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Synthesis And Applications Of Cyclopalladated Complexes Containing An (sp3)c-pd Bond

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SYNTHESIS AND APPLICATIONS OF CYCLOPALLADATED COMPLEXES CONTAINING AN $(sp^{3})$C–Pd BOND

By

Gerard C. Dickmu
Bachelor of Science, University of Buea, 2008

A Dissertation
Submitted to the Graduate School
of the
University of North Dakota
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for the degree of
Doctor of Philosophy

Grand Forks, North Dakota
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2015
This dissertation, submitted by Gerard Chepnda Dickmu in partial fulfillment of the requirements for the degree of Doctor of Philosophy from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done, and is hereby approved.

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Degree Doctor of Philosophy

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Gerard Chepnda Dickmu

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Date
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ABSTRACT

Cyclopalladated complexes (CPCs) possess a number of important properties and have been used in various application studies. However, preparation and uses of optically active CPCs with an \((sp^3)C\text{–}Pd\) bond have not been thoroughly investigated.

In this dissertation, the synthesis and applications of new enantiopure CPCs derived from naturally occurring and optically active \(D\)-camphor and \(L\)-fenchone are described. The preparation of these CPCs, which contain an \((sp^3)C\text{–}Pd\) bond, was accomplished by cyclopalladation of \(D\)-camphor \(O\)-methylxime, \(L\)-fenchone \(O\)-methylxime, \(L\)-fenchone oxime and camphor \(N,N\)-dimethylhydrazone using Pd(II) salts such as Pd(OAc)$_2$ and Pd(MeCN)$_2$Cl$_2$.

Phosphination reactions of CPCs derived from \(D\)-camphor \(O\)-methylxime and \(L\)-fenchone \(O\)-methylxime, as well as other \(CN\)-, \(CS\)- and \(CP\)-dimeric CPCs having an \((sp^3)C\text{–}Pd\) bond, were investigated using KPPh$_2$. These alternative CPCs were obtained from 8-methylquinoline, tri-(\(O\)-tolyl)phosphine, 2,6-dimethylthioanisole and trimesitylphosphine. In each case, when the CPC reacted with 4.5 equiv. of KPPh$_2$, the corresponding \(NP\)-, \(SP\)- and \(PP\)-ligands were isolated in 13–51% yield. Reactions using only 1 equiv. of KPPh$_2$ gave \(\mu\)-chloro-\(\mu\)-diphenylphosphido-CPCs as main products in 26–56% yield.

Proposed structures of new compounds obtained in the reactions were confirmed by spectroscopic methods and in some cases by X-ray crystallography. Purity and
elemental composition of the synthesized complexes and organic compounds were confirmed by either satisfactory elemental analysis or high resolution mass spectra data.
CHAPTER I

INTRODUCTION

I.1. Cyclopalladated Complexes Containing an \((sp^3)\)C–Pd Bond

Cyclopalladated complexes (CPCs) are organometallic compounds with a sigma C–Pd bond, intramolecularly stabilized by a dative bond between Pd and a heteroatom to form three-, four-, five-, six- or seven-membered palladacycles. The heteroatoms commonly involved in CPC formation include N and P and more rarely S, Se, As and O.

Cyclopalladated compounds have been known since the beginning of 1960s. In 1963, Kleiman and Dubeck investigated the reaction of dicyclopentadienylnickel (NiCp\(_2\)) and azobenzene (1) under both solvent and solvent-free conditions to furnish a new complex 2 (Scheme 1).\(^1\)

![Scheme 1. Synthesis of compound 2 and CPC 3 from azobenzene.](image)

In 1965, Cope and Siekman reported an analogous reaction with PdCl\(_2\) in an alcoholic solution to generate the first known palladacycle (3) (Scheme 1).\(^2\) Soon after this study, five-membered palladacycles were obtained when \(N,N\)-dimethylbenzylamines were reacted with PdCl\(_2\) under similar conditions.\(^2\) These first palladacycles contained an
aromatic \((sp^3)\)C–Pd bond.\(^2\) Cope et al. later investigated the reaction between Pd(II) reagents and allylic amines.\(^3\) They found that \(N,N\)-dimethyl-2-methylallylamine (4) reacted with \(\text{Li}_2\text{PdCl}_4\) or \(\text{PdCl}_2\) in an alcohol to give the corresponding CPCs 6 and 7 (Scheme 2).\(^3\) These are the first examples of the palladacycles with an \((sp^3)\)C–Pd bond.\(^3\)

![Scheme 2. Synthesis of CPCs from \(N,N\)-dimethyl-2-methylallylamine.](image)

Cyclometallation reactions have been observed with many transition metals, including Ru, Rh, Os, Pt, Ir, Fe, Ni, Co, Mn and others.\(^2,4-8\) Organopalladium compounds are especially valuable for several reasons. The C–Pd bond is known to react with numerous reagents to reliably yield functionalized products.\(^9-13\) This versatility is in part due to the tolerance of palladium reagents to many functional groups and also due to the selective reactivity of cyclopalladated intermediates at the C–Pd bond.\(^14-16\) Thus, cyclopalladation is an excellent route to many different bond linkages, including carbon-carbon, carbon-oxygen, carbon-nitrogen, carbon-sulfur, carbon-phosphorus and carbon-halogen bonds. Furthermore, the compatibility of palladium reagents such as \(\text{Pd(OAc)}_2\) with a variety of directing groups enables the use of a wider variety of substances compared to other transition metal reagents. Finally, most reactions involving palladacycles are not
sensitive to moisture and air, making the synthesis of complex organic molecules more facile.

Aliphatic palladacycles (here and later, all CPCs and palladacycles with an \((sp^3)C–Pd\) will be called aliphatic) have a characteristic \(\sigma\)-bond between palladium and an \(sp^3\)-hybridized carbon of the ligand.\(^{17-19}\) The \((sp^3)C–H\) bond is generally inert due to the absence of either empty low-energy orbitals or filled high-energy orbitals, which can overlap with metal orbitals.\(^{20, 21}\) Thus, reports of CPCs with an \((sp^3)C–Pd\) bond are far outnumbered by those of palladacycles containing an \((sp^2)C–Pd\) bond.

I.2. Classification of CPCs with an \((sp^3)C–Pd\) Bond

CPCs containing an \((sp^3)C–Pd\) bond are broadly divided into two types: benzylic (e.g., 8–10 in Chart 1) and aliphatic (e.g., 5–7 in Scheme 2). Benzylic CPCs are those in which the metal is bonded to a benzylic carbon, while palladium in aliphatic CPCs is bonded to an \(sp^3\)-hybridized carbon. The organic moiety of both benzylic and aliphatic CPCs can be either an anionic four-electron (CY) or six-electron (YCY) donor (Figure 1).\(^4\) CPCs of the latter type are examples of pincer complexes.

Figure 1. CY- and YCY-palladacycles.
While all YCY-type complexes are mononuclear, the CY-analogs can be mono-, di-, and trinuclear.\textsuperscript{4, 22} Di- and trinuclear complexes can exist as cis and trans geometric isomers with halogen, acetate or other bridging moieties (Figure 2).\textsuperscript{4, 22} Acetato-bridged trinuclear aliphatic CPCs derived from 1-\textit{tert}-butylpyrazole,\textsuperscript{23} \textit{N},\textit{N}-dimethylneopentylamine\textsuperscript{24} and 2-\textit{tert}-butyl-4,4-dimethyl-2-oxazoline\textsuperscript{25} have been reported by the research groups of Alonso, Hiraki, and Balavoine, respectively. Preparation of the acetato-bridged trinuclear benzylic CPC derived from 2-(dimethylamino)toluene has been discussed by Pfeffer.\textsuperscript{26, 27} Although acetate and chloride are the most common bridging ligands in CPCs with \textit{(sp}^2\textit{)}C–Pd bonds, \textit{N},\textit{O}-imidate ligands like succinimidate, phthalimidate and maleimidate\textsuperscript{28, 29} as well as carboxylato groups like oxalato, \textit{n}-alkylcarboxylato, \textit{n}-oxaalkylcarboxylato, \textit{p}-alkoxyphenylacetato and \textit{p}-alkoxybenzoato have also been reported.\textsuperscript{30}
CPCs can also be classified based on the donor heteroatom bonded to the metal, e.g., CN-, CP-, CS- and CO-type palladacycles. The donor atom Y is responsible in part for the ring size of CPCs since it delivers the palladium reagent to a particular C–H bond where palladation occurs. While CY-type benzylic CPCs contain mostly five- or six-membered palladacycles, their aliphatic counterparts can also be three- or four-membered.

I.2.1. CN-Palladacycles

Common directing groups for benzylic CN-CPCs include the pyridine, aniline and imine moieties. Hartwell et al. synthesized the first example of a benzylic CN-palladacycle (10) from 8-methylquinoline in 1970 via C–H bond activation using Li₂PdCl₄. Thereafter, many research groups reported other examples, particularly those derived from 2-substituted 8-alkylquinolines, ortho-alkyl-substituted N,N-dialkylanilines, and N-mesitylbenzylideneamines. In 1978–1981, Deeming and Rothwell studied the cyclopalladation of 8-alkylquinolines with various substituents (Me, Br, CHO, CH=NMe, CH₂OH and CO₂H) at the 2 position. They determined that the 2-substituted
derivatives of 8-alkylquinolines were readily palladated using Pd(OAc)$_2$ when the substituent was either CH=NMe, CH$_2$OH or CO$_2$H, while every attempt to metalate the analogs with Me, Br, or CHO groups did not work.$^{42,43,47}$ During the same time, Pfeffer et al., while studying reactions of ortho-alkyl-substituted N,N-dialkylanilines with LiPdCl$_4$, observed demethylation at the NMe$_2$ group to give N-alkylanilines.$^{26,27,56}$ Reactions of ortho-alkyl-substituted N,N-dialkylanilines with Pd(PhCN)$_2$Cl$_2$ and Pd(OCCF$_3$)$_2$ provided coordination complexes.$^{26,27,56}$ They were able to palladate only ortho-methyl-substituted N,N-dialkylanilines using Pd(OAc)$_2$ to get trinuclear CPCs which were converted to the dinuclear chloro-bridged analogs upon treatment with LiCl.$^{26,27,56}$ The dinuclear µ-Cl-CPC was subsequently reacted with AgOAc to regenerate the acetate-complexes.$^{26,27,56}$

The research groups of Gómez, Sales, Liu, Fernández and Munno have investigated the cyclopalladation of N-mesitylbenzylideneamines using Pd(OAc)$_2$.Palladation preferentially took place at the aromatic carbon to give five-membered endo-palladacycles.$^{52-55}$ The six-membered analogs generated via palladation at a benzylic carbon required higher temperatures.$^{52-55}$

Aliphatic CN-palladacycles have been reported with a variety of nitrogen-containing directing groups: oxime (including their O-substituted derivatives), hydrazone, ketazine, oxazoline, pyridine, amine, benzothiazole, pyrazole, urethane and acetanilide. Aliphatic five- and six-membered oxime palladacycles 12 include those with ordinary oxime (NOH), O-methyl oxime (NOMe) or O-acetyl oxime (NOAc) directing groups.$^{17,58-65}$ In 1978, Shaw et al., synthesized the first example of a CPC$^{58}$ containing an NOH directing group while those containing the NOAc directing group were introduced simultaneously in 1985 by the groups of Nishilyama,$^{60}$ and Baldwin.$^{59,61}$ CPCs with a
hydrazone directing group (13a) are usually five-membered and were first introduced by Shaw and his collaborators in 1978. 58 Such CPCs have an sp³ nitrogen coordinated to the Pd center. In 1983, Galli and Gasparrini reported a case of a hydrazone CPC (13b) in which the sp² nitrogen was coordinated to the Pd center. 66 This could be attributed to the stability of five-membered palladacycles compared to the six-membered rings that are formed if coordination occurs at the sp³ nitrogen. 66 In 1994 and 1995, Echavarren et al. worked on the synthesis of the PPh₃ adducts of type 13 CPCs upon reaction of the preligand (N,N-dimethylhydrazone) with Pd(PPh₃)₂Cl₂ and NaOAc in MeCN. 67, 68 Shaw et al. synthesized five-membered ring CPCs of type 14 containing ketazine as the directing group. 63 Clinet et al. worked on the five-membered ring CPCs derived from oxazoline (type 15). 25 Our group also reported such CPCs. 18, 69 In 1983 through 1992, Hiraki and his collaborators studied five- and six-membered ring CPCs (16) containing the pyridine moiety as the directing group. 70-72 Recently, Rourke et al. reported five-membered ring CPCs 16 containing the pyridine moiety as the directing group. 73, 74 Aliphatic CN-palladacycles (17) containing the amino directing group were introduced in 1967 by Cope et al. 3 and since then many of such CPCs have been reported. 19, 24, 75-85 In 1986, Hiraki et al. reported five-membered CPCs (18) with the benzothiazole moiety as the directing group, 86 while in 1992, Alonso et al. synthesized five-membered CPCs (19) with the pyrazole moiety as the directing group. 23 In 1994, Henderson et al. reported four-membered palladacycles 20 and 21 derived from urethane and acetanilide ligands. 87-89
I.2.2. CP-Palladacycles

Benzylic CP-CPCs are usually five-membered and synthesized from aryl- or benzylphosphines. Benzylic CPCs 22 were first reported in 1972 by Shaw et al.\textsuperscript{90} and since then many groups have either worked on their synthesis or their application as catalysts in cross-coupling reactions.\textsuperscript{31, 32, 91-105} Recently, Hou et al. prepared rare six-membered benzylic CPCs 23.\textsuperscript{101} Joshaghani et al. also recently synthesized a benzylic biphenyl-based phosphine CPC 25.\textsuperscript{93} A unique three-membered benzylic palladacycles 24 was obtained from bidentate derivatives of a phosphaalkene.\textsuperscript{106}
The majority of aliphatic $CP$-CPCs prepared from alkylphosphines are five-membered. Examples include palladacycles (type 26) obtained by the palladation of $^t$Bu$_2$PrP and $^t$Pr$_3$P. Four-membered P-containing palladacycles are also known. In 1977, Goel et al. synthesized the four-membered ring CPC 27 from $^t$Bu$_3$P. Later, Werner and Kraus developed a method to form similar palladacycles from $^t$Bu$_3$P and $^t$Bu$_2$PhP by the reaction of their coordination complexes with AgOAc. Interestingly, Milstein isolated the dinuclear five-membered aliphatic $CP$-palladacycle 28 with a monobridging diphosphine.


Chart 4. Examples of $CP$-palladacycles.
I.2.3. CS-Palladacycles

Like phosphorus, sulfur is a relatively soft donor atom and well suited for the soft Lewis acid Pd(II). Both benzylic and aliphatic palladacycles containing a sulfur directing group have been reported.

In 1989, Pfeffer et al. reported benzylic five-membered CS-CPCs (29) synthesized from 2,6-dimethylthioanisole.\textsuperscript{111,112} More recently, Vicente et al. discussed the synthesis of benzylic five-membered CS-CPCs from aryldithioacetals.\textsuperscript{113,114}

Aliphatic CS-palladacycles can be derived from a sulfide, thioamide, or thiourea. The first sulfide-derived palladacycle 30 was published by Okawara et al. in 1976.\textsuperscript{35} That complex had a rare three-membered ring.\textsuperscript{35} The five-membered ring sulfide palladacycles of type 31 were reported by the groups of Holton and Pfeffer.\textsuperscript{75, 82, 111, 112} An unusual method was described by Albéniz et al. for four- to six-membered palladacycles of type 30 by insertion reactions at the Pd-aryl bond.\textsuperscript{115} Leaver et al. made available the five-membered thioamide-derived aliphatic CS-CPC 32.\textsuperscript{116} Groups of Dunina and Pfeffer reported related five-membered thioamide-derived CPCs 33.\textsuperscript{111, 117, 118}

![Chart 5. Examples of CS-palladacycles.](image-url)
I.2.4. CO-Palladacycles

Despite the fact that oxygen-containing moieties are relatively hard ligands, CO-CPCs have also been reported. Palladacycles derived from aldehydes (34) were obtained by the groups of Elsevier, Vrieze, Sen and Osakada. Singh et al. also reported the aliphatic CO-palladacycle 35 with a hydroxyl donor moiety. Recently, Lindsell et al. observed the oxidation addition of 2-hydroxymethylbenzyl chloride with Pd(PPh₃)₄ in toluene to afford the benzylic CPC 36.

![Chart 6](image)


I.2.5. CC-Palladacycles

In 1999, Catellani et al. reported the CC-palladacycles 37, in which one of the carbon atoms bonded to the palladium center was $sp^3$-hybridized while the other was $sp^2$-hybridized. Earlier in 1998, Hashni et al. obtained complex 38 with both carbon atoms $sp^2$-hybridized.
1.2.6. Pincer Palladacycles

Pincer palladacycles contain ligands with three or sometimes four chelating atoms. They can be subdivided based on the number (tridentate or tetradentate) and type of chelating atoms, e.g., tridentate $CNO$, $NCN$, $NCO$, $NNC$, $CNN$, $CNC$, $CNS$ and $PCP$ and tetradentate $CNNC$ and $CNNO$. 

Chart 7. Examples of $CC$-palladacycles.
I.2.7. Spiro Palladacycles

These are bis-chelated mononuclear palladacycles formed by two bidentate ligands bound to a single Pd center. They have a characteristic C2 axis perpendicular to the plane of the molecule and passing through the Pd center. The chelation at the Pd center must be trans; cis chelations give mononuclear CPCs which are not spiro. There are only three
types of the ligands which were used to prepare such complexes. The research group of Newkome has synthesized five- and six-membered spiro palladacycles 50 and 51 from pyridine and pyrazine derivatives, respectively (Chart 9).\textsuperscript{138, 151} Fedorov et al. reported the spiro CPC 52 from the reaction of 3,3-dinitropropylamine with PdCl\textsubscript{2}.\textsuperscript{152}

![Chart 9. Examples of spiro palladacycles.](image)

I.3. Synthesis of Palladacycles Containing an (sp\textsuperscript{3})C–Pd Bond

The methods available for the synthesis of palladacycles include C–H activation with a Pd(II) reagent, oxidative addition, transmetalation and nucleophilic addition.

I.3.1. Pd(II)-Promoted C–H Bond Activation

Direct cyclopalladation using Pd(II) salts such as Pd(OAc)\textsubscript{2}, M\textsubscript{2}PdCl\textsubscript{4} (M = Na, Li, K) and Pd(MeCN)\textsubscript{2}Cl\textsubscript{2} is the most common method for synthesizing palladacycles in general and those containing an (sp\textsuperscript{3})C–Pd bond in particular. Ligands that have been palladated using this method include amines,\textsuperscript{24, 56, 76, 77, 136, 152} imines,\textsuperscript{51-55, 132, 150} pyridines,\textsuperscript{42, 43, 47, 70-72, 133, 134, 138-141, 151} pyrazines,\textsuperscript{151} hydrazones,\textsuperscript{58, 63, 66-68} oximes,\textsuperscript{58, 59, 61, 63} pyrazoles,\textsuperscript{23, 149} ketazines,\textsuperscript{63} oxazolines,\textsuperscript{18, 25, 69} phosphines,\textsuperscript{31, 32, 37, 90, 91, 97, 100, 101, 105, 107, 109, 110, 143-148, 153} sulfides,\textsuperscript{111} thioureas,\textsuperscript{111, 116, 117} thioamides,\textsuperscript{116} acetanilides,\textsuperscript{89} and thiazoles.\textsuperscript{86} Pd(OAc)\textsubscript{2} in acetic acid, benzene or toluene is the most common way to achieve palladation at an (sp\textsuperscript{3})C–H bond.\textsuperscript{17-19, 23, 25, 31, 32, 42, 51, 54, 70, 72, 86, 111, 132, 134, 153, 154} For example, in 1990,
Clinet et al. reported, the synthesis of CPC 15 through the activation of an \((sp^3)\)C–H bond on the tert-butyl group of 2-tert-butyl-4,4-dimethyl-2-oxazoline using Pd(OAc)$_2$ in AcOH followed by chloride substitution (Scheme 3).\(^{25}\)

Scheme 3. Synthesis of aliphatic CPC 15 from 2-tert-butyl-4,4-dimethyl-2-oxazoline 53.

Alkali salts of tetrachloropalladate, though weaker palladating agents than palladium acetate, have also been used for palladations at \((sp^3)\)C–H bonds.\(^{40, 42, 43, 59, 62, 64, 149, 153}\) In 1972, Cheney and Shaw succeeded in cyclopalladating di-tert-butyl-\(O\)-tolylphosphine 55 using Na$_2$PdCl$_4$. The product was the racemic P*-chiral phosphapalladacycle 56 with an \((sp^3)\)C–Pd bond,\(^{153}\) which turned out to possess a very high catalytic activity in C–C coupling reactions.\(^{92, 94-96, 155-158}\) Dunina et al. reported the resolution of P*-chiral phosphapalladacycle \(rac-56\) using potassium (S)-prolinate (Scheme 4).\(^{100}\)
Scheme 4. Synthesis of the optically active $P^*$-chiral benzylic $CP$-$CPC$ ($SpSp$)-$56$.

Synthesis of aliphatic CPCs through C–H activation can also be achieved by transcyclopalladation.\textsuperscript{34, 159, 160} Transcyclopalladation is a ligand-exchange reaction between a nonmetallated preligand and a palladacycle to form a new CPC.\textsuperscript{159} This reaction often requires the presence of either AcOH or CF$_3$CO$_2$H as a reaction promoter.\textsuperscript{159, 160} In 1984, Ryabov et al. reported the synthesis of CPC 8, which has a benzylic ($sp^3$)C–Pd bond, in 64% yield in the reaction of palladacycle 58 with 8-methylquinoline (59) at 50 °C for 24 h in AcOH–CHCl$_3$.\textsuperscript{159} Later, the same researchers increased the yield of complex 8 to 94% upon using the acetate-bridged CPC 58.\textsuperscript{161} The same reaction was also performed on SiO$_2$ without a solvent. In order to remove the product from SiO$_2$, the dimeric complex 8 was converted to the more soluble triphenylphosphine adduct 60 upon treatment with PPh$_3$ (Scheme 5).\textsuperscript{34} The yield of 60 was 46%.
Ryabov in one of his reviews on mechanism of C‒H bond activation stated that cyclopalladation through C‒H bond activation follows an electrophilic mechanism when an aromatic ligand is involved.\(^6\) The other suggested mechanistic routes include oxidative addition and \(\sigma\)-bond metathesis.\(^8\) It is now obvious that there is no single mechanism for C‒H bond activation that is applicable to all types of substrates and Pd(II) reactants.\(^{136}\) Furthermore, the mechanisms of C‒H bond activations for aromatic and aliphatic substrates should be different. Cyclopalladation at \((sp^3)\)C‒H bonds is usually believed to proceed through the transition state which exhibits agostic (three-center two-electron) interactions between the C‒H bond and the metal atom.\(^{162}\) Agostic interactions have been observed for metallations at \((sp^3)\)C‒H bonds using transition metal reagents.\(^{73, 163-165}\) In 2009, Rouke and his group reported the X-ray structure of an agostic complex while working on the metallation of 2-\(\text{tert}\)-butyl-6-(4-fluorophenyl)pyridine using K\(_2\)PtCl\(_4\).\(^{73}\) Later, they were able to obtain an X-ray structure for the agostic complex when Pd(OAc)\(_2\) was used as the metallating agent.\(^{74}\)

**Challenges in the Synthesis of Aliphatic Palladacycles Through C‒H Bond Activation**

Besides the inertness of \((sp^3)\)C‒H bonds, synthesis of aliphatic palladacycles through C‒H bond activation has two other fundamental challenges: (1) how to selectively palladate an \((sp^3)\)C‒H bond in the presence of a competing aromatic \((sp^3)\)C‒H bond and
(2) how to achieve palladation of 2° and 3° carbons instead of primary, particularly those in the tert-butyl moiety.

In general, aromatic C–H bond activation is favored over aliphatic C–H bond activation. Nonetheless, several research groups have reported palladation at a \((sp^3)\)C–H bond in the presence of a competing aromatic C–H bond achieved using the appropriate palladation agent and conditions. In 1994, Echavarren and Cardenas reported the palladation of acetophenone \(N,N\)-dimethylhydrazone (61) at the aliphatic C–H bond using Pd(PPh\(_3\))\(_2\)Cl\(_2\) and NaOAc in MeCN to furnish palladacycle 63. When the researchers used Na\(_2\)PdCl\(_4\) and NaOAc in MeOH, they observed exclusive palladation at the ortho position of the aromatic ring to give palladacycle 62. In the \(^1\)H NMR spectrum of complex 62, two \(N\)-methyl groups gave rise to a singlet at \(\delta 3.09\) ppm confirming that the \(sp^3\)-hybridized nitrogen atom is not the donor atom (Scheme 6). In contrast, two \(N\)-methyl substituents of 63 appeared as two singlets, proving diastereotopicity of these two groups and, therefore, Pd coordination with the \((sp^3)\)-N atom. Compound 62 remained unchanged when it was refluxed with NaOAc in MeCN. This observation allowed the authors to conclude that it is not an intermediate in the formation of aliphatic CPC 63.

![Scheme 6](image)


Cinellu et al. reported that the selective palladation of an unactivated \((sp^3)\)C–H bond in the presence of a competing aromatic \((sp^3)\)C–H bond in 6,6′-dimethoxy-2,2′-
bipyridine (64) depends on the solvent used. They observed that the use of a protic solvent like AcOH led to metalation at the unactivated \((sp^3)\)C–H bond to give palladacycles 66a,b. The use of the same Pd reagent in the aprotic solvent toluene led to palladation at the \((sp^2)\)C–H bond to yield complex 65 (Scheme 7).

