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

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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.

Keywords: Cyclopalladated complex; N,P , S,P , P,P Ligands; (sp^3)C–Pd Bond; Phosphination; $KPPh_2$

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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 $KPPh_2$.

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

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

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

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 $(sp^2)\text{C-Pd}$ 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 $\mu\text{-Cl-}\mu\text{-PPh}_2$ complex **3a** in 16%. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of one of the fractions contained the singlet of complex **4a** at δ -64.7 ppm [in C_6D_6 relative to $\text{P}(\text{OEt})_3$] and two doublets, δ 21.8 and 113.5 ppm, $J_{\text{P,P}} = 36$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of 123.2 ppm has been reported for complexes with the PAR_2 group as a terminal ligand bonded to $\text{Pd}(\text{II})$ [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 $\text{Pd}(\text{II})$ 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**.

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

To test whether the μ -Cl- μ -PPh₂ complex **3a** could be converted to its di- μ -PPh₂ analog **4a** and/or phosphine **2a**, it was reacted with 1 equiv. of KPhP₂. 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 -PPh₂ CPC **4a** was converted to compound **2a** in 27% yield by reaction with 2.5 equiv. of KPhP₂ in THF (rt, 96 h). It is noteworthy that the formation of the *N,P* ligand **2a** from CPC **4a** was slower than that from CPC **1a** using 4.5 equiv. of KPhP₂ in the same solvent (³¹P{¹H} NMR data).

Then we studied the fenchone-derived CPC **1b** [22] in reactions with KPhP₂. The reaction of CPC **1b** with 4.5 equiv. of KPhP₂ in THF furnished the enantiopure *N,P* ligand **2b** in 51% yield (Scheme 4). Using 1 equiv. of KPhP₂, CPC **1b** was converted to the μ -Cl- μ -PPh₂-bridged derivative **3b** in 56% yield. ¹H, ¹³C{¹H} and ³¹P{¹H} NMR data for complex **3b** suggest that this and other μ -Cl- μ -PPh₂-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.

Scheme 4. Reactions of the fenchone-derived CPC **1b** with KPPH_2 .

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 $\text{P}(\text{OEt})_3$ [24], Figure 1) was detected either in the $^{31}\text{P}\{^1\text{H}\}$ 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 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.

Scheme 5. Reaction of CPC **1c** with KPPH_2 .

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

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].

Scheme 6. Reactions of CPCs **1d** with KPPH_2 .

When 1 equiv. of KPPH_2 was used in the reaction, the $\mu\text{-Cl-}\mu\text{-PPh}_2$ -bridged derivative **3d** was isolated in 56% (Scheme 7). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3d** had a singlet at δ 10.2 ppm [CDCl_3 relative to $\text{P}(\text{OEt})_3$] 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 $\mu\text{-OAc-1d}$ 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.

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

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).

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

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 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).

Scheme 9. Reaction of complexes **1f** and $\mu\text{-OAc-1f}$ with KPPH_2 .

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 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).

Scheme 10. Reaction of CPC **1g** with KPPH_2 .

2.2. Structure confirmation

According to the literature [30], non-coordinated tertiary phosphines provide $^{31}\text{P}\{^1\text{H}\}$ 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). ³¹P{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 ¹³C{¹H} NMR signals of the CH₂P fragment in compounds **2a,b** and **8a,d,f,g** displayed J_{H,P} and J_{C,P} coupling constants. Diastereotopic hydrogens of the CH₂P 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 PCH₂ 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 ¹³C{¹H} NMR spectra. The CH₂P 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 ¹³C{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 $\mu\text{-Cl-}\mu\text{-PPh}_2$ Pd(II) complexes **3a,c** presumably have a syn configuration with the PPh₂ bridging ligand trans to both nitrogen atoms. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of CPCs **3a,c** in CDCl₃ exhibited singlets at δ 4.9 and -1.9 ppm, respectively. In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these complexes, the signal of the CH₂Pd fragment appeared as a doublet ($^2J_{\text{C,P}} = 2.2$ 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 ($^2J_{\text{C,P}} = 1.8$ Hz) [11]. The ^1H NMR spectra of complexes **3a,c** confirmed a 1:2 ratio of the PPh₂ group and cyclopalladated ligands in their structures. The elemental composition and purity of these compounds were confirmed by satisfactory elemental analysis.

