Journal of Organometallic Chemistry 797 (2015) 13–20

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Communication

Reactivity of dimeric cyclopalladated complexes with an (sp^3)C–Pd bond toward $KPPh_2$

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ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form
17 July 2015
Accepted 18 July 2015
Available online 26 July 2015

Keywords:
Cyclopalladated complex
N,P, S,P, P,P ligands
(sp^3)C–Pd bond
Phosphination
$KPPh_2$

ABSTRACT

Reactions of $KPPh_2$ with dimeric *C,N*, *C,P* and *C,S* cyclopalladated complexes (CPCs) **1a**–**g** containing an (sp^3)C–Pd bond were investigated. The CPCs used in the study were obtained from D-camphor *O*-methyloxime (**a**), L-fenchone *O*-methyloxime (**b**), 4,4-dimethyl-2-phenyl-2-oxazoline (**c**), 8-methylquinoline (**d**), trimesitylphosphine (**e**), tri(*O*-tolyl)phosphine (**f**) and 2,6-dimethylthioanisole (**g**). The dichloro-bridged CPCs **1a,b,d,f,g** and the diacetato-bridged analog **μ-OAc-1d** reacted with 4.5 equiv. of $KPPh_2$ at room temperature in THF to give either phosphines **2a,b** or phosphine oxides **8d,f,g** in 20–51% yield. Complexes **1a,b,d** reacted with 1 equiv. of $KPPh_2$ to produce the corresponding μ-chloro-μ-diphenylphosphido-CPCs **3a,b,d** in 33–56% yield. In the reaction of CPC **1c** with 4.5 equiv. of $KPPh_2$, complex **4c** with two PPh_2 bridging ligands was isolated in 36% yield. Structures of phosphines **2a,b**, phosphine oxides **8a,d,f,g** as well as complexes **3a,b,d** and **4c** were confirmed by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy.

1. Introduction

Reactions involving a C–Pd bond in cyclopalladated complexes (CPCs) represent a valuable approach for the synthesis of compounds that are not readily available by other methods [1]. Also, studies of these reactions shed light on mechanisms of palladium-catalyzed transformations [2]. Despite the abundance of reported reactions at the (sp^2)C–Pd bond of palladacycles [1], there are only a limited number of aliphatic CPCs and reagents studied in this type of transformation. The reagents that have been used in reactions of CPCs at the (sp^3)C–Pd bond include electron-deficient alkynes [3], benzyl isocyanide [4], CO with or without MeOH [4,5], I_2 [6,7], Cl_2 [8], Et_3BnNCl [7], methyl vinyl ketone [5], and alkyl iodides [5]. Several research groups reported oxidation of *C,N* CPCs obtained from oximes with bulky alkyl substituents [9]. The formation of an (sp^3)C–(sp^2)C bond was observed in the reaction of Me_3SnPh with a *C,P* palladacycle having a benzylic C–Pd bond [10].

Our group [11–13] and others [14] have investigated reactions of CPCs with lithium and potassium phosphides to form aminophosphines and related bidentate ligands (Scheme 1). All CPCs used in these studies contained an (sp^2)C–Pd bond. In this paper, we report our data on reactivity of *C,N*, *C,P* and *C,S* palladacycles with an (sp^3)C–Pd bond toward $KPPh_2$.

2. Results and discussion

2.1. $KPPh_2$ reactions of CPCs with an (sp^3)C–Pd bond

Previously, we showed that both $LiPPh_2$ and $KPPh_2$ are capable of reacting with dimeric chloro-bridged CPCs [11,12]. However, the outcome of the $LiPPh_2$ reactions with CPCs was highly sensitive to the phosphide structure in the solution, which in turn, depended on the preparation method, concentration and age of the chemical. $KPPh_2$ in a solution appears to exist only in a monomeric form, and reactivity of the commercial reagent and the one prepared in our lab from $ClPPh_2$ and K in THF was proven to be the same. In the present investigation, we used only commercially available $KPPh_2$ as a phosphide source.

The dimeric dichloro-bridged *C,N* CPC **1a** derived from *O*–Me camphor oxime [15] was chosen as a model complex for our study. Complex **1a** reacted with 4.5 equiv. of $KPPh_2$ in THF at rt for 18 h to give the desired *N,P* ligand **2a** in 21% yield (Scheme 2). Increasing the reaction temperature to 40 °C resulted in 5% yield of **2a**. Considering that the bidentate ligand **2a** might be coordinated to the metal, 1,2-bis(diphenylphosphino)ethane was added at the end of the room temperature reaction to release the *N,P* ligand in its free

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http://dx.doi.org/10.1016/j.jorganchem.2015.07.023
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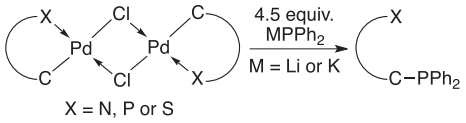


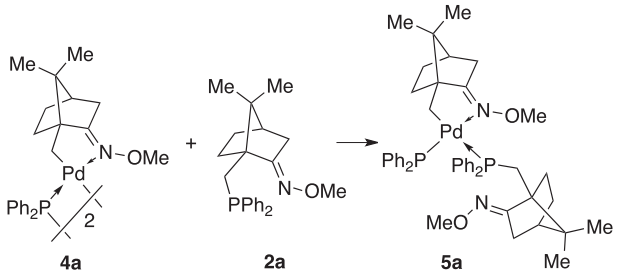
Scheme 1. Formation of bidentate ligands by reacting $MPPh_2$ with dimeric CPCs.

form. The yield, indeed, was improved, but not significantly (28%).

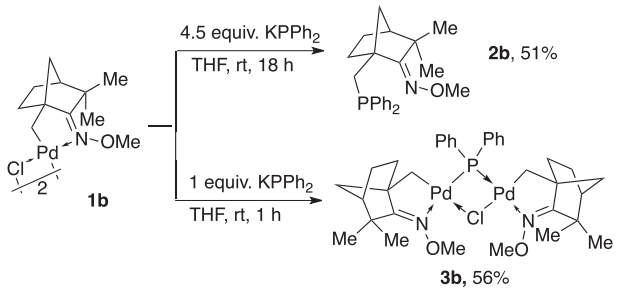
CPC **1a** was also reacted in THF with 1 equiv. of $KPPh_2$. As in the previously reported reactions of metal phosphides with CPCs having an (sp^2)C—Pd bond [12], no phosphine **2a** was formed and only complex **3a** was isolated (Scheme 2). The best yield of this complex (31%) was obtained when the reaction time was shortened to 1 h.

Then, the reaction of CPC **1a** with 4.5 equiv. of $KPPh_2$ (THF, 18 h, rt) was performed using ethyl acetate instead of halogenated solvents on the separation step. This modification allowed for isolation of phosphine **2a** in 17% yield and complex **4a** in 24% yield. The latter compound presumably has a dimeric structure with two PPh_2 bridges (Scheme 2). Attempted purification of complex **4a** using preparative TLC and CH_2Cl_2 as the eluent provided the μ-Cl-μ-PPh_2 complex **3a** in 16%. The $^{31}P\{^1H\}$ NMR spectrum of one of the fractions contained the singlet of complex **4a** at δ −64.7 ppm [in C_6D_6 relative to $P(OEt)_3$] and two doublets, δ 21.8 and 113.5 ppm, $J_{P,P}$ = 36 Hz. We hypothesize that these doublets belong to compound **5a**, which can be formed by reacting free phosphine **2a** with complex **4a** (Scheme 3). The $^{31}P\{^1H\}$ NMR chemical shift of 123.2 ppm has been reported for complexes with the PAr_2 group as a terminal ligand bonded to Pd(II) [16] (*cf.* the chemical shift of −7.8 ppm for the terminal PPh_2 ligand bonded to Pt [17]), while the chemical shifts in a range of 20–35 ppm are typical for tertiary phosphines bonded to Pd(II) as terminal ligands [11,18]. The value of the coupling constant suggests [18–20] that there are two phosphorus atoms in complex **5a** that are cis to each other. According to the transphobia concept [21], complexes of type **5** are expected to have a terminal PPh_2 group cis to the CH_2 fragment of the cyclopalladated ligand. Thus, we suggest that the diphosphido-bridged complexes of type **4** can react with other ligands, including compound **2a**, to form mononuclear complexes of type **5**.

