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Mechanistic Insights into the Palladium-Catalysed Asymmetric Phosphination of Cyclohexenyl Triflate

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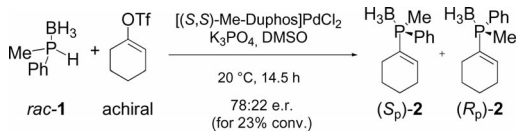
Preliminary results on the mechanism of the asymmetric phosphination involving an achiral alkenyl triflate (cyclohexenyl triflate) and a secondary phosphane–borane, (methyl)-phenylphosphane–borane (**1**) are reported. A catalytic cycle is proposed based on the variable-temperature ^{31}P NMR characterization of the individual steps (oxidative addition, transmetallation and reductive elimination). Each likely intermediate involved in this asymmetric C–P coupling reaction has been identified and characterized. Hence, cationic oxidative addition complex **3** has been readily synthesized and engaged in the stoichiometric reaction with highly enantio-enriched secondary phosphane–borane (S_P)-**1** enabling to isolate the corresponding diastereomerically pure transmetallation adduct (S,S,R_P)-**5**. Its structure has been confirmed by X-ray crystallography. Its decomposition by reductive elimination affords the highly enantio-enriched coupling product (S_P)-**2**. This study also provides information on the origin of the enantioselectivity.

Introduction

Alkenylphosphanes are key compounds in organophosphorus chemistry.[1] They proved to be useful in coordination chemistry, polymer chemistry, organic synthesis for the preparation of polyphosphanes and more recently in catalysis as ligands in cross-coupling reactions.[2] However, chiral derivatives and particularly P-chirogenic ones are scarce.[1] Possible reasons are the lack of general synthetic routes and tedious preparations using a stoichiometric amount of a chiral catalyst (resolution processes or asymmetric syntheses).[1] A promising new approach for their synthesis is asymmetric catalysis. Although a few examples have been recently reported in the literature through the use of catalytic hydrophosphination of alkynes[3] and C–P cross-coupling reaction of an alkenyl triflate,[4] the enantioselectivity reached and/or the scope of the reactions are too modest to envision preparing efficiently P-chirogenic tertiary phosphanes through these methodologies. Information on the mechanism and the factors, which affect the enantioselectivity of these reactions, would certainly be helpful to develop more efficient reactions. In this context, we report herein preliminary results on the mechanism of the palladium catalysed asymmetric phosphination of an alkenyl triflate using a secondary phosphane–borane as phosphinating agent.

Results and Discussion

After reporting a general and efficient access to achiral alkenylphosphanes involving the palladium-catalysed C–P cross-coupling reaction between secondary phosphane–boranes and alkenyl triflates,[5] we focused our work on the asymmetric version of this C–P cross-coupling reaction and recently reported that an enantio-enriched P-chirogenic alkenylphosphane could be formed by asymmetric C–P cross-coupling reaction (Scheme 1).[4] Promising enantiomeric ratios, up to 78:22, could be obtained in the study involving achiral cyclohexenyl triflate and the racemic (methyl)phenylphosphane–borane **1** when using (*S*,*S*)-Me-DUPHOSPdCl$_2$ as precatalyst (Scheme 1).



Scheme 1. Asymmetric C–P cross-coupling between cyclohexenyl triflate and phosphane–borane **1**.

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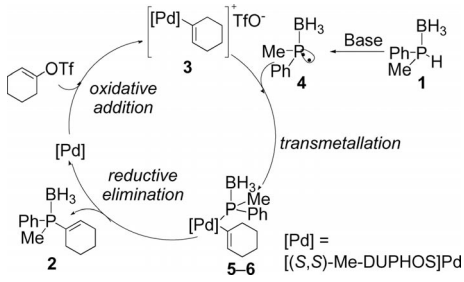
To get insights into the origin of the enantioselection, we embarked in a study aiming at characterizing likely intermediates involved in the different steps of the putative catalytic cycle by using ^{31}P NMR spectroscopy. To the best of our knowledge, there is no mechanistic information available on the coupling between a triflate derivative and a phosphane–borane in the literature. A plausible mechanism based on previous investigations on the C–P cross-coupling reaction between secondary phosphane–borane and aryl iodide,[6] is proposed in Scheme 2.



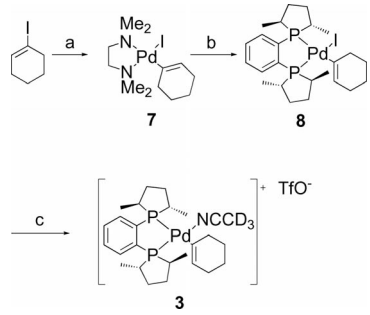
Scheme 2. Plausible catalytic cycle for the palladium-catalysed vinylation of phosphane–borane.

The putative first step is the oxidative addition of the alkenyl triflate to the low valent Pd^0 complex leading to cationic complex **3**.[7] Then, transmetallation with boron phosphide **4** resulting from the deprotonation of secondary phosphane–borane **1** occurs, leading to transmetallation adduct **5** and/or **6**. Lastly, reductive elimination enables the C–P bond formation and regenerates the Pd catalyst.

Synthesis of the Precursors: Secondary Phosphane–Borane 1 and Putative Cationic Oxidative Complex 3

Racemic secondary phosphane–borane **1** was prepared according to a literature procedure.[8] Enantiopure (S_P)-**1**, readily accessible by following the procedure reported by Livinghouse,[9] was efficiently prepared with an enantiomeric ratio of 98:2 (See Supporting Information). Alkenyl cationic oxidative palladium complexes with a labile ligand and a *cis* chelating diphosphane being depicted as unstable species,[7] compound **3** could not be obtained by direct oxidative addition to [(*S*,*S*)-Me-Duphos]Pd^0 complex. Hence, the putative catalyst **3** was prepared following the route described in Scheme 3, through a synthesis inspired by the chemistry developed by Brown on arylic cationic oxidative complexes for the study of reactive intermediates in the Heck reaction.[10]

The first step is the preparation of the new iodide complex **7** following an adapted procedure inspired by Glueck[11] and Drago's[12] works on the preparation of aryl-iodide oxidative addition complexes. $Pd_2(dba)_3{\cdot}CHCl_3$ was first treated with TMEDA and iodocyclohexene,[13] to give, after work-up, the air stable complex Pd(TMEDA)(cyclohexenyl)(*I*) **7** in 77% yield. Complex **7** was fully characterized by NMR spectroscopy, elemental analysis and HRMS. Its structure was also confirmed by X-ray crystallography after crystallisation from a mixture of Et_2O and



Scheme 3. Synthesis of complex **3**. a) $Pd_2(dba)_3{\cdot}CHCl_3$, TMEDA, toluene, 50 °C, 3 h, 77%; b) (*S*,*S*)-Me-DUPHOS, THF, 40 °C, 2 h, 84%; c) AgOTf, CD_3CN, –20 °C.

CH_2Cl_2.[14] The ORTEP diagram is shown in Figure 1. Selected bond lengths and angles are given in Table 1. Complex **7** adopts a near square-planar geometry at palladium with the cyclohexenyl group oriented orthogonal to the square plane of the molecule.

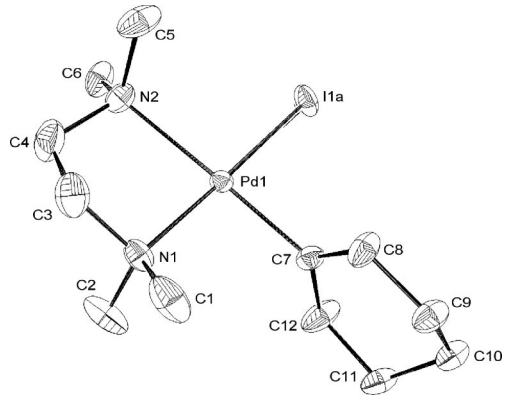


Figure 1. ORTEP diagram of Pd(TMEDA)(cyclohexenyl)(*I*) **7**. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and bond angles [°] for Pd(TMEDA)(cyclohexenyl)(*I*) **7**.