Di- $\mu\text{-PPh}_2$ 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of known di- $\mu\text{-PPh}_2$ Pd(II) complexes usually have the signals of the bridging PPh₂ group between -100 and -140 ppm [19,20,34,35]. We were able to isolate two complexes, **4a,c**, which presumably have dimeric cyclopalladated structure with two bridging PPh₂ ligands. The ^1H NMR spectrum of the oxazoline-derived complex **4c** suggests a 1:1 ratio of the PPh₂ fragment and the cyclopalladated ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the same compound in CDCl₃ exhibited a lone singlet at δ -85.1 ppm (-72.5 ppm in C₆D₆), which suggests the anti configuration of the cyclopalladated ligands. The $^{13}\text{C}\{^1\text{H}\}$ NMR signal of the CH₂Pd fragment in **4c** appeared at δ 42.2 ppm as a triplet with $J_{\text{C,P}}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4c** and **6c** were quite different. The $^{31}\text{P}\{^1\text{H}\}$ 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 $\mu\text{-Cl-}\mu\text{-PPh}_2$ complexes of type **3**. The $^{13}\text{C}\{^1\text{H}\}$ 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 $(sp^3)\text{C-Pd}$ 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 $(sp^3)\text{C-PPh}_2$ 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 KPh_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 1H (500 MHz), $^{13}C\{^1H\}$ (126 MHz), and $^{31}P\{^1H\}$ (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 (1H 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 (F₂₅₄) 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, CH₂Cl₂ and hexane were purified by distillation over CaH₂. 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 KPPH₂ (1 mL, 0.5 mmol). During the dropwise addition of KPPH₂ 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 CH₂Cl₂ (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). $[\alpha]_D^{22} +154$, $[\alpha]_{546}^{22} +173$ (*c* 0.0460, EtOH). *R_f* 0.63 (10:1 hexane–ethyl acetate). ¹H NMR (δ, ppm): 0.83 (s, 3H, CH₃), 0.94 (s, 3H, CH₃), 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} ≈ ⁴*J*_{3exo,5exo} ≈ 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, OCH₃), 7.32 (m, 6H, *m*- and *p*-PPh), 7.51 (m, 4H, *o*-PPh). ¹³C{¹H} NMR (δ, ppm): 19.8 and 20.1 (two CH₃), 27.5 (d, ¹*J*_{C,P} = 18,