To test whether the μ-Cl-μ-PPh_2 complex **3a** could be converted to its di-μ-PPh_2 analog **4a** and/or phosphine **2a**, it was reacted with 1 equiv. of $KPPh_2$. Two compounds were isolated after preparative TLC: free *N,P* ligand **2a** in 23% yield and complex **4a** in 14% yield. Next, the di-μ-PPh_2 CPC **4a** was converted to compound **2a** in 27% yield by reaction with 2.5 equiv. of $KPPh_2$ in THF (rt, 96 h). It is noteworthy that the formation of the *N,P* ligand **2a** from CPC **4a** was



Scheme 3. Proposed reaction of dimer **4a** with phosphine **2a**.

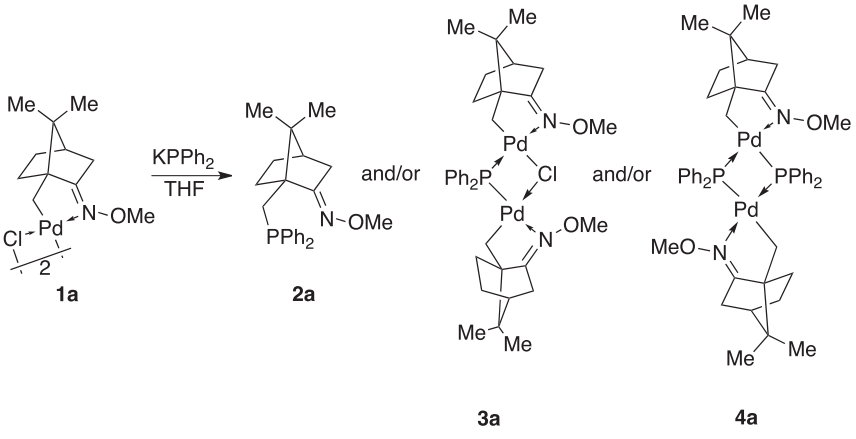


Scheme 4. Reactions of the fenchone-derived CPC **1b** with $KPPh_2$.

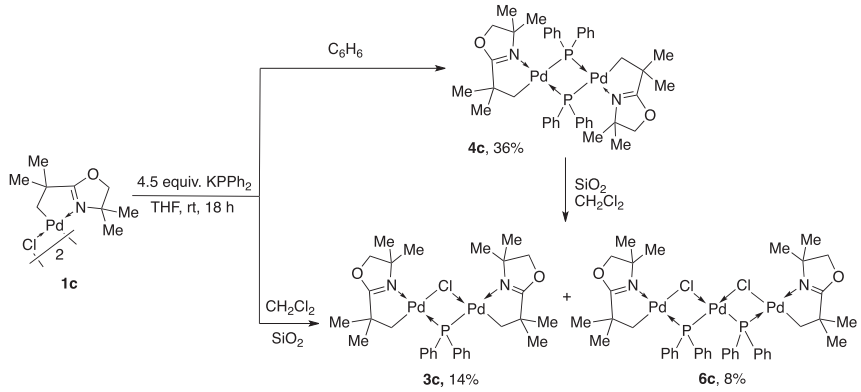
slower than that from CPC **1a** using 4.5 equiv. of $KPPh_2$ in the same solvent ($^{31}P\{^1H\}$ NMR data).

Then we studied the fenchone-derived CPC **1b** [22] in reactions with $KPPh_2$. The reaction of CPC **1b** with 4.5 equiv. of $KPPh_2$ in THF furnished the enantiopure *N,P* ligand **2b** in 51% yield (Scheme 4). Using 1 equiv. of $KPPh_2$, CPC **1b** was converted to the μ-Cl-μ-PPh_2-bridged derivative **3b** in 56% yield. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR data for complex **3b** suggest that this and other μ-Cl-μ-PPh_2-bridged CPCs reported in the literature [11–13], as well as the others described in this study, exist in solutions as single isomers with trans-*N,P* geometry.

The next complex studied was the oxazoline-derived dimer **1c**, synthesis of which was described previously [5,23]. Using standard conditions (rt, 18 h, 4.5 equiv. of $KPPh_2$), three new complexes were obtained: **3c**, **4c** and **6c** (Scheme 5). No traces of the desired phosphino-oxazoline **2c** (δ −37.8 ppm in $CDCl_3$ relative to $P(OEt)_3$) [24], Fig. 1) was detected either in the $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture or in the spectra of the fractions obtained after chromatographic separation. As in the case of the camphor-based



Scheme 2. Reaction of CPC **1a** with $KPPh_2$.



Scheme 5. Reaction of CPC **1c** with $KPPh_2$.

complex **4a**, the oxazoline-derived analog **4c** was unstable on SiO_2 in the presence of CH_2Cl_2 and provided two chloro-containing complexes **3c** and **6c** in 14 and 8% yield, respectively.

The 8-methylquinoline-derived complex **1d** [25] differs from CPCs **1a**–**c** by having a benzylic carbon bonded to the metal. Reactions of CPC **1d** with 4.5 equiv. of $KPPh_2$ at rt gave only 8-methylquinoline (**7d**, Scheme 6). The isolation of free preligands was previously reported in $KPPh_2$ reactions with CPCs containing an (sp^2)C–Pd bond [13] as well as in the Pd-catalyzed phosphination reactions of aryl triflates with PPh_3 [26]. The formation of such products can be explained by β-hydride elimination of the alkoxide-containing Pd(II) intermediate, which could be formed after the adventitious cleavage of a C–O bond in THF by the phosphide [11,13].

When 1 equiv. of $KPPh_2$ was used in the reaction, the μ-Cl-μ-PPh_2-brigded derivative **3d** was isolated in 56% (Scheme 7). The $^{31}P\{^1H\}$ NMR spectrum of complex **3d** had a singlet at δ 10.2 ppm [$CDCl_3$ relative to $P(OEt)_3$] and matched the data for this compound prepared by a different method [24].

Complex **1d** had a limited solubility in THF. The use of the more soluble compound ***μ*-OAc-1d** in the same reaction provided a mixture of phosphine **2d** and its oxide **8d**. In the next experiment, air was bubbled through the reaction mixture before purification, and oxide **8d** was isolated in 21% (Scheme 7). This reaction is the first example of converting acetato-bridged CPCs to the corresponding phosphines (or phosphine oxides) using metal phosphides.

It was of interest to investigate $KPPh_2$ reactivity toward CPCs with donor atoms other than nitrogen. The trimesitylphosphine-derived complex **1e** [27] reacted with 4.5 equiv. of $KPPh_2$ at rt to provide only the free preligand **7e** (Scheme 8).

