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PCN- and PCS-Pincer Palladium Complexes as Tandem Catalysts in Homoallylation Reactions

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Dedicated to Prof. Dr. Carmen Najera on the occasion of an important birthday in friendship and with great admiration for her excellent contribution to synthetic organic chemistry.

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Abstract: Novel PCN- and PCS-pincer palladium complexes 2-(dimethylamino)methyl-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) bromide (**1**), 2-(phenylimino)-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) bromide (**2**), 2-(phenylthiomethyl)-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) bromide (**3**), 2-(phenylthio)methyl-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) chloride (**4**) have been synthesized (55–95% yield) by using a flexible and straightforward synthetic route starting from isovanillin as the common precursor. The structures of complexes **1**, **2** and, **4** in the solid state were determined using X-ray diffraction and showed a typical pincer-type geometry. The catalytic activities of **1**–**3** in the homoallylation reactions of aldehydes and allyl(tributyl)stannane as well as of their corresponding cationic complexes **1a**–**3a** in the tandem reaction of aldehydes or sulfonimines with allyl chlorides and hexamethyldistannane were investigated. It was found that the catalytic activities are very dependent on the combination of the E-donor moieties in the pincer ligand. Generally, PCS-pincer complex **3** and its cationic complex **3a** outperform PCN-pincer complexes **1** and **2** as well as their cationic complexes **1a** and **2a** in both the homoallylation and tandem reaction. PCS-pincer palladium complexes **3** and **3a** seem to benefit in a positive sense from the combination and cooperativity of a π-accepting phosphorus donor and a σ-donating sulfur donor.

Keywords: homoallylation; palladium; pincer complexes; tandem catalysis

Introduction

In the past decades, ECE-pincer metal complexes have attracted much attention and a variety of structures with various donor atom containing groups, e.g., $E=NR_2$, SR, PR_2, SeR, OPR_2, $OP(OR)_2$ have been synthesized.[1a,b,c] A common characteristic of some of these complexes is their robustness, i.e., thermal stability and stability of the σ-M–C bond against oxidation and hydrolysis. In addition, a range of ECE-pincer metal complexes show remarkable performances as catalysts in C–C cross coupling, transfer hydrogenation, Michael addition, aldol condensation, homoallylation, and a number of other reactions.[1]

The greater part of the known ECE-pincer metal complexes have identical *ortho*-substituents along the C_{ipso}–metal bond, i.e., these are of the NCN,[2] PCP,[3] or SCS[4] types. Recently, ECE′-type ($E \neq E'$) pincer complexes, i.e., pincer ligands in which the *ortho*-substituents are different, have opened a new aspect of pincer chemistry.[5–7] As elaborated in Figure 1, some examples of PCN- and PCS-pincer palladium complexes and their applications in C–C cross coupling reactions,[5] aldol condensations and tandem catalysis[6] have been independently reported by different

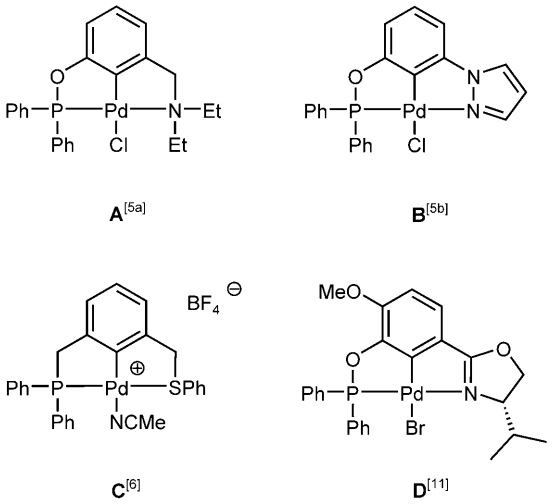


Figure 1. Representative examples of PCN- and PCS-pincer palladium complexes.

groups. The PCN-pincer Pd complexes **A** and **B** are able to catalyze the Suzuki–Miyaura arylation of benzyl halides and other non-activated coupling partners,[5b,c] while the PCS-pincer complex $[Pd\{C_6H_3(CH_2PPh_2)\text{-}2\text{-}(CH_2SPh)\text{-}6\}(MeCN)](BF_4)$ **C** is an excellent catalyst in the stannylation/homoallylation tandem reaction of allyl chloride, hexamethylditin and aldehydes or aryl sulfonimines (Scheme 1).[6] It is worthy of note that several pincer palladium complexes have been reported as active catalysts for only one of the two reactions that are part of this tandem reaction.[6,8–10] For example, the corresponding PCP-pincer palladium complex $[Pd\{C_6H_3(CH_2PPh_2)_2\text{-}2,6\}(MeCN)](BF_4)$ is an active catalyst in the homoallylation of aldehydes or sulfonimines with allylstannane,[8a] but is not able to catalyze the stannylation reaction. *Vice versa*, NCN-pincer palladium complexes catalyze the stannylation reaction, but not the homoallylation.[10] On the other hand, SCS-pincer palladium complexes, like complex **C**, are able to catalyze each of the two reactions of the tandem reaction.[6]

These observations prompted us to study the syntheses of ECE′-pincer palladium complexes bearing other combinations of σ-donating (i.e., N or S) and π-accepting (i.e., P) donors in order to study their catalytic performances in the stannylation/homoallylation tandem reaction.

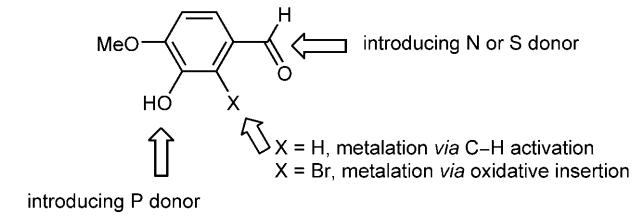


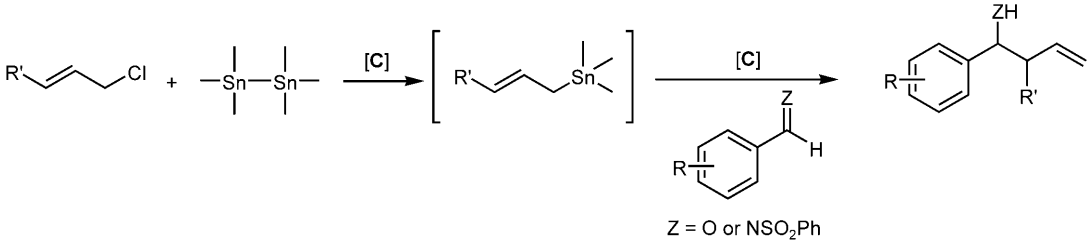
Figure 2. Strategy to access PCN- and PCS-pincer palladium complexes.

The use of isovanillin as the key building block, as pioneered by Nishiyama and co-workers (see complex **D** in Figure 1),[11] has allowed the regioselective introduction of oxazolinyl nitrogen donor and diphenylphosphinite phosphorus donor functionalities by chemoselective conversion of the two independent functional groups, i.e., the aldehyde and hydroxy groups. Here, we report on the development of a synthetic methodology to synthesize ECE′-pincer arene and aryl bromide ligands along with their corresponding palladium complexes starting from isovanillin as the general building block (Figure 2).

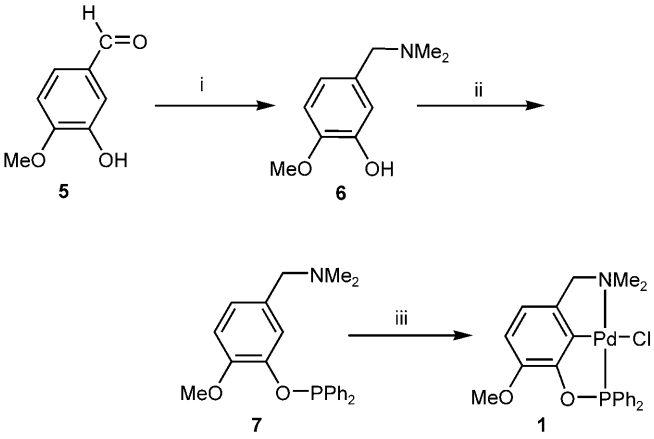
Results

Synthesis of PCN-Pincer Palladium Complex 1

Different from the literature procedure,[5a,12] which involved subsequent reduction, bromination and amination reaction steps, in the present synthetic route to **6** the aldehyde group of isovanillin **5** was directly converted into a (dimethylamino)methyl moiety in moderate yield through a one-pot reductive amination reaction (Scheme 2).[13] The resulting **6** was then reacted with diphenylphosphine chloride in the presence of triethylamine to yield the corresponding ECE′-pincer arene ligand **7** in good yield and acceptable purity. Compound **7** was used in the next metallation step without further purification. A stoichiometric amount of $PdCl_2$ was added to a solution of **7** in toluene and the resulting reaction mixture was refluxed at 110 °C under N_2 for 18 h. After purification, the desired



Scheme 1. Cationic PCS-pincer Pd complex **C**-catalyzed stannylation/homoallylation tandem reaction.



Scheme 2. Synthesis of PCN-pincer palladium complex **1**. *Reagents and conditions:* i) $NMe_2H{\cdot}HCl$, NaOAc, $NaBH_3CN$, ethanol, 24 h, 53%; ii) Ph_2PCl, Et_3N, 0 °C to room temperature, 16 h, quantitative yield; iii) $PdCl_2$, toluene, 110 °C, 18 h, 55%.

PCN-pincer palladium chloride complex **1** was obtained in 55% yield.

The molecular geometry of **1** in the solid state was determined by single crystal X-ray diffraction analysis at 150(2) K. Suitable (colourless) single crystals of **1** were obtained by slow diffusion of hexanes into a dichloromethane solution containing the complex at room temperature. As shown in Figure 3, the monoanionic pincer aryl ligand adopts the typical *mer*-PCN-pincer coordination mode. The palladium atom is located at the central position of a distorted square-planar structure, with the chloride group occupying the remaining *trans*-position with respect to C_{ipso}. The nitrogen donor and phosphorus donor are mutually *trans*-positioned, with a P1–Pd1–N1 angle of 159.53(5)°. The phenyl group C11/C16 is disordered. The value of the occupancy factor given for the major component of the disordered phenyl group refined to 0.646(14).