PCH₂), 27.8 (CH₂, C(5)), 30.9 (CH₂, d, ³J_{C,P} = 12, C(6)), 33.7 (CH₂, C(3)), 44.2 (CH, C(4)), 49.8 (quat. C, d, ³J_{C,P} = 3.9, C(7)), 54.6 (quat. C, d, ²J_{C,P} = 14, C(1)), 61.8 (OCH₃), 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, ²J_{C,P} = 19, *o*-PPh^A), 133.7 (CH, d, ²J_{C,P} = 20, *o*-PPh^B), 141.2 (quat. C, d, ¹J_{C,P} = 15, *ipso*-PPh^A), 141.3 (quat. C, d, ¹J_{C,P} = 17, *ipso*-PPh^B), 167.9 (quat. C, C=N). ³¹P{¹H} NMR (CDCl₃, δ, ppm): -36.9. ³¹P{¹H} NMR (C₆D₆, δ, ppm): -23.2. HRMS: [M + H]⁺ calcd for C₂₃H₂₈NOP 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 KPh₂ 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); [α]_D²² -189, [α]₅₄₆²² -190 (c 0.0650, EtOH). IR (Nujol mull, ν, cm⁻¹): 1674 (C=N). ¹H NMR (δ, ppm): 0.62 (s, 3H, CH₃), 0.72 (s, 3H, CH₃), 0.74 (m, 1H, PdCH^A), 1.27 (ddd, 1H, ³J_{5endo,6endo} = 13, ²J_{5endo,5exo} = 9.6, ³J_{5endo,6exo} = 4.3, H(5endo)), 1.39 (d, 1H, ²J_{H,H} = 10, PdCH^B), 1.64 (td, 1H, ²J_{6exo,6endo} = ³J_{6endo,5endo} = 13, ³J_{6endo,5exo} = 4.5, H(6endo)), 1.79 (m, 1H, H(5exo)), 1.91 (d, 1H, ²J_{3endo,3exo} = 19, H(3endo)), 1.96 (ddd, 1H, ²J_{6exo,6endo} = 13, ³J_{6exo,5exo} = 9.6, ³J_{6exo,5endo} = 4.3, H(6exo)), 1.99 (t, 1H, ³J_{4,5exo} = ³J_{4,3exo} = 4, H(4)), 2.37 (dt, 1H, ²J_{3exo,3endo} = 19, ³J_{3exo,4} = ⁴J_{3exo,5exo} = 4, H(3exo)), 3.97 (s, 3H, OCH₃), 7.30 (m, 6H, *m*- and *p*-PPh), 7.84 (m, 4H, *o*-PPh). ¹³C{¹H} NMR (δ, ppm): 18.5 and 20.2 (two CH₃), 19.4 (d, ¹J_{C,P} = 2.2, PCH₂), 27.3 (CH₂, C(5)), 33.4 (CH₂, C(3)), 33.8 (CH₂, C(6)), 46.8 (CH, C(4)), 48.2 (quat. C, C(7)), 62.7 (OCH₃), 65.9 (quat. C, C(1)), 127.9 (CH, d, ³J_{C,P} = 10, *m*-

PPh), 128.5 (CH, d, $^4J_{C,P} = 2.2$, *p*-PPh), 134.4 (CH, d, $^2J_{C,P} = 12$, *o*-PPh), 138.3 (quat. C, d, $^1J_{C,P} = 32$, *ipso*-PPh), 186.1 (quat. C, C=N). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 4.9; $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , δ , ppm): 18.0. Anal. Calcd for $\text{C}_{34}\text{H}_{46}\text{ClN}_2\text{O}_2\text{PPd}_2$: 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): -76.9; $^{31}\text{P}\{^1\text{H}\}$ 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. $[\alpha]_D^{23} -18$, $[\alpha]_{546}^{23} -13$ (*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). ^1H 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, $^2J_{3\text{endo},3\text{exo}} = 18$, H(3endo)), 2.15 (t, 1H, $^2J_{\text{H,H}} = ^3J_{\text{H,P}} = 16$, PCH^{A}), 2.40 (m, 2H, H(6exo), H(3exo)), 3.06 (dd, 1H, $^2J_{\text{H,H}} = ^3J_{\text{H,P}} = 16$, 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). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 19.6 and 19.9 (two CH_3), 27.3 (d, $^1J_{C,P} = 73$, PCH_2), 28.0 (CH_2 , C(5)), 29.4 (CH_2 , d, $^3J_{C,P} = 5.1$, C(6)), 33.8 (CH_2 , C(3)), 43.2 (CH, C(4)), 50.3 (quat. C, d, $^3J_{C,P} = 4.6$, C(7)), 53.2 (quat. C, d, $^2J_{C,P} = 4.9$, C(1)), 61.7 (OCH_3), 128.6 (CH, d, $^2J_{C,P} = 12$, *o*-PPh^A), 128.8 (CH, d, $^2J_{C,P} = 12$, *o*-PPh^B), 130.8 (CH, d,

