP} = 5.0$, C(3) arom.), 126.7 (s, C(4) arom.), 128.3 (m, *m*-PPh), 129.1 (s, *p*-PPh_A), 133.7 (d, $^{1}J_{CP} = 13.8$, *ipso*-PPh), 133.8 (s, *p*-PPh_B), 134.0 (d, $^{2}J_{CP} = 10.1$, *o*-PPh), 135.7 (d, $^{2}J_{CP} = 13.8$, C(6) arom.), 137.3 (d, $^{3}J_{CP} = 10.1$, C(5) arom.), 138.0 (d, $^{2}J_{CP} = 12.6$, C(2) arom.), 150.1 (d, $^{1}J_{CP} = 21.4$, C(1) arom.).

4.5.2. (S)-4-tert-Butyl-2-(2-diphenylphosphino)phenyl-2-oxazoline [(S)-8]

The phosphino-oxazoline was prepared from CPC (*S,S*)-**7** (20.6 mg) in 43% yield (10.0 mg) as colorless crystals using the procedure described for compound (*S*)-**6**. The eluent used for the preparative TLC was a 5:1 mixture of hexane–ethyl acetate. R_f 0.68 (4:1 hexane–ethyl acetate); $[\alpha]_D^{21}$ −60° (*c* 0.0011, CH_2Cl_2) [lit. [26] $[\alpha]_D^{20}$ −62° (*c* 0.0018, $CHCl_3$)]. ^{1}H NMR (δ, ppm): 0.72 (s, 9H, *t*-Bu), 3.88 (dd, 1H, $^{2}J = 10.1$, $^{3}J = 8.2$, H(5A) oxaz.), 4.01 (t, 1H, $^{3}J = 8.2$, H(4) oxaz.), 4.08 (dd, 1H, $^{2}J = 10.1$, $^{3}J = 8.2$, H(5B) oxaz.), 6.87 (ddd, 1H, $^{3}J = 7.6$, $^{3}J_{HP} = 4.1$, $^{4}J = 1.0$, H(6) arom.), 7.22–7.38 (m, 12H, PPh_2 and H(4,5) arom.), 7.94 (ddd, 1H, $^{3}J = 7.6$, $^{4}J_{HP} = 4.1$, $^{4}J = 1.3$, H(3) arom.); ^{31}P{^{1}H} NMR (δ, ppm): −20.76 (lit. data ($CDCl_3$, δ, ppm, relative to $PO(OPh)_3$): −6.3 [25]). The ^{13}C{^{1}H} NMR spectrum matched the literature data [26].

4.5.3. [2-(Methylthiomethyl)phenyl]diphenylphosphine (**11**)

Compound **11** was prepared from CPC **10** (26.0 mg) in 51% yield (14.5 mg) as a colorless syrup with an unpleasant odor using the procedure described for compound (*S*)-**6**. The eluent used for the preparative TLC was benzene. R_f 0.82 (benzene); ^{1}H NMR (δ, ppm): 1.99 (s, 3H, CH_3), 3.96 (d, 2H, $^{4}J_{HP} = 1.5$, CH_2), 6.92 (ddd, 1H, $^{3}J = 7.9$, $^{3}J_{HP} = 4.2$, $^{4}J = 1.2$, H(6) arom.), 7.15 (td, 1H, $^{3}J_{HH} = 7.3$, H(5) arom.), 7.28 (m, 4H, *m*-PPh), 7.33 (br m, 6H, *o*-PPh and *p*-PPh), 7.47 (br m, 2H, H(3) and H(4) arom.). ^{13}C{^{1}H} NMR (δ, ppm): 15.4 (s, CH_3), 36.8 (d, $^{3}J_{CP} = 24.8$, SCH_2), 127.3, 129.0 and 134.1 (three s, C(3), C(4) and C(5) arom.), 128.5 (d, $^{3}J_{CP} = 6.9$, *m*-PPh), 128.6 (s, *p*-PPh), 129.6 (d, $^{2}J_{CP} = 4.6$, C(6) arom.), 133.8 (d, $^{2}J_{CP} = 19.8$, *o*-PPh), 136.2, 136.8 and 142.8 (three d, $J_{CP} = 13.4$, 10.4 and 24.9, respectively, *ipso*-PPh, C(1) and C(2) arom.). ^{31}P{^{1}H} NMR (δ, ppm): −31.3. HRMS: $[M + H]^+$ calcd for $C_{20}H_{20}PS$ 323.1028, found 323.1014.

