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Synthesis of New Palladium Catalysts: First Isolation and Characterization of all Intermediates in a Cyclopalladation Reaction

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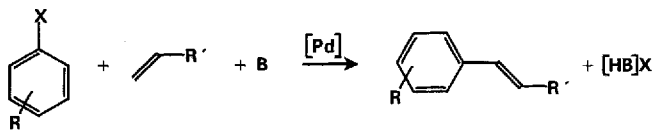
In order to synthesize chiral palladacycles for stereoselective C–C coupling reactions we studied the cyclopalladation of P-chiral phosphanes **2** and **3**. New palladium complexes of the type L_2PdX_2 (**6**, **8**) and $LXPd-\mu-X_2-PdXL$ (**5**, **9**, X = Cl; L = **2**, **3**) were isolated. A detailed study of the reactivity of all intermediates towards cyclopalladation proved the mechanism of cyclometalation reactions of *o*-tolylphosphanes for the first time. Different deuteration experiments clearly demonstrated the higher reactivity of dimeric palladium complexes towards metalation compared to monomeric species. In agreement with this observation only **5** and **9** gave the cyclopalladated products **4** and **10** as revealed by FAB mass spectrometric investigations. Under the described reaction conditions the synthesis of the corresponding palladacycles **4**, **10** is not possible because cyclometalation is a reversible process with $LXPd-\mu-X_2-PdXL$ as thermodynamic more stable products. The results demonstrate the importance of free coordination sites on the metal atom for cyclometalation reactions or more general CH activation processes.

C–C coupling reactions catalyzed by transition metals are of fundamental interest in modern synthetic chemistry. In this respect, the arylation and vinylation of olefins catalyzed by palladium complexes (Heck reaction) are widely used[2].

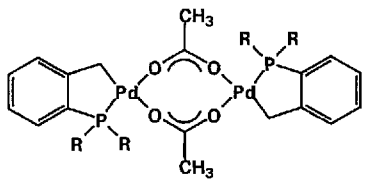
Scheme 1. Palladium-catalyzed arylation of olefins with aryl halides (Heck reaction); X = I, Br, N_2BF_4, C(=O)Cl, CF_3SO_3; B = base: NR_3, K_2CO_3, NaOAc; R, R′ = substituents



Recently, because of its excellent control of regio- and stereoselectivity intra-[3] and intermolecular[4] asymmetric variations of Heck reactions were developed[5]. Here standard catalyst systems use chiral bisphosphanes as auxiliary reagents to stabilize the catalytically active palladium(0) species. So far enantioselective Heck reactions are limited to aryl triflates and aryl iodides as arylating agents. In the case of aryl iodides a stoichiometric amount of silver salts is necessary to obtain good yields and high enantiomeric excesses[6]. All stereoselective Heck reactions suffer from insufficient catalyst turnover frequencies (TOF $< 10\ h^{-1}$) and catalyst turnover numbers (TON < 100). To overcome these problems we initiated a program for the development of new chiral palladium catalysts for stereoselective C–C coupling reactions.

Recently, we discovered palladacycles **1** as superior catalysts in Heck and related reactions of aryl bromides with catalyst turnover numbers up to 500000[7]. These structural well-defined single-site catalysts offer new opportunities to design optically pure palladacycles for asymmetric C–C coupling reactions, especially Heck reactions.

Scheme 2. Structurally well-defined palladacycle (**1** R = *o*-tolyl) as effective catalyst in Heck reactions



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Looking at the structure of **1** there are two possibilities with either C or P chirality. On the one hand the metalated methylene group can be replaced by a suitable alkyl or aryl group, on the other hand a phosphane containing a stereogenic P atom with an *o*-tolyl substituent suitable for cyclopalladation can be used.

Because of the easy access we started to study systems of the latter type. Thus, we synthesized phosphanes **2** and **3** as

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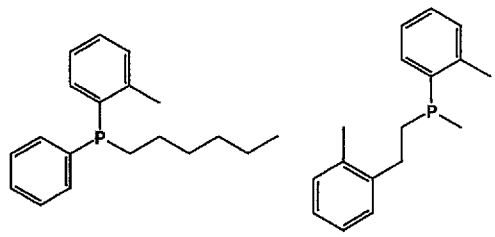
Scheme 3. Chiral phosphanes for the synthesis of P-chiral palladacycles



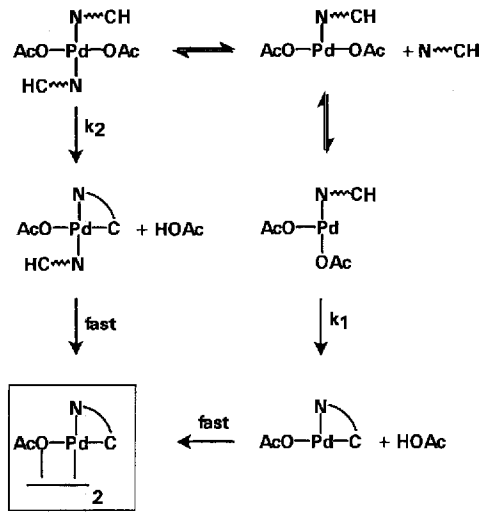
2 3

racemates. Optical resolution of the corresponding palladacycles should be possible[8].