$^3J_{C,P} = 8.9$, *m*-PPh^A), 131.6 (CH, br. s, *p*-PPh), 131.7 (CH, d, $^3J_{C,P} = 9.4$, *m*-PPh^B), 134.9 (quat. C, d, $^1J_{C,P} = 98$, *ipso*-PPh^A), 136.6 (quat. C, d, $^1J_{C,P} = 99$, *ipso*-PPh^B), 167.5 (quat. C, d, $^4J_{C,P} = 5.3$, C=N). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ , ppm): 15.1. $^{31}\text{P}\{^1\text{H}\}$ NMR (C₆D₆, δ , ppm): 25.0. HRMS: [M + H]⁺ calcd for C₂₃H₂₈NO₂P 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** (0.0794g, 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). $[\alpha]^{24}_{\text{D}} +138$, $[\alpha]^{24}_{546} +171$, $[\alpha]^{24}_{435} +246$ (*c* 0.150, EtOH). *R*_f 0.65 (10:1 hexane–ethyl acetate). ^1H NMR (δ , ppm): 1.19, 1.25 (two s, 6H, 2CH₃), 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, $^2J_{6\text{exo},6\text{endo}} = ^3J_{6\text{exo},5\text{endo}} = 12.0$, $^3J_{6\text{exo},5\text{exo}} \approx ^4J_{6\text{exo},P} \approx 1.8$, 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, OCH₃), 7.30 (m, 6H, *m*- and *p*-PPh), 7.47 (m, 4H, *o*-PPh). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 22.5 and 23.1 (two CH₃), 25.0 (CH₂, C(5)), 30.7 (d, $^1J_{C,P} = 13.1$, PCH₂), 33.3 (d, CH₂, $^3J_{C,P} = 9.2$, C(6)), 41.2 (CH₂, 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 (OCH₃), 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ , ppm): -37.1. HRMS: [M + H]⁺ calcd for C₂₃H₂₈NOP 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). $[\alpha]_D^{23}$ -121, $[\alpha]_{546}^{23}$ -147, $[\alpha]_{435}^{23}$ -204 (*c* 0.222, EtOH). Mp: 209–211 °C; *R_f* 0.55 (10:1 hexane–ethyl acetate). ¹H NMR (δ , ppm): 1.05 (dd, 1H, ²*J_{H,H}* = 9.6, ³*J_{H,P}* = 4.8, PdCH^A), 1.14, 1.20 (two s, 6H, 2CH₃), 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, OCH₃), 7.29 (m, 6H, *m*- and *p*-PPh), 7.82 (m, 4H, *o*-PPh). ¹³C{¹H} NMR (δ , ppm): 22.5 and 23.0 (two CH₃), 25.6 (CH₂, C(5)), 25.7 (PCH₂), 35.1 (CH₂, C(6)), 43.4 (CH₂, C(7)), 44.0 (C, C(3)), 52.3 (CH, C(4)), 62.6 (OCH₃), 64.3 (C, C(1)), 127.9 (d, ³*J_{C,P}* = 10.2, *m*-PPh), 128.4 (s, *p*-PPh), 134.4 (d, ²*J_{C,P}* = 12.2, *o*-PPh), 138.6 (d, ¹*J_{C,P}* = 31.1, *ipso*-PPh), 190.6 (C=N). ³¹P{¹H} NMR (CDCl₃, δ , ppm): 2.2. Anal. Calcd for C₃₄H₄₆N₂O₂PClPd₂: 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); ¹H NMR (δ , ppm): 1.08 and 1.45 (two s, 6H each, two (CH₃)₂C), 1.21 (d, 2H, ³*J_{H,P}* = 2.6, PdCH₂), 4.06 (s, 2H, OCH₂), 7.27 (m, 3H, *o*- and *m*-PPh), 7.83 (m, 2H, *p*-PPh);

