# Synthesis of Palladium and Platinum Complexes with Phosphine-Functionalized Benzimidazolin-2-ylidene Ligands

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Phosphine-functionalized benzimidazolium salts of the type *N*-(2-phosphinoethyl)-*N*′-alkylbenzimidazolium chloride (**4**, alkyl = ethyl; **5**, alkyl = *n*-propyl; **6**, alkyl = *n*-butyl) and *N*,*N*′-bis(2-phosphinoethyl)-5,6-dimethylbenzimidazolium chloride (**9**) have been prepared. The reaction of **4**−**6** with silver oxide followed by a carbene transfer reaction from silver to palladium or platinum gave complexes of the type *cis*-[M($PC^{NHC}$)$Cl_2$] **13**−**18** (M = Pd, Pt; $PC^{NHC}$ = *N*-(2-phosphinoethyl)-*N*′-alkylbenzimidazolin-2-ylidene). The pincer-type complexes [M($PC^{NHC}$P)Cl]Cl (M = Pd (**20**), Pt (**21**); $PC^{NHC}$P = *N*,*N*′-bis(2-phosphinoethyl)benzimidazolin-2-ylidene) with a diphosphine-functionalized carbene ligand have been synthesized by carbene transfer from the corresponding silver complex [Ag($PC^{NHC}$P)Cl] (**19**) to [$PdCl_2$(cod)] or [$PtCl_2$-$(PhCN)_2$]. The metathesis reaction of **20** with silver tetrafluoroborate in pyridine produced [Pd($PC^{NHC}$P)-py]$(BF_4)_2$ (**22**). Compounds **13**, **15**, and **22**·0.5MeOH have been characterized by X-ray diffraction. Heck-type coupling reactions of several aryl halides with styrene and *n*-butyl acrylate have been studied with the palladium complexes containing phosphine-functionalized carbene ligands as catalysts.

## Introduction

Starting with the isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo et al.[1] in 1991, a large number of stable NHC ligands have been prepared.[2] The preparation and the properties of NHCs derived from imidazole,[3] benzimidazole,[4] imidazolidine,[5] and triazole[6] have been studied in detail. Apart from the free carbene ligands, metal complexes of NHCs have attracted much interest because of the unique coordination chemistry of the NHC ligands and the application of such complexes as catalysts in various catalytic processes.[7] Selected catalytic applications for NHC complexes are the ruthenium-catalyzed olefin metathesis[8] and the rhodium-catalyzed hydroformylation.[9] Palladium-catalyzed C−C coupling reactions such as the Heck or Suzuki reaction are, however, the most common applications for catalytically active NHC complexes.[7]

N-Heterocyclic carbene ligands are often used as an alternative to the more expensive phosphine ligands. Among the advantages of the NHC ligands are their stronger $\sigma$-donor properties compared to tertiary phosphine ligands[10] with M→L $\pi$-back-bonding of no significance,[11] although its existence is still subject to debate.[12] The strong metal−carbon bond causes the enhanced stability of NHC complexes toward heat and moisture compared to phosphine complexes.[13] In addition, the strong $\sigma$-donation of NHC ligands leads to a stabilization of the metal center during the catalytic process since a charge deficit at the metal atom can be compensated.[14]

Complexes bearing bidentate or pincer-type ligands with a combination of different donor moieties have found widespread use in catalytic processes.[15] Heteroatom-functionalized carbene ligands with P (**A**),[16] N (**B**),[17] or S[18] donor function have been prepared. In addition, pincer-type complexes with group 15 donor groups and one (**C**)[19] or two (**D**)[20] imidazolin-2-ylidene functions are known. The combination of the carbene moiety

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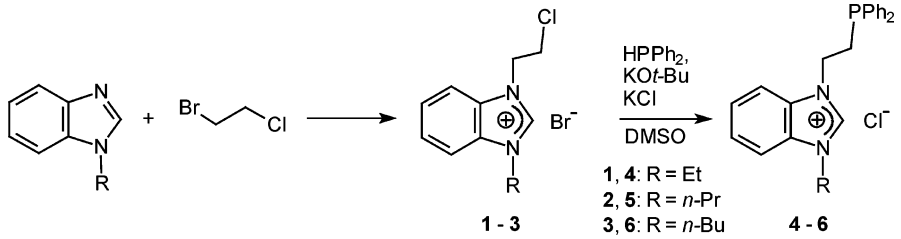
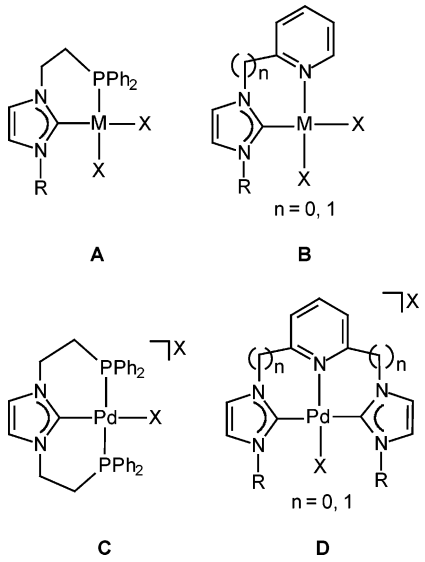
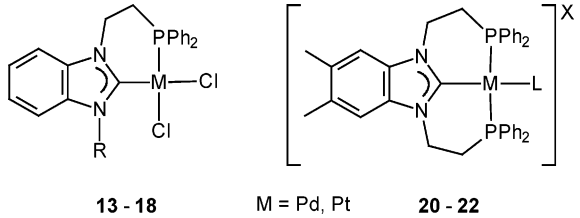
**Scheme 1. Preparation of the Phosphine-Functionalized Benzimidazolium Chlorides 4−6**




with classical donor functions allows a tuning of the metal coordination sphere. While the strongly bonded carbene donor function normally remains coordinated, the heteroatom donor groups can reversibly dissociate from the metal center, thereby generating vacant coordination sites for substrate binding in catalytic processes.[21]




Complexes with donor-functionalized bidentate or pincer-type carbene ligands have been employed as catalysts for a number of catalytic transformations. Most of these complexes, however, contain imidazolin-2-ylidenes as a carbene function, although a few donor-functionalized benzimidazolin-2-ylidene ligands are known.[22] We became interested in pincer-type ligands containing the benzimidazolin-2-ylidene donor function since this benzannulated N-heterocyclic carbene[1c,4] has been shown to occupy an intermediate position between the saturated imidazolidin-2-ylidene and the ubiquitous unsaturated imidazolin-2-ylidene. It was hoped that complexes with tuned electronic and catalytic properties would emerge from the use of ligands with benzimidazolin-2-ylidene donor groups. Here we present the synthesis of phosphine-functionalized benzimidazolium salts, which were used for the preparation of complexes with donor-functionalized **13**−**18** ($PC^{NHC}$) and pincer-type ($PC^{NHC}P$) carbene ligands **20**−**22**.




## Results and Discussion

**Preparation of the Benzimidazolium Salts.** The preparation of the *N*-(2-phosphinoethyl)-*N*′-alkylbenzimidazolium salts **4**−**6** is depicted in Scheme 1. It is based on the initial alkylation reaction of N-alkylbenzimidazole derivatives with 1-bromo-2-chloroethane giving the 2-chloroethyl-functionalized benzimidazolium salts **1**−**3**. This procedure failed when *N*-methylbenzimidazole was used as a starting material. Due to the higher reactivity of this derivative, both C−X bonds of the 1-bromo-2-chloroethane react to give an ethylene-bridged dibenzimidazolium salt. Reaction of compounds **1**−**3** with in situ-generated $KPPh_2$ in DMSO afforded the phosphine-functionalized benzimidazolium salts **4**−**6**.

The benzimidazolium salts **4**−**6** were obtained as white, air-sensitive solids. The $^1$H NMR spectra of these salts exhibit the NCHN resonance around $\delta$ 10.1 ppm. A single resonance with a chemical shift in the range $\delta$ −17.5 to −17.7 ppm was

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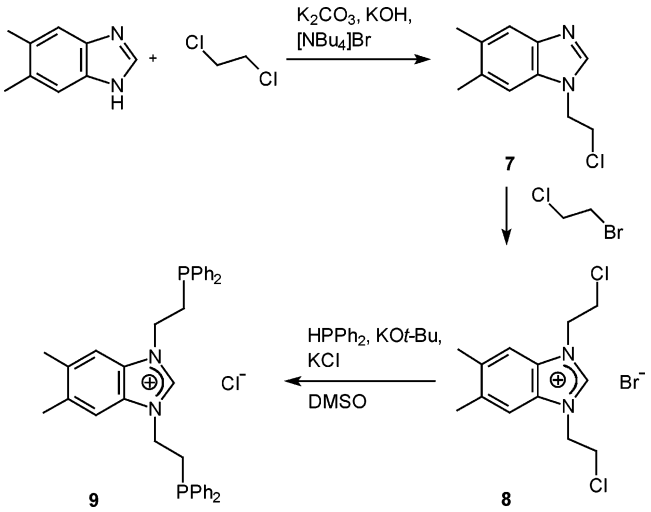
**Scheme 2. Synthesis of the Diphosphine-Functionalized Benzimidazolium Salt 9**



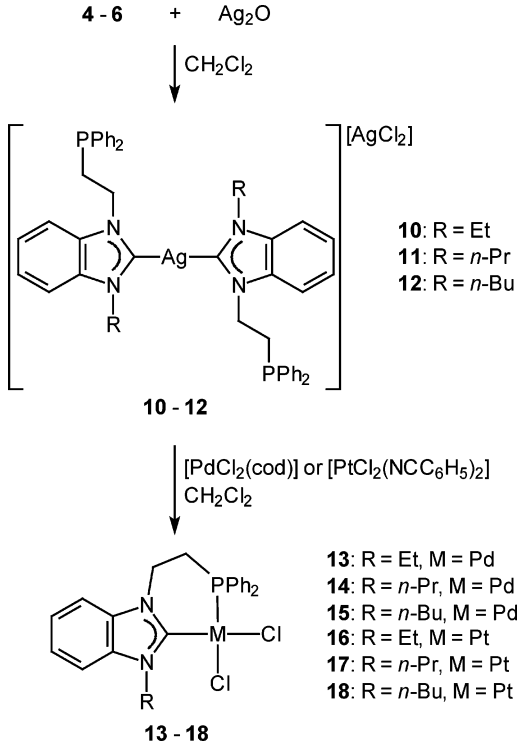

observed for the phosphorus atoms of the phosphine functions in the $^{31}$P NMR spectra. Coupling of the phosphorus atoms with the phenylene carbon atoms as well as with both carbon atoms of the ethylene bridge was observed in the $^{13}$C NMR spectra of the benzimidazolium salts **4**−**6**.

The benzimidazolium salt with two phosphine donor functions **9** (Scheme 2) was obtained in a reaction sequence similar to the one reported by Lee and co-workers[19a] for the related imidazolium derivatives. However, the described phase-transfer catalysis approach[23] did not yield the pure *N*-(2-chloroethyl)-benzimidazole. Instead, we obtained compound **7** by alkylation of 5,6-dimethylbenzimidazole with 1,2-dichloroethane. The second 2-chloroethyl group was introduced by stirring **7** in 1-bromo-2-chloroethane. Attempts to obtain the bromine-free salt by reaction with a second equivalent of 1,2-dichloroethane failed due to the lack of reactivity of the 1,2-dichloroethane. Reaction of compound **8** with $KPPh_2$ in DMSO gave the diphosphine-functionalized benzimidazolium salt **9** in good yield as an off white, air-sensitive solid.

