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Synthesis and Catalytic Application of Palladium Complexes with Picoline-Functionalized Benzimidazolin-2-ylidene Ligands

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The picoline-functionalized benzimidazolium salts *N*-alkyl-*N*′-picolylbenzimidazolium bromide [alkyl = methyl (**1**), ethyl (**2**), *n*-propyl (**3**), *n*-butyl (**4**)] and the dipicoline-functionalized benzimidazolium bromide **5** have been synthesized. Reaction of the salts **1**–**4** with palladium acetate leads to the formation of the palladium complexes of the type $[Pd(L)_2]Br_2$ (**6**–**9**; L = *N*-alkyl-*N*′-picolylbenzimidazolin-2-ylidene). Subsequent reaction of these complexes with $AgBF_4$ gave the palladium complexes **10**–**13**. The pincer-type palladium complex [PdBrL]Br (**14**, L = *N*,*N*′-dipicolylbenzimidazolin-2-ylidene) was prepared by deprotonation of the benzimidazolium salt **5** with *n*-butyllithium and subsequent coordination of the unstable carbene intermediate to $[PdBr_2cod]$. The molecular structures of the benzimidazolium salts **3** and **5** and the palladium complexes **7**–**9** and **11** have been determined by X-ray diffraction. The bis(carbene) palladium complexes **6**–**9** as well as the monocarbene pincer-type complex **14** have been used as precatalysts in Heck-type coupling reactions of several aryl halides with styrene and *n*-butyl acrylate as olefinic substrates.

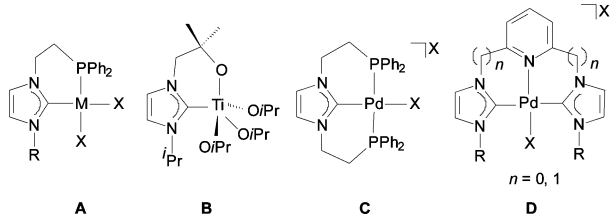
Introduction

The isolation of the first stable N-heterocyclic carbene (NHC) in 1991 by Arduengo et al.[1] caused a renewed and intense interest in this type of compounds.[2] A large number of different NHCs derived from imidazole,[3] imidazolidine,[4] benzimidazole,[5] and triazole[6] have been synthesized in addition to NHCs with extended ring sizes derived from six-[7] and seven-membered[8] heterocycles. Moreover, stable heterocyclic carbenes containing only one nitrogen atom within the heterocycle (CAAC)[9] or with two phosphorus atoms for the stabilization of the carbene center (PHC)[10] have been prepared by Bertrand et al.

Apart from the free carbenes, the number of complexes with NHC ligands has increased enormously because of the application of such complexes as catalysts in a variety of chemical transformations.[11] NHC ligands have become a cheap and easy accessible alternative to phosphanes in the design of new organometallic catalysts. In addition to the rhodium-catalyzed hydroformylation[12] and the ruthenium-catalyzed olefin metathesis reactions,[13] the most common applications for complexes bearing NHC ligands are the palladium- and nickel-catalyzed Heck- and Suzuki-type C–C coupling reactions.[11,14]

Relative to phosphane ligands, NHCs are widely considered stronger σ-donors without any significant M→L π-backbonding,[15] although the absence of backbonding is still a subject of debate.[16] The good σ-donor properties lead to highly stable NHC complexes. In contrast to the more-labile coordinated phosphane ligands, the carbene donor groups tend to remain coordinated to the metal center during catalytic transformation. Another positive aspect of the strong σ-donation is the efficient compensation of a charge deficiency at the metal atom during catalytic processes.[17]

A number of complexes with bridged bis(carbene) ligands[18] have been described in addition to complexes bearing bidentate heteroatom-functionalized carbene ligands with an additional heteroatom donor such as P (**A**),[19] N,[20] O (**B**)[21] or S.[22] Moreover, pincer-type complexes with one carbene (**C**)[23] and two additional group 15 donors or two carbene donor moieties and a pyridine- or phenylene-based bridging unit (**D**)[24] have been prepared.



Complexes bearing donor-functionalized NHC ligands sometimes show an increased catalytic activity.[11,14] The combination of NHCs with additional donor functions also allows for fine tuning of the catalyst's electronic properties. Normally, the σ-donor properties of the NHC ligand and that of the additional heteroatom are different, and this situation can lead to the generation of a vacant coordination

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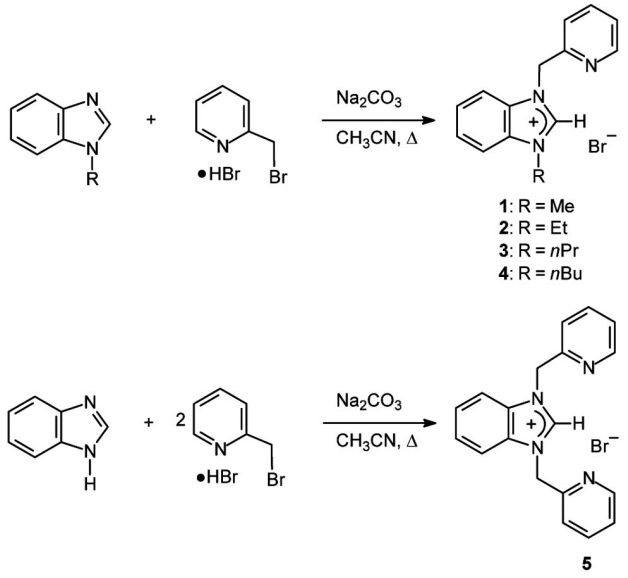
site for substrate binding during the catalytic process by temporary dissociation of the heteroatom donor from the metal.[25]

Most heterodonor-functionalized NHC ligands contain imidazolin-2-ylidenes as the carbene source, while benzimidazolin-2-ylidenes are much less encountered as the carbene moiety, although several complexes with donor-functionalized benzimidazolin-2-ylidene ligands are known.[26] The preparation of *N*-methyl-*N*′-picolylbenzimidazolium chloride has recently been described.[27] We have modified this synthesis and prepared a series of picoline-functionalized benzimidazolium salts. These compounds have been used for the synthesis of palladium complexes containing bi- and tridentate picoline-functionalized benzimidazolin-2-ylidene ligands. Here we report the molecular structures of selected palladium complexes with these ligands, together with their catalytic activity in Heck-type C–C coupling reactions.

Results and Discussion

Picoline-Functionalized Benzimidazolium Salts

Reaction of a suitably *N*-substituted benzimidazole derivative[26e,28] with 2-picolyl bromide hydrobromide in acetonitrile gave the picoline-functionalized benzimidazolium salts **1**–**4** with yields in the range 71–85% (Scheme 1). The dipicoline-functionalized benzimidazolium salt **5** was prepared by reaction of 2 equiv. 2-picolyl bromide hydrobromide with 1 equiv. benzimidazole and sodium carbonate as a base in acetonitrile with a yield of 76%.



Scheme 1. Synthesis of the picoline-functionalized benzimidazolium salts **1**–**5**.

The ^{1}H NMR spectra of the benzimidazolium salts **1**–**5** exhibit the signal for the NCHN proton as a singlet between δ = 9.90 and 11.50 ppm.[26–28] The resonances of the NCHN groups in the ^{13}C NMR spectra of **1**–**5** (δ = 143.8–143.1 ppm) are also found in the expected range.[26,28]

Preparation of the free carbene ligands or their dibenzotetraazafulvalene dimers by deprotonation of the acidic NCHN group failed. This is most likely due to the acidity of the methylene protons of the bridge. Attempted deprotonation of the C^2 carbon atom of the heterocycle with strong bases leads to undesired side reactions.[29]

Crystals suitable for an X-ray diffraction study of the benzimidazolium salts **3** and **5** were obtained by slow evaporation of the solvent from methanol solutions of the salts. The molecular structures of the benzimidazolium cations in **3** and **5**·H_2O are depicted in Figure 1. The N1–C1 and N2–C1 bond lengths and the N1–C1–N2 bond angles are typical for benzimidazolium salts.[26a,26c,28] No interaction between the nitrogen donor function of the picoline group and the acidic hydrogen atom of the benzimidazolium heterocycle exists since the N···H separations are too great to indicate such an interaction (in **3** 3.063 Å; in **5** 2.845 Å and 3.409 Å).