Since this first synthesis and characterization of a metallacycle by Kleiman and Dubeck in 1963[9] some mechanistic discussions appeared in the literature[10]. It is generally assumed that the coordination of the ligand via its donor atom is the first step in a cyclopalladation reaction[11]. The general nature of this adduct is not yet clear because, depending on the reaction conditions, different products were isolated. For example, the cyclopalladation of *N,N*-dimethyl-*o*-toluidine was successful only with palladium(II) acetate. Different types of adducts were obtained with other palladium precursors[12].

Based on kinetical data for the orthometalation of *N,N*-dimethylbenzylamine in glacial acetic acid, Ryabov postulated that the rate-determing step is the formation of a vacant coordination site and that cyclopalladation proceeds via a 14-electron intermediate (Scheme 4)[13].

Scheme 4. Cyclopalladation of *N,N*-dimethylbenzylamine ($k_1 \gg k_2$) according to Ryabov et al.[13]



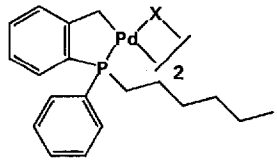
Recently, van Koten et al. (cyclopalladation of arylamines) and Milstein et al. (cycloplatination of alkylphosphanes) also reported that the formation of a coordinately unsaturated 14-electron complex is a necessary step in the cyclometalation reaction[14]. Interestingly, to the best of our knowledge there has been no proof for the mechanism of the important cyclopalladation of phosphanes.

Results and Discussion

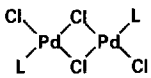
Study of the Cyclopalladation of Phosphane **2**: *n*-Hexylphenyl-*o*-tolylphosphane (**2**) was synthesized straightforwardly from chloro(diisopropylamino)phenylphosphane. Grignard reaction with *n*-hexyl bromide, exchange of the diisopropylamino group for chloride by treatment with HCl and an additional Grignard reaction with 2-bromotoluene afforded to the desired product in 47% yield.

In order to synthesize the palladacycle **4** we first tried the direct synthesis of **4** with palladium(II) acetate in toluene at 50°C analogously to the synthesis of **1**. Unfortunately, palladium complexes of **2** are much better soluble in common organic solvents compared to **1**. So no precipitate formed on addition of an excess of *n*-hexane to the cooled toluene solution.

4a: X = OAc
4b: X = Cl



Palladium chloride complexes are generally less soluble than their acetate derivatives. Thus, an excess of tetra-*n*-butylammonium chloride was added to the reaction mixture, and it was stirred at room temperature. After 24 h mainly palladium black had formed. Nevertheless, we were able to isolate the chloro-bridged dimer **5** as an orange solid in 13% yield after aqueous workup.



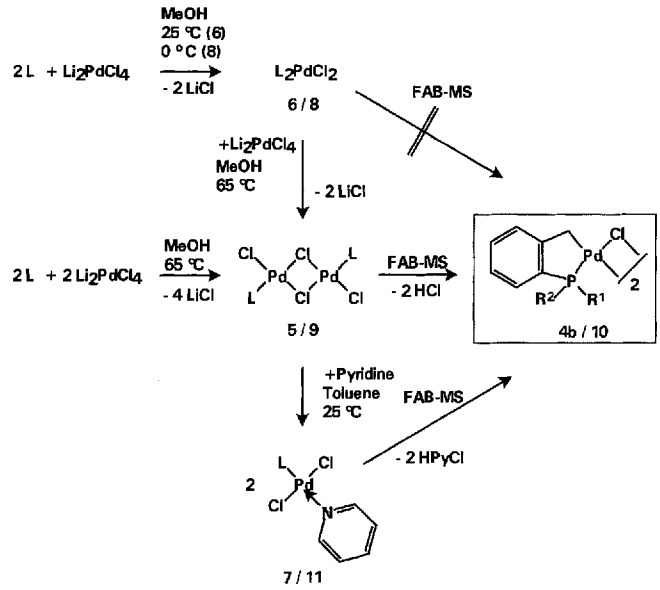
5: L = *n*-Hexylphenyl-*o*-tolylphosphane (**2**)

The reaction of **2** with various amounts of lithium tetrachloropalladate (ligand/palladium = 1:1.2–1:2) in methanol was investigated. Interestingly, bis(*n*-hexylphenyl-*o*-tolylphosphane)palladium(II) chloride (**6**) was isolated at room temperature as a yellow solid in 77–80% yield based on the phosphane. Performing the reaction in boiling methanol, we observed the selective formation of the chloro-bridged dimer **5** (93% yield).

