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# Elimination of an Alkyl Group from Imidazolium Salts: Imidazole-Coordinated Dinuclear Monodentate NHC–Palladium Complexes Driven by Self-Assembly and Their Application in the Heck Reaction

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**Keywords:** Heck reaction / Carbene ligands / Palladium / Self-assembly / NHCs (N-Heterocyclic carbenes)

A new family of imidazole-coordinated monodentate NHC–metal complexes **9** was obtained as well as *cis*-chelated bidentate NHC–metal complexes **10** from novel bis(imidazolium) salts **4** with a biphenyl backbone. The structures of complexes **9a** and **10b** were determined by X-ray crystal-structure diffraction, and their application in the Heck reaction showed good to excellent catalytic activities under very mild conditions.

## Introduction

N-Heterocyclic carbenes (NHCs), first reported by Öfele and Wanzlick,[1] have become a very important class of ligands due to their stability to air and moisture and their strong σ-donor but poor π-acceptor abilities. The design and synthesis of novel and effective NHCs have attracted a great deal of attention from both academia and industry.[2]

Unlike phosphanes, the coordination of NHCs to metal centers requires the activation or deprotonation of an imidazolium salt precursor. Thus far, many activation strategies have been used to prepare NHC–metal complexes.[3] Among these methods, the most important one is the deprotonation of the corresponding imidazolium salt with a base (for example, *t*BuOK, *n*BuLi, or $Cs_2CO_3$) to generate the NHC ligand.[4] Under basic conditions, imidazolium salts can also be converted into the corresponding imidazoles, but this process only takes place for imidazolium salts bearing an electron-withdrawing β substituent.[5] Recently, Whittlesey and coworkers reported ruthenium-induced elimination of an isopropyl group from an imidazolium salt to provide the corresponding imidazole-coordinated ruthenium complex through C–N bond activation and tautomerization.[6] It is conceivable that novel NHC–metal complexes **3** can be designed on the basis of such an elimination of an alkyl group $R^4$ to give imidazole **2** and deprotonation from the imidazolium salt precursor to give NHC **1** (Figure 1). However, up till now, complexes **3** have yet to be reported, except those generated from the coordination of an extra imidazole with NHC metal complexes.[7]

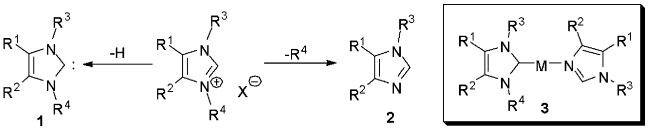

Figure 1. The transformation of imidazolium salts.

Encouraged by the development of monodentate NHCs[8] and combined with other coordination groups such as oxazolines and phosphanes and the successful applications of their palladium catalysts in bond–bond activations, such as $C(sp^3)$–H bond activation,[9] we envisaged that it might be feasible to use $C_2$-symmetric bis(imidazolium) salts as precursors for the preparation of monodentate NHC and imidazole-coordinated metal complex **3** in the presence of palladium salts. Herein, we wish to report the elimination of an alkyl group from imidazolium salts and a novel self-assembly strategy for the preparation of imidazole-coordinated dinuclear monodentate NHC palladium complexes from $C_2$-symmetric bis(imidazolium) salts.

## Results and Discussion

A novel family of bis(imidazolium) salts with a 1,1′-binaphthalenyl-2,2′-diamine (binam) framework (R = Me) was developed in our research group.[10] Their *cis*-chelated bidentate NHC–$Pd^{II}$ complexes could be obtained by treatment with $Pd(OAc)_2$ in the presence of a base such as *t*BuOK. However, an imidazole-coordinated monodentate NHC–Pd complex was not obtained, presumably as a result of the fact that elimination of an alkyl group from the benzimidazole ring in the sterically bulky binaphthalene scaffold