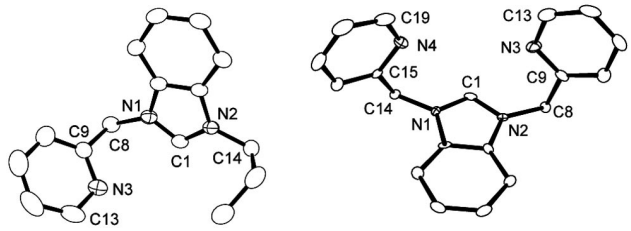
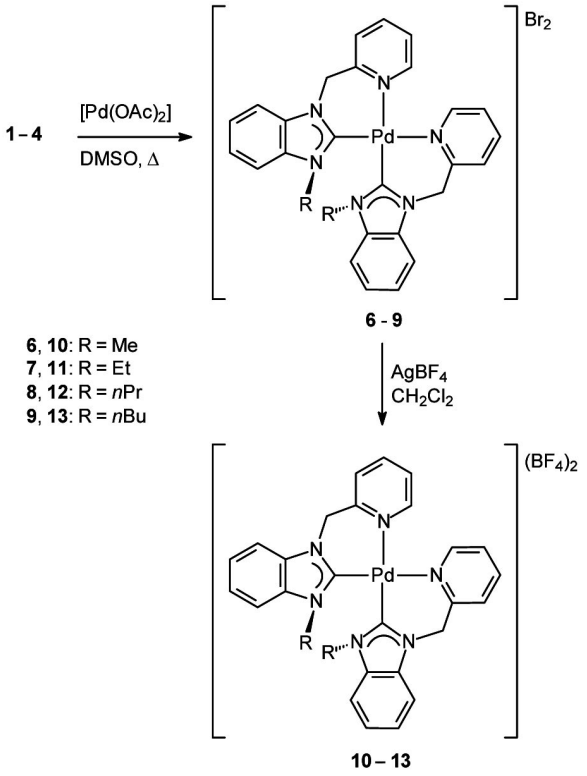


Figure 1. Molecular structures of the picoline-functionalized benzimidazolium cations in **3** and **5**·H_2O. Hydrogen atoms, the bromide counteranion, and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°] in **3**: N1–C1 1.328(3), N1–C8 1.464(4), N2–C1 1.328(3), N2–C14 1.472(3), N3–C9 1.341(4), N3–C13 1.335(4); N1–C1–N2 110.4(2), N1–C8–C9 110.3(2), C9–N3–C13 116.7(3). Selected bond lengths [Å] and angles [°] in **5**·H_2O: N1–C1 1.318(6), N1–C14 1.468(6), N2–C1 1.325(7), N2–C8 1.462(6), N3–C9 1.341(7), N3–C13 1.346(7), N4–C15 1.342(6), N4–C19 1.344(7); N1–C1–C2 111.6(5), N2–C8–C9 111.2(4), N1–C14–C15 110.8(4), C9–N3–C13 116.7(5), C15–N4–C19 116.3(5).

Palladium Complexes with Picoline-Functionalized Benzimidazolin-2-ylidene Ligands

Whereas a monocarbene palladium complex bearing an *N*-methyl-*N*′-picolyl-benzimidazolin-2-ylidene ligand has been prepared,[27] bis(carbene) palladium complexes with *N*-picoline-functionalized benzannulated carbene ligands have not yet been reported. Bis(carbene) palladium complexes bearing two *N*-picoline-functionalized benzimidazolin-2-ylidene ligands were synthesized by in situ deprotonation of the benzimidazolium salts **1**–**4** with palladium acetate and subsequent coordination of the carbene species to the palladium center (Scheme 2). After purification, the bright yellow palladium complexes **6**–**9** were obtained with yields in the range 75–86%. Complexes **6**–**9** are soluble in dichloromethane or a mixture of dichloromethane and methanol.

The formation of complexes **6**–**9** was verified by NMR spectroscopy. The characteristic ^{1}H NMR resonance for the acidic proton of the NCHN group in **1**–**4** ($\delta \approx 10$ ppm) is



Scheme 2. Synthesis of palladium complexes with picoline-functionalized benzimidazolin-2-ylidene ligands.

missing in the spectra of complexes **6**–**9**. In contrast to the rather simple spectra of the salts **1**–**4**, the spectra of complexes **6**–**9** show multiple resonances for the aromatic protons. The ^{13}C NMR spectra of **6**–**9** exhibit a double set of resonances that can be assigned to the picoline carbon atoms. The resonances of the carbene carbon atoms that are *cis* to each other are broad signals found in the narrow range 166.1–167.9 ppm.

The NMR spectra indicate that the palladium complexes **6**–**9** do not possess C_2 symmetry in solution. This might be due to a dynamic process involving the picoline donors, which could be coordinated to the metal center or act as a dangling ligand arm. The decoordination of a picoline donor was also indicated by mass spectrometry, which, instead of the dicationic complexes depicted in Scheme 2, shows one bromido ligand coordinated to the metal center instead of a picoline donor.

Crystals suitable for an X-ray diffraction study of compounds **7**, **8**·2MeOH, and **9**·2H_2O were grown by slow evaporation of the solvents from dichloromethane/methanol solutions of the complexes. The molecular structures of **7**, **8**, and **9** are depicted in Figure 2, and selected bond lengths and angles for these complexes are summarized in Table 1. All three complexes possess a C_2 symmetry in the solid state, and the palladium atom resides on a crystallographic twofold axis. Contrary to the dynamic behavior observed in solution, the picoline-functionalized NHC ligands act as a bidentate chelate ligand in all cases.

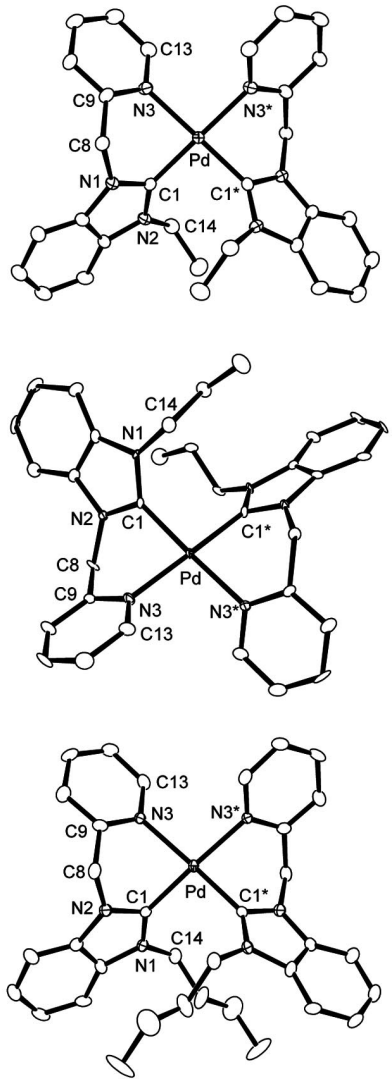


Figure 2. Molecular structures of the dicationic palladium complexes in **7** (top), **8**·2MeOH (middle), and **9**·2H_2O (bottom). Hydrogen atoms, bromide counterions, and solvent molecules have been omitted for clarity.

The Pd–$C_{carbene}$ bond lengths in **7** [1.962(3) Å], **8** [1.975(5) Å], and **9** [1.965(5) Å] fall in the expected range for complexes with a *cis* arrangement of the two benzimidazolin-2-ylidene donors [1.972(3)–1.991(7) Å].[30] They are shorter than the Pd–$C_{carbene}$ separations in both neutral and cationic palladium complexes with a *trans* orientation of the two benzimidazolin-2-ylidene ligands [Pd–$C_{carbene}$ 2.019(4)–2.047(4) Å].[26a–26c,31] The Pd–$N_{picoline}$ bond lengths in **7**–**9** fall in the range 2.082(3)–2.104(4) Å. They are similar to the Pd–N distances observed in palladium complexes with lutidine-bridged bis(benzimidazolin-2-ylidene) ligands reported recently [2.048(2)–2.072(3) Å].[26a,26b]

The palladium atoms in **7**–**9** have a slightly distorted square-planar arrangement of the coordinating ligands. The bond angle N3–Pd–N3* [for **7** 94.65(2)°; for **8** 96.3(2)°; for **9** 96.8(2)°] shows the greatest deviation from a perfect square-planar arrangement. The complexes appear to exist without strain, and the N–C–C bond angles at the methyl-

Table 1. Selected bond lengths [Å] and angles [°] in **7**, **8**·2MeOH, **9**·2H_2O, and **11**·CH_2Cl_2.

	7	**8**·2MeOH	**9**·2H_2O	**11**·CH_2Cl_2
Bond lengths				
Pd–C1	1.962(3)	1.975(5)	1.965(5)	1.976(3)
Pd–C21	–	–	–	1.974(3)
Pd–N3	2.082(3)	2.087(4)	2.104(4)	2.086(3)
Pd–N6	–	–	–	2.097(3)
N1–C1	1.341(4)	1.355(6)	1.341(6)	1.355(4)
N2–C1	1.351(4)	1.331(6)	1.349(6)	1.346(4)
N4–C21	–	–	–	1.357(4)
N5–C21	–	–	–	1.340(4)
Bond angles				
C1–Pd–C1*	93.92(2)	93.3(3)	93.8(3)	–
C1–Pd–C21	–	–	–	97.91(14)
N3–Pd–C1	85.74(12)	85.2(2)	85.1(2)	86.82(13)
N6–Pd–C21	–	–	–	84.93(13)
N3*–Pd–C1	178.48(12)	176.9(2)	173.3(2)	–
N3–Pd–C21	–	–	–	174.42(12)
N6–Pd–C1	–	–	–	177.08(12)
N3–Pd–N3*	94.65(15)	96.3(2)	96.8(2)	–
N3–Pd–N6	–	–	–	90.38(3)
N1–C1–N2	107.2(3)	109.0(4)	107.2(4)	106.6(3)
N4–C21–N5	–	–	–	107.5(3)
C9–N3–C13	118.8(3)	118.7(5)	119.4(4)	118.9(3)
C29–N6–C33	–	–	–	119.3(3)

ene carbon atom that links the carbene and the picoline donors are close to that for a tetrahedral arrangement [for **7** 111.1(3)°; for **8** 110.2(5)°; for **9** 110.7(4)°].