Dunina et al. observed a similar but opposite effect when they used different solvents in the reaction of 1-thiobenzoylpyrrolidine (67) with PdCl₂ or K₂PdCl₄. Reaction of 67 with K₂PdCl₄ in the protic solvent MeOH gave CPC 68 with an \((sp^2)\)C–Pd bond, while the use of the aprotic solvent HMPA and PdCl₂ led to palladation at \((sp^3)\)C–H bond to furnish CPC 69 (Scheme 8).

Both Sales’ and Minghetti’s groups have shown that regioselectivity of palladation can be governed by using different temperatures. In 1991, Sales et al. studied the
palladation of \(N\)-mesitylbenzylideneamine 70 using \(\text{Pd(OAc)}_2\). They observed that refluxing the reaction mixture led to metallation at the \(\text{(sp}^3\text{)}\text{C–H bond to give palladacycle 72}^\text{54}\). When the reaction was carried out at lower temperatures, palladation preferentially took place at the aromatic \(\text{(sp}^2\text{)}\text{C–H bond to furnish compound 71 (Scheme 9)}^\text{54}\). These data suggest that complex 72 with the benzylic C–Pd bond is more thermodynamically stable than its anlog 71.

Scheme 9. Temperature effect on the cyclopalladation of preligand 70 using \(\text{Pd(OAc)}_2\).

The research groups of Sales and Minghetti together with that of Fernandez have investigated the ring size preference in the palladation of \(\text{(sp}^3\text{)}\text{C–H bonds}^\text{53, 54, 139}\). Minghetti et al. obtained the six-membered palladacycle 74 upon reaction of preligand 73 with \(\text{Pd(OAc)}_2\) in \(\text{AcOH}\) under reflux^\text{139}. Palladacycle 74 was converted quantitatively to the five-membered-ring analog 75 upon refluxing in \(\text{AcOH}\) (Scheme 10)^\text{139}. This is an example of the general trend that five-membered aliphatic palladacycles appear to be more stable than related six-membered aromatic palladacycles^\text{167-169}. 
In 2004, while studying the palladation of \((R)-4\)-phenyl-2-oxazolines using \(\text{Pd(OAc)}_2\) in AcOH, our research group observed regioselectivity towards the formation of endo-palladacycles derived from imines.\(^{170}\) Later, our group also investigated reactions of \((S)-2\text{-}\text{tert-butyl}-4\text{-phenyl}-2\text{-oxazoline} 76\) with Pd(II) salts in an effort to determine whether the endo-effect-driven regioselectivity would lead to metalation at the \((sp^3)\text{C}–\text{H}\).\(^{69}\) This reaction provided endo-palladacycle 77 with the \((sp^3)\text{C}–\text{Pd}\) as the major product while the alternative exo-palladacycle 78 with an \((sp^2)\text{C}–\text{Pd}\) bond, was isolated in much lower yield (Scheme 11).\(^{69}\) It is noteworthy that palladacycle 77 was obtained exclusively when the reaction was performed solvent-free on silica gel (Scheme 11).\(^{18}\)

Scheme 11. Palladation of preligand 76.
As a rule, aliphatic palladations proceed with very high selectivity for \(1^\circ \) (sp\(^3\))C–H bonds especially those in the tert-butyl fragment.\(^{167}\) The reason for such selectivity appears to be due to the possibility of \(\beta\)-hydride elimination in cyclopalladated complexes with \(2^\circ\) and \(3^\circ \) (sp\(^3\))C–Pd bonds. In the case of metalation of the tert-butyl group, \(\beta\)-elimination is impossible because of the absence of \(\beta\)-hydrogens. Sanford et al. has reported the selective palladation and subsequent oxygenation of a \(1^\circ \) (sp\(^3\))C–H bond in the presence of a competing \(2^\circ \) (sp\(^3\))C–H bond in 3-methyl-2-pentanone O-methyl oxime 79 (Scheme 12).\(^{171-173}\) Compound 79 could undergo both \(1^\circ \) (sp\(^3\))C–H bond and \(2^\circ \) (sp\(^3\))C–H bond palladation to form two different five-membered palladacycles; however, no traces of the palladation product at the \(2^\circ \) (sp\(^3\))C–H bond were observed due to a more statistically probable \(\beta\)-hydride elimination.\(^{171, 172}\) Palladation occurred at the \(1^\circ \) (sp\(^3\))C–H bond of the methyl group to give palladacycle 80, which has just a single \(\beta\)-hydrogen.

Scheme 12. Regioselectivity in the palladation of 3-methyl-2-pentanone O-methyl oxime.

Recently, McNally et al. reported the cyclopalladation of aliphatic amines using Pd(OAc)$_2$.\(^{19}\) The amines used in this study (e.g., 83) have C–H bonds in the positions that could not give rise to conventional five-membered-ring palladacycles.\(^{19}\) Metalation of
these amines led to strained four-membered palladacycles. The effect of β-hydride elimination on selectivity was evident when the researchers selected amine 83, which could undergo cyclopalladation at an \((sp^3)\)C–H bond of either methyl or ethyl group.

Cyclopalladation of amine 83 at one of the three methyl group would give a strained four-membered palladacycle, while metalation at the ethyl group would furnish a conventional five-membered ring. Interestingly, palladation took place at the methyl group to give the four-membered palladacycle 84 (Scheme 13). No product of cyclopalladation at the 1° \((sp^3)\)C–H bond of the ethyl group was obtained.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \quad \text{H} \\
\text{O} & \quad \text{R} \quad \text{Me} \quad \text{Me}
\end{align*}
\]

1) Pd(OAc)$_2$, PhMe, 60 °C
2) PAr$_3$, acetone, rt
3) NaCl, acetone, rt

R = Et (83)  
Me (85)

R = Et (84), Me (86)  
Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$

Scheme 13. Selectivity in palladation of aliphatic amines 83 and 85.

McNally et al. isolated four-membered CPCs by selecting aliphatic amines that possess no C–H bonds in the positions amenable to the formation of five-membered rings (Scheme 13). These four-membered CPCs are the first (and only) examples of their kind. Interestingly, four-membered metalacycles were also obtained when McNally and his collaborators used amines capable of forming five-membered analogs.

I.3.2. Oxidative Addition

Oxidative addition can be used for the synthesis of palladacycles with an \((sp^3)\)C–Pd bond when C–H bond activation is impossible in the preligand. In this method, the two-electron donor group of an alkyl halide oxidatively adds to a Pd(0) or Pd(II) source.
increasing both its formal oxidation state and coordination number by two. This approach is particularly convenient for the preparation of palladacycles with an \((sp^2)\)C–Pd bond.

The synthesis of palladacycles with an \((sp^3)\)C–Pd bond through direct oxidative addition is still a great challenge due to the relative inertness of alkyl halides toward Pd(0) reagents. However, in 1975, Okawara et al. reported the direct oxidative addition of chloromethyl methyl sulfide (87) to Pd(PPh\(_3\))\(_4\) to give the aliphatic palladacycle 30 in 87% yield (Scheme 14).

![Scheme 14. Synthesis of the aliphatic palladacycle 30 by oxidative addition.](image)

I.3.3. Transmetalation

Transmetallation is another method to form a C–Pd bond. In this reaction, Pd replaces a metal within an organometallic compound. Organolithium reagents are the most commonly used to furnish palladacycles, particularly those with an \((sp^3)\)C–Pd bond. Tin, silicon and magnesium have also been used, though to a lesser extent.

There are several examples of using transmetalation to obtain aliphatic CPCs. Thus, attempts by Strohmann et al. to palladate silane 88 at the 1° carbon using Pd(OAc)\(_2\) did not work. Ligand 88 was recovered from the reaction mixture unchanged and palladium black was observed. When silane 88 was treated with 'BuLi in \(n\)-pentane at -90 °C, metallation took place at the methyl group to give the organolithium derivative 89 in 90% yield. The organolithium reagent 89 was then treated with \(trans\)-PdCl\(_2\)(SM\(_2\))\(_2\) in THF at -78 °C to form the aliphatic dimeric chloro-bridged CPC 90 in 72% yield (Scheme 15).
Pfeffer and co-workers have used transmetallation to access the silicon-containing dimeric chloro-bridged CPC 94, which is difficult to synthesize using other methods.\textsuperscript{48,49} The organolithium reagent 91 did not react with Pd(SEt\textsubscript{2})Cl\textsubscript{2}.\textsuperscript{48} However, the same compound 91 readily underwent transmetalation with the dimeric chloro-bridged N,N-dimethylbenzylamine-derived CPC 92 in Et\textsubscript{2}O to furnish compound 93 in 60\% yield (Scheme 17).\textsuperscript{48} Refluxing compound 93 with trans-Pd(SMe\textsubscript{2})Cl\textsubscript{2} in toluene gave complexes 92 and 94 (Scheme 16).\textsuperscript{49}

Nishiyama et al. synthesized ketoxime-based aliphatic palladacyles by transmetallation of stannyl and silyl ketoximes (e.g., 95) with Pd(PhCN)\textsubscript{2}Cl\textsubscript{2} in CH\textsubscript{2}Cl\textsubscript{2}.\textsuperscript{60} Complex 96 was isolated in 78\% yield from the reaction of (\textit{E})-β-tributylstannyl ketoxime...
with 1 equiv. of Pd(PhCN)$_2$Cl$_2$ at 0 °C for 30 min in CH$_2$Cl$_2$ (Scheme 17). For comparison, Shaw and his co-workers have reported that direct cyclopalladation of aliphatic oxime derivatives using Pd(II) salts typically takes three days at rt to furnish CPCs with yields up to 70%.$^{63}$ This is strong evidence that (sp$^3$)C–Pd bond is formed faster during transmetallation than in case of C–H bond activation to access ketoxime-based aliphatic palladacycles. However, this transformation suffers significant drawbacks, which are 1) the use of highly poisonous tin derivatives and 2) a laborious synthesis of the tin derivatives prior to transmetallation.

Scheme 17. Synthesis of the ketoxime-based aliphatic palladacycle 96 by transmetallation.

Cámpora et al. have reported the synthesis of CC-palladacycle 99 via transmetallation.$^{183}$ The Grignard reagent 98 underwent transmetallation by Pd(COD)Cl$_2$ in THF followed by base-catalyzed (sp$^3$)C–H activation to afford palladacycle 99 in 80% yield (Scheme 18).$^{183}$

I.3.4. Nucleophilic Addition

The preparation of palladacycles through nucleophilic addition involves the formation of a carbon-carbon or a carbon-oxygen bond between the \( \beta \)-carbon of an allylic amine or sulfide and a nucleophile. This reaction spontaneously results in the formation of a carbon-palladium bond at the \( \delta \)-carbon of the allylic and homoallylic amine or sulfide. The nucleophile used in this reaction is either an alcohol or a stable enolate ion such as sodiodiethylmalonate; the palladating agent most often used is \( \text{Li}_2\text{PdCl}_4 \). Nucleophilic additions have been used in the synthesis of diverse types of palladacycles including those with an \( (sp^3) \)C–Pd bond.\(^3,44,75,80-83\) As mentioned above (Scheme 2), the first CPC with an \( (sp^3) \)C–Pd bond was prepared by this method from allylic amines. Later in 1977, Kjonaas et al. expanded the substrate scope in this reaction to include the allylic sulfide \( \textbf{100} \).\(^75,82\) They also found that carbon nucleophiles like sodiodiethylmalonate can also be used in this method (Scheme 19).\(^75,82\)

![Scheme 19. Synthesis of palladacycle \( \textbf{31} \) by nucleophilic addition.](image)

I.3.5. Miscellaneous Methods

I.3.5.1. Modification of a Preformed Palladacycle

It is also possible to obtain one palladacycle from another. For example, a preformed \( (sp^3) \)C–Pd bonded palladacycle can then undergo a rearrangement or insertion reaction at the C–Pd bond to generate an \( (sp^3) \)C–Pd bonded palladacycle.\(^113,114,185,186\) In
2004, Solé et al. reported the synthesis of azapalladacycle 102 by the oxidative addition of \(N,N\)-dialkyl-2-iodoaniline 101 to Pd(PPh\(_3\))\(_4\) or Pd\(_2\)(dba)\(_3\)/PPh\(_3\).\(^{185}\) As expected, the strained four-membered ring in complex 102 underwent carbene insertion into the C–Pd bond to give the more stable five-membered ring palladacycle 103 (Scheme 20).\(^{185}\)

![Scheme 20. Synthesis of palladacycle 103 by carbene insertion at the C–Pd bond of CPC 102.](image)

Vicente and his collaborators have reported the unusual rearrangement of ortho-palladated arylthioacetals.\(^{113, 114}\) The oxidative addition of arylthioacetal 104 to Pd(dba)\(_2\) gave the unexpected iodine-bridged palladacycle 107 (Scheme 21).\(^{114}\) When this reaction occurred in the presence of TlOTf and 2,2'-bipyridine (bipy), the expected monomeric product 105 was obtained (Scheme 21).\(^{114}\) Compound 105 rearranged to palladacycle 106 upon refluxing in 1,2-dichloroethane (Scheme 21).\(^{114}\) This rearrangement resulted from the cleavage of one (\(sp^3\))C–Pd and one (\(sp^3\))C–S bond and the formation of one (\(sp^3\))C–Pd and one (\(sp^3\))C–S bond.
I.3.5.2. Modification of a Preformed Pd–Aryl Unit

Oxidative addition of an aryl halide to a Pd(0) source is the first step in another method used for preparation of CPCs. The aryl–Pd compound then reacts with an norbornene followed by treatment with a base to form a CC-palladacycle. Catellani et al. have worked extensively on the synthesis of CC-palladacycles using this methodology. In the example shown in Scheme 16, the first step of this transformation was oxidative addition of phenyl iodide to Pd(0)L₂ to give compound. The subsequent insertion of norbornene into the (sp²)C–Pd bond of compound provided the stable product. Compound then underwent base-catalyzed intramolecular C–H activation to furnish CC-palladacycle (Scheme 22).

Scheme 21. Synthesis of palladacycle by a rearrangement of CPC.

Scheme 22. Synthesis of palladacycle by modification of the preformed Pd–aryl unit.
I.4. Applications of Palladacycles Containing an (sp$^3$)C–Pd Bond

CPCs containing an (sp$^3$)C–Pd bond have been used in synthetic organic chemistry as 1) catalysts or precatalysts in the Mizoroki-Heck,\textsuperscript{95, 96, 104} Suzuki\textsuperscript{57, 92, 96} and other reactions,\textsuperscript{92, 101, 188-194} 2) reagents for chiral resolution of racemic ligands,\textsuperscript{195} 3) reagents for chiral coordinative derivatizing agents to determine optical activity,\textsuperscript{195} 4) chiral auxiliaries,\textsuperscript{195} and 5) ligand modifications using reactions at the Pd–C bond.\textsuperscript{196} CPCs containing an (sp$^3$)C–Pd bond have mostly been used as catalysts\textsuperscript{92-96, 98, 101, 154, 197} and to a lesser extent in ligand modifications using reactions at the Pd–C bond.\textsuperscript{62, 84, 85, 119, 198} To the best of our knowledge, aliphatic CPCs have never been utilized as reagents for chiral resolution of racemic ligands and chiral coordinative derivatizing agents, as well as chiral auxiliaries.

I.4.1. Use as Catalysts or Precatalysts

The first CPC with an (sp$^3$)C–Pd bond used as a catalyst in cross-coupling reactions is the Herrmann palladacycle \textbf{114}.\textsuperscript{96} The catalytic activity of complex \textbf{114} in the Heck reaction surpassed that of all previously used catalysts in the same transformation.\textsuperscript{96} The exceptional stability and a possibility of activating less reactive chloroarenes made this and related complexes target compounds for potential application in industries.\textsuperscript{22, 96} Herrmann et al. obtained 100\% yield of product \textbf{115} when CPC \textbf{114} was used as a catalyst in the reaction of 4-bromobenzaldehyde (\textbf{112}) with \textit{n}-butyl acrylate (\textbf{113}) (Scheme 23).\textsuperscript{96} The product yield of this reaction remained the same when the equivalence of the catalysts was reduced to thousand times its initial amount.\textsuperscript{96} Kinetic studies showed that the standard catalyst, a mixture of Pd(OAc)$_2$ and triarylphosphine, was deactivated at temperatures
above 120 °C due to the breaking of a P–C bond in the phosphine. This led to the deposition of Pd black usually observed in Heck reactions and explained why this catalyst cannot be used for less reactive chloroarenes and deactivated bromoarenes, which are often unreactive under mild reaction conditions and require temperatures above 120 °C. For comparison, thermal gravimetric/mass spectrometric studies of compound 114 indicated that it decomposes only at temperatures above 250 °C; hence it can be used in Heck reactions requiring high temperatures.

![Scheme 23. Catalytic activity of CPC 114 in Heck reaction.](image)

In an effort to compare the catalytic activity of pincer palladacycles with an \((sp^3)\)C–Pd and an \((sp^2)\)C–Pd bond, Milstein and his group used three PCP pincer CPCs in a Heck reaction. They reported that iodobenzene (116) reacted with tert-butyl acrylate (117) in the presence of catalytic amounts of the PCP pincer complex 119 containing an \((sp^2)\)C–Pd bond to furnish product 118 in 4% yield (Scheme 24). To their surprise, when the PCP pincer complex 120 with an \((sp^3)\)C–Pd bond was used, this reaction gave product 118 in 100% yield (Scheme 24). They screened many reagents and reaction conditions, and in each case the PCP pincer complex 120 provided better yields of the product than the PCP pincer complex 119. Although both pincer complexes showed very high thermal stability
with no decomposition up to 180 °C, CPC 120 had a higher turnover rate.\textsuperscript{200} Complex 120 was an effective catalyst even in Heck reactions of nonactivated aryl bromides, in which CPC 119 was not.\textsuperscript{200} The researchers concluded that the higher catalytic activity of CPC 120 could be due to electronic factors since the metal center in CPC 120 is more electron rich than in CPC 119.\textsuperscript{200}

Scheme 24. Catalytic activity of PCP pincer CPCs in Heck reaction.

To examine whether the Herrmann palladacycle 114 was also effective in Suzuki reactions, Beller et al. used this complex as a catalyst in cross-coupling reactions of aryl halides with arylboronic acids.\textsuperscript{95} These researchers found that 4-bromoacetophenone (112) reacted with phenylboronic acid (121) in the presence of compound 114 to give the desired 4-acetylbiphenyl (122) in yields above 90\% (Scheme 25).\textsuperscript{95} Complex 114 was also found to be effective in Suzuki reactions with less reactive chloroarenes.\textsuperscript{95}
Liu and her group have used the imine-derived CPC 124 as a catalyst in a similar Suzuki-Miyaura reaction (Scheme 26). They reported a quantitative yield of the product even though these reactions were carried out in air and protic solvents. The use of activated aryl chlorides like p-nitrophenyl chloride and p-acetylphenyl chloride both gave 100% yields of the respective products. However, they observed poor conversions for deactivated aryl halides and phenyl chloride. Deactivated aryl halides had electron-donating groups on the benzene ring.

Recently, Joshaghani et al. described the use of the biphenyl-based phosphine-derived CPC 127 as a catalyst in Suzuki couplings (Scheme 27). Previously, the researchers reported high catalytic activity of 2-(diphenylphosphino)-2′-methylbiphenyl in the presence of Pd(0) in several coupling reactions, which they assumed was due to the
formation of the palladacycle intermediate 127. CPC 127 was synthesized and tested as a catalyst for Suzuki cross-coupling reactions. The catalytic activity of CPC 127 improved with increasing reactivity of the aryl chloride used. They observed quantitative yield of the product when highly activated aryl chlorides with electron-withdrawing groups were used. It is worth noting that compound 127 was still effective in the reactions with electron-rich aryl halides like 3-chloroanisole (126). They also observed that the catalytic activity of CPC 127 surpassed that of its preligand.


Hou and his group have observed a rather different phenomenon. When CP-CPCs containing either an (sp$^3$)C–Pd or (sp$^2$)C–Pd bond were used as catalysts in the reaction of oxabicyclic alkenes and terminal alkynes, different products were obtained. When the reaction of 7-oxabenzonorbornadiene (129) with phenylacetylene (130) was catalyzed by CP-CPC 132 containing an (sp$^3$)C–Pd bond, the cyclic ether 133 was formed as the major product (Scheme 28). A switch to alcohol 134 was observed when CP-CPC 131 with an (sp$^2$)C–Pd bond was used (Scheme 28). DFT calculations showed that this selectivity resulted from the difference in trans effects of the carbon donors in the CPCs. The (sp$^3$)C atom possess a greater trans effect than the (sp$^2$)C because the former is a stronger donor. In the transition state (TS1) leading to compound 134, the O–Pd bond being formed is trans to the (sp$^2$)C–Pd bond of CPC 131. This trans-(sp$^2$)C,O geometry resulted in predominant
$\beta$-O elimination. In the transition state TS2 leading to compound 133 the C–Pd bond being broken is trans to the ($sp^3$)C–Pd bond of CPC 132. This trans-($sp^3$)C,O geometry favored protonolysis.\textsuperscript{101}

Scheme 28. Reaction of oxabicyclic alkenes with terminal alkynes using CPCs.

The Herrmann palladacycle has also been used in palladium-catalyzed homocoupling of aryl iodides.\textsuperscript{92} Luo et al. observed homocoupling of 4-iodotoluene (135) in DMF in the presence of complex 114 to give product 136 in 87% yield (Scheme 29).\textsuperscript{92} The yield of the products changed only a little when substituents on the benzene ring were varied.\textsuperscript{92} However, the reaction was faster with arenes having electron-withdrawing substituents than with those bearing electron-donating groups.\textsuperscript{92}
Scheme 29. Palladium-catalyzed homocoupling of 4-iodotoluene using CPC 114.

I.4.2. Ligand Modifications Using Reactions at the Pd–C Bond

Similarly to other organometallic compounds, CPCs can react with a number of substrates resulting in ligand modifications. Only a small fraction of these reactions involve CPCs with \((sp^3)C\text{–}Pd\) bonds. For example, the research group of Sheppard has reported the synthesis of novel compounds via cyclopalladation of lanosterol and cholesterol.\textsuperscript{62} These products could potentially be used as new adjuvant saponins.\textsuperscript{62} Holton, R. A. synthesized a prostaglandin by using the cyclopalladation of cyclopentadiene as the first step.\textsuperscript{84} Lindsell et al. have utilized reactions at the Pd–C bond of the benzylic CPC 138 to prepare lactone 140, which is a precursor of pharmaceutical agents.\textsuperscript{125} Their lactone synthesis started with the oxidative addition of 2-hydroxymethylbenzyl chloride (137) to Pd(PPh\textsubscript{3})\textsubscript{4} in toluene to afford CPC 138.\textsuperscript{125} Insertion of CO into the Pd–C bond of CPC 138 gave compound 140 in 71% yield (Scheme 30).\textsuperscript{125}

Scheme 30. Synthesis of compound 140 using CPC 138 as a reactant.

Pfeffer et al. have accessed novel heterocyclic compounds containing a bridgehead nitrogen via reactions at the Pd–C bond of the 8-methylquinoline-derived CPC 8.\textsuperscript{198} The
researchers reacted CPC 8 with 1 equiv. of dimethyl acetylenedicarboxylate to afford compound 141 in 91% yield (Scheme 31).^{198}

Scheme 31. Synthesis of compound 141 by the ligand modification method.
CHAPTER II
GOALS OF THE STUDY

II. 1. Types of Optically Active Cyclopalladated Complexes

Known optically active CPCs possess either 1) a chiral center,\(^{201}\) 2) chiral plane,\(^{202}\) 3) chiral axis\(^{203}\) or 4) a combination of two chiral elements.\(^{204}\) The first examples of optically active C*-chiral CPCs were derived from \(\alpha\)-arylalkylamines and were reported as early as 1971 (Chart 10).\(^{201,205}\) Later in the 1980s, Sokolov et al. introduced the planar chiral 1-dimethylaminoethylferrocene-derived complex \(\text{142}\) (Chart 10).\(^{204,206}\) Presently, there are many examples of optically active CPCs, which include both mono- and dinuclear \(CN-, CS-,\) and \(CP\)-complexes as well as mononuclear \(SCS, NCN, PCP\) and \(PCN\) pincer derivatives. The majority of optically active CPCs reported in literature have an \((sp^3)C-Pd\) bond,\(^{192}\) although optically active aliphatic CPCs have also been known (Chart 10).\(^{32,207-209,133}\)

Chart 10. Examples of optically active CPC containing 1) a chiral center [(\(R_C\))\(\text{-141}\), \((R_C)\)-8, \((S_P,S_P)\)-56 and \((S_P,R_C)\)-142], 2) chiral plane [(\(S_P,R_C)\)-142] and 3) chiral axis [(\(R_o,R_o)\)-131].
II.1.1. Optically Active Cyclopalladated Complexes Containing an \((sp^3)C\text{--Pd}\) Bond

Optically active CPCs containing an \((sp^3)C\text{--Pd}\) bond are the most abundant group of chiral CPCs and can be differentiated by the type of chirality into those with a chiral plane, chiral center or chiral axis. CPCs with central chirality contain one or more chiral atoms, which can be C, N, P or S. Chart 11 provides examples of C*-chiral CPCs 78 (see Scheme 11) and 141 (Chart 10),\(^{201}\) C*- and N*-chiral complex 143,\(^{210}\) C*- and S*-chiral analog 144,\(^{211}\) CS-CPC 69 (see Scheme 8)\(^{117}\) and C*- and P*-chiral CPC 145 (Chart 11).\(^ {212}\) Examples of CPCs with only planar chirality include CN-CPCs 146\(^ {213}\) and 147\(^ {214}\) (Chart 11). The majority of planar chiral CPCs also contain a chiral center, e.g., 148 and 149 (Chart 11).\(^ {214}\) Phosphapalladacycle 131 derived from binaphthalene exhibits axial chirality (see Chart 10).\(^ {203}\)

![Chart 11. Examples of optically active CPCs with an \((sp^3)C\text{--Pd}\) bond.](image)

Pincer CPCs with a stereocenter have been studied by several groups.\(^ {215\ 216\ 217\ 133}\)

\(^{218\ 219\ 194}\) Examples of these pincer complexes include CNO-44 (see Chart 8),\(^ {133}\) NCN-150,\(^ {215}\) NCNO-151,\(^ {216}\) OCNO-152,\(^ {217}\) PCP-153 and PCP-154,\(^ {219}\) PCN-155\(^ {194}\) and SCS-
156 (Chart 12). There are also reports of pincer complexes with axial chirality, e.g., *PCP*-157 as well as complexes with both axial and central chirality, e.g., *NCN*-158

Chart 12. Examples of optically active pincer complexes.
II.1.2. Optically Active Cyclopalladated Complexes with an (sp$^3$)C–Pd Bond

Most aliphatic CPCs containing a chiral center exist as racemates due to the tedious process of chiral resolution. This is one of the reasons why only a limited number of optically active CPCs of this kind have been known to date. Their examples include phosphapalladacycles $56$ (see Scheme 4),$^{207, 222}$ $161$,$^{223}$ $CS$-CPC $69$ (Scheme 8),$^{117}$ CC-CPC $38$ (Chart 7),$^{130, 131}$ pyrazole-derived CN-CPC $19$ (Chart 2),$^{23}$ and oxazoline-based CN-CPCs $159$ and $160$ (Chart 13).$^{208, 209, 224}$


II.2. Synthesis of Optically Active Cyclopalladated Complexes

Two common methods to access optically active CPCs with an (sp$^3$)C–Pd bond have been reported: 1) cyclometalation of enantiopure preligands$^{209, 225}$ and 2) chiral resolution of racemic cyclopalladated complexes.$^{32, 133}$ The third approach, enantioselective palladation,$^{226, 227}$ has also been used to prepare optically active CPCs, but all of them contain an (sp$^2$)C–Pd bond.