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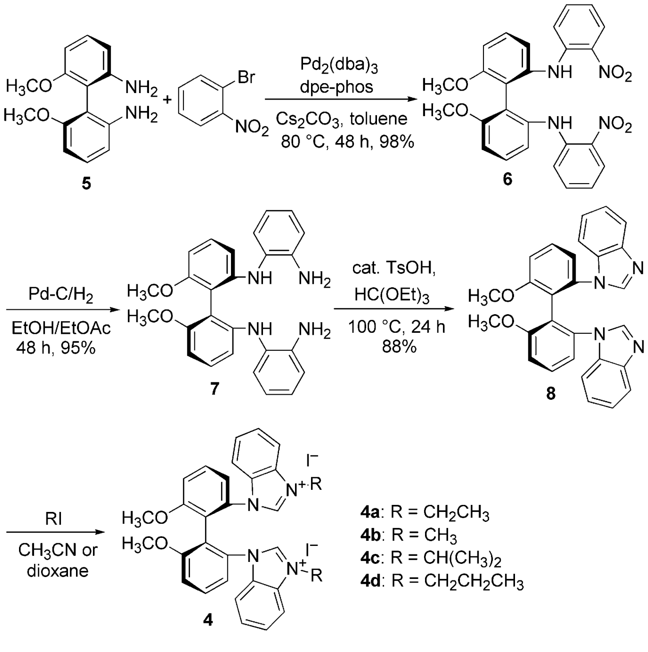
is difficult, which was ascertained on the basis of the X-ray crystal structure of the *cis*-chelated bidentate NHC–Pd$^{II}$ complex.[10c] Relative to the rigid binaphthalene skeleton, sterically more flexible bis(imidazolium) salts **4** were designed and synthesized. These substrates posses a biphenyl scaffold bearing a variety of alkyl groups and it was believed that elimination of one of the alkyl groups from the benzimidazole ring would be possible.

According to our previously reported synthetic procedure,[10] the preparation of bis(imidazolium) salts **4** is shown in Scheme 1. Racemic 6,6′-dimethoxybiphenyl-2,2′-diamine **5** was treated with 2-bromonitrobenzene in toluene at 80 °C to produce desired compound **6** in 98% yield after 48 h. Reduction of **6** with 10% Pd–C/$H_2$ at 60 °C afforded compound **7** in 95% yield. Subsequent cyclization with triethyl orthoformate catalyzed by toluenesulfonic acid (TsOH) at 100 °C gave benzimidazole **8** in 88% yield after 24 h. Quaternization of the benzimidazole ring of **8** with a variety of alkyl iodides upon heating in acetonitrile or dioxane provided the corresponding dibenzimidazolium salts **4a**–**d** in quantitative yields.



Scheme 1. The synthesis of bis(imidazolium) salts **4**.

To evaluate the coordinating behavior of bis(imidazolium) salts **4** to the metal center, the reactions of **4** with $Pd(OAc)_2$ in thf were carried out under reflux in the presence of *t*BuOK for 24 h. It was surprisingly found that the use of **4a** as the precursor led to isolation of new NHC–Pd$^{II}$ complex **9a** as the major product after silica-gel column chromatography, but only 15% yield of *cis*-chelated bidentate NHC–Pd$^{II}$ complex **10a** was produced on the basis of $^1H$ NMR spectroscopy.[10b] The $^1H$ NMR spectrum of complex **9a** revealed that the corresponding two methoxy groups of the biphenyl framework located at 2.59 and 2.83 ppm, respectively, and one ethyl group was eliminated on the basis of proton integration. Single crystals of this complex suitable for X-ray crystal structure analysis were grown from dichloromethane/hexane (1:4), and its ORTEP drawing is shown in Figure 2. From the crystal structure of **9a**, it can be seen that benzimidazole was formed with the elimination of an ethyl group from **4a**, which coordinated with $Pd(OAc)_2$ through the nitrogen atom, combined with the NHC ligand to give the $C_2$-symmetric dinuclear palladium complex driven by self-assembly. However, by using **4b** as the precursor, *cis*-chelated bidentate NHC–Pd$^{II}$ complex **10b** was obtained in 70% yield without the formation of complex **9b** under the standard conditions.[10b] Single crystals of complex **10b** suitable for X-ray crystal structure analysis were grown from dichloromethane/hexane (1:3), and its ORTEP drawing is shown in Figure 3.