The ^{1}H-NMR spectra of **5** and **6** are fairly identical. An exception is the resonance of the methyl group of the *o*-tolyl substituent which is shifted downfield from $\delta = 2.61$ in **6** to 2.88 in **5**.

The $^{31}P\{^1H\}$-NMR spectrum of **6** shows two signals at $\delta = 12.5$ and 12.7. This is in agreement with the formation of diastereomers from the chiral ligand. The $^{31}P\{^1H\}$-NMR resonance of **5** is shifted downfield to $\delta = 26.8$. Because of the longer distance of the two phosphorus nuclei only one resonance can be detected for the two diastereomers. In mass spectrometric investigations of **5** [CI-MS (70 eV) and FAB-MS] in all cases only the molecular peak of the cyclometalated compound **4b** ($C_{38}H_{48}Cl_2P_2Pd_2$: $m/z = 848$) can be found[15]. CI-MS investigations of **6** also led to cyclometalation in the mass spectrometer, but "milder" FAB-MS in-

Scheme 5. Reactions of the phosphanes **2** and **3** with lithium tetrachloropalladate



vestigations confirmed the expected molecular mass of **6** ($C_{38}H_{50}Cl_2P_2Pd$: *m/z* = 744).

Because of the possible cyclopalladation of **5** during mass spectrometric investigations we searched for alternative chemical methods to synthesize **4**. First, we heated **5** in *o*-xylene at reflux until the formation of palladium black was observed (4 h). Only starting material and some phosphane oxide ($^{31}P\{^1H\}$ NMR: δ = 53.5) could be isolated after aqueous workup. The reaction solution changed its color reversibly from red to yellow until heating. In order to understand the underlying complex chemistry we performed a high-temperature NMR study in [D_2]-1,1,2,2-tetrachloroethane, but no other species than **5** were detected up to 100 °C.

Heating of **5** without any solvent to 160 °C led partly to decomposition to palladium(II) chloride and the bis adduct **6**. In solution the reverse reaction was observed (see above).

Next reactions of **5** with different bases to support HCl elimination were investigated. In the presence of sodium acetate in protic solvents like methanol or 2-methoxyethanol (25 °C, 50 °C and reflux temperature) **5** decomposed while **6** could be isolated again. Moreover, reaction of **5** with potassium carbonate in acetonitrile led to the formation of palladium black upon heating.

Clearly, cyclometalation should be favored by free coordination sites on the metal center. To test this concept silver tetrafluoroborate was used to abstract chloride ions from **5** in various solvents (toluene, THF, ethyl acetate). A solution of **5** was stirred with the silver salt for one hour at room temperature, then tetra-*n*-butylammonium chloride was added to obtain stable chloro-bridged complexes. Only dark red oils were isolated after filtration and aqueous workup. The $^{31}P\{^1H\}$-NMR spectra indicate a complex mixture of compounds, and no defined product could be isolated.

To enhance the reactivity for cyclometalation monomeric base adducts were synthesized. Bridge splitting reactions of **5** with an excess of pyridine at room temperature led directly to the formation of **7** as an orange powder in 80% yield.

The ^{1}H-NMR spectrum of **7** is similar to that of **5** except for the resonances of the pyridine protons. The resonance of the methyl group of the *o*-tolyl substituent appears at δ = 3.00. In comparison with the free ligand the downfield shift is larger compared to **5**. The mass spectra (FAB-MS and CI-MS) are identical with those of **5** (*m/z* = 848). Thus, the downfield shift of the signal or the methyl group of the *o*-tolyl substituent correlates with the tendency of cyclopalladation in the mass spectrometer.

The problems of cyclopalladation of **2** could be attributed either to the low reactivity of the coordinated palladium atom or to the low stability of the resulting metallacycle because of steric effects[16].

To check the latter hypothesis, we studied the reactivity of **5** in [D_4]methanol. A sample of this solution was measured by ^{1}H-NMR spectroscopy and then stirred at room temperature for 5 days and measured again. The resonance of the methyl group decreased by about 20%, and simultaneously the resonance of the hydroxyl group of the methanol increased. *This H/D exchange between the methyl group of the ligand and the hydroxyl group of the methanol clearly demonstrates a reversible cyclopalladation process for the phosphane* **2**.