The N–C–N angles at the carbene center fall in the range 107.2(3)°–109.0(4)°. They are, as expected,[2] slightly smaller than the equivalent angles in the benzimidazolium salts **3** and **5**, but larger than the N–C–N angles observed for the free benzimidazolin-2-ylidenes.[5a,5c] The C–N–C bond angles within the picoline donor functions [for **7** 118.8(3)°; for **8** 118.7(5)°; for **9** 119.4(4)°] increase slightly upon coordination relative to the angles observed for the benzimidazolium salts **3** and **5**.

Reaction of the palladium complexes **6**–**9** with 2 equiv. silver tetrafluoroborate gave the complexes **10**–**13** (Scheme 2). This anion exchange removes the potentially competing ligand Br^-, which is capable of coordinating to the palladium atom. Consequently, both donor functions of the picoline-functionalized carbene ligands remain coordinated in solution. This behavior is revealed by the NMR spectra of compounds **10**–**13**, which exhibit only one set of resonances for the picoline functions. In addition, the protons of the methylene bridge become diastereotopic and lead to two doublets in the ^{1}H NMR spectra. The ^2J coupling constants exhibit values of about 14 Hz, which is typical for geminal coupling of diastereotopic protons.[26c]

Crystals of **11**·CH_2Cl_2 suitable for an X-ray diffraction study were obtained by slow evaporation of the solvents from a dichloromethane/methanol solution of **11**. As the complex cations in **7** and **11** are identical, they exhibit almost identical structural parameters. The major differences between **7** and **11**·CH_2Cl_2 is found in the space groups –*C*2/*c* for **7** (Z = 4) and $P2_1/n$ for **11**·CH_2Cl_2 (Z = 4). Additional crystal data for **11**·CH_2Cl_2 are summarized in Table 1, and Figure 3 shows a plot of the complex cation.

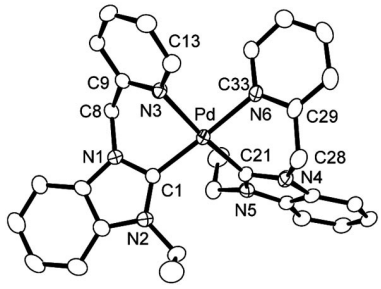
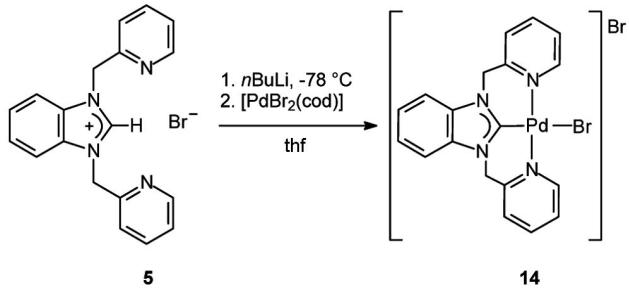


Figure 3. Molecular structure of the dicationic palladium complex in **11**·CH_2Cl_2. Hydrogen atoms and the two tetrafluoroborate anions have been omitted for clarity.

The potentially tridentate dipicoline-functionalized benzimidazolin-2-ylidene ligand obtained from **5** should be capable of forming a pincer-type palladium carbene complex like **14**. However, reaction of the benzimidazolium salt **5** with palladium acetate only afforded the undesired bis(carbene) palladium complex.[26a,26b,30a,31] Pincer complex **14** was obtained by in situ deprotonation of the benzimidazolium salt **5** with *n*BuLi at –78 °C, followed by trapping of the unstable carbene with [$PdBr_2$(cod)] (Scheme 3).



Scheme 3. Preparation of the pincer-type palladium complex **14**.

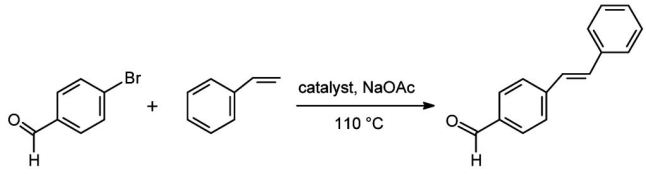
Formation of the palladium complex **14** was detected by NMR spectroscopy. The characteristic downfield signal for the NCHN proton of salt **5** at δ = 11.5 ppm is absent in the ^{1}H NMR spectrum of the palladium complex **14**. The resonance of the proton in the ε position of the pyridine ring (δ = 8.45 ppm in **5**) is shifted downfield upon coordination of the pyridine nitrogen to the palladium atom (δ = 9.42 ppm in **14**). The ^{13}C NMR spectrum exhibits the resonance of the coordinated carbene carbon atom at δ = 160.4 ppm.

Catalysis

The palladium complexes **6**–**9** and **14** were tested as precatalysts in Heck-type coupling reactions of differently *para*-functionalized aryl bromides with styrene and *n*-butyl acrylate. Because of the thermal stability of these complexes and their inertness towards air and moisture both in the solid state and in solution, the catalytic experiments were carried out under aerobic conditions.

Initially we studied the catalytic Heck-type coupling reaction of 4-bromobenzaldehyde and styrene with the cationic palladium complexes **6**–**9** and **14** as precatalysts (Table 2). After a reaction time of 24 h, almost complete conversion was observed with the four palladium complexes **6**–**9** bearing two picoline-functionalized benzimidazolin-2-ylidene ligands (Entries 1–4). Shortening of the reaction time to 2 h led to a drastic decrease in the conversion to between 27 and 32% (Entries 5–8). Only the pincer-type palladium complex **14** exhibited an acceptable conversion of 82% after a reaction time of only 2 h (Entry 9). We cannot rule out the formation of palladium colloids from the palladium complexes **6**–**9**, which then catalyzed the reaction heterogeneously.

Table 2. Palladium-catalyzed Heck-type coupling reaction of 4-bromobenzaldehyde and styrene.[a]



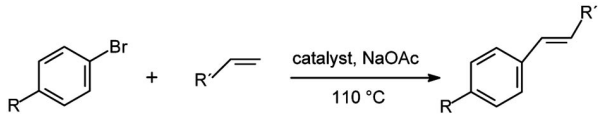
Entry	Catalyst	Time [h]	Conversion [%]
1	**6**	24	98
2	**7**	24	99
3	**8**	24	100
4	**9**	24	100
5	**6**	2	30
6	**7**	2	28
7	**8**	2	32
8	**9**	2	27
9	**14**	2	82

[a] Reaction conditions: 1 mmol 4-bromobenzaldehyde, 1.4 mmol styrene, 2 mmol NaOAc, 1 mol-% palladium catalyst, and 3 mL dimethylacetamide (dmac). Yields were determined by gas chromatography.

The palladium complexes **6**–**9** and **14** were also tested as precatalysts in several other coupling reactions of *para*-functionalized aryl bromides with styrene and *n*-butyl acrylate as olefinic substrates (Table 3). The first five entries in Table 3 show the conversions for the reaction of 4-bromoacetophenone with styrene catalyzed by the palladium complexes **6**–**9** and **14** for 2 h. Again, over this short reaction time, the pincer-type complex **14** exhibited the highest conversion, although the total conversion is not satisfying when compared to related complexes bearing benzimidazolin-2-ylidenes as the carbene source.[26d]

As previously observed, the conversion rate in catalytic Heck-type coupling reactions is also influenced by the electronic nature of the aryl bromides. In the reaction of 4-bromoanisole with styrene even after 24 h only low conversions to the desired coupling product were observed with the palladium complexes **6**–**9** (Entries 6–9). The conversion for aryl bromides with electron-withdrawing groups such as 4-bromoacetophenone and 4-bromobenzaldehyde (Table 2) is relatively high when compared to this data.

Table 3. Palladium-catalyzed Heck-type coupling reactions.[a]



Entry	Catalyst	R	R′	Time [h]	Conversion [%]
1	**6**	COMe	Ph	2	18
2	**7**	COMe	Ph	2	26
3	**8**	COMe	Ph	2	31
4	**9**	COMe	Ph	2	34
5	**14**	COMe	Ph	2	57
6	**6**	OMe	Ph	24	5
7	**7**	OMe	Ph	24	5
8	**8**	OMe	Ph	24	12
9	**9**	OMe	Ph	24	4
10	**6**	CHO	*n*BuOC(O)	2	21
11	**7**	CHO	*n*BuOC(O)	2	20
12	**8**	CHO	*n*BuOC(O)	2	19
13	**9**	CHO	*n*BuOC(O)	2	22
14	**14**	CHO	*n*BuOC(O)	2	65
15	**6**	COMe	*n*BuOC(O)	2	16
16	**7**	COMe	*n*BuOC(O)	2	15
17	**8**	COMe	*n*BuOC(O)	2	17
18	**9**	COMe	*n*BuOC(O)	2	22
19	**14**	COMe	*n*BuOC(O)	2	34

[a] Reaction conditions: 1 mmol 4-aryl halides, 1.4 mmol styrene, 2 mmol NaOAc, 1 mol-% palladium catalyst, and 3 mL dmac. Yields were determined by gas chromatography.

