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[2] Cross-linked dendrimers as polymers without catalytic properties: a) N. Moszner, T. Volkel, V. Rheinberger, *Macromol. Chem. Phys.* **1996**, *197*, 621–631; b) M. Trollsås, M. A. Kelly, H. Claesson, R. Siemens, J. L. Hedrick, *Macromolecules* **1999**, *32*, 4917–4924.

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[4] a) A different concept has been used by Seebach, et al., according to which modified TADDOLs having styrene units in the outer first-generation dendritic branches are embedded in a cross-linked organic polymer by copolymerization with styrene, followed by treatment with $Ti(OiPr)_4$ with formation of recyclable Ti catalysts: H. Sellner, D. Seebach, *Angew. Chem.* **1999**, *111*, 2039–2041; *Angew. Chem. Int. Ed.* **1999**, *38*, 1918–1920. Numerous related examples of the embedment of ligands in cross-linked polymers are known, for example: b) S. J. Fritschel, J. J. H. Ackerman, T. Keyer, J. K. Stille, *J. Org. Chem.* **1979**, *44*, 3152–3157; c) S. Itsuno, Y. Sakurai, K. Ito, T. Maruyama, S. Nakahama, J. M. J. Fréchet, *J. Org. Chem.* **1990**, *55*, 304–310; d) K. Nozaki, Y. Itoi, F. Shibahara, E. Shirakawa, T. Ohta, H. Takaya, T. Hiyama, *J. Am. Chem. Soc.* **1998**, *120*, 4051–4052.

[5] a) S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15–27; b) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1996**, *118*, 8977–8978; c) S. Kobayashi, S. Nagayama, *Synlett* **1997**, 653–654; d) D. Longbottom, *Synlett* **1999**, 2023.

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[8] In order to further increase mechanical stability, we were able to show in preliminary experiments that **3**, once ground in a mortar, can be entrapped in silica matrices using a sol–gel procedure, $Si(OCH_3)_4$ or $CH_3Si(OCH_3)_3$ serving as the precursors. Such gels are catalytically active.

A New Palladium-Catalyzed Intramolecular Cyclization: Synthesis of 1-Aminoindole Derivatives and Functionalization of their Carbocylic Rings

Makoto Watanabe,* Toshihide Yamamoto, and Masakazu Nishiyama

Palladium-catalyzed cyclization reactions are a versatile and efficient method for the synthesis of a large number of heterocycles.[1] The formation of the indole ring system is of interest and has been carried out by many methods[2] because indole derivatives exhibit pharmacological[3] and physiological activity.[4] The palladium-catalyzed synthesis of indoles from *o*-haloaniline precursors is one of the most useful methods for the preparation of this class of compounds.[5]

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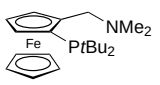
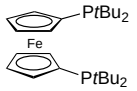
Palladium-catalyzed C–N bond formation of amines with aryl halides recently proved to be a versatile method for the synthesis of a wide range of arylamines.[6] Transformation of the amination products into indole derivatives was examined. First, palladium-catalyzed cyclization of *o*-bromo-*β*-phenethylamines followed by dehydrogenation of the resulting indolines with Pd/C gave indoles with substituents in the 7-position.[7] Second, palladium-catalyzed coupling of benzophenone hydrazone with aryl bromides was also reported to give *N*-arylhydrazones, which were used as substrates for Fischer indole synthesis.[8] However, palladium-catalyzed direct formation of the indole ring by N-arylation of aryl halides has not been reported.