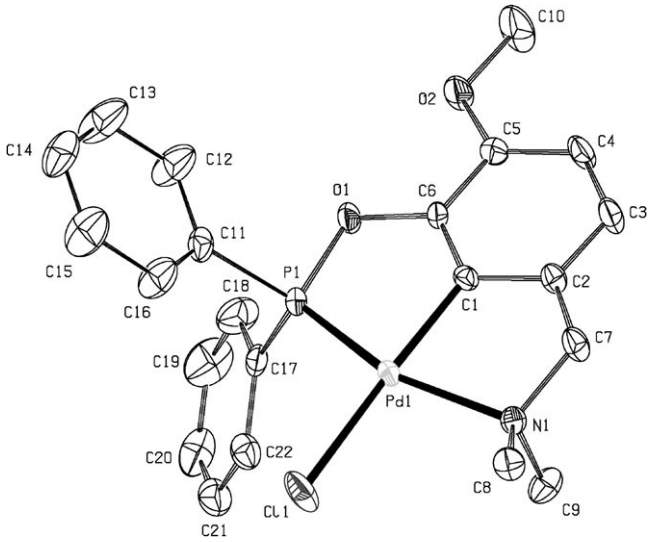
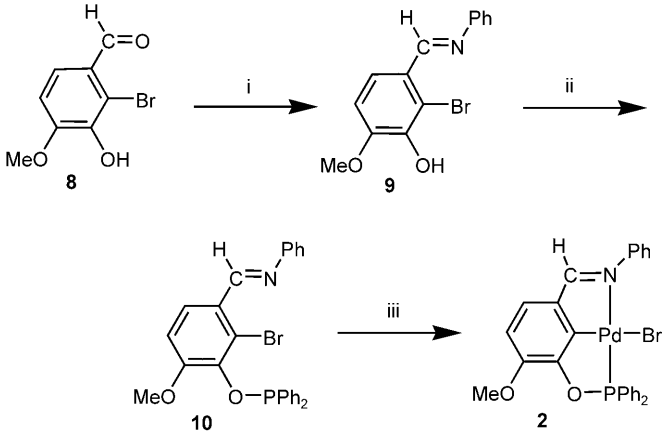


Figure 3. Displacement ellipsoid plot (50% probability level) of the asymmetric unit of **1** at 150(2) K. H atoms and the minor components of the disordered phenyl ring C11/C16 are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.957(2), Pd1–P1 2.1858(6), Pd1–N1 2.1592(17), Pd1–Cl1 2.3695(6), N1–C7 1.488(3), P1–O1 1.6380(16), P1–Pd–N1, 159.53(5), C1–Pd1–Cl1 177.26(7).

Synthesis of PCN-Pincer Palladium Complex 2

As depicted in Scheme 3, the novel PCN pincer palladium complex **2** has been derived from isovanillin bromide **8**.[14] Reaction of **8** with aniline in refluxing chloroform gave imine **9** in good yield. A subsequent reaction with diphenylphosphine chloride in the presence of triethylamine afforded the new PCN-pincer aryl bromide ligand **10** in quantitative yield. After removing $NEt_3{\cdot}HCl$ by simple filtration and without further purification, a solution of **10** in toluene was added to a solution of a zerovalent Pd precursor {i.e., $[Pd_2(dba)_3{\cdot}CHCl_3]$} in toluene. The reaction mixture was warmed to 80 °C for 5 h to yield PCN-pincer palladium chloride complex **2** in 84% yield.

The structure of **2** in the solid state (slow diffusion of hexanes into a dichloromethane solution of **2**) was determined by single crystal X-ray diffraction analysis at 150(2) K. As shown in Figure 4, **2** adopts a typical *mer*-pincer coordination mode. Different to complex **1**, complex **2** possesses an almost perfect square-planar structure, as the double bond of the imine can become conjugated with the aromatic backbone. The palladium atom is located at the central position of this square-planar structure, while the bromine atom



Scheme 3. Synthesis of PCN-pincer complex **2**. *Reagents and conditions:* i) $PhNH_2$, $CHCl_3$, $MgSO_4$, reflux, 16 h, 85%; ii) Ph_2PCl, Et_3N, 0 °C to room temperature, 16 h, quantitative yield; iii) $Pd_2(dba)_3{\cdot}CHCl_3$, toluene, 80 °C, 5 h, 84%.

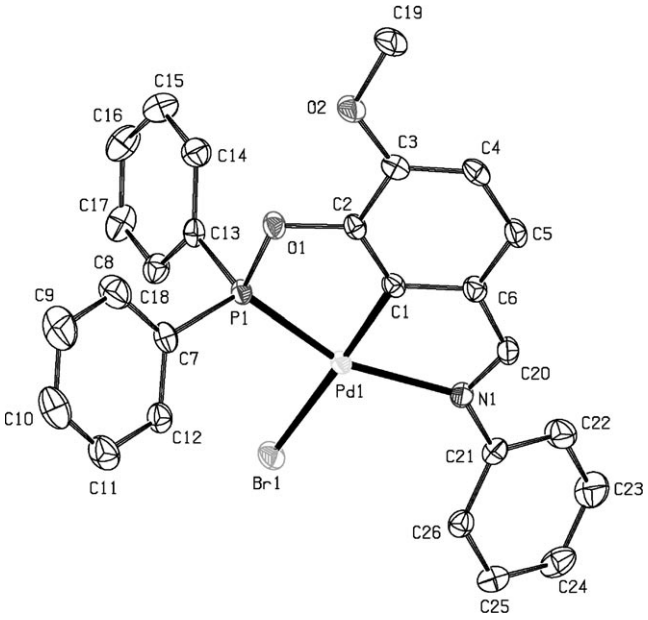
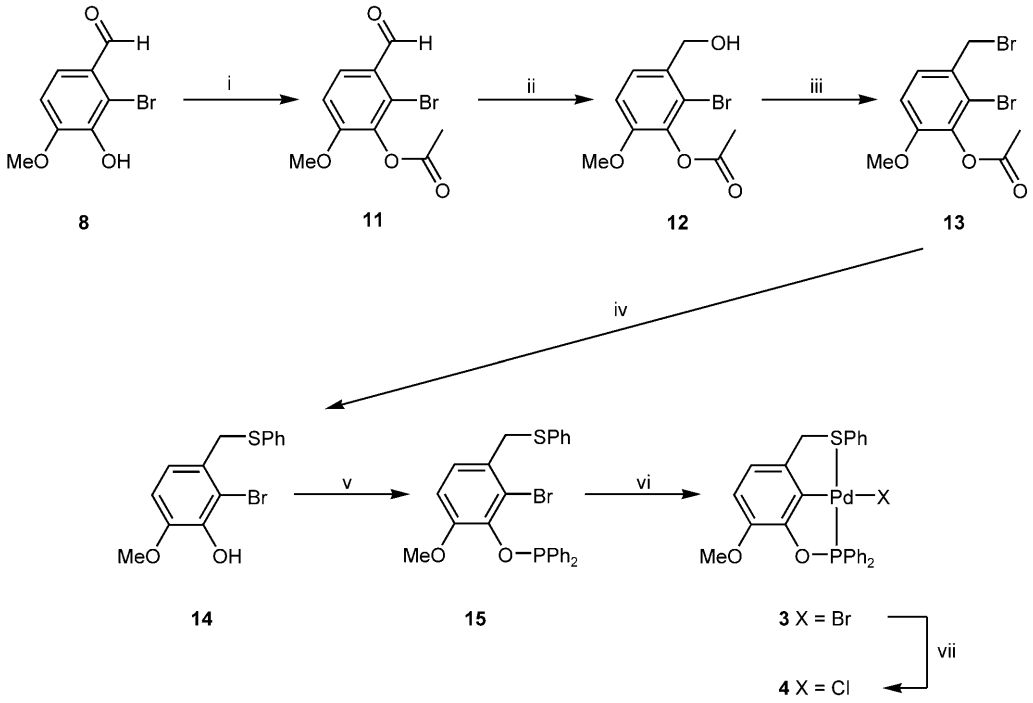


Figure 4. Displacement ellipsoid plot (50% probability level) of the asymmetric unit of **2** at 150(2) K. H atoms are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.9658(16), Pd1–P1 2.2020(5), Pd1–N1 2.1777(14), Pd1–Br1 2.5037(2), N1–C20 1.297(2), P1–O1 1.6513(12), P1–Pd–N1, 158.08(4), C1–Pd1–Br1 177.68(5).

occupies a position *trans* to C_{ipso}. The nitrogen and phosphorus donors are mutually located in *trans*-positions with a P1–Pd1–N1 angle of 158.08(4)°, which is very similar to that of **1** (*vide supra*).

Synthesis of PCS-Pincer Palladium Complexes 3 and 4

Besides PCN-pincer Pd complexes **1** and **2**, the novel PCS-pincer complexes **3** and **4** were synthesized as a proof of principle. As depicted in Scheme 4, the hydroxy group of isovanillin bromide **8** was first protected by an acetyl group to prevent side product formation during the bromination step. Subsequently, aldehyde **11** was converted into alcohol **12** by reduction in the presence of $NaBH_4$ in ethanol. Benzylic bromine **13** was prepared by reacting alcohol **12** with a small excess of PBr_3 under mild conditions. These first three steps produced the respective products in sufficient purity to enable their direct use in the next step. Thioether formation to afford compound **14** was accomplished by reacting **13** with NaSPh in dry THF at room temperature. Without purification, the resulting acetyl ester product was saponified and the resulting crude mixture was subjected to flash chromatography on silica gel to isolate compound **14** in a yield of 57%. The phosphorus donor was introduced *via* a



Scheme 4. Synthesis of PCS-pincer palladium complexes **3** and **4**. *Reagents and conditions:* i) Ac_2O, pyridine, 80 °C, 40 min, 90%; ii) $NaBH_4$, EtOH, room temperature, 30 min, 95%; iii) 1.3 equiv. PBr_3, Et_2O, 0 °C, 2 h, 87%; iv) a) NaSPh, THF, room temperature, 16 h; b) 3 mL 2.5 N NaOH water solution, EtOH, 30 min, 57%; v) $ClPPh_2$, Et_3N, THF, room temperature, 16 h, quantitative yield; vi) $Pd_2(dba)_3{\cdot}CHCl_3$, toluene, 80 °C, 5 h, 78%; vii) $AgBF_4$, wet acetone, aqueous NaCl solution, 1 h, 95%.