The application of the palladium complexes **6**–**9** and **14** as precatalysts for the C–C coupling reaction of 4-bromobenzaledehyde or 4-bromoacetophenone with *n*-butyl acrylate was also studied. In both coupling reactions the pincer-type palladium complex **14** is superior to the bis(carbene) palladium complexes **6**–**9**. After a reaction time of 2 h, a conversion of 65% (Entry 14) and 34% (Entry 19), respectively, was found for catalyst **14**, while the conversion for both investigated coupling reactions are much lower for the palladium complexes **6**–**9**.

Attempts to use the less-reactive 4-chlorobenzaldehyde as substrate also showed no satisfying results. In a manner similar to the less-reactive 4-bromoanisole, the conversion for the C–C coupling reaction of 4-chlorobenzaldehyde with styrene catalyzed by the bis(carbene) palladium complexes **6**–**9** was low (2–4%) after a reaction time of 24 h.

Therefore, we conclude that the application of palladium complexes with picoline-functionalized benzimidazolin-2-ylidene ligands seems to be limited to activated aryl bromides. Moreover, the bis(carbene) palladium complexes **6**–**9** with two bidentate ligands are less active than the pincer-type palladium complex **14**. We suppose that the difference in catalytic activity is based on steric effects, which makes substrate coordination to the catalytically active metal center more difficult in complexes **6**–**9**.

Conclusions

New picoline-functionalized benzimidazolium salts have been obtained by the reaction of benzimidazole derivatives

with picolyl bromide hydrobromide. Reaction of these salts with palladium acetate gives the square-planar bis(carbene) palladium complexes **6**–**9** in which the picoline-functionalized benzimidazolin-2-ylidene ligands and the carbene donors are in *cis* positions. A hemilabile coordination of the picoline arms was observed in solution for these complexes. Nevertheless, X-ray diffraction studies with single crystals of compounds **7**–**9** reveal picolyl coordination in the solid state. Anion exchange of the bromide anions with silver tetrafluoroborate gives the palladium complexes **10**–**13** in which the picolyl donors are coordinated in the solid state and in solution. Complexes **6**–**9** and **14** exhibit catalytic activity in Heck-type coupling reactions of activated aryl bromides with styrene or *n*-butyl acrylate. The highest catalytic activity is observed for the pincer-type complex **14**. All complexes show a low catalytic activity in coupling reactions of aryl chlorides or deactivated aryl bromides.

Experimental Section

General Procedures: All operations except for the preparation of complex **14** were carried out in air by using commercially available solvents. 2-Picolyl bromide hydrobromide and palladium acetate were purchased from Sigma–Aldrich or Fluka. The *N*-alkylated benzimidazole derivatives were prepared by using published procedures.[26e,28] Mass spectra were measured on a Varian MAT 212 instrument. Elemental analyses (C, H, N) were obtained for all compounds with a Vario EL III elemental analyzer at the Westfälische Wilhelms-Universität, Münster.

General Procedure for the Synthesis of *N*-Alkyl-*N*′-picolylbenzimidazolium Bromides 1–4: The *N*-alkylated benzimidazole derivative (1.2 mmol), 2-picolyl bromide hydrobromide (1.0 mmol, 0.252 g), and excess potassium carbonate (2.0 mmol, 0.276 g) as base were suspended in acetonitrile (50 mL). This mixture was heated under reflux for 48 h. The solvent was then removed in vacuo, and the residue was suspended in dichloromethane (30 mL). Filtration and removal of the solvent from the filtrate yielded a viscous residue, which was again dissolved in a small amount of dichloromethane. This solution was added dropwise to ice-cold diethyl ether (200 mL). A brown precipitate formed, which was separated by filtration. The solid was washed three times diethyl ether (25 mL each) and dried in vacuo.

***N*-Methyl-*N*′-picolylbenzimidazolium Bromide (1):** Yield: 0.215 g (71%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 9.90 (s, 1 H, NCHN), 8.49 (d, ^3J = 4.8 Hz, 1 H, pyridine-H$_\varepsilon$), 8.05–7.95 (m, 2 H, Ar-H), 7.94–7.89 (m, 2 H, pyridine-H$_\beta$ and pyridine-H$_\gamma$), 7.73–7.65 (m, 2 H, Ar-H), 7.37 (d, ^3J = 4.8 Hz, 1 H, pyridine-H$_\delta$), 5.93 (s, 2 H, NCH$_2$-pyridine), 4.15 (s, 3 H, NCH$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 153.4 (pyridine-C$_\alpha$), 150.0 (pyridine-C$_\varepsilon$), 143.8 (NCHN), 137.9 (pyridine-C$_\gamma$), 132.2, 131.5, 127.1 (Ar-C), 124.1 (pyridine-C$_\delta$), 123.1 (pyridine-C$_\beta$), 114.1, 114.0 (Ar-C), 51.2 (NCH$_2$-pyridine), 33.9 (CH$_3$) ppm. MS (MALDI): *m*/*z* = 224 [M – Br]$^+$. $C_{14}H_{14}BrN_3$ (304.19): calcd. C 55.28, H 4.64, N 13.81; found C 55.23, H 4.96, N 13.39.

***N*-Ethyl-*N*′-picolylbenzimidazolium Bromide (2):** Yield: 0.262 g (82%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 10.11 (s, 1 H, NCHN), 8.49 (d, ^3J = 4.8 Hz, 1 H, pyridine-H$_\varepsilon$), 8.15–8.06 (m, 2 H, Ar-H), 7.98–7.84 (m, 2 H, pyridine-H$_\beta$ and pyridine-H$_\gamma$), 7.74–7.61 (m, 2 H, Ar-H), 7.37 (d, ^3J = 4.8 Hz, 1 H, pyridine-H$_\delta$), 5.95 (s, 2 H, NCH$_2$-pyridine), 4.60 (q, ^3J = 7.2 Hz, 2 H, NC*H*$_2$CH$_3$), 1.57 (t, ^3J = 7.2 Hz, 3 H, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 153.4 (pyridine-C$_\alpha$), 149.9 (pyridine-C$_\varepsilon$), 143.1 (NCHN), 137.9 (pyridine-C$_\gamma$), 131.7, 131.3, 127.1, 126.9 (Ar-C), 124.0 (pyridine-C$_\delta$), 123.2 (pyridine-C$_\beta$), 114.3, 114.2 (Ar-C), 51.2 (NCH$_2$-pyridine), 42.6 (N*C*H$_2$CH$_3$), 14.7 (NCH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 238 [M – Br]$^+$. $C_{15}H_{16}BrN_3$ (318.22): calcd. C 56.62, H 5.07, N 13.20; found C 56.40, H 5.21, N 12.82.

***N*-Propyl-*N*′-picolylbenzimidazolium Bromide (3):** Yield: 0.268 g (81%). ^{1}H NMR (400.1 MHz, [D$_6$]dmso): δ = 10.14 (s, 1 H, NCHN), 8.47 (d, ^3J = 4.5 Hz, 1 H, pyridine-H$_\varepsilon$), 8.13 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 7.97 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 7.89 (t, ^3J = 7.8 Hz, 1 H, Ar-H), 7.71 (d, ^3J = 7.8 Hz, 1 H, Ar-H), 7.69–7.60 (m, 2 H, pyridine-H$_\beta$, pyridine-H$_\gamma$), 7.36 (d, ^3J = 4.5 Hz, 1 H, pyridine-H$_\delta$), 5.98 (s, 2 H, NCH$_2$-pyridine), 4.57 (t, ^3J = 7.3 Hz, 2 H, NC*H*$_2$CH$_2$CH$_3$), 1.95 (sext, ^3J = 7.3 Hz, 2 H, NCH$_2$C*H*$_2$CH$_3$), 0.94 (t, ^3J = 7.3 Hz, 3 H, NCH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (100.1 MHz, [D$_6$]dmso): δ = 153.4 (pyridine-C$_\alpha$), 149.9 (pyridine-C$_\varepsilon$), 143.5 (NCHN), 137.9 (pyridine-C$_\gamma$), 131.7, 131.4, 127.1, 126.9 (Ar-C), 124.1 (pyridine-C$_\beta$), 123.1 (pyridine-C$_\delta$), 114.3 (Ar-C), 51.2 (NCH$_2$-pyridine), 48.6 (N*C*H$_2$CH$_2$CH$_3$), 22.4 (NCH$_2$*C*H$_2$CH$_3$), 11.0 (NCH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 252 [M – Br]$^+$. $C_{16}H_{18}BrN_3$ (332.25): calcd. C 57.84, H 5.46, N 12.65; found C 57.72, H 5.67, N 12.38.

***N*-Butyl-*N*′-picolylbenzimidazolium Bromide (4):** Yield: 0.293 g (85%). ^{1}H NMR (300.1 MHz, [D$_6$]dmso): δ = 10.14 (s, 1 H, NCHN), 8.46 (d, ^3J = 4.5 Hz, 1 H, pyridine-H$_\varepsilon$), 8.13 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.96 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.89 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.11 (d, ^3J = 7.7 Hz, 1 H, Ar-H), 7.68–7.62 (m, 2 H, pyridine-H$_\beta$, pyridine-H$_\gamma$), 7.36 (d, ^3J = 4.5 Hz, 1 H, pyridine-H$_\delta$), 5.97 (s, 2 H, NCH$_2$-pyridine), 4.59 (t, ^3J = 7.3 Hz, 2 H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.91 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.35 (m, 2 H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.93 (t, ^3J = 7.3 Hz, 3 H, NCH$_2$CH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]dmso): δ = 153.4 (pyridine-C$_\alpha$), 149.9 (pyridine-C$_\varepsilon$), 143.5 (NCHN), 137.9 (pyridine-C$_\gamma$), 131.7, 131.1, 127.1, 126.9 (Ar-C), 124.0 (pyridine-C$_\beta$), 123.1 (pyridine-C$_\delta$), 114.3, 114.2 (Ar-C), 51.2 (NCH$_2$-pyridine), 46.9 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 30.9 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.4 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.7 (NCH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 266 [M – Br]$^+$. $C_{17}H_{20}BrN_3$ (346.27): calcd. C 57.97, H 5.82, N 12.14; found C 57.77, H 5.61, N 11.91.