The acidic NCHN proton of **9** was observed at $\delta$ 10.18 ppm in the $^1$H NMR spectrum, and the $^{31}$P spectrum exhibits a singlet at $\delta$ −17.7 ppm for the phosphorus atoms. The $^{13}$C NMR spectrum shows P−C coupling of the phosphorus atoms with the carbon atoms of the ethylene bridge and the phenyl substituents. The resonances for the methylene groups appear as doublets at $\delta$ 44.2 ($NCH_2$, $^2J_{PC}$ = 26.0 Hz) and 26.5 ppm ($CH_2PPh_2$, $^1J_{PC}$ = 14.2 Hz). Three doublets were observed for the carbon atoms of the phenyl substituents at $\delta$ 136.5, 133.1, and 132.1 ppm. Only the $C_\delta$ carbon atoms of the phenyl rings appear as a singlet at $\delta$ 128.9 ppm.

**Complexes of Bidentate Benzimdazolin-2-ylidene Ligands.** The phosphine-functionalized benzimidazolium salts **4**−**6** have been treated with silver oxide in dichloromethane to give the silver complexes **10**−**12**, which were subsequently used as carbene transfer agents[24] for the preparation of the palladium and platinum complexes **13**−**18** (Scheme 3). The silver complexes are colorless solids. Mass spectra indicate that two carbene ligands are coordinated to one silver atom. The characteristic downfield signal for the NCHN proton of the salts **4**−**6** around $\delta$ 10.1 ppm is missing in the $^1$H NMR spectra of the silver complexes **10**−**12**. The $^{13}$C NMR spectra show the

**Scheme 3. Synthesis of the Silver, Palladium, and Platinum Complexes with Phosphine-Functionalized Benzimidazolin-2-ylidene Ligands**




resonances for the coordinated carbene carbon atom in the region between $\delta$ 190.5 and 194.2 ppm which are typical values for silver NHC complexes.[25] The carbene carbon resonance could not be detected in the $^{13}$C NMR spectrum of **11**.

Both the $^1$H and the $^{13}$C NMR spectra of **10**−**12** show only broad resonances for the nuclei of the ethylene bridge caused by the flexibility of the noncoordinated phosphine donor function. The absence of coordination of the phosphine donor can also be concluded from the chemical shift for the phosphorus atoms (range $\delta$ −2.9 to −6.7 ppm) in the $^{31}$P NMR spectra, which are similar to the chemical shifts observed for the phosphorus atoms in the benzimidazolium salts **4**−**6** and other silver complexes with phosphine-substituted NHC ligands.[19a] Occasionally, the resonances for the carbon atoms of the six-membered ring of the benzimidazole moiety were not resolved, resulting in the observation of a reduced number of signals.

The palladium and platinum complexes **13**−**18** (Scheme 3) were obtained by a carbene transfer[24] reaction of the silver complexes **10**−**12** with $[PdCl_2(cod)]$ or $[PtCl_2(PhCN)_2]$ in dichloromethane for 12 h at ambient temperature. The bright yellow palladium complexes **13**−**15** and the white platinum complexes **16**−**18** were obtained as air-stable solids in about 80% yield.

The $^1$H NMR spectra of the palladium complexes **13**−**15** exhibit some differences compared to those of the benzimidazolium salts **4**−**6** or the silver complexes **10**−**12**. The protons of the $N-CH_2CH_2-P$ bridge become diastereotopic upon coordination of the phosphorus donor and appear as multiplets around $\delta \approx 5.0$ ppm ($NCH_2$) and $\delta \approx 3.0$ ppm ($PCH_2$). The same holds for the methylene protons of the other *N*-alkyl substituents. The bidentate coordination of the carbene/phosphine ligands is also visible in the $^{13}$C NMR spectra. The resonances for the carbene carbon atoms were observed upfield (range $\delta$ 169.1−

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169.3 ppm) from the resonances for the corresponding silver complexes. These values are close to those found for neutral bis(benzimidazolin-2-ylidene) palladium complexes with a *cis* arrangement of the NHC donor functions (*cis*-[$PdI_2$(benzimidazolin-2-ylidene)$_2$], range $\delta$ 172.06−175.14 ppm),[26] demonstrating again the electronic similarities between phosphine and carbene donors. No $^2J_{PC(carbene)}$ coupling was observed for the palladium complexes **13**−**15**. The $^{13}$C NMR spectra of the benzimidazolium salts **4**−**6** exhibit $^1J_{PC}$ and $^2J_{PC}$ coupling of the phosphorus atom and the carbon atoms of the ethylene bridge. Upon coordination of the ligands to palladium, the $^2J_{PC}$ coupling was no longer observed, while the coupling constant for the $^1J_{PC}$ coupling increased from $^1J_{PC} \approx 14$ Hz for the benzimidazolium salts to about 37 Hz (range $^1J_{PC}$ 36.9−38.0 Hz) for the complexes **13**−**15**. Coordination of the phosphorus atom was also evident from the downfield shift of the resonance for the phosphorus atom in the $^{31}$P NMR spectra from about $\delta$ −17.5 ppm for the benzimiazolium salts **4**−**6** or the silver complexes **10**−**12** (range $\delta$ −2.9 to −6.7 ppm) to values of $\delta$ 28.6−30.0 ppm for complexes **13**−**15**.

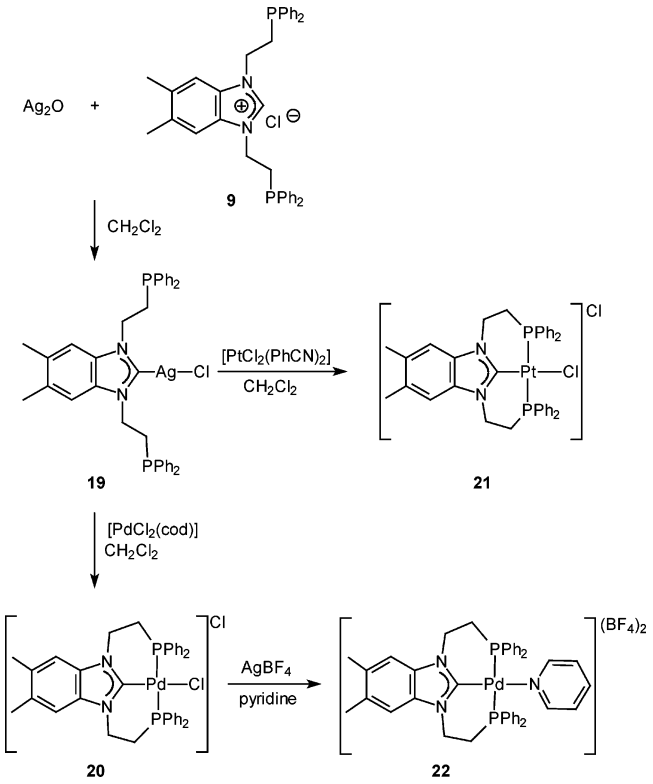
The NMR spectroscopic data of the platinum complexes **16**−**18** with the mixed phosphine/carbene ligands are very similar to those of the palladium complexes **13**−**15**. The resonances for the carbene carbon atoms in these complexes appear in the $^{13}$C NMR spectra as broad singlets (**16**) or doublets (chemical shift in the range $\delta$ 154.6−155.7 ppm) with $^2J_{PC}$ coupling constants of about 10 Hz. These are typical values for benzimidazolin-2-ylidene complexes of platinum.[27] The $^{31}$P NMR spectra reveal singlets in the range $\delta$ 4.2−9.6 ppm with Pt satellites ($^1J_{PPt} \approx 3700$ Hz) clearly demonstrating the interaction between the phosphorus and platinum nuclei.

**Pincer Complexes with Diphosphine-Functionalized Benzimidazolin-2-ylidene Ligands.** Silver complex **19** has been prepared from the benzimidazolium salt **9** and silver oxide (Scheme 4). Mass spectroscopy together with elemental analysis indicated the presence of a monocarbene complex, in contrast to the dicarbene complexes **10**−**12** (Scheme 3) obtained with the monophosphine-substituted benzimidazolium salts. The resonance for the carbene carbon atom was not detected in the $^{13}$C NMR spectrum of **19**, a behavior that has been seen previously with monocarbene complexes of silver(I).[19a,25] The resonance of the phosphorus atoms was observed at $\delta$ −3.0 ppm in the $^{31}$P NMR together with a broadening of the resonances for the carbon atoms ($^{13}$C NMR) and the protons ($^1$H NMR) of the ethylene bridge, indicating that the phosphine groups are not metal coordinated.

The carbene transfer reaction from silver to [$PdCl_2$(cod)] or [$PtCl_2$(PhCN)$_2$] was used to generate complexes **20**−**22** with the tridentate carbene/diphosphine ligand. Reaction of the pincer-type palladium complex **20** with silver tetrafluoroborate in pyridine produced the dicationic palladium complex **22**, which possesses a pyridine ligand coordinated in *trans*-position to the carbene donor function (Scheme 4).

The resonance for the carbene carbon atom in complex **20** was observed as a singlet at $\delta$ 161.8 ppm in the $^{13}$C NMR spectrum. As observed for the palladium complexes **13**−**15**, no coupling between the carbene carbon atom and the phosphorus donor functions was detected. Both phosphine phosphorus atoms exhibit coupling interactions with the carbon atoms of the attached phenylene rings, leading to the observation of triplets for three carbon atoms of the phenylene rings at $\delta$ 133.8, 129.5 and 128.7 ppm. P−C coupling interactions were also observed with the α-methylene group of the ethylene bridge, but not with the carbon atom in $\beta$-position. The coordination of both phosphine donors in **20** was confirmed by the observation of the downfield phosphorus resonance in the $^{31}$P NMR spectrum ($\delta$ 12.4 ppm) relative to the corresponding signal in the free benzimidazolium salt **9** ($\delta$ −17.7 ppm) or the silver complex **19** ($\delta$ −3.0 ppm).

**Scheme 4. Synthesis of the Silver (19), Palladium (20, 22), and Platinum (21) Complexes with the Diphosphine-Functionalized Benzimidazolin-2-ylidene Ligand**




Halide abstraction from **20** with $AgBF_4$ in pyridine gave complex **22** (Scheme 4). Surprisingly, the resonance for the carbene carbon atom *trans* to the pyridine donor is shifted upfield in **22** relative to **20** by about 10 ppm to $\delta$ 150.5 ppm. This upfield shift is apparently caused by the donor properties of the pyridine ligand. As expected, the phosphorus resonance in the $^{31}$P NMR of **22** is shifted downfield relative to **20** by about 10 ppm to $\delta$ 21.9 ppm.

The palladium complex **20** and its platinum analogue **21** exhibit very similar spectroscopic properties. Among the differences are the coupling of the carbene carbon atom and the phosphorus atoms via the platinum nucleus in the $^{13}$C NMR spectra, which led to the observation of a triplet for the carbene carbon atom with a with a $^2J_{PC}$ coupling constant of 9.0 Hz. Pt−P coupling has been observed in the $^{31}$P NMR spectrum of **21**, resulting in a singlet for the phosphine phosphorus atom at $\delta$ 14.1 ppm with Pt satellites ($^1J_{PPt} = 2434$ Hz). This interaction is also visible in the $^{195}$Pt NMR spectrum of **21**, which shows a triplet at $\delta$ −4482 ppm with a coupling constant of $^1J_{PPt} = 2450$ Hz.