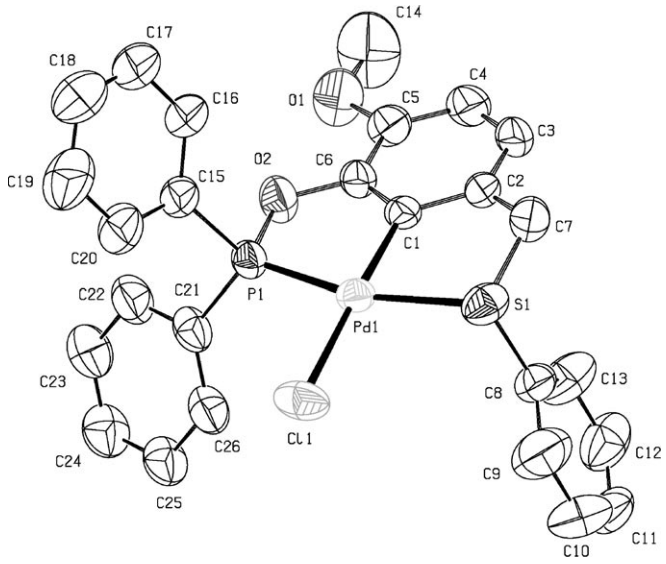


Figure 5. Displacement ellipsoid plot (50% probability level) of the asymmetric unit of **4** at 295(2) K. H atoms and the minor components of the three phenyl groups are omitted for the sake of clarity. Selected bond lengths [Å] and angles [°]: Pd1–C1 1.982(3), Pd1–P1 2.2011(9), Pd1–S1 2.3774(10), Pd1–Cl1 2.3718(9), S1–C7 1.807(4), P1–O2 1.632(2), P1–Pd–S1, 165.02(3), C1–Pd1–Cl1 176.35(8).

P–O coupling by reacting **14** with diphenylphosphine chloride in the presence of triethylamine. Finally, palladation was smoothly carried out by oxidatively inserting a zerovalent Pd species {i.e., $[Pd_2(dba)_3{\cdot}CHCl_3]$} into the C–Br bond of **15**, which gave the novel PCS-pincer palladium complex **3** in good yields after purification.

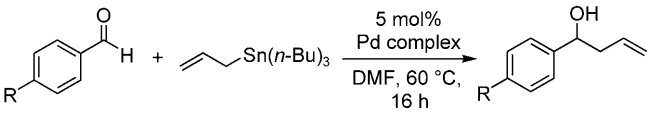
As we could not obtain suitable single crystals for **3**, complex **4** bearing a chloride anion was prepared.[15] Colourless crystals of this complex were obtained by slow diffusion of hexanes into a dichloromethane solution of **4** at room temperature. The structure of **4** was determined by single X-ray diffraction analysis at room temperature. As shown in Figure 5, the palladium atom is located at the central position of a distorted square-planar structure, in which the chloride group occupies a *trans* position with respect to C_{ipso}. The sulfur and phosphorus donors are mutually located in *trans* positions, with a P1–Pd1–S1 angle of 165.02(3)°, which is larger than those of PCN pincer complexes **1** [159.53(5)°] and **2** [158.08(4)°]. The values of the occupancy factors given for the major components of the disordered phenyl groups C8/C13, C15/C20 and C21/C26 refined to 0.743(6), 0.504(10) and 0.52(2), respectively.

PCN- and PCS-Pincer Palladium Complex-Catalyzed Homoallylation

The catalytic performances of the new PCN- and PCS-pincer complexes were initially evaluated in the homoallylation of aryl aldehydes with allyl(tributyl)stannane (Table 1).

For the typical benchmark substrate benzaldehyde (**16**), PCS-pincer complex **3** affords the desired homoallylic alcohol **16a** in good yield (Table 1, entry 3), whereas complexes **1** and **2** merely gave 68% and 21% yields, respectively (Table 1, entries 1 and 2). Improved product yields were obtained for all three pincer complexes when *para*-NO_2 functionalized electrophile **17**, which is an activated substrate (i.e., Hammett constant of *p*-NO_2 group is $\sigma_p = 0.78$[18]), was used (Table 1, entries 4–6 *vs.* entries 1–3). According to these initial tests, complex **3** showed the best catalytic activities amongst the three new pincer complexes. Remarkably, in the case of complexes **1** and **2**, some Pd black was found to be present in the reaction mixture after 5 h, whereas no Pd black was observed for complex **3**. This observation strongly indicated that PCN complexes **1** and **2** decomposed during the catalytic processes at 60 °C in DMF. Another substrate, *p*-methylbenzaldehyde **18** (i.e., Hammett constant of *p*-methyl group is $\sigma_p = -0.17$[18]) was evaluated as a slightly less electrophilic substrate using complex **3** as catalyst. The yield of its homoallylic alcohol product **18a** dramatically decreased to 33% (Table 1, entry 7). Finally, **3** catalyzes the conversion of *p*-bromobenzaldehyde **19** (i.e., Hammett constant of *p*-Br

Table 1. Homoallylation reactions of aryl aldehydes and allyl(tributyl)stannane catalyzed by Pd complexes **1**–**3**.



16, R = H
17, R = NO_2
18, R = Me
19, R = Br

16a, R = H
17a, R = NO_2
18a, R = Me
19a, R = Br

Entry	Electrophile	Catalyst	Product	Yield [%][a]
1	**16**	**1**	**16a**	68 (75)
2	**16**	**2**	**16a**	21 (30)
3	**16**	**3**	**16a**	84 (90)
4	**17**	**1**	**17a**	90 (>95)
5	**17**	**2**	**17a**	85 (>95)
6	**17**	**3**	**17a**	93 (>95)
7	**18**	**3**	**18a**	33 (40)
8	**19**	**3**	**19a**	71 (75)

[a] Isolated yields; product formation estimated by ^{1}H NMR spectroscopy with mesitylene as internal standard presented in parentheses.

group is $\sigma_p = 0.23$[18]) into homoallylic alcohol **19a** in a yield of 71% (Table 1, entry 8).

PCN- and PCS-Pincer Palladium Complex-Catalyzed in Tandem Catalysis

As cationic PCS-pincer palladium complex **C** was found to be an active catalyst for the stannylation/homoallylation tandem reaction,[6] we were interested in investigating the catalytic performance of the corresponding cationic PCN- and PCS-pincer palladium complexes **1a–3a**. These cationic complexes, comprising one equivalent of H_2O as co-ligand, were easily prepared by reacting the corresponding pincer halide complexes **1–3** with $AgBF_4$ in CH_2Cl_2 in the presence of water (Figure 6). The catalytic activities of these complexes in the tandem reaction are summarized in Table 2, Table 3, and Table 4.

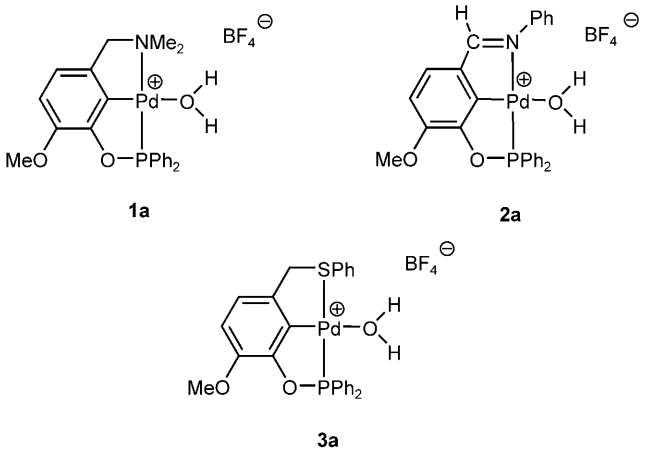
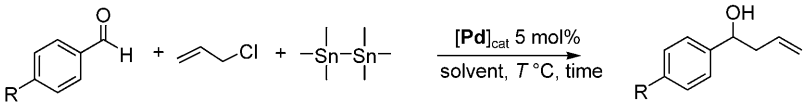


Figure 6. Cationic PCN- and PCS-pincer complexes **1a–3a**.

In order to compare their catalytic activities, the cationic PCN- and PCS-pincer complexes, **1a–3a** were tested in the tandem reaction of *p*-NO_2-benzaldehyde **17** and allyl chloride in the presence of hexamethyldistannane. Complexes **1a** and **3a** afforded comparable isolated yields as earlier reported (63%) for the PCS-pincer complex **C** (see Figure 1),[6] while the PCN-pincer complex **2a** showed a slightly lower catalytic activity. Complex **3a** outperformed PCN-pincer complexes **1a** and **2a** as well as PCS-pincer complex **C** according to the conversions of electrophile **17** and the isolated yields of homoallyl product **17a** (Table 2, entry 3 *vs.* entries 1 and 2).

A reaction condition optimization was then carried out with complex **3a** and electrophile **17**. It was found that the conversions of **17** depended highly on the polarity of the solvent in which the reaction was carried out. Polar solvents like THF and DMF afforded good conversions and isolated yields (Table 2, entries 3 and 4), whereas non-polar solvents like benzene and dichloromethane gave moderate conversions of 30–50% (Table 2, entries 5 and 6). Accordingly, DMF was kept as the optimal solvent in further catalytic tests.