II.2.1. Cyclopalladation of Enantiopure Preligands

The most straightforward approach for preparation of optically active CPCs is cyclopalladation of preligands derived from naturally occurring optically active compounds. Examples include complexes obtained from (i) 4-substituted 2-oxazolines,$^{228, 229}$ which are prepared from readily available enantiopure $\alpha$-amino alcohols, (ii) derivatives
of natural phenols L-(-)-tyrosine and (+)-estrone\textsuperscript{230} and (iii) derivatives of L-phenylalanine\textsuperscript{231} and (R)-2-phenylglycine.\textsuperscript{232} Only a small fraction of known enantiomerically pure or scalemic CPCs have an \((sp^3)\text{C–Pd bond (see Chart 13).}\textsuperscript{32, 207-209}

Our research group has also synthesized optically active CPCs via the cyclopalladation of enantiopure preligands. Previously, we studied the cyclopalladation of \((S)-4\text{-}\text{tert}-\text{butyl-2-methyl-2-oxazoline (165).}\textsuperscript{209} \text{Preligand 165 was synthesized according to a procedure reported by Meyers and Shipman from (S)-\text{\text{tert}-leucinol and ethylacetimidate hydrochloride (Scheme 32).}\textsuperscript{225} Reaction of 165 with Pd(OAc)\textsubscript{2} in acetic acid gave the exo-palladacycle 160 (Scheme 32).\textsuperscript{209} The yield of the product was not high, possibly because 1) the structure of 165 allows only the less favored exo-cyclopalladation and 2) the difficulty associated with the activation of an \((sp^3)\text{C–H bond.}\textsuperscript{209} This is in contrast to the observed endo-cyclopalladation of \((S)-2\text{-}\text{tert}-\text{butyl-4-phenyl-2-oxazoline and 2-tert-butyl-4,4-dimethyl-2-oxazoline previously discussed in this dissertation (see Scheme 3).}\textsuperscript{208}

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\chemfig{\text{\text{Bu}^+\text{OH} + \text{HCl}}\rightarrow [\text{CH}_2\text{Cl}_2, \text{rt, 12 h}] \text{(S}C\text{-)163 164}} \rightarrow \text{(S}C\text{-)165, 79%}} \text{(S}C\text{-)160, 43%}}
\end{tikzpicture}
\end{center}

Scheme 32. Synthesis of CPC \((S_C\text{-)160 from (S}_C\text{-)163.}
II.2.2. Synthesis of Optically Active Cyclopalladated Complexes through Chiral Resolution

Examples of preparation of optically active aliphatic CPCs using chiral resolution includes synthesis of 56 and 44. The preparation of enantiomerically pure phosphapalladacycle 56 by chiral resolution using optically active amino acid derivatives was described in Chapter I (see Scheme 4). The pincer CNO-complex 44 has also been successfully accessed through chiral resolution. Reaction of compound 166 with K₂PdCl₄ in EtOH followed by addition of pyridine gave rac-44, which upon stirring with S-(-)-1-phenylethylamine furnished a mixture of two diastereomers (Scheme 3). The diastereomeric mixture was separated using column chromatography, and a subsequent ligand exchange with pyridine gave both enantiomers of CPCs 44 (Scheme 3).
II.2.3. Synthesis of Optically Active CPCs through Enantioselective Palladation

All optically active complexes obtained by this method have an \( (sp^3)C-Pd \) bond.

The synthesis of optically active CPCs via enantioselective palladation was first introduced in 1979 by Sokolov and his research group.\(^{226}\) In this study, the researchers obtained dimer \textbf{170} with 79\% ee using 1 equiv. of (S)-N-acetylleucine (\textbf{169}) in the palladation of (dimethylaminomethyl)ferrocene (\textbf{170}) by \( \text{Na}_2\text{PdCl}_4 \) (Scheme 34).\(^{226}\) Recently, Richards and Günay investigated the same reaction in an attempt to confirm the enantioselectivity.
observed by Sokolov (Scheme 34).\textsuperscript{227} To obtain CPC 170, they used the same reaction conditions described by Sokolov. The product analysis by chiral chromatography provided 96% ee.\textsuperscript{227} The research groups of Ryabov and Richards used enantioselective palladation to access other optically active CPCs.\textsuperscript{159, 233, 234} To the best of our knowledge, optically active aliphatic CPCs have never been prepared using this method.

Scheme 34. Synthesis of the optically active CPC 170 via enantioselective palladation.

II. 3. Applications of Optically Active Cyclopalladated Complexes

Optically active CPCs have many applications. For example, in asymmetric synthesis, they can play three roles: catalyst/precatalyst,\textsuperscript{189, 190, 235-238} chiral auxiliary\textsuperscript{239-241} and reactant.\textsuperscript{14, 207, 242, 243} Optically active CPCs have also been used in chiral resolution,\textsuperscript{244-247} for determination of enantiopurity of amines, phosphines and other substrates possessing ligand properties\textsuperscript{248-250} as well as functioning as a reference point for determination of absolute configuration.\textsuperscript{245, 246, 251-253} In the majority of the application studies (except for the use of CPCs as chiral catalysts), only a small group of optically active CPCs are commonly employed; they are derivatives of optically active 1-phenylethylamine,\textsuperscript{248, 250} 1-(1-naphthyl)ethylamine\textsuperscript{205} and 1-(2-naphthyl)ethylamine.\textsuperscript{254}

Amongst the optically active CPCs obtained from compounds available in the chiral pool,\textsuperscript{255} only CPCs containing the oxazoline moiety were used in applications involving
chiral induction, predominantly as catalysts in asymmetric transformations. Moreover, the best results were obtained for quite complex structures, particularly those containing not only the oxazoline ring, but also a planar-chiral moiety. Only a small fraction of known enantiopure or scalemic CPCs have an \((\text{sp}^3)\text{C--Pd}\) bond, and none of them have been used as either resolving agents or catalysts in enantioselective transformations.

II.4. Goals of the Present Study

As was presented above, enantiopure CPCs have many important applications. However, most of these complexes are derivatives of 1-phenylethylamine and have an \((\text{sp}^3)\text{C--Pd}\) bond. It is of interest to 1) prepare new types of enantiopure aliphatic CPCs from readily accessible chiral compounds, 2) characterize their structures using available spectrometric methods and 3) study them as chiral inductors in various asymmetric transformations.

Readily available enantiopure D-camphor and other bicyclic monoterpenoids possess rigid structures that may be an advantageous feature in asymmetric reactions; therefore, CPCs based on compounds of this type are important research targets. If new CPCs based on inexpensive compounds from the chiral pool become available, applications of metallacycles in catalysis can be broadened and enriched. In this dissertation, we proposed and studied the synthesis, structural peculiarities and applications of new enantiopure CPCs derived from D-camphor and L-fenchone. Among various possible applications of the new camphor- and fenchone-based CPCs, we selected and investigated their transformations using KPPh₂.
Recently, our research group\textsuperscript{14, 15} and others\textsuperscript{258, 259} have shown that LiPPh\textsubscript{2} and KPPPh\textsubscript{2} are capable of reacting with aromatic CPCs at the C–Pd bond to give hemilabile *NP*-ligands containing an \((sp^2)\)C–P bond. *NP*-*, *PP*- and *SP*-bidentate ligands are efficient catalysts in a number of reactions. New types of chiral hemilabile *NP*-*, *PP*- and *SP*-ligands obtained from inexpensive and naturally optically active compounds can greatly broaden and enrich the applications of these compounds in catalysis. In this dissertation, we proposed and studied the synthesis of new enantiopure *NP*- and other bidentate ligands through the reaction of aliphatic CPCs with KPPPh\textsubscript{2}. Bidentate ligands having an \((sp^2)\)C–P bond have primarily been synthesized using lithium-mediated substitution.\textsuperscript{260-262}

The specific goals of the present study are: (1) to prepare D-camphor and L-fenchone derivatives capable of forming cyclopalladated complexes; (2) to synthesize and structurally characterize new enantiopure CPCs based on D-camphor- and L-fenchone derivatives and (3) to investigate a possibility of the *NP*-ligand preparation by reactions of aliphatic CPCs with KPPPh\textsubscript{2} (Schemes 35 and 36).
Scheme 35. Proposed synthesis and applications of D-camphor-derived CPCs.

Scheme 36. Proposed synthesis and applications of L-fenchone-derived CPCs.
CHAPTER III
RESULTS AND DISCUSSION

III.1. Synthesis of CPCs

III.1.1. Oxime of D-Camphor

There are a few reports about CPCs based on D-camphor; however, their structures are either quite complex (see structures 171 and 172 in Chart 14)\textsuperscript{263} or the bornane carbon framework is not a part of the metalacycle (compound 173).\textsuperscript{264} In 1983, Constable et al. reported unsuccessful attempts to cyclopalladate D-camphor oxime (HL) (174a) using Na\textsubscript{2}PdCl\textsubscript{4}.\textsuperscript{265} The main product of the reaction was the corresponding coordination complex, PdCl\textsubscript{2}(HL)\textsubscript{2}. Attempts to convert the coordination complexes PdCl\textsubscript{2}(HL)\textsubscript{2} and PdI\textsubscript{2}(HL)\textsubscript{2} to their cyclopalladated analogs by heating in high-boiling solvents were also unsuccessful.\textsuperscript{265} For comparison, the oximes of 2,2-dimethylcyclohexanone and related substrates undergo cyclopalladation using the same palladating reagent in high yields.\textsuperscript{64}

![Chart 14. Known CPCs containing the D-camphor carbon framework.](Image)
The Sanford group reported Pd(OAc)$_2$-catalyzed C–H bond oxygenation of $O$-methyl camphor oxime ($\text{174b}$) using K$_2$S$_2$O$_8$ in a mixture of AcOH and Ac$_2$O (100 °C, 12 h, 63%)$^{172}$ or PhI(OAc)$_2$ in AcOH (100 °C, 12 h, 75%).$^{172, 173}$ The same year, Thu et al. disclosed the results of the Pd(OAc)$_2$-catalyzed amidation of the same camphor derivative using K$_2$S$_2$O$_8$ and H$_2$NCOR (R = p-ClC$_6$H$_4$) and resulting in the conversion of the 1-methyl group to 1-CH$_2$NHSO$_2$R (80 °C, 14–20 h, 93%).$^{266}$ Both groups suggested that the reactions preceded through the formation of a cyclopalladated intermediate; however, no attempts were made to isolate it.

**Synthesis of Compounds 174-178 and Spectral Characterization**

On the basis of the aforementioned literature data, $O$-methyl camphor oxime $\text{174b}$ was chosen as a simple preligand for synthesis. First, attempts were made to obtain oxime $\text{174b}$ following the procedure, according to which a solution of D-camphor, methoxyamine hydrochloride and pyridine in isopropanol was refluxed for 7 h.$^{267}$ The $^1$H NMR spectrum of the reaction mixture showed that only ca. 10% of D-camphor was converted to the oxime. The Booth method,$^{268}$ following which a mixture of D-camphor, methoxyamine hydrochloride and pyridine was stirred at rt for 48 h, was also unsuccessful in our hands. When a mixture of D-camphor, methoxyamine hydrochloride and NaOAc in ethanol was refluxed for 5 h following the procedure by Kumar and Verma,$^{269}$ the desired product was prepared in 25% yield. When two-fold excess of methoxyamine hydrochloride and NaOAc was used and the reaction time was increased to 24 h, the pure product was isolated in 74% yield (Scheme 37). According to the $^1$H NMR, the prepared oxime was a 92:8 mixture of two geometrical isomers. Refluxing HONH$_2$.HCl with D-camphor and NaOAc in EtOH...
for 48 h gave preligand 174a in 80% yield. The structure of 174a was confirmed using $^1$H and $^{13}$C NMR spectra.

Scheme 37. Preparation of oxime 174 from D-camphor.

The coordination complex PdCl$_2$(HL)$_2$ (175) was prepared as a reference compound before attempting the cyclopalladation of the oxime. The coordination complex 175 was isolated in 67% yield by stirring camphor oxime 174b with 0.5 equiv of Na$_2$PdCl$_4$ at rt for 18 h (Scheme 38). According to the NMR spectroscopy data, the compound was a mixture of two isomers in ca. 9:1 ratio, possibly due to the presence of $E$ and $Z$ isomers in the starting oxime, although the existence of trans/cis forms of the complex in the solution cannot be excluded.

Scheme 38. Preparation of the coordination complex 175.

Cyclopalladation of oxime 174b was first tested with equimolar amounts of Na$_2$PdCl$_4$ and NaOAc by stirring the reagents in abs. MeOH at rt. Analytical TLC and $^1$H NMR spectrum of the product indicated that this reaction gave only complex 175 (33% yield). Repeating this reaction at reflux for 6 h still showed only the coordination complex.
An equimolar mixture of camphor oxime 174b and Pd(OAc)$_2$ was then stirred in glacial acetic acid at 80 °C for 5 h. After treatment with LiCl, the chloro-bridged CPC 177 was obtained in 66% yield (Scheme 39). The dimeric complex was converted to the mononuclear triphenylphosphine adduct 178 in 98% yield by stirring a 2:1 mixture of PPh$_3$ and CPC 177 in acetone at rt (Scheme 39).


The proposed structures of the obtained coordination and cyclopalladated complexes 175, 177 and 178 were supported by NMR spectroscopy. Signal assignment in the $^1$H and $^{13}$C NMR spectra was done using DEPT, COSY and HMQC spectra. Purity and elemental composition of the compounds were proven by satisfactory elemental analysis.

The $^1$H NMR spectra of the free oxime and the coordination complex contained four 3H singlets confirming the presence of one methoxy and three methyl groups in their structures. The striking difference between the two spectra was a significant downfield shift of the singlet belonging to the 1-Me group of complex 175 from $\delta$ 1.02 to 2.42 ppm. Such downfield shifts of some signals in the spectra of coordination complexes in comparison to those of free ligands have been observed earlier$^{56, 111, 270, 271}$ and can be explained by the position of the corresponding hydrogens above or below the PdCl$_2$N$_2$.
plane of the coordination complex. Such positioning of the C–H bond is considered a possible step of cyclopalladation.

As expected, $^1$H NMR spectra of the cyclopalladated derivatives 176 and 178 had signals of only two methyl groups instead of three (in addition to the singlet of the NOMe fragment). Each of the two diastereotopic hydrogens in the PdCH$_2$ group provided a doublet (or a doublet of doublets due to $^3J_{HP}$ for one of the hydrogens in complex 178): $^2J = 8$ Hz at 2.22 and 2.58 ppm for 177 and $^2J = 10$ Hz at 0.53 and 1.86 ppm for 178. The observed coupling constants and chemical shift values are similar to those reported previously for other dimeric CPCs and PPh$_3$ derivatives with the (sp$^3$)C–Pd bond.

It is noteworthy that the $^1$H and $^{13}$C NMR spectra in C$_6$D$_6$ of the dimeric CPC 177 showed doubling of some signals (in a 5:3 ratio). This can be explained by the presence of two geometrical isomers, cis and trans. Such isomerism is well known for dimeric CPCs including those with the (sp$^3$)C–Pd bond.

The $^1$H, $^{13}$C and $^{31}$P NMR spectra of the mononuclear CPC 178 had one set of signals that suggests the existence of only one isomer in a solution. This complex appears to have the trans-$P,N$ geometry as practically all known PPh$_3$ adducts of CN-cyclopalladated complexes. The 1D NOE experiment with the irradiating frequency corresponding to the resonance frequency of the ortho hydrogens of the PPh$_3$ ligand ($\delta$ 7.78 ppm) showed a positive enhancement of the signal at 1.86 ppm, which belongs to one of the hydrogens of the CH$_2$Pd fragment. Also, the $^1$H NMR signal of one of the hydrogens of the CH$_2$Pd group ($\delta$ 0.53 ppm) appeared as a doublet of doublets with $^2J_{HH} = 10$ Hz and $^3J_{HP} = 8$ Hz. A similar value of the $^3J_{HP}$ coupling constant observed for only one of the two
hydrogens of the CH$_2$PdP fragment was reported for a related PPh$_3$ complex with trans-$P,N$ geometry proven by X-ray crystallographic study.$^{209}$

When the cyclopalladation $O$-methyl camphor oxime (174) was achieved in our lab, we learned that Kuchin et al. just published the cyclopalladation of a closely related derivative of camphor, $N$-benzylimine 179 (Scheme 40).$^{274, 275}$ When our work was compared with Kuchin’s, we concluded that their spectral data and ours were similar (Scheme 40).$^{274, 275}$

Scheme 40. D-Camphor-derived palladacycle 180 with the $(sp^3)C$–Pd bond.

**X-ray Crystallographic Study of CPC 177**

The X-ray single crystal study of complex 177 unambiguously proved its dimeric and cyclopalladated structure. The molecular structure of the compound and the numbering scheme are presented in Fig. 3. Several crystallographic studies of chloro-bridged dimeric five-membered CN-CPCs with the $(sp^3)$C–Pd bond have been reported, including structures 90, 181–184, which will be used for comparison (Chart 15).$^{63, 181, 276, 277}$ Only one of these studies describes the molecular structure of a cyclopalladated oxime with a $(sp^3)$C–Pd bond (184); that oxime was obtained from tert-butyl methyl ketone.$^{63}$
Figure 3. ORTEP drawing of the molecular structure of CPC 177. Thermal ellipsoids are shown at the 50% probability level.

Chart 15. Examples of chloro-bridged dimeric CN-CPCs with the \((sp^3)\)C–Pd bond and a known molecular structure.

Complex 177 crystallizes from hexane/dichloromethane in the orthorhombic crystal system and in the space group \(P2_12_12_1\). The dimeric molecule consists of two independent halves, which are slightly different in their structural parameters. The structure showed trans geometry of the cyclopalladated ligands typical for the majority of known chloro-bridged CN-CPCs with a five-membered palladacycle in solid state. The \(\text{Pd}_2\text{Cl}_2\) ring in 177 is almost planar as in many other chloro-bridged CN-CPCs with trans-configuration. Four torsion angles in the \(\text{Pd}_2\text{Cl}_2\) ring are between 7.28 and 7.89 Å. The Pd…Pd distance in the complex is 3.500 Å, which is similar to those reported for CN-CPCs with trans-geometry.\(^{278}\) For comparison, the closest analog 184 has very rare cis ligand geometry in solid state and displays a significant bending of the \(\text{Pd}_2\text{Cl}_2\) ring that results in an unusually short Pd…Pd distance of 2.99 Å.\(^{63}\)
The Pd–Cl bond trans to the metalated carbon is longer, 2.4996 Å, than that trans to the nitrogen, 2.3311 Å (Δ 0.1685 Å), (here and later, the given values represent the average of two numbers obtained for each half of the dimeric molecule). Similar findings were reported for trans complexes 90, 181–183, in which the Pd–Cl bond length differences are 0.188, 0.156, 0.128 and 0.162 Å, respectively.181,276,277 For three representative chloro-bridged dimeric CN-CPCs with (i) the (sp²)C–Pd bond, (i) a five-membered palladacycle and (iii) trans ligand geometry, the difference between two Pd–Cl bonds (cis and trans to the aromatic carbon) has also been observed, although that difference is smaller, 0.1053, 0.125 and 0.131 Å.4,170,228,279 These data reflect a stronger trans influence of (i) the carbon donor atom compared to nitrogen and (ii) the (sp³)C atom compared to (sp²)C.

The (sp³)C–Pd bond length in 177 is 2.019 Å. This value is within the range reported for complexes 90, 181–184 (1.959–2.034 Å). The (sp³)N–Pd bond in 177 is a little bit longer than the (sp³)C–Pd bond, 2.037 Å, as it is reported for other chloro-bridged dimeric CN-CPCs with the (sp³)N and (sp³)C donor atoms and trans geometry of cyclopalladated ligands.170, 228, 279, 280 For comparison, in complexes 182 and 184, the (sp³)N–Pd bond lengths are 1.996(13) and 1.986(1) Å, respectively.63,277

In complex 177, the bite angles C(10)-Pd-N(1) and C(30)-Pd(2)-N(2) are 82.14(10) and 82.39(10)°, respectively. This value falls in the range reported for compounds 181–183: 84.5(1), 80.7(7) and 82.9(6)°, respectively.276,277 In complex 183 with a silicon atom in the metalacycle, the angle reaches 86.81(9)°.181 For comparison, the C-Pd-N angle for chloro-bridged CPCs with the (sp²)N and (sp²)C donor atoms varies from 80.3 to 81.2°;170,228,279 for the corresponding complexes with (sp³)N and (sp³)C, the C-Pd-N bite angle is slightly larger, 80.6–82.8°.278,280
Both palladium atoms in complex 177 are nearly in square-planar coordination with a slight tetrahedral distortion. The angle between the planes \{N(1)Pd(1)C(10)\} and \{Cl(1)Pd(1)Cl(2)\} is only 0.56°; the angle between the corresponding planes \{N(2)Pd(2)C(30)\} and \{Cl(1)Pd(2)Cl(2)\} is just slightly bigger, 3.26°. It appears that such almost ideal square-planar geometry is a characteristic feature of aliphatic palladacycles.\(^{209}\)

Two metalacycles of dimer 177 can be described as slightly twisted envelopes with C(10) and C(21) serving as the envelope flaps. To estimate the distortion of each metalacycle from planarity, the sum of absolute values of intrachelate torsion angles was used as was proposed by Dunina.\(^{281}\) For one of the rings in CPC 177, the sum is 65.67° with the average angle of 13.13°. For the second metalacycle, the sum is 31.7° with the average angle of 6.34°. The closely related dimer 181 displays a significantly higher distortion of the metalacycle with the sum of torsion angles equal to 158°, with an average angle of 31.6°.\(^{276}\) For comparison, chloro-bridged CN-CPCs with the \(sp^2\)C and \(sp^3\)N donor atoms have the sum of intrachelate torsion angles in the range of 99–135.5°.

III.1.2. N,N-Dimethylhydrazone of D-Camphor

The \(N,N\)-dimethylhydrazone of D-camphor (185) was first reported by Chelucci et al. in 1986 in their study of pyridoannelation of hindered ketones.\(^{282}\) As mentioned before, aliphatic CPCs containing the hydrazone directing group have been investigated by Cardenas et al.\(^{67, 68}\) There are no literature reports on the attempted cyclopalladation of compound 185 or its involvement in palladium-catalyzed reactions.

Preligand 185 was synthesized as a single isomer (\(^1\)H and \(^{13}\)C\(^{1}\)H) NMR data) in 89% yield following the published procedure by Chelucci et al.\(^{282, 283}\) D-Camphor, \(N,N\)-dimethylhydrazine and a catalytic amount of 4-toluenesulfonic acid were refluxed for
seven days in ethanol to give product 185 in 89% yield (Scheme 41). The product of this reaction can exist as two geometric, E/Z, isomers. According to $^1$H and $^{13}$C{$^1$H} NMR data, the hydrazone was isolated as a single geometric isomer. To determine whether the compound has either E or Z geometry, an NOE test was carried out. Irradiation of the protons on the NMe$_2$ group during the NMR experiment showed positive NOE for the endo hydrogen on C(3). Based on this observation, it could be concluded that compound 185 has the E geometry.

Scheme 41. Synthesis of camphor N,N-dimethylhydrazone 185.