**Molecular Structures of 13, 15, and 22·0.5MeOH.** The molecular structures of **13**, **15**, and **22** in **22**·0.5MeOH are depicted in Figures 1 and 2, and selected bond parameters are summarized in Table 1. The Pd−$C_{Carbene}$ bond lenghts in **13** [1.966(5) Å] and in **15** [1.973(3) Å] compare well with the corresponding parameters in palladium complexes with

(26) Hahn, F. E.; Foth, M. *J. Organomet. Chem.* **1999**, *585*, 241.
(27) Hahn, F. E.; Langenhahn, V.; Lügger, T.; Pape, T.; Le Van, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 3759

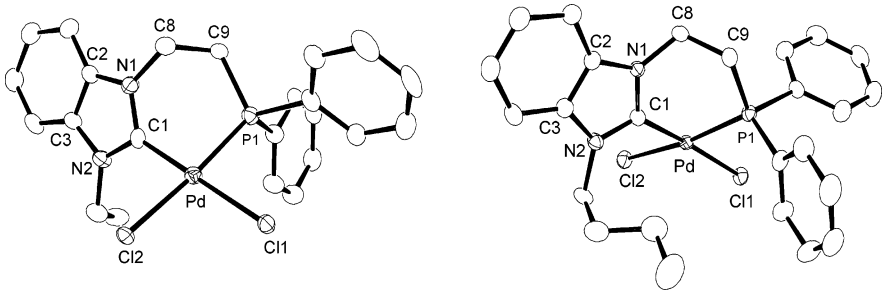



**Figure 1.** Molecular structures of **13** and **15**. Hydrogen atoms are omitted for clarity.

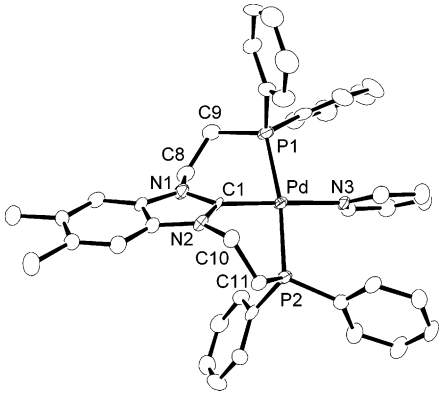



**Figure 2.** Molecular structure of **22**. Hydrogen atoms, the two tetrafluoroborate anions, and the solvent molecule are omitted for clarity.

**Table 1. Selected Bond Lengths [Å] and Angles (deg) of 13, 15, and 22·0.5MeOH**

| | | | **22**·0.5 MeOH | |
|---|---|---|---|---|
| | **13** | **15** | molecule 1 | molecule 2 |
| Pd−C1 | 1.966(5) | 1.973(3) | 1.974(5) | 1.980(6) |
| Pd−P1 | 2.2417(14) | 2.2248(8) | 2.3330(12) | 2.326(2) |
| Pd−Cl1 | 2.3656(13) | 2.3575(7) | | |
| Pd−P2 | 2.3056(13) | 2.3180(14) | | |
| Pd−Cl2 | 2.3903(13) | 2.3529(7) | | |
| Pd−N3 | 2.076(4) | 2.079(5) | | |
| C1−N1 | 1.362(7) | 1.353(3) | 1.347(6) | 1.357(8) |
| C1−N2 | 1.357(7) | 1.347(3) | 1.371(6) | 1.340(8) |
| C1−Pd−P1 | 87.6(2) | 88.80(8) | 84.70(14) | 86.6(2) |
| C1−Pd−Cl1 | 177.7(2) | 174.88(8) | | |
| C1−Pd−N3 | 177.6(2) | 177.8(2) | | |
| C1−Pd−Cl2 | 91.1(2) | 90.78(8) | | |
| C1−Pd−P2 | 87.23(14) | 85.7(2) | | |
| P1−Pd−Cl1 | 91.48(5) | 90.35(3) | | |
| P1−Pd−N3 | 95.2(1) | 95.00(13) | | |
| P1−Pd−Cl2 | 174.01(5) | 171.34(3) | | |
| P1−Pd−P2 | 171.69(5) | 171.20(6) | | |
| Cl1−Pd−Cl2 | 90.10(4) | 90.82(3) | | |
| P2−Pd−N3 | 92.82(11) | 92.64(13) | | |
| N1−C1−N2 | 105.6(5) | 106.8(2) | 106.4(4) | 108.5(6) |

phosphine-functionalized imidazolin-2-ylidene ligands [Pd−C ≈ 1.99 Å][16b,d,e] and also fall in the range described for neutral dicarbene complexes of the type *cis*-[$PdI_2$(benzimidazolin-2-ylidene)$_2$] [Pd−$C_{Carbene}$ ≈ 1.990 Å].[26] They are, however, shorter than reported for palladium complexes with benzimidazolin-2-ylidene ligands in *trans* configuration [range Pd−$C_{Carbene}$ 2.019(2)−2.040(3) Å].[22a,c] Otherwise the Pd−P bonds are in the expected range for complexes with chelating phosphine/carbene ligands [2.276(9)−2.461(7) Å].[16]

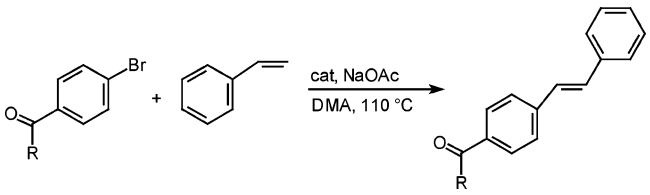
The Pd−Cl bonds in **13** show different bond lenghts [Pd−Cl1 2.3656(13) Å, Pd−Cl2 2.3903(13) Å], with the longer separation associated with the Pd−Cl2 bond *trans* to the phosphine donor. A different order of Pd−Cl bond lenghts would have been expected on the basis of the relative *trans* influence of the phosphine and carbene ligands. This situation has been noticed previously[16b] and is further complicated by the observation of essentially equal Pd−Cl bond distances in the related complex **15**. The reasons for this behavior are currently not understood. Both complexes are coordinated in a slightly distorted square-planar fashion. The angle C1−Pd−P1 within the chelate ring is smaller than 90° for both complexes. The P−Pd−Cl2 angle shows the greatest deviation (174.01(5)° for **13** and 171.34(4)° for **15**) from a perfect square-planar arrangement in both complexes.

The asymmetric unit of **22**·0.5MeOH contains two nearly identical independent molecules. Only one of these is depicted in Figure 2. Selected bond distances and angles for both molecules are listed in Table 1. The palladium atom in **22** adopts a square-planar coordination geometry. The benzimidazole ring is oriented almost perpendicular to the Pd/C1/P1/P2/N3 plane. This orientation is essential to allow the coordination of both phosphorus atoms. It has, however, been observed previously with sterically more flexible palladium complexes with benzimidazolin-2-ylidene ligands.[26] A comparison of **22** with the similar palladium complex bearing a diphosphine-substituted imidazolin-2-ylidene ligand reported by Lee et al.[19a] revealed similarities regarding the Pd−$C_{carbene}$ bond distance of 1.985(5) Å [1.974(5) and 1.980(6) Å for **22**]. The Pd−P distances in **22** are also very similar to those found in the palladium complex with the imidazolin-2-ylidene ligand (2.3300(11) Å).[19a] The Pd−P bond distances in **22** are longer than in complexes **13** and **15**.

**Catalysis.** The Pd-catalyzed coupling reaction of *para*-functionalized aryl bromides and styrene was studied using the complexes **13**−**15** and **20** as precatalysts (Table 2). The coupling of 4-bromobenzaldehyde with styrene proceeded with good yield over 2 h with 1.0 mol % of precatalyst at the relatively low temperature of 110 °C. Complete conversion was reached using only 0.01 mol % of catalyst but a prolonged reaction time of 24 h at 110 °C. The coupling of 4-bromoacetophenone with styrene proceeded with lower yield. The pincer-type complex **20** showed the lowest activity in the coupling reactions.

The conversion rate for the coupling reactions (1.0 mol % catalyst, reaction time 2 h) was also studied (Figure 3). As shown in the diagram, the conversion is fast for 4-bromobenzaldehyde and the palladium complexes **13**−**15** with more than 80% conversion after 2 h (Figure 3, left). The pincer-type palladium complex **20** is less active, with only 72% conversion over 2 h. The rate of the C−C coupling of 4-bromoacetophenone with styrene was also monitored over 2 h (Figure 3, right). Again compounds **13**−**15** catalyzed the coupling reaction with more than 70% conversion within 2 h, while only 52% conversion was reached with the pincer-type palladium complex **20**. From these data we conclude that complexes with bidentate mixed phosphine/carbene ligands such as **13**−**15** are more active

**Table 2. Pd-Catalyzed Coupling Reaction of *para*-Functionalized Aryl Bromides and Styrene[a]**




| entry | catalyst | mol % | R | time, h | yield, % |
|---|---|---|---|---|---|
| 1 | **13** | 1.0 | H | 2 | 86.0 |
| 2 | **14** | 1.0 | H | 2 | 95.9 |
| 3 | **15** | 1.0 | H | 2 | 90.4 |
| 4 | **20** | 1.0 | H | 2 | 72.0 |
| 5 | **13** | 0.01 | H | 24 | 99.8 |
| 6 | **14** | 0.01 | H | 24 | 100.0 |
| 7 | **15** | 0.01 | H | 24 | 100.0 |
| 8 | **20** | 0.01 | H | 24 | 100.0 |
| 9 | **13** | 1.0 | $CH_3$ | 2 | 74.0 |
| 10 | **14** | 1.0 | $CH_3$ | 2 | 78.1 |
| 11 | **15** | 1.0 | $CH_3$ | 2 | 79.4 |
| 12 | **20** | 1.0 | $CH_3$ | 2 | 52.0 |

[a] Reaction conditions: 1 mmol of the aryl bromide, 1.4 mmol of styrene, 2 mmol of NaOAc, Pd catalyst, and 3 mL of DMA, 110 °C. Yields were determined by gas chromatography.

catalysts than complex **20**, with the sterically more demanding tridentate pincer-type ligand.

Instead of styrene, *n*-butyl acrylate was used as olefinic substrate in C−C coupling reactions with 4-functionalized aryl bromides. More than 90% conversion was observed with 0.1 mol % of the palladium precatalysts **13**−**15** and **20**. Smaller amounts of precatalysts (0.01 mol %) gave more than 70% conversion after 24 h at 110 °C.

The catalytic activity of palladium complexes with mixed phosphine/benzimidazolin-2-ylidene ligands compares favorably with other palladium carbene complexes.[16,17,28] Particularly complexes **13**−**15** with a benzimidazolin-2-ylidene and only one phosphine donor are more active than pincer-type bis(benzimidazolin-2-ylidene) palladium complexes reported by us earlier[22a] or the pincer complexes of type **20** with a monocarbene/diphosphine ligand. Additional coupling experiments with deactivated aryl bromides and aryl chlorides are in progress.

## Conclusions

We described the preparation of mono- and diphosphine-functionalized benzimidazolium chlorides. These salts have been used for the synthesis of palladium and platinum complexes with bidentate $PC^{NHC}$ and tridentate $PC^{NHC}P$ ligands via the corresponding silver complexes. Reaction of [Pd($PC^{NHC}P$)Cl]Cl (**20**) and silver tetrafluoroborate in pyridine gave the dicationic complex **22** with the pyridine donor in *trans* position to the carbene carbon atom. The palladium complexes **13**−**15** show a high activity in C−C coupling reactions of *para*-functionalized aryl bromides with styrene and *n*-butyl acrylate at 110 °C, while the pincer complex [Pd($PC^{NHC}P$)Cl]Cl is less active in such coupling reactions.