Table 2. Tandem reactions of aldehydes catalyzed by pincer complexes **1a–3a**.[a]



16, R = H
17, R = NO_2
20, R = CF_3

16a, R = H
17a, R = NO_2
20a, R = CF_3

Entry	Electrophile	Cat.	Conditions (solvent/*T* [°C]/time)	Product	Conversion [%][b]	Yield [%][c]
1	**17**	**1a**	DMF/r.t./18 h	**17a**	70	59
2	**17**	**2a**	DMF/r.t./18 h	**17a**	60	43
3	**17**	**3a**	DMF/r.t./18 h	**17a**	85	70
4	**17**	**3a**	THF/r.t./18 h	**17a**	80	65
5	**17**	**3a**	DCM/r.t./18 h	**17a**	50	–
6	**17**	**3a**	Benzene/r.t./18 h	**17a**	30	–
7	**17**	**3a**	DMF/40/18 h	**17a**	80	68
8[d]	**17**	**3a**	DMF/40/18 h	**17a**	80	71
9	**20**	**3a**	DMF/r.t./16 h	**20a**	71[e]	68[e]
10	**16**	**3a**	DMF/r.t./16 h	**16a**	19[e]	18[e]

[a] *Reagents and conditions:* 0.1 mmol of aldehyde, 0.12 mmol of allyl chloride, 0.12 mmol of $Me_3SnSnMe_3$, 0.005 mmol of Pd complex, appointed solvent, reaction temperature and time.
[b] Conversions of electrophiles were monitored by ^1H NMR with mesitylene as internal standard.
[c] Isolated yields after column chromatography.
[d] 2.0 equivalents of allyl chloride were used.
[e] Detected by GC with mesitylene as internal standard.

The reaction temperature was then slightly elevated to 40 °C using 2.0 equivalents of allyl chloride, which did not show an improvement of the conversions (Table 2, entry 3 vs. entries 7 and 8). The catalytic activities of **3a** in reactions with two other electrophiles were then investigated. The trifluoromethyl-functionalized electrophile **20** (i.e., Hammett constant of *p*-CF_3 group is $\sigma_p = 0.54$[18]) gave a slightly decreased conversion and isolated yield compared to those of benchmark electrophile **17** (Table 2, entry 9). In contrast, the conversion and isolated yield dramatically decreased to less than 20% for benzaldehyde **16** (R = H) (Table 2, entry 10).

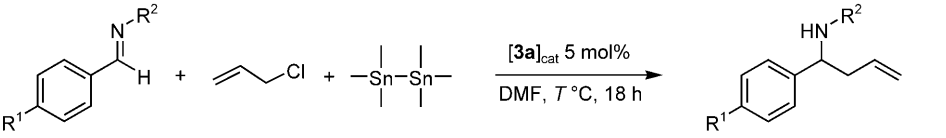
Next to aryl aldehyde substrates, a series of sulfonimines were tested as electrophiles in the tandem reaction by using the optimized conditions (Table 3). *N*-(4-Nitrobenzylidene)benzenesulfonamide **21** was converted into its homoallylic amine product **21a** in 63% isolated yield at room temperature. This yield increased to 77% when the reaction was carried out at 40 °C (Table 3, entries 1 and 2). Surprisingly, the conversions and yields were not significantly affected by using less electrophilic sulfonimines. For instance, *N*-benzylidenebenzenesulfonamide **22** achieved 80% conversion and 65% isolated yield, which is considerably different than the conversion and isolated yield observed in the tandem reaction for benzaldehyde (Table 3, entry 3 *vs.* Table 2, entry 10). Even the *N,N*-dimethylsulfamoyl-protected sulfonimines **23** and **24** were converted providing reasonable yields of the corresponding allylic products (Table 3, entries 4 and 5). These two homoallylsulfonamides belong to a novel class of homoallylic compounds that allow facile deprotection to yield primary allylamines.[16]

In addition, cinnamyl chloride was examined as allylic reagent in order to reveal the diastereoselectivity of **3a** in the tandem catalysis. Entries 1 and 2 in Table 4 show that both the isolated yield and diastereoselectivity of this reaction are dependent on the nature of the solvent in which the reaction was carried out. For *p*-NO_2-benzaldehyde **17** both the yield and diastereomeric ratio (i.e., *anti/syn*) were remarkably improved by using DMF instead of THF as the solvent (Table 4, entry 1 *vs.* entry 2). In contrast to the strong solvent effect, an increase of the temperature did not significantly affect the yield and diastereoselectivity (Table 4, entry 2 *vs.* 3). Moreover, the desired homoallylsulfonamide product **21b** was isolated in the same yield and similar stereoselectivity as the homoallylic product **17b** but with opposite steric configuration when *N*-(4-nitrobenzylidene)benzenesulfonamide **21** was used as electrophile. Interestingly, as earlier observed by Szabó et al.,[8a,17] formation of the *anti*-product is favoured for aldehyde electrophile **17**, whereas sulfonimine electrophile **21** prefers formation of the *syn* product.

Discussion

In general, the title ECE′-pincer palladium complexes are able to catalyze the homoallylation and stannylation/homoallylation tandem reactions with aldehydes and sulfonimines as electrophiles. Probably due to the

Table 3. Cationic PCS-pincer palladium complex **3a**-catalyzed tandem allylation of sulfonimines.[a]



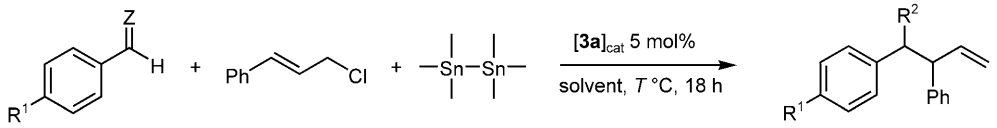
21, $R^1 = NO_2$, $R^2 = SO_2C_6H_5$
22, $R^1 = H$, $R^2 = SO_2C_6H_5$
23, $R^1 = NO_2$, $R^2 = SO_2NMe_2$
24, $R^1 = H$, $R^2 = SO_2NMe_2$

21a, $R^1 = NO_2$, $R^2 = SO_2C_6H_5$
22a, $R^1 = H$, $R^2 = SO_2C_6H_5$
23a, $R^1 = NO_2$, $R^2 = SO_2NMe_2$
24a, $R^1 = H$, $R^2 = SO_2NMe_2$

Entry	Electrophile	Product	Conversion [%][b]	Yield [%][c]
1[d]	**21**	**21a**	80	63
2	**21**	**21a**	90	77
3	**22**	**22a**	80	65
4	**23**	**23a**	75	60
5	**24**	**24a**	60	45

[a] *Reagents and conditions:* 0.1 mmol of sulfonimine, 0.12 mmol of allyl chloride, 0.12 mmol of $Me_3SnSnMe_3$, 0.005 mmol of Pd complex, 1 mL of DMF, 40 °C unless otherwise stated.
[b] Conversions of electrophiles were monitored by ^1H NMR with mesitylene as internal standard.
[c] Isolated yields.
[d] The reaction was performed at room temperature.

Table 4. PCS-pincer complex **3a** catalyzed tandem allylation reactions with cinnamyl chloride.[a]



17, $R^1 = NO_2$, Z = O
21, $R^1 = NO_2$, $Z = NSO_2C_6H_5$

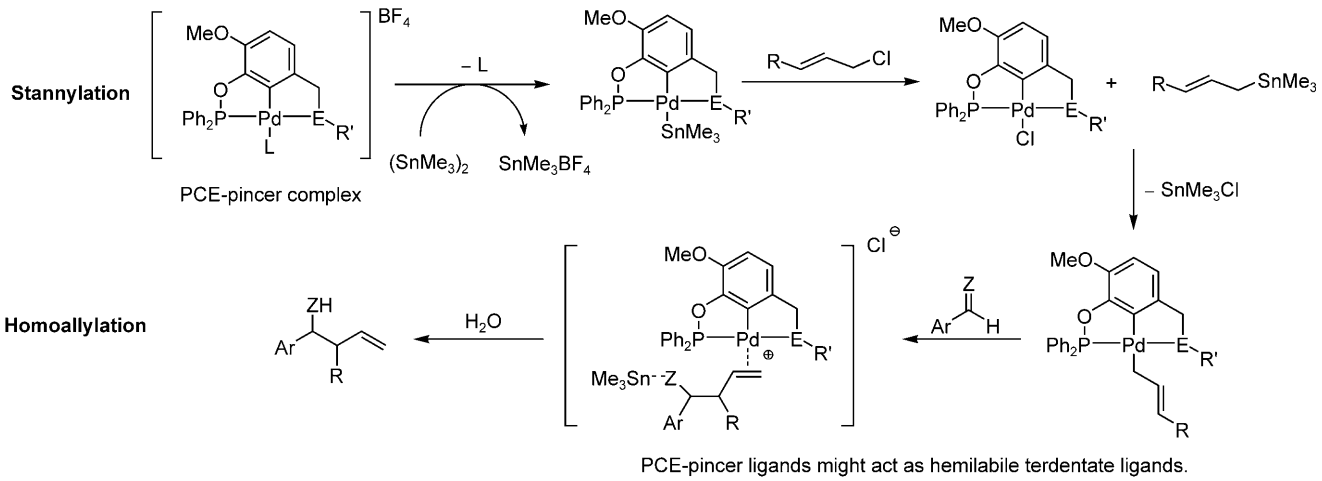
17b, $R^1 = NO_2$, $R^2 = OH$
21b, $R^1 = NO_2$, $R^2 = NHSO_2C_6H_5$

Entry	Electrophile	Product	Conditions (solvent/*T* [°C])	Conversion [%][b]	Yield [%][c]	*dr*[d]
1	**17**	**17b**	THF/r.t.	50	30	3:2
2	**17**	**17b**	DMF/r.t.	85	65	5:1
3	**17**	**17b**	DMF/40	85	63	6:1
4	**21**	**21b**	DMF/40	80	48[e]	1:5

[a] *Reagents and conditions:* 0.1 mmol of aldehyde or sulfonimine, 0.12 mmol of cinnamyl chloride, 0.12 mmol of $Me_3SnSnMe_3$, 0.005 mmol of Pd complex **3a**, appointed solvent, temperature and reaction time.
[b] Conversions of electrophiles were detected by ^1H NMR with mesitylene as internal standard.
[c] Isolated yields.
[d] Diastereomeric ratio: *anti/syn*.
[e] Only the pure *syn* product was isolated.

combination and cooperation of two different donor moieties, these pincer complexes display quite dissimilar catalytic activities not only to each other, but also to the previously reported symmetrical ECE-pincer complexes. For instance, PCN-pincer complexes **1** and **2** showed low catalytic activities towards the benchmark electrophile benzaldehyde in the homoallylation reactions, and Pd black formed during the course of the reactions. Presumably, PCN-pincer ligands are hemi-labile under the reaction conditions (60 °C, DMF), and the Pd atoms might dissociate from the complexes during catalysis (see Scheme 5). Differently, PCS-pincer complex **3** could take advantage of the combination of S and P donors, and conserves its configuration during catalysis. Thus, it shows better catalytic activities without the concomitant formation of Pd black.