Figure 4. Expected and observed NOE effect upon irradiation of the NMe$_2$ group on 185.

Cyclopalladation of the camphor hydrazone 185 was attempted using a variety of conditions; the successful results are summarized in Table 1. All reactions in AcOH resulted in deprotection of the carbonyl group to give camphor. Palladation of 185 using Pd(OAc)$_2$ in MeCN or toluene furnished the desired product 186, although in low yields. The yield of compound 186 was increased to 72% when Na$_2$PdCl$_4$ was used in the presence
of the weak base NaOAc in MeCN. The best yield (92%) of the cyclopalladated complex was achieved with Pd(MeCN)\(_2\)Cl\(_2\)/NaOAc in MeCN (Scheme 42).

Scheme 42. Cyclopalladation of camphor \(N,N\)-dimethylhydrazone 185.

Table 1. Cyclopalladation of camphor \(N,N\)-dimethylhydrazone 185.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd source/base</th>
<th>Rxn temp. (^\circ)C</th>
<th>Rxn time (h)</th>
<th>Solvent</th>
<th>Yield of 186 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(OAc)(_2)</td>
<td>reflux</td>
<td>4</td>
<td>MeCN</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>Na(_2)PdCl(_2)/AcONa</td>
<td>reflux</td>
<td>4</td>
<td>MeCN</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>Pd(OAc)(_2)</td>
<td>60</td>
<td>6</td>
<td>PhMe</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>Pd(CH(_3)CN)(_2)Cl(_2)/NaOAc</td>
<td>reflux</td>
<td>4</td>
<td>MeCN</td>
<td>92</td>
</tr>
</tbody>
</table>

Cyclopalladation of 185 occurred at the methylene group. This conclusion was made based on the \(^1\)H and \(^{13}\)C\({}^1\)H NMR spectra of CPC 186 which showed signals of the three methyl groups on the camphor moiety in addition to the nonequivalent methyl groups on the \((sp^3)N\) atom. This suggested that palladation takes place at C(3) (the methylene carbon) and the \((sp^3)N\) atom is coordinated to the Pd center leading to the possibility of endo/exo palladation. The \(^1\)H and \(^{13}\)C\({}^1\)H NMR spectra of product 186 were complex. This complexity is not only due to possible formation of endo and exo isomers but also cis and trans isomers (Chart 16). In addition, conformational flexibility of trans- and cis-186
is plausible, resulting in three diastereomers for each conformation. This was observed by Perera et al. for complexes of molybdenum derived from 3-diphenylphosphino-(1R)-(+)camphor dimethylhydrazone.284

Repeated attempts to get only one isomer by varying the reagents and reaction conditions gave the same mixture (1H and 13C{1H} NMR data). All efforts to separate the isomers by preparative thin-layer chromatography (TLC) using different eluents were unsuccessful. The mixture of CPCs was refluxed in MeOH in the hope that it would isomerize to give a single isomer, but instead deprotection of the carbonyl group occurred to give D-camphor. Refluxing CPCs 186 over 6 h in aprotic solvents like MeCN and toluene also led to the breakdown of the complex with the deposition of Pd black. Separation of CPCs 186 by recrystallization using common solvents was unsuccessful.

Because the 1H and 13C{1H} NMR spectra for the dimeric complex 186 were difficult to interpret, it was reacted with 2 equiv. of PPh3 in acetone to give the mononuclear triphenylphosphine adduct 187 (Scheme 43). The 1H and 13C{1H} NMR spectra of complexes 187 showed a mixture of two stereoisomers in a 1:1 isomeric ratio, one with an

Chart 16. Possible isomers of CPC 186.
endo C–Pd bond (endo-187) and the other with an exo C–Pd bond (exo-187, Scheme 43).

Attempts to separate the isomers by preparative TLC using different eluents were also unsuccessful. Similar to dimers 186, deprotection of the carbonyl group occurred to give D-camphor when the mixture of complexes 187 was refluxed in MeOH. Refluxing complexes 187 in aprotic solvents like MeCN and toluene also led to the breakdown of the complex with the deposition of Pd black. Separation of CPCs 187 by recrystallization using common organic solvents failed.

![Scheme 43. Reaction of camphor N,N-dimethylhydrazone CPC 186 with PPh₃.](image)

There are many reports of the conversion of dimeric CPCs to their mononuclear adducts by reaction with Na(acac). Na(acac) was prepared by slow addition of a solution of NaOH to acetylacetone. CPC-186 was also converted to the mononuclear acetylacetonate adducts endo- and exo-188 in 96% yield by stirring with 3 equiv. of Na(acac) in CHCl₃ (Scheme 44). The yield of endo- and exo-188 was similar to those reported in the literature (80–98%). The ¹H and ¹³C{¹H} NMR spectra of product 188 showed a mixture of two diastereomers, which differ by stereochemistry at C(3) (Scheme 44). Attempts to separate the two isomers using preparative TLC were unsuccessful.
The best ratios of endo- and exo-188, 83:17 for the former and 19:81 for the latter, were obtained using preparative TLC (silica gel, 1:2 ethyl acetate–hexane). The 83:17 mixture of endo and exo complexes were left in CDCl$_3$ for 3 weeks resulting to a 3:2 ratio of endo and exo complexes which suggested a slow isomerization of the former compound to the latter. The two isomers can be differentiated by a distinct $^1$H NMR signal of the hydrogen bonded to C(3). The singlet at $\delta$ 3.99 ppm was assigned to isomer exo-188 with the endo hydrogen at C(3) since no coupling is expected between hydrogens of C(3) and C(4). The exo hydrogen of C(3) in isomer endo-188 was coupled with both the hydrogen of C(4) and the exo hydrogen of C(5) providing a triplet at $\delta$ 4.82 ppm with a coupling constant of 3.5 Hz. These data point to the fact that endo-188 has C–Pd bond in endo position, while exo-188 is the exo isomer as shown in scheme 44. The identity of the endo isomer could further be confirmed by comparing the $^1$H NMR signals of the three methyl groups of the camphor fragment as they appear in three compounds: preligand 185 and complexes endo- and exo-188. The three methyl groups of the camphor moiety of the endo isomer are arranged in a similar pattern to those of the preligand 185 while those in the exo isomer are not. The interaction of the acac ligand with (pro-S)-Me at C(7) in the exo isomer led to a downfield shift of its $^1$H NMR signal.
The X-ray single crystal study of complex 186 unambiguously proved its dimeric and cyclopalladated structure. The molecular structure of the compound and the numbering scheme are presented in Fig. 4. To the best of our knowledge, there are no reported crystal structures for CN-CPCs with a 2° (sp³)C–Pd bond. However, several crystallographic studies of chloro-bridged dimeric five-membered CN-CPCs with 1° (sp³)C–Pd bonds have been reported, including structures 90, 177, 181–184, which will be used for comparison (Chart 17).63, 181, 276, 277 Only two of these studies describe the molecular structure of a cyclopalladated hydrazone with a (sp³)C–Pd bond (182, 183); these hydrazones were obtained from tert-butyl methyl ketone.277

Figure 5. ORTEP drawing of the molecular structure of CPC 186. Thermal ellipsoids are shown at the 50% probability level.
Chart 17. Examples of chloro-bridged dimeric CN-CPCs with an \((sp^3)\)C–Pd bond and a known molecular structure.

Complex \(\text{186}\) crystallizes from hexane/dichloromethane in the monoclinic crystal system and in the space group \(P2_1\). The dimeric molecule consists of two independent halves, which are slightly different in their structural parameters. The structure showed trans geometry of the cyclopalladated ligands typical for the majority of known chloro-bridged \(CN\)-CPCs with a five-membered palladacycle in solid state. The \(\text{Pd}_2\text{Cl}_2\) ring in \(\text{186}\) is almost planar as in many other chloro-bridged \(CN\)-CPCs with trans configuration. Four torsion angles in the \(\text{Pd}_2\text{Cl}_2\) ring are between 2.17 and 2.38 Å. The \(\text{Pd}...\text{Pd}\) distance in the complex is 3.466 Å, which is similar to those reported for \(CN\)-CPCs with trans-geometry.\(^{278}\) For comparison, the closest analog \(\text{177}\) has a \(\text{Pd}...\text{Pd}\) distance of 3.500 Å while another close analog, \(\text{184}\), possesses very rare cis ligand geometry in solid state and displays a significant bending of the \(\text{Pd}_2\text{Cl}_2\) ring that results in an unusually short \(\text{Pd}...\text{Pd}\) distance of 2.99 Å.\(^{63}\)

The \(\text{Pd}–\text{Cl}\) bond trans to the metalated carbon is longer, 2.4906 Å (here and later, the given values represent the average of two numbers obtained for each half of the dimeric molecule), than that trans to the nitrogen, 2.3374 Å (\(\Delta 0.1532\) Å). Similar findings were reported for trans complexes \(\text{90, 177, 181–183}\), in which the \(\text{Pd}–\text{Cl}\) bond length differences are 0.188, 0.169, 0.156, 0.128 and 0.162 Å, respectively.\(^{181, 276, 277}\) For three representative chloro-bridged dimeric \(CN\)-CPCs with (i) the \((sp^3)\)C–Pd bond, (ii) a five-membered
palladacycle and (iii) trans ligand geometry, the difference between two Pd–Cl bonds (cis and trans to the aromatic carbon) has also been observed, although that difference is smaller, 0.1053, 0.125 and 0.131 Å. These data reflect a stronger trans influence of (i) the carbon donor atom compared to nitrogen and (ii) the (sp^3)C atom compared to (sp^2)C.

The (sp^3)C–Pd bond length in complex 177 is 1.982 Å. This value is within the range reported for complexes 90, 177, 181–184 (1.959–2.034 Å). The (sp^3)N–Pd bond (2.078 Å) in 186 is a little bit longer than the (sp^3)C–Pd bond (1.982 Å), as it is reported for other chloro-bridged dimeric CN-CPCs with the (sp^3)N and (sp^3)C or (sp^3)N and (sp^3)C donor atoms and trans-geometry of cyclopalladated ligands.17, 170, 228, 279, 280 For comparison, in complexes 177, 182 and 184, the (sp^2)N–Pd bond lengths are 2.037(2) 1.996(13) and 1.986(1) Å, respectively63, 277 while in complex 183 the (sp^3)N–Pd bond length is 2.063(1) Å.277

In complex 186, the bite angles C(3)-Pd(1)-N(2) and C(3A)-Pd(1A)-N(2A) are equivalent, 80.8(2)°. This value falls in the range reported for compounds 177, 181–183: 82.27(10), 84.5(1), 80.7(7) and 82.9(6) °, respectively.17, 276, 277 In complex 183 with a silicon atom in the metalacyle, the angle reaches 86.81(9)°.181 For comparison, the C-Pd-N angle for chloro-bridged CPCs with the (sp^2)N and (sp^2)C donor atoms varies from 80.3 to 81.2°;170, 228, 279 for the corresponding complexes with (sp^3)N and (sp^3)C, the C-Pd-N bite angle is slightly larger, 80.6–82.8°.278, 280

Both palladium atoms in complex 186 are nearly in square-planar coordination with a slight tetrahedral distortion. The angle between the planes {N(2)Pd(1)C(3)} and {Cl(1)Pd(1)Cl(1A)} is only 6.02°; the angle between the corresponding planes
\{N(2A)Pd(1A)C(3A)\} and \{Cl(1)Pd(1A)Cl(1A)\} is just slightly bigger, 3.60°. It appears that such almost ideal square-planar geometry is a characteristic feature of aliphatic palladacycles.\textsuperscript{209}

Two metalacycles of dimer 177 can be described as slightly twisted envelopes with C(10) and C(21) serving as the envelope flaps. To estimate the distortion of each metalacycle from planarity, the sum of absolute values of intrachelate torsion angles was used as was proposed by Dunina.\textsuperscript{281} For one of the rings in CPC 177, the sum is 65.67° with the average angle of 13.13°. For the second metalacycle, the sum is 31.7° with the average angle of 6.34°. The closely related dimer 181 displays a significantly higher distortion of the metalacycle with the sum of torsion angles equal to 158°, with an average angle of 31.6°.\textsuperscript{276} For comparison, chloro-bridged CN-CPCs with the (\(sp^2\))C and (\(sp^3\))N donor atoms have the sum of intrachelate torsion angles in the range of 99–135.5°.

III.1.3. \(N,N\)-Diphenylhydrazone of D-Camphor

Previously, Kuchin et al. synthesized CPC 190 from camphor \(N\)-benzylimine 189 using Pd(OAc)\(_2\) in toluene at 60 °C. Preligand 189 can undergo either palladation at the (\(sp^2\))C of the phenyl group or at the (\(sp^3\))C of the camphor moiety. This research group observed regioselective metalation at the (\(sp^2\))C of the phenyl group of camphor \(N\)-benzylimine 189 to give CPC 190 in 45% yield (Scheme 45).\textsuperscript{274, 275, 290}

\begin{equation}
\text{D-camphor} \xrightarrow{\text{Ph}_2\text{CHNH}_2, \text{BF}_3(\text{OEt})_2, \text{PhMe}, \text{reflux, 15 h}} \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{189, 51%}
\end{equation}

\begin{equation}
\text{1. Pd(OAc)}_2, \text{PhMe, 60 °C, 3 h} \quad \text{Me} \quad \text{Me} \quad \text{Ph} \quad \text{N} \quad \text{Ph} \quad \text{190, 45%}
\end{equation}

Scheme 45. D-Camphor-derived palladacycles with the (\(sp^2\))C–Pd bond.
It was of interest to investigate regioselectivity of cyclopalladation for the related preligand, \( N,N \)-diphenylhydrazone of D-camphor 191. There are no literature reports on \( N,N \)-diphenylhydrazone of D-camphor 191. Attempts were made to obtain hydrazone 191 following the published procedure for the synthesis of the phenylhydrazone of D-camphor 192 by Schantl et al. \(^{291} \)

According to their procedure, \( N,N \)-diphenylhydrazine, D-camphor and a catalytic amount of AcOH were refluxed for 3 h in ethanol (Scheme 46). \(^1\)H NMR spectrum of the reaction mixture indicated the presence of the product in ca. 70% yield, but upon purification the \( N,N \)-diphenylhydrazone of D-camphor completely decomposed to D-camphor.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{N-NPh}_2 \\
\text{D-camphor} & \quad \text{D-camphor}
\end{align*}
\]

Scheme 46. Synthesis of camphor \( N,N \)-diphenylhydrazone 191.

III.1.4. Phenylhydrazone of D-Camphor

The phenylhydrazone of D-camphor (192) was synthesized in 50% yield following the published procedure by Schantl et al. \(^{291} \)

According to their procedure, D-camphor, phenylhydrazine and a catalytic amount of AcOH were refluxed for 3 h in ethanol (Scheme 47). The structure of the phenylhydrazone product was confirmed using \(^1\)H NMR spectroscopy. As the authors mentioned, elevated temperatures or traces of acids readily converted phenylhydrazone 192 to D-camphor. It is worth noting that we observed decomposition of this compound immediately after purification even at rt as the brown oily product was turning green. All attempts to cyclopalladate the freshly prepared compound
using Na$_2$PdCl$_2$/AcONa, Pd(OAc)$_2$ or Pd(CH$_3$CN)$_2$Cl$_2$/NaOAc at rt in aprotic solvents such as MeCN and toluene failed due to too rapid decomposition of the preligand to the starting carbonyl compound.

Scheme 47. Synthesis of camphor phenylhydrazone 192.

III.1.5. O-(Diphenylphosphinyl)oxime of D-Camphor

The aim of this work was to access a chiral aliphatic CP-palladacycle based on D-camphor. The presence of a phosphorus atom in the desired CPC allows one to use $^{31}$P NMR spectroscopy for characterization. There are no reports of O-(diphenylphosphinyl) oxime of D-camphor 193 in literature. The synthesis of the acetone analog has been reported by the research groups of Harger and Jennings.\textsuperscript{292-294} According to their procedure, diphenylphosphinic chloride, D-camphor oxime and Et$_3$N were stirred at rt in CH$_2$Cl$_2$/petroleum ether for three weeks (Scheme 48). The $^1$H NMR spectrum of the reaction mixture showed ca. 91% conversion to product 193; however, several attempts to isolate this compound in pure form were unsuccessful.

III.1.6. *tert*-Butylimine of D-Camphor

The *tert*-butylimine of D-camphor 194 has not been reported in literature. TiCl\textsubscript{4} has been shown to be a very effective catalyst for the condensation of sterically hindered ketones and alkyl amines to furnish N-alkylimines.\textsuperscript{295-297} Based on this information, D-camphor, *tert*-butylamine and TiCl\textsubscript{4} were refluxed in benzene for three weeks (Scheme 49). Analysis of the reaction mixture using \textsuperscript{1}H NMR spectroscopy showed no conversion to the product.

Scheme 49. Failed attempt to obtain *tert*-butylimine of D-camphor 194.

III.1.7. Thiocamphor

A sulfur-containing D-camphor derivative 195 was synthesized in order to attempt preparation of the corresponding CS-palladacycle. Since there was a report of the cyclopalladation of thioketones,\textsuperscript{117} we decided to obtain thioketone 195 (also known as thiocamphor). Attempts to synthesize this compound by refluxing D-camphor with Lawesson’s reagent in toluene were unsuccessful.\textsuperscript{298} The reaction gave a complex mixture that was difficult to separate. The Polshettiwar and Kaushik procedure, according to which D-camphor and P\textsubscript{4}S\textsubscript{10}/Al\textsubscript{2}O\textsubscript{3} were refluxed in MeCN for 2 h, gave thiocamphor in 51% yield (Scheme 50).\textsuperscript{299} The structure of thiocamphor 195 was confirmed using \textsuperscript{1}H NMR spectroscopy. All attempts to cyclopalladate thiocamphor using Na\textsubscript{2}PdCl\textsubscript{2}/AcONa, Pd(OAc)\textsubscript{2} or Pd(CH\textsubscript{3}CN)\textsubscript{2}Cl\textsubscript{2}/NaOAc led to the formation of D-camphor.
Scheme 50. Synthesis and the failed cyclopalladation of thiocamphor 195.

### III.1.8. Oxime of L-Fenchone

After succeeding to synthesize and cyclopalladate D-camphor O-methyloxime, we decided to try a closely related bicyclic derivative, L-fenchone. Since there is not a single report in the literature on the cyclopalladation of any L-fenchone derivative or their involvement in palladium-catalyzed reactions, we thought that it would be interesting to study their cyclopalladation. The rigidity of inexpensive and naturally optically active L-fenchone could be an advantageous feature in cyclopalladation and subsequently in the applications of the fenchone based CPCs.

#### Preparation of CPCs Based on L-Fenchone Oximes and their Spectral Characterization

Readily available and inexpensive L-fenchone was converted to two preligands: oxime 196a and its O-methyl derivative 196b (Scheme 51). Oximes 196b were synthesized using the Kumar and Verma procedure\(^{269}\) according to which a mixture of L-fenchone, methoxyamine hydrochloride and NaOAc in ethanol was refluxed for 48 h furnishing the desired product in ca. 50:50 isomeric ratio. All attempts to get a single isomer or predominantly one isomer ratio did not work. Palladation of oxime 196b using Pd(OAc)\(_2\) in AcOH with the hope that isomerization would occur during this process instead gave an inseparable mixture of CPCs. The Jennequin procedure was used to prepare compound 196a according to which a mixture of L-fenchone, hydroxylamine hydrochloride (HONH\(_2\)·HCl) and pyridine was refluxed in EtOH for 48 h to afford oxime 196a in 64%
The $^1$H and $^{13}$C NMR spectra of 196a contained only one set of signals suggesting that the oxime was in the form of one isomer. When HONH$_2$HCl was replaced with its O-methyl analog, oxime 196b was isolated in 82% yield. The $^{13}$C NMR spectrum of 196b contained two sets of signals; the 94:6 ratio of two geometric isomers was determined by integration of two MeO signals in the $^1$H NMR spectrum.

Scheme 51. Preparation of preligands 196a,b from L-fenchone.

Cyclopalladation of oximes 196a,b was accomplished using the same reagent and conditions as reported for the preparation of CPC 177$^\text{17}$: Pd(OAc)$_2$, AcOH, 80 °C, 5 h.$^{55,60}$ The dimeric acetato-bridged complexes 197a,b were converted in situ to their chloro-bridged analogs 198a,b using LiCl in acetone. In a separate reaction, the latter complexes were converted to mononuclear derivatives 199a,b using PPh$_3$ as a monodentate auxiliary ligand (Scheme 52). Chemical composition and purity of complexes 198a,b and 199a,b as well as the fenchone derivative 196b were confirmed by satisfactory elemental analysis.
Scheme 52. Preparation of L-fenchone-derived CPCs 198a,b.

Cyclopalladation of preligands 196a,b and the proposed structures of new complexes 198a,b were supported by NMR spectroscopy. The $^1$H NMR spectra of oxime 196a and its O-methyl derivative 196b contained three 3H singlets in the region of 1.20–1.35 ppm assigned to the methyl groups at positions 1 and 3. In the $^1$H NMR spectra of complexes 198a,b, one of the three singlets in that region was replaced by two one-proton signals with the chemical shifts between 2.15 and 2.80 ppm. Compared to oximes 196a,b, the DEPT spectra of dimers 198a,b contained one more CH$_2$ signal (at 24.6 ppm for 198a and at 25.8 ppm for 198b). For comparison, the $^1$H NMR signals of two diastereotopic hydrogens of the PdCH$_2$ group in the camphor-derived complexes 177 and 180 appeared at 1.55 and 2.59 ppm (180) and 1.89 and 2.41 ppm (177); the $^{13}$C{$^1$H} NMR signal of the carbon bonded to the metal in complexes 177 and 180 was observed at 30.2 and 29.9 ppm, respectively. $^{17, 275}$ $^{13}$C{$^1$H} NMR spectra of dimers 198a,b in CDCl$_3$ contained only one set of signals suggesting that these complexes exist in solution as one isomer. For comparison, the $^{13}$C{$^1$H} NMR spectra of the camphor-derived dimeric
complex 177 in CDCl$_3$ and C$_6$D$_6$ contained two sets of signals signifying the existence of this complex in solution as a mixture of cis and trans isomers.$^{17}$

$^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectra of mononuclear CPCs 199a,b in CDCl$_3$ contained only one set of signals suggesting that these complexes are single geometric isomers in solutions. The $^{13}$C{$^1$H} NMR signals assigned to the carbon of the PdCH$_2$ fragment in compounds 199a,b appeared as singlets at 32.8 and 33.0 ppm. The fact that these signals appeared as singlets ($^3J_{C,P} \approx 0$ Hz) may be indicative of the cis position of PPh$_3$ relative to the methylene group bonded to the palladium.$^{24}$ For comparison, the $sp^3$-hybridized carbons bonded to the metal in the PPh$_3$ derivatives of 177 and 180 of trans geometry provided singlets in the $^{13}$C{$^1$H} NMR spectra at 35.1 and 27.0 ppm, respectively.$^{17,275}$ As reported for related PPh$_3$ derivatives with the ($sp^3$)C–Pd bond and proven trans-$N,P$ geometry,$^{76,208,209}$ one of the two $^1$H NMR signals of the PdCH$_2$ group in 199a,b appeared as a doublet ($^2J_{H,H} = 10.1$ and 10.7 Hz, respectively), while the other hydrogen gave a doublet of doublets due to additional splitting on the phosphorus atom ($^3J_{H,P} = 7.2$ and 9.0 Hz, respectively). One of the two hydrogens of the PdCH$_2$ fragment in both complexes 199a,b provided a signal in a significantly higher field (at 1.09 ppm for 199a and 0.84 ppm for 199b) compared to the other hydrogen (2.28 and 2.16 ppm, respectively). The significant signal shift to a higher field for one of the two hydrogens of the PdCH$_2$ group in the $^1$H NMR spectra of the PPh$_3$ adducts 199a,b suggests that the hydrogen is under the influence of magnetic anisotropy caused by phenyl groups of the PPh$_3$ auxiliary ligand.$^{301-303}$ This, in turn, suggests trans-$N,P$ geometry of complexes 199a,b. For comparison, both $^1$H NMR signals of the PdCH$_2$ group in the chloro-bridged CPCs 198a,b were observed above 2.15 ppm. To note, the chemical shift of the signals in
the $^{31}$P{$^1$H} NMR spectra of 199a,b (19.70 and 20.32 ppm relative to P(OEt)$_3$, respectively) is within the range reported for related mononuclear CPCs with the (sp$^3$)C–Pd bond, the PPh$_3$ auxiliary ligand, and proven trans-N,P geometry.\textsuperscript{76, 208, 209, 304}

**X-ray Structural Analysis of Complexes 199a,b**

Cyclopalladated structure of complexes 199a,b and their trans-N,P geometry were unambiguously proven by X-ray crystallographic studies. Molecular structures of the complexes and the numbering schemes are presented in Figures 5 and 6. Crystal, data collection, and refinement parameters for 199a,b are presented in Table 15–20. The data obtained for complexes 199a,b are compared to those reported for dimer 177\textsuperscript{17} and the closely related five-membered CN-palladacycles 200–204 containing the (sp$^3$)C–Pd bond and PPh$_3$ as the auxiliary ligand (Chart 18).\textsuperscript{74, 76, 208, 209, 304}

![Chart 18](image.png)

Chart 18. Examples of PPh$_3$ adducts of CN-CPCs with the (sp$^3$)C–Pd bond and a known molecular structure.
Figure 6. ORTEP drawing of the molecular structure of complex 199a. Thermal ellipsoids are shown at the 50% probability level.