***N*,*N*′-Dipicolylbenzimidazolium Bromide (5):** Benzimidazole (0.45 mmol, 0.054 g), 2-picolyl bromide hydrobromide (1.0 mmol, 0.250 g), and an excess of sodium carbonate as base (0.212 g, 2.0 mmol) were suspended in acetonitrile (80 mL). The reaction mixture was heated under reflux for 48 h. Subsequently, the solvent was removed in vacuo, and the oily residue was dissolved in a small amount of dichloromethane. This solution was added dropwise to ice-cold diethyl ether (200 mL) whilst stirring. A reddish precipitate formed, which was isolated by filtration. The solid was washed three times with diethyl ether (25 mL each) and dried in vacuo. Yield: 0.131 g (76%). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ = 11.50 (s, 1 H, NCHN), 8.45 (d, ^3J = 4.7 Hz, 2 H, pyridine-H$_\varepsilon$), 7.84–7.77 (m, 4 H, Ar-H), 7.33–7.65 (m, 4 H, Ar-H), 7.48 (d, ^3J = 5.0 Hz, 2 H, pyridine-H$_\gamma$), 7.22, 7.19 (both d, ^3J = 5.0 Hz, 2 H, pyridine-H$_\beta$, pyridine-H$_\delta$), 5.97 (s, 4 H, NCH$_2$-pyridine) ppm. ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 152.7 (pyridine-C$_\alpha$), 150.1 (pyridine-C$_\varepsilon$), 143.8 (NCHN), 138.1 (pyridine-C$_\gamma$), 132.0, 127.5 (Ar-C), 124.3 (pyridine-C$_\beta$), 124.1 (pyridine-C$_\delta$), 114.6 (Ar-C), 53.0 (NCH$_2$-pyridine) ppm. MS (MALDI): *m*/*z* = 301 [M – Br]$^+$. $C_{19}H_{17}BrN_4$ (381.3): calcd. C 59.85, H 4.49, N 14.69; found C 59.31, H 4.12, N 14.23.

General Synthesis of {Bis[*N*-alkyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium(II)} Dibromides 6–9: Palladium acetate (0.22 mmol, 0.050 g) and one of the benzimidazolium salts **1**–**4** (0.44 mmol) were dissolved in argon-saturated dmso (10 mL). The orange solution was stirred at room temperature for 2 h. The temperature was then raised to 50 °C for another 12 h. Finally, the solution was stirred at 120 °C for 3 h. The solvent was removed in vacuo, and the solid residue was dissolved in a mixture of dichloromethane and methanol (1:1, v/v). This solution was added dropwise to ice-cold diethyl ether (200 mL). A bright yellow precipitate formed, which was isolated by filtration. The isolated solid was washed twice with diethyl ether (5 mL each) and dried in vacuo.

{Bis[*N*-methyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium(II)} Dibromide (6): Yield: 0.118 g (75%). ^{1}H NMR (200 MHz, [D$_6$]-dmso): δ = 9.06–9.04 (m, 1 H, pyridine-H), 8.12–7.10 (m, 15 H, Ar-H, pyridine-H), 6.01 (s br., 4 H, NCH$_2$-pyridine), 4.15 (s, 6 H, NCH$_3$) ppm. ^{13}C NMR (100.1 MHz, [D$_6$]dmso): δ = 167.9 (NCN), 154.2, 153.0 (pyridine-C$_\alpha$), 150.7, 149.4 (pyridine-C$_\varepsilon$), 140.6 (pyridine-C$_\gamma$), 134.2, 133.9, 124.2, 123.9 (Ar-C), 122.7 (pyridine-C$_\beta$, pyridine-C$_\delta$), 111.7, 111.2 (Ar-C), 51.7 (NCH$_2$-pyridine), 34.5 (NCH$_3$) ppm. MS (MALDI): *m*/*z* = 633 [M – Br]$^+$. $C_{28}H_{26}Br_2N_6Pd$ (712.8): calcd. C 47.18, H 3.68, N 11.79; found C 45.97, H 3.45, N 11.53.

{Bis[*N*-ethyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium(II)} Dibromide (7): Yield: 0.134 g (82%). ^{1}H NMR (200.1 MHz, [D$_6$]-dmso): δ = 9.01 (d, ^3J = 5.5 Hz, 1 H, pyridine-H), 8.10–8.06 (m, 1 H, pyridine-H), 7.99 (d, ^3J = 7.9 Hz, 4 H, Ar-H), 7.82–7.79 (m, 2 H, pyridine-H), 7.77–7.74 (m, 2 H, pyridine-H), 7.56 (t, ^3J = 7.9 Hz, 4 H, Ar-H), 7.45–7.41 (m, 2 H, pyridine-H), 6.09–5.99 (m, 2 H, NCH$_2$-pyridine), 5.97–5.91 (m, 2 H, NCH$_2$-pyridine), 4.88–4.68 (m, 4 H, NC*H*$_2$CH$_3$), 1.47 (t, ^3J = 7.2 Hz, 6 H, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 167.8 (NCN), 154.4, 153.7 (pyridine-C$_\alpha$), 152.6, 148.0 (pyridine-C$_\varepsilon$), 140.8, 140.4 (pyridine-C$_\gamma$), 132.8, 132.3, 124.7, 124.4 (Ar-C), 124.0, 123.9 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.2, 111.8 (Ar-C), 51.6 (NCH$_2$-pyridine), 42.2 (N*C*H$_2$CH$_3$), 13.6 (NCH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 661 [M – Br]$^+$. $C_{30}H_{30}Br_2N_6Pd$ (740.8): calcd. C 48.64, H 4.08, N 11.34; found C 48.33, H 3.87, N 10.98.

{Bis[*N*-propyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium-(II)} Dibromide (8): Yield: 0.146 g (86%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 9.01 (d, ^3J = 5.4 Hz, 1 H, pyridine-H), 8.10–8.06 (m, 1 H, pyridine-H), 8.03–7.97 (m, 4 H, Ar-H), 7.85–7.81 (m, 2 H, pyridine-H), 7.79–7.76 (m, 2 H, pyridine-H), 7.56 (t, ^3J = 8.0 Hz, 4 H, Ar-H), 7.48–7.41 (m, 2 H, pyridine-H), 6.28–6.20 (m, 2 H, NCH$_2$-pyridine), 5.96–5.88 (m, 2 H, NCH$_2$-pyridine), 4.66–4.46 (m, 4 H, NC*H*$_2$CH$_2$CH$_3$), 2.03–1.82 (m, 4 H, NCH$_2$C*H*$_2$CH$_3$), 0.88 (t, ^3J = 7.3 Hz, 6 H, NCH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 166.1 (NCN), 154.9, 154.4 (pyridine-C$_\alpha$), 153.1, 149.6 (pyridine-C$_\varepsilon$), 141.4, 141.0 (pyridine-C$_\gamma$), 133.8, 133.3, 125.8, 125.6 (Ar-C), 125.2, 124.7 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.7, 112.1 (Ar-C), 52.8, 52.3 (NCH$_2$-pyridine), 50.3 (N*C*H$_2$CH$_2$CH$_3$), 23.3 (NCH$_2$*C*H$_2$CH$_3$), 11.6 (NCH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 689 [M – Br]$^+$. $C_{32}H_{34}Br_2N_6Pd$ (768.9): calcd. C 49.99, H 4.46, N 10.93; found C 49.53, H 4.21, N 10.52.

{Bis[*N*-butyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium-(II)} Dibromide (9): Yield: 0.148 g (85%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 9.01 (d, ^3J = 5.5 Hz, 1 H, pyridine-H), 8.11–8.05 (m, 1 H, pyridine-H), 8.02–7.95 (m, 4 H, Ar-H), 7.87–7.83 (m, 2 H, pyridine-H), 7.81–7.77 (m, 2 H, pyridine-H), 7.56 (t, ^3J = 8.0 Hz, 4 H, Ar-H), 7.53–7.41 (m, 2 H, pyridine-H), 6.33–6.14 (m, 2 H, NCH$_2$-pyridine), 6.01–5.82 (m, 2 H, NCH$_2$-pyridine), 4.66–4.46 (m, 4 H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.96–1.69 (m, 4 H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.41–1.22 (m, 4 H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.56 (t, ^3J = 7.3 Hz, 6 H, NCH$_2$CH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 167.85 (NCN), 153.7, 152.4 (pyridine-C$_\alpha$), 149.9 (pyridine-C$_\varepsilon$), 140.9, 140.4 (pyridine-C$_\gamma$), 133.2, 132.7, 125.1, 124.9 (Ar-C), 124.1, 123.9 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.0, 111.5 (Ar-C), 52.3, 52.2 (NCH$_2$-pyridine), 48.3, 47.4 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 31.1, 30.8 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.1 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.2 (NCH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 717 [M – Br]$^+$. $C_{34}H_{38}Br_2N_6Pd$ (796.9): calcd. C 51.24, H 4.81, N 10.55; found C 50.87, H 4.43, N 10.21.