Bond	Length	Bond	Angle
Pd1–C7	1.9795(16)	N1–Pd1–N2	83.17(7)
Pd1–N1	2.1322(15)	N2–Pd1–I1	95.08(10)
Pd1–N2	2.2249(16)	C7–Pd1–I1	89.20(9)
Pd1–I1	2.545(5)	C7–Pd1–N1	92.66(7)
		C7–Pd1–N2	174.21(6)
		N1–Pd1–I1	177.54(13)

Displacement of the TMEDA ligand by (*S*,*S*)-Me-DUPHOS afforded iodide complex **8** in 84% yield. This new complex was fully characterized by NMR spectroscopy, elemental analysis and HRMS. It proved to be less stable than its precursor **7** both in solution and in solid state. Although it is possible to handle this complex in air, it is necessary to store it at –20 °C to avoid decomposition. The low stability of **8** was also demonstrated during crystallization attempts, which all led to the known by-product [(*S*,*S*)-Me-DUPHOS]PdI_2[11a] whatever the technique used (evaporation, diffusion at low temperature). The assignment of the cyclohexenyl and DUPHOS ligand pro-

tons was established via a ^{1}H COSY experiment and long-range ^{13}C, ^{1}H correlations. The coordinated cyclohexenyl fragment exhibited a signal about 5.5 ppm in the ^{1}H NMR spectrum and a resonance in ^{13}C NMR about 154 ppm with a characteristic *trans* coupling constant $^2J_{\text{C-P}trans}$ value of ca. 130 Hz for the σ-bounded alkene (See Supporting Information). This high frequency chemical shift is quite similar to those observed in the literature for aryl complex derivatives.[11] Insight into the structure was then obtained by ^{1}H NOESY in order to determine how the cyclohexenyl ligand and the auxiliary Me-DUPHOS interact in solution. A section of the ^{1}H NOESY spectrum of **8** is shown in Figure 2 and clearly reveals fairly strong NOEs between the methyl (Me_{12}) and the methine (H^8) of the DUPHOS phospholane ring and the vinylic proton of the cyclohexenyl group (H^1) (Figure 3). Correlation was also observed between the methyl (Me_{18}) and the methine (H^{11} and H^{14}) of the DUPHOS and the *ortho* protons (H^{21} and H^{24}) of the aromatic ring of DUPHOS, as shown in Figure 3.

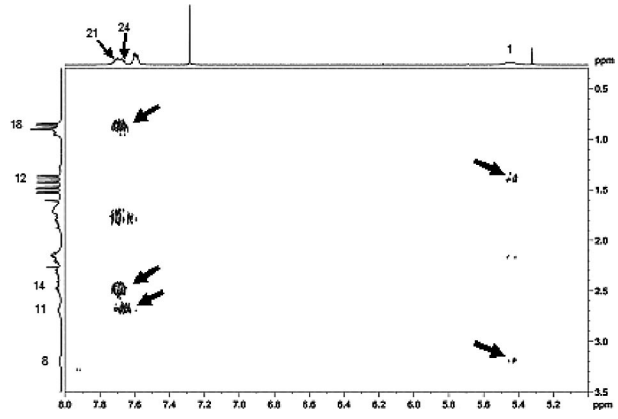
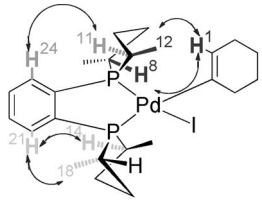


Figure 2. Section of the ^{1}H NOESY spectrum of **8** ($CDCl_3$, 400 MHz).



Correlation	H^{12}	H^8	H^{11}	H^{14}	H^{18}
H^1	✓	✓	-	-	-
H^{24}	-	-	✓	-	-
H^{21}	-	-	-	✓	✓

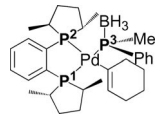
Figure 3. Representation of **8** showing intra- and inter-ligand NOEs.

The putative oxidative addition product **3** was then obtained after treatment of alkenyliodide complex **8** with silver triflate in CD_3CN at –20 °C followed by low temperature filtration of the precipitated silver salts. Due to its low stability in solution (decomposition about 20 °C), **3** was characterized by multinuclear NMR spectroscopy at low temperature and by HRMS (see Supporting Information). The ^{31}P NMR spectrum shows two peaks at δ = 68.6 and 65.4 ppm (in CD_3CN) with a characteristic *cis* coupling constant J_{pp} value about 29 Hz (see Supporting Information).

Study of the Catalytic Cycle by vt-NMR Spectroscopy Using (S_P)-1: Transmetallation Step

Having in hand phosphane **1** and catalyst precursor **3**, the catalytic cycle was studied by vt-NMR spectroscopy using first the highly enantio-enriched (S_P)-**1** phosphane–borane. Treatment of **3** at –60 °C in a mixture of solvents, {[D_8]THF/[D_7]DMF (10 equiv. to Pd complex)},[15] with (S_P)-**1** (98:2 e.r.) in stoichiometric amount, in the presence of Me_3SiOK as base,[16] led to the clean formation of a new complex. Low-temperature ^{31}P NMR spectroscopy (see Table 2 and the Supporting Information) supports the formation of the transmetallation complex **5** (Scheme 2). No trace of a silanolate palladium complex resulting from the reaction between silanolate and **3** could be detected.[17] This observation indicates that deprotonation of **1** is fast[18] and that boron phosphide **4** directly reacts with **3** to give **5**. It is worth noting that since the phosphorus in **5** is tetrahedral, the inversion process at phosphorus should be arrested. Therefore, only one diastereomer of the transmetallation adduct **5** having a controlled stereochemistry at phosphorus is expected if the coordination of the phosphide **4** to the metal centre occurs with high stereocontrol.[19] In fact, we observed in the ^{31}P NMR spectrum two isomers of the transmetallation adduct **5** in a 1:1.5 ratio.[20] The extra isomer **5***min* appeared to be a conformational isomer, which arose from slow rotation about the Pd–C bond on the NMR time scale. Similar behaviour was reported in the related Pt(DIOP)(*o*-An)(*I*)[21] and [Pd(DUPHOS)(*o*-An)-{PPhMe(BH_3)}] complexes.[11]

Table 2. ^{31}P{H} NMR spectroscopic data for **5** at –30 °C.[a]



Complex	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{P1P2}	J_{P1P3}	J_{P2P3}
5*maj*[b]	61.6	63.3	–19.7	26.0	294.2	24.4
5*min*[c]	59.2	59.8	–15.1	25.1	300.1	29.8

[a] Solvent: [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF. [b] Major conformational isomer. [c] Minor conformational isomer.

In the ^{31}P NMR spectrum, each isomer of the boron phosphide complex **5** shows a characteristic broad doublet due to the [P^3(Me)(Ph)(BH_3)] phosphido group and two doublets of doublets due to the non equivalent P^1 and P^2 phosphorus atoms of DUPHOS ligand with small (ca. 25 Hz) and large (ca. 295 Hz) coupling constants, which are consistent with J_{PP} *cis* and J_{PP} *trans* values, respectively (see Table 2 and Figure 4).[6d]

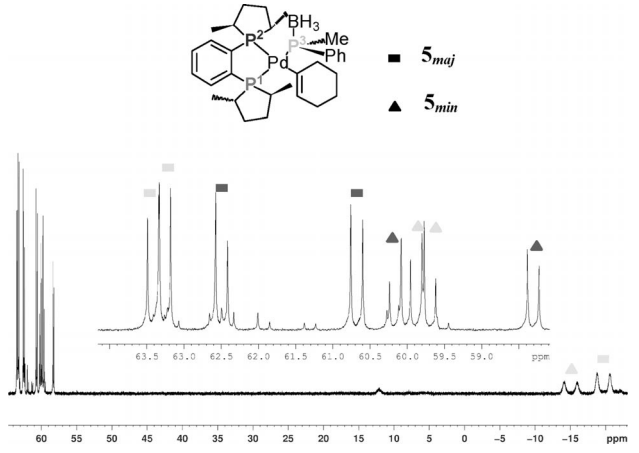


Figure 4. $^{31}P\{H\}$ spectrum of complex **5** in [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF at –30 °C.