Figure 7. ORTEP drawing of the molecular structure of complex 199b. Thermal ellipsoids are shown at the 50% probability level.
Bond lengths in 199a,b are similar to those reported for related complexes.\textsuperscript{17, 74, 76, 208, 209, 304} It is noteworthy that the C–Pd bond (2.063 Å) in complex 199b is the longest among those found in the related complexes (2.000–2.051 Å). Interestingly, the Pd–N bond (2.115 Å) in the same complex 199b is also the longest among the camphor- and fenchone-derived CPCs 177 and 199a,b. The Pd–P bond (2.2218 and 2.2250 Å, respectively) in 199a,b are the shortest among the related CN-palladacycles chosen for the comparison (2.2340–2.2563 Å).

The values of the C(1)-Pd-N angle (81.43° and 79.25°, respectively) in both complexes 199a,b fall in the range of reported values for related compounds (78.15–83.43°).\textsuperscript{17, 74, 76, 208, 209, 304} Other bond angles in 199a,b are also similar to those found in complexes 177 and 200–203.

The palladium atom in complexes 199a,b has square-planar coordination with a slight distortion. In both compounds, the torsion angles Pd-N-C(1)-P, Pd-C(1)-P-Cl, Pd-P-Cl-N and Pd-Cl-N-C(1) have the same sign; therefore, the distortion can be described as pyramidal. The distance from the mean plane \{PClC(1)N\} to the metal in 199a,b is 0.049 and 0.075 Å, respectively, indicating that the distortion is greater in 199b. The angle between the planes \{NPdC(1)\} and \{PPdCl\} is equal to 4.3° in 199a and 6.8° in 199b. For comparison, the angle between planes \{NPdC(1)\} and \{PPdCl\} in the reported mononuclear complexes 200 and 201 is equal to 7.7° (the average for four independent molecules) and 2.9°, respectively.\textsuperscript{208, 209}

Palladacycle’s conformation in complexes 199a,b can be described as a slightly twisted envelope with the Pd atom serving as the envelope flap. The sum of absolute values of intrachelate torsion angles in the palladacycle of 199a is found to be 93.50° with the
average angle value of 18.70°. The metalacycle in 199b is more distorted than that in 199a: the sum of absolute values of intrachelate torsion angles in palladacycle 199b is equal to 123.24° with the average angle value of 24.65°. These values suggest that distortion of palladacycles 199a,b from planarity is about average compared to related palladacycles.\textsuperscript{17} For example, for the closely related dichloro-bridged dimer 177, the sum of the intrachelate torsion angles in palladacycle is 48.69° (the average for two palladacycles in the dimer), while the angle sum in the palladacycle of complex 200 is found to be 97.56°. The most distorted palladacycle appears to be in complex 201,\textsuperscript{209} where the sum of intrachelate torsion angles reaches 171.24°.

A notable feature of the crystal structure of complex 199a is the participation of the OH fragment in an intramolecular hydrogen bond with the Cl acceptor. There are two other reports of hydrogen bonding involving the oxime group in camphor-derived Pd(II) complexes.\textsuperscript{265, 305} One of these two studies describes the molecular structure of the coordination complex PdCl\textsubscript{2}L\textsubscript{2}, L = camphor oxime.\textsuperscript{265} The authors drew attention to two hydrogen bonds involving one of the two Cl atoms and both hydroxyl groups suggesting that such a geometry makes the cyclopalladation difficult as it is impossible for the carbon atom of CH\textsubscript{3}(7) to approach the metal. All attempts to palladate camphor oxime with halogen-containing Pd salts were unsuccessful.\textsuperscript{265} Our own attempts to synthesize a CPC from this oxime using Pd(AcO)\textsubscript{2} also failed. This makes the cyclopalladation of the closely related fenchone oxime 196a especially rewarding.

III.2. Reactions of KPPh\textsubscript{2} with CPCs having the (sp3)C–Pd Bond

Stoichiometric and catalytic transformations using palladium and other transition-metal derivatives are rightfully considered a cornerstone of organic and organometallic
chemistry. During the last decade, a variety of atom-economical Pd-catalyzed C–H bond functionalization reactions have gained recognition as a powerful and versatile synthetic approach.\textsuperscript{306-317} Most recently, the focus of these investigations has shifted toward aliphatic C–H bond activation\textsuperscript{220, 306, 307, 318-321} because possible synthetic applications appear to be more diverse and, therefore, more useful. However, metal-catalyzed reactions at the (\textit{sp}^3)C–H bond are difficult to achieve in comparison to those at the (\textit{sp}^2)C–H bond\textsuperscript{171, 306, 317} due to the absence of both empty low-energy orbitals and filled high-energy orbitals that facilitate interaction with orbitals from the metal.\textsuperscript{306, 322} To attain the C–H bond activation by a metal and to increase the regioselectivity of this process, a directing heteroatom or auxiliary is introduced into in the substrate structure.\textsuperscript{317, 323-329} As a result, the first step in many Pd-catalyzed C–H bond functionalization reactions is the formation of a palladacycle.\textsuperscript{330} Additionally, it has been noted that many examples of C–H bond activation, including cyclopalladation reactions, appear to occur under thermodynamic control; therefore, the outcome is dependent on the relative stability of the palladacycle and the strength of the nascent C–Pd bond.\textsuperscript{331} By analogy with data previously reported for Rh complexes,\textsuperscript{331} (\textit{sp}^2)C–Pd bonds are expected to be stronger then (\textit{sp}^3)C–Pd bonds; this may explain frequently observed\textsuperscript{4, 8, 332} (with rare exceptions)\textsuperscript{47, 51, 54, 63, 76, 136, 139, 208, 333} regioselective aromatic cyclopalladation in the presence of a competing aliphatic fragment. Besides the C–Pd bond forming step, a typical catalytic cycle includes the reaction of this bond with a second reagent. Therefore, investigating possible Pd-catalyzed C–H bond functionalization transformations by a certain reagent, it is important to consider the reactivity of the corresponding C–Pd bond toward that chemical. The fact that palladacycles are intermediates of the auxiliary-directing Pd-catalyzed C–H bond
functionalization reactions warrants further studies of stoichiometric reactions of cyclopalladated complexes (CPCs), particularly those with the $(sp^3)$C–Pd bond.

Despite the abundance of reported reactions at the C–Pd bond of palladacycles, there are only a limited number of transformations involving the $(sp^3)$C–Pd bond. Moreover, most of these infrequent studies describe reactions at the benzylic position. The earliest examples of reactions at the $(sp^3)$C–Pd bond of CPCs were reported by the Pfeffer group. They investigated mono- and bis-insertions of hexafluorobutyne and other electron-deficient alkynes into the C–Pd bond of various CN-CPCs including dimeric complexes obtained from $N,N$-dimethyl-o-toluidine. Later, the same group reported reactions of benzyl isocyanide with several CS-CPCs, including one with a benzylic C–Pd bond and one with an aliphatic C–Pd bond (derived from methyl 2,2-dimethylphenyl sulfide and tert-butyl phenyl sulfide, respectively). The same CPCs were also tested in reactions with CO at rt; however, only the complex obtained from tert-butyl phenyl sulfide provided a new insertion product. The authors noted that (i) the yields of the isocyanide insertion products were comparable for all studied CPCs regardless of the hybridization of the carbon atom bonded to the metal and (ii) CS-palladacycles were more reactive towards insertion reactions of isocyanides and CO compared to CN-analogs.

In 1984, Carr and Sutherland studied the iodination of an aliphatic five-membered $C,N$ palladacycle with I$_2$. Later, chlorinations using Cl$_2$ and Et$_3$BnNCl were reported for one $C,N$ and one $C,S$ complex, respectively. In 2005, the Yu group described the iodination of 2,4-di-tert-butyl-2-oxazoline with I$_2$ using stoichiometric and catalytic amounts of Pd(OAc)$_2$. The CPC used in the Yu study was first synthesized by Balavoine and Clinet, who reacted the complex with methyl vinyl ketone, MeI, $n$-BuI, allyl iodide
and CO with and without MeOH to give substituted oxazolines with new C–C bonds. However, no information was provided about the products formed in these reactions except for the yields.  

Several research groups reported oxidation of CN-CPCs obtained from oximes with bulky alkyl substituents.  

The formation of an \((sp^3)C–(sp^2)C\) bond was observed in the reaction of Me₃SnPh with a \(CP\)-palladacycle having a benzylic C–Pd bond. All of these reports suggest that palladacycles with benzylic and aliphatic \((sp^3)C–Pd\) bonds can be used in the same reactions as analogous \((sp^2)C–Pd\)-bonded CPCs; however, no proper comparison of their reactivity can be made because of the limited data available.

Our group and others have investigated reactions of CPCs with lithium and potassium phosphides to form aminophosphines and related bidentate ligands (Scheme 53). All CPCs used in these studies contained an \((sp^2)C–Pd\) bond. In this section of the dissertation, we report our data on reactivity of CN-, CP- and CS-palladacycles with an \((sp^3)C–Pd\) bond toward KPPh₂ and compare these results with the those reported for the \((sp^2)C–Pd\)-bonded CPCs in the same reaction.

![Scheme 53](image)

**Scheme 53.** Formation of bidentate ligands by reacting MPPh₂ with dimeric CPCs containing an \((sp^2)C–Pd\) bond.

Previously, we showed that both LiPPh₂ and KPPh₂ are capable of reacting with dimeric chloro-bridged CPCs. However, the outcome of the LiPPh₂ 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. KPPh₂ 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 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 CN-CPC 177 derived from O-Me camphor oxime$^{17}$ was chosen as a model complex for our study. Complex 177 reacted with 4.5 equiv. of KPPH$_2$ in THF at rt for 18 h to give the desired $NP$-ligand 205 in 21% yield (Scheme 54). The conditions used for this transformation were the same as those previously reported in reactions with CPCs derived from aromatic substrates,$^{14,15,342}$ but the obtained yield of the phosphine was less than half.$^{14,15}$ Increasing the reaction temperature to 40 °C resulted in 5% yield of 205. Considering that the bidentate ligand 205 might be coordinated to the metal, 1,2-bis(diphenylphosphino)ethane was added at the end of the room temperature reaction to release the $NP$-ligand in its free form. The yield, indeed, was improved, but not significantly (28%).

Scheme 54. Reaction of CPC 177 with KPPH$_2$. 

![Scheme 54. Reaction of CPC 177 with KPPH2.](image)
In an attempt to improve the yield of the camphor-based phosphine 205 and learn more about this reaction, the dimeric CPC 177 was reacted in THF with 1 equiv. of KPh2 (corresponds to a 1:2 ratio of Pd and PPh2). As in the previously reported reactions of CPCs with 1 equiv. of KPh2,15 no phosphine 205 was formed and only complex 206 was isolated (Scheme 54). The best yield of this complex (31%) was obtained when the reaction time was shortened to 1 h.

Then, the reaction of CPC 177 with 4.5 equiv. of KPh2 was performed using the standard conditions (THF, 18 h, rt) with a modified purification procedure. Use of ethyl acetate instead of halogenated solvents allowed for isolation of the unstable complex 207 (24%), which presumably has a dimeric structure with two PPh2 bridges. Phosphine 205 was obtained from the same reaction in 17% yield. Further chromatographic purification of complex 207 using CH2Cl2 provided several compounds, some of which were isolated in a pure form or identified using 31P{1H} NMR data. The μ-Cl-μ-PPh2 complex 206 and HP(O)Ph2 were obtained in 16% and 5% yield, respectively, and phosphine 205 was detected by 31P{1H} NMR (<5% yield). The 31P{1H} NMR spectrum of one of the fractions contained the singlet of complex 207 at δ -64.7 ppm [in C6D6 relative to P(OEt)3] and two doublets, δ 21.8 and 113.5 ppm, JPP = 36 Hz. We hypothesize that these doublets belong to compound 208, which can be formed by reacting free phosphine 205 with complex 207 (Scheme 55). The 31P{1H} NMR chemical shift of 123.2 ppm has been reported for complexes with the PAr2 group as a terminal ligand bonded to Pd(II)343 (cf. the chemical shift of -7.8 ppm for the terminal PPh2 ligand bonded to Pt),344,345 while the chemical shifts in a range of 20–35 ppm are typical for tertiary phosphines bonded to Pd(II) as terminal ligands.342,346 The value of the coupling constant suggests that there are two phosphorus
atoms in complex 208 that are cis to each other. Also, the values of the $^{31}$P NMR chemical shifts and the coupling constant of compound 208 are remarkably similar to the analogous complex 209 (Figure 8), which was previously isolated and fully characterized (including a satisfactory elemental analysis). According to the transphobia concept, complexes of type 208 and 209 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 207 can a) slowly produce the corresponding N,P ligands (in this case 205) as a result of reductive elimination and b) react with other ligands, including compound 205, to form mononuclear complexes of type 208 and 209.

Scheme 55. Proposed reaction of dimer 207 with phosphine 205.

Figure 8. Structure of complex 209.
To test whether the $\mu$-Cl-$\mu$-PPh$_2$ complex 206 could be converted to its di-$\mu$-PPh$_2$ analog 207 and/or phosphine 205, it was reacted with 1 equiv. of KPPh$_2$. Two compounds were isolated after preparative TLC: free N,P ligand 205 in 23% yield and complex 207 in 14% yield. It is noteworthy that the $\mu$-Cl-$\mu$-PPh$_2$ CPC obtained from N,N-dimethylbenzylamine can also be converted to the corresponding free aminophosphine in 38% yield by reacting with LiPPh$_2$.$^{342}$

Next, we studied whether the free phosphine could be obtained directly from the di-$\mu$-PPh$_2$ CPC 207 by reacting it with 2.5 equiv. of KPPh$_2$ in THF. To our surprise, after 18 h at rt, no free phosphine 205 was detected in the $^{31}$P{$_1$H} NMR spectrum of the reaction mixture. Chromatographic separation of the reaction mixture allowed for 31% recovery of the starting complex 207. Carrying out the same reaction over 36 h provided no free phosphine either. In the third experiment, which lasted 96 h, the non-coordinated N,P-ligand 205 was finally isolated in 27% yield. Therefore, the di-$\mu$-PPh$_2$ CPC 207 can be converted to compound 205 by reaction with KPPh$_2$; however, this produces the N,P-ligand much more slowly than the direct reaction of CPC 177 with 4.5 equiv. of KPPh$_2$ in THF. In another experiment, the di-$\mu$-PPh$_2$ dimer 207 was treated with 2 equiv. of LiCl before addition of 2.5 equiv. of KPPh$_2$. The $^{31}$P{$_1$H} NMR spectrum of the reaction mixture after 18 h at rt already contained the signal of non-coordinated phosphine 205 suggesting that the reaction of complex 207 with KPPh$_2$ to give phosphine 205 is faster in the presence of chloride ions.

The $^{31}$P{$_1$H} NMR spectra of the sample from the reaction of CPC 177 with 4.5 equiv. of KPPh$_2$ (rt, 18 h) had signals of free phosphine 205, complex 207, PPh$_3$PPh$_2$ and its monoxide, as well as several compounds, which we could not identify, including two
complexes apparently having two different P atoms cis to each other and separated by two bonds \((J_{PP} = 30–40\, \text{Hz})\). The formation of \(\text{PPh}_2\text{PPh}_2\) and its monoxide was also observed in all other reactions of CPCs with metal phosphides.

Encouraged by our results for the camphor-based complex 177, we tested the fenchone-derived CPC 198 in reactions with KPPH₂. The reaction of CPC 198 with 4.5 equiv. of KPPH₂ in THF furnished the enantiopure NP-ligand 210 \((\delta -37.1\, \text{ppm})\) in 51% yield (Scheme 57). Using 1 equiv. of KPPH₂, CPC 198 was converted to the \(\mu\)-Cl-\(\mu\)-PPh₂-bridged derivative 211 \((\delta 2.2\, \text{ppm})\) in 56% yields (Scheme 57). \(^1\text{H}, \, ^{13}\text{C}\{^1\text{H}\} \) and \(^{31}\text{P}\{^1\text{H}\}\) NMR data for complex 211 suggest that this and other \(\mu\)-Cl-\(\mu\)-PPh₂-bridged CPCs reported in the literature,\(^{14,\,15,\,342}\) as well as the others described in this study, exist in solutions as single isomers with trans-\(N,P\) geometry.

The 8-methylquinoline-derived complex 212\(^{42}\) studied next differs from the previously used CPCs 177 and 198 by having a benzylic carbon bonded to the metal. Reactions of CPC 212 with 4.5 equiv. of KPPH₂ at rt gave only 8-methylquinoline (Scheme 58). The isolation of free preligands was previously reported in KPPH₂ reactions with CPCs.
containing an \((sp^2)\)C–Pd bond\(^{14}\) as well as in the Pd-catalyzed phosphination reactions of aryl triflates with PPh\(_3\).\(^{354}\) The formation of such products can be explained by \(\beta\)-hydride elimination of the alkoxide-containing Pd(II) intermediate,\(^{14}\) which could be formed after the adventitious cleavage of a C–O bond in THF by the phosphide.\(^{342}\)

![Scheme 57. Reactions of CPCs 212 with KPPh\(_2\).](image)

When 1 equiv. of KPPh\(_2\) was used in the reaction, the \(\mu\)-Cl-\(\mu\)-PPh\(_2\)-brigded derivative 214 was isolated in 56% (Scheme 58). The \(^{31}\)P\{\(^1\)H\} NMR spectrum of complex 214 had a singlet at \(\delta\) 10.2 ppm [CDCl\(_3\) relative to P(OEt)\(_3\)] and matched the data for this complex prepared by a different method.\(^{347}\)

Complex 212 had a limited solubility in THF. To test if the more soluble complex \(\mu\)-OAc-212 could provide the phosphination product 215, the reaction of this CPC with 4.5 equiv. of KPPh\(_2\) at rt was carried out. Preparative TLC provided a mixture of the desired product 215 and its oxide 216. In the next experiment, air was bubbled through the reaction mixture for 18 h before preparative TLC. The change in the work-up resulted in the isolation of compound 216 in 21% (Scheme 59). 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 such as trimesitylphosphine-derived complex 217 containing a benzylic C–Pd bond. This compound reacted with 4.5 equiv. of KPPH$_2$ at rt to provide only the free preligand 218 (Scheme 60).

Reactions of KPPH$_2$ with two tri-ortho-tolylphosphine-derived complexes, dichloro-bridged dimer 219 and its acetato-bridged analog $\mu$-OAc-219$^{31}$ 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 219 furnished phosphine oxide 220 in 20% yield (Scheme 61). In contrast to the KPPH$_2$ reactions with the 8-methylquinoline-derived CPCs, the use of $\mu$-OAc-219 instead of its chloro-bridged analog provided only traces of the phosphination product 220. It is worth mentioning that, according to $^{31}$P NMR data, only one of the two phosphino groups in the
product was oxidized. In both reactions, along with compound 220, tri-ortho-tolylphosphine 211 was isolated as well (Scheme 61).

Scheme 60. Reaction of complexes 219 and μ-OAc-219 with KPPh2.

Finally, the reactivity of the CS-CPC 222 was studied. This complex reacted with 4.5 equiv. of KPPh2 to provide the phosphination product 223 in low yield. Because of the rapid conversion of 223 to the corresponding oxide 224 during purification, 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 225 was isolated in all reactions of CPC 222 (Scheme 62).

Scheme 61. Reaction of CPC 222 with KPPh2.

2.2. Structure confirmation
According to the literature, non-coordinated tertiary phosphines provide \(^{31}\text{P}\{^{1}\text{H}\}\) NMR signals in the -70 to +70 ppm interval (relative to H\(_{3}\)PO\(_{4}\)), 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 the synthesized phosphines 205 and 210 contained a single peak 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 corresponding phosphine oxides with \(^{31}\text{P}\{^{1}\text{H}\}\) NMR signals at \(\delta\) 15.1 and 15.0 ppm, respectively. \(^{31}\text{P}\{^{1}\text{H}\}\) NMR spectra of phosphine oxides 216 and 224 exhibited singlets at \(\delta\) 16.5 and 15.0 ppm, respectively, whereas the spectrum of product 9f with two phosphorus atoms contained two doublets at \(\delta\) -45.1 and 15.4 ppm (\(^{4}\text{J}_{\text{P,P}} = 9.2\) Hz).

\(^{1}\text{H}\) and \(^{13}\text{C}\{^{1}\text{H}\}\) NMR signals of the CH\(_{2}\)P fragment in compounds 205 and 210 and 226, 216, 220 and 224 displayed \(J_{\text{H,P}}\) and \(J_{\text{C,P}}\) coupling constants. Diastereotopic hydrogens of the CH\(_{2}\)P group in 205 and 210 and 226 (Figure 9) provided two doublets of doublets between \(\delta\) 2.15 and 3.06 ppm. The \(^{1}\text{H}\) NMR signal of the benzylic CH\(_{2}\) group bonded to the phosphorus atom in phosphine oxides 216, 220 and 224 appeared as a doublet between \(\delta\) 4.00 and 4.56 ppm. It is noteworthy that the values of the coupling constant \(^{2}\text{J}_{\text{H,P}}\) for phosphines 205 and 210 were 3.5 and 4.1 Hz, while those for phosphine oxides 226, 216, 220 and 224 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 \(^{13}\text{C}\{^{1}\text{H}\}\) NMR spectra. The CH\(_{2}\)P group in phosphines 205 and 210 gave a doublet at \(\delta\) 27.5 and 30.7 ppm with \(^{1}\text{J}_{\text{C,P}}\) equal to 18 and 13 Hz, respectively. The \(^{13}\text{C}\{^{1}\text{H}\}\) NMR signal of the same group in phosphine oxides 226, 216,
220 and 224 appeared between δ 27.3 and 36.6 ppm and displayed the coupling constant $^{1}J_{C,P}$ in a range of 67–73 Hz. The oxidation of the phosphino group in compounds 226, 216, 220 and 224 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. The elemental composition of phosphines 205 and 210 and phosphine oxides 213, 221 and 225 was confirmed by HRMS data.

Figure 9. Oxide of 205.

Pd(II) complexes with both a chloro and phosphido bridge are rather uncommon in the literature. Moreover, there are only two known cyclopalladated complexes of this type. They were obtained from $N,N$-dimethylbenzylamine and its $\alpha$-tert-butyl-derivative. Three isomers can be predicted for such complexes; however, it was shown that in the solid form and in a solution, they exist as syn isomers with the trans-$N,P$ ligand configuration. The $\mu$-Cl-$\mu$-PPh$_2$ Pd(II) complex (206) obtained in this study presumably have a syn configuration with the PPh$_2$ bridging ligand trans to both nitrogen atoms. The $^{31}$P{$^{1}$H} NMR spectra of CPC 206 in CDCl$_3$ exhibited a singlet at δ 4.9 ppm, respectively. In the $^{13}$C{$^{1}$H} NMR spectra of this complex, the signal of the CH$_2$Pd fragment appeared as a doublet ($^{2}J_{C,P}$ = 2.2 Hz) at 19.4 ppm. For comparison, the reported complex of this type synthesized from $N,N$-dimethylbenzylamine provided the $^{31}$P NMR signal at δ 25.1 ppm ($^{2}J_{C,P}$ = 1.8 Hz). The $^{1}$H NMR spectra of complex 206 confirmed a
1:2 ratio of the PPh₂ group and cyclopalladated ligands in it structure. The elemental composition and purity of this compound was confirmed by satisfactory elemental analysis.

Di-μ-PPh₂ complexes of Pd(II) and especially Pt(II) are well known. 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. Unfortunately, only the X-ray crystallographic data for this compound are available. The ³¹P{¹H} NMR spectra of known di-μ-PPh₂ Pd(II) complexes usually have the signals of the bridging PPh₂ group between -100 and -140 ppm. In the present study, we were able to isolate complex, 207, which presumably have dimeric cyclopalladated structure with two bridging PPh₂ ligands. The ¹H NMR spectrum of the oxazoline-derived analog of complex 207 previously synthesized in our lab suggests a 1:1 ratio of the PPh₂ fragment and the cyclopalladated ligand. The ³¹P{¹H} 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 ¹³C{¹H} NMR signal of the CH₂Pd fragment in oxazoline-derived analog of complex 207 appeared at δ 42.2 ppm as a triplet with J_C,P equal to 55.1 Hz. Regrettably, the camphor-derived complex 207 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 PPh₂ fragment and the cyclopalladated ligand. The only reliable spectroscopic data for this complex that can be reported are its ³¹P{¹H} NMR signal at δ -64.8 ppm in C₆D₆ and -76.9 ppm in CDCl₃.
CONCLUSIONS

As a result of the experimental work, all three major goals (see page 47) have been accomplished.

1. Enantiopure D-camphor O-methyloxime, L-fenchone oximes and camphor N,N-dimethylhydrazone were synthesized according to published procedures in 64–89% yield from readily available compounds in the chiral pool. Structures of these preligands were confirmed using NMR spectroscopy.

2. Direct cyclopalladation of D-camphor O-methyloxime, L-fenchone oximes and camphor N,N-dimethylhydrazone with Pd(OAc)$_2$ and/or Pd(MeCN)$_2$Cl$_2$, afforded new optically active aliphatic cyclopalladated complexes in 49–92% yield. NMR spectral and single crystal X-ray crystallographic studies were used to confirm the presence of an $(sp^3)$C–Pd bond in the complexes.

