CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200902071

σ-Alkylpalladium Intermediates in Intramolecular Heck Reactions:Isolation and Catalytic Activity

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Abstract: The isolation of σ-alkylpalladium Heck intermediates, possible when β-hydride elimination is inhibited, is a rather rare event. Performing intramolecular Heck reactions on *N*-allyl-2-halobenzylamines in the presence of $[Pd(PPh_3)_4]$, we isolated and characterized a series of stable bridged palladacycles containing an iodine or bromine atom on the palladium atom. Indolyl substrates were also tested for isolation of the corresponding complexes. X-ray crystallographic analysis of one of the indolyl derivatives revealed the presence of a five-membered palladacycle with the metal center bearing a PPh_3 ligand and an iodine atom in a *cis* position with respect to the nitrogen atom. The stability of the σ-alkylpalladium complexes is probably a consequence of the strong constraint resulting from the bridged junction that hampers the *cisoid* conformation essential for β-hydride elimination. Subsequently, the thus obtained bridged five-membered palladacycles were proven to be effective precatalysts in Heck reactions as well as in cross-coupling processes such as Suzuki and Stille reactions.

Keywords: Heck reaction · homogeneous catalysis · metallacycles · palladium · X-ray diffraction

Introduction

Palladium-catalyzed reactions represent one of the most valuable tools in organic synthesis over the last 30 years.[1] The importance of these reactions is reflected by the numerous reports of such reactivity in almost every issue of the journals dealing with organic synthesis. The broad utility of palladium in organic chemistry comes from the facile interconversion between the Pd^0, Pd^{II}, and Pd^{IV} oxidation states during the reaction course, because each oxidation state behaves differently.[2]

Among the different Pd-catalyzed reaction types, the Mizoroki–Heck reaction allows the direct coupling of activated arenes/heteroarenes and olefins with an unactivated alkene by a formal C–H activation creating a σ bond between two sp^2 carbon centers.[3] Compared to cross-coupling processes,[4] this reaction has the practical and economical advantages of being able to start from very simple and readily available materials by substituting the organometallic coupling partner with a simple unsaturated system. During the past decades, the Heck reaction has been developed and improved significantly with regard to scope and reactivity.[5] In particular, proper catalyst and ligand design has led to a variety of very efficient catalytic systems that provide high reaction rates and turnover numbers (TON), often affording good selectivity and product yields.

The standard catalytic cycle generally assumed for the Heck reaction involves a homogeneous palladium catalyst that cycles between the Pd^0 and Pd^{II} oxidation states during the course of the reaction.[6] As shown in Scheme 1, a Pd^0 catalyst, which may also be obtained in situ by reduction of a precatalyst in the Pd^{II} oxidation state, oxidatively adds to the aryl halide to give a Pd^{II} intermediate. The olefin can next bind to the Pd^{II} complex, with subsequent insertion into the aryl–Pd bond, forming a new carbon–carbon bond. β-Hydride elimination gives the product, with a $[PdH(L)_2X]$ species generated in the process. According to the traditionally proposed mechanism, the Pd^0 species is then regenerated by deprotonating reductive action of the $[PdH(L)_2X]$ complex in the presence of a base.

Other plausible mechanisms of the Heck reaction based on cationic[3d] and anionic versions,[7] or on a Pd^{II}–Pd^{IV} se-

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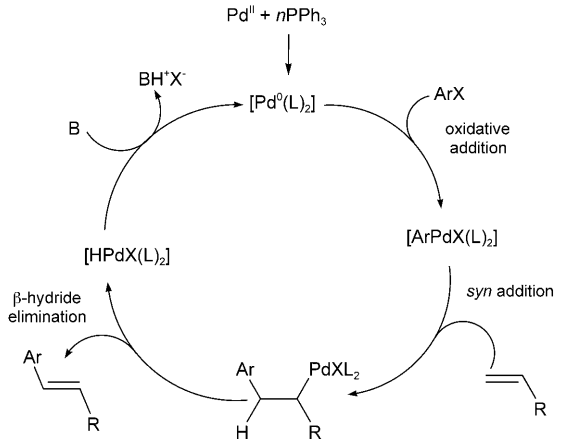
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200902071.

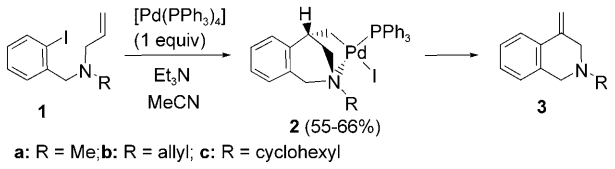


Scheme 1. Typically accepted catalytic cycle for the Heck reaction.

quence[8] have been proposed, although the latter has been demonstrated to be unlikely.

However, each of these mechanisms involves a σ-alkylpalladium complex, from which the different products evolve. Despite the well-established assumption that such an intermediate forms, the capture of σ-alkylpalladium Heck intermediates with inhibition of β-hydride elimination is an uncommon event. This has been described in only two publications concerning intramolecular reactions that recently appeared in the literature.[9] Overman isolated [alkyl–Pd(L)$_n$] palladacycles that were obtained by intramolecular trapping of a cationic intermediate species [alkyl–Pd(L)$_n$]$^+$OTf$^-$ (Tf = trifluoromethylsulfonyl) by an internal nitrogen atom.[9a,b] Balme obtained a phosphine-coordinated [σ-alkyl–PdI] complex stabilized through chelation by the nitrogen atom of a proline moiety contained in the carbon ligand backbone.[9c] Moreover, the literature cases of stable σ-alkylpalladium complexes having a hydrogen atom in the β-position with respect to the metal are rare.[10]

Our contribution in the field of palladium-catalyzed processes concerns studies to synthesize complex polyheterocyclic systems.[11] In the course of our investigations to obtain 4-spiroannulated tetrahydroisoquinolines by a one-pot sequential intramolecular Heck reaction/1,3-dipolar cycloaddition,[12] we disclosed that cyclization of allylamines **1** in the presence of [Pd(PPh$_3$)$_4$] and Et$_3$N in acetonitrile gave rise to the isolation of the σ-alkylpalladium complexes **2** (Scheme 2), instead of the expected isoquinoline derivatives **3**. These bridged palladacycles containing an iodine atom and a triphenylphosphine ligand were found to be highly stable towards air, moisture, heat, and bases.



Scheme 2. Previously reported behavior of allyl(benzyl)amines **1** to give σ-alkyl complexes **2**.

Among the organopalladium complexes, palladacycles have received special attention in the literature due to their unique properties that make them suitable for a variety of applications in many fields. Starting from the original work of Herrmann and Beller,[8a] palladacycles have proven to be convenient and efficient precatalysts for the construction of C–C and C–heteroatom bonds.[13] Noteworthy are the palladacycles containing phosphorus ligands that can stabilize the catalytically active Pd species usually involved in the catalytic cycle.

As a consequence of these aspects, and in light of our preliminary results, we decided 1) to expand the scope to shed light on the structural requirements of the substrates necessary for the stability of the σ-alkylpalladium intermediates, and 2) to test the properties of the new palladium complexes as precatalysts in C–C bond-forming reactions.

Results and Discussion

Determination of structural features for isolation of σ-alkyl complexes: First, we wanted to determine the key framework essential for assuring the stability of σ-alkylpalladium Heck intermediates. In Figure 1, the features of the basic skeleton that have been modified for our purposes are highlighted, namely 1) the type of the benzylic carbon, 2) the nature of the aryl halide, and 3) the substitution pattern of the aromatic ring.

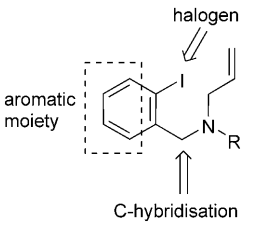
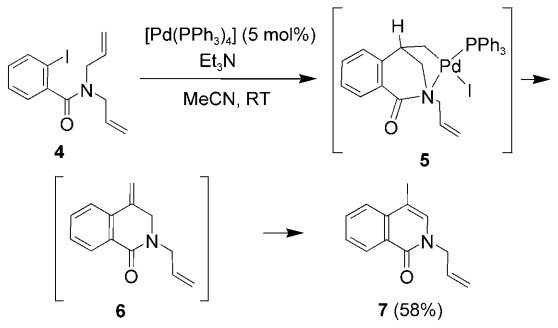


Figure 1. Structural modifications of the basic skeleton

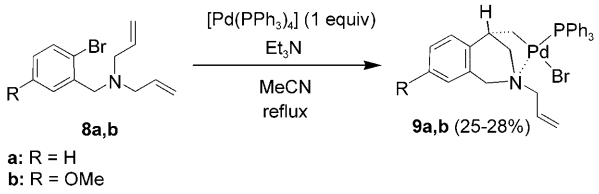
First of all, we tried to change the nature of the benzylic carbon, by considering an aryl iodide with an sp^2-hybridized carbon atom. Thus, diallylamide **4** was chosen as a substrate for treatment with a catalytic amount of [Pd(PPh$_3$)$_4$] and Et$_3$N in acetonitrile (Scheme 3). When the reaction was carried out at room temperature, the formation of the Heck product **6** and its isomerization derivative **7** occurred. The corresponding σ-Pd-complex intermediate **5** was neither isolated, nor detected in the ^{1}H NMR spectrum of the crude



Scheme 3. Reaction of allyl(benzoyl)amine **4** in the presence of a catalytic amount of [Pd(PPh$_3$)$_4$] and Et$_3$N as a base.

mixture. As expected, the use of a much higher amount of $[Pd(PPh_3)_4]$ (1 equiv) did not provide intermediate **5**. It is worth noting that chromatographic separation of the crude mixture provided only isoquinolin-2-one **7** in 58% yield, whereas 4-exomethylene derivative **6** underwent degradation during the silica gel purification. According to this evidence, an sp^3-hybridized carbon atom in the benzylic position seems to be necessary for the stability of the σ-alkylpalladium complex intermediate.