However, palladium catalyst systems employing P*t*Bu$_3$ and mono- and bidentate phosphanes bearing P–*t*Bu bonds were reported for amination,[9] aryl ether formation,[10] Suzuki coupling,[9b, 11] the Heck reaction,[12] and ketone arylation,[13] after we disclosed that bulky electron-rich P*t*Bu$_3$ afforded much higher catalytic activity than other phosphanes in the palladium-catalyzed amination of aryl halides with both aliphatic and aromatic amines.[14] One of the advantages of such phosphanes is the possibility of using unreactive aryl chlorides as substrates. Here we report a new method for the direct conversion of *o*-chloroarylacetaldehyde *N*,*N*-disubstituted hydrazones (**1**) into 1-aminoindole derivatives **2** and **4** by palladium-catalyzed intramolecular ring closure of **1** in the presence of P*t*Bu$_3$, 1,1′-bis(di-*tert*-butylphosphanyl)ferrocene (DB^{t}PF), and 2-(dimethylaminomethyl)-1-(di-*tert*-butylphosphanyl)ferrocene (**3**) as ligands [see Eqs. (1) and (2)].



3



DB^{t}PF

o-Chloroarylacetaldehydes can be synthesized from commercially available *o*-chloroarylmethyl chlorides.[10c] Hydrazone derivatives **1** were prepared from the above aldehydes and *N*,*N*-disubstituted hydrazines, and isolated in 90–93% yield by distillation.[15] The palladium-catalyzed cyclization of **1** gave a 1-aminoindole ring system. The results of the indolization of **1** are summarized in Table 1. The reaction with sodium *tert*-butoxide in *o*-xylene at 120 °C in the presence of [Pd_2(dba)$_3$] (dba = dibenzylideneacetone) and a bulky electron-rich phosphane gave a moderate yield of 1-(dimethylamino)indole (entry 1). A low yield was obtained in dioxane (entry 2). Whereas the yield of the reaction with the bidentate bis-phosphane DB^{t}PF[16] was lower than with P*t*Bu$_3$ (entry 3), the reaction in the presence of the P,N ligand **3** gave 78% yield (entry 4).[17] Although many P,N ligands bearing *t*Bu–P bonds are available, we chose **3** because it can be readily synthesized in one step from commercially available dimethylaminomethylferrocene.[18] Cs_2CO_3 and Rb_2CO_3 could also be used as bases (entries 5 and 6). Synthesis of indoles with substituents on the carbocyclic rings was also possible (entries 7–9). Since indole derivatives bearing a Cl substituent on the carbocyclic ring can be utilized as substrates for more elaborate indoles in palladium-catalyzed reactions such as

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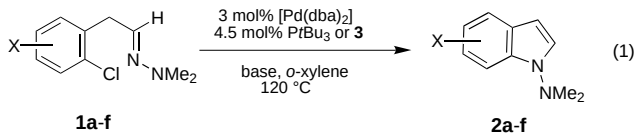
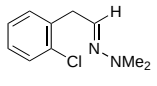
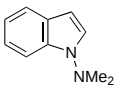
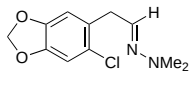
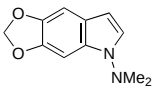
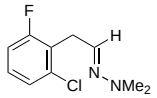
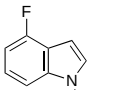
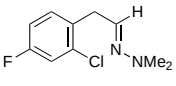
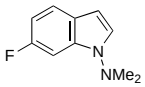
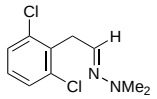
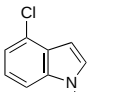
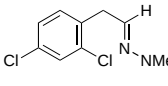
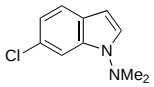


1a-f **2a-f**

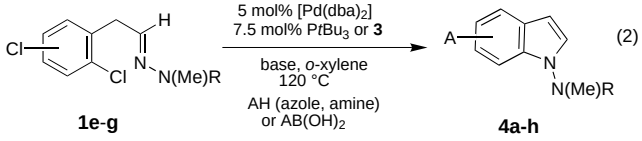
Table 1. Palladium-catalyzed intramolecular cyclization of *o*-chloroarylacetaldehyde *N*,*N*-dimethylhydrazones **1**.[a]