4.5.4. [2-(Methylthiomethyl)phenyl]diphenylphosphine oxide (**11A**)

The compound was obtained upon the exposure of phosphine **11** to air. R_f 0.29 (5:1 benzene–acetone). ^{1}H NMR (δ, ppm): 1.85 (s, 3H, CH_3), 4.09 (s, 2H, CH_2), 7.04 (dd, 1H, $^{3}J_{HH} = 7.1$, $^{3}J_{HP} = 14.7$, H(6) arom.), 7.18 (br t, 1H, $J = 8.2$, H(5) arom.), 7.46 (m, 4H, *m*-PPh), 7.50 (m, 1H, H(4) arom.), 7.53 (m, 2H, *p*-PPh), 7.65 (m, 4H, *o*-PPh), 7.74

(dd, 1H, $^3J_{HH}$ = 8.2, $^4J_{HP}$ = 4.1, H(3) arom.). $^{13}C\{^1H\}$ NMR (δ, ppm): 15.4 (s, CH_3), 36.3 (s, CH_2), 126.2 (d, $^3J_{CP}$ = 12.6, C(6) arom.), 128.6 (d, $^2J_{CP}$ = 11.9, *m*-PPh), 130.7 (br s, C(3) arom.), 131.1 (d, $^1J_{CP}$ = 10.4, C(5) arom.), 131.5 (d, $^2J_{CP}$ = 7.9, C(2) arom.), 131.9 (d, $^4J_{CP}$ = 2.8, *p*-PPh), 132.0 (d, $^3J_{CP}$ = 9.7, *o*-PPh), 132.4 (d, $^1J_{CP}$ = 37.7, *ipso*-PPh), 133.3 (s, C(4) arom.), 133.5 (d, $^1J_{CP}$ = 12.9, C(1) arom.). $^{31}P\{^1H\}$ NMR (δ, ppm): 16.9. HRMS: $[M + H]^+$ calcd for $C_{20}H_{20}PSO$ 339.0977, found 339.0969.

4.5.5. [2-(Diphenylphosphoryl)benzyl]diphenylphosphine oxide (**14**)

The dioxide was obtained from CPC **12** (25.0 mg) as a white solid in 35% yield (9.9 mg) following the procedure described for (*S*)-**6**. In the end of the reaction, air was bubbled through the mixture for 1 h to ensure the oxidation of the product. The eluent used for the preparative TLC was a 3:1 benzene–acetone mixture. R_f 0.57 (3:1 benzene–acetone); m.p. 172–175 °C, dec.; ^1H NMR (δ, ppm): 3.36 (dd, 2H, $^2J_{HP}$ = 10.7, $^4J_{HP}$ = 5.4, CH_2), 6.74 (dd, 1H, $^3J_{HH}$ = 7.9, $^3J_{HP}$ = 10.4, H(3) arom.), 7.00 (br t, 1H, ^3J = 6.4, $^4J_{HP}$ = 6.0, H(6) arom.), 7.20 (t, 1H, ^3J = 8.0, H(4) arom.), 7.31 (t, 1H, ^3J = 7.4, H(5) arom.), 7.38 (m, 4H, *m*-PPh^1), 7.46 (m, 2H, *p*-PPh^1), 7.51 (m, 4H, *m*-PPh^2), 7.59 (m, 2H, *p*-PPh^2), 7.73 (br. m, 8H, *o*-PPh^1 and *o*-PPh^2). ^{13}C NMR (δ, ppm): 33.5 (dd, $^1J_{CP}$ = 27.4, $^3J_{CP}$ = 15.8, CH_2), 125.5 (dd, $^1J_{CP}$ = 51.3, $^3J_{CP}$ = 11.5, C(2) arom.), 127.9 (d, $^1J_{CP}$ = 58.9, *ipso*-PPh^1), 128.2 (d, $^1J_{CP}$ = 56.4, *ipso*-PPh^2), 128.4 (dd, $^3J_{CP}$ = 8.9, $^5J_{CP}$ = 3.1, C(4) arom.), 128.7 (d, $^3J_{CP}$ = 11.6, *m*-PPh^2), 129.0 (d, $^3J_{CP}$ = 11.9, *m*-PPh^1), 131.8 (d, $^4J_{CP}$ = 2.6, *p*-PPh^2), 132.0 (m, C(5) and C(6) arom.), 132.1 (d, $^4J_{CP}$ = 2.3, *p*-PPh^1), 133.5 (d, $^2J_{CP}$ = 10.6, *o*-PPh^2), 134.0 (d, $^3J_{CP}$ = 5.2, C(3) arom.), 134.8 (d, $^2J_{CP}$ = 11.7, *o*-PPh^1), 137.3 (dd, $^2J_{CP}$ = 11.8, $^2J_{CP}$ = 2.3, C(1) arom.). $^{31}P\{^1H\}$ NMR (δ, ppm): 35.4 and 8.9 (two d, $^4J_{PP}$ = 6.4). IR (ν, cm^{-1}, CH_2Cl_2): 1266 s (P=O), 1225 s (CH_2P=O). HRMS $[M + Na]^+$ calcd for $C_{31}H_{26}O_2NaP_2$ 515.13002, found 515.13159.