Reactions of $KPPh_2$ with two tri-*ortho*-tolylphosphine-derived complexes, dichloro-bridged dimer **1f** and its acetato-bridged analog ***μ*-OAc-1f** [28] were investigated as well. In all experiments with these two CPCs, air was bubbled into the reaction mixtures before purification to ensure oxidation of the phosphine product. Reaction of complex **1f** furnished phosphine oxide **8f** in 20% yield (Scheme 10). In contrast to the $KPPh_2$ reactions with the 8-methylquinoline-derived CPCs, the use of ***μ*-OAc-1f** instead of its

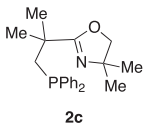
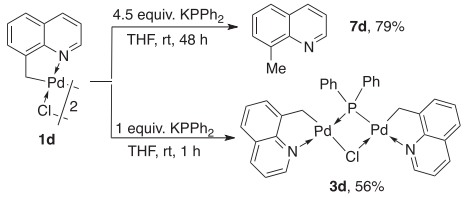
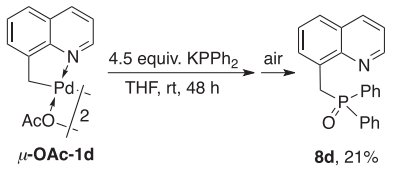


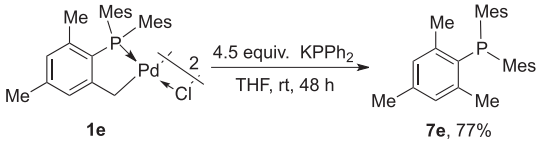
Fig. 1. Structure of compound **2c**.



Scheme 6. Reactions of CPCs **1d** with $KPPh_2$.



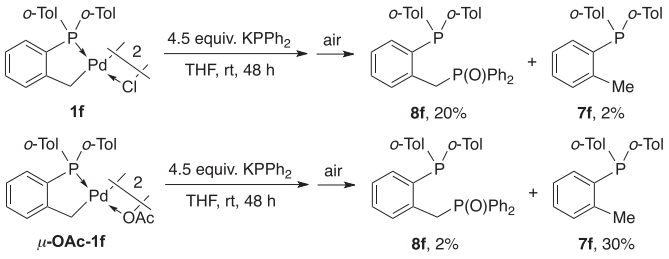
Scheme 7. Reaction of CPC ***μ*-OAc-1d** with 4.5 equiv. of $KPPh_2$.



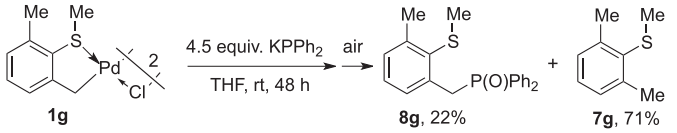
Scheme 8. Formation of compound **7e** in the reaction of CPC **1e** with $KPPh_2$.

chloro-bridged analog provided only traces of the phosphination product **8f**. According to ^{31}P NMR data, only one of the two phosphino groups in the product was oxidized. In both reactions, along with compound **8f**, tri-*ortho*-tolylphosphine **7f** was isolated as well (Scheme 9).

The reactivity of the *CS* CPC **1g** [29] toward $KPPh_2$ was also studied. The complex reacted with 4.5 equiv. of the phosphide to



Scheme 9. Reaction of complexes **1f** and ***μ*-OAc-1f** with $KPPh_2$.



Scheme 10. Reaction of CPC **1g** with $KPPh_2$.

provide product **2g** in low yield. Because of the rapid conversion of phosphine **2g** to the corresponding oxide **8g**, the crude product was oxidized before preparative TLC. The best yield of the phosphine oxide was 22%. It is noteworthy that a significant amount of the free sulfide **7g** was isolated in all reactions of CPC **1g** (Scheme 10).

2.2. Structure confirmation

According to the literature [30], non-coordinated tertiary phosphines provide $^{31}P\{^1H\}$ NMR signals in the −70 to +70 ppm interval (relative to H_3PO_4), diphenyl-substituted tertiary phosphines give signals with negative chemical shift values, and signals of phosphine oxides usually have positive chemical shift values between 10 and 30 ppm. The spectra of phosphines **2a,b** contained a singlet at −23.2 and −37.1 ppm [relative to $P(OEt)_3$], respectively. These phosphines were slowly, within a week, oxidized by oxygen in air to give the corresponding phosphine oxides (δ 15.1 and 15.0 ppm, respectively). $^{31}P\{^1H\}$ NMR spectra of phosphine oxides **8d**,**g** exhibited singlets at δ 16.5 and 15.0 ppm, respectively, whereas the spectrum of product **8f** with two phosphorus atoms contained two doublets at δ −45.1 and 15.4 ppm ($^4J_{P,P} = 9.2$ Hz).

^1H and $^{13}C\{^1H\}$ NMR signals of the CH_2P fragment in compounds **2a,b** and **8a,d,f,g** displayed $J_{H,P}$ and $J_{C,P}$ coupling constants. Diastereotopic hydrogens of the CH_2P group in **2a,b** and **8a** provided two doublets of doublets between δ 2.15 and 3.06 ppm. The ^1H NMR signal of the PCH_2 group in oxides **8d,f,g** appeared as a doublet between δ 4.00 and 4.56 ppm. The values of the coupling constant $^2J_{H,P}$ for phosphines **2a,b** were 3.5 and 4.1 Hz, while those for oxides **8a,d,f,g** were much larger: 16.0, 14.2, 9.6 and 14.1 Hz, respectively. The difference in the values of coupling constants when comparing phosphines to phosphine oxides was especially noticeable in $^{13}C\{^1H\}$ NMR spectra. The CH_2P group in phosphines **2a,b** gave a doublet at δ 27.5 and 30.7 ppm with $^1J_{C,P}$ equal to 18 and 13 Hz, respectively. The $^{13}C\{^1H\}$ NMR signal of the same group in oxides **9a,d,f,g** appeared between δ 27.3 and 36.6 ppm and displayed the coupling constant $^1J_{C,P}$ in a range of 67–73 Hz. The oxidation of the phosphino group in compounds **8a,d,f,g** was also confirmed by IR spectroscopy. IR spectra of these compounds had an absorption band at 1187–1199 cm^{-1} assigned to the stretching vibrations of the P═O group [31]. The elemental composition of phosphines **2a,b** and phosphine oxides **8d,f,g** was confirmed by HRMS data.

Pd(II) complexes with both a chloro and phosphido bridge are rather uncommon in the literature [11,12,32,33]. Moreover, there are only two known cyclopalladated complexes of this type [11,12,33]. Three isomers can be predicted for such complexes; however, it was shown that in the solid form [33] and in a solution [11], they exist as syn isomers with the trans-*N,P* ligand configuration. Two μ-Cl-μ-PPh_2 Pd(II) complexes **3a**,**c** presumably have a syn configuration with the PPh_2 bridging ligand trans to both nitrogen atoms. The $^{31}P\{^1H\}$ NMR spectra of CPCs **3a**,**c** in $CDCl_3$ exhibited singlets at δ 4.9 and −1.9 ppm, respectively. In the $^{13}C\{^1H\}$ NMR spectra of these complexes, the signal of the CH_2Pd fragment appeared as a doublet ($^2J_{C,P} = 2.2$ Hz) at 19.4 ppm and as a singlet at 33 ppm, respectively. For comparison, the reported complex of this type synthesized from *N,N*-dimethylbenzylamine provided the ^{31}P NMR signal at δ 25.1 ppm ($^2J_{C,P} = 1.8$ Hz) [11]. The ^1H NMR spectra of complexes **3a**,**c** confirmed a 1:2 ratio of the PPh_2 group and cyclopalladated ligands in their structures. The elemental composition and purity of these compounds were confirmed by satisfactory elemental analysis.