On warming (–10 °C), one of the isomer disappeared: a section of $^{31}P\{H\}$ spectra of complex **5** at various temperatures (from –50 °C to 20 °C) is reported in Figure 5.

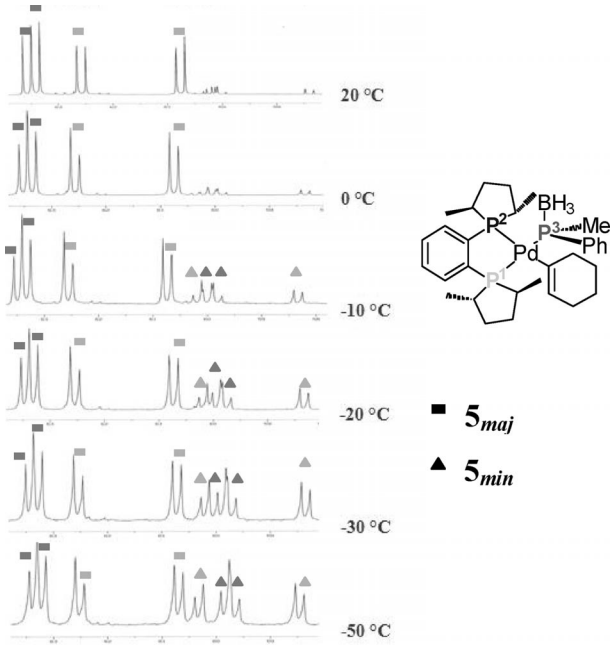


Figure 5. Section of $^{31}P\{H\}$ spectra corresponding to phosphorus P^1 and P^2 of DUPHOS ligand in complex **5** at various temperature; experiments were done in [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF.

As illustrated in Figure 6, the ^{31}P NMR spectrum at 0 °C indicates the presence of only one species, which is consistent with the boron phosphide complex **5** (see Table 3 for ^{31}P NMR spectroscopic data). This observation points out that treatment of the chiral cationic complex **3** with the highly enantio-enriched (S_P)-**1** (98:2 e.r.) gives **5** with high *dr* (98:2) at low temperature (–60 °C).

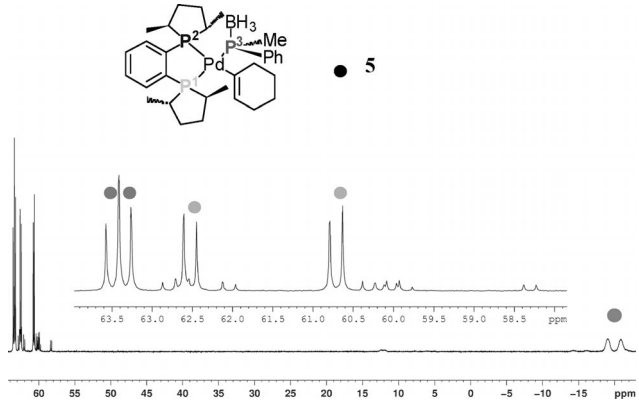
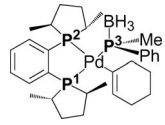


Figure 6. $^{31}P\{H\}$ spectrum of complex **5** in [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF at 0 °C.

Table 3. $^{31}P\{H\}$ NMR spectroscopic data for **5** at 0 °C.[a]



Complex	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{P1P2}	J_{P1P3}	J_{P2P3}
5	61.6	63.4	–19.7	26.0	294.0	24.5

[a] Solvent: [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF.

Single crystals of **5** were obtained by slow diffusion of pentane into a concentrated CH_2Cl_2 solution at –20 °C.[22] ORTEP diagram is shown in Figure 7; selected bond lengths and angles are given in Table 4. Additional information appears in the Supporting Information. Complex **5** shows a great distortion from planarity as judged by the distances of ligand atoms from the P1P2PdCP3 plan (up to 0.20 Å for P3). This result is consistent with a great steric congestion around the palladium atom caused by the [P^3(Me)(Ph)(BH_3)] phosphido–borane group and is in agreement with the behavior of complex **5** in solution. Absolute configuration (*R*) of the phosphido center P^3 in **5** was established by X-ray crystallography, suggesting that the transmetallation step proceeds with retention of configuration (Figure 7).[23]

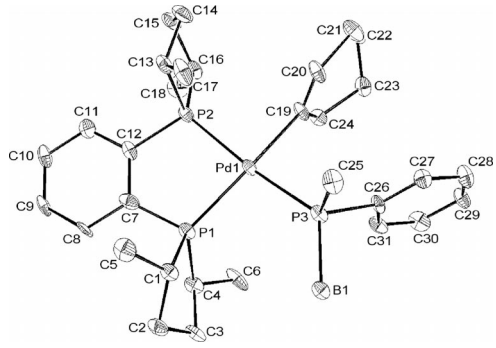


Figure 7. ORTEP diagram of [Pd{(*S*,*S*)-Me-DUPHOS}(cyclohexenyl)–{P(Me)(Ph)(BH_3)}] (**5**). Hydrogen atoms are omitted for clarity.

Table 4. Selected bond lengths [Å] and bond angles [°] for [Pd{(*S*,*S*)-Me-DUPHOS}(cyclohexenyl){P(Me)(Ph)(BH_3)}] **5**.

Bond	Length	Bond	Angle
Pd1–P1	2.3310(18)	P1–Pd1–P3	99.28(6)
Pd1–P2	2.2849(19)	P2–Pd1–P1	85.80(7)
Pd1–P3	2.3531(18)	C19–Pd1–P2	90.1(2)
Pd1–C19	2.070(6)	C19–Pd1–P3	86.3(2)
P3–C26	1.831(6)	C19–Pd1–P1	171.21(19)
P3–C25	1.839(7)	P2–Pd1–P3	167.79(6)
P3–B1	1.947(8)		

Study of the Catalytic Cycle by vt-NMR Spectroscopy Using (S_P)-1: Reductive Elimination Step

Decomposition of **5** on warming to 20 °C through reductive elimination led as expected to tertiary phosphane–borane **2** along with Pd[(*S*,*S*)-Me-Duphos]$_2$, which was characterized by comparison with an authentic sample.[11a] Surprisingly, a third product was detected in the reaction mixture at 20 °C (Figure 8). The $^{31}P\{H\}$NMR spectrum of this unknown compound shows the presence of two doublets of doublets, indicating that the two phosphorus atoms P^1 and P^2 of the [(Me-DUPHOS)Pd] fragment are non equivalent, along with a broad signal, which is consistent with the phosphorus atom P^3 of the tertiary phosphane–borane group [MePh(cyclohexenyl)P(BH_3)]. These observations are in agreement with a palladium complex, having the 3 phosphorus atoms in its coordination sphere. However, no large J_{pp} coupling constant (about 300 Hz) between the phosphorus atoms of the phosphane–borane group and one of the DUPHOS group could be observed contrarily to what was observed in **5** (J_{P1P3} = 294 Hz, see Table 3). Instead, rather small coupling constants (J_{P1P3} = 8.9, J_{P2P3} = 26.5 Hz) were measured (Table 5). From this set of observations, we can determine that phosphorus P^3 in [MePh(cyclohexenyl)P(BH_3)] is not directly bound to the metal centre in the palladium complex. We propose structure **9** for this new complex, which would arise from the coordination of the C=C bond of the cyclohexenyl group of the coupling product **2** to the unstable [(Me-DUPHOS)Pd] complex released in the reaction mixture during the reductive elimination step. A second lower-intensity signal (set of doublet of doublets) close to that of the major compound was also observed. This signal might be due to an isomer of **9**, in which palladium binds the other enantioface of the alkene.