The catalytic use of complex **3** in the homoallylation is limited to relatively strong electrophiles bearing electron-withdrawing groups and shows a rather low catalytic activity towards weak electrophilic substrates in comparison with earlier reported phosphite or phosphonite PCP-pincer palladium complexes (Table 1, entries 7 and 8).[8a,b,e,f,9] Importantly, it was found that the increasing order of yields agreed with the increasing order of Hammett constants of the *para*-functional groups in the aldehyde substrates. This observation implies that the electrophilic character of the aldehydes can affect the rate-determining step in the homoallylation of aldehydes. This observa-



Scheme 5. Reaction pathway of PCE-pincer Pd complexes-catalyzed stannylation/homoallylation tandem reaction.

tion strongly suggests that the catalytic activity of ECE′-pincer complexes in homoallylation reactions might not be further improved by simply combining one electron-enriched donor and one electron-deficient donor.

The stannylation/homoallylation tandem reaction involves three independent steps (Scheme 5): (i) stannylation of allyl chloride, which is favoured by an electron-enriched Pd metal center;[10] (ii) transmetalation of allylstannane and pincer palladium complex to generate an η^1-allyl Pd intermediate, which requires an electron-deficient Pd metal center;[8a–c] and (iii) an aryl aldehyde or aryl sulfonimine substrate electrophilically attacks the γ position of the η^1-allyl moiety, which is enhanced by an electron-enriched Pd metal center.[8a–c] Clearly, these reactions proceed under very complicated electronic requirements, and thus the rational design of pincer ligands and the fine-tuning of the electronic properties of their donor moieties are crucial for the further development of these catalyzed reactions. Electronically tuneable ECE′-pincer metal complexes seem to be an ideal choice in this respect, particularly when the complexes bear both σ-donating (i.e., N or S) and π-accepting (i.e., P) donors.

In the tandem reactions of aldehydes, allyl chloride and hexamethyldistannane, cationic aqua PCS-pincer complex **3a** also outperformed PCN-pincer complexes **1a** and **2a**, albeit that its catalytic activity towards less electrophilic substrates is still not ideal, which is consonant with the results observed for the corresponding, neutral PCS-pincer palladium chloride **3** in homoallylation reactions (*vide supra*). Interestingly, the catalytic activity of complex **3a** was not significantly affected by using less electrophilic sulfonimine substrates, which indicates that the electrophilic character of sulfonimines cannot predominate the rate-determining step in their homoallylation. Importantly, under mild ambient conditions Pd-black was not formed in any of the tandem catalysis reactions. Electron-deficient phosphinite PCS-pincer complex **3a** overall showed comparable catalytic activities and stereoselectivities to the relatively electron-enriched phosphine cationic PCS-pincer complex **C** [Pd{$C_6H_3(CH_2PPh_2)$-2-(CH_2SPh)-6}(MeCN)] (BF_4),[6] regardless of the combination of electrophile [i.e., *p*-NO_2-benzaldehyde and *N*-(4-nitrobenzylidene)benzenesulfonamide] and allyl chloride (i.e., allyl chloride and cinnamyl chloride). Yet, **3a** is outperformed by SCS-pincer complex [Pd{$C_6H_3(CH_2SPh)_2$-2,6}(MeCN)] (BF_4) bearing an electron-donating SCS-pincer ligand in both catalytic activity and diastereoselectivity.[6] These observations imply that the better catalytic activity in the tandem reaction could require pincer complexes bearing relatively stronger electron-donating pincer ligands and less electrophilic palladium(II) metal centers.

According to the Hammett constant for a *meta*-OMe group with respect to the C–Pd σ-bond, i.e., $\sigma_m = 0.12$,[18] the *meta*-OMe groups in the ECE′-pincer complexes **1**–**3** and **1a**–**3a** withdraw electron density from the C_{ipso}–Pd bonds and thus polarize the C_{ipso}–Pd bonds in the direction of C_{ipso}, consequently, it makes the Pd metal centers more positively charged. Therefore, these pincer complexes can be considered as relatively electron-deficient and they are expected to accelerate the transmetallation step in the allylation process but to slow down both the stannylation of allyl chlorides and homoallylation of Pd η^1-allyl moieties according to previous reports.[8a–c] Efforts are currently ongoing to corroborate this line of reasoning with the analogous complex that does not have a OMe group.

Conclusions

In this paper, we have developed a series of unsymmetrical PCN- and PCS-pincer palladium complexes starting from isovanillin as the common building block, by using tuneable and straightforward synthetic routes. Their syntheses enjoy good yields, mild reaction conditions, and excellent flexibility. Additionally, the detailed structures of the PCN- (**1** and **2**) and PCS- (**3a**) pincer palladium complexes in the solid state have been determined by single crystal X-ray analyses. The catalytic performances of these complexes have been examined in homoallylation reactions of aldehydes with allyl(tributyl)stannane as well as the tandem reactions of allyl chlorides, aldehydes or sulfonimines, and hexamethyldistannane in order to understand the influence of the combination of different E-donors on the course of these reactions. In the homoallylation reactions, PCS-pincer complex **3** outperforms PCN-pincer complexes **1** and **2** to afford yields warranting further investigations for strong electrophiles, although its catalytic activity is rather low towards less electrophilic substrates. In the tandem reaction, it was also found that cationic PCS-pincer complex **3a** is superior to cationic PCN-pincer complexes **1a** and **2a** in terms of catalytic activities towards both aryl aldehydes and aryl sulfonimines. Remarkably, aryl sulfonimines generally present higher reactivities in comparison with aryl aldehydes when PCS-pincer complex **3a** is used as the catalyst. These investigations have shown the remarkable catalytic properties of PCS-pincer palladium complexes in the stannylation/homoallylation tandem reaction, but also showed that these are inferior to the activity of symmetrical SCS-pincer palladium complexes. Due to the flexible synthetic strategy, the catalytic performances of PCS-pincer complexes could be further improved by varying either the thioether or the phosphinite functionalities with different substituents. Current ef-

forts in our laboratory aim at both the development of more active PCS-pincer complexes and of their chiral analogues in asymmetric tandem catalysis, as well as at the understanding of the subtle electronic demand of the catalytic stannylation/homoallylation reaction.

Experimental Section

General Remarks

All reactions were performed under a dry N_2 atmosphere using standard Schlenk techniques unless stated otherwise. Glassware was oven dried or flame dried prior to use. Diethyl ether and THF were freshly distilled over metallic sodium prior to use. Toluene, Et_3N, and DMF were distilled over CaH_2 and stored under N_2 at −30 °C. Diphenylphosphine chloride was freshly distilled under reduced pressure prior to use. 2-Bromo-3-hydroxy-4-methoxybenzaldehyde **8** was prepared according to a reported procedure.[14] All other reagents were purchased from ACROS Organics and Sigma–Aldrich Chemical Co. Inc, and used as received. ^{1}H NMR (400.0 MHz), ^{13}C NMR (100.6 MHz), and ^{31}P NMR (161.9 MHz) spectra were recorded at room temperature in $CDCl_3$ on a Varian 400 MHz spectrometer. Chemical shift values are reported in ppm (δ) relative to $(CH_3)_4Si$ (^{1}H and ^{13}C NMR) or a capillary containing 85% H_3PO_4 in D_2O (^{31}P{^{1}H} NMR). Flash chromatography was performed using ACROS silica gel, 0.06–0.200 mm, pore diameter *ca.* 6 nm. MS measurements were carried out on an Applied Biosystems Voyager DE-STR MALDI-TOF MS. Elemental microanalyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a/d Ruhr, Germany.

1-(Dimethylamino)methyl-3-hydroxy-4-methoxybenzene (6)

Isovanillin (2 g, 13.15 mmol) was reacted with dimethylamine hydrochloride (2.32 g, 28.45 mmol) and sodium cyanoborohydride (1.44 g, 22.85 mmol) in methanol (100 mL) in the presence of sodium acetate (1.82 g, 22.20 mmol). The pH value of the solution was maintained in the range of 7–8 throughout the reaction, if necessary by the addition of concentrated HC1. The solution was stirred at room temperature during 24 h. Acetone (## mL) was then added, followed by 6 N HCl (until pH 2–3 was reached). The solvent was removed under vacuum, and the residue was dissolved in water (50 mL) and extracted with EtOAc (4×15 mL). The combined organic layers upon evaporation of the solvent yielded a mixture of starting aldehyde and the corresponding alcohol. The remaining aqueous phase was made basic (pH 8–9) and extracted with EtOAc (5×25 mL). The organic extracts were dried over $MgSO_4$, and the solvent was removed under vacuum, thus yielding an amber oil residue. An analytical sample was recrystallized from a saturated hot hexanes solution of the crude product. Yield: 1.27 g (53%), white solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.83–6.91 (m, 3H, ArH), 6.05 (br s, 1H, OH), 3.91 (s, 3H, OCH_3), 3.39 (s, 2H, CH_2NMe_2), 2.28 (s, 6H, NMe_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 146.2, 145.8, 131.5, 121.0, 116.0, 110.7, 63.9, 56.2, 45.2; anal. calcd. for C 66.27, H 8.34, N 7.73; found: C 66.26, H 8.40, N 7.69.