Di-μ-PPh_2 complexes of Pd(II) and especially Pt(II) are well known [19,20,34,35]. However, to the best of our knowledge, only one cyclometallated derivative of this type has been reported, the Pt(II) complex derived from 7,8-benzoquinoline [36]. Unfortunately, only the X-ray crystallographic data for this compound are available. The $^{31}P\{^1H\}$ NMR spectra of known di-μ-PPh_2 Pd(II) complexes usually have the signals of the bridging PPh_2 group between −100 and −140 ppm [19,20,34,35,37]. We were able to isolate two complexes, **4a,c**, which presumably have dimeric cyclopalladated structure with two bridging PPh_2 ligands. The ^1H NMR spectrum of the oxazoline-derived complex **4c** suggests a 1:1 ratio of the PPh_2 fragment and the cyclopalladated ligand. The $^{31}P\{^1H\}$ NMR spectrum of the same compound in $CDCl_3$ exhibited a lone singlet at δ −85.1 ppm (−72.5 ppm in C_6D_6), which suggests the anti configuration of the cyclopalladated ligands. The $^{13}C\{^1H\}$ NMR signal of the CH_2Pd fragment in **4c** appeared at δ 42.2 ppm as a triplet with $J_{C,P}$ equal to 55.1 Hz. Unfortunately, the camphor-derived complex **4a** could not be obtained in the pure form to allow its complete characterization by NMR spectroscopy. The ^1H NMR spectrum of this compound was too complex to assign all signals; however, the signal integration suggested a 1:1 ratio of the PPh_2 fragment and the cyclopalladated ligand. The only reliable spectroscopic data for this complex that can be reported are its $^{31}P\{^1H\}$ NMR signal at δ −64.8 ppm in C_6D_6 and -76.9 ppm in $CDCl_3$.

We suggest that complex **6c** has a trinuclear structure with both Cl and PPh_2 acting as the bridging ligands. The elemental composition of the unusual complex was supported by a satisfactory elemental analysis. The ^1H NMR spectrum proved a 1:1 ratio of the PPh_2 group and the cyclopalladated ligand in the structure. The 1:1 ratio of the PPh_2 ligand and the cyclopalladated oxazoline moiety was also evident for di-phosphido-bridged complex **4c**; however, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **4c** and **6c** were quite different. The $^{31}P\{^1H\}$ NMR spectrum of **6c** had only one signal at δ 10.3 ppm. This chemical shift value is within the range reported [12] or observed in this study for the corresponding dinuclear μ-Cl-μ-PPh_2 complexes of type **3**. The $^{13}C\{^1H\}$ NMR signals of the CH_2Pd fragment in the trinuclear complex **6c** and its binuclear analog **3c** appeared as singlets, suggesting that the CH_2 group is cis to the PPh_2 ligand in both compounds.

3. Conclusions

Dimeric cyclopalladated complexes of the *C,N*, *C,P* and *C,S* type and containing an (sp^3)C–Pd bond reacted with $KPPh_2$ to provide several products types. The main product structure depended on the molar equivalents of $KPPh_2$ used in the reaction. When 4.5 equiv. of $KPPh_2$ were applied, the majority of CPCs provided either phosphine **2** or phosphine oxide **8**. In spite of low yields (20–51%) of the desired phosphination products with an (sp^3)C–PPh_2 bond and the use of expensive palladium, this method is presently the only reported two-step sequence for the synthesis of such compounds from readily available substrates, i.e., preligands of type **7**. It appears that CPCs with an (sp^3)C–Pd bond are somewhat less reactive toward $KPPh_2$ than their analogs with an (sp^2)C–Pd bond. A diphosphido-bridged cyclopalladated complex, **4c**, was for the first time isolated and fully characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. Using the knowledge obtained in our studies of stoichiometric reactions of CPCs with metal phosphides, we are currently investigating related Pd-catalyzed transformations.

4. Experimental

4.1. General methods and materials

Routine ^{1}H (500 MHz), $^{13}C\{^{1}H\}$ (126 MHz), and $^{31}P\{^{1}H\}$ (202 MHz) as well as DEPT, COSY, and HSQC 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, *J*, are given in Hz. Spectra were recorded in $CDCl_3$ unless stated otherwise. Melting points were measured on a Laboratory Devices Mel-Temp apparatus and are uncorrected. Optical rotations were measured at rt on a Rudolph Autopol III automatic polarimeter. Analytical TLC was performed on Whatman silica gel 60 (F_{254}) 250 precoated plates. Preparative TLC was carried out using 200 × 250 mm glass plates with an unfixed layer of Merck silica gel 60 (230 mesh) containing ca. 5% of silica gel with fluorescent indicator (Aldrich). Compounds were visualized on TLC plates using UV light (254 nm) and/or iodine stain. Methoxyamine hydrochloride was purchased from Alfa Aesar, D-camphor from Fisher Scientific. All other reagents were acquired from Sigma-Aldrich and used as purchased. $Pd(OAc)_2$ was purified by dissolving in hot benzene, filtering the solution and removing the solvent on a rotavapor. NaOAc and $Pd(OAc)_2$ were dried in vacuum prior to use. Benzene, CH_2Cl_2 and hexane were purified by distillation over CaH_2. Toluene and THF were dried by refluxing over K/benzophenone ketyl and distilled under Ar immediately before starting a reaction.

4.2. Synthesis of the starting compounds **1a**–**g**

Complexes **1a**–**g** were synthesized using published procedures [5,15,22,25,27–29]. The NMR spectra of the obtained compounds matched those reported in the literature.

4.3. Synthesis and characterization of new compounds

4.3.1. (R,R)-1-{(Diphenylphosphino)methyl}-7,7-dimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (**2a**)

CPC **1a** (0.0723 g, 0.112 mmol) was added to a 25-mL Schlenk flask containing a magnetic stirring bar. The flask was evacuated and filled with Ar 5 times. Abs. THF (15 mL) was then added using a syringe followed by a 0.5 M solution of $KPPh_2$ (1 mL, 0.5 mmol). During the dropwise addition of $KPPh_2$ for 5 min, the yellow solution turned dark red. The mixture was stirred at rt for 18 h in Ar. The Schlenk flask was then placed on a rotavapor to remove THF. The dark-red solid residue was dissolved in CH_2Cl_2 (2 mL) and quickly separated into several fractions using preparative TLC (10:1 hexane–ethyl acetate). Fraction 3 corresponded to the product (0.0492 g, 0.135 mmol, 21%, colorless oil). $[\alpha]^{22}_{D}$ +154, $[\alpha]^{22}_{546}$ +173 (*c* 0.0460, EtOH). R_f 0.63 (10:1 hexane–ethyl acetate). ^{1}H NMR (δ, ppm): 0.83 (s, 3H, CH_3), 0.94 (s, 3H, CH_3), 1.20 (m, 1H, H(5endo)), 1.64 (m, 1H, H(6endo)), 1.77 (m, 2H, H(5exo), H(6exo)), 1.84 (m, 1H, H(4)), 1.95 (d, 1H, $^{2}J_{3endo,3exo}$ = 17.6, H(3endo)), 2.15 (dd, 1H, $^{2}J_{H,H}$ = 15.0, $^{3}J_{H,P}$ = 4.1, PCH^{A}), 2.48 (ddd, 1H, $^{2}J_{3exo,3endo}$ = 17.6, $^{3}J_{3exo,4} \approx {}^{4}J_{3exo,5exo} \approx$ 4.3, H(3exo)), 2.52 (dd, 1H, $^{2}J_{H,H}$ = 15.0, $^{3}J_{H,P}$ = 4.1, PCH^{B}), 3.76 (s, 3H, OCH_3), 7.32 (m, 6H, *m*- and *p*-PPh), 7.51 (m, 4H, *o*-PPh). $^{13}C\{^{1}H\}$ NMR (δ, ppm): 19.8 and 20.1 (two CH_3), 27.5 (d, $^{1}J_{C,P}$ = 18, PCH_2), 27.8 (CH_2, C(5)), 30.9 (CH_2, d, $^{3}J_{C,P}$ = 12, C(6)), 33.7 (CH_2, C(3)), 44.2 (CH, C(4)), 49.8 (quat. C, d, $^{3}J_{C,P}$ = 3.9, C(7)), 54.6 (quat. C, d, $^{2}J_{C,P}$ = 14, C(1)), 61.8 (OCH_3), 128.27, 128.47, 128.52, 128.76, 128.81 (all CH, *m*- and *p*-PPh; the signal at 128.81 ppm has a double intensity), 133.0 (CH, d, $^{2}J_{C,P}$ = 19, *o*-PPh^{A}), 133.7 (CH, d, $^{2}J_{C,P}$ = 20, *o*-PPh^{B}), 141.2 (quat. C, d, $^{1}J_{C,P}$ = 15, *ipso*-PPh^{A}), 141.3 (quat. C, d, $^{1}J_{C,P}$ = 17, *ipso*-PPh^{B}), 167.9 (quat. C, C=N). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, ppm): −36.9. $^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, ppm): −23.2. HRMS: $[M + H]^+$ calcd for $C_{23}H_{28}NOP$ 366.1981, found 366.1979.