Subsequently, we modified the halide atom with the aim to test the stability of σ-alkyl(bromo) complexes. Diallyl(benzyl)amine **8a** was treated directly with a stoichiometric amount of $[Pd(PPh_3)_4]$ in the presence of Et_3N in acetonitrile (Scheme 4). Its conversion required heating at reflux to

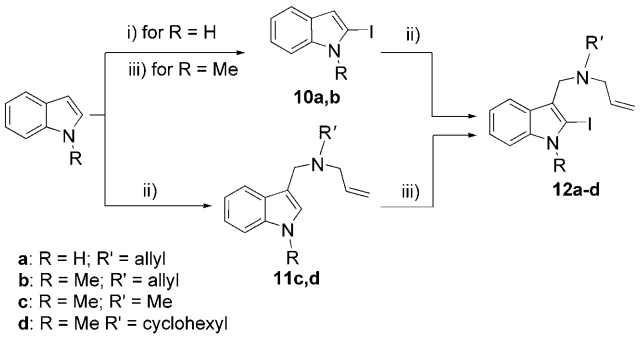


Scheme 4. Preparation of aryl-σ-alkyl bromo complexes as Heck intermediates.

provide the bromide complex **9a** as the sole product, although isolated in lower yield than that obtained for **2b** from the corresponding precursor **1** (25 vs. 66%[12]). Similar to iodide complex **2b**, σ-alkyl(bromo) complex **9a** showed high stability as well as a poor tendency for transforming into the Heck product.

The stability of the σ-alkyl–Pd–PPh_3–bromo Heck intermediate **9a** encouraged us to extend the range of Pd complexes by introducing a functional group on the benzene ring. Starting from the commercially available 2-bromo-5-methoxybenzyl bromide, diallylamine **8b** was synthesized and converted into bromo complex **9b** through a reaction outcome strictly closed to unfunctionalized compound **8a**.

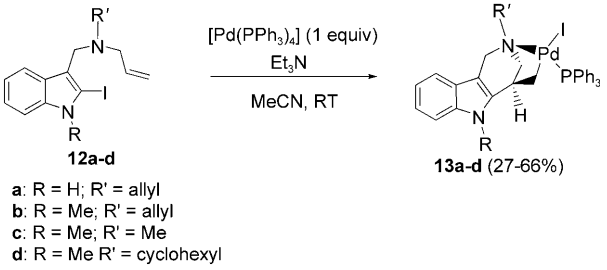
Intramolecular Heck coupling on heteroaromatic frameworks was also investigated. We planned to construct compounds with the iodine atom and the (allylamino)methyl group tied to an indole nucleus. To this end, the series of new 2-iodoindole derivatives **12a–d** was prepared by iodination and Mannich condensation to introduce the [alkyl(allyl)amino]methyl substituent to the 3-position of the indole (Scheme 5). These functionalization reactions on an indole nucleus were equally possible by both sequences shown in Scheme 5, but the most convenient synthetic outcome was strongly dependent on the allylamine. In the case of diallylamine, the highest yields were obtained when the Mannich reactions were performed in the presence of 37% aqueous formaldehyde and 60% acetic acid (AcOH) on 2-iodoindoles, while with methyl- and cyclohexylallylamines the 3-aminomethyl functionalization was more conveniently achieved on 1-methylindole with subsequent introduction of the iodine atom. In the case of indole, the iodination was accomplished under Bergman's conditions,[14] which involve in



Scheme 5. Synthesis of indole derivatives **12** by Mannich reactions with alkyl(allyl)amines. i) BuLi, CO_2, LDA, I_2, THF, −70°C; ii) alkyl(allyl)-amine, CH_2O(aq) 37%, AcOH 60%, reflux; iii) BuLi, I_2, Et_2O, reflux.

situ preventive protection of the nitrogen atom in the presence of BuLi and CO_2, whereas 1-methylindoles underwent direct regioselective iodination at the 2-position.[15]

The behavior of iodosubstituted pseudobenzylamines **12a–d** under our standard Heck conditions revealed close similarities to the previous results involving benzylamines. Compounds **12a–d** were smoothly converted into σ-alkylpalladium complexes **13a–d** at room temperature (Scheme 6), and Heck products were not detected even after heating at reflux.



Scheme 6. Preparation of indolyl-σ-alkyl iodo complexes as Heck intermediates.

The structure of complexes **13a–d** was confirmed by means of an X-ray crystal structure analysis carried out on a suitable single crystal of **13b**.[16] As already observed in the case of **2**, the square-planar stereochemistry of the Pd^{II} center is a consequence of the formation of a five-membered metallacycle and the presence of a PPh_3 ligand and an iodine atom *cis* with regard to the nitrogen atom of the metallacycle (Figure 2).

The results concerning the structural requirements for the isolation of σ-alkylpalladium complexes highlighted that an sp^3 benzylic carbon is an essential feature, while the nature of the halide as well as the aromatic moiety may be varied. The marked stability of the isolated complexes could be due to the electronic nature of the nitrogen atom as well as the strong constraint imposed by the bridged junction. The latter hampers two essential requirements for β-hydride elimination, namely, *cisoid* conformation and agostic interactions. The two following explanations may account for the

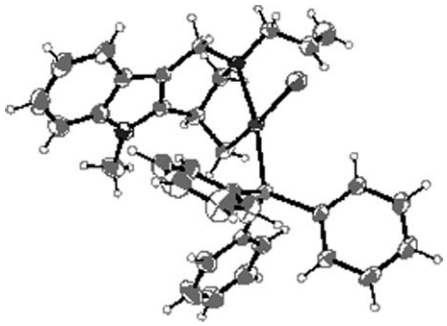


Figure 2. ORTEP representation (30% probability level) of the molecular structure of compound **13b**.

different behavior of species **5** compared to **2**, **9**, and **13**: 1) the carbonyl group imposes a geometry that favors β-elimination of the metal and 2) the stability of an intermediate complex resulting from coordination of the metal with an sp^2-hybridized nitrogen is lower than that of an intermediate arising from coordination with an sp^3-hybridized nitrogen.

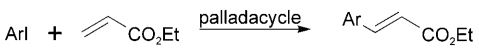
σ-Alkyl complexes as precatalysts in Pd-promoted reactions: Palladacycles are extensively investigated organometallic compounds and some of them are efficient catalyst precursors for C–C bond formation. However, these reactions often have to be carried out under a controlled atmosphere due to the air- and moisture-sensitivity of the palladacycles. The high thermal stability of our palladacycles in the presence of air and moisture suggested a possible effective application as precatalysts in Pd-catalyzed couplings such as Heck, Suzuki, and Stille reactions.

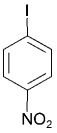
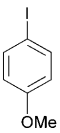
First, we tested the catalytic efficacy of our palladacycles in the Heck reaction between aryl iodides and ethyl acrylate in the presence of Et_3N as base in DMF as solvent at 120°C or under "Jeffery conditions"[17] in the presence of sodium acetate as base and Bu_4NCl as additive in acetonitrile heated under reflux or DMF at 120°C as solvent. Table 1 shows the results of the coupling reactions. Palladacycle **2b** was effective in the first procedure with iodobenzene as substrate, giving ethyl cinnamate quantitatively after 2 h at a loading of 0.01 mol% or after 24 h at a loading of 0.001 mol% (entries 1 and 2). When the loading of **2b** was reduced to 0.0001 mol%, the Heck product was obtained in 12% yield (entry 3), corresponding to a turnover number (TON) of 120000.

In the literature there are many examples of Heck reactions of activated substrates such as aryl iodides in which palladacycles act as a source of the catalytically active Pd^0 species, usually with TONs in the order of 10^3–10^{10} cycles. Among the reactions of iodobenzene with acrylates, compound **2b** is comparable to other catalytic systems such as sulfur-[18] or rhenium-containing[19] and imine-[20] or oxime-derived[21] palladacycles, even if there are other systems that perform better.[22]

Similar catalytic activity was shown by iodo(indolyl)palladacycles **13a** and **13b** (Table 1, entries 4 and 5). In contrast, bromopalladacycle **9a** was less efficient (entries 6 and 7 vs. 1–5), requiring a higher loading to accomplish the formation of ethyl cinnamate. The ability of palladacycles **2** and **13** to operate as precursors of Heck catalysts diminished in the presence of sodium acetate and Bu_4NCl in DMF or acetonitrile as the solvent. In these solvents, ethyl cinnamate was obtained in satisfactory yields only in the presence of complexes **2b** and **13b** at a loading of 0.1 mol% (entries 8, 9, and 11). Palladacycle **2b** was studied further in the coupling of 4-nitro- and 4-methoxy-1-iodobenzene with ethyl acrylate (entries 12 and 13). In both cases, the precatalyst performs well at 0.001 mol% giving the corresponding cinnamates in good yields.

Table 1. Palladacycle-catalyzed Heck reaction of aryl iodides and ethyl acrylate.