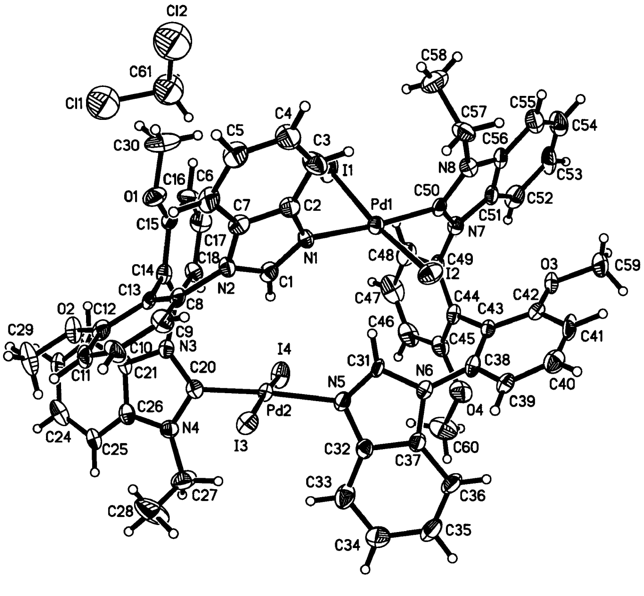


Figure 2. ORTEP drawing of bis(NHC)–Pd$^{II}$ complex **9a** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Pd1–N1 2.089(7), N2–C1 1.373(12), N1–C1 1.297(11), N2–C1 1.408(12), Pd1–C50 2.014(9), N7–C50 1.347(11), N8–C50 1.330(11), Pd1–I1 2.6164(10), Pd1–I2 2.6071(10), Pd2–C20 1.961(9), Pd2–I3 2.5962(10), Pd2–I4 2.6074(10); C1–N1–C2 106.6(8), N1–C1–N2 112.2(8), I1–Pd1–N1 90.4(2), I1–Pd1–I2 171.75(4), N1–Pd1–N2 90.6(2), N1–Pd1–C50 175.3(4), N8–C50–Pd1 122.8(7), N7–C50–Pd1 128.4(7), C50–Pd1–I1 C50–Pd1–I1 91.2(2).

It should be noted that complex **9a** was a self-assembled cyclodimer possessing a chiral “parallelogram” grid[11] by ligand and metal coordination. The chirality of the biphenyl axis was found to have the (*S*,*S*)-configuration, as determined by the crystal structure (Figure 2). The imidazole nitrogen atom has a weaker *trans* effect than that of the iodine anion, and the NHC has a stronger *trans* effect than that of the iodine anion.[12] That is the reason why complex **9a** is a *trans*-chelated NHC–Pd$^{II}$ complex with a bite angle (C50–Pd1–N1) of 175.3°, whereas complex **10b** is a *cis*-chelated bidentate NHC–Pd$^{II}$ complex with a bite angle (C1–Pd–C8) of 93.2°. The benzimidazole ring in **4a** is almost perpendicular to the benzene ring, and relative to the repulsion observed when (*S*)-**4a** coordinates with (*S*)-**4a**, this can produce higher steric repulsion between the imidazole and the