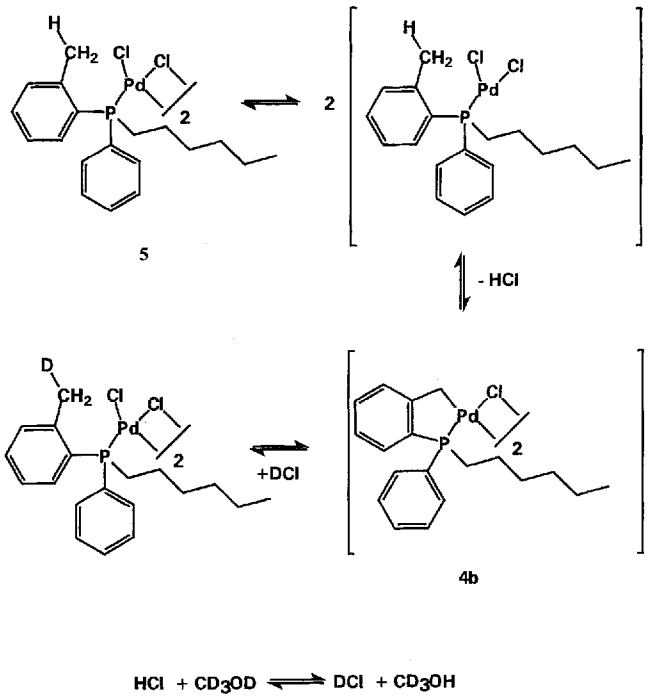
No H/D exchange was detected under similar conditions by the free ligand **2**, neither by the monomeric compound **6**. This indicates the higher reactivity of **5** towards internal CH activation compared to **6** and the necessity of free coordination sites on metal atoms for CH activation processes. Additional proof for the H/D exchange was provided by the preparation of **5** in boiling [D_4]methanol (74% yield). The resulting complex was analyzed by ^{2}H-NMR spectroscopy. The spectrum shows a signal at δ = 2.70 (and some water from the workup at δ = 5.10). As reference [D_8]toluene was added, and the resonance of the [D_3]methyl group was set to δ = 2.09.

The mechanistic consequences of these results are shown in Scheme 6. In the first step **4b** is formed from **5** by elimination of HCl. HCl is in equilibrium with DCl via the deuterated methanol. Deuterolysis of the Pd–C bond is the final step of the H/D exchange.

Again only for the preparation of the dimeric chloro-bridged compound **5** the incorporation of deuterium was detected. No reaction was observed for the monomeric complex **6**. The results of our deuteration studies as well as the FAB mass spectrometric investigations prove for the first time a general mechanism of cyclopalladation for simple phosphanes which is in agreement with the suggested mechanism of other cyclometalations[13,14].

Study of the Cyclopalladation of Phosphane **3**: Reaction of the phosphane **3**[17] with lithium tetrachloropalladate in methanol gave similar results compared to **2**. In this respect bis[methyl-*o*-tolyl(2-*o*-tolylethyl)phosphane]palladium(II) chloride (**8**) could be isolated as a yellow powder by stirring of **3** with 1.3 eq. of lithium tetrachloropalladate in meth-

Scheme 6. Mechanistic explanation of the experimentally detected regioselective H/D exchange of **5**; the monomeric species **6** cannot form an analogous coordinatively unsaturated species, and thus no similar CH activation is observed



$$HCl + CD_3OD \rightleftharpoons DCl + CD_3OH$$

anol at 0 °C (45% yield). Cooling is necessary; otherwise the product distribution is shifted to the chloro-bridged dimeric complex **9** at higher reaction temperature. Thus, reaction at room temperature resulted in the formation of a mixture of **8** and **9** (1.7:1), while reaction in boiling methanol afforded **9** (orange powder) as a single product in 73% yield.

The $^{31}P\{^1H\}$-NMR spectrum of **8** shows four resonances at δ = 4.0, 3.9, 0.0, and −0.1 according to the two diastereomers of the *cis* and *trans* isomer. Compared to the resonance in the $^{31}P\{^1H\}$-NMR spectrum of the monomeric compound **8**, there is a downfield shift to δ = 16.8 in **9**.

In agreement with the aforementioned mechanistic consequences and analogy to **5**, complex **9** could not be identified by mass spectrometry. All attempts to obtain a mass spectrum of **9** (CI-MS or FAB-MS) led to the formation of the corresponding cyclometalated compound **10**, which again could be identified by its molecular mass (*m/z* = 792, $C_{34}H_{40}Cl_2P_2Pd_2$) and its isotopic pattern. In contrast, FAB-MS investigations confirmed the molecular mass of **8** (*m/z* = 688, $C_{34}H_{42}Cl_2P_2Pd$), while under the conditions of chemical ionization (CI-MS) cyclopalladation to **10** (*m/z* = 792) was observed.