It is well known that coordination of an olefin fragment to a transition metal complex lowers the stretching frequency of olefin C=C bond.[24] Thus, to get more information, we performed the infrared spectrum of a reaction mixture sample containing complex **9** and coupling product **2**. The C=C absorption frequency in **2** is observed at 1649 cm^{-1} while that of **9** is at 1633 cm^{-1} (see Supporting Information). This low-frequency shift of the C=C band is in agreement with the coordination of the cyclohexenyl C=C bond on the Pd^0.

To confirm the structure of **9**, a sample of the reaction mixture containing compound **2** and complex **9**, was heated into the NMR probe from 20 °C to 50 °C and evolution

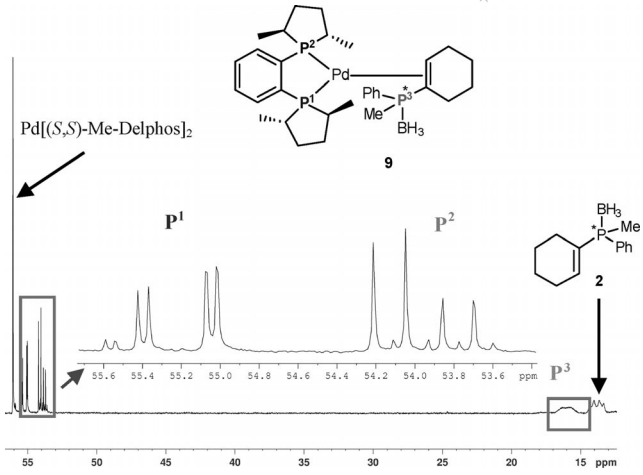
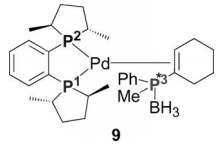


Figure 8. $^{31}P\{H\}$ spectrum of the reaction mixture after reductive elimination in [D_8]THF/[D_7]DMF with the signal locked to [D_8]-THF at 20 °C.

Table 5. $^{31}P\{H\}$ NMR spectroscopic data for **9** at 20 °C.[a]



Complex	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{12}	J_{13}	J_{23}
9	55.2	53.9	16.0	56.7	8.9	26.5

[a] Solvent: [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF.

was monitored by $^{31}P\{H\}$ NMR spectroscopy (Figure 9). As expected, increase of the temperature led to the evolution of complex **9** into the coupling product **2** and Pd[(*S*,*S*)-Me-Duphos]$_2$. This reaction proved to be irreversible since the decrease of the temperature from 50 to 20 °C did not modify the phosphorus NMR spectrum, indicating that the palladium complex initially involved in the complexation has evolved (Figure 9).

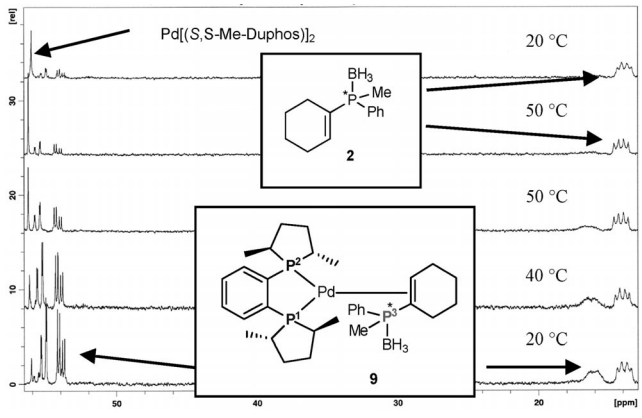


Figure 9. $^{31}P\{H\}$ spectrum of the reaction mixture resulting from reductive elimination, at different temperatures between 20 °C and 50 °C, in [D_8]THF/[D_7]DMF with the signal locked to [D_8]THF.

Hydrolysis of the reaction mixture containing tertiary phosphane–borane **2** and Pd[(*S*,*S*)-Me-Duphos]$_2$, followed by extraction and purification by flash column chromatography afforded pure coupling product **2**. HPLC analysis showed that enantiomer $\mathbf{e_2}$ ($\mathbf{e_2}$: t_R 9.34 min, enantiomer $\mathbf{e_1}$: t_R 10.95 min, see Supporting Information) was formed with a 98:2 er. This result indicates that under the conditions used (transmetallation at low temperature and reductive elimination at room temp.), loss of *P*-stereochemistry is not observed.[25] This information is significant since it suggests that interconversion of phosphide enantiomers **4** does not occur before Pd–P bond formation or occurs more slowly than transmetallation at –60 °C (Scheme 2). This observation also highlights the high electrophilic reactivity of **3** even at low temperature. The group of Glueck having previously demonstrated in the synthesis of the Pamp ligand that P–C reductive elimination from Pd^{II} derivatives proceeded through retention of configuration,[11] (S_P) configuration was assigned to the major enantiomer of phosphane–borane **2** obtained in the coupling. The correlation with HPLC, thus enabled us to assign (S_P) configuration to enantiomer $\mathbf{e_2}$ and (R_P) to enantiomer $\mathbf{e_1}$.

Study of the Catalytic Cycle by vt-NMR Spectroscopy Using (+/–)-1

The mechanistic investigation was then performed with a 3:1 ratio of racemic phosphane–borane **1** and complex **3** in order to parallel the conditions used in catalytic reactions (Scheme 2). Other conditions were similar to those employed in the mechanistic investigation using enantio-enriched (S_P)-**1**. Upon reaction between *rac*-**1** and complex **3**, four new sets of signals were observed by ^{31}P vt-NMR at temperatures between –60 °C and –10 °C. ^{31}P{H} NMR spectrum and data are reported in Figure 10 and Table 6, respectively. The observed ^{31}P NMR signals were attributed to the two expected diastereomers of the transmetallation complex **5***maj* and **6***maj* and to their conformational isomers **5***min* and **6***min* (Table 6).

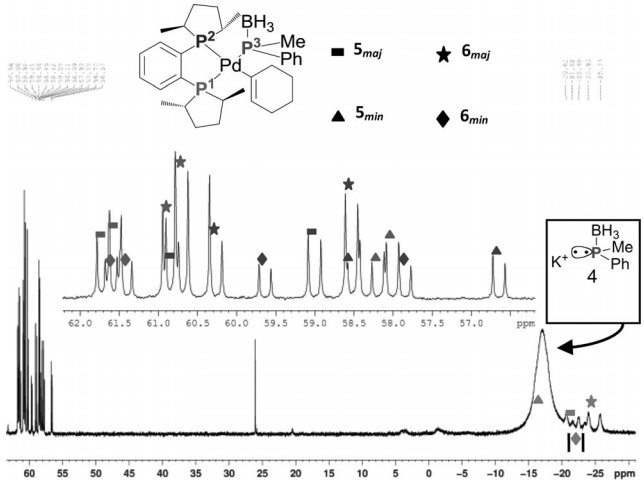
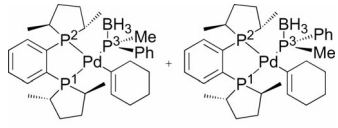


Figure 10. ^{31}P{H} spectrum of complex **5** and **6** in [D$_8$]THF/[D$_7$]-DMF with the signal locked to [D$_8$]THF at –30 °C.