4.3.2. (R,R)-μ-Chloro-μ-(diphenylphosphido)bis{[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N} dipalladium(II) (**3a**)

The reaction was performed as described above for **2a** except that 1 equiv. of $KPPh_2$ was used and the reaction time was 1 h. After solvent removal, the crude product was dissolved in ethyl acetate (2 mL) and separated into several fractions using preparative TLC (10:1 hexane–ethyl acetate). Fraction 2 corresponded to complex **3a** (0.0198 g, 0.0249 mmol, 31%, orange solid). Mp: 194–196 °C; R_f 0.50 (10:1 hexane–ethyl acetate); $[\alpha]^{22}_{D}$ −189, $[\alpha]^{22}_{546}$ −-190 (*c* 0.0650, EtOH). IR (Nujol mull, ν, cm^{-1}): 1674 (C=N). ^{1}H NMR (δ, ppm): 0.62 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 0.74 (m, 1H, $PdCH^{A}$), 1.27 (ddd, 1H, $^{3}J_{5endo,6endo}$ = 13, $^{2}J_{5endo,5exo}$ = 9.6, $^{3}J_{5endo,6exo}$ = 4.3, H(5endo)), 1.39 (d, 1H, $^{2}J_{H,H}$ = 10, $PdCH^{B}$), 1.64 (td, 1H, $^{2}J_{6exo,6endo} = {}^{3}J_{6endo,5endo}$ = 13, $^{3}J_{6endo,5exo}$ = 4.5, H(6endo)), 1.79 (m, 1H, H(5exo)), 1.91 (d, 1H, $^{2}J_{3endo,3exo}$ = 19, H(3endo)), 1.96 (ddd, 1H, $^{2}J_{6exo,6endo}$ = 13, $^{3}J_{6exo,5exo}$ = 9.6, $^{3}J_{6exo,5endo}$ = 4.3, H(6exo)), 1.99 (t, 1H, $^{3}J_{4,5exo} = {}^{3}J_{4,3exo}$ = 4, H(4)), 2.37 (dt, 1H, $^{2}J_{3exo,3endo}$ = 19, $^{3}J_{3exo,4} = {}^{4}J_{3exo,5exo}$ = 4, H(3exo)), 3.97 (s, 3H, OCH_3), 7.30 (m, 6H, *m*- and *p*-PPh), 7.84 (m, 4H, *o*-PPh). $^{13}C\{^{1}H\}$ NMR (δ, ppm): 18.5 and 20.2 (two CH_3), 19.4 (d, $^{1}J_{C,P}$ = 2.2, PCH_2), 27.3 (CH_2, C(5)), 33.4 (CH_2, C(3)), 33.8 (CH_2, C(6)), 46.8 (CH, C(4)), 48.2 (quat. C, C(7)), 62.7 (OCH_3), 65.9 (quat. C, C(1)), 127.9 (CH, d, $^{3}J_{C,P}$ = 10, *m*-PPh), 128.5 (CH, d, $^{4}J_{C,P}$ = 2.2, *p*-PPh), 134.4 (CH, d, $^{2}J_{C,P}$ = 12, *o*-PPh), 138.3 (quat. C, d, $^{1}J_{C,P}$ = 32, *ipso*-PPh), 186.1 (quat. C, C=N). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, ppm): 4.9; $^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, ppm): 18.0. Anal. Calcd for $C_{34}H_{46}ClN_2O_2PPd_2$: C, 51.43; H, 5.84; N, 3.53%. Found: C, 51.14; H, 5.85; N, 3.49%.

4.3.3. (R,R)-Di-μ-(diphenylphosphido)bis{[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N}dipalladium(II) (**4a**)

The reaction was performed as described above for **2a**. The purification by preparative TLC was performed using 5:1 hexane–ethyl acetate as an eluent. The use of halogenated solvents, such as CH_2Cl_2 and $CHCl_3$, was avoided during all steps of the product purification. The upper fraction on the TLC plate corresponded to the product (0.0163 g, 0.0173 mmol, ca. 26%, brown solid). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, ppm): −76.9; $^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, ppm): −64.3.

4.3.4. (R,R)-1-{(Diphenyloxophosphino)methyl}-7,7-dimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (**8a**)

Phosphine **2a** was exposed to the air to give the corresponding oxide as an orange-yellow oil in a quantitative yield. $[\alpha]^{23}_{D}$ −18, $[\alpha]^{23}_{546}$ −13 (*c* 0.099, EtOH). R_f 0.57 (5:3 hexane–acetone). IR (CH_2Cl_2, ν, cm^{-1}): 1671 (C=N), 1184 (P=O). ^{1}H NMR (δ, ppm): 0.81 (s, 3H, CH_3), 1.04 (s, 3H, CH_3), 1.12 (m, 1H, H(5endo)), 1.30 (m, 1H, H(6endo)), 1.82 (m, 2H, H(5exo), H(4)), 1.88 (d, 1H, $^{2}J_{3endo,3exo}$ = 18, H(3endo)), 2.15 (t, 1H, $^{2}J_{H,H} = {}^{3}J_{H,P}$ = 16, PCH^{A}), 2.40 (m, 2H, H(6exo), H(3exo)), 3.06 (dd, 1H, $^{2}J_{H,H} = {}^{3}J_{H,P}$ = 16, PCH^{B}), 3.72 (s, 3H, OCH_3), 7.45 (m, 6H, *o*- and *p*-PPh), 7.77 (m, 2H, *m*-PPh^{A}), 7.95 (m, 2H, *m*-PPh^{B}). $^{13}C\{^{1}H\}$ NMR (δ, ppm): 19.6 and 19.9 (two CH_3), 27.3 (d, $^{1}J_{C,P}$ = 73, PCH_2), 28.0 (CH_2, C(5)), 29.4 (CH_2, d, $^{3}J_{C,P}$ = 5.1, C(6)), 33.8 (CH_2, C(3)), 43.2 (CH, C(4)), 50.3 (quat. C, d, $^{3}J_{C,P}$ = 4.6, C(7)), 53.2 (quat. C, d, $^{2}J_{C,P}$ = 4.9, C(1)), 61.7 (OCH_3), 128.6 (CH, d, $^{2}J_{C,P}$ = 12, *o*-PPh^{A}), 128.8 (CH, d, $^{2}J_{C,P}$ = 12, *o*-PPh^{B}), 130.8 (CH, d, $^{3}J_{C,P}$ = 8.9, *m*-PPh^{A}), 131.6 (CH, br. s, *p*-PPh), 131.7 (CH, d, $^{3}J_{C,P}$ = 9.4, *m*-PPh^{B}), 134.9 (quat. C, d, $^{1}J_{C,P}$ = 98, *ipso*-PPh^{A}), 136.6 (quat. C, d, $^{1}J_{C,P}$ = 99, *ipso*-PPh^{B}), 167.5 (quat. C, d, $^{4}J_{C,P}$ = 5.3, C=N). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, δ, ppm): 15.1. $^{31}P\{^{1}H\}$ NMR (C_6D_6, δ, ppm): 25.0. HRMS: $[M + H]^+$ calcd for $C_{23}H_{28}NO_2P$ 382.1894, found 382.1894.