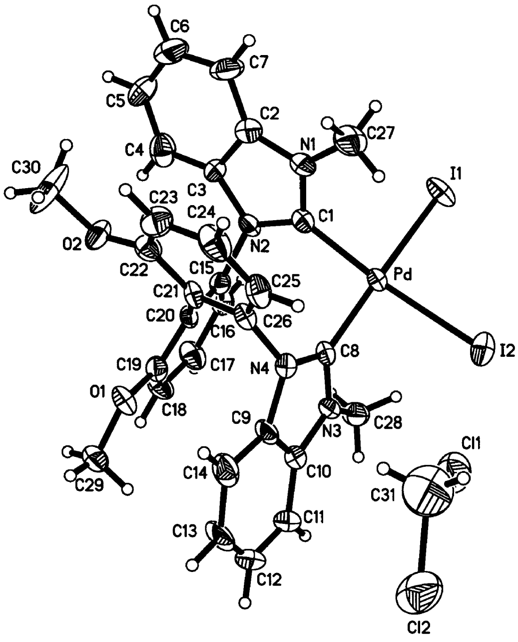


Figure 3. ORTEP drawing of bis(NHC)–Pd$^{II}$ complex **10b** with thermal ellipsoids at the 30% probability level. Selected bond lengths [Å] and angles [°]: Pd–C1 1.996(12), Pd–C8 1.959(11), Pd–I1 2.6691(11), Pd–I2 2.6715(13), C1–Pd–I1 88.4(3), C1–Pd–C8 93.2(5), C1–Pd–I1 167.3(4), I1–Pd–I2 92.54(4), C8–Pd–I1 167.8(3), C8–Pd–I2 88.5(3).

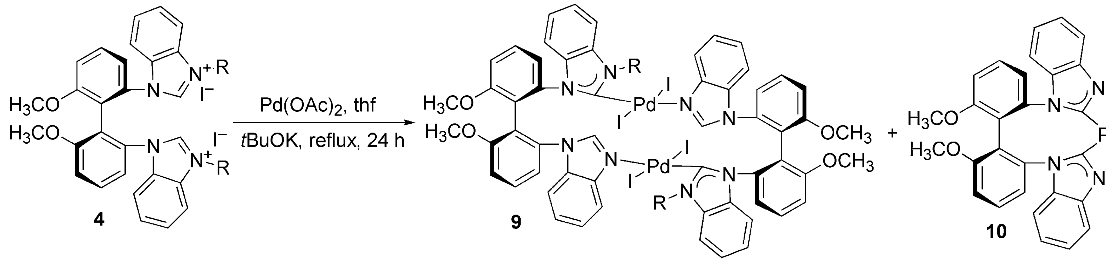
NHC moiety containing the benzene rings and methoxy groups if (*S*)-**4a** coordinates with (*R*)-**4a**. Therefore, the coordinative self-assembly gave the imidazole-coordinated dinuclear monodentate NHC–Pd complexes as (*R*,*R*)-**9a** and (*S*,*S*)-**9a** from racemate **4a** exclusively.

When the alkyl (R) group in bis(imidazolium) salt **4c** is an isopropyl group, Pd$^{II}$ complex **9c** was obtained in only 22% yield along with trace amounts of *cis*-chelated bidentate NHC–Pd$^{II}$ complex **10c**, presumably as a result of the steric hindrance of the isopropyl group under the identical conditions (Table 1, Entry 3). Moreover, as for bis(imidazolium) salt **4d** in which the R group is a normal propyl group, Pd$^{II}$ complex **9d** was obtained in 46% yield along with trace amounts of NHC–Pd$^{II}$ complex **10d** (Table 1, Entry 4).

The influence of a base in the preparation of the palladium complexes was also investigated, and the results of these experiments are summarized in Table 1 (Entries 5–7). It was found that the use of $Cs_2CO_3$ or $NaOCH_3$ as the base could also give dinuclear NHC–Pd complex **9a** in 48 and 42% yield, respectively, along with **10a** in 23 and 16% yield, respectively (Table 1, Entries 5 and 6). Only 5% yield of **9a** was obtained without the formation of complex **10a** in the absence of a base, suggesting that a base is required in this interesting coordination process (Table 1, Entry 7).

It was interestingly found that imidazolium salt **4** bearing a β-H on the alkyl group was converted into the corresponding imidazole as well as the carbene intermediate. This β-H may be activated by palladium to release an ethylene molecule in a mechanism similar to that observed for dealkylation induced by ruthenium complexes.[6] To determine whether Pd was involved in the dealkylation process, a control experiment was carried out by using bis(imidazolium) salt **4a** and *t*BuOK as the substrates in thf (10 mL) under reflux for 12 h without the addition of $Pd(OAc)_2$ (Scheme 2). Surprisingly, new compound **11** was isolated in 90% yield. Although imidazolin-2-one is well known to be prepared by deprotonation and oxidation of the corresponding benzimidazolium salt under an ambient atmo-