## Experimental Section

**General Procedures.** All operations were carried out in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried with standard methods and freshly distilled prior to use. Diphenylphosphine and [$PtCl_2(NCC_6H_5)_2$] were purchased from Aldrich and Fluka. [$PdCl_2$(cod)][29] and the *N*-alkylated benzimidazole derivatives[22] were prepared using published procedures. NMR spectra were recorded on Bruker AC 200 (200 MHz) or Bruker AMX 400 (400 MHz) spectrometers. Mass spectra were measured on a Varian MAT 212 instrument. Elemental analyses (C, H, N) were obtained for all compounds using an Elementar Vario EL III elemental analyzer at the Westfälische Wilhelms-Universität Münster.

**General Procedure for the Synthesis of *N*-(2-Chloroethyl)-*N*′-alkylbenzimidazolium Bromides 1−3.** An *N*-alkylated benzimidazole derivative (10 mmol) was stirred in 20 mL of 1-bromo-2-chloroethane for one week under exclusion of light. The liquid was removed, and the white residue was dissolved in 3 mL of methanol. This solution was added dropwise to ice cold diethyl ether. A white precipitate formed, which was collected by filtration, washed two times with a small amount of diethyl ether, and dried in vacuo.

***N*-(2-Chloroethyl)-*N*′-ethylbenzimidazolium Bromide (1).** Yield: 83.0%. $^1$H NMR (200.1 MHz, $CD_3OD$): $\delta$ 9.79 (s, 1H, NCHN), 8.10 − 8.02 (m, 2H, Ar−H), 7.77−7.72 (m, 2H, Ar−H), 4.98 (t, 2H, $^3J$ = 5.5 Hz, NC$H_2$CH$_2$Cl), 4.64 (q, 2H, $^3J$ = 7.3 Hz, NC$H_2$CH$_3$), 4.16 (t, 2H, $^3J$ = 5.5 Hz, NCH$_2$C$H_2$Cl), 1.69 (t, 3H, $^3J$ = 7.3 Hz, NCH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, $CD_3OD$): $\delta$ 143.8 (NCHN), 133.7, 133.6, 129.4, 129.3, 115.6, 115.5 (Ar−C), 50.8 (NCH$_2$CH$_2$Cl), 44.8 (NCH$_2$CH$_3$), 44.0 (NCH$_2$CH$_2$Cl), 15.6 (NCH$_2$-CH$_3$). MS (MALDI): *m*/*z* 209 ([M − Br]$^+$). Anal. Calcd for $C_{11}H_{14}N_2BrCl$ (289.7): C, 45.61; H, 4.87; N, 9.67. Found: C, 45.23; H, 4.43; N, 9.56.

***N*-(2-Chloroethyl)-*N*′-propylbenzimidazolium Bromide (2).** Yield: 85.4%. $^1$H NMR (200.1 MHz, $CD_3OD$): $\delta$ 9.84 (s, 1H, NCHN), 8.16−8.00 (m, 2H, Ar−H), 7.81−7.69 (m, 2H, Ar−H), 5.00 (t, 2H, $^3J$ = 5.5 Hz, NC$H_2$CH$_2$Cl), 4.59 (t, 2H, $^3J$ = 7.3 Hz, NC$H_2$CH$_2$CH$_3$), 4.17 (t, 2H, $^3J$ = 5.5 Hz, NCH$_2$C$H_2$Cl), 2.08 (sext, 2H, $^3J$ = 7.3 Hz, NCH$_2$C$H_2$CH$_3$), 1.04 (t, 3H, $^3J$ = 7.3 Hz, NCH$_2$-CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, $CD_3OD$): $\delta$ 143.5 (NCHN), 132.9, 132.7, 128.8, 128.4, 114.8, 114.7 (Ar−C), 50.1 (NCH$_2$CH$_2$Cl), 49.9 (NCH$_2$CH$_2$CH$_3$), 43.2 (NCH$_2$CH$_2$Cl), 23.6 (NCH$_2$CH$_2$CH$_3$), 11.1 (NCH$_2$CH$_2$CH$_3$). MS (MALDI): *m*/*z* 223 ([M − Br]$^+$). Anal. Calcd for $C_{12}H_{16}N_2BrCl$ (303.7): C, 47.46; H, 5.31; N, 9.22. Found: C, 46.68; H, 4.97; N, 9.18.

***N*-(2-Chloroethyl)-*N*′-butylbenzimidazolium Bromide (3).** Yield: 93.4%. $^1$H NMR (200.1 MHz, $CD_3OD$): $\delta$ 9.85 (s, 1H, NCHN), 8.17−8.04 (m, 2H, Ar−H), 7.84−7.72 (m, 2H, Ar−H), 5.02 (t, 2H, $^3J$ = 5.5 Hz, NC$H_2$CH$_2$Cl), 4.65 (t, 2H, $^3J$ = 7.4 Hz, NC$H_2$CH$_2$CH$_2$CH$_3$), 4.20 (t, 2H, $^3J$ = 5.5 Hz, NCH$_2$C$H_2$Cl), 2.08 (quint, 2H, $^3J$ = 7.4 Hz, NCH$_2$C$H_2$CH$_2$CH$_3$), 1.50 (sext, 2H, $^3J$ = 7.4 Hz, NCH$_2$CH$_2$C$H_2$CH$_3$), 1.05 (t, 3H, $^3J$ = 7.4 Hz, NCH$_2$CH$_2$-CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, $CD_3OD$): $\delta$ 145.7 (NCHN), 133.5, 129.4, 129.3, 115.7, 115.5 (Ar−C), 50.8 (NCH$_2$CH$_2$Cl), 49.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 44.0 (NCH$_2$CH$_2$Cl), 33.0 (NCH$_2$CH$_2$CH$_2$-CH$_3$), 21.5 (NCH$_2$CH$_2$CH$_2$CH$_3$), 14.7 (NCH$_2$CH$_2$CH$_2$CH$_3$). MS (MALDI): *m*/*z* 237 ([M − Br]$^+$). Anal. Calcd for $C_{13}H_{18}N_2BrCl$ (317.7): C, 49.15; H, 5.71; N, 8.82. Found: C, 48.55; H, 5.56; N, 8.73.

**General Procedure for the Synthesis of *N*-(2-Diphenylphosphinoethyl)-*N*′-alkylbenzimidazolium Chlorides (4−6).** A sample

(28) (a) McGuinness, D. S.; Green, M. J., Cavell, K. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1998**, *565*, 165. (b) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596. (c) McGuinness, D. S.; Cavell, K. J. *Organometallics* **2000**, *19*, 741. (d) Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, A. J. P., Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617*−*618*, 546. (e) Herrmann, W. A.; Reisinger, C.-P.; Spiegler, M. *J. Organomet. Chem.* **1998**, *557*, 93. (f) Herrmann, W. A.; Schwarz, J.; Gardiner, M. G.; Spiegler, M. *J. Organomet. Chem.* **1999**, *575*, 80. (g) Gardiner, M. G.; Herrmann, W. A.; Reisinger, C.-P.; Schwarz, J.; Spiegler, M. *J. Organomet. Chem.* **1999**, *572*, 239. (h) Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*−*618*, 616. (i) Huynh, H. V.; Neo, T. C.; Tan, G. K. *Organometallics* **2006**, *25*, 1298.

(29) Drew, D.; Doyle, J. R. *Inorg. Synth.* **1972**, *13*, 47.

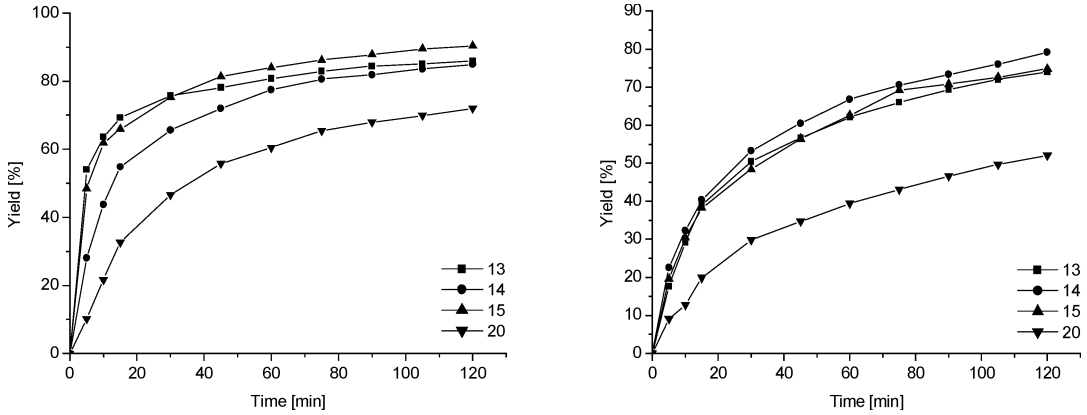



**Figure 3.** Reaction profiles for the coupling reaction of 4-bromobenzaldehyde (left) and 4-bromoacetophenone (right) with styrene catalyzed by 1 mol % of **13**−**15** and **20**.

of KO$^t$Bu (1 mmol, 0.112 g) was dissolved in 2 mL of DMSO, and diphenylphosphine (1.1 mmol, 0.21 mL) was added. The color of the solution changed immediately from bright yellow to red. The solution was stirred for 2 h at ambient temperature. The reaction mixture was then added dropwise to a stirred solution containing one of the benzimidazolium salts **1**−**3** (0.95 mmol) and KCl (5 mmol, 0.373 g) in DMSO (1 mL). The solvent was removed under reduced pressure after stirring at ambient temperature for 12 h. The residue was then dissolved in 10 mL of methanol and filtered through Celite. The solvent was removed and the air-sensitive oily residue washed two times with diethyl ether (3 mL each) and dried in vacuo.

***N*-(2-Diphenylphosphinoethyl)-*N*′-ethylbenzimidazolium Chloride (4).** Yield: 86.4%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 10.06 (s, 1H, NCHN), 8.02−7.91 (m, 2H, Ar−H), 7.67−7.57 (m, 2H, Ar−H), 7.45−7.25 (m, 10H, PPh−H), 4.64 (t, 2H, $^3J$ = 7.4 Hz, NC$H_2$CH$_2$PPh$_2$), 4.38 (q, 2H, $^3J$ = 7.2 Hz, NC$H_2$CH$_3$), 2.88 (t, 2H, $^3J$ = 7.4 Hz, NCH$_2$C$H_2$PPh$_2$), 1.48 (t, 3H, $^3J$ = 7.2 Hz, NCH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 141.7 (NCHN), 136.6 (d, $J_{PC}$ = 12.2 Hz, PPh−C), 133.5 (d, $J_{PC}$ = 15.9 Hz, PPh−C), 132.3 (d, $J_{PC}$ = 19.6 Hz, PPh−C), 130.3, 130.0 (Ar−C), 128.5 (d, $J_{PC}$ = 6.2 Hz, PPh−C), 126.3, 113.6, 113.4 (Ar−C), 48.5 (N$CH_2$CH$_3$), 44.6 (d, $^2J_{PC}$ = 24.4 Hz, N$CH_2$CH$_2$PPh$_2$), 26.4 (d, $^1J_{PC}$ = 14.1 Hz, NCH$_2$$CH_2$PPh$_2$), 14.0 (NCH$_2$$CH_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ −17.5. MS (MALDI): *m*/*z* 359 ([M − Cl]$^+$). Anal. Calcd for $C_{23}H_{24}N_2ClP$ (394.9): C, 69.96; H, 6.13; N, 7.09. Found: C, 69.54; H, 6.23; N, 6.94.