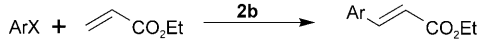
Entry	ArI	Palladacycle [mol%]	Procedure[a]	Solvent	T [°C]	t [h]	Yield [%][b]
1	PhI	**2b** (0.01)	i	DMF	120	2	98
2	PhI	**2b** (0.001)	i	DMF	120	24	98
3	PhI	**2b** (0.0001)	i	DMF	120	24	12
4	PhI	**13a** (0.0001)	i	DMF	120	24	10
5	PhI	**13b** (0.0001)	i	DMF	120	24	9
6	PhI	**9a** (0.1)	i	DMF	120	2	76
7	PhI	**9a** (0.01)	i	DMF	120	24	–
8	PhI	**2b** (0.1)	ii	DMF	120	2	63
9	PhI	**2b** (0.1)	ii	CH_3CN	reflux	2	73
10	PhI	**2b** (0.01)	ii	CH_3CN	reflux	2	8
11	PhI	**13b** (0.1)	ii	CH_3CN	reflux	2	61
12		**2b** (0.001)	i	DMF	120	20	95
13		**2b** (0.001)	i	DMF	120	20	92

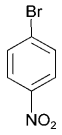
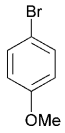
[a] Procedure i): Et_3N (1 equiv); procedure ii) AcONa (1 equiv), Bu_4NCl (1 equiv). [b] Isolated yield.

The catalytic efficacy of palladacycle **2b** was also evaluated in the Heck reaction with aryl bromides as substrates (Table 2). In general, more drastic conditions (higher precatalyst loading and/or activation under microwave irradiation) were required compared to when the corresponding iodides were used as substrates.

Ethyl cinnamate was produced in very low yield from phenyl bromide and ethyl acrylate when 1 mol% of precatalyst was used with Et_3N or AcONa as base in DMF or acetonitrile as solvent (entries 1–3). Better results were obtained when microwave activation was used, in particular under "Jeffery conditions", which led to the Heck product in 70% yield (Table 2, entry 5 vs. 4). However, when the precatalyst loading was reduced to 0.1 mol%, the reaction conversion markedly decreased (entry 6). Subsequently, we tried the coupling of different aryl and heteroaryl bromides with ethyl acrylate under the conditions shown in entry 5. Bromo derivatives with an activating group (including the pyridine

Table 2. Heck reaction of aryl halides and ethyl acrylate catalyzed by palladacycle **2b**.



Entry	ArX	**2b** [mol%]	Procedure[a]	Solvent	*T* [°C][b]	*t* [h]	Yield [%][c]
1	PhBr	1	i	DMF	120	24	25
2	PhBr	1	ii	DMF	120	48	8
3	PhBr	1	ii	CH_3CN	reflux	48	–
4	PhBr	1	i	DMF	MW	1	27
5	PhBr	1	ii	DMF	MW	1	70
6	PhBr	0.1	ii	DMF	MW	4	<5
7		1	ii	DMF	MW	1	98
8		1	ii	DMF	MW	1	81
9		1	ii	DMF	MW	1	98
10		1	ii	DMF	MW	1	62
11		1	ii	DMF	MW	1	87
12	PhCl	1	ii	DMF	MW	1	trace

[a] Procedure i): Et_3N (1 equiv); procedure ii) AcONa (1 equiv), Bu_4NCl (1 equiv). [b] MW (microwave) conditions: 15–20 W, 170°C, 3.0 bar. [c] Isolated yields.

ring) were converted into the corresponding ethyl cinnamates in high yields (entries 7–9); 1-bromo-4-methoxybenzene and 2-bromothiophene gave the corresponding Heck products in 62% and 87% yield, respectively (entries 10 and 11). Complex **2b** was almost inactive when chlorobenzene was used as substrate (entry 12).

When olefin arylations by use of palladacycles as precatalysts on aryl bromides are taken into account, the result of entry 10 is the most appropriate to compare the effectiveness of compound **2b** with literature data, 4-bromoanisole being the most suitable substrate to this end.[13b] Palladacycle **2b** shows a TON similar to the Herrmann–Beller catalyst and its close analogues,[23] imine- and amine-derived palladacycles,[24] oxime-derived palladacycles,[22e,25] and sulfur-containing palladacycles.[18] However, it should be mentioned that there are other systems with higher activity.[26]

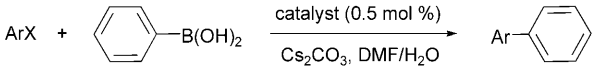
On the basis of the results obtained by using σ-alkylpalladium–iodine complexes as effective precatalysts for Heck reactions, we next examined whether they could also facilitate Pd-catalyzed cross-coupling reactions. In this field, the Suzuki reaction is a method widely used for the construction of biaryl or substituted aromatic moieties.[27]

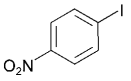
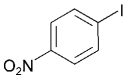
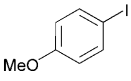
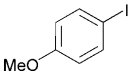
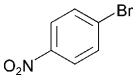
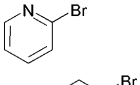
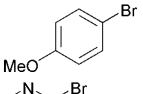
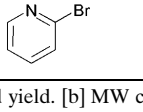
The impact of σ-alkylpalladium–iodine complexes on the performance of the Suzuki reaction was evaluated by employing phenylboronic acid and Cs_2CO_3 as a base in DMF/H_2O (4:1) as the solvent mixture. To our satisfaction, it was found that **2b** and **13b** were active enough to promote the C–C bond formation under relatively mild conditions in air and in the presence of water. As shown in Table 3, in the presence of 0.5 mol% of complex **2b**, a series of electronically different (hetero)aryl iodides and bromides underwent coupling to afford the corresponding biphenyls, although full conversion was never observed (entries 1, 2, 4, and 6–9). This means that as a catalyst precursor for Suzuki reactions on activated aryl halides, palladacycle **2b** cannot compete with highly performing systems such as triaryl phosphite palladacycles capable of TONs on the impressive order of 10^7–10^8.[23a] However, its behavior towards 4-bromoanisole (entry 9) is similar to that of sulfur-[18,28] or hydrazone-containing[29] palladacycles as well as imine-based palladium complexes.[20]

The behavior of indolyl complex **13b** was very similar to that of **2b** (entries 3 and 5). Lowering the precatalyst load affected the reaction course adversely. The attempt to improve the yields by decreasing the reaction time by using microwave activation did not give the desired results (entry 10).[30]

Finally, we turned our attention to investigating our palladacycles as precatalysts in Stille reactions.[31] In designing our experiments with aryl halides in combination with two different stannanes, we fixed iodide-bridged palladacycle **2b**

Table 3. Palladacycle-catalyzed Suzuki coupling of aryl halides and phenylboronic acid.



Entry	ArX	Catalyst	*T* [°C]	*t* [h]	Yield [%][a]
1	PhI	**2b**	50	18	73
2		**2b**	50	18	81
3		**13b**	50	18	78
4		**2b**	50	18	66
5		**13b**	50	18	60
6	PhBr	**2b**	100	24	48
7		**2b**	100	24	67
8		**2b**	100	24	62
9		**2b**	100	24	42
10		**2b**	MW[b]	1	18

[a] Isolated yield. [b] MW conditions: 15–20 W, 170°C, 3.0 bar.

as precatalyst, DMF as the solvent, and 80 °C as the reaction temperature. The best results, collected in Table 4, were always obtained at 0.01 mol % precatalyst loading. The cross-coupling reactions also proceeded well when the loading of **2b** was decreased to 0.001 mol %, but the product yields were lower (see yields in parentheses in Table 4).

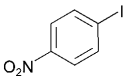
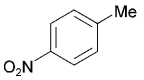
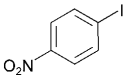
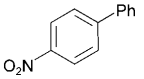
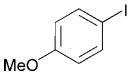
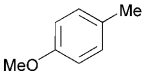
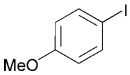
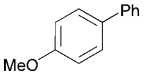
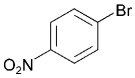
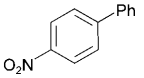
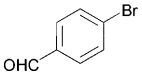
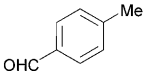
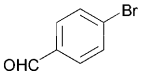
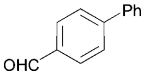
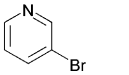
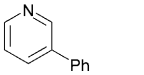
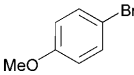
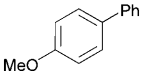
The coupling between $PhBu_3Sn$ and iodo- or bromobenzene gave biphenyl in satisfactory yields (Table 4, entries 1 and 6). A variety of aryl halides containing electron-withdrawing groups, including 3-bromopyridine, were converted into coupling products with Me_4Sn and $PhBu_3Sn$ in high yields (entries 2, 3, and 7–10). For 4-methoxyphenyl iodide and bromide the coupling products were obtained in 30–59 % yield (entries 4, 5, and 11).

Compared to Heck and Suzuki reactions, Stille coupling has been under-investigated. Palladacycle **2b**, reaching a TON of 59000 in the reaction of 1-bromo-4-nitrobenzene, is better than oxime–Pd complexes[32] and the Herrmann–Beller catalyst[33] in coupling activated aryl bromides. The effectiveness of **2b** towards 4-bromoanisole (TON 5100) also reflects the behavior of other palladacycles such as the PCP pincer,[34] and works better than palladacyclopentadienyl complexes.[35] However, its coupling ability is lower than those of triaryl phosphite palladacycles, which are again shown to be the best-performing precatalysts in cross-coupling reactions.[36]

It is worth noting that all palladacycles retained their activity even after being stored in air at room temperature for a few months, and demonstrated excellent thermal stability, decomposing only after being heated for more than 48 h in the presence of a base. This means that they are much more stable towards air, moisture, and heating than the [Pd-$(PPh_3)_4$] used for their generation.

Table 4. Stille coupling of aryl halides and stannanes catalyzed by palladacycle **2b**.