General Procedure for the Synthesis of {Bis[*N*-alkyl-*N*′-(α-picolyl)-benzimidazolin-2-ylidene]palladium(II)} Tetrafluoroborate 10–13: One of the palladium complexes **6**–**9** (1.0 mmol) and silver tetrafluoroborate (2.1 mmol, 0.220 g) were dissolved in dichloromethane (60 mL). The solution was stirred under exclusion of light for 12 h. It was then filtered, and the filtrate was dried in vacuo. A bright yellow residue was obtained, which was dissolved in dichloromethane (2 mL) and added dropwise to diethyl ether while stirring. A yellow precipitate formed, which was collected by filtration. The solid was washed twice with diethyl ether (5 mL each) and dried in vacuo.

{Bis[*N*-methyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium-(II)} Tetrafluoroborate (10): Yield: 0.487 g (67%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 8.79 (d, ^3J = 5.4 Hz, 2 H, pyridine-H$_\varepsilon$), 8.46–8.04 (m, 5 H, Ar-H and pyridine-H), 7.87–7.65 (m, 4 H, Ar-H and pyridine-H), 7.62–7.56 (m, 5 H, Ar-H and pyridine-H), 6.50, (d, ^2J = 14.0 Hz, 2 H, NCH$_2$-pyridine), 6.36 (d, ^2J = 14.0 Hz, 2 H, NCH$_2$-pyridine), 4.23 (s, 6 H, NCH$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]dmso): δ = 167.2 (NCN), 153.9 (pyridine-C$_\alpha$), 152.2 (pyridine-C$_\varepsilon$), 141.8 (pyridine-C$_\gamma$), 134.0, 132.6 (Ar-C), 125.5, 125.1 (Ar-C), 124.5, 124.2 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.0, 111.5 (Ar-C), 50.5 (NCH$_2$-pyridine), 34.8 (NCH$_3$) ppm. MS (MALDI): *m*/*z* = 551 [M + H – 2BF$_4$]$^+$.

{Bis[*N*-ethyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium-(II)} Tetrafluoroborate (11): Yield: 0.556 g (74%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 8.39 (d, ^3J = 5.5 Hz, 2 H, pyridine-H$_\varepsilon$), 8.28–8.16 (m, 6 H, Ar-H, pyridine-H), 7.86 (d, ^3J = 8.1 Hz, 2 H, Ar-H), 7.69–7.59 (m, 4 H, Ar-H, pyridine-H$_\beta$, pyridine-H$_\delta$), 7.56 (d, ^3J = 5.5 Hz, 2 H, pyridine-H), 6.44 (d, ^2J = 14.1 Hz, 2 H, NCH$_2$-pyridine), 6.39 (d, ^2J = 14.1 Hz, 2 H, NCH$_2$-pyridine), 4.43–4.23 (m, 2 H, NC*H*$_2$CH$_3$), 3.88–3.65 (m, 2 H, NC*H*$_2$CH$_3$), 1.17 (t, ^3J = 7.2 Hz, 6 H, NCH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.3 MHz, [D$_6$]-dmso): δ = 167.1 (NCN), 153.9 (pyridine-C$_\alpha$), 152.7 (pyridine-C$_\varepsilon$), 141.8 (pyridine-C$_\gamma$), 133.4, 132.8, 125.4, 125.1 (Ar-C), 124.6, 124.2 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.0, 111.6 (Ar-C), 51.3 (NCH$_2$-pyridine), 43.6 (N*C*H$_2$CH$_3$), 14.7 (NCH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 579 [M + H – 2BF$_4$]$^+$.

{Bis[*N*-propyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium-(II)} Tetrafluoroborate (12): Yield: 0.604 g (77%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 8.43 (d, ^3J = 5.6 Hz, 2 H, pyridine-H$_\varepsilon$), 8.32–8.14 (m, 6 H, Ar-H, pyridine-H), 7.88 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 7.69–7.47 (m, 6 H, Ar-H, pyridine-H), 6.46 (d, ^3J = 14.1 Hz, 2 H, NCH$_2$-pyridine), 6.40 (d, ^3J = 14.1 Hz, 2 H, NCH$_2$-pyridine), 4.39–4.19 (m, 2 H, NC*H*$_2$CH$_2$CH$_3$), 3.61–3.41 (m, 2 H, NC*H*$_2$CH$_2$CH$_3$), 1.61–1.40 (m, 4 H, NCH$_2$C*H*$_2$CH$_3$), 0.54 (t, ^3J = 7.2 Hz, 6 H, NCH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.1 MHz, [D$_6$]-dmso): δ = 167.1 (NCN), 153.9 (pyridine-C$_\alpha$), 152.6 (pyridine-C$_\varepsilon$), 141.8 (pyridine-C$_\gamma$), 133.3, 133.1, 125.1, 124.9 (Ar-C), 124.2, 124.1 (pyridine-C$_\beta$, pyridine-C$_\delta$), 111.8, 111.4 (Ar-C), 51.5 (NCH$_2$-pyridine), 49.7 (N*C*H$_2$CH$_2$), 22.5 (NCH$_2$*C*H$_2$CH$_3$), 11.4 (NCH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 607 [M + H – 2BF$_4$]$^+$.

{Bis[*N*-butyl-*N*′-(α-picolyl)benzimidazolin-2-ylidene]palladium(II)} Tetrafluoroborate (13): Yield: 0.586 g (72%). ^{1}H NMR (200.1 MHz, [D$_6$]dmso): δ = 8.43 (d, ^3J = 5.5 Hz, 2 H, pyridine-H$_\varepsilon$), 8.30–8.15 (m, 6 H, Ar-H, pyridine-H), 7.87 (d, ^3J = 8.2 Hz, 2 H, Ar-H), 7.69–7.61 (m, 4 H, Ar-C, pyridine-H), 7.57 (d, ^3J = 5.5 Hz, 2 H, pyridine-H), 6.47 (d, ^3J = 14.6 Hz, 2 H, NCH$_2$-pyridine), 6.40 (d, ^3J = 14.6 Hz, 2 H, NCH$_2$-pyridine), 4.39–4.20 (m, 2 H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 3.74–3.54 (m, 2 H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.96–1.69 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.40–1.20 (m, 2 H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.03–0.87 (m, 4 H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.51 (t, ^3J = 7.3 Hz, 6 H, NCH$_2$CH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (50.1 MHz, [D$_6$]dmso): δ = 167.3 (NCN), 153.9 (pyridine-C$_\alpha$), 152.6 (pyridine-C$_\varepsilon$), 141.9 (pyridine-C$_\gamma$), 133.3, 133.1, 125.9, 125.5 (Ar-C), 124.9, 124.7 (pyridine-C$_\beta$, pyridine-C$_\delta$), 112.6, 112.0 (Ar-C), 51.5 (NCH$_2$-pyridine), 49.7 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 29.9 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 22.5 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 11.0 (NCH$_2$CH$_2$CH$_2$*C*H$_3$) ppm. MS (MALDI): *m*/*z* = 635 [M + H – 2BF$_4$]$^+$.

{Bromo[*N*,*N*′-Dipicolylbenzimidazolin-2-ylidene]palladium(II)} Bromide (14): Compound **5** (1.0 mmol, 0.380 g) was suspended in thf (70 mL), and the suspension was cooled down to –78 °C. *n*BuLi (1.1 mmol, 0.44 mL of a 2.5 M hexane solution) was then added dropwise to the suspension. After stirring at –78 °C for 30 min, [PdBr$_2$(cod)] (1.0 mmol, 0.374 g) was added. The reaction mixture was warmed to ambient temperature, and it was then heated under reflux for an additional 12 h. The solvent was removed in vacuo, and the solid residue was extracted twice with dichloromethane (20 mL each). The resulting solution was filtered, and the solvent was removed in vacuo. A red solid was obtained, which was dissolved in a small amount of dichloromethane. This solution was added dropwise to stirred diethyl ether (200 mL). A precipitate formed, which was collected by filtration, washed with diethyl ether (5 mL), and dried in vacuo. Yield: 0.358 g (63%). ^{1}H NMR (300.1 MHz, [D$_6$]dmso): δ = 9.42 (d, ^3J = 6.4 Hz, 2 H, pyridine-H$_\varepsilon$), 8.27–8.18 (m, 6 H, Ar-H, pyridine-H$_\gamma$), 7.71 (t, ^3J = 6.4 Hz, 2 H, pyridine-H$_\beta$), 7.50 (m, 2 H, pyridine-H$_\delta$), 6.19 (s, 4 H, NCH$_2$-pyridine) ppm. ^{13}C NMR (75.1 MHz, [D$_6$]dmso): δ = 160.4 (NCN), 156.1 (pyridine-C$_\alpha$), 153.2 (pyridine-C$_\varepsilon$), 141.0 (pyridine-C$_\gamma$), 132.6 (Ar-C), 127.0 (pyridine-C$_\beta$), 125.7 (pyridine-C$_\delta$), 124.9, 112.7 (Ar-C), 51.0 (NCH$_2$-pyridine) ppm. MS (MALDI): *m*/*z* = 486 [M – Br]$^+$. C$_{19}$H$_{16}$Br$_2$N$_4$Pd (566.6): calcd. C 40.28, H 2.85, N 9.89; found C 40.01, H 2.53, N 9.73.