Table 6. ^{31}P{H} NMR spectroscopic data for diastereomers **5** and **6** at –30 °C.[a]



Complex	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{P1P2}	J_{P1P3}	J_{P2P3}
5*maj*[b]	60.0	61.6	–21.5	26.0	294.4	24.3
5*min*[c]	57.6	58.1	[d]	25.1	300.3	29.7
6*maj*[b]	59.4	60.8	–24.8	25.5	280.1	[e]
6*min*[c]	58.7	61.5	–22.5	24.7	289.0	30.5

[a] Solvent: [D$_8$]THF/[D$_7$]DMF with the signal locked to [D$_8$]THF. [b] Major conformational isomer. [c] Minor conformational isomer. [d] Broad doublet is overlapped by the signal of **1**, which is in excess. [e] Not observed.

As anticipated, at –10 °C, signals of the minor isomers almost disappeared leading to diastereomers (*S*,*S*,*R*$_P$)-**5** and (*S*,*S*,*S*$_P$)-**6** in an approximate 1:1.4 ratio (within experimental error due to the inaccuracy of ^{31}P NMR integration). The ^{31}P{H} NMR spectrum and data are reported in Figure 11 and Table 7, respectively.

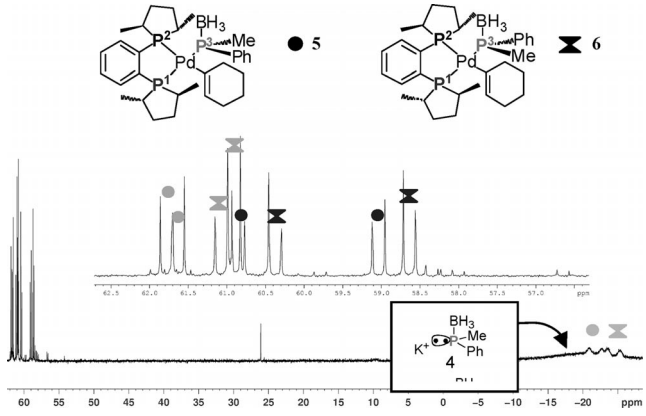
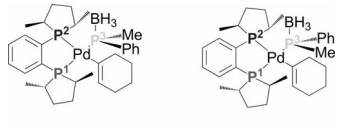


Figure 11. ^{31}P{H} spectrum of complex **5** and **6** in [D$_8$]THF/[D$_7$]-DMF with the signal locked to [D$_8$]THF at 0 °C.

Table 7. ^{31}P{H} NMR spectroscopic data for diastereomers **5** and **6** at 0 °C.[a]

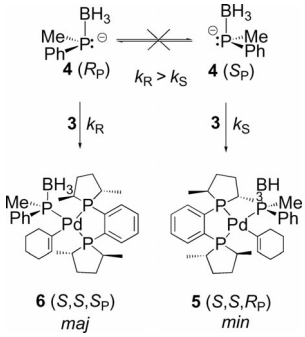


Complex	$\delta(P^1)$	$\delta(P^2)$	$\delta(P^3)$	J_{P1P2}	J_{P1P3}	J_{P2P3}
5	59.9	61.7	–21.8	26.0	294.3	24.4
6	59.5	61.0	–24.5	25.8	281.8	[b]

[a] Solvent: [D$_8$]THF/[D$_7$]DMF (10 equiv. to Pd complex) with the signal locked to [D$_8$]THF. [b] Not observed.

Since no interconversion of anion **4** was observed at low temperature using enantiopure (*S*)-**1**, the fact that diastereomers (*S*,*S*,*R*$_P$)-**5** and (*S*,*S*,*S*$_P$)-**6** are formed in unequal

amounts suggests that one enantiomer, here (R_P)-**4**, reacts more quickly with chiral **3** than the other one, i.e. (S_P)-**4**, ($k_R > k_S$), Scheme 4.



Scheme 4. Faster reaction of (R_P)-**4** vs. (S_P)-**4**.

Warming the solution to 20 °C did not show any significant modification of the diastereomeric ratio. Approximate half-lives of **5** and **6** under these conditions are 1.25 h and 1 h, respectively. At 20 °C, diastereomers **5** and **6** smoothly undergo reductive elimination at rather similar rates leading to the formation of coupling product **2** in a 68:32 enantiomeric ratio. As expected HPLC analysis shows that enantiomer $\mathbf{e_1}$, i.e. (R_P)-**2**, is the major one. These observations are consistent: i) with a reductive elimination, which proceeds with retention of configuration, enantiomer (R_P)-**2** arising from the major diastereomer (S,S,S_P)-**6**,[23] and ii) with a faster reaction of (R_P)-**4** with **3** compared to (S_P)-**4**.

Conclusions

In summary, we have determined the individual steps and characterized the main intermediates in a potential mechanism for the [(*S*,*S*)-Me-DUPHOS]$PdCl_2$-catalysed coupling reaction involving a racemic secondary phosphane–borane and an alkenyl triflate. This mechanistic study also provides information on the origin of enantioselectivity. Both Pd–P (transmetallation) and P–C bond formation (reductive elimination) proceeds with retention of configuration; and the enantioselectivity is proposed to result from a kinetic resolution when transmetallation and reductive elimination are performed under mild conditions (–60 °C for transmetallation and room temp. for reductive elimination). Influence of higher temperature and extension to more dissymmetric and bulky secondary phosphane–boranes in order to favour the anion interconversion and improve the transmetallation selectivity are currently in progress.

Experimental Section

General: All reactions were carried out under nitrogen atmosphere. All glassware was flame-dried before use. (Methyl)phenylphosphane–borane[8] and 1-iodocyclohexene[13] were prepared according to literature procedures. (*S*,*S*)-Me-DUPHOS, commercially available, was used as purchased.

Toluene, diethyl ether, tetrahydrofuran, acetonitrile and dichloromethane were purified by an Innovative technology Pure Solv. device (activated alumina column containing a copper catalyst and molecular sieves). Pentane was distilled from calcium hydride before use.

The solvents used for the preparation of complexes were distilled (or purified by an Innovative technology Pure Solv. device) and degassed. $CDCl_3$, CD_2Cl_2, CD_3CN, [D_8]THF and [D_7]DMF were dried with molecular sieves (4 Å) before use.

Column chromatography was performed on Merck silica gel Si 60 (40–63 μm). Solvents were used as purchased. Thin-layer chromatography (TLC) was performed on silica gel 60 F-254 plates (0.1 mm) with iodine or UV detection.

^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were obtained on Bruker DPX 250 or AC 400 spectrometers, ^{11}B NMR spectra were recorded on a Bruker AC 400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to Me_4Si used as an internal standard. ^{31}P, ^{19}F and ^{11}B NMR chemical shifts are reported relative to H_3PO_4 (85%), $CFCl_3$ and $BF_3{\cdot}Et_2O$ used as external references, respectively. Coupling constants are reported in Hertz (Hz). The following symbols were used to describe signal multiplicities: s stands for singlet, d for doublet, t for triplet, q for quadruplet, quint for quintuplet, sept for septuplet, oct for octuplet, m for multiplet, and br. for broad.

Elemental analyses were obtained from a ThermoQuest NA 2500 CHNS-O instrument.

Mass spectroscopy was performed on a QTOF Micro WATERS.

Infrared spectroscopy was performed on a Perkin–Elmer Spectrum One ATR-FTIR spectrometer.

High-Performance Liquid Chromatography (HPLC) separations were achieved using the following components: For flow up to 0.5 mL/min, the components are: a Waters 600 pump, a Waters 996 photodiode array detector (190–250 nm) and Millenium software. For flow below 0.5 mL/min, the components are: a Waters Alliance 2695 pump, a Waters 2996 photodiode array detector (190–250 nm) and Empower Software.