Bridge splitting of **9** with an excess of pyridine at room temperature gave the monomeric pyridine adduct [methyl-*o*-tolyl(2-*o*-tolylethyl)phosphane](pyridine)palladium(II) chloride (**11**) (90% yield). Except for the resonances of the pyridine protons, the ^1H-NMR spectrum of **11** is similar to the one of complex **7**. Again the resonance of the methyl group of the *o*-tolyl substituent is shifted downfield to δ = 3.06. Again **11** cannot be detected by mass spectrometric investigations. In FAB- and CI-MS only the molecular peak of the cyclometalated species **10** is observed.

All other attempts to achieve cyclopalladation to obtain **10** from **8** or **9** analogously to the reactions of **5** and **6** failed.

Conclusion

In this paper we report on the isolation and characterization of intermediates generated in the cyclopalladation reaction of the new phosphanes **2** and **3**. In our study we confirmed the suggested mechanism of cyclopalladation reactions by isolating the postulated intermediates for the first time and proving their different ability for CH activation. It is shown that the first intermediate formed during cyclometalation reactions of **2** and **3** are complexes **6** and **8** of the type L_2PdX_2. With another equivalent of the palladium precursor the next intermediates **5** and **9**, complexes of the type $LXPd-\mu-X_2-PdXL$, are formed selectively. These complexes undergo cyclopalladation under the conditions of FAB mass spectrometry in contrast to **6** and **8**.

Further evidence for the enhanced tendency towards CH activation was found in a regioselective H/D exchange of **5**. Neither the free ligand **2** nor **6** shows similar results. These results demonstrate strikingly the importance of free coordination sites on palladium for successful CH activation.

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Experimental

Commercial compounds and solvents were used as received. Lithium tetrachloropalladate[18] and chloro(diisopropylamino)-phenylphosphane[19] were prepared according to a previously described procedure. – Analyses: Analytical Laboratory of the Hoechst AG (Frankfurt/M.).

n-Hexylphenyl-o-tolylphosphane (**2**)

1. *(Diisopropylamino)-n-hexylphenylphosphane:* To a stirred suspension of 14.95 g (0.615 mol) of magnesium turnings in 90 ml of THF a solution of 101.5 g (0.615 mol) of *n*-hexyl bromide in 250 ml of THF was added dropwise under nitrogen. The reaction mixture was heated at reflux and cooled to 10 °C. Then a solution of 146.1 g (0.60 mol) of chloro(diisopropylamino)phenylphosphane in 180 ml of THF was added dropwise at 10 °C. After stirring at room temp., the solid was separated by filtration, washed with THF, and the solvent was removed from the combined filtrate under reduced pressure. The remaining product was extracted with toluene and distilled in vacuo (b.p. 112–113 °C/0.15 mbar) to afford 136 g (77%) of (diisopropylamino)-*n*-hexylphenylphosphane.

2. *Chloro-n-hexylphenylphosphane:* A stirred solution of 136 g (0.464 mmol) of (diisopropylamino)-*n*-hexylphenylphosphane in 400 ml of *o*-xylene was allowed to react with 45.0 g (1.23 mol) of hydrogen chloride at room temp. overnight. The reaction solution was filtered, and the residue was washed with *o*-xylene. Distillation in vacuo yielded 83.0 g (78%) of chloro-*n*-hexylphenylphosphane, b.p. 115 °C/0.2 mbar.

3. *n-Hexylphenyl(o-tolyl)phosphane* (**2**): To a stirred suspension of 3.9 g (0.16 mol) of magnesium turnings in 20 ml of THF a solution of 27.4 g (0.16 mol) of 2-bromotoluene in 80 ml of THF was added dropwise. The reaction mixture was heated at reflux until complete reaction. After cooling to 5°C, a solution of 34.3 g (0.15 mol) of chloro-*n*-hexylphenylphosphane in 30 ml of THF was added dropwise. The solution was stirred overnight at room temp., the solid was filtered off and washed with THF. The solvent was removed in vacuo, and the remaining residue was extracted with toluene and filtered off. After distillation in vacuo, 33.5 g (79%) of the product (b.p. 163°C/0.15 mbar) was obtained. – $C_{19}H_{25}P$ (284.4): calcd. C 80.2, H 8.9, P 10.9; found C 80.0, H 8.7, P 11.3.