ArX + $RSnR'_3$ —(**2b** (0.01 mol %), DMF, 80 °C, 24 h)→ ArR

Entry	ArX	Stannane	Product	Yield [%][a]
1	PhI	$PhBu_3Sn$		83 (64)
2		Me_4Sn		98
3		$PhBu_3Sn$		99 (75)
4		Me_4Sn		30
5		$PhBu_3Sn$		59
6	PhBr	$PhBu_3Sn$		69
7		$PhBu_3Sn$		82 (59)
8		Me_4Sn		83
9		$PhBu_3Sn$		93
10		$PhBu_3Sn$		96
11		$PhBu_3Sn$		51

[a] Isolated yield. Yields in parentheses were obtained when 0.001 mol % of **2b** was used.

Conclusions

In summary, the development of stable σ-alkylpalladium Heck intermediates was well established. The present results constitute the first example of the systematic isolation of the σ-alkylpalladium intermediates in Heck processes. Previously, only two cases led to the unusual isolation of Heck intermediates containing a six-membered palladacycle in a fused-ring structure[9a,b] or a five-membered palladacycle in a bridged-ring structure.[9c] The allylamine nature of the involved nitrogen atom in the starting substrate was proven to be the key feature necessary for the isolation of stable Pd complexes.

Notably, this series of σ-alkylpalladium complexes was found to provide versatile and robust precatalysts suitable for a wide range of C–C bond-forming processes such as Heck, Suzuki, and Stille reactions. Finally, these palladacycles offer an alternative to the use of traditional palladium catalysts in C–C bond-forming reactions in view of their excellent stability.

Experimental Section

General: Melting points were determined by the capillary method on a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded on an AVANCE 400 Bruker spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 162 MHz for ^{31}P NMR. Chemical shifts are given as δ values in ppm relative to the residual solvent peaks ($CHCl_3$) as the internal reference. ^{31}P NMR spectra were recorded with external H_3PO_4 as reference. ^{13}C NMR spectra were ^{1}H-decoupled and the multiplicities were determined by the APT pulse sequence. ^{31}P NMR spectra were decoupled. Mass spectra were determined on a VG-7070 EQ-HF instrument. Elemental analyses were carried out on a Perkin–Elmer CHN Analyzer Series II 2400. Thin-layer chromatographic separations were performed on precoated Merck silica gel 60 F254. Preparative separations were performed by flash chromatography on Merck silica gel (0.035–0.070 mm).

General procedure for *N*-alkyl-*N*-allyl-substituted 3-(aminomethyl)indoles 11 and 12: A mixture of a solution of the appropriate allylamine (10.5 mmol, 1.2 equiv) and a 37 % aq solution of formaldehyde (0.76 mL, 10.1 mmol, 1.2 equiv) in 60 % acetic acid (2.11 mL, 22.6 mmol, 2.7 equiv) was cooled at 0 °C. A solution of the indolyl substrate (8.5 mmol, 1 equiv) in cold absolute EtOH (8 mL) was then added dropwise to the preceding solution. The mixture was stirred for 30 min at room temperature and for 2 h under heating at reflux. After cooling of the mixture, 1 N

aq NaOH was added until an alkaline pH was obtained, and then the mixture was extracted with Et_2O (3×25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated under reduced pressure. The crude products were purified by flash chromatography on silica gel.

***N*-Allyl-*N*-methyl-1-methyl-3-aminomethylindole (11c)**: Yield: 94%; R_f= 0.16 (petroleum ether/EtOAc 1:1, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.74 (d, ^3J=7.8 Hz, 1H; Ar*H*), 7.12–7.35 (m, 3H; Ar*H*), 7.03 (s, 1H; =C*H*NCH$_3$), 5.99 (ddt, ^3J=6.3, J_{cis}=10.2, J_{trans}= 17.2 Hz, 1H; =C*H*CH$_2$), 5.25 (d, J_{trans}=17.2 Hz, 1H; =CH*H*$_{trans}$), 5.19 (d, J_{cis}=10.2 Hz, 1H; =CH*H*$_{cis}$), 3.80 (s, 3H; CCHNC*H*$_3$), 3.74 (s, 2H; NC*H*$_2$Ar), 3.11 (d, ^3J=6.3 Hz, 2H; NC*H*$_2$CH=), 2.28 ppm (s, 3H; CH$_2$CH$_2$NC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.7 (s, *C*$_{Ar}$), 136.8 (d, CH$_2$*C*H=CH$_2$), 129.2 (d, *C*H$_{Ar}$), 129.1 (s, *C*$_{Ar}$), 122.2 (d, *C*H$_{Ar}$), 120.1 (d, *C*H$_{Ar}$), 119.7 (d, *C*H$_{Ar}$), 118.1 (t, CH=*C*H$_2$), 111.8 (s, *C*CH$_2$N), 109.8 (d, *C*H$_{Ar}$), 60.9 (t, *C*H$_2$CH=CH$_2$), 52.7 (t, NC*H*$_2$Ar), 42.6 (q, CCHNC*H*$_3$), 33.0 ppm (q, CH$_2$CH$_2$NC*H*$_3$); MS: *m/z*: 214 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{18}N_2$: C 78.46, H 8.47, N 13.07; found: C 78.32, H 8.58, N 13.10.

***N*-Allyl-*N*-cyclohexyl-1-methyl-3-aminomethylindole (11d)**: Yield: 70%; R_f=0.36 (petroleum ether/EtOAc 2:1, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.77 (d, ^3J=7.9, 1H; Ar*H*), 7.30 (d, ^3J=8.2, 1H; Ar*H*), 7.23 (dd, ^3J=8.2 Hz, ^3J=6.9 Hz, 1H; Ar*H*), 7.11 (dd, ^3J=7.9 Hz, ^3J=6.9 Hz, 1H; Ar*H*), 6.98 (s, 1H; =C*H*NCH$_3$), 5.89 (ddt, ^3J=6.2, J_{cis}= 10.2, J_{trans}=17.2 Hz, 1H; =C*H*CH$_2$), 5.19 (d, J_{trans}=17.2 Hz, 1H; = CH*H*$_{trans}$), 5.07 (d, J_{cis}=10.2 Hz, 1H; =CH*H*$_{cis}$), 3.82 (s, 2H; NC*H*$_2$Ar), 3.77 (s, 3H; NC*H*$_3$), 3.20 (d, ^3J=6.3 Hz, 2H; NC*H*$_2$CH=), 2.66 (tt, ^3J= 11.5 Hz, ^3J=3.3 Hz, 1H; NC*H*cy), 1.87–1.92 (m, 2H; cy*H*), 1.78–1.83 (m, 2H; cy*H*), 1.60–1.68 (m, 1H; cy*H*), 1.13–1.38 ppm (m, 5H; cy*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.0 (d, CH$_2$*C*H=CH$_2$), 137.9 (s, *C*$_{Ar}$), 128.8 (s, *C*$_{Ar}$), 128.4 (d, *C*H$_{Ar}$), 122.0 (d, *C*H$_{Ar}$), 120.5 (d, *C*H$_{Ar}$), 119.2 (d, *C*H$_{Ar}$), 116.3 (t, CH=*C*H$_2$), 114.3 (s, *C*CH$_2$N), 109.6 (d, *C*H$_{Ar}$), 58.9 (d, NC*H*cy), 53.5 (t, *C*H$_2$CH=CH$_2$), 45.6 (t, NC*H*$_2$Ar), 33.1 (q, NC*H*$_3$), 29.4 (t, *C*H$_2$cy), 27.2 (t, *C*H$_2$cy), 26.9 ppm (t, *C*H$_2$cy); MS: *m/z*: 282 $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{26}N_2$: C 80.80, H 9.28, N 9.92; found: C 80.95, H 9.15, N 9.90.

General procedure for 3-(aminomethyl)-substituted 2-iodoindoles 12: The products were prepared according to literature procedures.[14]

***N,N'*-Diallyl-2-iodo-3-aminomethylindole (12a)**: Yield: 52%; R_f=0.32 (petroleum ether/EtOAc 85:15, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.06 (br s, 1H; N*H*), 7.82 (d, ^3J=7.7 Hz, 1H; Ar*H*), 7.30 (d, ^3J=7.8 Hz, 1H; Ar*H*), 7.15 (dd, ^3J=7.7 Hz, ^3J=6.3 Hz, 1H; Ar*H*), 7.11 (dd, ^3J=7.8 Hz, ^3J=6.3 Hz, 1H; Ar*H*), 5.96 (ddt, ^3J=6.4, J_{cis}=10.2, J_{trans}=17.2 Hz, 2H; =C*H*CH$_2$), 5.23 (d, J_{trans}=17.2 Hz, 2H; =CH*H*$_{trans}$), 5.16 (d, J_{cis}=10.2 Hz, 2H; =CH*H*$_{cis}$), 3.69 (s, 2H; NC*H*$_2$Ar), 3.14 ppm (d, ^3J=6.4 Hz, 4H; NC*H*$_2$CH=). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.2 (s, *C*$_{Ar}$), 136.8 (d, CH$_2$*C*H=CH$_2$), 128.9 (s, *C*$_{Ar}$), 122.4 (d, *C*H$_{Ar}$), 119.8 (d, *C*H$_{Ar}$), 119.7 (d, *C*H$_{Ar}$), 119.6 (s, *C*CH$_2$N), 117.8 (t, CH=*C*H$_2$), 110.7 (d, *C*H$_{Ar}$), 89.8 (s, *C*I), 57.1 (t, *C*H$_2$CH=CH$_2$), 51.8 ppm (t, NC*H*$_2$Ar); MS: *m/z*: 352 $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{17}IN_2$: C 51.15, H 4.86, N 7.95; found: C 51.36, H 4.75, N 8.04.