Enantiomeric ratio of compound **2** was measured by HPLC using two different conditions, determined using racemic **2**:[5]

Conditions A: Daicel Chiralpack OJ-H (250 × 4.6 mm, L × ID) column (*n*-heptane/2-propanol 90:10, 1 mL min^{-1}, t_{R1} = 9.34 min: enantiomer $\mathbf{e_2}$, t_{R2} = 10.95 min: enantiomer $\mathbf{e_1}$) at 20 °C.

Conditions B: Daicel Chiralpack AD-H (250 × 4.6 mm, L × ID) column [*n*-heptane/(MeOH/EtOH, 50:50) 98:2, 0.2 mL min^{-1}, t_{R1} = 37.08 min, t_{R2} = 39.48 min] at 12 °C

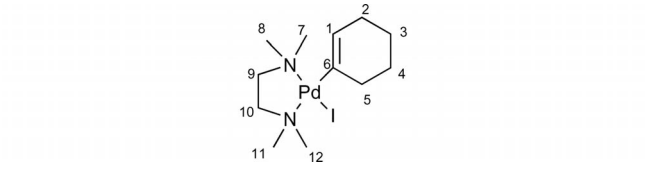
Given enantiomeric ratio of compound **2** are average of at least two experiments.

Xray structures were recorded using a Bruker Kappa Apex II CCD diffractometer.

Synthesis of (S_p)-(Methyl)phenylphosphane–borane (1): The enantio-enriched (S_p)-(methyl)phenylphosphane–borane **1** (98:2 e.r.) was prepared by asymmetric lithiation/trapping−reductive elimination as reported by Livinghouse.[9] The enantiomeric ratio of compound **1** was measured by HPLC using conditions described in the literature:[25a] Daicel Chiralpack OJ-H (250 × 4.6 mm, L × ID) column (*n*-heptane/2-propanol 90:10, 1 mL min^{-1}, t_{R1} = 14.72 min, t_{R2} = 15.54 min) at 20 °C.

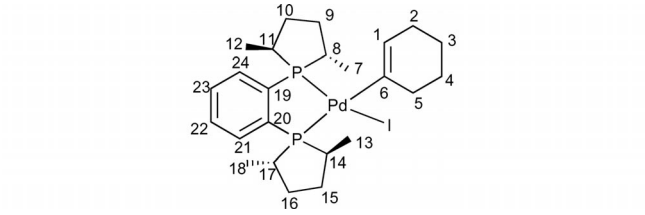
Synthesis of Pd(TMEDA)(cyclohexenyl)(I) (7): In a Schlenk tube, flushed under nitrogen, TMEDA (102 μL, 0.68 mmol, 2.6 equiv.) and 1-iodocyclohexene (130 mg, 0.62 mmol, 2.4 equiv.) are added to a dark suspension of $Pd_2(dba)_3{\cdot}CHCl_3$ (269.5 mg, 0.26 mmol) in

toluene (3 mL). The reaction mixture is heated to 50 °C for 3 h in darkness. During the reaction, the mixture turns green and then yellow. After cooling to room temperature, the reaction mixture is filtered and an orange solid is obtained. This solid is washed with diethyl ether (6 × 2 mL) to remove dba, then dissolved in dichloromethane, and filtered (through a 0.2 μm Nylon filter) to remove Pd metal particles. The solution is concentrated under reduced pressure affording a yellow-orange solid (172 mg, 77%).



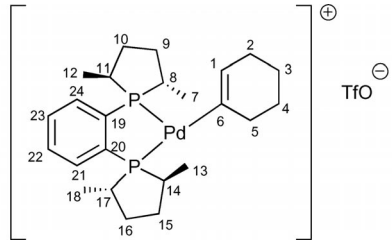
^{1}H NMR (400.1 MHz, CD_2Cl_2): δ = 5.02–4.96 (m, 1 H, H^1), 3.01–2.87 (m, 1 H, H^{9a}), 2.71–2.44 (m, 2 H, H^{9b} and H^{10a}), 2.65 (s, 3 H, H^7), 2.56 (s, 6 H, H^8 and H^{11}), 2.51 (s, 3 H, H^{12}), 2.42–2.29 (m, 2 H, H^{5a} and H^{10b}), 2.22–2.09 (m, 3 H, H^2 and H^{5b}), 1.69–1.43 (m, 4 H, H^3 and H^4) ppm. ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 142.8 (s, C^6), 123.3 (s, C^1), 62.3 (s, C^9), 58.1 (s, C^{10}), 51.5 (s, C^8), 50.7 (s, C^{11}), 48.1 (s, C^{12}), 47.6 (s, C^7), 38.8 (s, C^5), 28.5 (s, C^2), 26.5 (s, C^4), 24.4 (s, C^3) ppm. $C_{12}H_{25}IN_2Pd{\cdot}0.11CH_2Cl_2$ (438.75): C 32.85, H 5.74, N 6.30; found C 32.87, H 6.08, N 6.52. HRMS calcd. for $C_{12}H_{25}IN_2Pd{\cdot}CH_3CN$ $[M + H]^+$: 472.0441, found 472.0457 (CH_3CN is the solvent used for HRMS analysis).

Synthesis of [Pd{(*S*,*S*)-Me-DUPHOS}(cyclohexenyl)](I) (8): In a Schlenk tube, flushed under nitrogen, a solution of Pd(TMEDA)(cyclohexenyl)(*I*) (140 mg, 0.32 mmol) and (*S*,*S*)-Me-DUPHOS (99.6 mg, 0.32 mmol) in THF (3.6 mL) is stirred in darkness at 40 °C for 2 h. After cooling to room temperature, the reaction mixture is partially concentrated under reduced pressure and the orange product is precipitated by addition of pentane at 0 °C, filtered and washed with pentane (5 × 3 mL). The orange solid obtained is dissolved in dichloromethane, and filtered (through 0.2 μm Nylon filter). The solution is concentrated under reduced pressure giving a pale orange solid (169 mg, 84%).



^{31}P NMR (161.9 MHz, $CDCl_3$): δ = 65.9 (d, $^2J_{PP}$ = 31.8 Hz), 60.4 (d, $^2J_{PP}$ = 31.8 Hz) ppm. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 7.77–7.64 (m, 2 H, H^{21} and H^{24}), 7.64–7.56 (m, 2 H, H^{22} and H^{23}), 5.45 (dm, $^4J_{HP}$ = 12.0 Hz, 1 H, H^1), 3.62–3.46 (m, 1 H, H^{17}), 3.30–3.10 (m, 1 H, H^8), 2.80–2.60 (m, 1 H, H^{11}), 2.56–2.40 (m, 2 H, H^{4a} and H^{14}), 2.38–2.26 (m, 3 H, H^{9a}, H^{10a} and H^{16a}), 2.26–2.04 (m, 5 H, H^2, H^{4b} and H^{15}), 1.92–1.72 (m, 3 H, H^{9b}, H^{10b} and H^{16b}), 1.72–1.62 (m, 4 H, H^3 and H^5), 1.50 (dd, $^3J_{HP}$ = 18.4, $^3J_{HH}$ = 6.8 Hz, 3 H, H^{13}), 1.40 (dd, $^3J_{HP}$ = 18.8, $^3J_{HH}$ = 6.8 Hz, 3 H, H^{12}), 0.93 (dd, $^3J_{HP}$ = 15.6, $^3J_{HH}$ = 7.6 Hz, 3 H, H^7), 0.87 (dd, $^3J_{HP}$ = 14.0, $^3J_{HH}$ = 7.2 Hz, 3 H, H^{18}) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 153.7 (d, $^2J_{CP}$ = 130.4 Hz, C^6), 144.7 (dd, $^1J_{CP}$ = 45.7, $^2J_{CP}$ = 33.1 Hz, C^{19} *or* C^{20}), 143.0 (dd, $^1J_{CP}$ = 31.9, $^2J_{CP}$ = 23.7 Hz, C^{19} *or* C^{20}), 133.2 (d, $^2J_{CP}$ = 13.9 Hz, C^{21}), 132.4 (d, $^2J_{CP}$ = 15.4 Hz, C^{24}), 130.8 (s, C^{22} *or* C^{23}), 130.7 (s, C^{22} *or* C^{23}), 127.4 (br., C^1), 43.5 (br., C^{11}), 42.2 (d, $^1J_{CP}$ = 18.7 Hz, C^{14}), 37.7 (d, $^2J_{CP}$ = 2.7 Hz, C^{16}), 36.7 (s, C^9), 36.6 (d, $^1J_{CP}$ = 19.2 Hz, overlapping with other signals, C^{17}), 36.4 (d, $^2J_{CP}$ = 2.8 Hz, C^{15}), 35.9 (d, $^2J_{CP}$ = 4.7 Hz, C^{10}), 33.7 (br., C^8), 29.5 (dd, $^4J_{CP}$ = 12.2, $^4J_{CP}$ = 2.7 Hz, C^2), 26.5 (d, $^3J_{CP}$ = 6.5 Hz, C^5), 25.6 (s, C^4), 24.0 (s, C^3), 17.4 (d, $^2J_{CP}$ = 12.4 Hz, C^{13}), 15.9 (d, $^2J_{CP}$ = 8.7 Hz, C^{12}), 14.7 (d, $^2J_{CP}$ = 1.7 Hz, C^{18}), 14.4 (d, $^2J_{CP}$ = 1.0 Hz, C^7) ppm. $C_{24}H_{37}IP_2Pd$ (620.82): C 46.43, H 6.01; found C 46.21, H 6.28. HRMS calcd. for $C_{24}H_{37}INaP_2Pd$ $[M + Na]^+$: 643.0348, found 643.0328.