Entry	Substrate	Ligand	Base	Product	Yield [%][b]
1	 **1a**	P*t*Bu$_3$	NaO*t*Bu	 **2a**	39 (42)
2[c]	**1a**	P*t*Bu$_3$	NaO*t*Bu	**2a**	(7)
3	**1a**	DB^{t}PF	NaO*t*Bu	**2a**	(28)
4	**1a**	**3**	NaO*t*Bu	**2a**	73 (78)
5	**1a**	**3**	Cs_2CO_3	**2a**	(75)
6	**1a**	**3**	Rb_2CO_3	**2a**	(73)
7	 **1b**	**3**	NaO*t*Bu	 **2b**	30
8	 **1c**	**3**	NaO*t*Bu	 **2c**	60
9	 **1d**	**3**	NaO*t*Bu	 **2d**	74
10	 **1e**	P*t*Bu$_3$	NaO*t*Bu	 **2e**	46
11	**1e**	**3**	NaO*t*Bu	**2e**	34
12	**1e**	**3**	Cs_2CO_3	**2e**	33
13[d]	**1e**	**3**	NaO*t*Bu	**2e**	48
14	 **1f**	P*t*Bu$_3$	Rb_2CO_3	 **2f**	18

[a] All reactions were carried out with 3 mol% of [Pd(dba)$_2$], 4.5 mol% of **3** or P*t*Bu$_3$, 1.2 equiv of base, and 1.5–2.2 mmol of substrate at 120 °C for 2–20 h in *o*-xylene, unless otherwise noted. [b] Yield of product isolated by column chromatography on Al_2O_3 (elution with hexane/diethyl ether). Yields in parentheses were measured by GC analysis with *tert*-butylbenzene as internal standard. [c] Dioxane was used in place of *o*-xylene. [d] The reaction was carried out with 6 mol% of [Pd(dba)$_2$] and 9 mol% of **3**.

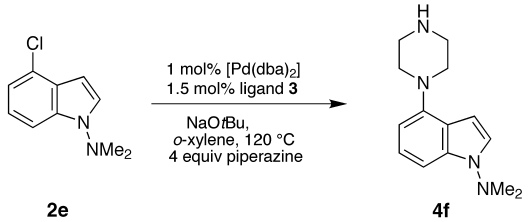
aminationand Suzuki coupling, we attempted cyclization of dichloroarylacetaldehyde hydrazones. Indeed, 4-chloro- and 6-chloro-1-dimethylaminoindoles were obtained (entries 10–14). A slightly higher yield was obtained by using P*t*Bu$_3$. The catalytic cycle is terminated when oxidative addition of these chloroindoles to Pd^0 species takes place in this reaction. Therefore, yields of chloroindoles are lower than those of unsubstituted indoles and fluoroindoles, and the yield increases with a larger amount of catalyst (entry 13).

Although chloroindole derivatives are attractive intermediates for synthesis of amino- and aryl-functionalized indoles, isolation of chloroindoles is expected to be unnecessary in the case of cyclization with coupling reagents that can react with the intermediate chloroindoles **2e–f** and **1** (X = Cl) and thus circumvent the termination of the catalytic cycle. Therefore, we examined a palladium-catalyzed cyclization of **1** (X = Cl) in the presence of phenylboronic acid, azoles, and amines to give 4- and 6-substitued indole derivatives **4** [Eq. (2)]. The