***N*-(2-Diphenylphosphinoethyl)-*N*′-propylbenzimidazolium Chloride (5).** Yield: 91.2%. $^1$H NMR (400.1 MHz, DMSO-$d_6$): $\delta$ 10.14 (s, 1H, NCHN), 8.00−7.90 (m, 2H, Ar−H), 7.60−7.55 (m, 2H, Ar−H), 7.44−7.39 (m, 2H, PPh−H$_\delta$), 7.38−7.32 (m, 4H, PPh−H$_\beta$), 7.30−7.24 (m, 4H, P−PhH$_\gamma$), 4.64 (t, 2H, $^3J$ = 7.5 Hz, NC$H_2$CH$_2$PPh$_2$), 4.36 (t, 2H, $^3J$ = 7.2 Hz, NC$H_2$CH$_2$CH$_3$), 2.88 (t, 2H, $^3J$ = 7.5 Hz, NCH$_2$C$H_2$PPh$_2$), 1.84 (sext, 2H, $^3J$ = 7.2 Hz, NCH$_2$C$H_2$CH$_3$), 0.86 (t, 3H, $^3J$ = 7.2 Hz, NCH$_2$CH$_2$C$H_3$). $^{13}$C NMR (100.6 MHz, DMSO-$d_6$): $\delta$ 142.1 (NCHN), 136.5 (d, $J_{PC}$ = 12.4 Hz, PPh−C), 133.5 (d, $J_{PC}$ = 16.5 Hz, PPh−C), 132.3 (d, $J_{PC}$ = 19.4 Hz, PPh−C), 130.8, 130.7 (Ar−C), 128.4 (d, $J_{PC}$ = 6.3 Hz, PPh−C), 126.3, 113.6, 113.5 (Ar−C), 47.9 (N$CH_2$CH$_2$CH$_3$), 44.5 (d, $^2J_{PC}$ = 24.3 Hz, N$CH_2$CH$_2$PPh$_2$), 26.5 (d, $^1J_{PC}$ = 14.3 Hz, NCH$_2$$CH_2$PPh$_2$), 22.0 (NCH$_2$$CH_2$CH$_3$), 10.6 (NCH$_2$CH$_2$$CH_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ −17.7. MS (MALDI): *m*/*z* 373 ([M − Cl]$^+$). Anal. Calcd for $C_{24}H_{26}N_2ClP$ (408.9): C, 70.50; H, 6.41; N, 6.85. Found: C, 69.53; H, 6.28; N, 6.37.

***N*-(2-Diphenylphosphinoethyl)-*N*′-butylbenzimidazolium Chloride (6).** Yield: 90.2%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 10.03 (s, 1H, NCHN), 7.99−7.90 (m, 2H, Ar−H), 7.63−7.54 (m, 2H, Ar−H), 7.33−7.22 (m, 10H, PPh−H), 4.64 (t, 2H, $^3J$ = 7.4 Hz, NC$H_2$CH$_2$PPh$_2$), 4.37 (t, 2H, $^3J$ = 7.2 Hz, NC$H_2$CH$_2$CH$_2$CH$_3$), 2.87 (t, 2H, $^3J$ = 7.4 Hz, NCH$_2$C$H_2$PPh$_2$), 1.79 (quint, 2H, $^3J$ = 7.2 Hz, NCH$_2$C$H_2$CH$_2$CH$_3$), 1.29 (sext, 2H, $^3J$ = 7.2 Hz, NCH$_2$CH$_2$C$H_2$CH$_3$), 0.87 (t, 3H, $^3J$ = 7.2 Hz, NCH$_2$CH$_2$CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 142.0 (NCHN), 136.5 (d, $J_{PC}$ = 12.4 Hz, PPh−C), 133.5 (d, $J_{PC}$ = 15.6 Hz, PPh−C), 132.2 (d, $J_{PC}$ = 19.7 Hz, PPh−C), 130.2, 130.0 (Ar−C), 128.6 (d, $J_{PC}$ = 6.1 Hz, P−PhC), 126.4, 126.3, 113.6, 113.4 (Ar−C), 48.0 (N$CH_2$CH$_2$CH$_2$CH$_3$), 45.2 (d, $^2J_{PC}$ = 24.1 Hz, N$CH_2$CH$_2$PPh$_2$), 30.5 (NCH$_2$$CH_2$CH$_2$CH$_3$), 26.2 (d, $^1J_{PC}$ = 14.2 Hz, NCH$_2$$CH_2$PPh$_2$), 18.9 (NCH$_2$CH$_2$$CH_2$CH$_3$), 13.3 (NCH$_2$CH$_2$CH$_2$$CH_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ −17.7. MS (MALDI): *m*/*z* 387 ([M − Cl]$^+$). Anal. Calcd for $C_{25}H_{28}N_2ClP$ (422.9): C, 71.00; H, 6.67; N, 6.62. Found: C, 70.53; H, 6.52; N, 6.47.

***N*-(2-Chloroethyl)-5,6-dimethylbenzimidazole (7).** A sample of 5,6-dimethylbenzimidazole (34.2 mmol, 5.0 g) was dissolved in 100 mL of 1,2-dichloroethane together with potassium hydroxide (225 mmol, 12.6 g), potassium carbonate (72 mmol, 10.0 g), and a catalytic amount of tetrabutyl ammonium bromide (0.7 mmol, 0.237 g). The mixture was stirred for 48 h at ambient temperature. The resulting suspension was filtered, and the filtrate was washed twice with water (25 mL each). The organic layer was dried over magnesium sulfate and the solvent was removed. Then the bright yellow residue was washed twice with petroleum ether (10 mL each) and dried in vacuo. Yield: 83.1%. $^1$H NMR (200.1 MHz, CD$_3$OD): $\delta$ 8.05 (s, 1H, NCHN), 7.43 (s, 1H, Ar−H), 7.34 (s, 1H, Ar−H), 4.55 (t, 2H, $^3J$ = 5.8 Hz, NC$H_2$CH$_2$Cl), 3.93 (t, 2H, $^3J$ = 5.8 Hz, NCH$_2$C$H_2$Cl), 2.39 (s, 3H, CH$_3$), 2.35 (s, 3H, CH$_3$). $^{13}$C NMR (50.3 MHz, CD$_3$OD): $\delta$ 141.7 (NCHN), 132.8, 129.7, 120.4, 120.2, 112.2, 111.3 (Ar−C), 47.6 (NCH$_2$$CH_2$Cl), 43.8 (N$CH_2$CH$_2$Cl), 20.6 (CH$_3$), 20.4 (CH$_3$). MS (MALDI): *m*/*z* 209 ([M]$^+$). Anal. Calcd for $C_{11}H_{13}N_2Cl$ (208.7): C, 63.29; H, 6.28; N, 13.42. Found: C, 62.93; H, 5.87; N, 13.18.

***N*,*N*′-Bis(2-chloroethyl)-5,6-dimethylbenzimidazolium Bromide (8).** A sample of **7** (6.0 mmol, 1.251 g) was dissolved in 1-bromo-2-chloroethane (10 mL). The reaction mixture was stirred at ambient temperature under exclusion of light for one week. The solvent was removed in vacuo, and the residue was dissolved in 3 mL of methanol. This solution was added dropwise to 150 mL of diethyl ether. A pale yellow precipitate formed, which was collected, washed with 5 mL of diethyl ether, and dried. Yield: 82.3%. $^1$H NMR (200.1 MHz, CD$_3$OD): $\delta$ 9.67 (s, 1H, NCHN), 7.85 (s, 2H, Ar−H), 4.92 (t, 4H, $^3J$ = 5.4 Hz, NC$H_2$CH$_2$Cl), 4.13 (t, 4H, $^3J$ = 5.4 Hz, NCH$_2$C$H_2$Cl), 2.51 (s, 6H, CH$_3$). $^{13}$C NMR (50.3 MHz, CD$_3$OD): $\delta$ 143.3 (NCHN), 136.3, 131.0, 114.3 (Ar−C), 48.6 (NCH$_2$$CH_2$Cl), 43.1 (N$CH_2$CH$_2$Cl), 20.6 (CH$_3$). MS (MALDI): *m*/*z* 272 ([M − Br]$^+$). Anal. Calcd for $C_{13}H_{17}N_2BrCl_2$ (352.1): C, 44.34; H, 4.87; N, 7.96. Found: C, 43.87; H, 5.02; N, 7.98.

***N*,*N*′-Bis(2-diphenylphosphinoethyl)-5,6-dimethylbenzimidazolium Chloride (9).** A sample of KO$^t$Bu (2.0 mmol, 0.224 g) was dissolved in 2 mL of DMSO, and 2.2 mmol (0.42 mL) of

diphenylphosphine was added to this solution. The resulting red solution was stirred for 2 h at ambient temperature. Then the reaction mixture was added dropwise to a stirred solution containing 1.0 mmol (0.352 g) of **8** and 10 mmol (0.746 g) of KCl dissolved in 2 mL of DMSO. The reaction mixture was stirred for 12 h at ambient temperature, and the solvent was removed in vacuo. Methanol (10 mL) was added to the residue. The resulting suspension was filtered through Celite and the filtrate brought to dryness. The oily, pale yellow residue was washed with 5 mL of diethyl ether and dried in vacuo. Yield: 76.8%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 10.18 (s, 1H, NCHN), 7.94−7.80 (m, 8H, Ar−H, PPh−H), 7.73−7.37 (m, 14H, PPh−H), 4.65 (t, 4H, $^3J$ = 7.4 Hz, NC$H_2$CH$_2$PPh$_2$), 2.98 (t, 4H, $^3J$ = 7.4 Hz, NCH$_2$C$H_2$PPh$_2$), 2.53 (s, 6H, CH$_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 140.6 (NCHN), 136.5 (d, $^1J_{PC}$ = 12.2 Hz, PPh−C$_\alpha$), 136.0, 133.3 (Ar−C), 133.1 (d, $^2J_{PC}$ = 19.5 Hz, PPh−C$_\beta$), 132.1 (d, $^3J_{PC}$ = 7.3 Hz, PPh−C$_\gamma$), 128.9 (s, PPh−C$_\delta$), 112.8 (Ar−C), 44.2 (d, $^2J_{PC}$ = 26.0 Hz, NCH$_2$CH$_2$PPh$_2$), 26.5 (d, $^1J_{PC}$ = 14.2 Hz, NCH$_2$CH$_2$PPh$_2$), 19.8 (CH$_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ −17.7. MS (MALDI): $m/z$ 571 ([M − Cl]$^+$). Anal. Calcd for $C_{37}H_{37}N_2ClP_2$ (607.1): C, 73.20; H, 6.14; N, 4.61. Found: C, 72.51; H, 5.89; N, 4.23.

**General Procedure for the Synthesis of Bis{*N*-(2-diphenylphosphinoethyl)-*N*′-alkylbenzimidazolin-2-ylidene}silver(I) Dichloroargentates (10−12).** A sample of a phosphine-functionalized benzimidazolium salt **4**−**6** (1 mmol) and silver oxide (1.2 mmol, 0.278 g) were dissolved in 50 mL of dichloromethane. The mixture was stirred for 2 days under exclusion of light and then filtered through Celite. The filtrate was brought to dryness in vacuo. The solid residue obtained was dissolved in a few milliliters of dichloromethane, and this solution was added dropwise to 100 mL of diethyl ether. A colorless, air-sensitive precipitate formed, which was isolated by filtration and dried in vacuo.