4.3.5. (S,S)-1-{(Diphenylphosphino)methyl}-3,3-dimethylbicyclo [2.2.1]heptan-2-one O-Methyloxime (**2b**)

The reaction was performed as described above for **2a** using complex **1b** (0.0794 g, 0.123 mmol). The reaction mixture was separated into several fractions using preparative TLC (10:1 hexane–ethyl acetate). Fraction 3 corresponded to compound **2b** (0.0461 g, 0.126 mmol, 51%, colorless oil). $[\alpha]^{24}_{D}$ +138, $[\alpha]^{24}_{546}$ +171, $[\alpha]^{24}_{435}$ +246 (*c* 0.150, EtOH). R_f 0.65 (10:1 hexane–ethyl acetate). ^{1}H NMR (δ, ppm): 1.19, 1.25 (two s, 6H, $2CH_3$), 1.31 (d, 1H, $^2J_{7A,7B}$ = 10.1, H(7A)), 1.42 (m, 1H, H(6endo)), 1.50 (m, 1H, H(5endo)), 1.58 (br. d, 1H, H(7B)), 1.75 (m, 2H, H(4), H(5exo)), 1.92 (tq, 1H, $^2J_{6exo,6endo} = {}^3J_{6exo,5endo}$ = 12.0, $^3J_{6exo,5exo} \approx {}^4J_{6exo,P} \approx$ 1.8, H(6exo)), 2.46 (dd, 1H, $^2J_{H,H}$ = 14.7, $^2J_{H,P}$ = 3.5, PCH^A), 2.59 (dd, 1H, $^2J_{H,H}$ = 14.7, $^2J_{H,P}$ = 4.1, PCH^B), 3.73 (s, 3H, OCH_3), 7.30 (m, 6H, *m*- and *p*-PPh), 7.47 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (δ, ppm): 22.5 and 23.1 (two CH_3), 25.0 (CH_2, C(5)), 30.7 (d, $^1J_{C,P}$ = 13.1, PCH_2), 33.3 (d, CH_2, $^3J_{C,P}$ = 9.2, C(6)), 41.2 (CH_2, C(7)), 44.3 (CH, C(4)), 48.3 (d, C, C(3)), 52.6 (d, C, $^2J_{C,P}$ = 16.7, C(1)), 61.2 (OCH_3), 128.22, 128.27, 128.32 (*m*- and *p*-PPh), 132.8 (d, $^2J_{C,P}$ = 19.2, *o*-PPh^A), 133.0 (d, $^2J_{C,P}$ = 19.3, *o*-PPh^B), 139.9 (d, $^1J_{C,P}$ = 12.6, *ipso*-PPh^A), 140.0 (d, $^1J_{C,P}$ = 10.8, *ipso*-PPh^B), 171.9 (C=N). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): −37.1. HRMS: $[M + H]^+$ calcd for $C_{23}H_{28}NOP$ 366.1981, found 366.1964.

4.3.6. (S,S)-μ-Chloro-μ-(diphenylphosphido)bis{[2-(methoxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl]methyl-C,N} dipalladium(II) (**3b**)

The reaction was performed as described above for the preparation of **3a** using complex **1b** (0.0817 g, 0.1268 mmol). The reaction mixture was separated into several fractions using preparative TLC (10:1 hexane–ethyl acetate). Fraction 2 corresponded to complex **3b** (0.0180 g, 0.0227 mmol, 56%, orange solid). $[\alpha]^{23}_{D}$ −121, $[\alpha]^{23}_{546}$ −147, $[\alpha]^{23}_{435}$ −204 (*c* 0.222, EtOH). Mp: 209–211 °C; R_f 0.55 (10:1 hexane–ethyl acetate). ^{1}H NMR (δ, ppm): 1.05 (dd, 1H, $^2J_{H,H}$ = 9.6, $^3J_{H,P}$ = 4.8, PdCH^A), 1.14, 1.20 (two s, 6H, $2CH_3$), 1.17 (m, 1H, H(7A)), 1.53 (m, 2H, H(6endo), 5endo)), 1.63 (m, 2H, H(7B), PdCH^B), 1.80 (m, 1H, H(5exo)), 1.91 (m, 2H, H(4), H(6exo)), 3.93 (s, 3H, OCH_3), 7.29 (m, 6H, *m*- and *p*-PPh), 7.82 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (δ, ppm): 22.5 and 23.0 (two CH_3), 25.6 (CH_2, C(5)), 25.7 (PCH_2), 35.1 (CH_2, C(6)), 43.4 (CH_2, C(7)), 44.0 (C, C(3)), 52.3 (CH, C(4)), 62.6 (OCH_3), 64.3 (C, C(1)), 127.9, (d, $^3J_{C,P}$ = 10.2, *m*-PPh), 128.4 (s, *p*-PPh), 134.4 (d, $^2J_{C,P}$ = 12.2, *o*-PPh), 138.6 (d, $^1J_{C,P}$ = 31.1, *ipso*-PPh), 190.6 (C=N). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): 2.2. Anal. Calcd for $C_{34}H_{46}N_2O_2PClPd_2$: C, 51.43; H, 5.84; N, 3.53%. Found: C, 51.30; H, 5.84; N, 3.52%.

4.3.7. μ-Chloro-μ-(diphenylphosphido)bis{2-[2-(4,4-dimethyloxazolin-2-yl)-2-methyl]propyl-C,N}dipalladium(II) (**3c**) and di-μ-chloro-μ-(diphenylphosphido)bis{2-[2-(4,4-dimethyloxazolin-2-yl)-2-methyl]propyl-C,N}tripalladium(II) (**6c**)

The reaction was performed as described for compound **2a** using CPC **1c** (30.2 mg, 0.0512 mmol) as a starting reactant. The reaction mixture first appeared yellow, then dark red, and finally dark yellow. The reaction mixture was separated into fractions using preparative TLC (3:1 benzene–acetone). Two pure compounds were isolated: complex **3c** as a white solid in 14% yield (5.2 mg) and complex **6c** as a bright yellow solid in 8% yield (2.9 mg). *Data for complex* ***3c***: R_f 0.48 (benzene); ^{1}H NMR (δ, ppm): 1.08 and 1.45 (two s, 6H each, two $(CH_3)_2C$), 1.21 (d, 2H, $^3J_{H,P}$ = 2.6, $PdCH_2$), 4.06 (s, 2H, OCH_2), 7.27 (m, 3H, *o*- and *m*-PPh), 7.83 (m, 2H, *p*-PPh); ^{13}C{^{1}H} NMR (δ, ppm): 27.8 and 28.0 (two $(CH_3)_2C$), 31.0 (CH_2Pd), 41.6 and 66.2 (two quat. C, two $C(CH_3)_2$), 81.8 (OCH_2), 127.4 (CH, d, $^3J_{C,P}$ = 9.8, *m*-PPh), 127.5 (CH, *p*-PPh), 134.2 (CH, d, $^2J_{C,P}$ = 11.3, *o*-PPh), 138.7 (quat. C, d, $^1J_{C,P}$ = 28.9, *ipso*-PPh), 181.1 (quat. C, C=N); ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): −1.93. Anal. Calcd for $C_{30}H_{42}N_2O_2PClPd_2$: C, 48.57; H, 5.71; N, 3.78%. Found: C, 48.77; H, 5.84; N, 3.59%. *Data for complex* ***6c***: R_f 0.07 (benzene), 0.70 (5:1 benzene–acetone); ^{1}H NMR (δ, ppm, C_6D_6): 1.05 and 1.24 (two s, 6H each, two $(CH_3)_2C$), 1.32 (s, 2H, $PdCH_2$), 3.31 (s, 2H, OCH_2), 6.85 (t, 4H, ^3J = 7.3, *m*-PPh), 6.94 (t, 2H, ^3J = 7.3, *p*-PPh), 7.58 (m, 4H, *o*-PPh); ^{13}C{^{1}H} NMR (δ, ppm, C_6D_6): 27.9 and 28.4 (two $(CH_3)_2C$), 33.7 (CH_2Pd), 42.2 and 66.9 (two $C(CH_3)_2$), 81.9 (OCH_2), 127.9 (t, $^3J_{CP}$ = 5.0, *m*-PPh), 128.9 (*p*-PPh), 135.0 (t, $^2J_{CP}$ = 7.5, *o*-PPh), 135.4 (t, $^1J_{CP}$ = 17.0, *ipso*-PPh), 182.1 (C=N); ^{31}P{^{1}H} NMR (δ, ppm, $CDCl_3$): 10.3; ^{31}P{^{1}H} NMR (δ, ppm, C_6D_6): 23.3. Anal. Calcd for $C_{42}H_{52}Cl_2N_2O_2P_2Pd_2$: C, 47.19; H, 4.90; N, 2.62%. Found: C, 47.32; H, 4.99; N, 2.58%.