***N,N'*-Diallyl-1-methyl-2-iodo-3-aminomethylindole (12b)**: Yield: 72%; R_f=0.78 (petroleum ether/EtOAc 1:1, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.83 (d, ^3J=7.9, 1H; Ar*H*), 7.32 (d, ^3J=8.2, 1H; Ar*H*), 7.20 (dd, ^3J=8.2 Hz, ^3J=7.2 Hz, 1H; Ar*H*), 7.11 (dd, ^3J=7.9 Hz, ^3J=7.2 Hz, 1H; Ar*H*), 5.98 (ddt, ^3J=6.4, J_{cis}=10.2, J_{trans}=17.2 Hz, 2H; = C*H*CH$_2$), 5.24 (d, J_{trans}=17.2 Hz, 2H; =CH*H*$_{trans}$), 5.18 (d, J_{cis}=10.2 Hz, 2H; =CH*H*$_{cis}$), 3.79 (s, 3H; NC*H*$_3$), 3.75 (s, 2H; NC*H*$_2$Ar), 3.15 ppm (d, ^3J=6.4 Hz, 4H; NC*H*$_2$CH=). ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.2 (s, *C*$_{Ar}$), 136.8 (d, CH$_2$*C*H=CH$_2$), 128.8 (s, *C*$_{Ar}$), 122.4 (d, *C*H$_{Ar}$), 119.8 (d, *C*H$_{Ar}$), 119.6 (d, *C*H$_{Ar}$), 118.4 (s, *C*CH$_2$N), 117.6 (t, CH=*C*H$_2$), 109.8 (d, *C*H$_{Ar}$), 89.7 (s, *C*I), 57.0 (t, *C*H$_2$CH=CH$_2$), 51.8 (t, NC*H*$_2$Ar), 34.7 ppm (q, NC*H*$_3$); MS: *m/z*: 366 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{19}IN_2$: C 52.47, H 5.23, N 7.65; found: C 52.56, H 5.14, N 7.51.

***N*-Allyl-*N*-methyl-1-methyl-2-iodo-3-aminomethylindole (12c)**: Yield: 34%; R_f=0.38 (petroleum ether/EtOAc 7:3, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.75 (d, ^3J=7.9 Hz, 1H; Ar*H*), 7.32 (d, ^3J= 8.2 Hz, 1H; Ar*H*), 7.19 (dd, ^3J=8.2 Hz, ^3J=7.1 Hz, 1H; Ar*H*), 7.10 (dd, ^3J=7.9 Hz, ^3J=7.1 Hz, 1H; Ar*H*), 6.00 (ddt, ^3J=6.5, J_{cis}=10.2, J_{trans}= 17.2 Hz, 1H; =C*H*CH$_2$), 5.24 (d, J_{trans}=17.2 Hz, 1H; =CH*H*$_{trans}$), 5.17 (d, J_{cis}=10.2 Hz, 1H; =CH*H*$_{cis}$), 3.80 (s, 3H; CCNC*H*$_3$), 3.67 (s, 2H; NC*H*$_2$Ar), 3.13 (d, ^3J=6.5 Hz, 2H; NC*H*$_2$CH=), 2.25 ppm (s, 3H; CH$_2$CH$_2$NC*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.1 (s, *C*$_{Ar}$), 137.0 (d, CH$_2$*C*H=CH$_2$), 128.8 (s, *C*$_{Ar}$), 122.4 (d, *C*H$_{Ar}$), 120.1 (d, *C*H$_{Ar}$), 119.5 (d, *C*H$_{Ar}$), 118.2 (s, *C*CH$_2$N), 117.7 (t, CH=*C*H$_2$), 110.4 (d, *C*H$_{Ar}$), 90,1 (s, *C*I), 61.4 (t, *C*H$_2$CH=CH$_2$), 54.9 (t, NC*H*$_2$Ar), 42.7 (q, CCNC*H*$_3$), 34.7 ppm (q, CH$_2$CH$_2$NC*H*$_3$); MS: *m/z*: 340 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{17}IN_2$: C 49.43, H 5.04, N 8.23; found: C 49.57, H 4.88, N 8.32.

***N*-Allyl-*N*-cyclohexyl-1-methyl-2-iodo-3-aminomethylindole (12d)**: Yield: 69%; R_f=0.68 (EtOAc, UV); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.85 (d, ^3J=7.9, 1H; Ar*H*), 7.30 (d, ^3J=8.2, 1H; Ar*H*), 7.23 (dd, ^3J= 8.2 Hz, ^3J=7.0 Hz, 1H; Ar*H*), 7.11 (dd, ^3J=7.9 Hz, ^3J=7.0 Hz, 1H; Ar*H*), 5.89 (ddt, ^3J=6.3, J_{cis}=10.1, J_{trans}=17.2 Hz, 1H; =C*H*CH$_2$), 5.19 (d, J_{trans}=17.2 Hz, 1H; =CH*H*$_{trans}$), 5.05 (d, J_{cis}=10.1 Hz, 1H; =CH*H*$_{cis}$), 3.79 (s, 2H; NC*H*$_2$Ar), 3.78 (s, 3H; NC*H*$_3$), 3.14 (d, ^3J=6.3 Hz, 2H; NC*H*$_2$CH=), 2.48–2.62 (m, 1H; NC*H*cy), 1.15–1.92 ppm (m, 10H; cy*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.4 (s, *C*$_{Ar}$), 139.1 (d, CH$_2$*C*H=CH$_2$), 128.9 (s, *C*$_{Ar}$), 121.8 (d, *C*H$_{Ar}$), 120.0 (d, *C*H$_{Ar}$), 119.9 (d, *C*H$_{Ar}$), 119.8 (s, *C*CH$_2$N), 116.3 (t, CH=*C*H$_2$), 109.8 (d, *C*H$_{Ar}$), 89.4 (s, *C*I), 58.6 (d, NC*H*cy), 53.3 (t, *C*H$_2$CH=CH$_2$), 48.1 (t, NC*H*$_2$Ar), 34.6 (q, NC*H*$_3$), 29.2 (t, *C*H$_2$cy), 27.1 (t, *C*H$_2$cy), 22.8 ppm (t, *C*H$_2$cy); MS: *m/z*: 408 $[M]^+$; elemental analysis calcd (%) for $C_{19}H_{25}IN_2$: C 55.89, H 6.17, N 6.86; found: C 55.78, H 6.25, N 6.94.

General procedure for palladacycles 9 and 13: $[Pd(PPh_3)_4]$ (1.154 g, 1 mmol) and Et_3N (0.42 mL, 3 mmol) in CH_3CN (2 mL) were added to a solution of **8** or **12** (1 mmol) in CH_3CN (3 mL). The mixture was stirred at room temperature (**12**) or under heating at reflux (**8**) for 2 h. After removal of the solvent under reduced pressure, H_2O (10 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried (Na_2SO_4) and eluted through a silica gel column.

Palladacycle 9a: Yield: 25%; R_f=0.12 (petroleum ether/EtOAc 8:2, UV); brown solid; m.p. 145–147°C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.25–7.36 (m, 18H; Ar*H*), 6.97 (d, ^3J=7.3 Hz, 1H; Ar*H*), 6.64–6.69 (m, 1H; =C*H*CH$_2$), 5.44 (d, J_{cis}=11.5 Hz, 1H; = CH*H*$_{cis}$), 5.40 (d, J_{trans}=17.3 Hz, 1H; =CH*H*$_{trans}$), 5.07 (d, ^2J=14.7 Hz, 1H; ArCH*H*N), 4.71 (dd, ^2J=3.7 Hz, ^3J=11.4 Hz, 1H; NCH*H*CH=), 3.78 (dd, ^3J=5.5 Hz, ^2J=14.7 Hz, 1H; ArCH*H*N), 3.20 (d, ^3J=11.4 Hz, 1H; NCH*H*CH=), 3.04–3.11 (m, 1H; NCH*H*CH), 2.58 (s br, 1H; NCH*H*CH), 2.40–2.42 (m, 1H; ArC*H*CH$_2$), 1.72 (dd, ^3J=3.2 Hz, ^2J= 12.5 Hz, 1H; PdCH*H*CH), 1.58–1.60 ppm (m, 1H; PdCH*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.3 (s, *C*$_{Ar}$), 135.0 (d, *C*H$_{Ar}$), 134.9 (d, CH$_2$*C*H=CH$_2$), 134.8 (d, *C*H$_{Ar}$PPh$_3$), 134.4 (d, *C*H$_{Ar}$), 132.9 (s, *C*$_{Ar}$), 132.8 (s, *C*$_{Ar}$), 132.2 (s, *C*$_{Ar}$), 131.7 (s, *C*$_{Ar}$), 130.4 (d, *C*H$_{Ar}$PPh$_3$), 128.4 (d, *C*H$_{Ar}$PPh$_3$), 128.3 (d, *C*H$_{Ar}$PPh$_3$), 128.1 (d, *C*H$_{Ar}$), 127.4 (d, *C*H$_{Ar}$), 127.2 (d, *C*H$_{Ar}$), 126.6 (d, *C*H$_{Ar}$), 121.0 (t, CH$_2$CH=*C*H$_2$), 63.8 (t, *C*H$_2$CH= CH$_2$), 60.8 (t, NC*H*$_2$CH), 60.3 (t, ArC*H*$_2$N), 45.9 (t, PdC*H*$_2$CH), 45.0 ppm (d, ArC*H*CH$_2$); ^{31}P NMR (162 MHz, $CDCl_3$): δ=34.5 ppm (s); MS: *m/z*: 633 $[M]^+$ (calculated for the most abundant Pd isotope, ^{106}Pd); elemental analysis calcd (%) for $C_{31}H_{31}BrNPPd$: C 58.65, H 4.92, N 2.21; found: C 58.56, H 5.13, N 2.17.