**Bis{*N*-(2-diphenylphosphinoethyl)-*N*′-ethylbenzimidazolin-2-ylidene}silver(I) Dichloroargentate (10).** Yield: 75.5%. $^1$H NMR (200.1 MHz, CD$_2$Cl$_2$): $\delta$ 7.95−7.79 (m, 4H, Ar−H), 7.78−7.65 (m, 4H, Ar−H), 7.57−7.42 (m, 8H, PPh−H), 7.31−7.06 (m, 12H, PPh−H), 5.31−5.10 (m, 4H, NC$H_2$CH$_2$PPh$_2$), 4.37−4.17 (m, 4H, NC$H_2$CH$_3$), 3.28−2.99 (m, 4H, NCH$_2$C$H_2$PPh$_2$), 1.23 (t, 6H, NCH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, CD$_2$Cl$_2$): $\delta$ 194.2 (NCN), 132.9 (d, $J_{PC}$ = 15.7 Hz, PPh−C), 131.6 (d, $J_{PC}$ = 8.4 Hz, PPh−C), 130.0 (Ar−C), 128.5 (d, $J_{PC}$ = 9.9 Hz, PPh−C), 127.4 (d, $J_{PC}$ = 11.7 Hz, PPh−C), 123.4, 123.2, 111.2, 111.1 (Ar−C), 45.7 (d, $^2J_{PC}$ = 11.2 Hz, NCH$_2$CH$_2$PPh$_2$), 44.2 (NCH$_2$CH$_3$), 28.4 (d, $^1J_{PC}$ = 8.7 Hz, NCH$_2$CH$_2$PPh$_2$), 15.5 (NCH$_2$CH$_3$). $^{31}$P NMR (81.0 MHz, CD$_2$Cl$_2$): $\delta$ −6.7. MS (MALDI): $m/z$ 824 ([M − AgCl$_2$]$^+$). Anal. Calcd for $C_{46}H_{46}N_4Ag_2Cl_2P_2$ (1003.5): C, 55.06; H, 4.62; N, 5.58. Found: C, 54.48; H, 4.53; N, 5.47.

**Bis{*N*-(2-diphenylphosphinoethyl)-*N*′-propylbenzimidazolin-2-ylidene}silver(I) Dichloroargentate (11).** Yield: 78.1%. $^1$H NMR (200.1 MHz, CD$_2$Cl$_2$): $\delta$ 7.87−7.79 (m, 4H, Ar−H), 7.73 − 7.64 (m, 4H, Ar−H), 7.52−7.12 (m, 20H, PPh−H), 5.15 (m, 4H, NC$H_2$CH$_2$PPh$_2$), 4.14 (m, 4H, NC$H_2$CH$_2$CH$_3$), 3.03 (m, 4H, NCH$_2$C$H_2$PPh$_2$), 1.77 (m, 4H, NCH$_2$C$H_2$CH$_3$), 0.87 (t, 6H, NCH$_2$CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, CD$_2$Cl$_2$): $\delta$ 133.2 (d, $J_{PC}$ = 15.7 Hz, PPh−C), 132.9, 132.8 (Ar−C), 131.9 (d, $J_{PC}$ = 8.6 Hz, PPh−C), 129.3 (d, $J_{PC}$ = 11.3 Hz, PPh−C), 127.8 (d, $J_{PC}$ = 11.3 Hz, PPh−C), 123.7, 123.6, 111.8, 111.4 (Ar−C), 51.1 (NCH$_2$CH$_2$CH$_3$), 46.4 (s, br, NCH$_2$CH$_2$PPh$_2$), 28.5 (s, br, NCH$_2$CH$_2$PPh$_2$), 24.0 (NCH$_2$CH$_2$CH$_3$), 11.6 (NCH$_2$CH$_2$CH$_3$). The resonance for the carbene carbon atom was not observed. $^{31}$P NMR (81.0 MHz, CD$_2$Cl$_2$): $\delta$ −5.7. MS (MALDI): $m/z$ 852 ([M − AgCl$_2$]$^+$). Anal. Calcd for $C_{48}H_{50}N_4Ag_2Cl_2P_2$ (1031.5): C, 55.89; H, 4.89; N, 5.43. Found: C, 54.79; H, 4.47; N, 5.31.

**Bis{*N*-(2-diphenylphosphinoethyl)-*N*′-butylbenzimidazolin-2-ylidene}silver(I) Dichloroargentate (12).** Yield: 81.1%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 7.59−7.45 (m, 8H, Ar−H), 7.32−7.11 (m, 20H, PPh−H), 5.24−5.05 (m, 4H, NC$H_2$CH$_2$PPh$_2$), 4.16 (t, 4H, $^3J$ = 7.2 Hz, NC$H_2$CH$_2$CH$_2$CH$_3$), 3.02 (m, 4H, NCH$_2$C$H_2$-PPh$_2$), 1.71 (quint, 4H, $^3J$ = 7.2 Hz, NCH$_2$C$H_2$CH$_2$CH$_3$), 1.32 (sext, 4H, $^3J$ = 7.2 Hz, NCH$_2$CH$_2$C$H_2$CH$_3$), 0.91 (t, 6H, $^3J$ = 7.2 Hz, NCH$_2$CH$_2$CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 190.5 (NCN), 133.1 (d, $J_{PC}$ = 16.4 Hz, PPh−C), 131.8 (d, $J_{PC}$ = 7.4 Hz, PPh−C), 130.4 (Ar−C), 128.8 (d, $J_{PC}$ = 9.8 Hz, PPh−C), 127.7 (d, $J_{PC}$ = 11.1 Hz, PPh−C), 123.6, 111.6, 111.3 (Ar−C), 49.4 (NCH$_2$CH$_2$CH$_2$CH$_3$), 46.4 (d, $^2J_{PC}$ = 10.6 Hz, NCH$_2$CH$_2$PPh$_2$), 32.6 (NCH$_2$CH$_2$CH$_2$CH$_3$), 28.2 (s, br, NCH$_2$CH$_2$PPh$_2$), 20.5 (NCH$_2$-CH$_2$CH$_2$CH$_3$), 14.0 (NCH$_2$CH$_2$CH$_2$CH$_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ −2.9. MS (MALDI): $m/z$ 880 ([M − AgCl$_2$]$^+$). Anal. Calcd for $C_{50}H_{54}N_4Ag_2Cl_2P_2$ (1059.3): C, 56.68; H, 5.14; N, 5.29. Found: C, 56.09; H, 4.98; N, 5.17.

**General Procedure for the Synthesis of {*N*-(2-Diphosphinoethyl)-*N*′-alkylbenzimidazolin-2-ylidene}palladium(II) Dichlorides (13−15).** One equivalent of one of the silver complexes **10**−**12** (0.5 mmol) was dissolved in 60 mL of dichloromethane. To this solution was added [PdCl$_2$(cod)] (1.0 mmol, 0.285 g), and the reaction mixture was stirred for 14 h at ambient temperature. The reaction mixture was filtered through Celite, and the solvent was removed in vacuo. The residue was dissolved in a small amount of dichloromethane, and the solution was added dropwise to cold diethyl ether (200 mL). The bright yellow precipitate obtained was collected by filtration, washed with 5 mL of diethyl ether, and dried in vacuo.

**{*N*-(2-Diphenylphosphinoethyl)-*N*′-ethylbenzimidazolin-2-ylidene}palladium(II) Dichloride (13).** Yield: 83.4%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 7.83−7.63 (m, 4H, Ar−H), 7.57 − 7.37 (m, 10H, PPh−H), 5.12−5.02 (m, 1H, NC$H_2$CH$_3$), 4.99−4.78 (m, 2H, NC$H_2$CH$_2$PPh$_2$), 4.59−4.34 (m, 1H, NC$H_2$CH$_3$), 3.19 (m, 2H, NCH$_2$C$H_2$PPh$_2$), 1.22 (m, 3H, NCH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 169.1 (NCN), 133.2 (Ar−C), 133.0 (d, $^3J_{PC}$ = 9.3 Hz, PPh−C$_\gamma$), 132.2 (d, $^4J_{PC}$ = 12.1 Hz, PPh−C$_\delta$), 130.7 (d, $^2J_{PC}$ = 9.8 Hz, PPh−C$_\beta$), 128.5 (d, $^1J_{PC}$ = 10.9 Hz, PPh−C$_\alpha$), 124.0, 123.8, 111.7, 111.4 (Ar−C), 51.2 (NCH$_2$CH$_3$), 44.7 (NCH$_2$CH$_2$-PPh$_2$), 27.5 (d, $^1J_{PC}$ = 38.0 Hz, NCH$_2$CH$_2$PPh$_2$), 14.8 (NCH$_2$CH$_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ 30.0. MS (MALDI): $m/z$ 499 ([M − Cl]$^+$). Anal. Calcd for $C_{23}H_{23}N_2Cl_2PPd$ (535.8): C, 51.56; H, 4.33; N, 5.23. Found: C, 50.89; H, 4.03; N, 5.13.

**{*N*-(2-Diphenylphosphinoethyl)-*N*′-propylbenzimidazolin-2-ylidene}palladium(II) Dichloride (14).** Yield: 87.3%. $^1$H NMR (200.1 MHz, CDCl$_3$): $\delta$ 7.98−7.87 (m, 2H, Ar−H), 7.78−7.70 (m, 2H, Ar−H), 7.56−7.40 (m, 10H, PPh−H), 5.10−4.64 (m, 3H, NC$H_2$CH$_2$PPh$_2$ and NC$H_2$CH$_2$CH$_3$), 4.46−4.31 (m, 1H, NC$H_2$CH$_2$-CH$_3$), 2.77−2.56 (m, 2H, NCH$_2$C$H_2$PPh$_2$), 1.29 (m, 2H, NCH$_2$C$H_2$-CH$_3$), 0.61 (t, 3H, NCH$_2$CH$_2$C$H_3$). $^{13}$C NMR (50.3 MHz, CDCl$_3$): $\delta$ 169.2 (NCN), 134.7 (PPh−C), 133.6, 133.4 (Ar−C), 132.0, 130.5 (PPh−C), 128.7 (d, $J_{PC}$ = 11.7 Hz, PPh−C), 124.6, 124.4, 111.9, 111.0 (Ar−C), 50.6 (NCH$_2$CH$_2$CH$_3$), 45.0 (NCH$_2$CH$_2$PPh$_2$), 29.2 (d, $^1J_{PC}$ = 36.9 Hz, NCH$_2$CH$_2$PPh$_2$), 23.4 (NCH$_2$CH$_2$CH$_3$), 11.3 (NCH$_2$CH$_2$CH$_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ 30.0. MS (MALDI): $m/z$ 514 ([M − Cl]$^+$). Anal. Calcd for $C_{24}H_{25}N_2Cl_2$-PPd (549.8): C, 52.43; H, 4.58; N, 5.10. Found: C, 52.09; H, 4.83; N, 4.98.