4.3.8. Di-μ-(diphenylphosphido)bis{2-[2-(4,4-dimethyl-2-oxazolin-2-yl)-2-methyl]propyl-C,N}dipalladium(II) (**4c**)

The complex was obtained as a bright orange solid using the reaction conditions described for complexes **3c** and **6c** except for the purification step. After solvent removal from the reaction mixture, freshly distilled CH_2Cl_2 (ca. 1.5 mL) was added to the solid residue. The part of the reaction mixture soluble in CH_2Cl_2 was then purified by preparative TLC (3:1 benzene–acetone) to give **3c** and **6c**. The remaining reaction mixture (which was insoluble in CH_2CH_2) was dissolved in benzene. The solution was filtered and then the solvent was removed on a rotary evaporator yielding an orange solid. This solid was transferred to a filter, rinsed with hexane and dried under vacuum. Yield 23.9 mg (36%). R_f 0.97 (benzene); 0.70 (hexane). M.p. 152–155 °C (dec.). IR (CH_2Cl_2, ν, cm^{-1}): 1632 s (C=N). ^{1}H NMR (δ, ppm, C_6D_6): 0.57 and 1.31 (two s, 6H each, two $(CH_3)_2C$), 1.65 (s, 2H, $PdCH_2$), 3.37 (s, 2H, OCH_2), 7.06 (m, 2H, *p*-PPh), 7.11(m, 4H, *m*-PPh), 8.13 (m, 4H, *o*-PPh). ^{13}C{^{1}H} NMR (δ, ppm, C_6D_6): 27.3 and 30.0 (two $(CH_3)_2C$), 42.2 (t, $^2J_{CP}$ = 55.1, CH_2Pd), 43.0 and 65.8 (two quat. C, two $C(CH_3)_2$), 81.7 (OCH_2), 127.3 (CH, *p*-PPh), 127.8 (CH, t, $^3J_{CP}$ = 3.6, *m*-PPh), 136.1 (CH, t, $^2J_{CP}$ = 5.6, *o*-PPh), 142.5 (quat. C, t, $^1J_{CP}$ = 3.0, *ipso*-PPh), 184.9 (quat. C, C=N). ^{31}P{^{1}H} NMR (δ, ppm, $CDCl_3$): −85.1; ^{31}P{^{1}H} NMR (δ, ppm, C_6D_6): −72.5.

4.3.9. 8-[(Diphenyloxophosphino)methyl]quinoline (**8d**)

Complex **1d** (0.1636 g, 0.2659 mmol) was added to an oven dried Ar-filled 50-mL Schlenk flask containing a magnetic stirring bar. The flask was evacuated and filled with Ar 5 times. Then abs. THF (17 mL) was added followed by a 0.5 M solution of $KPPh_2$ in THF (3.2 mL, 1.6 mmol). During the dropwise addition, the orange solution turned dark red, and then black. The mixture was stirred at rt for 48 h in Ar. The reaction mixture was then filtered through celite (h = 1 cm), and the flask with the filtrate was placed on a rotavapor to remove solvent. The crude product was dissolved in CH_2Cl_2 and separated into several fractions using preparative TLC (10:1 ethyl acetate–acetone). Fraction 1 corresponded to 8-methylquinoline **7d** (0.0450 g, 0.314 mmol, 48%, colorless oil). Fraction 3 corresponded to compound **8d** (0.0321 g, 0.0231 mmol, 21%, colorless oil). R_f 0.40 (10:1 ethyl acetate–acetone). ^{1}H NMR (δ, ppm): 4.56 (d, 2H, $^2J_{H,P}$ = 14.2, PCH_2), 7.28 (t, 1H, $^3J_{H,H}$ = 4.2, arom. H(3)), 7.31 (m, 4H, *o*-PPh), 7.38 (dt, 2H, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 1.3, *p*-PPh), 7.46 (t, 1H, $^2J_{H,P}$ = 15.4, arom. H(6)), 7.64 (d, 1H, $^3J_{H,P}$ = 8.2, arom. H(7)), 7.78 (m, 4H, *m*-PPh), 8.03 (dd, 1H, $^3J_{H,H}$ = 8.2, $^5J_{H,H}$ = 1.6, arom. H(5)), 8.05 (m, 1H, arom. H(4)), 8.76 (dd, 1H, $^3J_{H,H}$ = 4.1, $^5J_{H,H}$ = 1.6, arom. H(2)). ^{13}C{^{1}H} NMR (δ, ppm): 21.2 (d, $^1J_{C,P}$ = 67.9, PCH_2), 121.2 (s, arom. CH(3)), 126.8 (d, $^3J_{C,P}$ = 2.8, arom. CH(6)), 127.2 (d, $^4J_{C,P}$ = 1.0, arom. CH(7)), 128.5 (d, $^2J_{C,P}$ = 11.6, *o*-PPh), 131.2 (d, $^2J_{C,P}$ = 7.7, *ipso*-PPh), 131.55 (s, arom. CH(5)), 131.56 (d, $^2J_{C,P}$ = 9.2, *m*-PPh), 131.8 (d, $^2J_{C,P}$ = 2.3, *p*-PPh), 133.0 (s, arom. C(10)), 133.8 (two s, (s, arom. CH(8)), 136.6 (s, arom. CH(4)), 146.7 (d, $^2J_{C,P}$ = 5.5, arom. CH(9)), 149.4 (s, CH, arom. CH(2)). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): 16.5. IR (Nujol mull, ν, cm^{-1}): 1199 s (P=O). HRMS: $[M + H]^+$ calcd for $C_{22}H_{19}NOP$ 343.1199, found 344.1108.

4.3.10. μ-Chloro-μ-(diphenylphosphido)bis(8-quinolinylmethyl-C,N)dipalladium (**3d**)

The reaction was performed as described above for preparation of **3a** using CPC **1d** (0.0498 g, 0.0693 mmol). The reaction mixture was separated into several fractions using preparative TLC (10:1 benzene–acetone). Fraction 1 corresponded to complex **3d** (0.0258 g, 0.0359 mmol, 56%, orange powder). Mp: 237–239 °C; R_f 0.65 (15:1 toluene–ethyl acetate). ^{1}H NMR (δ, ppm): 3.02 (s, 2H, CH_2), 7.35 (m, 6H, *m*- and *p*-PPh), 7.40 (t, 1H, $^3J_{H,H} = 7.5$, arom. CH), 7.45 (d, 1H, $^3J_{H,H} = 7.0$, arom. CH), 7.50 (dd, 1H, $^3J_{H,H} \approx 8.3$, $^4J_{H,H} \approx 4.7$, arom. CH), 7.56 (d, 1H, $^3J_{H,H} \approx 7.7$, arom. CH), 8.00 (m, 4H, *o*-PPh) 8.25 (dd, 1H, $^3J_{H,H} \approx 8.2$, $^4J_{H,H} \approx 1.3$, arom. CH), 9.11 (m, 1H, arom. CH). ^{13}C{^{1}H} NMR (δ, ppm): 25.7 (CH_2, CH_2), 120.9 (d, $^4J_{C,P} = 2.7$, CH), 123.4 (s, CH), 127.5 (s, CH), 127.9, (d, $^3J_{C,P} = 10.0$, *m*-PPh), 128.2 (d, $^4J_{C,P} = 2.5$, CH), 129.0 (s, C), 129.3 (s, *p*-PPh), 134.1 (d, $^2J_{C,P} = 11.9$, *o*-PPh), 137.7 (s, CH), 137.8 (d, $^1J_{C,P} = 32.1$, *ipso*-PPh), 146.8 (s, CH), 149.6 (s, C), 151.0 (d, $^4J_{C,P} = 1.9$, C). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): 10.2. Anal. Calcd for $C_{32}H_{26}N_2PClPd_2$: C, 53.54; H, 3.65; N, 3.90%. Found: C, 53.27; H, 3.80; N, 3.85%.