Palladacycle 9b: Yield: 28%; R_f=0.16 (petroleum ether/EtOAc 8:2, UV); brown solid; m.p. 156–158°C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.27–7.37 (m, 15H; Ar*H*), 6.88 (d, ^3J=8.3 Hz, 1H; Ar*H*), 6.82 (dd, ^4J=2.5 Hz, ^3J=8.3 Hz, 1H; Ar*H*), 6.76 (d, ^4J= 2.3 Hz, 1H; Ar*H*), 6.63–6.67 (m, 1H; =C*H*CH$_2$), 5.44 (d, J_{cis}=11.6 Hz, 1H; =CH*H*$_{cis}$), 5.40 (d, J_{trans}=17.2 Hz, 1H; =CH*H*$_{trans}$), 5.02 (d, ^2J= 14.7 Hz, 1H; ArCH*H*N), 4.69 (dd, ^2J=3.9 Hz, ^3J=12.6 Hz, 1H; NCH*H*CH=), 3.88 (s, 3H; C*H*$_3$), 3.75 (dd, ^3J=5.5 Hz, ^2J=14.7 Hz, 1H; ArCH*H*N), 3.18 (d, ^3J=10.3 Hz, 1H; NCH*H*CH=), 3.03–3.10 (m, 1H; NCH*H*CH), 2.52 (br s, 1H; NCH*H*CH), 2.37–2.40 (m, 1H; ArC*H*CH$_2$), 1.71 (dd, ^3J=3.2 Hz, ^2J=9.2 Hz, 1H; PdCH*H*CH), 1.53–1.59 ppm (m, 1H; PdCH*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.5 (s, *C*$_{Ar}$), 135.0 (d, *C*H$_{Ar}$PPh$_3$), 134.9 (d, *C*H$_{Ar}$PPh$_3$), 134.4 (d, CH$_2$*C*H=CH$_2$), 133.9 (s, *C*$_{Ar}$), 133.5 (s, *C*$_{Ar}$), 132.2 (s, *C*$_{Ar}$), 131.7 (s, *C*$_{Ar}$), 131.6 (s, *C*$_{Ar}$), 130.5 (d,

$CH_{Ar}PPh_3$), 129.0 (d, CH_{Ar}), 128.4 (d, $CH_{Ar}PPh_3$), 128.3 (d, $CH_{Ar}PPh_3$), 121.0 (t, $CH_2CH{=}CH_2$), 114.4 (d, CH_{Ar}), 111.1 (d, CH_{Ar}), 63.7 (t, $CH_2CH{=}CH_2$),60.9 (t, NCH_2CH), 60.6 (t, $ArCH_2N$), 55.8 (q, CH_3), 46.4 (t, $PdCH_2CH$), 44.2 ppm (d, $ArCHCH_2$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 36.5$ ppm (s); MS: *m/z*: 663 $[M]^+$ (calculated for the most abundant Pd isotope, ^{106}Pd); elemental analysis calcd (%) for $C_{32}H_{33}BrNOPPd$: C 57.80, H 5.00, N 2.11; found: C 57.97, H 4.86, N 2.33.

Palladacycle 13a: Yield: 45%; $R_f = 0.37$ (petroleum ether/EtOAc 2:1, UV); brown solid; m.p. 79–81 °C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.12$–7.76 (m, 20H; Ar*H*, N*H*), 6.74–6.79 (m, 1H; =C*H*CH_2), 5.48 (d, $J_{cis} = 11.5$ Hz, 1H; =CHH_{cis}), 5.43 (d, $J_{trans} = 18.1$ Hz, 1H; =CHH_{trans}), 5.31 (d, $^2J = 12.8$ Hz, 1H; ArCH*H*N), 4.93 (dd, $^3J = 11.6$ Hz, 1H; NCH*H*CH=), 3.86 (dd, $^3J = 6.9$ Hz, $^2J = 12.8$ Hz, 1H; ArCH*H*N), 3.23–3.35 (m, 2H; NCH*H*CH, NCH*H*CH=), 2.59–2.66 (m, 2H; NCH*H*CH, Ar*CH*CH_2), 1.84–1.87 (m, 1H; PdCH*H*CH), 1.44–1.61 ppm (m, 1H; PdCH*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.0$ (s, C_{Ar}), 136.2 (s, C_{Ar}), 135.6 (d, $CH_{Ar}PPh_3$), 135.5 (d, $CH_{Ar}PPh_3$), 135.2 (d, $CH_{Ar}PPh_3$), 135.0 (d, $CH_{Ar}PPh_3$), 134,9 (d, $CH_2CH{=}CH_2$), 132.8 (s, C_{Ar}), 132.3 (s, C_{Ar}), 130.5 (d, $CH_{Ar}PPh_3$), 128.6 (d, $CH_{Ar}PPh_3$), 128.4 (d, $CH_{Ar}PPh_3$), 128.3 (d, $CH_{Ar}PPh_3$), 128.1 (d, $CH_{Ar}PPh_3$), 126.3 (s, C_{Ar}), 122.0 (d, CH_{Ar}), 120.8 (t, $CH_2CH{=}CH_2$), 120.4 (d, CH_{Ar}), 119.1 (d, CH_{Ar}), 114.5 (s, C_{Ar}), 111.2 (d, CH_{Ar}), 106.8 (s, C_{Ar}), 64.7 (t, $CH_2CH{=}CH_2$), 61.0 (t, NCH_2CH), 57.1 (t, $ArCH_2N$), 47.3 (t, $PdCH_2CH$), 40.3 ppm (d, $ArCHCH_2$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 34.8$ ppm (s); MS: *m/z*: 720 $[M]^+$ (calculated for the most abundant Pd isotope, ^{106}Pd); elemental analysis calcd (%) for $C_{33}H_{32}IN_2PPd$: C 54.98, H 4.47, N 3.89; found: C 54.77, H 4.56, N 3.68.

Palladacycle 13b: Yield: 27%; $R_f = 0.25$ (petroleum ether/EtOAc 4:1, UV); brown solid; m.p. 179–181 °C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.12$–7.73 (m, 19H; Ar*H*), 6.75–6.80 (m, 1H; =C*H*CH_2), 5.49 (d, $J_{cis} = 10.4$ Hz, 1H; =CHH_{cis}), 5.45 (d, $J_{trans} = 17.2$ Hz, 1H; =CHH_{trans}), 5.31 (d, $^2J = 12.5$ Hz, 1H; ArCH*H*N), 4.93 (d, $^3J = 13.3$ Hz, 1H; NCH*H*CH=), 3.84–3.89 (m, 1H; ArCH*H*N), 3.39 (s, 3H; CH_3), 3.30–3.41 (m, 2H; NCH*H*CH=, NCH*H*CH), 2.67 (br s, 1H; NCH*H*CH), 2.60 (d, $^3J = 10.3$ Hz, 1H; Ar*CH*CH_2), 1.88–1.91 (m, 1H; PdCH*H*CH), 1.51–1.56 ppm (m, 1H; PdCH*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 140.3$ (s, C_{Ar}), 137.4 (s, C_{Ar}), 135.6 (d, $CH_{Ar}PPh_3$), 135.3 (d, $CH_{Ar}PPh_3$), 135.2 (d, $CH_{Ar}PPh_3$), 135.0 (d, $CH_{Ar}PPh_3$), 134.9 (d, $CH_2CH{=}CH_2$), 133.0 (s, C_{Ar}), 132.5 (s, C_{Ar}), 130.5 (d, $CH_{Ar}PPh_3$), 128.8 (d, $CH_{Ar}PPh_3$), 128.6 (d, $CH_{Ar}PPh_3$), 128.3 (d, $CH_{Ar}PPh_3$), 128.2 (d, $CH_{Ar}PPh_3$), 125.7 (s, C_{Ar}), 121.5 (d, CH_{Ar}), 120.8 (t, $CH_2CH{=}CH_2$), 120.0 (d, CH_{Ar}), 119.1 (d, CH_{Ar}), 114.8 (s, C_{Ar}), 109.3 (d, CH_{Ar}), 105.6 (s, C_{Ar}), 64.6 (t, $CH_2CH{=}CH_2$), 61.2 (t, NCH_2CH), 57.2 (t, $ArCH_2N$), 46.0 (t, $PdCH_2CH$), 39.0 (d, $ArCHCH_2$), 29.2 ppm (q, NCH_3); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 35.2$ ppm (s); MS: *m/z*: 734 $[M]^+$ (calculated for the most abundant Pd isotope, ^{106}Pd); elemental analysis calcd (%) for $C_{34}H_{34}IN_2PPd$: C 55.56, H 4.66, N 3.81; found: C 55.42, H 4.84, N 3.61.

Palladacycle 13c: Yield: 64%; $R_f = 0.59$ (petroleum ether/EtOAc 1:1, UV); brown solid; m.p. 132–133 °C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.11$–7.56 (m, 19H; Ar*H*), 5.25 (d, $^2J = 13.5$ Hz, 1H; ArCH*H*N), 3.64–3.69 (m, 1H; ArCH*H*N), 3.36–3.41 (m, 6H; NCH_3, NCH_3), 3.12 (d, $^2J = 10.3$ Hz, 1H; NCH*H*CH), 2.89 (d, $^2J = 10.3$ Hz, 1H; NCH*H*CH), 2.68 (br s, 1H; Ar*CH*CH_2), 1.89–1.92 (m, 1H; PdCH*H*CH), 1.54–1.66 ppm (m, 1H; PdCH*H*CH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 139.8 (s, C_{Ar}), 137.5 (s, C_{Ar}), 135.1 (d, $CH_{Ar}PPh_3$), 135.0 (d, $CH_{Ar}PPh_3$), 134.9 (d, $CH_{Ar}PPh_3$), 134.8 (d, $CH_{Ar}PPh_3$), 132.9 (s, C_{Ar}), 132.4 (s, C_{Ar}), 130.5 (d, $CH_{Ar}PPh_3$), 128.6 (d, $CH_{Ar}PPh_3$), 128.4 (d, $CH_{Ar}PPh_3$), 128.3 (d, $CH_{Ar}PPh_3$), 128.2 (d, $CH_{Ar}PPh_3$), 125.6 (s, C_{Ar}), 121.5 (d, CH_{Ar}), 120.0 (d, CH_{Ar}), 119.1 (d, CH_{Ar}), 114.7 (s, C_{Ar}), 109.3 (d, CH_{Ar}), 105.4 (s, C_{Ar}), 66.5 (t, NCH_2CH), 58.5 (t, $ArCH_2N$), 53.1 (q, $CCNCH_3$), 46.5 (t, $PdCH_2CH$), 39.1 (d, $ArCHCH_2$), 29.2 ppm (q, $CH_2CH_2NCH_3$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 37.2$ ppm (s); MS: *m/z*: 708 $[M]^+$ (calculated for the most abundant Pd isotope, ^{106}Pd); elemental analysis calcd (%) for $C_{32}H_{32}IN_2PPd$: C 54.22, H 4.55, N 3.95; found: C 54.07, H 4.69, N 4.06.