3. Phosphination reactions of new complexes derived from the O-methyloximes of D-camphor and L-fenchone as well as other dimeric CN-, CP- and CS-CPCs with an $(sp^3)$C–Pd bond were investigated. Using 4.5 equiv. of KPPh$_2$, CPCs were converted to the corresponding phosphines or phosphine oxides in 20–51% yield. When CPCs reacted with 1 equiv. of KPPh$_2$, unique mono-chloro-mono-phosphido-bridged CPCs were isolated in 31–56% yield.
CHAPTER VI

EXPERIMENTAL

VI.1. General Methods and Materials

Routine $^1$H (500 MHz) and $^{13}$C($^1$H) (126 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. IR spectra were recorded on a Perkin Elmer Spectrum 400 FT-IR/FT-FIR Spectrometer. 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 in a 1-dm tube. Elemental analyses were carried out by Atlantic Microlabs Inc., Norcross, GA. Analytical TLC was performed on Whatman silica gel 60 (F$_{254}$) 250 precoated plates. Preparative TLC was carried out using 200 $\times$ 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, hydroxylamine hydrochloride and L-(−)-fenchone were purchased from Acros Organics Co., PPh$_3$ from Eastman Kodak, D-camphor ([α]$_D$ = +44.1° (c = 10.0, EtOH)) from Fisher Scientific. These reagents were used as purchased as their purity was confirmed by $^1$H NMR spectroscopy. Pd(OAc)$_2$ purchased from Aldrich 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$_2$Cl$_2$, hexane and ethyl acetate were distilled over CaH$_2$. Toluene and THF were dried by refluxing over K/benzophenone ketyl and distilled under Ar immediately before starting a reaction. These reagents were used as purchased. The enantiometric purity of L(-)-fenchone was 97%, [α]$^{24}_D$ - 48.9 (neat). Other chemicals were acquired from Sigma-Aldrich Co. and were used without purification unless indicated.

VI.2. Preparation of D-Camphor Derivatives and Their Cyclopalladation

Compounds 174b, 185, 191, 192 and 195 were synthesized using published procedures. The NMR spectra of the obtained compounds matched those reported in the literature.

VI.2.1. Synthesis and Characterization of New Compounds

$(1R,4R)$-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (D-Camphor O-Methyloxime (174b)). Enantiopure D-camphor (0.2000 g, 1.314 mmol) was added to a solution of methoxylamine hydrochloride (0.3007 g, 3.600 mmol) and sodium acetate (0.4676 g, 5.700 mmol) in water (1.2 mL). Ethanol (2 mL) was added, and the mixture was refluxed for 48 h. The mixture was then filtered to remove any solid residue, and ethanol was evaporated under reduced pressure to get an oily residue. The crude product was purified by extraction using CH$_2$Cl$_2$ (5 mL × 3). The combined organic layers were dried over Na$_2$SO$_4$. After filtration, the solvent was removed on a rotavapor to obtain the pure product as a colorless oil in 74% (0.1744 g, 0.9625 mmol). According to the $^1$H NMR spectrum, the product was a mixture of two geometric isomers in a ratio of 92:8. $R_f$ 0.60 (100:1 hexane–acetone); [α]$^{22}_D$ -29.7, [α]$^{22}_{546}$ -42.7, [α]$^{22}_{435}$ -67.9 (c 0.781, EtOH). IR (film, ν, cm$^{-1}$): 1654 and 1667 (C=N), 1045 (N-O). $^1$H NMR (δ, ppm) [63]: 0.80 (s, 3H,
CH$_3$), 0.91 (s, 3H, CH$_3$), 1.02 (s, 3H, CH$_3$), 1.22 (ddd, 1H, $^2$J$_{5\text{endo},5\text{exo}}$ = 12.8, $^3$J$_{5\text{endo},6\text{endo}}$ = 9.3, $^3$J$_{5\text{endo},4}$ = 4.2, H(5endo)), 1.45 (ddd, 1H, $^2$J$_{6\text{endo},6\text{exo}}$ = 14.5, $^3$J$_{6\text{endo},5\text{endo}}$ = 9.3, $^3$J$_{6\text{endo},5\text{exo}}$ = 4.4, H(6endo)), 1.69 (td, 1H, $^2$J$_{6\text{exo},6\text{endo}}$ = $^3$J$_{6\text{exo},5\text{exo}}$ = 12.0, $^3$J$_{6\text{exo},5\text{endo}}$ = 4.3, H(6exo)), 1.82 (m, 1H, H(5exo)), 1.86 (t, 1H, $^3$J$_{4,5\text{exo}}$ = $^3$J$_{4,3\text{exo}}$ = 4.3, H(4)), 1.98 (d, 1H, $^2$J$_{3\text{endo},3\text{exo}}$ = 18.1, H(3endo)), 2.47 (dt, 1H, $^2$J$_{3\text{exo},3\text{endo}}$ = 18.1, $^3$J$_{3\text{exo},4}$ = $^4$J$_{3\text{exo},5\text{exo}}$ = 4.3, H(3exo)), 3.73 (minor isomer) and 3.82 (major isomer) (two s, 3H, OCH$_3$).

$^{13}$C{$_^1$H} NMR ($\delta$, ppm): 11.2, 18.6, 19.5 (three CH$_3$), 27.4 (CH$_2$, C(5)), 32.9 (CH$_2$, C(6)), 33.6 (CH$_2$, C(3)), 43.8 (CH, C(4)), 48.1 and 51.6 (two quat. C, C(1) and C(7)), 61.2 (OCH$_3$), 169.2 (C=N).

(1R,4R)-Dichlorobis{2-(methoxyimino)-1,7,7-trimethylbicyclo[2.2.1]heptane}palladium(II) (175). To a small, one-neck round-bottomed flask containing a magnetic stirring bar and camphor oxime 174b (0.0245 g, 0.135 mmol), Na$_2$PdCl$_4$ (0.0206 g, 0.0700 mmol) was added. Abs. MeOH (1 mL) was added as well, and the flask was covered with a stopper. After stirring the mixture at rt for 18 h, MeOH was removed on a rotavapor. The red-brown crude product was purified using preparative TLC (silica gel, 5:1 hexane–acetone). The pure product was isolated as a yellow powder in 67% yield (0.0168 g, 0.0468 mmol). Mp: 180–182 °C; $R_f$ 0.36 (99:1 benzene–acetone); $[\alpha]^{22}_D$ +50.3, $[\alpha]^{22}_{546}$ +44.4 ($c$ 0.0510, EtOH). IR (Nujol mull, v, cm$^{-1}$): 1655 (C=N). $^1$H NMR ($\delta$, ppm): 0.84 (minor isomer) and 0.87 (major) (two s, 3H, CH$_3$), 0.94 (minor) and 0.98 (major) (two s, 3H, CH$_3$), 1.22 (m, 1H, H(5endo)), 1.81–1.99 (m, 4H, H(5exo, 6endo, 6exo, 4)), 2.29 (d, 1H, $^3$J$_{3\text{endo},3\text{exo}}$ = 18.5, H(3endo)), 2.42 (s, 3H, CH$_3$), 2.80 (m, 1H, H(3exo)), 4.20 (major) and 4.51 (minor) (two s, 3H, OCH$_3$). $^{13}$C{$_^1$H} NMR ($\delta$, ppm): 14.8, 19.2, 20.4 (three CH$_3$), 27.2 (CH$_2$, C(5)), 32.4 (CH$_2$, C(6)), 38.6 (CH$_2$, C(3)), 43.5 (CH, C(4)), 50.3 (C, C(7)), 55.4 (C, C(1)), 62.5 (OCH$_3$, C(10)), 188.0 (C=N).
Anal. Calcd for C$_{22}$H$_{38}$Cl$_2$N$_2$O$_2$Pd: C, 48.94; H, 7.09; N, 5.19. Found: C, 48.94; H, 7.18; N, 5.21%.

$(1S,4R)$-Di-$\mu$-chlorobis[[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N]dipalladium(II) (177). To a 10-mL one-neck round-bottomed flask containing a magnetic stirring bar, camphor oxime 174b (0.0797 g, 0.440 mmol), Pd(OAc)$_2$ (0.0987 g, 0.440 mmol) and glacial acetic acid (19 mL) were added. The resulting mixture was stirred at 80 °C for 5 h. The solvent was removed under reduced pressure to give a brown oily residue of the crude acetate-bridged analog of 176. Abs. acetone (19 mL) was added to the crude product followed by introduction of LiCl (0.0746 g, 1.76 mmol). The mixture was stirred at rt for 18 h. The solution was then filtered through celite (h = 1 cm), and the flask with the filtrate was placed on a rotavapor to remove acetone. The crude product was purified using preparative TLC (silica gel, 99:1 benzene-acetone). The pure product was isolated as an orange-yellow powder in 66% yield (0.0936 g, 0.145 mmol). Mp: 204–206 °C; $R_f$ 0.56 (99:1 benzene–acetone); [$\alpha$]$^{22\text{D}}$ -164, [$\alpha$]$^{22\text{S}46}$ -201, [$\alpha$]$^{22\text{S}435}$ -307 (c 0.100, EtOH). IR (Nujol mull, v, cm$^{-1}$): 1662 (C=N). $^1$H NMR ($\delta$, ppm): 0.80 (s, 3H, CH$_3$), 0.93 (s, 3H, CH$_3$), 1.32 (t, 1H, J$_{5\text{endo},5\text{exo}}$ = 3, J$_{5\text{endo},6\text{endo}}$ = 9.4, H(5endo)), 1.89 (m, 4H, H(5endo), H(6endo), PdCH), 2.06 (m, 1H, H(6exo)), 2.14 (t, 1H, J$_{4,3\text{exo}}$ = 3, J$_{4,5\text{exo}}$ = 4.0, H(4)), 2.41 (m, 2H, J$_{3\text{endo},3\text{exo}}$ = 18.1, J$_{3\text{exo},4}$ = 4.0, H(3exo), PdCH$^3$), 3.78 (s, 3H, OCH$_3$). $^{13}$C{$_1$H} NMR (δ, ppm): 18.3 and 19.6 (two CH$_3$), 26.7 (CH$_2$, C(5)), 31.9 (CH$_2$, C(6)), 33.3 (CH$_2$, C(3)), 46.7 and 66.4 (two quat. C, C(1) and C(7)), 47.6 (CH, C(4)), 62.2 (OCH$_3$), 193.6 (C=N). $^1$H NMR (C$_6$D$_6$, δ, ppm): 0.42 (s, 3H, CH$_3$), 0.56 (s, 3H, CH$_3$), 0.74 (ddd, 1H, J$_{5\text{endo},5\text{exo}}$ = 12.5, J$_{5\text{endo},6\text{endo}}$ = 9.2, J$_{5\text{endo},6\text{exo}}$ = 4.2, H(5endo)), 1.34 (m, 1H, H(5exo)), 1.43 (d, 1H, J$_{3\text{exo},3\text{endo}}$ = 19.0, H(3endo)), 1.47 (t,
1H, \(^3\)J\(_{4,5\text{exo}}\) = \(^3\)J\(_{4,3\text{exo}}\) = 4.0, H(4)), 1.51 (m, 1H, H(6\text{endo})), 1.71 (ddd, 1H \(^2\)J\(_{6\text{endo},6\text{exo}}\) = 13.0, \(^3\)J\(_{6\text{exo},5\text{endo}}\) = 9.2, \(^3\)J\(_{6\text{exo},5\text{endo}}\) = 4.2, H(6\text{exo})), 1.96 (dt, 1H, \(^2\)J\(_{3\text{endo},3\text{exo}}\) = 18.8, \(^3\)J\(_{3\text{exo},4}\) = \(^3\)J\(_{3\text{exo},5\text{exo}}\) = 4.0, H(3\text{exo})), 2.22 (d, 1H, \(^2\)J\(_{H,H}\) = 8.0, PdCH\(_{A}\)), 2.58 (d, 1H, \(^2\)J\(_{H,H}\) = 8, PdCH\(_B\)), 3.79 (s, 3H, OCH\(_3\)). Minor isomer: 2.06 and 2.42 (two br. s, PdCH\(_A\) and PdCH\(_B\)), 3.87 (s, 3H, OCH\(_3\)). The isomer ratio in C\(_6\)D\(_6\) solution was 5:2. \(^{13}\)C{\(^1\)H} NMR (C\(_6\)D\(_6\), \(\delta\), ppm): 16.7 and 18.1 (two CH\(_3\)), 25.3 (CH\(_2\), C(5)), 30.5 (CH\(_2\), C(6)), 31.8 (CH\(_2\), C(3)), 45.0 and 65.0 (two quat. C, C(1) and C(7)), 46.2 (CH, C(4)), 60.9 (OCH\(_3\)), 191.0 (C=N). Anal. Calcd for C\(_{22}\)H\(_{36}\)Cl\(_2\)N\(_2\)O\(_2\)Pd\(_2\): C, 41.01; H, 5.63; N, 4.35. Found: C, 41.02; H, 5.69; N, 4.38%.

\((1S,4R)\)-Chloro[[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N](triphenylphosphine-P)palladium(II) (178). To a 25-mL round-bottomed flask containing a magnetic stirring bar and CPC 177 (0.0148 g, 0.0230 mmol), abs. acetone (8 mL) and PPh\(_3\) (0.0121 g, 0.0460 mmol) were added. The resulting mixture was stirred at rt for 18 h. The solvent was removed under reduced pressure to give a pale-yellow residue. The crude product was purified using preparative TLC (silica gel, 1:2 ethyl acetate–hexane). The pure product was isolated as a pale yellow powder in 98% yield (0.0263 g, 0.0450 mmol). Mp 198–200 °C; \(R_f\) 0.40 (1:2 ethyl acetate–hexane); [\(\alpha\)]\(_{22}^D\) -237, [\(\alpha\)]\(_{22}^{246}\)-277, [\(\alpha\)]\(_{22}^{245}\)-462 (c 0.0730, EtOH). IR (Nujol mull, \(\nu\), cm\(^{-1}\)): 1662 (C=N). \(^1\)H NMR (\(\delta\), ppm): 0.53 (dd, 1H, \(^2\)J\(_{H,H}\) = 10, \(^3\)J\(_{H,P}\) = 8, PdCH\(_A\)), 0.56 (s, 3H, CH\(_3\)), 0.84 (s, 3H, CH\(_3\)), 1.29 (ddd, 1H, \(^3\)J\(_{6\text{endo},5\text{endo}}\) = 12.5, \(^2\)J\(_{5\text{endo},5\text{exo}}\) = 9.5, \(^3\)J\(_{5\text{endo},6\text{exo}}\) = 4.2, H(5\text{endo})), 1.61 (td, 1H, \(^2\)J\(_{6\text{exo},6\text{endo}}\) = \(^3\)J\(_{6\text{endo},5\text{endo}}\) = 12.5, \(^3\)J\(_{6\text{endo},5\text{exo}}\) = 4.2, H(6\text{endo})), 1.80 (m, 1H, H(5\text{exo})), 1.86 (d, 1H, \(^2\)J\(_{H,H}\) = 10, PdCH\(_B\)), 1.96 (ddd, 1H, \(^2\)J\(_{6\text{exo},6\text{endo}}\) = 12.5, \(^3\)J\(_{6\text{exo},5\text{exo}}\) = 9.3, \(^3\)J\(_{6\text{exo},5\text{endo}}\) = 4.2, H(6\text{exo})), 2.02 (d, 1H, \(^2\)J\(_{3\text{endo},3\text{exo}}\) = 18.7, H(3\text{endo})), 2.07 (t, 1H, \(^3\)J\(_{4,5\text{exo}}\) = \(^2\)J\(_{4,3\text{exo}}\) = 4.3, H(4)), 2.49 (dt, 1H, \(^2\)J\(_{3\text{exo},3\text{endo}}\) = 18.7, \(^3\)J\(_{3\text{exo},4}\) = 4.3, \(^4\)J\(_{3\text{exo},5\text{exo}}\) = 3.5, H(3\text{exo})), 4.12 (s, 3H, H(4)).
OCH₃), 7.40 (m, 9H, m- and p-PPh), 7.74 (m, 6H, o-PPh). ¹³C{¹H} NMR (δ, ppm): 18.2 and 20.2 (two CH₃), 27.0 (PdCH₂), 27.2 (CH₂, C(5)), 33.4 (CH₂, C(3)), 33.5 (CH₂, C(6)), 47.2 (CH, C(4)), 48.1 (C, C(7)), 63.3 (OCH₃), 66.0 (C, C(1)), 128.5 (d, ³J_C,P = 10.1, m-PPh), 130.7 (d, ⁴J_C,P = 2.4, p-PPh), 131.7 (d, ¹J_C,P = 51.6, ipso-PPh), 135.1 (d, ²J_C,P = 11.3, o-PPh), 192.2 (C=N). ³¹P{¹H} NMR (δ, ppm): 20.4. Anal. Calcd for C₂₉H₃₃ClNOPPd: C, 59.60; H, 5.69; N, 2.40. Found: C, 59.83; H, 5.68; N, 2.48%.

**Complexes 188.** To a 25-mL round-bottomed flask containing a magnetic stirring bar and the CPC of camphor N,N-dimethylhydrazone (0.0385 g, 0.0574 mmol), chloroform (12 mL) and Na(acac) (0.0216 g, 0.0177 mmol) were added. The resulting mixture was stirred at rt for 18 h. The solvent was removed under reduced pressure to give a pale yellow residue. The crude product was purified using preparative TLC (silica gel, 1:2 ethyl acetate–hexane) to give the pure product 188 as a pale yellow powder (0.0538 g, 0.0900 mmol, 96%).

**(1R,3S,4S)-Chloro[[2-(N,N-dimethylhydrazono)-1,7,7-trimethylbicyclo[2.2.1]heptyl]methylenyl-C,N](acetylacetonate–O,O)palladium(II) (endo-188).** Mp: 120–122 °C; R₇ 0.80 (2:1 hexane–ethyl acetate). IR (ν, cm⁻¹, mineral oil): 1656 (C=N). ¹H NMR (δ, ppm): 0.91, 0.93, 1.08 (three s, 9H, CH₃), 1.31 (ddd, 1H, ³J₅endo,6exo = 13, ³J₅endo,5exo = 9.2), 1.70 (m, 1H, H(5exo)), 1.75 (m, 1H, H(6exo)), 1.87 (s, 3H, acac CH₃), 1.89 (m, 1H, H(6exo)), 1.91 (s, 3H, acac CH₃), 2.02 (t, 1H, ³J₄,5exo = 4.0, H(4)), 2.66, 3.02 (two s, 6H, 2NCH₃), 4.82 (t, 1H, ³J₄,PdCH ≈ 3.5, PdCH), 5.22 (s, 1H, acac CH). ¹³C{¹H} NMR (δ, ppm): 11.2, 20.0, 21.3 (three CH₃), 26.3 (CH₂, C(5)), 27.7, 28.7 (two CH₃, (acac)), 37.2 (CH₂, C(6)), 48.3 (PdCH), 48.4 (C, C(7)), 48.9 (CH, C(4)), 51.92, 51.94 (two NCH₃), 53.0 (C,
(1R,3R,4S)-Chloro[(2-(N,N-dimethylhydrazono)-1,7,7-trimethylbicyclo[2.2.1]heptyl)methylene]-C,N(acetylacetonate-O,O)palladium(II) (exo-188). Mp: 120–122 °C; \( R_f \) 0.75 (2:1 hexane–ethyl acetate). IR (\( \nu \), cm\(^{-1}\), mineral oil): 1656 (C=N). \(^1\)H NMR (\( \delta \), ppm): 0.89, 0.99 (two s, 6H, 2CH\(_3\)), 1.33 (ddd, 1H, \( J_{5\text{endo},6\text{endo}} \approx 11.8, J_{5\text{endo},5\text{exo}} \approx 8.9, J_{5\text{endo},6\text{exo}} = 2.9, \) H(5endo)), 1.42 (s, 3H, CH\(_3\)), 1.69 (t, 1H, \( J_{4,5\text{exo}} \approx J_{4,3\text{exo}} \approx 3.4, \) H(4)), 1.76 (m, 2H, H(5exo), (6endo)), 1.888 (s, 3H, acac CH\(_3\)), 1.891 (m, 1H, H(6exo)), 1.893 (s, 3H, acac CH\(_3\)), 2.66, 3.04 (two s, 6H, 2NCH\(_3\)), 3.99 (s, 1H, PdCH), 5.21 (s, 1H, acac CH). \(^{13}\)C\(^{1}\)H NMR (\( \delta \), ppm): 12.1, 20.7, 21.3 (three CH\(_3\)), 27.9, 28.6 (two CH\(_3\), (acac)), 29.3 (CH\(_2\), C(5)), 30.9 (CH\(_2\), C(6)), 46.8 (CH, C(4)), 46.9 (CH, PdCH)), 50.7 (C, C(7)), 51.5 (C, C(1)), 52.1, 52.5 (two NCH\(_3\)), 99.9 (CH, (acac)), 186.3, 188.0 (two C, (acac)), 198.6 (C=N). Anal. Calcd for C\(_{17}\)H\(_{28}\)N\(_2\)O\(_2\)Pd: C, 51.19; H, 6.89; N, 7.02. Found: C, 50.89; H, 6.89; N, 7.03%.

VI.3. Preparation of L-Fenchone Derivatives and Their Cyclopalladation

\((1R,4S)-1,3,3\text{-Trimethylbicyclo[2.2.1]heptan-2-one oxime (196a)}\). To a solution of hydroxylamine hydrochloride (0.5483 g, 7.891 mmol) in abs. EtOH (10 mL) was added L-(−)-fenchone (0.4290 g, 2.818 mmol). Pyridine (0.60 mL, 7.5 mmol) was then added dropwise and the mixture was refluxed for 48 h. The mixture was filtered, and ethanol from the filtrate was evaporated under reduced pressure. 1M aq. HCl solution (30 mL) was added to the oily residue, and the product was extracted with Et\(_2\)O (3 × 5 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\). After filtration, the solvent was removed on a rotavapor to obtain the pure product as a white powder (0.3041 g, 1.818 mmol, 64%). Mp:
149–151 °C (lit. data 150–153 °C [14]); [α]D +3.00 (c 0.406, EtOH); Rf 0.53 (100:1 hexane–acetone). IR (ν, mineral oil): 1682 (C=N). 1H NMR (δ, ppm): 1.22 (s, 3H, CH3(8)), 1.30, 1.33 (two s, 3H each, CH3(9exo) and CH3(9endo)), 1.34 (m, 1H, H(7A)), 1.45 (m, 1H, H(6endo)), 1.55 (m, 2H, H(6exo), H(5endo)), 1.72 (d, J 7A,7B = 10.5 Hz, 1H, H(7B)), 1.79 (m, 1H, H(5exo)), 1.82 (d, J ≈ 1 Hz, 1H, H(4)), 8.61 (br s, 1H, OH). 13C{1H} NMR (δ, ppm): 17.1 (CH3(8)), 22.2, 22.9 (CH3(9exo) and CH3(9endo)), 25.2 (CH2, C(5)), 34.2 (CH2, C(6)), 43.2 (CH2, C(7)), 44.2 (quat. C, C(3)), 48.6 (CH, C(4)), 50.1 (quat. C, C(1)), 172.5 (C=N). HRMS: [M + H]+ calcd for C10H18NO 168.1388, found 168.1449.

(1R,4S)-1,3,3-Trimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (196b).

This compound was synthesized using the procedure described for oxime 196a in 82% yield (3.197 g, 17.63 mmol) using methoxylamine hydrochloride (5.000 g, 59.87 mmol), L-(−)-fenchone (3.255 g, 21.38 mmol) and pyridine (4.7 mL, 58 mmol) and abs. EtOH (50 mL). According to the 1H NMR spectrum, the product was a mixture of two geometric isomers in a ratio of 94:6. Bp: 86–88 °C; [α]D -20.0, [α]D 546 -35.0, [α]D 435 -67.0 (c 1.04, EtOH); Rf 0.66 (100:1 hexane–acetone). IR (ν, mineral oil): 1655 (C=N). 1H NMR (δ, ppm): 1.22, 1.23, 1.25 (three s, 9H, 3CH3), 1.31 (dd, J 7A,7B = 10.0, J 7,4 = 1.2, 1H, H(7A)), 1.43 (m, 1H, H(6endo)), 1.54 (m, 2H, H(6exo), H(5endo)), 1.70 (dq, J 7A,7B = 10.0, J 4,7B = 4J 5exo,7B ≈ J 5endo,7B = 4J 5endo,7B ≈ 1.8 Hz; 1H, H(7B)), 1.78 (m, 2H, H(5exo), H(4)), 3.71 (minor isomer) and 3.75 (major isomer) (two s, 3H, OCH3). 13C{1H} NMR (δ, ppm): 17.2, 22.5, 23.4 (three CH3), 25.3 (CH2, C(5)), 34.4 (CH2, C(6)), 43.4 (CH2, C(7)), 48.6 (CH, C(4)), 44.6 and 49.9 (two quat. C, C(1) and C(3)), 61.0 (OCH3), 172.6 (C=N). Anal. Calcd for C11H19NO: C, 72.88; H, 10.56; N, 7.73. Found: C, 72.59; H, 10.35; N, 7.78%.
(S,S)-Di-µ-chlorobis[[2-(hydroxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl]methyl-C,N]dipalladium(II) (198a). To a 25-mL one-neck round-bottomed flask containing a magnetic stirring bar, fenchone oxime 196a (0.0527 g, 0.315 mmol), Pd(OAc)$_2$ (0.0707 g, 0.315 mmol) and glacial acetic acid (5.6 mL) were added at rt. The resulting mixture was stirred at 80 °C for 5 h. The solvent was removed under reduced pressure to give a brown oily residue of the crude acetate-bridged dimer 197a. HPLC-grade acetone (5.6 mL) was added to the crude acetate-bridged dimer followed by introduction of LiCl (0.0534 g, 1.26 mmol). The mixture was stirred at rt for 18 h. The solution was then filtered through celite (h = 1 cm), and the flask with the filtrate was placed on a rotavapor to remove acetone. The crude product was separated into several fractions using preparative TLC (silica gel, 9:1 toluene–ethyl acetate). Complex 198a was isolated as an orange-yellow powder in 65% yield (0.0189 g, 0.0307 mmol). Mp: 189–191 °C; [α]$^2_{D}$ -57, [α]$^{24}_{546}$-70 (c 0.30, CH$_2$Cl$_2$); $R_f$ 0.56 (9:1 toluene–ethyl acetate). $^1$H NMR (δ, ppm): 1.20 (s, 3H, CH$_3$), 1.27 (s, 3H, CH$_3$), 1.39 (d, $^2$J$_{7A,7B}$ = 9.9, 1H, H(7A)), 1.59–1.71 (m, 2H, H(6endo), 5(endo)), 1.80–1.87 (m, 2H, H(7B), H(5exo)), 1.95 (m, 1H, H(6exo)), 2.14 (s, 1H, H(4)), 2.29 (d, 1H, $^2$J$_{A,B}$ = 8.8, PdCH$_A$), 2.76 (d, 1H, $^2$J$_{A,B}$ = 8.8, PdCH$_B$), 7.60 (br s, 1H, OH). $^{13}$C{[^1]}H NMR (δ, ppm): 21.3 and 22.4 (two CH$_3$), 24.6 (CH$_2$, PdC) [24], 25.2 (CH$_2$, C(5)), 34.0 (CH$_2$, C(6)), 41.0 (CH$_2$, C(7)), 43.9 and 65.6 (two quat. C, C(1) and C(3)), 54.1 (CH, C(4)), 190.4 (C=N). Anal. Calcd for C$_{20}$H$_{32}$Cl$_2$N$_2$O$_2$Pd$_2$: C, 38.98; H, 5.23; N, 4.55. Found: C, 39.23; H, 5.23; N, 4.55%.