$^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 27.8 and 28.0 (two $(\text{CH}_3)_2\text{C}$), 31.0 (CH_2Pd), 41.6 and 66.2 (two quat. C, two $\text{C}(\text{CH}_3)_2$), 81.8 (OCH_2), 127.4 (CH , d, $^3J_{\text{C,P}} = 9.8$, *m*-PPh), 127.5 (CH , *p*-PPh), 134.2 (CH , d, $^2J_{\text{C,P}} = 11.3$, *o*-PPh), 138.7 (quat. C, d, $^1J_{\text{C,P}} = 28.9$, *ipso*-PPh), 181.1 (quat. C, C=N); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): -1.93. Anal. Calcd for $\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_2\text{PClPd}_2$: 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); ^1H NMR (δ , ppm, C_6D_6): 1.05 and 1.24 (two s, 6H each, two $(\text{CH}_3)_2\text{C}$), 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); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm, C_6D_6): 27.9 and 28.4 (two $(\text{CH}_3)_2\text{C}$), 33.7 (CH_2Pd), 42.2 and 66.9 (two $\text{C}(\text{CH}_3)_2$), 81.9 (OCH_2), 127.9 (t, $^3J_{\text{CP}} = 5.0$, *m*-PPh), 128.9 (*p*-PPh), 135.0 (t, $^2J_{\text{CP}} = 7.5$, *o*-PPh), 135.4 (t, $^1J_{\text{CP}} = 17.0$, *ipso*-PPh), 182.1 (C=N); $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm, CDCl_3): 10.3; $^{31}\text{P}\{^1\text{H}\}$ NMR (δ , ppm, C_6D_6): 23.3. Anal. Calcd for $\text{C}_{42}\text{H}_{52}\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2\text{Pd}_2$: 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). ^1H NMR (δ , ppm, C_6D_6): 0.57 and 1.31