Di-μ-chloro-bis(n-hexylphenyl-o-tolylphosphane)dipalladium(II) Dichloride (**5**): To a solution of lithium tetrachloropalladate (1.1 g, 4.2 mmol) in 30 ml of boiling methanol a solution of **2** (1.0 g, 3.5 mmol) in 20 ml of methanol was added dropwise. The mixture was heated at reflux for 2.5 h and then allowed to cool to room temp. After addition of 100 ml of dichloromethane and 80 ml of water, the phases were separated. The organic phase was extracted twice with 80 ml of water and the aqueous phase once with 50 ml of dichloromethane. The combined organic phases were dried with sodium sulfate, and the solvent was removed in vacuo to furnish **5** as an orange solid in 93% yield. – ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 7.79–7.63 (m, 2H, H_{Ar}), 7.51–7.01 (m, 7H, H_{Ar}), 2.88 (s, 3H, Ar-CH_3), 2.60 (m, 1H, PCH_2), 2.34 (m, 1H, PCH_2), 1.52–1.04 [m, 8H, $(CH_2)_4$], 0.75 (t, $^3J_{HH}$ = 8 Hz, 3H, CH_3). – ^{13}C{DEPT} NMR (75.43 MHz, $CDCl_3$, 20°C): δ = 132.3 (C_{Ar}-H), 131.5 (C_{Ar}-H), 130.9 (C_{Ar}-H), 130.7 (C_{Ar}-H), 127.9 (C_{Ar}-H), 124.2 (C_{Ar}-H), 30.0 ($CH_2CH_2CH_3$), 29.5 (PCH_2CH_2), 25.6 (PCH_2), 23.9 ($PCH_2CH_2CH_2$), 23.0 (Ar-CH_3), 21.4 (CH_2CH_3), 12.8 (CH_3). – ^{31}P{^{1}H} NMR (12.138 MHz, $CDCl_3$, 20°C): δ = 26.8. – IR (KBr): $\tilde{\nu}$ = 3058 cm^{-1} w, 2920 m, 1435 s, 1101 m, 745 vs, 692 m, 466 m. – IR (nujol): $\tilde{\nu}$ = 494 cm^{-1} m, 465 m, 351 s, 295 w, 256 s. – MS (FAB or CI, 70 eV), *m/z*: 848 [M^+ (cyclometalated)], 813 [M^+ (cyclometalated) – Cl]. – $C_{38}H_{50}Cl_4P_2Pd_2$ (923.4): calcd. C 49.4, H 5.5, Cl 15.3, P 6.7, Pd 23.0; found C 49.2, H 5.4, Cl 14.0, P 7.0, Pd 24.

Bis(n-hexylphenyl-o-tolylphoshane)palladium(II) Dichloride (**6**): To a solution of lithium tetrachloropalladate (0.55 g, 2.1 mmol) in 30 ml of methanol a solution of 1.0 g (3.5 mmol) of **2** in 20 ml of methanol was added dropwise. The solution was stirred for 22 h at room temp. After filtration of the yellow precipitate, the product was washed twice with 20 ml of methanol and 20 ml of pentane and dried (yield 80%). – ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 7.73–7.63 (m, 2H, H_{Ar}), 7.38–7.02 (m, 7H, H_{Ar}), 2.61 (s, 3H, Ar-CH_3), 2.58 (m, 1H, PCH_2), 2.25 (m, 1H, PCH_2), 1.64–1.06 [m, 8H, $(CH_2)_4$], 0.75 (t, $^3J_{HH}$ = 8 Hz, 3H, CH_3). – ^{13}C{DEPT} NMR (75.43 MHz, $CDCl_3$, 20°C): δ = 133.7 (C_{Ar}-H), 132.6 (C_{Ar}-H), 131.1 (C_{Ar}-H), 130.3 (C_{Ar}-H), 128.3 (C_{Ar}-H), 125.3 (C_{Ar}-H), 31.5 ($CH_2CH_2CH_3$), 31.2 (PCH_2CH_2), 25.0 (PCH_2), 24.9 ($PCH_2CH_2CH_2$), 23.3 (Ar-CH_3), 22.5 (CH_2CH_3), 14.0 (CH_3). – ^{31}P{^{1}H} NMR (12.138 MHz, $CDCl_3$, 20°C): δ = 12.7, 12.5. – IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} w, 2926 m, 1435 s, 1271 m, 1197 m, 1092 m, 1028 m, 869 vs, 695 s, 557 m, 505 s, 456 s. – IR (nujol): $\tilde{\nu}$ = 419 cm^{-1} m, 357 vs, 195 m. – MS (FAB), *m/z*: 744 [M^+], 709 [M^+ – Cl], 673 [M^+ – Cl – HCl]. – MS (CI, 70 eV), *m/z*: 848 [M^+ (cyclometalated)], 813 [M^+ (cyclometalated) – Cl]. – $C_{38}H_{50}Cl_2P_2Pd$ (746.1): calcd. C 61.2, H 6.8, Cl 9.5, P 8.4, Pd 14.3; found C 60.9, H 6.7, Cl 9.2, P 8.8, Pd 15.