General Method for the Heck Reactions: One of the palladium complexes **6**–**9** or **14** (1.0 mol-%), an aryl halide (1.0 mmol), styrene or *n*-butyl acrylate (1.4 mmol), and sodium acetate as base (2.0 mmol) were dissolved in dimethylacetamide (dmac, 3 mL). The reaction mixture was heated to 110 °C with stirring. After the selected reaction time had lapsed, the mixture was cooled down to ambient temperature, and the organic phase was cleaned by elution over a short silica gel column. The solution was then analyzed by quantitative GC chromatography (GC-FID) with a Shimadzu GC-2100 equipped with an Aglient Technologies HP 5 capillary column (30.0 m).

X-ray Diffraction Studies: Diffraction data for **3**, **5**·H$_2$O, **7**, and **11**·CH$_2$Cl$_2$ were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). For compounds **8**·2MeOH and **9**·2H$_2$O, diffraction data were obtained on a Bruker SMART CCD diffractometer with a rotating anode by using Cu-K_α radiation (λ = 1.54184 Å). Data were collected over the full sphere and were corrected for absorption. Data reduction was performed with the Bruker SMART[32] program package. For further crystal and data collection details see Table 4. All crystal structures were solved with SHELXS-97[33] by employing the heavy-atom method and were refined with SHELXL-97[34] by using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models at calculated positions, and their thermal parameters were fixed to 1.3 U$_{eqv.}$ of the parent atom. Ortep-3 for Windows[35] was used for all molecular plots. CCDC-713489 (**3**), -713490 (**5**·H$_2$O), -713491 (**7**), -713492 (**8**·2MeOH), -713493 (**9**·2H$_2$O), and -713494 (**11**·CH$_2$Cl$_2$) contain 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.

Table 4. Summary of crystallographic data for **3**, **5**·H$_2$O, **7**, **8**·2MeOH, **9**·2H$_2$O, and **11**·CH$_2$Cl$_2$.

	3	**5**·H$_2$O	**7**	**8**·2MeOH	**9**·2H$_2$O	**11**·CH$_2$Cl$_2$
Formula	C$_{16}$H$_{18}$N$_3$Br	C$_{19}$H$_{19}$N$_4$BrO	C$_{30}$H$_{30}$N$_6$Br$_2$Pd	C$_{34}$H$_{42}$N$_6$Br$_2$O$_2$Pd	C$_{34}$H$_{42}$N$_6$Br$_2$O$_2$Pd	C$_{31}$H$_{32}$N$_6$B$_2$Cl$_2$F$_8$Pd
M_r	332.24	399.29	740.82	832.96	832.96	839.55
Crystal size [mm]	0.25 × 0.25 × 0.21	0.17 × 0.06 × 0.03	0.09 × 0.05 × 0.03	0.31 × 0.25 × 0.24	0.22 × 0.13 × 0.06	0.10 × 0.06 × 0.04
a [Å]	10.328(2)	16.847(2)	8.972(3)	9.6057(3)	19.4769(5)	9.464(2)
b [Å]	14.559(3)	10.456(13)	21.584(6)	21.9015(5)	11.0235(3)	15.022(4)
c [Å]	11.502(2)	20.068(3)	15.981(5)	16.6005(5)	18.4314(5)	24.112(6)
α [°]	90	90	90	90	90	90
β [°]	114.854(3)	90	90.331(7)	97.118(2)	121.776(2)	98.732(5)
γ [°]	90	90	90	90	90	90
V [Å^3]	1569.2(5)	3521.4(8)	3095(2)	3465.5(2)	3364.1(2)	3388.3(15)
Z	4	8	4	4	4	4
Space group	*P*2$_1$/*c*	*Pbca*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*P*2$_1$/*n*
$\rho_{calcd.}$ [g cm^{-3}]	1.406	1.506	1.590	1.596	1.645	1.646
μ [mm^{-1}]	2.614 (Mo-K_α)	2.349 (Mo-K_α)	3.211 (Mo-K_α)	7.333 (Cu-K_α)	7.554 (Cu-K_α)	0.783 (Mo-K_α)
2θ range [°]	4.3–55.0	4.0–50.0	3.8–60.2	8.1–139.8	9.6–139.9	3.2–50.0
Data collected	15094	26727	17675	9819	9386	26798
Unique data, R_{int}	3595, 0.0336	3099, 0.0856	4531, 0.0787	3214, (0.0726)	2880	5951
Obsd. data [$I \geq 2\sigma(I)$]	2935	2508	3235	2250	1805	4849
R (all data)	0.0599	0.0820	0.0789	0.0755	0.0668	0.0543
wR (all data)	0.1095	0.1730	0.0880	0.1348	0.0837	0.0948
No. of variables	191	238	178	216	205	453
Peak/hole [e Å^3]	1.323/–1.099	0.681/–0.757	1.124/–0.711	1.138/–2.966	0.805/–0.557	0.675/–0.388