**{*N*-(2-Diphenylphosphinoethyl)-*N*′-butylbenzimidazolin-2-ylidene}palladium(II) Dichloride (15).** Yield: 85.7%. $^1$H NMR (400.1 MHz, CDCl$_3$): $\delta$ 7.83−7.78 (m, 2H, Ar−H), 7.67−7.63 (m, 2H, Ar−H), 7.54−7.38 (m, 10H, PPh−H), 4.93 (m, 2H, NC$H_2$-CH$_2$PPh$_2$), 4.78−4.66 (m, 1H, NC$H_2$CH$_2$CH$_2$CH$_3$), 4.32−4.20 (m, 1H, NC$H_2$CH$_2$CH$_2$CH$_3$), 2.51 (m, 2H, NCH$_2$C$H_2$PPh$_2$), 1.72 (m, 2H, NCH$_2$C$H_2$CH$_2$CH$_3$), 1.13 (sext, 2H, $^3J$ = 7.3 Hz, NCH$_2$CH$_2$C$H_2$-CH$_3$), 0.71 (t, 3H, $^3J$ = 7.3 Hz, NCH$_2$CH$_2$CH$_2$C$H_3$). $^{13}$C NMR (100.6 MHz CDCl$_3$): $\delta$ 169.3 (NCN), 134.0 (PPh−C), 133.1, 132.9 (Ar−C), 131.5, 130.1 (PPh−C), 128.7 (d, $J_{PC}$ = 11.7 Hz, PPh−C), 124.3, 124.0, 111.4, 110.9 (Ar−C), 48.3 (NCH$_2$CH$_2$CH$_2$CH$_3$), 44.2 (NCH$_2$CH$_2$PPh$_2$), 31.7 (NCH$_2$CH$_2$CH$_2$CH$_3$), 28.7 (d, $^1J_{PC}$ = 37.2 Hz, NCH$_2$CH$_2$PPh$_2$), 20.0 (NCH$_2$CH$_2$CH$_2$CH$_3$), 13.6 (NCH$_2$-

$CH_2CH_2CH_3$). $^{31}P$ NMR (162.0 MHz, $CDCl_3$): $\delta$ 28.6. MS (MALDI): *m*/*z* 528 ([M − Cl]$^+$). Anal. Calcd for $C_{25}H_{27}N_2Cl_2PPd$ (563.8): C, 53.26; H, 4.83; N, 4.97. Found: C, 52.86; H, 4.47; N, 4.66.

**General Procedure for the Synthesis of {*N*-(2-Diphosphinoethyl)-*N*′-alkylbenzimidazolin-2-ylidene}platinum(II) Dichlorides (16−18).** The platinum complexes of the phosphine-functionalized benzimidazolin-2-ylidene ligands were prepared in the same manner as described for the palladium complexes **13**−**15** from $[PtCl_2(PhCN)_2]$ and the silver complexes **10**−**12**.

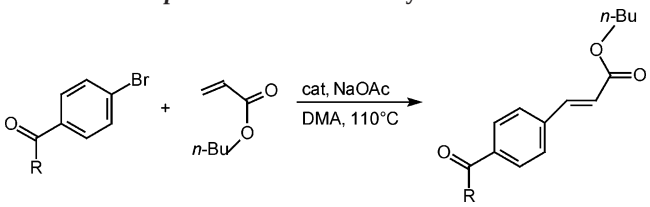
**{*N*-(2-Diphenylphosphinoethyl)-*N*′-ethylbenzimidazolin-2-ylidene}platinum(II) Dichloride (16).** Yield: 81.3%. $^1H$ NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 7.75−7.67 (m, 4H, Ar−H), 7.64−7.38 (m, 10H, PPh−H), 4.93 (m, 1H, $NCH_2CH_2PPh_2$), 4.60−4.48 (m, 2H, $NCH_2CH_3$), 4.20 (m, 1H, $NCH_2CH_2PPh_2$), 3.48−3.30 (m, 2H, $NCH_2CH_2PPh_2$), 1.54 (m, 3H, $NCH_2CH_3$). $^{13}C$ NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 154.6 (NCN), 133.5, 132.8 (PPh−C), 132.0 (Ar−C), 129.2, 128.3 (PPh−C), 123.9, 123.7, 111.7, 111.5 (Ar−C), 46.8 ($NCH_2CH_3$), 43.9 ($NCH_2CH_2PPh_2$), 26.2 (d, $^1J_{PC}$ = 44.3 Hz, $NCH_2CH_2PPh_2$), 13.4 ($NCH_2CH_3$). $^{31}P$ NMR (81.0 MHz, DMSO-$d_6$): $\delta$ 8.1 (s, Pt satellites, $^1J_{PPt}$ = 3695 Hz). MS (MALDI): *m*/*z* 589 ([M − Cl]$^+$). Anal. Calcd for $C_{23}H_{23}N_2Cl_2PPt$ (624.4): C, 44.24; H, 3.71; N, 4.49. Found: C, 43.56; H, 3.88; N, 4.03.

**{*N*-(2-Diphenylphosphinoethyl)-*N*′-propylbenzimidazolin-2-ylidene}platinum(II) Dichloride (17).** Yield: 85.6%. $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ 7.84−7.70 (m, 4H, Ar−H), 7.62−7.51 (m, 10H, PPh−H), 4.86 (s, br, 2H, $NCH_2CH_2PPh_2$), 4.74 (m, 2H, $NCH_2CH_2CH_3$), 2.42 (s, br, 2H, $NCH_2CH_2PPh_2$), 1.85 (m, 2H, $NCH_2CH_2CH_3$), 0.71 (t, 3H, $NCH_2CH_2CH_3$). $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 155.7 (d, $^2J_{PC}$ = 10.5 Hz, NCN), 134.2 (PPh−C), 132.8 (d, $J_{PC}$ = 7.9 Hz, PPh−C), 132.1 (Ar−C), 129.1 (PPh−C), 128.6 (d, $J_{PC}$ = 11.5 Hz, PPh−C), 124.1, 124.0, 111.4, 110.8 (Ar−C), 49.7 ($NCH_2CH_2CH_3$), 44.6 ($NCH_2CH_2PPh_2$), 27.6 (d, $^1J_{PC}$ = 44.4 Hz, $NCH_2CH_2PPh_2$), 22.8 ($NCH_2CH_2CH_3$), 11.1 ($NCH_2CH_2CH_3$). $^{31}P$ NMR (162.0 MHz, $CDCl_3$): $\delta$ 4.2 (s, Pt satellites, $^1J_{PPt}$ = 3718 Hz). $^{195}Pt$ NMR (85.8 MHz, $CDCl_3$): $\delta$ −2327.7 (s, br). MS (MALDI): *m*/*z* 603 ([M − Cl]$^+$). Anal. Calcd for $C_{24}H_{25}N_2Cl_2PPt$ (638.4): C, 45.15; H, 3.95; N, 4.39. Found: C, 44.46; H, 3.89; N, 4.27.

**{*N*-(2-Diphenylphosphinoethyl)-*N*′-butylbenzimidazolin-2-ylidene}platinum(II) Dichloride (18).** Yield: 85.9%. $^1H$ NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 7.83−7.74 (m, 4H, Ar−H), 7.62−7.36 (m, 10H, PPh−H), 4.83 (s, br, 2H, $NCH_2CH_2PPh_2$), 4.71 (m, 2H, $NCH_2CH_2CH_2CH_3$), 2.34 (s, br, 2H, $NCH_2CH_2PPh_2$), 1.75 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.68 (t, 2H, $NCH_2CH_2CH_2CH_3$). $^{13}C$ NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 155.7 (d, $^2J_{PC}$ = 10.1 Hz, NCN), 134.2 (PPh−C), 132.8 (d, $J_{PC}$ = 7.9 Hz, PPh−C), 132.0 (Ar−C), 129.3 (PPh−C), 128.6 (d, $J_{PC}$ = 11.5 Hz, PPh−C), 123.9, 123.7, 111.7, 111.5 (Ar−C), 48.8 ($NCH_2CH_2CH_2CH_3$), 43.9 ($NCH_2CH_2PPh_2$), 31.0 ($NCH_2CH_2CH_2CH_3$), 26.2 (d, $^1J_{PC}$ = 44.6 Hz, $NCH_2CH_2PPh_2$), 19.5 ($NCH_2CH_2CH_2CH_3$), 13.4 ($NCH_2CH_2CH_2CH_3$). $^{31}P$ NMR (81.0 MHz, DMSO-$d_6$): $\delta$ 9.6 (s with Pt satellites, $^1J_{PPt}$ = 3681 Hz). MS (MALDI): *m*/*z* 617 ([M − Cl]$^+$). Anal. Calcd for $C_{25}H_{27}N_2Cl_2PPt$ (652.5): C, 46.02; H, 4.17; N, 4.29. Found: C, 45.67; H, 3.87; N, 4.01.

**{*N*,*N*′-Bis(2-diphenylphosphinoethyl)-5,6-dimethylbenzimidazolin-2-ylidene}silver(I) Chloride (19).** A sample of $Ag_2O$ (0.6 mmol, 0.139 g) and compound **9** (1 mmol, 0.607 g) were dissolved in 40 mL of dichloromethane and stirred for 48 h under exclusion of light at ambient temperature. The resulting suspension was filtered through Celite, and the solvent was removed in vacuo. Dichloromethane (4 mL) was added to the residue, and the solution was added dropwise to ice cold diethyl ether (100 mL). The obtained white precipitate was collected by filtration, washed two times with diethyl ether (5 mL each), and dried in vacuo. Yield: 65.3%. $^1H$ NMR (200.1 MHz, $CD_2Cl_2$): $\delta$ 7.71−7.65 (s, 2H, Ar−H), 7.49−7.06 (m, 20H, PPh−H), 4.74 (s, br, 4H, $NCH_2CH_2PPh_2$), 2.79 (s, br, 4H, $NCH_2CH_2PPh_2$), 2.30 (s, 6H, $CH_3$). $^{13}C$ NMR (50.3 MHz, $CD_2Cl_2$): $\delta$ 133.2 (s, br, PPh−C), 132.2 (Ar−C), 131.9 (d, $J_{PC}$ = 8.5 Hz, PPh−C), 130.5 (Ar−C), 128.9 (s, br, PPh−C), 127.7 (d, $J_{PC}$ = 10.9 Hz, PPh−C), 111.4 (Ar−C), 46.0 (s, br, $NCH_2CH_2PPh_2$), 28.4 (s, br, $NCH_2CH_2PPh_2$), 20.4 ($CH_3$). The resonance for the carbene carbon atom was not observed. $^{31}P$ NMR (81.0 MHz, $CD_2Cl_2$): $\delta$ −3.0 (s, br). MS (MALDI): *m*/*z* 679 ([M − Cl]$^+$). Anal. Calcd for $C_{37}H_{36}N_2AgClP_2$ (714.0): C, 62.24; H, 5.08; N, 3.92. Found: C, 61.76; H, 4.89; N, 3.81.

**Table 3. Pd-Catalyzed Coupling Reaction of *n*-Butyl Acylate with *para*-Functionalized Aryl Bromides[a]**




| entry | catalyst | mol % | R | time, h | yield, % |
|---|---|---|---|---|---|
| 1 | **13** | 0.1 | H | 24 | 95.8 |
| 2 | **14** | 0.1 | H | 24 | 97.8 |
| 3 | **15** | 0.1 | H | 24 | 100.0 |
| 4 | **20** | 0.1 | H | 24 | 91.2 |
| 5 | **13** | 0.01 | H | 24 | 95.8 |
| 6 | **14** | 0.01 | H | 24 | 83.8 |
| 7 | **15** | 0.01 | H | 24 | 73.6 |
| 8 | **20** | 0.01 | H | 24 | |
| 9 | **13** | 1 | H | 2 | 86.8 |
| 10 | **14** | 1 | H | 2 | 85.7 |
| 11 | **15** | 1 | H | 2 | 83.0 |
| 12 | **20** | 1 | H | 2 | 56.7 |
| 13 | **13** | 0.1 | $CH_3$ | 24 | 84.6 |
| 14 | **14** | 0.1 | $CH_3$ | 24 | 97.5 |
| 15 | **15** | 0.1 | $CH_3$ | 24 | 100 |
| 16 | **20** | 0.1 | $CH_3$ | 24 | 62.1 |
| 17 | **13** | 0.01 | $CH_3$ | 24 | 84.6 |
| 18 | **14** | 0.01 | $CH_3$ | 24 | 60.2 |
| 19 | **15** | 0.01 | $CH_3$ | 24 | 59.2 |
| 20 | **20** | 0.01 | $CH_3$ | 24 | 52.3 |
| 21 | **13** | 1 | $CH_3$ | 2 | 53.5 |
| 22 | **14** | 1 | $CH_3$ | 2 | 57.9 |
| 23 | **15** | 1 | $CH_3$ | 2 | 54.0 |
| 24 | **20** | 1 | $CH_3$ | 2 | 46.7 |

[a] Reaction conditions: 1 mmol of 4-aryl bromide, 1.4 mmol of *n*-butyl acrylate, 2 mmol of NaOAc, Pd catalyst, and 3 mL of DMA. Yields were determined by gas chromatography.