1-(Dimethylamino)methyl-3-diphenylphosphinooxy-4-methoxybenzene (7)

Compound **6** (0.182 g, 1 mmol) was in dissolved dry toluene (20 mL) and pre-cooled to 0 °C on an ice bath. To this solution was consecutively added Et_3N (280 μL, 2 mmol) and Ph_2PCl (189 μL, 1 mmol) *via* an airtight syringe. After the addition, the reaction mixture was allowed to warm to room temperature and was vigorously stirred for 16 h. The resulting white suspension was filtered through a short pad of Celite, after which the filtrate was concentrated under reduced pressure to give crude compound **7**, which was obtained in quantitative yield and used in the next step without further purification. Yield:0. 037 g (quantitative); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66–7.74 (m, 4H, PPhH), 7.35–7.48 (m, 6H, PPhH), 6.71 (d, ^3J = 8.0 Hz, 1H, ArH), 6.42 (d, ^3J = 8.0 Hz, 1H, ArH), 6.38 (s, 1H, ArH), 3.98 (s, 3H, OCH_3), 3.41 (s, 2H, CH_2NMe_2), 2.34 (s, 6H, NMe_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 168.6, 153.9 (d, J = 3.0 Hz), 148.5, 144.7, 142.5 (d, J = 18 Hz), 131.2 (d, J = 7.6 Hz), 131.0 (d, J = 7.6 Hz), 129.8 (d, J = 4 Hz), 128.3 (d, J = 7.5 Hz), 126.1, 123.4, 110.9, 53.6, 50.7; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 126.4 (s).

2-(Dimethylamino)methyl-5-methoxy-6-(diphenylphosphinoxy)phenyl palladium(II) Bromide (1)

To a solution of compound **7** (0.19 g, 0.5 mmol) in dry toluene (15 mL) was added $PdCl_2$ (0.09 g, 0.5 mmol) and this mixture was refluxed at 110 °C under N_2 for 18 h. After cooling, the reaction mixture was filtered through a short pad of Celite and the filtrate was concentrated under reduced pressure to yield a yellowish solid. The solid was subjected to flash chromatography with EtOAc/hexanes (9:1, v/v) as eluent. Analytically pure product was obtained as a slightly yellow and air stable solid. Yield: 0.139 g (0.275 mmol, 55%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.97–8.03 (m, 4H, PPhH), 7.47–7.49 (m, 6H, PPhH), 6.70 (d, ^3J = 8.0 Hz, 1H, ArH), 6.64 (d, ^3J = 8.0 Hz, 1H, ArH), 4.05 (s, 2H, CH_2NMe_2), 3.86 (s, 3H, OCH_3), 2.89 (s, 6H, NMe_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 50.5 (d, J = 11 Hz), 146.8, 144.5 (d, J = 20 Hz), 140.3, 133.5 (d, J = 54 Hz), 131.8–132.2 (m), 128.8 (d, J = 20 Hz), 117.6, 110.9, 56.6, 50.5; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 155.4 (s). MS (MALDI-TOF): m/z = 470.81, calcd. for $[M-Cl]^+$: 470.82; anal. calcd. for $C_{22}H_{23}NClO_2PPd$: C 52.19, H 4.58, N 2.77, P 6.12, Pd 21.02; found: C 52.22, H 4.61, N 2.71, P 6.09, Pd 21.01;

1-Phenylimino-2-bromo-3-hydroxy-4-methoxybenzene (9)

Compound **8** (0.4620 g, 2 mmol),[13] aniline (184 μL, 2 mmol), and $MgSO_4$ (1 g) were suspended in $CHCl_3$ (20 mL) and refluxed at 75 °C under N_2 for overnight. After cooling, the reaction mixture was filtered through a short pad of Celite and the filter cake was washed with CH_2Cl_2 (3×5 mL). The combined filtrate was concentrated to dryness in vacuo to yield a yellow-brown solid that was used for the next step without further purification. An analytical

sample was recrystallized from a saturated hot hexanes solution of the crude product. Yield: 0.52 g (85%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.81 (s, 1H, PhN=CHAr), 7.91 (d, ^3J = 8.4 Hz, 1H, ArH), 7.40 (m, 2H, NPhH), 7.27 (m, 3H, NPhH), 6.93 (d, ^3J = 8.4 Hz, 1H, ArH), 6.06 (br s, 1H, OH), 3.98 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 159.4, 151.9, 149.7, 143.3, 129.4, 128.0, 126.4, 121.0, 112.7, 109.9, 56.7; anal. calcd.: C 54.92, H 3.95, N 4.58; found: C 54.96, H 3.91, N 4.53.

1-Phenylimino-2-bromo-3-diphenylphosphinoxy-4-methoxybenzene (10)

Compound **9** (0.3062 g, 1 mmol) was azeotropically dried on dry toluene (3 × 5 mL), and afterwards dissolved in dry toluene (20 mL) and precooled to 0 °C on an ice bath. To this solution was consecutively added Et_3N (280 μL, 2 mmol) and Ph_2PCl (189 μL, 1 mmol) *via* an airtight syringe. After addition, the reaction mixture was allowed to warm to room temperature and was vigorously stirred for 16 h. The resulting white suspension was filtered through a short pad of Celite and the filter cake was washed with EtOAc (3 × 5 mL). The filtrate was concentrated under reduced pressure and was fully dried in vacuum to give crude compound **10**, which was used in the next step without further purification. Yield:0.496 g (quantitative); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.84 (s, 1H, CH=NPh), 7.80 (t, ^3J = 4.4 Hz, 4H, PPhH), 7.43–7.47 (m, 6H, PPhH), 7.24–7.41 (m, 6H, ArH + NPhH), 6.94 (d, ^3J = 8.8 Hz, 1H, ArH), 3.64 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 159.6, 151.1, 142.1 (d, J = 18 Hz), 132.0 (d, J = 11 Hz), 131.3 (d, J = 23 Hz), 129.4 (d, J = 12 Hz), 128.6, 128.5, 128.4, 126.3, 124.5, 122.4, 121.3, 111.6, 56.2; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 126.8 (s).

2-(Phenylimino)-5-methoxy-6-(diphenylphosphinoxy)-phenylpalladium(II) Bromide (2)

To a solution of compound **10** (0.2450 g, 0.5 mmol) in dry toluene (15 mL) was added [Pd_2(dba)$_3$·$CHCl_3$] (0.258 g, 0.25 mmol) and this mixture was warmed to 80 °C under N_2 for 5 h. After cooling, the reaction mixture was filtered through a short pad of Celite and the filtrate was concentrated under reduced pressure to yield a yellowish solid mixture. The solid was subsequently subjected to flash chromatography with EtOAc/hexanes (3:7 v/v) as eluent. The product was obtained as a light yellow and air stable solid. Yield: 0.2387 g (0.4 mmol,80%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.07 (q, ^3J = 6.4 Hz, 4H, PPhH), 7.46–7.54 (m, 6H, PPhH), 7.40 (t, ^3J = 7.2 Hz, 2H, NPhH), 7.26–7.31 (m, 3H, NPhH), 8.24 (d, $^4J_{P,H}$ = 4.8 Hz, 1H, CH=NPh), 7.22 (d, ^3J = 8.0 Hz, 1H, ArH), 6.70 (d, ^3J = 8.0 Hz, 1H, ArH), 3.94 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 173.0, 156.5, 150.3 (d, J = 10.4 Hz), 148.3 (d, J = 20.7 Hz), 148.6, 138.1, 132.2–132.9 (m), 128.8–129.2 (m), 127.7, 125.6, 123.7, 109.5, 56.4; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 159.2 (s). MS (MALDI-TOF): m/z = 516.86, calcd. for $C_{26}H_{21}NO_2PPd$ [M−Br]$^+$: 516.84; Anal. calcd.: C 52.33, H 3.55, N 2.35, P 5.19, Pd 17.83; found: C 52.28, H, 3.65, N 2.38, P 5.14, Pd 17.81;

2-Bromo-3-formyl-6-methoxyphenyl Acetate (11)

Compound **8** (1.16 g, 5 mmol) and Ac_2O (0.47 mL, 5 mmol) were dissolved in pyridine (15 mL) and vigorously stirred at room temperature under N_2 for 1 h. Subsequently, pyridine was removed from the mixture under reduced pressure on a rotary evaporator. The resulting oily product was redissolved in demineralized water (20 mL) and the pH value of the mixture was then adjusted to 7 by adding saturated aqueous $NaHCO_3$ solution. The neutralized aqueous solution was extracted with EtOAc (3 × 15 mL) and the combined organic layers were dried over $MgSO_4$. After filtration, filtrate solution was evaporated to dryness to afford a white solid. The product was pure enough to be used in the next step without further purification. Yield: 1.22 g (90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.14 (s, 1H, ArC=OH), 7.76 (d, ^3J = 8.8 Hz, 1H, ArH), 6.94 (d, ^3J = 8.8 Hz, 1H, ArH), 3.83 (s, 3H, OCH_3), 2.33 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 190.3, 167.8, 157.4, 138.2, 128.9, 127.2, 122.6, 111.2, 56.8, 20.5; anal. calcd.: C 43.98, H 3.32, Br 29.26; found: C 43.91, H 3.28, Br 29.31.