4.5.6. Chloro-{2-[(diphenylphosphino)methyl]phenyl-C,P}(tetraphenyldiphosphine oxide-P)palladium(II) (**16**)

The complex was isolated as a yellow powder in 13% yield from the reaction of CPC **12** with $KPPh_2$ (see the preparation of compound **14**). R_f 0.26 (5:1 benzene–acetone); ^1H NMR (δ, ppm): 3.27 (dd, 2H, $^2J_{HP}$ = 10.1, $^4J_{HP}$ = 5.6, CH_2), 6.7 (m, 2H, H(3) arom. and H(6) arom.), 7.07 (m, 2H, H(4) arom. and H(5) arom.), 7.16–7.24 (br. m, 10H, *m*-PPh^1, *m*-PPh^2, and *p*-PPh^1), 7.35 (m, 2H, *p*-PPh^2), 7.46 (m, 4H, *m*-PPh^3), 7.51 (m, 2H, *p*-PPh^3), 7.67–7.60 (br. m, 12H, *o*-PPh^1, *o*-PPh^2, and *o*-PPh^3). ^{13}C NMR (δ, ppm): 38.5 (dd, $^1J_{CP}$ = 25.5, $^2J_{CP}$ = 17.5, CH_2), 127.0, (d, $^2J_{CP}$ = 10.8, *m*-PPh^1), 127.7, 130.7, 131.6 and 133.1 (four m, C(3), C(4), C(5) and C(6) arom.), 128.0 (d, $^2J_{CP}$ = 11.4, *m*-PPh^2), 128.1 (m, *ipso*-PPh^1), 128.2 (m, *ipso*-PPh^2), 128.8 (d, $^4J_{CP}$ = 2.8, *p*-PPh^1), 128.9 (d, $^2J_{CP}$ = 10.7, *m*-PPh^3), 130.7 (m, C(5) arom.), 130.8 (d, $^4J_{CP}$ = 2.4, *p*-PPh^2), 131.0 (d, $^4J_{CP}$ = 2.4, *p*-PPh^3), 131.1 (d, $^1J_{CP}$ = 12.3, *ipso*-PPh^3), 131.5 (d, $^3J_{CP}$ = 10.3, *m*-PPh^1), 133.9 (d, $^3J_{CP}$ = 11.1, *o*-PPh^2), 134.8 (d, $^3J_{CP}$ = 11.9, *o*-PPh^3), 137.9 (dd, $^2J_{CP}$ = 16.3, $^3J_{CP}$ = 4.0, C(2) arom.), 141.5 (m, C(1) arom.). $^{31}P\{^1H\}$ NMR (δ, ppm): 49.4 (dd, $^1J_{PP}$ = 449, $^3J_{PP}$ = 15.5, $P(O)Ph_2$), 31.4 (dd, $^2J_{PP}$ = 61.1, $^3J_{PP}$ = 15.5, CH_2PPh_2), −7.2 (dd, $^1J_{PP}$ = 449, $^2J_{PP}$ = 61.1, $PdPPh_2$).