1e-g **4a-h**

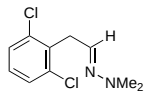
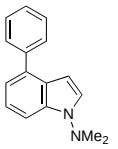
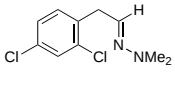
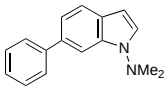
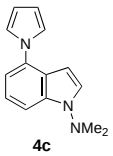
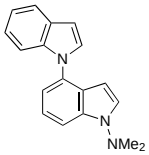
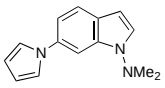
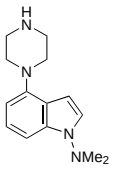
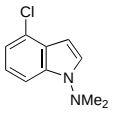
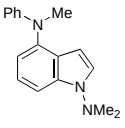
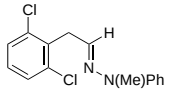
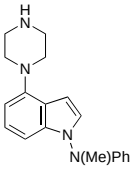
results are summarized in Table 2. Cyclization in the presence of phenylboronic acid gave 4- and 6-phenylindole derivatives **4a** and **4b** in one-pot reactions (entries 1–3). A slightly higher yield was obtained with ligand **3**. In this reaction, Suzuki coupling took place five times faster than the formation of chloroindole (2 h at 120 °C), and the conversion of the intermediate into the indole compound was then monitored by GC analysis. Reactions with azoles gave the azolylindoles **4c–e** (entries 4–7). In this case P*t*Bu$_3$ was superior to **3**, which gave only traces of **4c** and a low yield of the intermediate chloroindole **2e** (entry 4).[19] Rb_2CO_3 was preferably used because it was the most effective base in a Pd(OAc)$_2$/P*t*Bu$_3$-catalyzed synthesis of *N*-arylazoles from aryl halides and azoles.[20] Cyclization with amines was also examined. The reaction with piperazine in the presence of P*t*Bu$_3$ afforded dechlorinated derivatives of **1e** and formation of only traces of the indole nucleus (entry 9). However, the piperazinylindole **4f** was obtained with ligand **3** (entry 8). The presence of an *N*-methyl-*N*-phenylhydrazone moiety did not influence the yield (entry 12). Whereas cyclization with *N*-methylaniline gave the desired product **4g** (entry 11), the use of *N*-methylpiperazine resulted in selective formation of the 4-chloroindole derivative **2e** (entry 10). The initial formation of the chloroindole ring by C–N bond formation using azoles and amines occurred without formation of the product from the reaction of **1** with the azoles and amines. This result is in sharp contrast to C–C bond formation with phenylboronic acid. The yields obtained with amines are lower than those with phenylboronic acid and azoles. The reason might be a low tolerance of the acetaldehyde hydrazone moiety toward amines, since the reaction of isolated 4-chloro-1-dimethylaminoindole (**2e**) with piperazine at 120 °C for 2 h with palladium/**3** as catalyst furnished the desired 4-piperazinylindole (**4f**) in 94% yield [Eq. (3)].



2e **4f**

  1433-7851/00/3914-2502 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2000**, *39*, No. 14

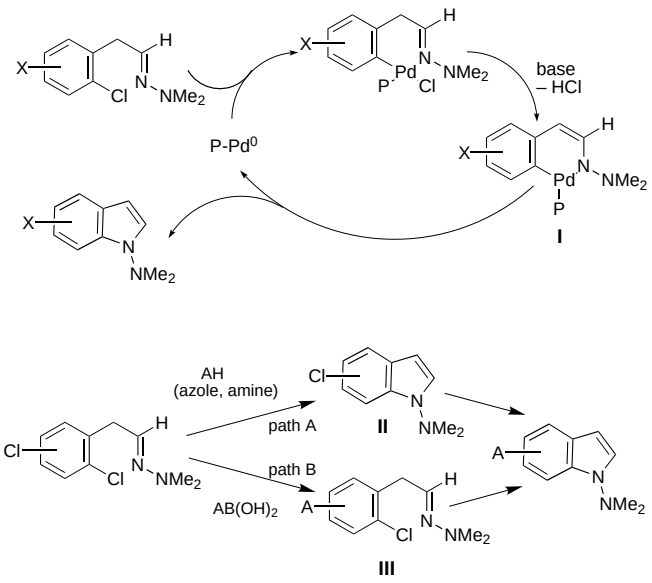
Table 2. Palladium-catalyzed synthesis of 4- and 6-substituted indoles.[a]