(two s, 6H each, two (CH₃)₂C), 1.65 (s, 2H, PdCH₂), 3.37 (s, 2H, OCH₂), 7.06 (m, 2H, *p*-PPh), 7.11 (m, 4H, *m*-PPh), 8.13 (m, 4H, *o*-PPh). ¹³C{¹H} NMR (δ, ppm, C₆D₆): 27.3 and 30.0 (two (CH₃)₂C), 42.2 (t, ²J_{CP} = 55.1, CH₂Pd), 43.0 and 65.8 (two quat. C, two C(CH₃)₂), 81.7 (OCH₂), 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). ³¹P{¹H} NMR (δ, ppm, CDCl₃): -85.1; ³¹P{¹H} NMR (δ, ppm, C₆D₆): -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 KPPH₂ 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 CH₂Cl₂ 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). ¹H NMR (δ, ppm): 4.56 (d, 2H, ²J_{H,P} = 14.2, PCH₂), 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)). ¹³C{¹H} NMR (δ, ppm): 21.2 (d, ¹J_{C,P} = 67.9, PCH₂), 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)). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 16.5. IR (Nujol mull, ν , cm^{-1}): 1199 s (P=O). HRMS: $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{19}\text{NOP}$ 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). ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , δ , ppm): 10.2. Anal. Calcd for $\text{C}_{32}\text{H}_{26}\text{N}_2\text{PClPd}_2$: 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). ^1H NMR (δ , ppm): 2.26 (s, 6H, CH₃), 4.00 (d, 2H, $^2J_{\text{H,P}} = 9.6$, PCH₂), 6.61 (dd, 2H, $^3J_{\text{H,P}} = 7.4$, $^3J_{\text{H,H}} = 4.6$, arom. CH of C₆H₄-CH₂P), 7.00 (dd, 1H, $^3J_{\text{H,H}} = 7.6$, $^4J_{\text{H,P}} = 3.9$, arom. CH of C₆H₄-CH₂P), 7.05 (m, 3H, arom. CH(3), CH(5) of tolyl), 7.20 (t, 2H, $^3J_{\text{H,H}} = 6.0$, arom. CH(4) of tolyl), 7.23–7.30 (m, 3H, arom. CH(3), CH(6) of tolyl), 7.35 (td, 4H, $^3J_{\text{H,P}} = 7.5$, $^3J_{\text{H,H}} = 2.8$, *o*-PPh), 7.42 (t, 2H, $^3J_{\text{H,H}} = 6.9$, *p*-PPh), 7.74 (dd, 4H, $^3J_{\text{H,P}} = 11.4$, $^3J_{\text{H,H}} = 7.4$, *m*-PPh), 7.95 (t, 1H, $^3J_{\text{H,H}} = 6.3$, arom. CH of C₆H₄-CH₂P). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 21.6, 21.8 (two s, CH₃), 35.0 (dd, $^1J_{\text{C,P}} = 67.2$, $^3J_{\text{C,P}} = 25.9$, PCH₂), 126.7 (s, arom. CH(5) of tolyl), 127.8 (s, arom. CH(3) of tolyl), 128.8 (d, $^3J_{\text{C,P}} = 11.7$, *o*-PPh), 129.3 (s, arom. CH(6) of tolyl), 129.6 (s, arom. CH(3) of tolyl), 130.5 (d, $^4J_{\text{C,P}} = 4.7$, arom. CH(4) of tolyl), 131.2 (t, $^4J_{\text{C,P}} = 4.3$, arom. CH of C₆H₄-CH₂P), 131.5 (d, $^3J_{\text{C,P}} = 9.4$, *m*-PPh), 132.0 (s, *p*-PPh), 133.3 (d, $^1J_{\text{C,P}} = 99.3$, arom. C(1) of tolyl), 133.5 (s, arom. CH of C₆H₄-CH₂P), 134.3 (s, arom. CH of C₆H₄-CH₂P), 134.5 (d, $^2J_{\text{C,P}} = 9.3$, PPh), 135.0 (t, $^3J_{\text{C,P}} = 8.4$, arom. CH of C₆H₄-CH₂P), 137.7 (dd, $^1J_{\text{C,P}} = 26.4$, $^3J_{\text{C,P}} = 6.3$, arom. C of C₆H₄-CH₂P), 142.8 (d, $^1J_{\text{C,P}} = 25.9$, C(2) of tolyl). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ , ppm): -45.08 and 15.35 (two d, $^4J_{\text{P,P}} = 9.2$). IR (Nujol mull, ν , cm⁻¹): 1198 s (P=O). HRMS: $[\text{M} + \text{Na} + \text{H}]^+$ calcd for C₃₃H₃₀O₂P₂Na 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). ^1H NMR (δ , ppm): 2.04 (s, 3H, CH₃), 2.48 (s, 3H, SCH₃), 4.24 (d, 2H, $^2J_{\text{H,P}} = 14.1$, PCH₂), 7.10 (m, 2H, arom. H(4), H(5)), 7.33 (m, 1H, arom. H(3)), 7.42 (dt, 4H, $^3J_{\text{H,P}} = ^3J_{\text{H,H}} = 7.7$, $^4J_{\text{H,H}} = 2.7$, *o*-PPh), 7.49 (dt, 2H, $^3J_{\text{H,H}} = 7.4$, $^4J_{\text{H,H}} = 1.3$, *p*-PPh), 7.72 (dd, 4H, $^3J_{\text{H,H}} = 7.2$, $^3J_{\text{H,H}} = 7.2$, *m*-PPh). $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , ppm): 19.1 (s, CH₃), 22.2 (s, SCH₃), 36.6 (d, $^1J_{\text{C,P}} = 67.0$, PCH₂), 128.6 (d, $^5J_{\text{C,P}} = 1.7$, arom. CH(5)), 128.8 (d, $^2J_{\text{C,P}} = 11.8$, *o*-PPh), 129.0 (d, $^3J_{\text{C,P}} = 4.8$, CH(3)), 129.7 (d, $^4J_{\text{C,P}} = 2.7$, arom. CH(4)), 131.7 (d, $^3J_{\text{C,P}} = 9.1$, *m*-PPh), 132.1 (d, $^4J_{\text{C,P}} = 2.8$, *p*-PPh), 132.7 (s, C(6)), 133.5 (s, C(2)), 136.36 (t, $^1J_{\text{C,P}} = 9.2$, *ipso*-PPh), 143.5 (s, C(1)). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl₃, δ , ppm): 15.03. IR (Nujol mull, ν , cm⁻¹): 1187 s (P=O). HRMS: $[\text{M} + \text{H}]^+$ calcd for C₂₁H₂₂OPS 353.1123, found 353.1005.

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Supplementary Data

Supplementary data for this article contain ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of compounds **2a,b**, **3a–d**, **4c**, **7c** and **9a,d,f,g**.

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