4.3.11. [2-(Di-ortho-tolylphosphino)benzyl]diphenylphosphine oxide (**8f**)

Complex **1f** (0.0690 g, 0.0775 mmol) was added to an oven dried Ar-filled 25-mL Schlenk flask containing a magnetic stirring bar. The flask was evacuated and filled with Ar 5 times. Then abs. THF (10 mL) was added followed by a 0.5 M solution of $KPPh_2$ in THF (0.7 mL, 0.3 mmol). During the dropwise addition, the yellow solution turned dark red, and then brown. The mixture was stirred at rt for 48 h in Ar and then 48 h in air. The reaction mixture was then filtered through celite (h = 1 cm), and the flask with the filtrate was placed on a rotavapor to remove solvent. The mixture was separated into several fractions using preparative TLC (10:1 ethyl acetate–acetone). Fraction 1 corresponded to tri(*O*-tolyl)phosphine **7f** (0.001 g, 0.003 mmol, 2%, white powder). Fraction 2 corresponded to product **8f** (0.00147 g, 0.0303 mmol, 20%, pale yellow oil). R_f 0.59 (10:1 ethyl acetate–acetone). ^{1}H NMR (δ, ppm): 2.26 (s, 6H, CH_3), 4.00 (d, 2H, $^2J_{H,P} = 9.6$, PCH_2), 6.61 (dd, 2H, $^3J_{H,P} = 7.4$, $^3J_{H,H} = 4.6$, arom. CH of C_6H_4–CH_2P), 7.00 (dd, 1H, $^3J_{H,H} = 7.6$, $^4J_{H,P} = 3.9$, arom. CH of C_6H_4–CH_2P), 7.05 (m, 3H, arom. CH(3), CH(5) of tolyl), 7.20 (t, 2H, $^3J_{H,H} = 6.0$, arom. CH(4) of tolyl), 7.23–7.30 (m, 3H, arom. CH(3), CH(6) of tolyl), 7.35 (td, 4H, $^3J_{H,P} = 7.5$, $^3J_{H,H} = 2.8$, *o*-PPh), 7.42 (t, 2H, $^3J_{H,H} = 6.9$, *p*-PPh), 7.74 (dd, 4H, $^3J_{H,P} = 11.4$, $^3J_{H,H} = 7.4$, *m*-PPh), 7.95 (t, 1H, $^3J_{H,H} = 6.3$, arom. CH of C_6H_4–CH_2P). ^{13}C{^{1}H} NMR (δ, ppm): 21.6, 21.8 (two s, CH_3), 35.0 (dd, $^1J_{C,P} = 67.2$, $^3J_{C,P} = 25.9$, PCH_2), 126.7(s, arom. CH(5) of tolyl), 127.8 (s, arom. CH(3) of tolyl), 128.8 (d, $^3J_{C,P} = 11.7$, *o*-PPh), 129.3 (s, arom. CH(6) of tolyl), 129.6 (s, arom. CH(3) of tolyl), 130.5 (d, $^4J_{C,P} = 4.7$, arom. CH(4) of tolyl), 131.2 (t, $^4J_{C,P} = 4.3$, arom. CH of C_6H_4–CH_2P), 131.5 (d, $^3J_{C,P} = 9.4$, *m*-PPh), 132.0 (s, *p*-PPh), 133.3 (d, $^1J_{C,P} = 99.3$, arom. C(1) of tolyl), 133.5 (s, arom. CH of C_6H_4–CH_2P), 134.3 (s, arom. CH of C_6H_4–CH_2P), 134.5 (d, $^2J_{C,P} = 9.3$, PPh), 135.0 (t, $^3J_{C,P} = 8.4$, arom. CH of C_6H_4–CH_2P), 137.7 (dd, $^1J_{C,P} = 26.4$, $^3J_{C,P} = 6.3$, arom. C of C_6H_4–CH_2P), 142.8 (d, $^1J_{C,P} = 25.9$, C(2) of tolyl). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): −45.08 and 15.35 (two d, $^4J_{P,P} = 9.2$). IR (Nujol mull, ν, cm^{-1}): 1198 s (P═O). HRMS: $[M + Na + H]^+$ calcd for $C_{33}H_{30}O_2P_2Na$ 543.1691, found 543.1440.

4.3.12. [6-Methyl-1-(methylthio)benzyl]diphenylphosphine oxide (**8g**)

The compound was obtained using the procedure described above for oxide **8f** using complex **1g** (0.1309 g, 0.2233 mmol). The reaction mixture was separated using preparative TLC (10:1 ethyl acetate–acetone). Fraction 1 corresponded to 2,6-dimethylthioanisole **7g** (0.0483 g, 0.317 mmol, 71%, colorless oil). Fraction 2 corresponded to compound **8g** (0.0351 g, 0.0996 mmol, 22%, purple oil). R_f 0.50 (10:1 ethyl acetate–acetone). ^{1}H NMR (δ, ppm): 2.04 (s, 3H, CH_3), 2.48 (s, 3H, SCH_3), 4.24 (d, 2H, $^2J_{H,P} = 14.1$, PCH_2), 7.10 (m, 2H, arom. H(4), H(5)), 7.33 (m, 1H, arom. H(3)), 7.42 (dt, 4H, $^3J_{H,P} = {}^3J_{H,H} = 7.7$, $^4J_{H,H} = 2.7$, *o*-PPh), 7.49 (dt, 2H, $^3J_{H,H} = 7.4$, $^4J_{H,H} = 1.3$, *p*-PPh), 7.72 (dd, 4H, $^3J_{H,H} = 7.2$, $^3J_{H,H} = 7.2$, *m*-PPh). ^{13}C{^{1}H} NMR (δ, ppm): 19.1 (s, CH_3), 22.2 (s, SCH_3), 36.6 (d, $^1J_{C,P} = 67.0$, PCH_2), 128.6 (d, $^5J_{C,P} = 1.7$, arom. CH(5)), 128.8 (d, $^2J_{C,P} = 11.8$, *o*-PPh), 129.0 (d, $^3J_{C,P} = 4.8$, CH(3)), 129.7 (d, $^4J_{C,P} = 2.7$, arom. CH(4)), 131.7 (d, $^3J_{C,P} = 9.1$, *m*-PPh)), 132.1 (d, $^4J_{C,P} = 2.8$, *p*-PPh), 132.7 (s, C(6)), 133.5 (s, C(2)), 136.36 (t, $^1J_{C,P} = 9.2$, *ipso*-PPh), 143.5 (s, C(1)). ^{31}P{^{1}H} NMR ($CDCl_3$, δ, ppm): 15.03. IR (Nujol mull, ν, cm^{-1}): 1187 s (P═O). HRMS: $[M + H]^+$ calcd for $C_{21}H_{22}OPS$ 353.1123, found 353.1005.

Acknowledgment

The authors acknowledge financial support from the University of North Dakota and ND EPSCoR through NSF grant No. EPS-0-0184442. We would also like to thank Dr. V.A. Stepanova for help with experimental techniques.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.07.023.

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