Entry	Substrate	Reagent	Ligand	Base	Product	Yield [%][b]
1	 **1e**	$PhB(OH)_2$	**3**	Cs_2CO_3	 **4a**	56
2	**1e**	$PhB(OH)_2$	P*t*Bu_3	Cs_2CO_3	**4a**	40
3	 **1f**	$PhB(OH)_2$	**3**	Cs_2CO_3	 **4b**	29
4	**1e**	pyrrole	**3**	Cs_2CO_3	 **4c**	Spur
5	**1e**	pyrrole	P*t*Bu_3	Rb_2CO_3	**4c**	54
6	**1e**	indole	P*t*Bu_3	Rb_2CO_3	 **4d**	40
7	**1f**	pyrrole	P*t*Bu_3	Rb_2CO_3	 **4e**	24
8[c]	**1e**	piperazine	**3**	NaO*t*Bu	 **4f**	30
9[c]	**1e**	piperazine	P*t*Bu_3	NaO*t*Bu	**4f**	trace
10	**1e**	*N*-methyl-piperazine	**3**	NaO*t*Bu	 **2e**	38
11	**1e**	PhN(Me)H	**3**	NaO*t*Bu	 **4g**	39
12[c]	 **1g**	piperazine	**3**	NaO*t*Bu	 **4h**	33

[a] All reactions were performed with 5 mol % of $[Pd(dba)_2]$, 7.5 mol % of **3** or P*t*Bu_3, 1.1 equiv of reagent, 2.2 equiv of base, and 1.5 mmol of substrate at 120 °C for 24 – 48 h in *o*-xylene, unless otherwise noted. [b] Yield of product isolated by column chromatography on Al_2O_3 (elution with hexane/diethyl ether for entries 1 – 7, 10, and 11; ethyl acetate/methanol for entries 8 and 12). [c] 4 equiv of piperazine relative to the substrate was used.

We also attempted the conversion of **1e** into 4-substituted indole derivatives using butyl acrylate and tribuyltin amides. Whereas cyclization followed by a Heck reaction took place to give approximately 10 % yield of the desired product (GC analysis), no products were obtained in the presence of the tin reagents.

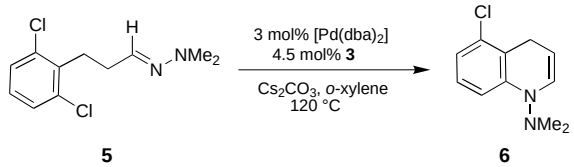
We believe that indole ring formation takes place via the aryl(enamido)palladium complex **I** (Scheme 1), although the mechanistic details of the reaction remain unknown.[21] When



Schema 1. Reaction pathways to the substituted indole derivatives and a plausible reaction sequence (neutral ligands are omitted for clarity).

coupling agents are present in the reaction mixture, the order of the cyclization and coupling reactions depends on the nature of the reagents. Chloroindole derivatives **II** were selectively formed as intermediates in the cases of azoles and amines (Scheme 1, path A), while the intermediate **III** was formed regardless of the position of the Cl substituent with phenylboronic acid (Scheme 1, path B). This means that C–C bond formation with $ArB(OH)_2$ is faster than both formation of the the indole ring and C–N bond formation with azoles and amines.

This palladium-catalyzed intramolecular indole formation could be extended to the formation of other heterocycles such as 1-amino-4*H*-quinolines. For instance, 2,6-dichlorophenylpropionaldehyde *N*,*N*-dimethylhydrazone (**5**)[22] was converted to 5-chloro-1-(dimethylamino)- 4*H*-quinoline (**6**) in 32 % yield [Eq. (4)].



5 **6** (4)

In conclusion, we have found a new palladium-catalyzed synthesis of indole rings that provides access to a wide range

of 1-aminoindoles that could formerly be synthesized by only limited methods.[23] This methodology also allows sequential reactions of this new cyclization and known palladium-catalyzed reactions with nucleophilic reagents in a single procedural operation to furnish indole derivatives with substituents on the carbocyclic rings. Indole derivatives that are not functionalized at both the 2- and 3-positions could be synthesized by using arylacetaldehyde hydrazones as substrates. Such compounds are important for the synthesis of more elaborate indole derivatives, because these positions can be easily functionalized by several methods.[5a,b] Furthermore, this methodology can be extended to the construction of six-membered ring systems such as 4*H*-quinolines.

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Spin Crossover in a Supramolecular Fe_4^{II} [2 × 2] Grid Triggered by Temperature, Pressure, and Light**

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In memory of Oliver Kahn

The development of advanced materials and devices for nanotechnology requires systems that form switchable domains on the molecular or supramolecular level, so as to

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