4.5.7. 2-[2-(Diphenylphosphino)benzyl]pyridine (**18**)

The compound was synthesized from CPC **17** (19.7 mg) as a pale yellow syrup in 47% yield (10.7 mg) using the procedure described for (*S*)-**6**. The eluent used for the preparative TLC was a 10:1 benzene–acetone mixture. R_f 0.69 (10:1 benzene–acetone); ^1H NMR (δ, ppm): 4.45 (s, 2H, CH_2), 6.93 (m, 2H, H(4) of Py and H(6) of C_6H_4), 6.91 (m, 1H, H(6) of C_6H_4), 7.00 (br dd, 1H, J = 8.3, J = 6.2, H(5) of Py), 7.14 (br t, 1H, ^3J = 6.8, H(4) of C_6H_4), 7.20–7.32 (m, 12H, PPh, H(3) of Py and H(3) of C_6H_4), 7.39 (td, 1H, J = 8.0, J = 1.7, H(5) of C_6H_4), 8.46 (d, 1H, J = 4.6, H(6) of Py). $^{13}C\{^1H\}$ NMR (δ, ppm): 42.8 (d, $^3J_{CP}$ = 21.8, CH_2), 121.0 (s, C(5) of Py), 123.6 (d, $^2J_{CP}$ = 2.3, C(6) of C_6H_4), 126.9 (s, C(4) of C_6H_4), 128.5 (d, $^3J_{CP}$ = 7.1, *m*-PPh), 128.6 (s, *p*-PPh), 129.1 (s, C(3) of Py), 130.3 (d, $^3J_{CP}$ = 4.8, C(3) of C_6H_4), 133.8 (s, C(4) of Py), 133.9 (d, $^2J_{CP}$ = 19.7, *o*-PPh), 136.1 (s, C(5) of C_6H_4), 136.2, 136.6 and 144.1 (three d, $^2J_{CP}$ = 11.3, $^1J_{CP}$ = 26.3, $^1J_{CP}$ = 10.3, respectively, C(1) of C_6H_4, PC(2) of C_6H_4 and *ipso*-PPh_2), 149.1 (s, C(6) of Py), 160.5 (s, C(2) of Py). $^{31}P\{^1H\}$ NMR (δ, ppm): −29.4. HRMS $[M + H]^+$ calcd for $C_{24}H_{21}NP$ 354.14116, found 354.14506.

4.5.8. 2′-(Diphenylphosphino)-N,N-dimethylbiphenyl-2-amine (**20**)

The compound was synthesized from CPC **19** (21.1 mg) as a white solid in 47% yield (11.2 mg) using the procedure described for (*S*)-**6**. The eluent used for the preparative TLC was benzene. R_f 0.77 (benzene). The ^1H and $^{13}C\{^1H\}$ NMR spectra matched the literature data [46]. $^{31}P\{^1H\}$ NMR (δ, ppm): −29.4 (lit. data: −13.9 ppm relative to 85% H_3PO_4 in $CDCl_3$ [46]).

4.5.9. [2,6-Bis(methylthiomethyl)phenyl]diphenylphosphine (**23**)

The highest yield of compound **23**, 49%, was obtained from CPC **22** and $KPPh_2$ in hexane using 1.2 equiv. of $KPPh_2$ and the CPC concentration of 3 mg/mL. The solvent used for preparative TLC was benzene. Disulfidophosphine **23** was obtained as a pale yellow syrup with an unpleasant odor. R_f 0.68 (benzene); ^1H NMR (δ, ppm): 1.81 (s, 6H, 2 CH_3), 3.77 (s, 4H, 2 CH_2), 7.27–7.34, 7.45–7.48 (three m, 13H, PPh_2 and C_6H_3). $^{13}C\{^1H\}$ NMR (δ, ppm): 15.4 (s, CH_3), 38.9 (d, $^3J_{CP}$ = 18.6, CH_2), 127.7 (s, *p*-PPh), 128.5 (d, $^3J_{CP}$ = 5.5, *m*-PPh), 129.3 (d, $^3J_{CP}$ = 3.9, C(3) and C(5) arom.), 130.4 (s, C(4) arom.), 131.4 (d, $^2J_{CP}$ = 17.5, *o*-PPh), 132.9 (d, $^1J_{CP}$ = 21.1, C(1) arom.), 136.1 (d, $^2J_{CP}$ = 15.1, C(2) and C(6) arom.), 146.1 (d, $^1J_{CP}$ = 14.5, 2C, *ipso*-PPh). $^{31}P\{^1H\}$ NMR (δ, ppm, $CDCl_3$): −34.7. HRMS: $[M + H]^+$ calcd for $C_{22}H_{24}PS_2$ 383.10625, found 383.10845.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.078.

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