2-Bromo-3-hydroxymethyl-6-methoxyphenyl Acetate (12)

To a solution of **11** (1.22 g, 4.5 mmol) in absolute ethanol (20 mL) was added $NaBH_4$ (0.1 g, 2.5 mmol) in one portion. The reaction mixture was stirred at room temperature for 1 h. Ethanol was removed on a rotary evaporator and the resulting mixture was diluted with water (20 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, followed by filtration. A white solid product was obtained after removing the solvent under vacuum. The product was enough pure to be used in the next step without further purification. An analytical sample was recrystallized from a saturated hot hexanes solution of the crude product. Yield: 1.18 g (95%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.23 (d, ^3J = 8.4 Hz, 1H, ArH), 6.86 (d, ^3J = 8.4 Hz, 1H, ArH), 4.59 (s, 2H, $ArCH_2OH$), 3.78 (s, 3H, OCH_3), 2.93 (s very br., 1H, CH_2OH), 2.34 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 168.4, 153.2, 151.8, 137.9, 130.5, 126.3, 117.6, 109.7, 64.6, 56.5, 21.2; anal. calcd.: C 43.66, H 4.03, Br 29.05; found: C 43.70, H 3.98, Br 29.09.

2-Bromo-3-bromomethyl-6-methoxyphenyl Acetate (13)

To a solution of **12** (1.18 g, 4.3 mmol) in dry THF (20 mL) pre-cooled at 0 °C on an ice bath was added freshly distilled PBr_3 (0.50 mL, 5 mmol) *via* syringe. After the addition, the ice bath was removed and the reaction was quenched by carefully adding saturated aqueous $NaHCO_3$ (10 mL) after being stirred at room temperature for 1.5 h. Afterwards, the mixture was extracted with EtOAc (3 × 20 mL) and the combined organic layers were dried over $MgSO_4$. Removal of all volatiles under vacuum yielded a yellowish oily product. The product was pure enough to be used in the next step without further purification. An analytical sample was obtained by high vacuum flash distillation (0.5 mmHg/185 °C). Yield: 1.26 g (3.74 mmol, 87%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26 (d, ^3J = 8.8 Hz, 1H, ArH), 6.84 (d, ^3J = 8.8 Hz, 1H, ArH), 4.56 (s, 2H, $ArCH_2Br$), 3.77 (s, 3H, OCH_3), 2.32 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 164.8, 138.3, 129.4, 129.1, 122.0, 114.3, 56.2, 26.7, 20.3;

anal. calcd.: C 35.54, H 2.98, Br 47.28; found: C 35.44, H 3.05, Br 47.23.

1-(Phenylthio)methyl-2-bromo-3-hydroxy-4-methoxybenzene (14)

Compound **13** (0.25 g , 0.76 mmol) and NaSPh (0.1 g, 0.76 mmol) were stirred in dry THF (20 mL) at room temperature for 16 h. After quenching the reaction with demineralized water (20 mL), the crude product was extracted with EtOAc (3×30 mL) and the combined organic layers were dried over $MgSO_4$. A yellow oily mixture was obtained after removing of all volatiles. Without further purification, it was directly treated with 2.5 N NaOH (3 mL) and ethanol (10 mL) at room temperature for 30 min. The reaction mixture was then diluted with demineralized water (50 mL) and neutralized with acetic acid. The mixture was extracted with EtOAc (3×30 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated on a rotary evaporator after filtration. The resulting beige oily product was subjected to flash chromatography with EtOAc/hexanes [1:1 (v/v)] as eluent, $R_f = 0.85$. The desired product was obtained as a beige viscous oil. Yield: 0.14 g (0.43 mmol, 57%); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.33$ (apparent d, $^3J = 7.6$ Hz, 2H, SPhH), 7.24 (t, $^3J = 7.6$ Hz, 2H, SPhH), 7.19 (apparent t, $^3J = 7.2$ Hz, 1H, SPhH), 6.78 (d, $^3J = 8.4$ Hz, 1H, ArH), 6.68, (d, $^3J = 8.4$ Hz, 1H, ArH), 6.04, (s br, 1H, ArOH), 4.19 (s, 2H, $ArCH_2SPh$), 3.85 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 158.0$, 141.9, 136.4, 129.9, 129.0, 126.8, 125.2, 123.6, 116.0, 114.7, 58.2, 37.8; anal. calcd.: C 51.70, H 4.03, Br 24.57, S 9.86; found: C 51.61, H 3.98, Br 24.59, S 9.79;

1-(Phenylthio)methyl-2-bromo-3-diphenylphosphinoxy-4-methoxybenzene (15)

Compound **14** (0.1630 g, 0.5 mmol) was azeotropically dried in dry toluene 3 times, dissolved in dry toluene (20 mL) and pre-cooled to 0 °C on an ice bath. To this solution was consecutively added Et_3N (140 μL, 1 mmol) and Ph_2PCl (94.5 μL, 0.5 mmol) *via* an airtight syringe. After addition, the reaction mixture was allowed to warm to room temperature and was vigorously stirred for 16 h. The resulting white suspension was filtered through a short pad of Celite, and the filtrate was concentrated under reduced pressure and thoroughly dried under vacuum to give crude compound **15**, which was obtained in quantitative yield and used in the next step without further purification. Yield: 0.260 g (quantitative); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.83$ (q, $^3J = 8.0$ Hz, 4H, PPhH), 7.58–7.75 (m, 2H, SPhH), 7.37–7.48 (m, 6H, PPhH), 7.24–7.31 (m, 3H, CH_2SPhH), 6.71 (d, $^3J = 7.6$ Hz, 1H, ArH), 6.43 (d, $^3J = 7.6$ Hz, 1H, ArH), 4.34 (s, 2H, $ArCH_2SPh$), 3.95 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 163.4$, 153.9 (d, $J = 3.6$ Hz), 148.5, 144.9, 142.1 (d, $J = 18$ Hz), 131.7 (d, $J = 7.5$ Hz), 131.4 (d, $J = 7.5$ Hz), 129.8 (d, $J = 4$ Hz), 128.3 (d, $J = 7.8$ Hz), 129.7, 128.6, 117.5, 110.5, 57.1, 23.4, 14.9; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): $\delta = 126.9$ (s).

2-(Phenylthiomethyl)-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) Bromide (3)

To a solution of compound **15** (0.2550 g, 0.5 mmol) in dry toluene (15 mL) was added $Pd_2(dba)_3{\cdot}CHCl_3$ (0.258 g, 0.25 mmol) and the mixture was warmed to 80 °C under N_2 for 5 h. After cooling, the reaction mixture was filtered through a short pad of Celite and the filtrate was concentrated under reduced pressure to yield a yellowish solid mixture. The solid was subjected to flash chromatography with EtOAc/hexanes [3:7 (v/v)] as eluent. An analytic sample was obtained as a light yellow and air stable solid. Yield: 0.2400 g (0.39 mmol, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.03$ (q, $^3J = 8.0$ Hz, 4H, PPhH), 7.79–7.82 (m, 2H, SPhH), 7.45–7.52 (m, 6H, PPhH), 7.34–7.36 (m, 3H, CH_2SPhH), 6.85 (d, $^3J = 8.0$ Hz, 1H, ArH), 6.70 (d, $^3J = 8.0$ Hz, 1H, ArH), 4.62 (s, 2H, $ArCH_2SPh$), 3.86 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 174.4$, 157.8, 152.0 (d, $J = 14$ Hz), 148.0, 142.5 (d, $J = 2$ Hz), 142.0, 133.3, 133.0, 132.5 (d, $J = 3$ Hz), 132.0 (d, $J = 14$ Hz), 130.0, 129.6 (d, $J = 14$ Hz), 118,9, 111.4, 57.1, 50.5; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): $\delta = 153.0$ (s). MS (MALDI-TOF): $m/z = 535.90$, calcd. for $C_{26}H_{21}NO_2PPd$ $[M-Br]^+$: 535.91; anal. calcd.: C 50.71, H 3.60, P 5.03, Pd 17.28, S 5.21; found: C 50.68, H 3.51, P 5.04, Pd 17.27, S 5.25;

2-(Phenylthio)methyl-5-methoxy-6-(diphenylphosphinoxy)phenylpalladium(II) Chloride (4)

To a solution of **3** (0.2400 g, 0.39 mmol) in acetone (20 mL), $AgBF_4$ (0.082 g, 0.42 mmol) was added and the reaction mixture was stirred at room temperature for 1 h. The resulting suspension was filtered over Celite and the residue was subsequently washed with CH_2Cl_2 (15 mL) and demineralized water (10 mL). A saturated aqeuous NaCl solution was added and the biphasic mixture was stirred at room temperature for 1 h. Afterwards, the two layers were separated and the aqueous layer was further washed with CH_2Cl_2 (3× 10 mL). The combined organic layers were dried over MgSO4 and evaporated to dryness. The residue was redissolved in a minimal amount of CH_2Cl_2, from which the product precipitated upon addition of hexanes. After centrifugation, **4** was isolated as a slightly yellow powder. Yield: 0.2120 g (0.37 mmol, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 8.03$ (q, $^3J = 8.0$ Hz, 4H, PPhH), 7.79–7.82 (m, 2H, SPhH), 7.45–7.52 (m, 6H, PPhH), 7.34–7.36 (m, 3H, CH_2SPhH), 6.82 (d, $^3J = 8.0$ Hz, 1H, ArH), 6.69 (d, $^3J = 8.0$ Hz, 1H, ArH), 4.59 (s, 2H, $ArCH_2SPh$), 3.86 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 171.4$, 158.6, 151.8 (d, $J = 14$ Hz), 147.9, 142.5 (d, $J = 2$ Hz), 141.7, 133.3, 132.8, 132.5 (d, $J = 3$ Hz), 131.5(d, J=14 Hz), 129.8, 129.5 (d, $J = 14$ Hz), 118,9, 110.8, 56.5, 50.0; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): $\delta = 150.8$ (s). MS (MALDI-TOF): $m/z = 535.90$, calcd. for $C_{26}H_{21}NO_2PPd$ $[M-Cl]^+$: 535.91; anal. calcd.: C 54.65, H 3.88, P 5.42, Pd 18.63, S 5.61; found: C 54.70, H 3.91, P 5.34, Pd 18.27, S 5.52.