(n-Hexylphenyl-o-tolylphosphane)(pyridine)palladium(II) Dichloride (**7**): To a solution of **5** (0.70 g, 0.75 mmol) in 30 ml of toluene pyridine (0.18 g, 2.3 mmol) was added. The reaction mixture was stirred for 30 min at room temp. and filtered through Celite. The solvent was removed in vacuo. The remaining solid was dissolved in toluene/*n*-hexane (1:3) and the solution cooled to –78°C. After a few days an orange precipitate had formed which was filtered off. After washing three times with 50 ml of pentane and drying, **7** was obtained in 82% yield. – ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 8.93 (m, 2H, 2-H_{Py}), 8.00–7.12 (m, 12H, H_{Ar}), 3.00 (s, 3H, P-Ar-CH_3), 2.85–2.44 (m, 2H, PCH_2-), 1.60–1.14 [m, 8H, $(CH_2)_4$], 0.83 (t, $^2J_{HH}$ = 7 Hz, 3H, CH_2CH_3). – ^{13}C{DEPT} NMR (75.43 MHz, $CDCl_3$, 20°C): δ = 151.5 (C_{Ar}-H), 139.3 (C_{Ar}-H), 138.2 (C_{Ar}-H), 133.7 (C_{Ar}-H), 132.5 (C_{Ar}-H), 131.6 (C_{Ar}-H), 131.0 (C_{Ar}-H), 125.2 (C_{Ar}-H), 124.5 (C_{Ar}-H), 31.2 (CH_2), 27.0 (CH_2), 26.6 (CH_2), 24.9 (CH_2), 23.9 (Ar-CH_3), 22.5 (CH_2), 14.0 (CH_3). – ^{31}P{^{1}H} NMR (12.138 MHz, $CDCl_3$, 20°C): δ = 20.0. – IR (KBr): $\tilde{\nu}$ = 3064 cm^{-1} w, 2925 m, 1602 s, 1446 s, 1216 m, 1100 m, 1069 s, 753 vs, 692 vs, 559 w. – IR (nujol): $\tilde{\nu}$ = 353 cm^{-1} s, 282 m, 229 s. – MS (FAB or CI, 70 eV), *m/z*: 848 [M^+ (cyclometalated)], 813 [M^+ (cyclometalated) – Cl]. – $C_{24}H_{29}Cl_2NPPd$ (539.8): calcd. C 53.4, H 5.4, N 2.6, P 5.7, Pd 19.7; found C 53.1, H 5.4, N 2.3, P 5.9, Pd 19.

Bis[methyl-o-tolyl(2-o-tolylethyl)phosphane]palladium(II) Dichloride (**8**): To a solution of lithium tetrachloropalladate (1.0 g, 3.9 mmol) in 75 ml of methanol, cooled to 0°C, a solution of methyl-*o*-tolyl(2-*o*-tolylethyl)phoshane (**3**) (2.0 g, 7.8 mmol) in 25 ml methanol was added dropwise. The reaction mixture was stirred at 0°C for 3 h, the precipitate was filtered off and washed three times with methanol and twice with pentane. After drying, **8** was obtained (yellow powder) in 45% yield as a mixture of 4 diastereomers. Therefore no clear relation of the corresponding signals could be obtained in ^{1}H and ^{13}C NMR. – ^{31}P{^{1}H} NMR (12.138 MHz, $CDCl_3$, 20°C): δ = 4.0, 3.9, 0.0, –0.1. – IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} m, 3008 m, 2912 m, 1603 w, 1490 s, 1451 vs, 1294 s, 1200 m, 1135 m, 1030 w, 955 s, 890 vs, 745 vs. – IR (nujol): $\tilde{\nu}$ = 447 cm^{-1} vs, 355 s, 303 vs, 284 m. – MS (FAB), *m/z*: 688 [M^+], 653 [M^+ – Cl], 617 [M^+ – Cl – HCl]; MS (CI, 70 eV), *m/z*: 792 [M^+ (cyclometalated)], 757 [M^+ (cyclometalated) – Cl]. – $C_{34}H_{42}Cl_2P_2Pd$ (690.0): calcd. C 59.2, H 6.1, Cl 10.3, Pd 15.4; found C 59.3, H 6.1, Cl 10.9, Pd 15.