**{*N*,*N*′-Bis(2-diphenylphosphinoethyl)-5,6-dimethylbenzimidazolin-2-ylidene}palladium(II) Dichloride (20).** The silver complex **19** (0.2 mmol, 0.143 g) was dissolved in 50 mL of dichloromethane. Complex $[PdCl_2(cod)]$ (0.2 mmol, 0.057 g) was added to this solution, and the reaction mixture was stirred for 1 day at ambient temperature. The mixture was filtered through Celite, and the solvent was removed in vacuo. The solid residue was dissolved in a small amount of dichloromethane, and this solution was added dropwise to ice cold diethyl ether (100 mL). A bright yellow precipitate formed, which was collected by filtration, washed with 5 mL of diethyl ether, and dried in vacuo. Yield: 89.7%. $^1H$ NMR (400.1 MHz, $CDCl_3$): $\delta$ 7.87 (s, 2H, Ar−H), 7.84−7.82 (m, 6H, PPh−H), 7.56−7.52 (m, 7H, PPh−H), 7.51−7.46 (m, 7H, PPh−H), 4.79−4.70 (m, 4H, $NCH_2CH_2PPh_2$), 2.73−2.66 (m, 4H, $NCH_2CH_2PPh_2$), 2.38 (s, 6H, $CH_3$). $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 161.8 (NCN), 135.5 (Ar−C), 133.8 (t, $J_{PC}$ = 6.3 Hz, PPh−C), 131.9 (s, PPh−C), 131.7 (Ar−C), 129.5 (t, $J_{PC}$ = 5.4 Hz, PPh−C), 128.7 (t, $J_{PC}$ = 26.3 Hz, PPh−C), 111.3 (Ar−C), 43.2 ($NCH_2CH_2PPh_2$), 25.6 (t, $^1J_{PC}$ = 16.0 Hz, $NCH_2CH_2PPh_2$), 20.3 ($CH_3$). $^{31}P$ NMR (162.0 MHz, $CDCl_3$): $\delta$ 12.4 (s). MS (MALDI): *m*/*z* 712 ([M − Cl]$^+$). Anal. Calcd for $C_{37}H_{36}N_2Cl_2P_2Pd$ (748.0): C, 59.41; H, 4.85; N, 3.75. Found: C, 59.28; H, 4.65; N, 3.56.

**Table 4. Summary of Crystallographic Data for 13, 15, and 22·0.5MeOH**

| | **13** | **15** | **22**·0.5MeOH |
|---|---|---|---|
| formula | $C_{23}H_{23}N_2Cl_2PPd$ | $C_{25}H_{27}N_2Cl_2PPd$ | $C_{42.5}H_{43}N_3B_2F_8O_{0.5}P_2Pd$ |
| $M_r$ | 535.70 | 563.76 | 945.76 |
| cryst size [mm] | 0.08 × 0.06 × 0.04 | 0.17 × 0.16 × 0.08 | 0.46 × 0.24 × 0.19 |
| *a* [Å] | 8.9474(13) | 15.896(3) | 11.3796(3) |
| *b* [Å] | 13.912(2) | 16.054(3) | 16.7644(5) |
| *c* [Å] | 17.268(3) | 18.968(3) | 22.7228(7) |
| α [deg] | 90 | 90 | 101.099(2) |
| *β* [deg] | 90 | 90 | 95.263(2) |
| *γ* [deg] | 90 | 90 | 93.406(2) |
| *V* [Å$^3$] | 2149.4(5) | 4840.5(14) | 4222.7(2) |
| *Z* | 4 | 8 | 4 |
| space group | $P2_12_12_1$ | *Pbca* | $P\bar{1}$ |
| $\rho_{calcd}$ [g cm$^{-3}$] | 1.655 | 1.547 | 1.488 |
| $\mu$ [mm$^{-1}$] | 1.199 (Mo Kα) | 1.069 (Mo Kα) | 4.883 (Cu Kα) |
| 2$\theta$ range [deg] | 3.9−55.0 | 4.2−60.2 | 4.0−140.0 |
| no. of data collected | 21 177 | 52 905 | 24 679 |
| no. of unique data | 4935 | 7076 | 13 986 |
| obsd data [$I \geq 2\sigma(I)$] | 4468 | 5961 | 9451 |
| *R* (all data) | 0.0534 | 0.0568 | 0.0788 |
| $R_w$ (all data) | 0.1058 | 0.0976 | 0.1474 |
| no. of variables | 264 | 281 | 1104 |
| peak/hole [e Å$^3$] | 0.836/−0.445 | 1.113/−0.486 | 1.301/−1.051 |

{***N,N′*-Bis(2-diphenylphosphinethyl)-5,6-dimethylbenzimidazolin-2-ylidene}platinum(II) Dichloride (21).** Complex **21** was prepared as described for **20** from $[PtCl_2(PhCN)_2]$ (0.2 mmol, 0.094 g) and silver complex **19** (0.2 mmol, 0.143 g). Yield: 82.4%. $^1$H NMR (400.1 MHz, DMSO-$d_6$): $\delta$ 7.94−7.86 (m, 6H, Ar−H and PPh−H), 7.73 (m, 2H, PPh−H), 7.63−7.53 (m, 6H, PPh−H), 7.51−7.42 (m, 6H, PPh−H), 7.39−7.34 (m, 2H, PPh−H), 4.73−4.60 (m, 4H, NC$H_2$CH$_2$PPh$_2$), 2.91−2.80 (m, 4H, NCH$_2$C$H_2$PPh$_2$), 2.38 (s, 6H, CH$_3$). $^{13}$C NMR (100.6 MHz, DMSO-$d_6$): $\delta$ 145.9 (t, $^2J_{PC}$ = 9.0 Hz, NCN), 133.9 (t,$^3J_{PC}$ = 6.0 Hz, PPh−C$_\gamma$), 133.5 (Ar−C), 132.0 (t,$^4J_{PC}$ = 5.5 Hz, PPh−C$_\delta$), 131.6 (Ar−C), 128.8 (t, $^2J_{PC}$ = 5.5 Hz, PPh−C$_\beta$), 128.3 (t, $^1J_{PC}$ = 15.0 Hz, PPh−C$_\alpha$), 111.6 (Ar−C), 43.2 (N*C*H$_2$CH$_2$PPh$_2$), 23.5 (t, $^1J_{PC}$ = 19.3 Hz, NCH$_2$*C*H$_2$PPh$_2$), 19.8 (CH$_3$). $^{31}$P NMR (162.0 MHz, DMSO-$d_6$): $\delta$ 14.1 (s, Pt satellites, $^1J_{PPt}$ = 2434 Hz). $^{195}$Pt NMR (85.8 MHz, DMSO-$d_6$): $\delta$ −4482 (t, $^1J_{PPt}$ = 2450 Hz). MS (MALDI): *m*/*z* 801 ([M − Cl]$^+$). Anal. Calcd for $C_{37}H_{36}N_2Cl_2P_2Pt$ (836.6): C, 53.12; H, 4.34; N, 3.35. Found: C, 52.91; H, 4.43; N, 3.24.

{**(*N,N′*-Bis(2-diphenylphosphinoethyl)-5,6-dimethylbenzimidazolin-2-ylidene}pyridinepalladium(II) Bis(tetrafluoroborate) (22).** Complex **20** (0.25 mmol, 0.187 g) was dissolved in 10 mL of pyridine. Silver tetrafluoroborate (0.55 mmol, 0.110 g) was added to this solution, and the reaction mixture was stirred at ambient temperature for 1 day and then filtered through Celite. The solvent was removed, and the brown residue was dried in vacuo. Yield: 69.7%. $^1$H NMR (200.1 MHz, DMSO-$d_6$): $\delta$ 8.22 (d, 2H, $^3J$ = 5.3 Hz, py-H$_\alpha$), 7.65−7.29 (m, 23H, Ar−H and PPh−H and py-H$_\gamma$), 6.96 (t, 2H, $^3J$ = 6.5 Hz, py-H$_\beta$), 5.12−4.99 (m, 4H, NC$H_2$CH$_2$-PPh$_2$), 3.23−3.05 (m, 4H, NCH$_2$C$H_2$PPh$_2$), 2.27 (s, 6H, CH$_3$). $^{13}$C NMR (50.3 MHz, DMSO-$d_6$): $\delta$ 150.3 (NCN), 151.0 (py-C$_\alpha$), 140.8 (py-C$_\gamma$), 134.0 (Ar−C), 132.8 (t, $^3J$ = 6.7 Hz, PPh−C$_\gamma$), 131.7 (Ar−C, PPh−C$_\delta$), 129.2 (t, $^2J$ = 5.6 Hz, PPh−C$_\beta$), 128.5 (t, $^1J$ = 6.7 Hz, PPh−C$_\alpha$), 127.3 (py−C$_\beta$), 112.0 (Ar−C), 45.2 (N*C*H$_2$CH$_2$-PPh$_2$), 24.6 (NCH$_2$*C*H$_2$PPh$_2$), 19.8 (CH$_3$). $^{31}$P NMR (81.0 MHz, DMSO-$d_6$): $\delta$ 21.9. MS (MALDI): *m*/*z* 677 ([M − py − 2BF$_4$ + H]$^+$).

**General Procedure for the C−C Coupling Experiments.** One of the palladium complexes **13**−**15** or **20** was dissolved in dimethylacetamide (3 mL). To this solution were added the aryl halide (1.0 mmol), styrene or *n*-butyl acrylate (1.4 mmol), and sodium acetate as base (2.0 mmol). The solution was heated to 110 °C with stirring. It was then allowed to cool to ambient temperature. Residual NaOAc and palladium complexes were removed by column chromatography with silica gel. 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.** Air-stable crystals of compounds **13** and **15** were obtained at ambient temperature by recrystallization from dichloromethane. Crystals of the solvate **22**·0.5MeOH were obtained from a dichloromethane/methanol solution at ambient temperature. Diffraction data for **13** and **15** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 153(2) K using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). Diffraction data for compound **22**·0.5MeOH were obtained with a Bruker SMART 6000 CCD diffractometer equipped with a rotating anode using Cu Kα radiation ($\lambda$ = 1.54184 Å) at 100(2) K. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART[30] program package. For further crystal and data collection details see Table 4. Structure solutions were found with the SHELXS-97[31] package using the heavy-atom method and were refined with SHELXL-97[32] against $F^2$ using first isotropic and later anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions. The asymmetric unit of **22**·0.5MeOH contains two almost identical molecules of **22** and one molecule of methanol.

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**Supporting Information Available:** Full crystallographic data for compounds **13**, **15**, and **22**·0.5MeOH are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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