General Procedure for Synthesizing Cationic Pincer Palladium Complexes 1a–3a

PCN- or PCS-pincer palladium complexes **1–3** (0.1 mmol) and $AgBF_4$ (0.020 g, 0.1 mmol) were suspended in dichloromethane (5 mL). A few drops of demineralized water were added to the reaction mixture and the resultant mixture was stirred at room temperature for 1 h. To the mixture was

added $MgSO_4$ (0.5 g) and the white suspension was further stirred for some time. Afterwards, the suspension was filtered over a short pad of Celite and the filter cake was washed with freshly distilled dichloromethane (3×5 mL). The combined solutions were concentrated under vacuum and the product was precipitated from the solution by the addition of hexanes or ether. A white solid was then collected by centrifuge and was completely dried under vacuum.

Data for complex 1a: Yield: 0.050 g (0.087 mmol, 87%), white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96–8.02 (m, 4H, PPhH), 7.47–7.50 (m, 6H, PPhH), 6.71 (d, ^3J = 8.0 Hz, 1H, ArH), 6.65 (d, ^3J = 8.0 Hz, 1H, ArH), 4.06 (s, 2H, CH_2NMe_2), 3.84 (s, 3H, OCH_3), 2.89 (s, 6H, NMe_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 171.9, 155.8, 150.5 (d, J = 10 Hz), 146.8, 144.5 (d, J = 18.8 Hz), 140.3, 133.5 (d, J = 50 Hz), 131.7–132.1 (m), 128.9 (d, J = 18.8 Hz), 118.6, 110.9, 56.7, 50.5; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 152.3 (br s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376.3 Hz): δ = −153.1 (s). MS (MALDI-TOF): m/z = 488.86, calcd. for $C_{22}H_{25}NO_3PPd$ $[M-BF_4]^+$: 488.83, m/z = 470.80, calcd. for $C_{22}H_{23}NO_2PPd$ $[M-BF_4-H_2O]^+$: 470.82; anal. calcd.: C 45.90, H 4.38, N 2.43, P 5.38, Pd 18.49; found: C 45.85, H 4.44, N 2.40, P 5.35, Pd 18.51.

Data for complex 2a: Yield: 0.049 g (0.08 mmol, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.23 (d, $^4J_{P,H}$ = 5 Hz, 1H, CH=NPh), 8.10 (q, ^3J = 6.8 Hz, 4H, PPhH), 7.46–7.54 (m, 6H, PPhH), 7.38 (t, ^3J = 7 Hz, 2H, NPhH), 7.26–7.33 (m, 3H, NPhH), 7.23 (d, ^3J = 8.0 Hz, 1H, ArH), 6.71 (d, ^3J = 8.0 Hz, 1H, ArH), 3.93 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 172.8, 156.5, 150.1 (d, J = 10 Hz), 148.6, 148.4 (d, J = 21 Hz), 138.5, 132.3–132.7 (m), 129.1 (m), 128.7, 127.9, 125.6, 123.8, 109.5, 56.3; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 156.2 (br s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376.3 Hz): δ = −153.3 (s); MS (MALDI-TOF): m/z = 534.80, calcd. for $C_{26}H_{23}NO_3PPd$ $[M-BF_4]^+$: 534.86, m/z = 516.88, calcd. for $C_{26}H_{21}NO_2PPd$ $[M-BF_4-H_2O]^+$: 516.84; anal. calcd.: C 50.23, H 3.73, N 2.25, P 4.98, Pd 17.12; found: C 50.30, H 3.78, N 2.20, P 4.91, Pd 17.14.

Data for complex 3a: Yield: 0.058 g (0.09 mmol, 90%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.02 (q, ^3J = 8.0 Hz, 4H, PPhH), 7.80–7.83 (m, 2H, SPhH), 7.46–7.53 (m, 6H, PPhH), 7.32–7.35 (m, 3H, CH_2SPhH), 6.88 (d, ^3J = 8.4 Hz, 1H, ArH), 6.72 (d, ^3J = 8.4 Hz, 1H, ArH), 4.63 (s, 2H, $ArCH_2SPh$), 3.87 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 174.2, 152.1 (d, J = 14 Hz), 148.0, 142.5 (d, J = 2 Hz), 142.1, 133.3, 133.0, 132.7 (d, J = 3 Hz), 132.5 (d, J = 14 Hz), 130.3, 129.9 (d, J = 14 Hz), 118,7, 111.5, 57.1, 50.6; ^{31}P{^{1}H} NMR ($CDCl_3$, 161.9 Hz): δ = 151.7 (br s); ^{19}F{^{1}H} NMR ($CDCl_3$, 376.3 Hz): δ = −153.2 (s); MS (MALDI-TOF): m/z = 553.85, calcd. for $C_{26}H_{24}O_3PPdS$ $[M-BF_4]^+$: 553.93, m/z = 535.85, calcd. for $C_{26}H_{22}O_2PPdS$ $[M-BF_4-H_2O]^+$: 535.91; anal. calcd.: C 48.74, H 3.78, P 4.83, Pd 16.61; found: C 48.65, H 3.80, P 4.81, Pd 16.58.

General Procedure for Catalytic Homoallylation Reactions

In a flame-dried Schlenk flask, aryl aldehyde (0.1 mmol), allylstannane (37 μL, 0.12 mmol), pincer complex (0.005 mmol), dry DMF (1 mL) and a stirring bar were loaded and the resulting mixture was vigorously stirred at 60 °C for 16 h. The reaction was quenched by the addition saturated aqueous KF solution (1 mL) and the reaction mixture was stirred at room temperature for another 12 h. Afterwards, the reaction mixture was extracted with EtOAc (3×2 mL) and the combined organic layers were dried over $MgSO_4$. The dry solution was concentrated on a rotary evaporator and was subjected to flash chromatography with EtOAc/hexanes (3:7 v/v) as eluent. Chemical conversions were estimated by ^{1}H NMR with mesitylene as internal standard. The ^{1}H and ^{13}C NMR spectral data of the resulting allylic alcohols agreed with those of reported compounds.[7c]

General Procedure for Catalytic Tandem Reactions

In a flame-dried Schlenk flask, aryl aldehyde or sulfonimine (0.1 mmol), hexamethyldistannane (25 μL, 0.12 mmol), pincer complex (0.005 mmol), solvent (1 mL), and a stirring bar were loaded and the resulting mixture was vigorously stirred at the indicated temperature for 16–18 h. The reaction was quenched by addition saturated aqueous KF solution (1 mL) and the reaction mixture was stirred at room temperature for another 12 h. Afterwards, the reaction mixture was extracted with EtOAc (3×2 mL) and the combined organic layers were dried over $MgSO_4$. The dry solution was concentrated on a rotary evaporator and was subjected to flash chromatography with EtOAc/hexanes (3:7 v/v) as eluent. Chemical conversions were estimated by ^{1}H NMR or GC with mesitylene as internal standard. The ^{1}H and ^{13}C NMR spectral data of the resulting allylic alcohols agreed with those of reported compounds.[6,8c]

X-Ray Diffraction Analysis

All reflection intensities were measured using a Nonius KappaCCD diffractometer equipped either with a rotating anode (**1** and **2**) or a sealed tube (**4**) with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å) under the program *COLLECT*.[19] The programs *PEAKREF*[20] or *HKL2000*[21] were used to refine the cell dimensions. Data reduction was done using the programs *EVALCCD*[22] or *HKL2000*.[21] The structures were solved either with the programs *DIRDIF08*[23] or *SHELXS-97*[24] and were refined on F^2 with *SHELXL-97*.[24] Multi-scan semi-empirical absorption corrections based on symmetry-related measurements were applied to all sets of data with the program *SADABS*.[25] The temperature of data collection was controlled using the system *OXFORD CRYOSTREAM 600* (manufactured by *OXFORD CRYOSYSTEMS*). The H-atoms (except for the H atom attached to C20 in **2**) were placed at calculated positions (*AFIX 23* or *AFIX 43* or *AFIX 137*) with isotropic displacement parameters having values 1.2 or 1.5 times *U*eq of the attached C atom. The coordinates and the isotropic displacement parameter of the H atom attached to C20 (**2**) were refined freely.

For **1**, data were collected at 150 K after the crystal had been flash cooled from room temperature. One phenyl ring of complex **1** is disordered. Restraints were applied so that the minor and major components of the disordered phenyl group have similar geometries (*FLAT*, *SADI* and *SAME* instructions). The *SIMU* instruction (i.e., a restraint for which neighbouring atoms have similar U_{ij}) had to be applied to all disordered atoms in order to get a satisfactory refinement.

For **2**, data were collected at 150 K after the crystal had been flash cooled from room temperature. The structure of complex **2** is ordered.

For **4**, crystals shattered if the temperature was set at 200 K or below. This behaviour may result from the existence of a destructive phase transition. Subsequently, no data could be collected at 150 K. Near 230 K, a few frames were collected but the diffraction pattern looked rather complicated (i.e., extra spots were not integrated correctly during the process of cell determination). Data were then collected near 295 K, at which the diffraction corresponds to that of a single crystal. It seems to be likely that a solid-solid phase transition occurs somewhere between room temperature and 230 K, but its study is beyond the scope of this paper. The structure of **4** is disordered: the phenyl groups attached to the P and S atoms are disordered. The anisotropic displacement parameters for the disordered C_{phenyl} atoms attached directly to P and S atoms (e.g., C8 and C8′) were constrained to be the same using the *EADP* instruction. The *ISOR* and *SIMU* instructions were applied to all disordered atoms in order to get a satisfactory refinement. Restraints were applied so that the minor and major components of the disordered rings have similar geometries using the *SADI* and *SAME* instructions.

CCDCC 741774, CCDC 71775, and CCDC 71776 contain the supplementary crystallographic data for compounds **1**, **2**, and **4**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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