Di-μ-chloro-bis[methyl-o-tolyl(2-o-tolylethyl)phopshane]dipalladium(II) Dichloride (**9**): To a solution of lithium tetrachloropalladate (2.8 g, 10.7 mmol) in 100 ml of boiling methanol a solution of methyl-*o*-tolyl(2-*o*-tolylethyl)phosphane (**3**) (2.5 g, 9.8 mmol) was added dropwise. The solution was heated at reflux for 2 h, the precipitate was filtered off, washed three times with 50 ml of methanol, twice with 50 ml of pentane and dried. A yellow-orange solid was obtained in 73% yield. – ^{1}H NMR (300 MHz, [D_6]DMSO, 20°C): δ = 7.55–7.06 (m, 8H, H_{Ar}), 3.08 (m, 1H, PCH_2), 3.02 (s, 3H, P–Ar–CH_3), 2.55 (m, 2H, –CH_2–Ar), 2.28 (m, 1H, PCH_2), 2.22 (s, 3H, CH_2–Ar–CH_3), 1.90 (d, $^2J_{PH}$ = 12 Hz, 3H, PCH_3). – ^{13}C{^{1}H} NMR (75.43 MHz, [D_6]DMSO, 20°C): δ = 140.8 (C_{Ar}-H), 139.7 (C_{Ar}-H), 135.9 (C_{Ar}-H), 131.9 (C_{Ar}-H), 131.6 (C_{Ar}-H), 130.8 (C_{Ar}-H), 130.7 (C_{Ar}-H), 130.0 (C_{Ar}-H), 129.1 (C_{Ar}-H), 126.9 (C_{Ar}-H), 126.0 (C_{Ar}-H), 28.2 (CH_2), 27.7 (CH_2), 23.3 (Ar-CH_3), 19.2 (CH_3). – ^{31}P{^{1}H} NMR (12.138 MHz, [D_6]DMSO, 20°C): δ = 16.8. – IR (KBr): $\tilde{\nu}$ = 3055 cm^{-1} m, 3002 m, 2917 m, 1591 w, 1453 s, 1301 s, 1202 s, 1136 s, 989 m, 957 s, 897 w, 882 vs, 750 vs. – IR (nujol): $\tilde{\nu}$ = 460 cm^{-1} m, 449 w, 351 vs, 288 m, 255 vs. – MS (FAB or CI, 70 eV), *m/z*: 792 [M^+ (cyclometalated)], 757 [M^+ (cyclometalated) – Cl]. – $C_{34}H_{42}Cl_4P_2Pd_2$ (867.3): calcd. C 47.1, H 4.9, P 7.2, Pd 24.6; found C 47.5, H 4.9, P 7.5, Pd 25.

[Methyl-o-tolyl(2-o-tolylethyl)phosphane](pyridine)palladium(II) Dichloride (**11**): To a suspension of **9** (0.50 g, 0.58

mmol) in 20 ml of toluene pyridine (0.14 g, 1.7 mmol) was added. After a few min the suspension became a clear solution which was filtered through Celite. The solvent was removed in vacuo, and the remaining solid was recrystallized from toluene/hexane (1:1). **11** was obtained as long yellow crystals in 87% yield. – ^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ = 8.86 (m, 2H, 2-H_{Py}), 7.74–7.02 (m, 11H, H_{Ar}), 3.13 (m, 1H, PCH_2), 3.06 (s, 3H, P–Ar–CH_3), 2.68 (m, 2H, CH_2–Ar), 2.27 (m, 1H, PCH_2), 2.22 (s, 3H, CH_2–Ar–CH_3), 1.90 (d, $^2J_{PH}$ = 12 Hz, 3H, PCH_3). – ^{13}C{^{1}H} NMR (75.43 MHz, $CDCl_3$, 20°C): δ = 151.3 (C_{Py}-1), 140.9 (C_{Ar}), 139.1 (C_{Ar}), 138.3 (C_{Ar}), 137.7 (C_{Ar}), 131.9 (C_{Ar}), 131.2 (C_{Ar}), 130.5 (C_{Ar}), 129.9 (C_{Ar}), 129.6 (C_{Ar}), 128.9 (C_{Ar}), 126.7 (C_{Ar}), 126.4 (C_{Ar}), 125.7 (C_{Ar}), 124.7 (C_{Ar}), 28.1 (PCH_2CH_2), 27.9 (PCH_2), 23.5 (P–Ar–CH_3), 19.3 (CH_2–Ar–CH_3). – ^{31}P{^{1}H} NMR (12.138 MHz, $CDCl_3$, 20°C): δ = 9.7. – IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1} w, 2960 m, 1601 s, 1443 vs, 1294 s, 1208 s, 1145 m, 1063 s, 998 m, 956 s, 892 vs, 879 s, 754 vs. – IR (nujol): $\tilde{\nu}$ = 351 cm^{-1} vs, 233 s, 150 m. – MS (FAB or CI, 70 eV), *m/z*: = 792 [M^+ (cyclometalated)], 757 [M^+ (cyclometalated) – Cl]. – $C_{22}H_{26}Cl_2NPPd$ (512.75): calcd. C 51.5, H 5.1, Cl 13.8, N 2.7, P 6.0, Pd 20.8; found C 51.7, H 5.1, Cl 14.1, N 2.7, P 6.2, Pd 21.

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