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[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[2] a) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; b) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–91.
[3] a) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921; b) N. Kuhn, T. Kratz, *Synthesis* **1993**, 561–562.
[4] a) A. J. Arduengo III, J. R. Goerlich, W. J. Marshall, *J. Am. Chem. Soc.* **1995**, *117*, 11027–11028; b) M. K. Denk, A. Thadani, K. Hatano, A. Lough, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2607–2609; c) F. E. Hahn, M. Paas, D. Le Van, T. Lügger, *Angew. Chem. Int. Ed.* **2003**, *42*, 5243–5246; d) R. S. Bon, F. J. J. de Kanter, M. Lutz, A. L. Spek, M. C. Jahnke, F. E. Hahn, M. B. Groen, R. V. A. Orru, *Organometallics* **2007**, *26*, 3639–3650; e) G. W. Nyce, S. Csihony, R. M. Waymouth, J. L. Hedrick, *Chem. Eur. J.* **2004**, *10*, 4073–4079.
[5] a) F. E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, *Chem. Eur. J.* **1999**, *5*, 1931–1935; b) F. E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, *Angew. Chem. Int. Ed.* **2000**, *39*, 541–544; c) N. I. Korotkikh, G. F. Raenko, T. M. Pekhtereva, O. P. Shvaika, A. H. Cowley, J. N. Jones, *Russ. J. Org. Chem.* **2006**, *42*, 1822–1833.
[6] D. Enders, K. Breuer, G. Raabe, J. Runsik, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021–1023.
[7] a) P. Bazinet, G. P. A. Yap, D. S. Richeson, *J. Am. Chem. Soc.* **2003**, *125*, 13314–13315; b) P. Bazinet, T.-G. Ong, J. S. O'Brien, N. Lavoie, E. Bell, G. P. A. Yap, I. Korobkov, D. S. Richeson, *Organometallics* **2007**, *26*, 2885–2895; c) M. Otto, S. Conejero, Y. Canac, V. D. Romanenko, V. Rudzevitch, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1016–1017.
[8] a) M. Iglesias, D. J. Beetstra, A. Stasch, P. N. Horton, M. B. Hursthouse, S. Coles, K. J. Cavell, A. Dervisi, I. A. Fallis, *Organometallics* **2007**, *26*, 4800–4809; b) M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi, I. A. Fallis, *Organometallics* **2008**, *27*, 3279–3289.
[9] a) V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709; b) R. Jazzar, R. D. Dewhurst, J.-B. Bourg, B. Donnadieu, Y. Canac, G. Bertrand, *Angew. Chem. Int. Ed.* **2007**, *46*, 2899–2902.
[10] a) D. Martin, A. Baceiredo, H. Gornitzka, W. W. Schoeller, G. Bertrand, *Angew. Chem. Int. Ed.* **2005**, *44*, 1700–1703; b) J. D. Masuda, D. Martin, C. Lyon-Saunier, A. Baceiredo, H. Gornitzka, B. Donnadieu, G. Bertrand, *Chem. Asian J.* **2007**, *2*, 178–187.
[11] a) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) A. T. Normand, K. J. Cavell, *Eur. J. Inorg. Chem.* **2008**, 2781–2800.
[12] a) M. Poyatos, P. Uriz, T. A. Mata, C. Claver, E. Fernandez, E. Peris, *Organometallics* **2003**, *22*, 440–444; b) M. T. Zarka, M. Bortenschlager, K. Wurst, O. Nuyken, R. Weberskirch, *Organometallics* **2004**, *23*, 4817–4820.
[13] a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18–29; b) R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765; c) S. J. Connon, S. Blechert, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900–1923; d) H. Clavier, K. Grela, A. Kirschning, M. Mauduit, S. P. Nolan, *Angew. Chem. Int. Ed.* **2007**, *46*, 6786–6801.
[14] E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.
[15] M.-T. Lee, C.-H. Hu, *Organometallics* **2004**, *23*, 976–983.
[16] a) H. M. J. Wang, C. S. Vasam, T. Y. R. Tsai, S.-H. Chen, A. H. H. Chang, I. J. B. Lin, *Organometallics* **2005**, *24*, 486–493; b) X. Hu, K. Meyer, *J. Organomet. Chem.* **2005**, *690*, 5474–5484; c) X. Hu, I. Castro-Rodriguez, K. Meyer, *Chem. Commun.* **2004**, 2164–2165; d) X. Hu, Y. Tang, P. Gantzel, K. Meyer, *Organometallics* **2003**, *22*, 612–614.
[17] K. Albert, P. Gisdakis, N. Rösch, *Organometallics* **1998**, *17*, 1608–1616.
[18] a) H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Cheng, *Tetrahedron* **2004**, *60*, 5807–5825; b) M. Muehlhofer, T. Strassner, E. Herdtweck, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *660*, 121–126; c) J. A. Mata, A. R. Chianese, J. R. Miecznikowski, M. Poyatos, E. Peris, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 1253–1263.
[19] a) N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch, M. E. Light, *Organometallics* **2003**, *22*, 4750–4758; b) A. A. Danopoulos, N. Tsoureas, S. A. Macgregor, C. Smith, *Organometallics* **2007**, *26*, 253–263; c) L. D. Field, B. A. Messerle, K. Q. Vuong, P. Turner, *Organometallics* **2005**, *24*, 4241–4250; d) C.-C. Lee, W.-C. Ke, K.-T. Chan, L.-C. Lai, C.-H. Hu, H. M. Lee, *Chem. Eur. J.* **2007**, *13*, 582–591; e) S. Nanchen, A. Pfaltz, *Helv. Chim. Acta* **2006**, *89*, 1559–1573; f) N. Stylianides, A. A. Danopoulos, N. Tsoureas, *J. Organomet. Chem.* **2005**, *690*, 5948–5958; g) E. Bappert, G. Helmchen, *Synlett* **2004**, 1789–1793; h) H. M. Lee, P. L. Chiu, J. Y. Zeng, *Inorg. Chim. Acta* **2004**, *357*, 4313–4321; i) T. Focken, G. Raabe, C. Bolm, *Tetrahedron: Asymmetry* **2004**, *15*, 1693–1706; j) J. Wolf, A. Labande, J.-C. Daran, R. Poli, *Eur. J. Inorg. Chem.* **2008**, 3024–3030.
[20] a) A. A. D. Tulloch, A. A. Danopoulos, R. P. Tooze, S. M. Cafferkey, S. Kleinhenz, M. B. Hursthouse, *Chem. Commun.* **2000**, 1247–1248; b) S. Gründemann, M. Albrecht, A. Kovacevic, J. W. Faller, R. H. Crabtree, *J. Chem. Soc., Dalton Trans.* **2002**, 2163–2167; c) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz, G. Eastham, *J. Chem. Soc., Dalton Trans.* **2000**, 4499–4506; d) A. A. D. Tulloch, S. Winston, A. A. Danopoulos, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, 699–708; e) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; f) X. Wang, S. Liu, G.-X. Jin, *Organometallics* **2004**, *23*, 6002–6007; g) A. A. D. Tulloch, A. A. Danopoulos, S. Kleinhenz, M. E. Light, M. B. Hursthouse, G. Eastham, *Organometallics* **2001**, *20*, 2027–2031; h) J. C. C. Chen, I. J. B. Lin, *Organometallics* **2000**, *19*, 5113–5121; i) V. Cesar, S. Bellemin-Laponnaz, L. H. Gade, *Organometallics* **2002**, *21*, 5204–5208; j) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546–560; k) O. Kaufhold, F. E. Hahn, T. Pape, A. Hepp, *J. Organomet. Chem.* **2008**, *693*, 3435–3440.
[21] a) P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* **2004**, 1612–1613; b) P. L. Arnold, A. C. Scarisbrick, A. J. Blake, C. Wilson, *Chem. Commun.* **2001**, 2340–2341; c) P. L. Arnold, A. J. Blake, C. Wilson, *Chem. Eur. J.* **2005**, *11*, 6095–6099; d) H. Aihara, T. Matsuo, H. Kawaguchi, *Chem. Commun.* **2003**, 2204–2205; e) N. A. Jones, S. T. Liddle, C. Wilson, P. L. Arnold, *Organometallics* **2007**, *26*, 755–757; f) P. L. Arnold, C. Wilson, *Inorg. Chim. Acta* **2007**, *360*, 190–196; g) D. Zhang, H. Aihara, T. Watanabe, T. Matsuo, H. Kawaguchi, *J. Organomet. Chem.* **2007**, *692*, 234–242; h) D. Patel, S. T. Liddle, S. A. Mungur, M. Rodden, A. J. Blake, P. L. Arnold, *Chem. Commun.* **2006**, 1124–1126.
[22] a) D. Sellmann, W. Prechtel, F. Knoch, M. Moll, *Inorg. Chem.* **1993**, *32*, 538–546; b) J. A. Cabeza, I. del Rio, M. G. Sanchez-Vega, M. Suarez, *Organometallics* **2006**, *25*, 1831–1834; c) J. A. Cabeza, I. da Silva, I. del Rio, M. G. Sanchez-Vega, *Dalton Trans.* **2006**, 3966–3971; d) H. V. Huynh, C. H. Yeo, G. K. Tan, *Chem. Commun.* **2006**, 3833–3835; e) J. Wolf, A. Labande, J.-C. Daran, R. Poli, *Eur. J. Inorg. Chem.* **2007**, 5069–5079.
[23] a) H. M. Lee, J. Y. Zeng, C.-H. Hu, M.-T. Lee, *Inorg. Chem.* **2004**, *43*, 6822–6829; b) J. Y. Zeng, M.-H. Hsieh, H. M. Lee, *J. Organomet. Chem.* **2005**, *690*, 5662–5671; c) P. L. Chiu, H. M.

Lee, *Organometallics* **2005**, *24*, 1692–1702; d) A. E. Wang, J.-H. Xie, L.-X. Wang, Q.-L. Zhou, *Tetrahedron* **2005**, *61*, 259–266.

[24] a) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 201–202; b) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700–706; c) A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles, M. B. Hursthouse, R. S. Hay-Motherwell, W. B. Motherwell, *Chem. Commun.* **2001**, 1270–1271; d) A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, 1009–1015; e) S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485–5488; f) J. R. Miecznikowski, S. Gründemann, M. Albrecht, C. Megret, E. Clot, J. W. Faller, O. Eisenstein, R. H. Crabtree, *Dalton Trans.* **2003**, 831–838; g) M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, *Organometallics* **2003**, *22*, 1110–1114; h) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2002**, *327*, 116–125; i) D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2006**, *359*, 1855–1869; j) R. S. Simons, P. Custer, C. A. Tessier, W. J. Youngs, *Organometallics* **2003**, *22*, 1979–1982; k) A. A. D. Danopoulos, J. A. Wright, W. B. Motherwell, S. Ellwood, *Organometallics* **2004**, *23*, 4807–4810; l) D. S. McGuinness, V. C. Gibson, J. W. Steed, *Organometallics* **2004**, *23*, 6288–6292; m) D. Pugh, J. A. Wright, S. Freeman, A. A. Danopoulos, *Dalton Trans.* **2006**, 775–782. For a recent review see: D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610–641.

[25] P. Braunstein, F. Naud, *Angew. Chem. Int. Ed.* **2001**, *40*, 680–699.

[26] a) F. E. Hahn, M. C. Jahnke, V. Gomez Benitez, D. Morales-Morales, T. Pape, *Organometallics* **2005**, *24*, 6458–6463; b) M. C. Jahnke, T. Pape, F. E. Hahn, *Z. Naturforsch.* **2007**, *62b*, 357–361; c) F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2007**, *26*, 150–154; d) F. E. Hahn, M. C. Jahnke, T. Pape, *Organometallics* **2006**, *25*, 5927−5936; e) F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203−2209.

[27] N. T. Barczak, R. E. Grote, E. R. Jarvo, *Organometallics* **2007**, *26*, 4863−4865

[28] E. A. Goreshnik, D. Schollmeyer, M. G. Mys′kiv, O. V. Pavl′uk, *Z. Allg. Anorg. Chem.* **2000**, *626*, 1016−1019.

[29] a) C. Holtgrewe, C. Diedrich, T. Pape, S. Grimme, F. E. Hahn, *Eur. J. Org. Chem.* **2006**, 3116−3124 ; b) H. V. Huynh, N. Meier, T. Pape, F. E. Hahn, *Organometallics* **2006**, *25*, 3012−3018

[30] a) F. E. Hahn, M. Foth, *J. Organomet. Chem.* **1999**, *585*, 241−245; b) F. E. Hahn, T. v. Fehren, L. Wittenbecher, R. Fröhlich, *Z. Naturforsch.* **2004**, *59b*, 541−543; c) F. E. Hahn, T. von Fehren, T. Lügger, *Inorg. Chim. Acta* **2005**, *358*, 4137−4144.

[31] F. E. Hahn, C. Holtgrewe, T. Pape, *Z. Naturforsch.* **2004**, *59b*, 1051−1053.

[32] *SMART*, Bruker AXS, **2000**.

[33] G. M. Sheldrick, *SHELXS-97*, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[34] G. M. Sheldrick, *SHELXL-97*, Universität Göttingen, Germany, **1997**

[35] L. J. Farrugia, *ORTEP-3*, University of Glasgow, Scotland, **1999**

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