Palladacycle 13d: Yield: 66%; $R_f = 0.43$ (petroleum ether/EtOAc 2:1, UV); brown solid; m.p. 68–70 °C (diisopropyl ether); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.11$–7.57 (m, 19H; Ar*H*), 5.17 (d, $^2J = 13.1$ Hz, 1H; ArCH*H*N), 4.36–4.41 (m, 1H; ArCH*H*N), 4.01 (br s, 1H; NC*H*cy), 3.37 (s, 3H; NCH_3), 3.30 (br s, 1H; NCH*H*CH), 3.08 (d, $^2J = 8.1$ Hz, 1H; NCH*H*CH), 2.71 (br s, 1H; Ar*CH*CH_2), 2.24 (d, $^2J = 10.7$ Hz, 1H; PdCH*H*CH), 1.90–1.99 (m, 2H; PdCH*H*CH, cy*H*), 1.20–1.37 ppm (m, 9H; cy*H*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 140.2$ (s, C_{Ar}), 137.4 (s, C_{Ar}), 135.2 (d, $CH_{Ar}PPh_3$), 135.0 (d, $CH_{Ar}PPh_3$), 134.9 (d, $CH_{Ar}PPh_3$), 134.8 (d, $CH_{Ar}PPh_3$), 133.3 (s, C_{Ar}), 132.8 (s, C_{Ar}), 130.4 (d, $CH_{Ar}PPh_3$), 128.4 (d, $CH_{Ar}PPh_3$), 128.3 (d, $CH_{Ar}PPh_3$), 128.1 (d, $CH_{Ar}PPh_3$), 127.9 (d, $CH_{Ar}PPh_3$), 126.0 (s, C_{Ar}), 121.4 (d, CH_{Ar}), 120.0 (d, CH_{Ar}), 119.1 (d, CH_{Ar}), 114.7 (s, C_{Ar}), 109.3 (d, CH_{Ar}), 106.0 (s, C_{Ar}), 65.5 (d, NCHcy), 56.0 (t, NCH_2CH), 53.3 (t, $ArCH_2N$), 44.7 (t, $PdCH_2CH$), 39.5 (d, $ArCHCH_2$), 30.1 (t, CH_2cy), 29.2 (q, NCH_3), 26.9 (t, CH_2cy), 26.1 ppm (t, CH_2cy); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 36.5$ ppm (s); MS: *m/z*: 776 $[M]^+$ calculated for the most abundant Pd isotope, ^{106}Pd; elemental analysis calcd (%) for $C_{37}H_{40}IN_2PPd$: C 57.19, H 5.19, N 3.61; found: C 57.37, H 5.16, N 3.48.

Acknowledgements

The authors thank the Ministero dell'Istruzione, dell'Università e della Ricerca for financial support and for the Ph.D. fellowships to M.R. (Progetto Giovani 2006).

[1] a) J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, Wiley, New York, **1995**; b) E. I. Negishi, *Handbook of Organopalladium Chemistry for Organic Synthesis*, Wiley, New York, **2002**; c) J. J. Li, G. W. Gribble, *Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist*, Pergamon, New York, **2000**.

[2] a) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318–5365; b) A. J. Canty, *Acc. Chem. Res.* **1992**, *25*, 83–90; c) A. R. Dick, J. W. Kampf, M. S. Sanford, *J. Am. Chem. Soc.* **2005**, *127*, 12790–12791.

[3] a) T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581–581; b) R. F. Heck, J. P. Nolley, *J. Org. Chem.* **1972**, *37*, 2320–2322; c) M. Oestreich, *The Mizoroki–Heck Reaction*, Wiley, New York, **2009**; d) W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2–7; e) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; f) A. B. Dounay, L .E. Overman, *Chem. Rev.* **2003**, *103*, 2945–2964; g) V. Farina, *Adv. Synth. Catal.* **2004**, *346*, 1553–1582; h) A. T. Lindhardt, T. Skrydstrup, *Chem. Eur. J.* **2008**, *14*, 8756–8766.

[4] a) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473; b) E. I. Negishi, Z. Huang, G. Wang, S. Mohan, C. Wang, H. Hattori, *Acc. Chem. Res.* **2008**, *41*, 1474–1485; c) S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486–1499; d) J. Terao, N. Kambe, *Acc. Chem. Res.* **2008**, *41*, 1545–1554; e) M. Kosugi, K. Fugami in *Handbook of Organopalladium Chemistry for Organic Synthesis, Vol. 2* (Ed.: E. I. Negishi), Wiley, New York, **2002**, pp. 263–284.

[5] For reviews on the asymmetric Heck reaction, see: a) A. G. Coyne, M. O. Fitzpatrick, P. J. Guiry in *The Mizoroki–Heck Reaction* (Ed.: M. Oestreich), Wiley, New York, **2009**, pp. 405–431; b) J. T. Link, C. K. Wada in *The Mizoroki–Heck Reaction* (Ed.: M. Oestreich), Wiley, New York, **2009**, pp. 433–462; c) A. B. Dounay, L. E. Overman in *The Mizoroki–Heck Reaction* (Ed.: M. Oestreich), Wiley, New York, **2009**, pp. 533–568. For some recent advanced studies, see d) A. B. Dounay, K. Hatanaka, J. J. Kodanko, M. Oestreich, L. E. Overman, L. A. Pfeifer, M. M. Weiss, *J. Am. Chem. Soc.* **2003**, *125*, 6261–6271; e) D. Yang, Y. C. Chen, N. Y. Zhu, *Org. Lett.* **2004**, *6*, 1577–1580; f) D. Yang, Y. C. Chen, N. Y. Zhu, *Org. Lett.* **2004**, *6*, 2125–2128; g) A. L. Hansen, J. P. Ebran, M. Ahlquist, P. O. Norrby, T. Skrydstrup, *Angew. Chem.* **2006**, *118*, 3427–3431; *Angew. Chem. Int. Ed.* **2006**, *45*, 3349–3353; h) C. Yi, R. Hua, *Tetrahedron Lett.* **2006**, *47*, 2573–2576; i) A. T. Lindhardt (neé Hansen), M. L. H. Mantel, T. Skrydstrup, *Angew. Chem.* **2008**, *120*, 2708–2712; *Angew. Chem. Int. Ed.* **2008**, *47*, 2668–2672; j) A. L. Hansen, T. Skrydstrup, *Org. Lett.* **2005**, *7*, 5585–5587.