Synthesis of the Cationic Complex [Pd{(*S*,*S*)-MeDUPHOS}(cyclohexenyl)]$^+$ (TfO)$^-$ (3): In a Schlenk tube, flushed under nitrogen, a cooled solution (–20 °C) of [Pd{(*S*,*S*)-Me-DUPHOS}(cyclohexenyl)](I) (20 mg, 0.032 mmol) in CD_3CN (0.5 mL) is added to AgOTf (8.3 mg, 0.032 mmol) at –20 °C in darkness. After 5 min, the precipitate is removed by filtration (through a 0.2 μm Nylon filter) leading to a clear and pale-yellow solution which is immediately used for NMR analysis.



^{31}P NMR (161.9 MHz, CD_3CN, at –20 °C): δ = 68.6 (d, $^2J_{PP}$ = 28.8 Hz), 65.4 (d, $^2J_{PP}$ = 28.8 Hz) ppm. ^{1}H NMR (400.1 MHz, CD_3CN, at –20 °C): δ = 8.02–7.63 (m, 4 H, H^{21}, H^{22}, H^{23} and H^{24}), 5.51–5.42 (m, 1 H, H^1), 3.16–3.00 (m, 1 H, H^{17}), 2.89–2.69 (m, 3 H, H^8, H^{11} and H^{14}), 2.58–2.19 (m, 6 H, H^{4a}, H^{9a}, H^{10a}, H^{15} and H^{16a}), 2.15–2.06 (m, 2 H, H^2), 2.02–1.94 (m, 1 H, H^{4b}), 1.92–1.75 (m, 3 H, H^{9b}, H^{10b} and H^{16b}), 1.73–1.60 (m, 4 H, H^3 and H^5), 1.37 (dd, $^3J_{HP}$ = 18.0, $^3J_{HH}$ = 7.2 Hz, 3 H, H^{13}), 1.32 (dd, $^3J_{HP}$ = 18.0, $^3J_{HH}$ = 6.8 Hz, 3 H, H^{12}), 0.84 (dd, $^3J_{HP}$ = 14.8, $^3J_{HH}$ = 7.2 Hz, 3 H, H^7), 0.83 (dd, $^3J_{HP}$ = 15.6, $^3J_{HH}$ = 7.2 Hz, 3 H, H^{18}) ppm. ^{13}C NMR (100.6 MHz, CD_3CN, at –20 °C): δ = 153.9 (d, $^2J_{CP}$ = 112.7 Hz, C^6), 143.1 (br., C^{19} *or* C^{20}), 137.9 (br., C^{19} *or* C^{20}), 134.2 (d, $^2J_{CP}$ = 13.0 Hz, C^{21}), 133.7 (d, $^2J_{CP}$ = 16.2 Hz, C^{24}), 132.4 (d, $^3J_{CP}$ = 6.5 Hz, C^{22} *or* C^{23}), 132.2 (br., C^{22} *or* C^{23}), 128.3 (br., C^1), 121.3 (q, $^1J_{CF}$ = 320.7 Hz, overlapping with solvent signal, CF_3), 42.9 (br., C^{11}), 40.4 (d, $^1J_{CP}$ = 19.4 Hz, C^{14}), 37.0 (s, C^{16}), 36.6 (d, $^2J_{CP}$ = 4.0 Hz, C^9), 36.4 (d, $^1J_{CP}$ = 20.8 Hz, C^{17}), 36.3 (s, C^{15}), 35.9 (d, $^2J_{CP}$ = 5.3 Hz, C^{10}), 35.1 (br., C^8), 29.0 (dd, $^4J_{CP}$ = 11.3, $^4J_{CP}$ = 3.6 Hz, C^2), 25.9 (d, $^3J_{CP}$ = 5.7 Hz, C^5), 25.7 (s, C^4), 23.8 (s, C^3), 17.6 (d, $^2J_{CP}$ = 12.7 Hz, C^{13}), 16.1 (d, $^2J_{CP}$ = 6.2 Hz, C^{12}), 14.1 (d, $^2J_{CP}$ = 2.5 Hz, C^{18}), 14.0 (s, C^7) ppm. ^{19}F NMR (376.5 MHz, [D$_7$]DMF, at –50 °C): δ = –79.4 (s) ppm. HRMS calcd. for $C_{24}H_{37}P_2Pd$ $[M]^+$: 493.1405, found 493.1384. ESI MS (CF_3O_3S): *m*/*z* 149 $[M]^-$

NMR Spectroscopy Monitoring of the Catalytic Cycle

From (S_p)-(Methyl)phenylphosphane–Borane (1). Stoichiometric Conditions: In a Schlenk tube, flushed under nitrogen, a cooled solution (–60 °C) of the oxidative addition complex **3** (30 mg, 0.048 mmol) in a [D$_8$]THF (0.2 mL)/[D$_7$]DMF (38 μL) solvent mixture is added to AgOTf (12.4 mg, 0.048 mmol) at –60 °C in darkness. The reaction mixture is stirred for 5 min giving a yellow precipitate. The solution is filtered (through a 0.2 μm Nylon filter), affording a clear and pale-yellow solution, which was transferred into a precooled NMR tube (–60 °C) fitted with a rubber septum. In another Schlenk, flushed under nitrogen, (S_p)-(methyl)phenylphosphane–borane **1** (6.7 μL, 0.048 mmol, 98:2 e.r.) is added to a solution of Me_3SiOK (7.45 mg, 0.058 mmol, 1.2 equiv.) in [D$_8$]THF

(0.2 mL) at –60 °C. The solution is stirred for 1 min at –60 °C and then transferred rapidly into the precooled NMR tube (–60 °C) containing the solution of the cationic oxidative addition complex. The tube is stirred and placed into the precooled NMR probe and the reaction is monitored by $^{31}P\{H\}$ NMR spectroscopy from –60 °C to 20 °C. At 20 °C, the transmetallation adduct **5** undergoes reductive elimination. The reaction is completed after 14 h, giving the cross-coupling product. Then, the mixture is hydrolyzed with degassed water (0.5 mL). The aqueous layer is extracted with diethyl ether (3 × 2 mL). The combined organic layers are dried with $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica-gel column chromatography with pentane/AcOEt (95:5, R_f = 0.30) as eluent affording the pure coupling product **2**[5] as a yellow oil with an enantiomeric ratio of 98:2 in favour of enantiomer $\mathbf{e_2}$ (the enantiomeric ratio was measured by chiral HPLC using conditions described above, see Supporting Information).