(S,S)-Di-µ-chlorobis[[2-(methoxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl]methyl-C,N]dipalladium(II) (198b). This compound was isolated as an orange–yellow powder in 49% yield (0.1453 g, 0.2255 mmol) using the
procedure described for complex 198a and the following reagents: fenchone O-methyloxime 196b (0.3164 g, 1.745 mmol), Pd(OAc)$_2$ (0.3918 g, 1.745 mmol) and LiCl (0.2960 g, 6.981 mmol). Mp: 202–204 °C; $[\alpha]_{D}^{22}$ -172, $[\alpha]_{22}$ -226, (c 0.416, CH$_2$Cl$_2$); $R_f$ 0.56 (9:1 toluene–ethyl acetate). $^1$H NMR (δ, ppm): 1.19, 1.21 (two s, 6H, 2CH$_3$), 1.38 (d, $^2$J$_{7A,7B}$ = 10.2, 1H, H(7A)), 1.63 (m, 1H, 5(endo)), 1.74 (m, 1H, H(6(endo))), 1.81 (m, 2H, H(7), H(5exo)), 2.01 (m, 1H, H(6exo)), 2.08 (d, $J = 3.5$, 1H, H(4)), 2.17 (br. s, 1H, PdCH$^A$), 2.58 (br. s, 1H, PdCH$^B$), 3.78 (s, 3H, OCH$_3$). $^{13}$C{$^1$H} NMR (δ, ppm): 22.4 and 23.3 (two CH$_3$), 25.3 (CH$_2$, C(5)), 25.8 (PdC) [24], 33.9 (CH$_2$, C(6)), 41.3 (CH$_2$, C(7)), 44.6 and 64.9 (two quat. C, C(1) and C(3)), 53.7 (CH, C(4)), 62.4 (OCH$_3$), 198.6 (C=N). Anal. Calcd for C$_{22}$H$_{36}$Cl$_2$N$_2$O$_2$Pd$_2$: C, 41.01; H, 5.63; N, 4.35. Found: C, 41.28; H, 5.52; N, 4.28%.

\((S,S)\)-Chloro[2-(hydroxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl]methyl-C,N \((\text{triphenylphosphine-P})\text{palladium(II)} \) (199a). To a 50-mL round-bottomed flask with a magnetic stirring bar, a solution of complex 198a (0.0505 g, 0.0820 mmol) in acetone (32 mL) and PPh$_3$ (0.0430 g, 0.164 mmol) were added. The resulting mixture was stirred at rt for 18 h. The solvent was removed under reduced pressure to give a white residue. The crude product was purified using preparative TLC (silica gel, 1:2 ethyl acetate–hexane). The pure complex was isolated as a white powder in 99% yield (0.0921 g, 0.0164 mmol). Mp: 148–150 °C; $[\alpha]_{D}^{22}$ -76.0, $[\alpha]_{22}$ -96.0, $[\alpha]_{22}$ -212 (c 0.366, EtOH); $R_f$ 0.65 (2:1 hexane–ethyl acetate). $^1$H NMR (δ, ppm): 1.09 (dd, 1H, $^2$J$_{H,H} = 10.1$, 2J$_{H,P} = 7.2$, PdCH$^A$), 1.22 (d, 1H, 2J$_{7A,7B}$ = 10.4, H(7A)), 1.27, 1.29 (two s, 6H, 2CH$_3$), 1.52 (m, 1H, H(6(endo))), 1.58 (m, 1H, H(5(endo))), 1.76 (br. d, 1H, 2J$_{7A,7B}$ = 10.4, H(7B)), 1.8–1.9 (m, 2H, H(5exo), H(6exo)), 2.08 (poorly resolved d, 1H, $J \approx 1.0$, H(4)), 2.28 (d, 1H, 2J$_{H,H} = 10.1$, PdCH$^B$), 7.41 (m, 9H, $m$- and p-PPh), 7.65 (m, 6H, o-PPh), 9.70 (s, 1H, OH).
\(^{13}\text{C}\{^1\text{H}\}\text{ NMR (δ, ppm):} 21.0 \text{ and } 22.1 \text{ (two CH\textsubscript{3}),} \text{ 25.1 (CH\textsubscript{2}, C(5)),} \text{ 32.8 (PdC),} \text{ 34.7 (CH\textsubscript{2}, C(6)),} \text{ 42.1 (CH\textsubscript{2}, C(7)),} \text{ 42.9 (C, C(3)),} \text{ 53.2 (CH, C(4)),} \text{ 64.9 (C, C(1)),} \text{ 128.3 (d,} \text{ }^3J_{C,P} = 10.8, m-\text{PPh),} \text{ 130.5 (d,} \text{ }^4J_{C,P} = 1.7, p-\text{PPh),} \text{ 131.0 (d,} \text{ }^1J_{C,P} = 49.6, \text{ipso-} \text{PPh),} \text{ 134.5 (d,} \text{ }^2J_{C,P} = 12.2, o-\text{PPh),} \text{ 187.9 (C=N).} \text{ }^{31}\text{P}\{^1\text{H}\}\text{ NMR (δ, ppm):} 19.7.\text{ Anal. Calcd for C}_{28}\text{H}_{31}\text{ClNOPPd: C, 58.96; H, 5.48; N, 2.46. Found: C, 58.70; H, 5.68; N, 2.49%.} (S,S)-\text{Chloro[2-(methoxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl} \text{methyl-C,N]} \text{ (triphenylphosphine-P)palladium(II) (199b).} \text{ This compound was obtained as a white powder in 74% yield (0.0579 g, 0.0991 mmol) using complex 198b (0.0430 g, 0.0667 mmol) and PPh\textsubscript{3} (0.0350 g, 0.134 mmol) and following the procedure described for compound 199a. Mp: 179–181 °C; [\alpha]^{24}\text{D} -134, [\alpha]^{24}\text{546} -169, [\alpha]^{24}\text{435} -373 (c 0.348, EtOH); R\text{f} 0.54 (2:1 hexane–ethyl acetate). }^{1}\text{H NMR (δ, ppm):} 0.84 \text{ (dd, 1H,} \text{ }^2J_{H,H} = 10.7, \text{ }^2J_{H,P} = 9.0, \text{PdCH}\textsubscript{A}), \text{ 1.18 (m, 1H, H(7)),} \text{ 1.25, 1.27 (two s, 6H,} \text{ 2CH\textsubscript{3}}, \text{ 1.50 (m, 1H, H(6endo)),} \text{ 1.55 (m, 1H, H(5endo)),} \text{ 1.72 (d, 1H,} \text{ }^2J_{7A,7B} = 9.9, \text{ H(7A)), } \text{ 1.82 (m, 1H, H(5exo)),} \text{ 1.91 (m, 1H, H(6exo)),} \text{ 2.00 (unresolved d, 1H, H(4)),} \text{ 2.16 (d, 1H,} \text{ }^2J_{H,H} = 10.7, \text{ PdCH}\textsubscript{B}), \text{ 4.10 (s, 3H, OCH\textsubscript{3}}, \text{ 7.39 (m, 9H,} \text{m- and} p-\text{PPh),} \text{ 7.71 (m, 6H, o-} \text{PPh)} \text{.}^{13}\text{C}\{^1\text{H}\}\text{ NMR (δ, ppm):} 22.8 \text{ and} 23.4 \text{ (two CH\textsubscript{3}),} \text{ 25.5 (CH\textsubscript{2}, C(5)),} \text{ 33.0 (PdC),} \text{ 34.8 (CH\textsubscript{2}, C(6)),} \text{ 43.4 (CH\textsubscript{2}, C(7)),} \text{ 44.2 (C, C(3)),} \text{ 52.9 (CH, C(4)),} \text{ 63.5 (OCH\textsubscript{3}}, \text{ 64.5 (C, C(1)),} \text{ 128.5 (d,} \text{ }^3J_{C,P} = 10.7, \text{ } m-\text{PPh),} \text{ 130.7 (s,} \text{p-} \text{PPh),} \text{ 131.8 (d,} \text{ }^1J_{C,P} = 50.3, \text{ipso-} \text{PPh),} \text{ 135.1 (d,} \text{ }^2J_{C,P} = 11.6, \text{ o-} \text{PPh),} \text{ 196.6 (C=N).} \text{ }^{31}\text{P}\{^1\text{H}\}\text{ NMR (δ, ppm):} 20.3.\text{ Anal. Calcd for C}_{29}\text{H}_{33}\text{ClNOPPd: C, 59.60; H, 5.69; N, 2.40. Found: C, 59.90; H, 5.71; N, 2.40%.}
VI.4. Preparation of CPCs and Their Reactions with KPPH₂

Complexes 177, 178, 212, 217, 219 and 222 were synthesized using published procedures. The NMR spectra of the obtained compounds matched those reported in the literature.

VI.4.1. Synthesis and Characterization of New Compounds

(R,R)-1-[(Diphenylphosphino)methyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (205). CPC 177 (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 pure product (0.0492 g, 0.135 mmol, 21%, colorless oil). [α]²²D +154, [α]²²546 +173 (c 0.0460, EtOH). Rf 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, ²J₃exo,₃endo = 17.6, H(3endo)), 2.15 (dd, 1H, ²J₃H,H = 15.0, ³J₃H,P = 4.1, PCH²), 2.48 (ddd, 1H, ²J₃exo,₃endo = 17.6, ³J₃exo,₄ ≈ ⁴J₃exo,5exo ≈ 4.3, H(3exo)), 2.52 (dd, 1H, ²J₄H,H = 15.0, ³J₄H,P = 4.1, PCH⁵), 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, ¹J₃C,P = 18, PCH₂), 27.8 (CH₂, C(5)), 30.9 (CH₂, d, ³J₃C,P = 12, C(6)), 33.7 (CH₂, C(3)), 44.2 (CH, C(4)), 49.8 (quat. C, d, ³J₃C,P = 3.9, C(7)) 54.6 (quat. C, d, ²J₃C,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$^\Lambda$), 133.7 (CH, d, $^2J_{C,P} = 20$, o-PPh$^B$), 141.2 (quat. C, d, $^1J_{C,P} = 15$, ipso-PPh$^\Lambda$), 141.3 (quat. C, d, $^1J_{C,P} = 17$, ipso-PPh$^B$), 167.9 (quat. C, C=N).

$^{31}$P{\sup1}H NMR (CDCl$_3$, $\delta$, ppm): -36.9. $^{31}$P{\sup1}H NMR (C$_6$D$_6$, $\delta$, ppm): -23.2. HRMS: [M + H]$^+$ calcd for C$_{23}$H$_{28}$NOP 366.1981, found 366.1979.

(R,R)-$\mu$-Chloro-$\mu$-(diphenylphosphido)bis[[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N]dipalladium(II) (206). The reaction was performed as described above for 205 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 206 (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, $[\alpha]_{22}^D$ 546 -190 (c 0.0650, EtOH). IR (Nujol mull, $\nu$, cm$^{-1}$): 1674 (C=N). $^1$H NMR ($\delta$, ppm): 0.62 (s, 3H, CH$_3$), 0.72 (s, 3H, CH$_3$), 0.74 (m, 1H, PdCH$^\Lambda$), 1.27 (ddd, 1H, $^3J_{5\text{endo},6\text{endo}} = 13$, $^2J_{6\text{exo},6\text{endo}} = 9.6$, $^3J_{6\text{endo},6\text{exo}} = 4.3$, H(5endo)), 1.39 (d, 1H, $^2J_{7\text{endo},7\text{exo}} = 10$, PdCH$^B$), 1.64 (td, 1H, $^2J_{7\text{endo},7\text{exo}} = 3J_{6\text{endo},5\text{endo}} = 13$, $^3J_{6\text{endo},5\text{exo}} = 4.5$, H(6endo)), 1.79 (m, 1H, H(5exo)), 1.91 (d, 1H, $^2J_{8\text{endo},8\text{exo}} = 19$, H(3endo)), 1.96 (ddd, 1H, $^2J_{8\text{exo},8\text{endo}} = 13$, $^3J_{8\text{endo},8\text{exo}} = 9.6$, $^3J_{8\text{exo},8\text{endo}} = 4.3$, H(6exo)), 1.99 (t, 1H, $^3J_{9.5\text{exo}} = 3J_{4.3\text{exo}} = 4$, H(4)), 2.37 (dt, 1H, $^2J_{9\text{exo},9\text{endo}} = 19$, $^3J_{9\text{exo},4} = 4J_{9\text{exo},9\text{endo}} = 4$, H(3exo)), 3.97 (s, 3H, OCH$_3$), 7.30 (m, 6H, m- and p-PPh), 7.84 (m, 4H, o-PPh). $^{13}$C{\sup1}H NMR ($\delta$, ppm): 18.5 and 20.2 (two CH$_3$), 19.4 (d, $^1J_{C,P} = 2.2$, 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, $^3J_{C,P} = 10$, 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). $^{31}$P{$^1$H} NMR (CDCl$_3$, $\delta$, ppm): 4.9; $^{31}$P{$^1$H} NMR (C$_6$D$_6$, $\delta$, ppm): 18.0. Anal. Calcd for C$_{34}$H$_{46}$ClN$_2$O$_2$PPd$_2$: C, 51.43; H, 5.84; N, 3.53%. Found: C, 51.14; H, 5.85; N, 3.49%.

$(R,R)$-Di-$\mu$-(diphenylphosphido)bis{[2-(methoxyimino)-7,7-dimethylbicyclo[2.2.1]heptyl]methyl-C,N}dipalladium(II) (207). The reaction was performed as described above for 205. The purification by preparative TLC was performed using 5:1 hexane–ethyl acetate as an eluent. The use of halogenated solvents, such as CH$_2$Cl$_2$ 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$_3$, $\delta$, ppm): -76.9; $^{31}$P{$^1$H} NMR (C$_6$D$_6$, $\delta$, ppm): -64.3.

$(S,S)$-1-{[(Diphenylphosphino)methyl]-3,3-dimethylbicyclo[2.2.1]heptan-2-one}

$O$-Methyloxime (210). The reaction was performed as described above for 205 using complex 198 (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 210 (0.0461 g, 0.126 mmol, 51%, colorless oil). $\lbrack \alpha \rbrack_{D}^{24} +138$, $\lbrack \alpha \rbrack_{D}^{546} +171$, $\lbrack \alpha \rbrack_{D}^{435} +246$ (c 0.150, EtOH). $R_f$ 0.65 (10:1 hexane–ethyl acetate). $^1$H NMR ($\delta$, ppm): 1.19, 1.25 (two s, 6H, 2CH$_3$), 1.31 (d, 1H, $^2$J$_{7A,7B}$ = 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, $^2$J$_{6exo,6endo}$ = $^3$J$_{6exo,5endo}$ = 12.0, $^3$J$_{6exo,5exo}$ $\approx$ $^4$J$_{6exo,P}$ $\approx$ 1.8, H(6exo)), 2.46 (dd, 1H, $^2$J$_{H,H}$ = 14.7, $^2$J$_{H,P}$ = 3.5, PCH$_3$), 2.59 (dd, 1H, $^2$J$_{H,H}$ = 14.7, $^2$J$_{H,P}$ = 4.1, PCH$_3$), 3.73 (s, 3H, OCH$_3$), 41.2 (CH$_2$, C(7)), 44.3 (CH, C(4)), 48.3 (d, C, C(3)), 52.6 (d, C, $^2$J$_{C,P}$ = 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-PPhᴬ), 133.0 (d, ²J_C,P = 19.3, o-PPhᴮ), 139.9 (d, ¹J_C,P = 12.6, ipso-PPhᴬ), 140.0 (d, ¹J_C,P = 10.8, ipso-PPhᴮ), 171.9 (C=N). ³¹P{¹H} NMR (CDCl₃, δ, ppm): -37.1. HRMS: [M + H]⁺ calcd for C₂₃H₂₈NOP 366.1981, found 366.1964.

(S,S)-µ-Chloro-µ-(diphenylphosphido)bis([2-(methoxyimino)-3,3-dimethylbicyclo[2.2.1]heptyl]methyl-C,N)dipalladium(II) (211). The reaction was performed as described above for the preparation of 206 using complex 198 (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 211 (0.0180 g, 0.0227 mmol, 56%, orange solid). [α]²³_D -121, [α]²³_{546} -147, [α]²³_{435} -204 (c 0.222, EtOH). Mp: 209–211 °C; Rₛ 0.55 (10:1 hexane–ethyl acetate). ¹H NMR (δ, ppm): 1.05 (dd, 1H, ²J_H,H = 9.6, ³J_H,P = 4.8, PdCHᴬ), 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), PdCHᴮ), 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, 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). ³¹P{¹H} NMR (CDCl₃, δ, ppm): 2.2. Anal. Calcd for C₃₄H₄₆N₂O₂PCl₂: C, 51.43; H, 5.84; N, 3.53%. Found: C, 51.30; H, 5.84; N, 3.52%.

µ-Chloro-µ-(diphenylphosphido)bis(8-quinolinylmethyl-C,N)dipalladium (214). The reaction was performed as described above for preparation of 206 using CPC 212 (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 214
(0.0258 g, 0.0359 mmol, 56%, orange powder). Mp: 237–239 °C; Rf 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, $^3$J$_{H,H}$ = 7.5, arom. CH), 7.45 (d, 1H, $^3$J$_{H,H}$ = 7.0, arom. CH), 7.50 (dd, 1H, $^3$J$_{H,H}$ ≥ 8.3, 4$J_{H,H}$ ≈ 4.7, arom. CH), 7.56 (d, 1H, $^3$J$_{H,H}$ ≈ 7.7, arom. CH), 8.00 (m, 4H, o-PPh) 8.25 (dd, 1H, $^3$J$_{H,H}$ ≈ 8.2, 4$J_{H,H}$ ≈ 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, $^4$J$_{C,P}$ = 2.7, CH), 123.4 (s, CH), 127.5 (s, CH), 127.9, (d, $^3$J$_{C,P}$ = 10.0, m-PPh), 128.2 (d, $^4$J$_{C,P}$ = 2.5, CH), 129.0 (s, C), 129.3 (s, p-PPh), 134.1 (d, $^2$J$_{C,P}$ = 11.9, o-PPh), 137.7 (s, CH), 137.8 (d, $^1$J$_{C,P}$ = 32.1, ipso-PPh), 146.8 (s, CH), 149.6 (s, C), 151.0 (d, $^4$J$_{C,P}$ = 1.9, C). $^{31}$P{$^1$H} NMR (CDCl$_3$, δ, ppm): 10.2. Anal. Calcd for C$_{32}$H$_{26}$N$_2$PClPd$_2$: C, 53.54; H, 3.65; N, 3.90%. Found: C, 53.27; H, 3.80; N, 3.85%.

8-[(Diphenyloxophosphino)methyl]quinoline (216). Complex 212 (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$_2$Cl$_2$ and separated into several fractions using preparative TLC (10:1 ethyl acetate–acetone). Fraction 1 corresponded to 8-methylquinoline 213 (0.0450 g, 0.314 mmol, 48%, colorless oil). Fraction 3 corresponded to compound 216 (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, $^2$J$_{H,P}$ = 14.2, PCH$_2$), 7.28 (t, 1H, $^3$J$_{H,H}$ = 4.2, arom. H(3)), 7.31 (m, 4H, o-PPh), 7.38 (dt, 2H, $^3$J$_{H,H}$ = 7.4, $^4$J$_{H,H}$ = 1.3, p-PPh), 7.46 (t, 1H, $^2$J$_{H,P}$
= 15.4, arom. H(6)), 7.64 (d, 1H, $^3J_{H,P} = 8.2$, arom. H(7)), 7.78 (m, 1H, arom. H(4)), 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 ($\delta$, 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$_3$, $\delta$, ppm): 16.5. IR (Nujol mull, $\nu$, cm$^{-1}$): 1199 s (P=O). HRMS: [M + H]$^+$ calcd for C$_{22}$H$_{19}$NOP 343.1199, found 344.1108.

[2-(Di-ortho-tolylphosphino)benzyl]diphenylphosphine oxide (220). Complex 219 (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 221 (0.001 g, 0.003 mmol, 2%, white powder). Fraction 2 corresponded to product 220 (0.00147 g, 0.0303 mmol, 20%, pale yellow oil). $R_f$ 0.59 (10:1 ethyl acetate–acetone). $^1$H NMR ($\delta$, ppm): 2.26 (s, 6H, CH$_3$), 4.00 (d, 2H, $^3J_{H,P} = 9.6$, PCH$_2$), 6.61 (dd, 2H, $^3J_{H,P} = 7.4$, $^3J_{H,H} = 4.6$, arom. CH of C$_6$H$_4$-CH$_2$P), 7.00 (dd, 1H, $^3J_{H,H} = 7.6$, $^4J_{H,P} = 3.9$, arom. CH of C$_6$H$_4$-CH$_2$P), 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, $^3J_{H,P} = 7.4, m$-PPh), 7.95 (t, 1H, $^3J_{H,H} = 6.3$, arom. CH of C$_6$H$_4$-CH$_2$P). $^{13}$C$\{^1$H$\}$ NMR ($\delta$, 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$_6$H$_4$-CH$_2$P), 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$_6$H$_4$-CH$_2$P), 134.3 (s, arom. CH of C$_6$H$_4$-CH$_2$P), 134.5 (d, $^2J_{C,P} = 9.3$, PPh), 135.0 (t, $^3J_{C,P} = 8.4$, arom. CH of C$_6$H$_4$-CH$_2$P), 137.7 (dd, $^1J_{C,P} = 26.4, ^3J_{C,P} = 6.3$, arom. C of C$_6$H$_4$-CH$_2$P), 142.8 (d, $^1J_{C,P} = 25.9$, C(2) of tolyl). $^{31}$P$\{^1$H$\}$ NMR (CDCl$_3$, $\delta$, ppm): -45.08 and 15.35 (two d, $^4J_{P,P} = 9.2$). IR (Nujol mull, $\nu$, cm$^{-1}$): 1198 s (P=O). HRMS: [M + Na + H]$^+$ calcd for C$_{33}$H$_{30}$O$_2$P$_2$Na 543.1691, found 543.1440.

[6-Methyl-1-(methylthio)benzyl]diphenylphosphine oxide (224). The compound was obtained using the procedure described above for oxide 220 using complex 222 (0.1309 g, 0.2233 mmol). The reaction mixture was separated into two fractions using preparative TLC (10:1 ethyl acetate–acetone). Fraction 1 corresponded to 2,6-dimethylthioanisole 225 (0.0483 g, 0.317 mmol, 71%, colorless oil). Fraction 2 corresponded to compound 224 (0.0351 g, 0.0996 mmol, 22%, purple oil). $R_f$ 0.50 (10:1 ethyl acetate–acetone). $^1$H NMR ($\delta$, 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, $^3J_{H,P} = 3^J_{H,H} = 7.7, ^4J_{H,H} = 2.7$, 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 ($\delta$, ppm): 19.1 (s, CH$_3$), 22.2
(s, SCH₃), 36.6 (d, J_C,P = 67.0, PCH₂), 128.6 (d, J_C,P = 1.7, arom. CH(5)), 128.8 (d, J_C,P = 1.8, o-PPh), 129.0 (d, J_C,P = 4.8, CH(3)), 129.7 (d, J_C,P = 2.7, arom. CH(4)), 131.7 (d, J_C,P = 9.1, m-PPh), 132.1 (d, J_C,P = 2.8, p-PPh), 132.7 (s, C(6)), 133.5 (s, C(2)), 136.3 (s, C(6))

31P{¹H} NMR (CDCl₃, δ, ppm): 15.03. IR (Nujol mull, ν, cm⁻¹): 1187 s (P=O).