[6] a) G. T. Crisp, *Chem. Soc. Rev.* **1998**, *27*, 427–436; b) J. P. Knowles, A. Whiting, *Org. Biomol. Chem.* **2007**, *5*, 31–44.
[7] a) C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314–321; b) F. d'Orlye, A. Jutand, *Tetrahedron* **2005**, *61*, 9670–9678; c) A. Jutand, *Pure Appl. Chem.* **2004**, *76*, 565–576; d) S. Kozuch, C. Amatore, A. Jutand, S. Shaik, *Organometallics* **2005**, *24*, 2319–2330; e) S. Kozuch, S. Shaik, A. Jutand, C. Amatore, *Chem. Eur. J.* **2004**, *10*, 3072–3080.
[8] a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989–1992; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1848; b) B. L. Shaw, *New J. Chem.* **1998**, *22*, 77–81; c) B. L. Shaw, S. D. Perera, *Chem. Commun.* **1998**, 1863–1865; d) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687–11688.
[9] a) M. Oestreich, P. R. Dennison, J. J. Kodanko, L. E. Overman, *Angew. Chem.* **2001**, *113*, 1485–1489; *Angew. Chem. Int. Ed.* **2001**, *40*, 1439–1442; b) B. J. Burke, L. E. Overman, *J. Am. Chem. Soc.* **2004**, *126*, 16820–16833; c) B. Clique, C. H. Fabritius, C. Couturier, N. Monteiro, G. Balme, *Chem. Commun.* **2003**, 272–273.
[10] a) R. C. Larock, S. S. Hershberger, K. Takagi, M. A. Mitchell, *J. Org. Chem.* **1986**, *51*, 2450–2457; b) R. Arnek, K. Zetterberg, *Organometallics* **1987**, *6*, 1230–1235; c) D. L. Reger, D. G. Garza, L. Lebioda, *Organometallics* **1991**, *10*, 902–906; d) L. Zhang, K. Zetterberg, *Organometallics* **1991**, *10*, 3806–3813; e) R. McCrindle, G. Ferguson, A. J. McAlees, G. J. Arsenault, A. Gupta, M. C. Jennings, *Organometallics* **1995**, *14*, 2741–2748; f) G. C. Lloyd-Jones, P. A. Slatford, *J. Am. Chem. Soc.* **2004**, *126*, 2690–2691; g) D. Tanaka, S. P. Romeril, A. G. Myers, *J. Am. Chem. Soc.* **2005**, *127*, 10323–10333.
[11] a) E. M. Beccalli, G. Broggini, G. Paladino, C. Zoni, *Tetrahedron* **2005**, *61*, 61–68; b) E. M. Beccalli, G. Broggini, M. Martinelli, G. Paladino, *Tetrahedron* **2005**, *61*, 1077–1082; c) E. M. Beccalli, G. Broggini, M. Martinelli, G. Paladino, C. Zoni, *Eur. J. Org. Chem.* **2005**, 2091–2096; d) G. Abbiati, E. M. Beccalli, G. Broggini, M. Martinelli, G. Paladino, *Synlett* **2006**, 73–76; e) E. M. Beccalli, E. Borsini, G. Broggini, G. Palmisano, S. Sottocornola, *J. Org. Chem.* **2008**, *73*, 4746–4749; f) E. M. Beccalli, E. Borsini, G. Broggini, M. Rigamonti, S. Sottocornola, *Synlett* **2008**, 1053–1057; g) E. M. Beccalli, G. Broggini, F. Clerici, S. Galli, C. Kammerer, M. Rigamonti, S. Sottocornola, *Org. Lett.* **2009**, *11*, 1563–1566.
[12] E. M. Beccalli, G. Broggini, M. Martinelli, N. Masciocchi, S. Sottocornola, *Org. Lett.* **2006**, *8*, 4521–4524.
[13] a) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082; b) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.* **2005**, *105*, 2527–2571; c) N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440–1449.
[14] J. Bergman, L. Venemalm, *J. Org. Chem.* **1992**, *57*, 2495–2497.
[15] J. Bergman, N. Eklund, *Tetrahedron* **1980**, *36*, 1439–1443.
[16] Crystal data for **13b**: $C_{34}H_{34}IN_2PPd$; $M_r = 734.9\ g\,mol^{-1}$; triclinic, $P\bar{1}$; $a = 9.305(1)$, $b = 12.529(2)$, $c = 14.220(3)$ Å; $\alpha = 84.25(2)$, $\beta = 72.87(2)$, $\gamma = 83.07(1)°$; $V = 1569.0(4)$ Å^3, $Z = 2$, $F(000) = 732$, $\rho_{calc} = 1.556\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.651\ mm^{-1}$; $R = 0.031$, $wR2 = 0.082$, Gof = 1.054 for 5035 observed $[I > 2\sigma(I)]$ reflections and 353 parameters; highest peak and deepest hole = 0.72 and −0.85 e Å^{-2}. CCDC-740279 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
[17] a) T. Jeffery, J.-C. Galland, *Tetrahedron Lett.* **1994**, *35*, 4103–4106; b) T. Jeffery, *Tetrahedron* **1996**, *52*, 10113–10130; c) T. Jeffery, M. David, *Tetrahedron Lett.* **1998**, *39*, 5751–5754.
[18] Z. Xiong, N. Wang, M. Dai, A. Li, J. Chen, Z. Yang, *Org. Lett.* **2004**, *6*, 3337–3340.
[19] F. K. Friedlein, F. Hampel, J. A. Gladysz, *Organometallics* **2005**, *24*, 4103–4105.
[20] J. M. Chitanda, D. E. Prokopchuk, J. Wilson Quail, S. R. Foley, *Dalton Trans.* **2008**, 6023–6029.
[21] a) S. Iyer, G. M. Kulkarni, C. Ramesh, *Tetrahedron* **2004**, *60*, 2163–2172; b) E. Alacid, C. Nàjera, *Synlett* **2006**, 2959–2964.
[22] a) M. Ohff, A. Ohff, D. Milstein, *Chem. Commun.* **1999**, 357–358; b) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, *Chem. Commun.* **2000**, 1247–1248; c) K. R. Reddy, K. Surekha, G.-H. Lee, S.-M. Peng, S.-T. Liu, *Organometallics* **2000**, *19*, 2637–2639; d) S. Sjövall, M. H. Johansson, C. Andersson, *Eur. J. Inorg. Chem.* **2001**, 2907–2911; e) E. Alacid, D. A. Alonso, L. Botella, C. Nàjera, M. C. Pacheco, *Chem. Rec.* **2006**, *6*, 117–132.
[23] a) W. A. Herrmann, C. Brossmer, C. P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357–1364; b) D. A. Albisson, R. B. Bedford, P. N. Scully, *Tetrahedron Lett.* **1998**, *39*, 9793–9796.
[24] a) J. Spencer, D. P. Sharratt, J. Dupont, A. L. Monteiro, V. I. Reis, M. P. Stracke, F. Rominger, I. M. McDonald, *Organometallics* **2005**, *24*, 5665–5672; b) C. Xu, J.-F. Gong, S.-F. Yue, Y. Zhu, Y.-J. Wu, *Dalton Trans.* **2006**, 4730–4739.
[25] L. Botella, C. Nàjera, *J. Org. Chem.* **2005**, *70*, 4360–4369.
[26] a) S. Gibson, D. F. Foster, G. R. Eastham, R. P. Tooze, D. J. Cole-Hamilton, *Chem. Commun.* **2001**, 779–780; b) C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling, J. Dupont, *Org. Lett.* **2003**, *5*, 983–986; c) Q. Yao, E. P. Kinney, C. Zheng, *Org. Lett.* **2004**, *6*, 2997–2999; d) E. A. B. Kantchev, G.-R. Peh, C. Zhang, J. Y. Ying, *Org. Lett.* **2008**, *10*, 3949–3952.
[27] For a selection of recent applications of palladacycle-promoted Suzuki reactions see: a) E. Alacid, C. Nájera, *J. Organomet. Chem.* **2009**, *694*, 1658–1665; b) X. Zhang, Y. Qiu, B. Rao, M. Luo, *Organometallics* **2009**, *28*, 3093–3099; c) H. Doucet, *Eur. J. Org. Chem.* **2008**, 2013–2030; d) M. Joshaghani, M. Daryanavard, E. Rafiee, S. Nadri, *J. Organomet. Chem.* **2008**, *693*, 3135–3140; e) D.-H. Lee; Y. H. Lee; D. I. Kim; Y. Kim; W. T. Lim; J. M. Harrowfield; P. Thuéry; M.-J. Jin; Y. C. Park; I.-M. Lee, *Tetrahedron* **2008**, *64*, 7178–7182; Y. H. Lee; D. I. Kim; Y. Kim; W. T. Lim; J. M. Harrowfield; P. Thuéry; M.-J. Jin; Y. C. Park; I.-M. Lee, *Tetrahedron* **2008**, *64*, 7178–7182.
[28] M.-T. Chen, C.-A. Huang, C.-T. Chen, *Eur. J. Inorg. Chem.* **2006**, 4642–4648.
[29] T. Mino, Y. Shirae, M. Sakamoto, T. Fujita, *Synlett* **2003**, 882–884.
[30] For a selection of applications of the Suzuki reaction under microwave irradiation, see: a) N. E. Leadbeater, M. Marco, *Org. Lett.* **2002**, *4*, 2973–2976; b) R. Lépine, J. Zhu, *Org. Lett.* **2005**, *7*, 2981–2984; c) Y. Wang, D. R. Sauer, *Org. Lett.* **2006**, *8*, 2793–2796; d) P. Cao, J. Qu, G. Burton, R. A. Rivero, *J. Org. Chem.* **2008**, *73*, 7204–7208; e) K. Damian, M. L. Clarke, C. J. Cobley, *J. Mol. Catal. A* **2008**, *284*, 46–51; f) N. Kopylovich, J. Lasri, M. F. C. G. da Silva, A. J. L. Pombeiro, *Dalton Trans.* **2009**, 3074–3084.
[31] For a selection of recent applications of palladacycle-promoted Stille reactions, see: a) M. P. Muñoz, B. Martín-Matute, C. Fernández-Rivas, D. J. Cárdenas, A. M. Echavarren, *Adv. Synth. Catal.* **2001**, *343*, 338–342; b) D. A. Alonso, L. Botella, C. Nájera, M. C. Pacheco, *Synthesis* **2004**, 1713–1718; c) N. Carrera, E. Gutiérrez, R. Benavente, M. M. Villavieja, A. C. Albéniz, P. Espinet, *Chem. Eur. J.* **2008**, *14*, 10141–10148; d) J. R. Naber, S. L. Buchwald, *Adv. Synth. Catal.* **2008**, *350*, 957–961.
[32] D. A. Alonso, C. Nàjera, M. C. Pacheco, *Org. Lett.* **2000**, *2*, 1823–1826.
[33] J. Louie, J. F. Hartwig, *Angew. Chem.* **1996**, *108*, 2531–2533; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2359–2361.
[34] D. Olsson, P. Nilsson, M. El Masnaouy, O. F. Wendt, *Dalton Trans.* **2005**, 1924–1929.
[35] C. M. Crawforth, I. J. S. Fairlamb, A. R. Kapdi, J. L. Serrano, R. J. K. Taylor, G. Sanchez, *Adv. Synth. Catal.* **2006**, *348*, 405–412.
[36] a) D. A. Albisson, R. B. Bedford, P. N. Scully, S. E. Lawrence, *Chem. Commun.* **1998**, 2095–2096; b) R. B. Bedford, S. L. Hazelwood, M. E. Limmert, D. A. Albisson, S. M. Draper, P. N. Scully, S. J. Coles, M. B. Hursthouse, *Chem. Eur. J.* **2003**, *9*, 3216–3227.

Received: July 24, 2009
Published online: December 18, 2009