^{31}P NMR Characterization of the Transmetallation Adduct 5: ^{31}P NMR {161.9 MHz, [D_7]DMF (10 equiv. to Pd complex)/[D_8]THF (signal locked), at –30 °C}: δ = 63.3 (dd, $^2J_{P2P1}$ = 26.0, $^2J_{P2P3}$ = 24.4 Hz, P^2, **5***maj*), 61.6 (dd, $^2J_{P1P2}$ = 26.0, $^2J_{P1P3}$ = 294.2 Hz, P^1, **5***maj*), 59.8 (dd, $^2J_{P2P1}$ = 25.1, $^2J_{P2P3}$ = 29.8 Hz, P^2, **5***min*), 59.2 (dd, $^2J_{P1P2}$ = 25.1, $^2J_{P1P3}$ = 300.1 Hz, P^1, **5***min*), –15.1 (br. d, $^2J_{P3P1}$ = 300.1 Hz, P^3, **5***min*), –19.7 (br. d, $^2J_{P3P1}$ = 294.2 Hz, P^3, **5***maj*) ppm.

^{31}P NMR {161.9 MHz, [D_7]DMF (10 equiv. to Pd complex)/[D_8]-THF (signal locked), at 0 °C}: δ = 63.4 (dd, $^2J_{P2P1}$ = 26.0, $^2J_{P2P3}$ = 24.5 Hz, P^2), 61.6 (dd, $^2J_{P1P2}$ = 26.0, $^2J_{P1P3}$ = 294.0 Hz, P^1), –19.7 (br. d, $^2J_{P3P1}$ = 294.0 Hz, P^3) ppm.

Recrystallisation of Diastereomerically Pure Transmetallation Adduct 5: At –10 °C, only the diastereomer (S,S,R_P) is observed by ^{31}P NMR spectroscopy. The reaction is stopped at –10 °C and the reaction mixture is concentrated under reduced pressure. The resulting residue is dissolved in CH_2Cl_2 (0.4 mL), filtered (through a 0.2 μm Nylon filter), and transferred into a precooled NMR tube (–20 °C) followed by addition of pentane. By this way, orange crystals suitable for X-ray analysis are obtained by slow diffusion of pentane into the CH_2Cl_2 solution at –20 °C.

From Excess Racemic (Methyl)phenylphosphane–borane (1): In a Schlenk tube, flushed under nitrogen, a cooled solution (–60 °C) of the oxidative addition complex **3** (30 mg, 0.048 mmol) in a [D_8]-THF (0.2 mL)/[D_7]DMF (38 μL, 0.48 mmol, 10 equiv.) solvent mixture is added to AgOTf (12.4 mg, 0.048 mmol) at –60 °C in darkness. The reaction mixture is stirred for **5***min* giving a yellow precipitate. The solution is filtered (through a 0.2 μm Nylon filter), resulting in a clear and pale-yellow solution and then transferred into a precooled NMR tube (–60 °C) fitted with a rubber septum. In another Schlenk, flushed under nitrogen, racemic (methyl)phenylphosphane–borane (+/–)-**1** (20 μL, 0.145 mmol, 3 equiv.) is added to a solution of Me_3SiOK (22.3 mg, 0.174 mmol, 3.6 equiv.) in [D_8]THF (0.2 mL) at –60 °C. The solution is stirred for 30 min at –60 °C and then transferred into the precooled NMR tube (–60 °C) containing the solution of the cationic oxidative addition complex. The tube is stirred and placed into the precooled NMR probe and the reaction is monitored by $^{31}P\{H\}$ NMR spectroscopy from –60 °C to 20 °C. At 20 °C, the transmetallation adducts **5** and **6** undergo reductive elimination. The reaction is completed after 14 h, giving the cross-coupling product. Then, the mixture is hydrolyzed with degassed water (0.5 mL). The aqueous layer is extracted with diethyl ether (3 × 2 mL). The combined organic layers are dried with $MgSO_4$ and concentrated under reduced pressure. The crude product is then purified by silica-gel column chromatography with pentane/AcOEt (95:5, R_f = 0.30) as eluent affording the pure coupling product **2**[5] as a yellow oil with an enantiomeric ratio of 68:32 in favour of enantiomer $\mathbf{e_1}$ (Enantiomeric ratio is measured by HPLC using conditions described above, see Supporting Information).

^{31}P NMR Characterization of the Transmetallation Adducts 5 and 6: ^{31}P NMR {161.9 MHz, [D_7]DMF (10 equiv. to Pd complex)/[D_8]THF (signal locked), at –30 °C}: δ = 61.6 (dd, $^2J_{P2P1}$ = 26.0, $^2J_{P2P3}$ = 24.3 Hz, P^2, **5***maj*), 61.5 (dd, $^2J_{P2P1}$ = 24.7, $^2J_{P2P3}$ = 30.5 Hz, P^2, **6** *min*), 60.8 (apparent t, $^2J_{P2P1}$ = 25.5 Hz, P^2, **6***maj*), 60.0 (dd, $^2J_{P1P2}$ = 26.0, $^2J_{P1P3}$ = 294.4 Hz, P^1, **5***maj*), 59.4 (dd, $^2J_{P1P2}$ = 25.5, $^2J_{P1P3}$ = 280.1 Hz, P^1, **6***maj*), 58.7 (dd, $^2J_{P1P2}$ = 24.7, $^2J_{P1P3}$ = 289.0 Hz, P^1, **6** *min*), 58.1 (dd, $^2J_{P2P1}$ = 25.1, $^2J_{P2P3}$ = 29.7 Hz, P^2, **5***min*), 57.6 (dd, $^2J_{P1P2}$ = 25.1, $^2J_{P1P3}$ = 300.3 Hz, P^1, **5***min*), –21.5 (br. d, $^2J_{P3P1}$ = 294.4 Hz, P^3, **5***maj*), –22.5 (br. d, $^2J_{P3P1}$ = 289.0 Hz, P^3, **6** *min*), –24.8 (br. d, $^2J_{P3P1}$ = 280.1 Hz, P^3, **6***maj*) ppm, P^3 of complex **5***min* is not observed (overlapping by signal of secondary phosphane–borane).

^{31}P NMR {161.9 MHz, [D_7]DMF (10 equiv. to Pd complex)/[D_8]-THF (signal locked), at 0 °C}: δ = 61.7 (dd, $^2J_{P2P1}$ = 26.0, $^2J_{P2P3}$ = 24.4 Hz, P^2, **5**), 61.0 (apparent t, $^2J_{P2P1}$ = 25.8 Hz, P^2, **6**), 59.9 (dd, $^2J_{P1P2}$ = 26.0, $^2J_{P1P3}$ = 294.3 Hz, P^1, **5**), 59.5 (dd, $^2J_{P1P2}$ = 25.8, $^2J_{P1P3}$ = 281.8 Hz, P^1, **6**), –21.8 (br. d, $^2J_{P3P1}$ = 294.3 Hz, P^3, **5**), –24.5 (br. d, $^2J_{P3P1}$ = 281.8 Hz, P^3, **6**) ppm.

Supporting Information (see also the footnote on the first page of this article): HPLC of **1** and **2**, NMR characterisation of **3**, **5**, **6**, **7** and **8**, X-ray structure of **5** and **7**, IR spectra of **2** and **9**.

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