(R,R)-1-[(Diphenyloxophosphino)methyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-one O-Methyloxime (226). Phosphine 205 was exposed to the air to give the corresponding oxide as an orange-yellow oil in a quantitative yield. [α]²⁴D -18, [α]²⁴₅₆ -13 (c 0.099, EtOH). Rf 0.57 (5:3 hexane‒acetone). IR (CH₂Cl₂, ν, cm⁻¹): 1671 (C=N), 1184 (P=O). ¹H NMR (δ, ppm): 0.81 (s, 3H, CH₃), 1.04 (s, 3H, CH₃), 1.12 (m, 1H, H(5endo)), 1.30 (m, 1H, H(6endo)), 1.82 (m, 2H, H(5exo), H(4)), 1.88 (d, 1H, J₃endo,3exo = 18, H(3endo)), 2.15 (t, 1H, J₃H,H = 3 J₃H,P = 16, PCH), 2.40 (m, 2H, H(6exo), H(3exo)), 3.06 (dd, 1H, J₃H,H = 3 J₃H,P = 16, PCH), 3.72 (s, 3H, OCH₃), 7.45 (m, 6H, o- and p-PPh), 7.77 (m, 2H, m-PPh), 7.95 (m, 2H, m-PPh). ¹³C{¹H} NMR (δ, ppm): 19.6 and 19.9 (two CH₃), 27.3 (d, J_C,P = 73, PCH₂), 28.0 (CH₂, C(5)), 29.4 (CH₂, C(3)), 33.8 (CH₂, C(3)), 43.2 (CH, C(4)), 50.3 (quat. C, d, J_C,P = 4.6, C(7)), 53.2 (quat. C, d, J_C,P = 4.9, C(1)), 61.7 (OCH₃), 128.6 (CH, d, J_C,P = 12, o-PPh), 128.8 (CH, d, J_C,P = 12, o-PPh), 130.8 (CH, d, J_C,P = 8.9, m-PPh), 131.6 (CH, br. s, p-PPh), 131.7 (CH, d, J_C,P = 9.4, m-PPh), 134.9 (quat. C, d, J_C,P = 98, ipso-PPh), 136.6 (quat. C, d, J_C,P = 99, ipso-PPh), 167.5 (quat. C, d, J_C,P = 5.3, C=N). ³¹P{¹H} NMR (CDCl₃, δ, ppm): 15.1. ³¹P{¹H} NMR (C₆D₆, δ, ppm): 25.0. HRMS: [M + H]⁺ calcd for C₂₃H₂₈NO₂P 382.1894, found 382.1894.

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APPENDICES
APPENDIX A

X-RAY DATA TABLES OF COMPLEX 177

Table 2. Crystal data, data collection, structure solution and structure refinement for 177.

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<td>(R) indices (all data)</td>
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Table 3. Selected bond lengths for 177.

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Table 4. Selected angles for 177.

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<td>C(24)-C(25)-C(26)</td>
<td>103.1(2)</td>
</tr>
<tr>
<td>C(1)-C(6)-C(5)</td>
<td>103.4(2)</td>
<td>C(25)-C(26)-C(21)</td>
<td>104.0(2)</td>
</tr>
<tr>
<td>C(9)-C(7)-C(8)</td>
<td>107.9(3)</td>
<td>C(29)-C(27)-C(28)</td>
<td>107.8(3)</td>
</tr>
<tr>
<td>C(9)-C(7)-C(4)</td>
<td>114.1(2)</td>
<td>C(29)-C(27)-C(24)</td>
<td>114.5(2)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(4)</td>
<td>114.1(2)</td>
<td>C(28)-C(27)-C(24)</td>
<td>114.7(2)</td>
</tr>
<tr>
<td>C(9)-C(7)-C(1)</td>
<td>113.8(2)</td>
<td>C(29)-C(27)-C(21)</td>
<td>113.5(2)</td>
</tr>
<tr>
<td>C(8)-C(7)-C(1)</td>
<td>113.4(2)</td>
<td>C(28)-C(27)-C(21)</td>
<td>112.9(2)</td>
</tr>
<tr>
<td>C(4)-C(7)-C(1)</td>
<td>93.1(2)</td>
<td>C(24)-C(27)-C(21)</td>
<td>93.1(2)</td>
</tr>
<tr>
<td>C(1)-C(10)-Pd(1)</td>
<td>109.25(17)</td>
<td>C(21)-C(30)-Pd(2)</td>
<td>110.95(18)</td>
</tr>
</tbody>
</table>
Table 5. Crystal data, data collection, structure solution and structure refinement for 156.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>$\text{C}<em>{24}\text{H}</em>{42}\text{Cl}<em>{2}\text{N}</em>{4}\text{Pd}_{2}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>670.31</td>
</tr>
<tr>
<td>Temperature</td>
<td>123(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>$a = 12.1816(17)$ Å, $\alpha = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 7.1564(10)$ Å, $\beta = 109.964(2)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 16.823(2)$ Å, $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>1378.4(3) Å $^3$</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.615 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.517 mm$^{-1}$</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>680</td>
</tr>
<tr>
<td>Crystal color, morphology</td>
<td>Yellow, Block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.220 x 0.200 x 0.180 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.779 to 27.617°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>$-15 \leq h \leq 15$, $-9 \leq k \leq 9$, $-21 \leq l \leq 21$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16179</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>6351 [$R_{\text{int}} = 0.0329$]</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>5902</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>100.0%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.4915 and 0.4383</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>6351 / 1 / 299</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.040</td>
</tr>
<tr>
<td>Final $R$ indices [$I &gt; 2\sigma(I)$]</td>
<td>$R_1 = 0.0298$, $wR_2 = 0.0570$</td>
</tr>
<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0336$, $wR_2 = 0.0596$</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>-0.04(2)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.680 and -0.503 e.$\text{Å}^{-3}$</td>
</tr>
</tbody>
</table>
Table 6. Selected bond lengths for 186.

<table>
<thead>
<tr>
<th>Bond</th>
<th>d/ Å</th>
<th>Bond</th>
<th>d/ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(1)-C(3)</td>
<td>1.982(5)</td>
<td>C(4)-C(7)</td>
<td>1.545(7)</td>
</tr>
<tr>
<td>Pd(1)-N(2)</td>
<td>2.076(5)</td>
<td>C(5)-C(6)</td>
<td>1.551(8)</td>
</tr>
<tr>
<td>Pd(1)-Cl(1A)</td>
<td>2.3331(14)</td>
<td>C(7)-C(9)</td>
<td>1.533(8)</td>
</tr>
<tr>
<td>Pd(1)-Cl(1)</td>
<td>2.5012(13)</td>
<td>C(7)-C(10)</td>
<td>1.536(8)</td>
</tr>
<tr>
<td>Pd(1A)-C(3A)</td>
<td>2.007(5)</td>
<td>N(1A)-C(2A)</td>
<td>1.267(7)</td>
</tr>
<tr>
<td>Pd(1A)-N(2A)</td>
<td>2.079(5)</td>
<td>N(1A)-N(2A)</td>
<td>1.489(6)</td>
</tr>
<tr>
<td>Pd(1A)-Cl(1)</td>
<td>2.3416(14)</td>
<td>N(2A)-C(11A)</td>
<td>1.468(8)</td>
</tr>
<tr>
<td>Pd(1A)-Cl(1A)</td>
<td>2.4799(14)</td>
<td>N(2A)-C(12A)</td>
<td>1.492(7)</td>
</tr>
<tr>
<td>N(1)-C(2)</td>
<td>1.271(7)</td>
<td>C(1A)-C(2A)</td>
<td>1.501(7)</td>
</tr>
<tr>
<td>N(1)-N(2)</td>
<td>1.495(6)</td>
<td>C(1A)-C(8A)</td>
<td>1.507(8)</td>
</tr>
<tr>
<td>N(2)-C(11)</td>
<td>1.474(7)</td>
<td>C(1A)-C(6A)</td>
<td>1.550(9)</td>
</tr>
<tr>
<td>N(2)-C(12)</td>
<td>1.475(8)</td>
<td>C(1A)-C(7A)</td>
<td>1.576(7)</td>
</tr>
<tr>
<td>C(1)-C(8)</td>
<td>1.507(7)</td>
<td>C(2A)-C(3A)</td>
<td>1.491(8)</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.521(7)</td>
<td>C(3A)-C(4A)</td>
<td>1.535(7)</td>
</tr>
<tr>
<td>C(1)-C(7)</td>
<td>1.557(8)</td>
<td>C(4A)-C(5A)</td>
<td>1.542(8)</td>
</tr>
<tr>
<td>C(1)-C(6)</td>
<td>1.569(7)</td>
<td>C(4A)-C(7A)</td>
<td>1.565(8)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.501(8)</td>
<td>C(5A)-C(6A)</td>
<td>1.539(8)</td>
</tr>
<tr>
<td>C(3)-C(4)</td>
<td>1.548(7)</td>
<td>C(7A)-C(9A)</td>
<td>1.511(7)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.513(8)</td>
<td>C(7A)-C(10A)</td>
<td>1.534(8)</td>
</tr>
</tbody>
</table>

Table 7. Selected angles for 186.

<table>
<thead>
<tr>
<th>Bond</th>
<th>angle/°</th>
<th>Bond</th>
<th>angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(3)-Pd(1)-N(2)</td>
<td>80.8(2)</td>
<td>C(3A)-Pd(1A)-Cl(1A)</td>
<td>175.46(16)</td>
</tr>
<tr>
<td>C(3)-Pd(1)-Cl(1A)</td>
<td>93.87(18)</td>
<td>N(2A)-Pd(1A)-Cl(1A)</td>
<td>96.00(13)</td>
</tr>
<tr>
<td>N(2)-Pd(1)-Cl(1A)</td>
<td>174.12(12)</td>
<td>Cl(1)-Pd(1A)-Cl(1A)</td>
<td>88.40(4)</td>
</tr>
<tr>
<td>C(3)-Pd(1)-Cl(1)</td>
<td>174.36(17)</td>
<td>Pd(1A)-Cl(1A)-Pd(1)</td>
<td>91.34(5)</td>
</tr>
<tr>
<td>N(2)-Pd(1)-Cl(1)</td>
<td>97.45(13)</td>
<td>Pd(1)-Cl(1A)-Pd(1A)</td>
<td>92.08(5)</td>
</tr>
<tr>
<td>Cl(1A)-Pd(1)-Cl(1)</td>
<td>88.08(4)</td>
<td>C(2)-N(1)-N(2)</td>
<td>108.5(4)</td>
</tr>
<tr>
<td>C(3A)-Pd(1A)-N(2A)</td>
<td>80.8(2)</td>
<td>C(11)-N(2)-C(12)</td>
<td>110.1(5)</td>
</tr>
<tr>
<td>C(3A)-Pd(1A)-Cl(1)</td>
<td>94.68(18)</td>
<td>C(11)-N(2)-N(1)</td>
<td>106.4(4)</td>
</tr>
<tr>
<td>N(2A)-Pd(1A)-Cl(1)</td>
<td>175.21(14)</td>
<td>C(12)-N(2)-N(1)</td>
<td>104.0(4)</td>
</tr>
</tbody>
</table>
C(11)-N(2)-Pd(1) 113.7(4) C(2A)-C(1A)-C(7A) 96.5(4)
C(12)-N(2)-Pd(1) 110.1(4) C(8A)-C(1A)-C(7A) 117.9(5)
N(1)-N(2)-Pd(1) 112.1(3) C(6A)-C(1A)-C(7A) 101.2(5)
C(8)-C(1)-C(2) 116.6(5) N(1A)-C(2A)-C(3A) 126.5(5)
C(8)-C(1)-C(7) 120.0(5) N(1A)-C(2A)-C(1A) 124.7(5)
C(2)-C(1)-C(7) 101.0(5) C(3A)-C(2A)-C(1A) 108.0(5)
C(8)-C(1)-C(6) 115.6(5) C(2A)-C(3A)-C(4A) 101.5(4)
C(2)-C(1)-C(6) 99.7(4) C(2A)-C(3A)-Pd(1A) 106.3(4)
C(7)-C(1)-C(6) 100.6(5) C(4A)-C(3A)-Pd(1A) 129.2(4)
N(1)-C(2)-C(3) 125.6(5) C(3A)-C(4A)-C(5A) 105.5(5)
N(1)-C(2)-C(1) 125.5(5) C(3A)-C(4A)-C(7A) 103.5(5)
C(3)-C(2)-C(1) 108.6(5) C(5A)-C(4A)-C(7A) 101.3(4)
C(2)-C(3)-C(4) 100.2(4) C(6A)-C(5A)-C(4A) 102.1(5)
C(2)-C(3)-Pd(1) 105.9(4) C(5A)-C(6A)-C(1A) 105.6(5)
C(4)-C(3)-Pd(1) 129.4(4) C(9A)-C(7A)-C(10A) 107.3(5)
C(5)-C(4)-C(7) 103.9(5) C(9A)-C(7A)-C(4A) 115.9(5)
C(5)-C(4)-C(3) 108.0(5) C(10A)-C(7A)-C(4A) 112.6(4)
C(7)-C(4)-C(3) 100.5(4) C(9A)-C(7A)-C(1A) 113.5(4)
C(4)-C(5)-C(6) 103.7(4) C(10A)-C(7A)-C(1A) 113.9(5)
C(5)-C(6)-C(1) 103.7(5) C(4A)-C(7A)-C(1A) 93.4(4)
C(9)-C(7)-C(10) 106.8(5)
C(9)-C(7)-C(4) 112.6(5)
C(10)-C(7)-C(4) 116.2(5)
C(9)-C(7)-C(1) 114.0(5)
C(10)-C(7)-C(1) 112.6(5)
C(4)-C(7)-C(1) 94.7(4)
C(2A)-N(1A)-N(2A) 108.9(4)
C(11A)-N(2A)-N(1A) 104.8(4)
C(11A)-N(2A)-C(12A) 109.7(5)
N(1A)-N(2A)-C(12A) 107.6(4)
C(11A)-N(2A)-Pd(1A) 109.5(4)
N(1A)-N(2A)-Pd(1A) 112.9(3)
C(12A)-N(2A)-Pd(1A) 112.1(4)
C(2A)-C(1A)-C(8A) 116.4(5)
C(2A)-C(1A)-C(6A) 107.5(5)
C(8A)-C(1A)-C(6A) 114.9(4)

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APPENDIX C

X-RAY DATA TABLES OF COMPLEX 199a

Table 8. Crystal data, data collection, structure solution and structure refinement for 199a.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C\textsubscript{28} H\textsubscript{31} Cl N O P Pd</td>
</tr>
<tr>
<td>Formula weight</td>
<td>570.36</td>
</tr>
<tr>
<td>Temperature</td>
<td>173(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a = 27.051(2) \ Å) (\alpha = 90^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b = 11.8212(11) \ Å) (\beta = 121.429(1)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 19.0231(17) \ Å) (\gamma = 90^\circ)</td>
</tr>
<tr>
<td>Volume</td>
<td>5190.7(8) \ Å\textsuperscript{3}</td>
</tr>
<tr>
<td>(Z)</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.460 Mg/m\textsuperscript{3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.900 mm\textsuperscript{-1}</td>
</tr>
<tr>
<td>(F(000))</td>
<td>2336</td>
</tr>
<tr>
<td>Crystal color, morphology</td>
<td>colourless, needle</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.40 x 0.13 x 0.10 mm\textsuperscript{3}</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.764 to 27.508°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>(-34 \leq h \leq 32, -15 \leq k \leq 15, -24 \leq l \leq 24)</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>23130</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5932 [(R\text{(int)} = 0.0502)]</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>4451</td>
</tr>
<tr>
<td>Completeness to theta = 25.242°</td>
<td>99.9%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5932 / 0 / 301</td>
</tr>
<tr>
<td>Goodness-of-fit on (F^2)</td>
<td>1.005</td>
</tr>
<tr>
<td>Final (R) indices [(I &gt; 2\sigma(I))]</td>
<td>(R_1 = 0.0432, \ wR2 = 0.0918)</td>
</tr>
<tr>
<td>(R) indices (all data)</td>
<td>(R_1 = 0.0659, \ wR2 = 0.1021)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.815 and -1.026 e.Å\textsuperscript{-3}</td>
</tr>
</tbody>
</table>
Table 9. Selected bond lengths for 199a.

<table>
<thead>
<tr>
<th>Bond</th>
<th>( d / \text{Å} )</th>
<th>Bond</th>
<th>( d / \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd1-C1</td>
<td>2.051(4)</td>
<td>P1-C23</td>
<td>1.822(4)</td>
</tr>
<tr>
<td>Pd1-N1</td>
<td>2.064(3)</td>
<td>C11-C12</td>
<td>1.381(5)</td>
</tr>
<tr>
<td>Pd1-P1</td>
<td>2.2218(10)</td>
<td>C11-C16</td>
<td>1.395(5)</td>
</tr>
<tr>
<td>Pd1-Cl1</td>
<td>2.4019(9)</td>
<td>C12-C13</td>
<td>1.385(6)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.526(5)</td>
<td>C13-C14</td>
<td>1.378(6)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.502(5)</td>
<td>C14-C15</td>
<td>1.371(6)</td>
</tr>
<tr>
<td>C2-C7</td>
<td>1.539(6)</td>
<td>C15-C16</td>
<td>1.373(6)</td>
</tr>
<tr>
<td>C2-C8</td>
<td>1.550(6)</td>
<td>C17-C22</td>
<td>1.391(6)</td>
</tr>
<tr>
<td>C3-N1</td>
<td>1.273(5)</td>
<td>C17-C18</td>
<td>1.391(6)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.507(5)</td>
<td>C18-C19</td>
<td>1.391(7)</td>
</tr>
<tr>
<td>N1-O1</td>
<td>1.391(4)</td>
<td>C19-C20</td>
<td>1.379(9)</td>
</tr>
<tr>
<td>C4-C9</td>
<td>1.521(6)</td>
<td>C20-C21</td>
<td>1.371(9)</td>
</tr>
<tr>
<td>C4-C10</td>
<td>1.545(7)</td>
<td>C21-C22</td>
<td>1.369(6)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.556(7)</td>
<td>C23-C24</td>
<td>1.378(5)</td>
</tr>
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<td>C5-C6</td>
<td>1.522(8)</td>
<td>C23-C28</td>
<td>1.390(5)</td>
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<tr>
<td>C5-C8</td>
<td>1.548(7)</td>
<td>C24-C25</td>
<td>1.395(5)</td>
</tr>
<tr>
<td>C6-C7</td>
<td>1.540(7)</td>
<td>C25-C26</td>
<td>1.366(7)</td>
</tr>
<tr>
<td>P1-C17</td>
<td>1.814(4)</td>
<td>C26-C27</td>
<td>1.352(7)</td>
</tr>
<tr>
<td>P1-C11</td>
<td>1.820(3)</td>
<td>C27-C28</td>
<td>1.388(6)</td>
</tr>
</tbody>
</table>

Table 10. Selected angles for 199a.

<table>
<thead>
<tr>
<th>Bond</th>
<th>angle/°</th>
<th>Bond</th>
<th>angle/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-Pd1-N1</td>
<td>81.43(14)</td>
<td>C3-C2-C8</td>
<td>99.5(3)</td>
</tr>
<tr>
<td>C1-Pd1-P1</td>
<td>89.70(11)</td>
<td>C1-C2-C8</td>
<td>119.9(3)</td>
</tr>
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<td>C18-C17-P1</td>
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<td>C26-C27-C28</td>
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APPENDIX D

X-RAY DATA TABLES OF COMPLEX 199b

Table 11. Crystal data, data collection, structure solution and structure refinement for 199b.

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<th>Property</th>
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<tr>
<td>Temperature</td>
<td>123(2) K</td>
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<tr>
<td>Wavelength</td>
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</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$a = 10.9541(7)$ Å $a = 90^\circ$</td>
</tr>
<tr>
<td></td>
<td>$b = 9.1372(7)$ Å $\beta = 108.297(4)^\circ$</td>
</tr>
<tr>
<td></td>
<td>$c = 13.8615(9)$ Å $\gamma = 90^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>1317.25(16) Å^{3}</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
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</tr>
<tr>
<td>Absorption coefficient</td>
<td>7.353 mm^{-1}</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>600</td>
</tr>
<tr>
<td>Crystal color, morphology</td>
<td>colorless, Needle</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.186 x 0.117 x 0.042 mm^{3}</td>
</tr>
<tr>
<td>Theta range for data collection</td>
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<tr>
<td>Index ranges</td>
<td>-13 $\leq h \leq 13$, -11 $\leq k \leq 9$, -17 $\leq l \leq 17$</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>34115</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>5246 [$R$(int) = 0.0417]</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>5083</td>
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<td>Completeness to theta = 67.679°</td>
<td>100.0%</td>
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<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.4709 and 0.3395</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5246 / 1 / 310</td>
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<tr>
<td>Goodness-of-fit on $F^2$</td>
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<tr>
<td>Final $R$ indices [$I&gt;2\sigma(I)$]</td>
<td>$R_1 = 0.0289$, $wR_2 = 0.0696$</td>
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<tr>
<td>$R$ indices (all data)</td>
<td>$R_1 = 0.0305$, $wR_2 = 0.0707$</td>
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<tr>
<td>Absolute structure parameter</td>
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Largest diff. peak and hole

0.578 and -0.594 eÅ⁻³

Table 12. Selected bond lengths for 199b.

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<th>Bond</th>
<th>d/ Å</th>
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<td>P1-C24</td>
<td>1.843(5)</td>
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<td>Pd1-N1</td>
<td>2.115(4)</td>
<td>C12-C13</td>
<td>1.379(6)</td>
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<tr>
<td>Pd1-P1</td>
<td>2.2250(12)</td>
<td>C12-C17</td>
<td>1.398(6)</td>
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<tr>
<td>Pd1-Cl1</td>
<td>2.3822(11)</td>
<td>C13-C14</td>
<td>1.388(7)</td>
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<tr>
<td>N1-C3</td>
<td>1.273(6)</td>
<td>C14-C15</td>
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</tr>
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<td>N1-O1</td>
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<td>C15-C16</td>
<td>1.388(7)</td>
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<tr>
<td>O1-C11</td>
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<td>C16-C17</td>
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</tr>
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<td>C1-C2</td>
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<td>C18-C19</td>
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Table 13. Selected angles for 199b.

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</table>
APPENDIX E

SELECTED SPECTRA
Figure 10. $^1$H NMR spectrum of 174b.
Figure 11. $^{13}$C\(^{1}{\text{H}}\) NMR spectrum of 174b.
Figure 12. $^1$H NMR spectrum of 177.
Figure 13. $^{13}$C($^1$H) NMR spectrum of 177.
Figure 14. $^1$H NMR spectrum of 178.
Figure 15. $^{13}\text{C}[^1\text{H}]$ NMR spectrum of 178.
Figure 16. $^1$H NMR spectrum of *endo-188*. 
Figure 17. $^{13}$C($^1$H) NMR spectrum of endo-188.
Figure 18. $^1$H NMR spectrum of *exo-188*. 
Figure 19. $^{13}$C($^1$H) NMR spectrum of exo-188.
Figure 20. $^1$H NMR spectrum of 196a.
Figure 21. $^{13}\text{C}^{\text{1H}}$ NMR spectrum of 196a.
Figure 22. $^1$H NMR spectrum of 196b.
Figure 23. $^{13}$C{$^1$H} NMR spectrum of 196b.
Figure 24. $^1$H NMR spectrum of 198a.
Figure 25. $^{13}$C$\{^1$H$\}$ NMR spectrum of 198a.
Figure 26. $^1$H NMR spectrum of 198b.
Figure 27. $^{13}\text{C}(^1\text{H})$ NMR spectrum of 198b.
Figure 28. $^1$H NMR spectrum of 199a.
Figure 29. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 199a.
Figure 30. $^1$H NMR spectrum of 199b.
Figure 31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 199b.
Figure 32. $^1$H NMR spectrum of 205.
Figure 33. $^{13}\text{C}[^1\text{H}]$ NMR spectrum of 205.
Figure 34. $^{31}\text{P}^\{^1\text{H}\}$ NMR spectrum of 205.
Figure 35. $^1$H NMR spectrum of 206.
Figure 36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 206.
Figure 37. $^{31}\text{P} \{^1\text{H}\}$ NMR spectrum of 206.
Figure 38. $^1$H NMR spectrum of 210.
Figure 39. $^{13}\text{C}(^1\text{H})$ NMR spectrum of 210.
Figure 40. $^{31}\text{P}^1\text{H}$ NMR spectrum of 210.
Figure 41. $^1$H NMR spectrum of 211.
Figure 42. $^{13}$C($^1$H) NMR spectrum of 211.
Figure 43. $^{31}$P{${^1}$H} NMR spectrum of 211.
Figure 44. $^1$H NMR spectrum of 214.
Figure 45. $^{13}$C($^1$H) NMR spectrum of 214.
Figure 46. $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 214.
Figure 47. $^1$H NMR spectrum of 216.
Figure 48. $^{13}$C{$^1$H} NMR spectrum of 216.
Figure 49. $^{31}\text{P}(\text{^1H})$ NMR spectrum of 216.
Figure 50. $^1$H NMR spectrum of 220.
Figure 51. $^{13}$C($^1$H) NMR spectrum of 220.
Figure 52. $^{31}\text{P}^{1}{\text{H}}\text{NMR}$ spectrum of 220.
Figure 53. $^1$H NMR spectrum of 224.
Figure 54. $^{13}$C($^1$H) NMR spectrum of 224.
Figure 55. $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 224.
Figure 56. $^1$H NMR spectrum of 226.
Figure 57. $^{13}$C($^1$H) NMR spectrum of 226.
Figure 58. $^{31}$P{$^1$H} NMR spectrum of 226.
REFERENCES


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