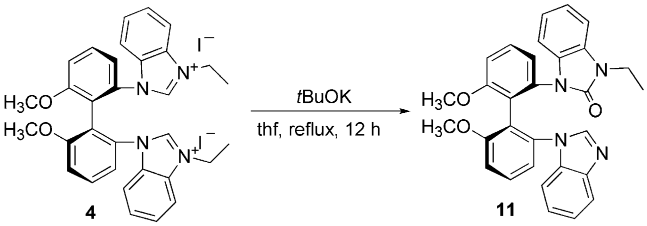
Table 1. The coordination of bis(imidazolium) salt with $Pd(OAc)_2$.[a]



| Entry | Imidazolium salt | Base | Yield of **9** [%][b] | Yield of **10** [%][c] |
|---|---|---|---|---|
| 1 | **4a** | *t*BuOK | **9a**, 63 | **10a**, 15 |
| 2 | **4b** | *t*BuOK | **9b**, none | **10b**, 70 |
| 3 | **4c** | *t*BuOK | **9c**, 22 | **10c**, trace |
| 4 | **4d** | *t*BuOK | **9d**, 46 | **10d**, trace |
| 5 | **4a** | $Cs_2CO_3$ | **9a**, 48 | **10a**, 23 |
| 6 | **4a** | $NaOCH_3$ | **9a**, 42 | **10a**, 16 |
| 7 | **4a** | none | **9a**, 5 | none |

[a] Reactions of imidazolium salts **4** with $Pd(OAc)_2$ in thf were carried out under reflux in the presence of a base for 24 h. [b] Isolated yield by silica-gel column chromatography. [c] Isolated yield by silica-gel column chromatography.

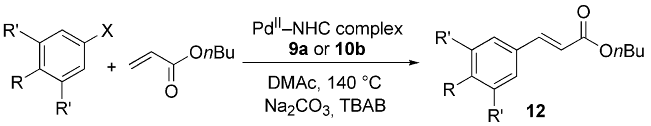
sphere,[13] to the best of our knowledge, this is the first example to indicate that imidazole and imidazolin-2-one could be both obtained from one molecule in the presence of *t*BuOK. On the basis of this control experiment, it is clear that Pd was not involved in the dealkylation process, although the exact mechanism for the transformation of the imidazolium salt to the corresponding imidazole and benzimidazolin-2-one to afford compound **11** is still obscure at the present stage.



Scheme 2. The synthesis of bis(imidazolium) salts **4**.

The palladium-catalyzed Heck reaction has turned out to be one of the most powerful methods for the formation of carbon–carbon bonds in organic synthesis.[14] A number of palladium/N-heterocyclic carbene catalyzed systems have been employed with great success.[15] Herein, we turned our interest to investigate the catalytic abilities of NHC–Pd complexes **9a** and **10b** in the Heck reaction. Typically, *n*-butyl acrylate was used as a model substrate with aryl halogenides for the Heck reaction with the use of NHC–Pd complexes (0.1 mol-% Pd) as the catalyst in the presence of $Na_2CO_3$ at 140 °C. The results are summarized in Table 2. It was found that Heck reaction products **12** were obtained in good to high yields in most cases (Table 2, Entries 1–5). The electronic properties of the R and R′ groups significantly affected the outcome of the Heck reactions catalyzed by **9a**. For electron-rich 4-bromoanisole, the reaction was somewhat sluggish and product **12a** was obtained in 80% yield under identical conditions (Table 2, Entry 1). For different halide atoms, iodobenzene gave product **12d** in 99% yield, but only trace amounts of cross-coupling product was obtained for chlorobenzene. NHC–Pd complex **10b** was also used as the catalyst to catalyze the Heck reaction, and it showed similar catalytic activity to that of **9a** (Table 2, entries 8–14).

Table 2. The coordination of bis(imidazolium) salt with $Pd(OAc)_2$.[a]



| Entry | R | R′ | X | Complex | Time [h] | Yield [%][b] |
|---|---|---|---|---|---|---|
| 1 | $OCH_3$ | H | Br | **9a** | 18 | **12a**, 80 |
| 2 | $CH_3$ | H | Br | **9a** | 18 | **12b**, 90 |
| 3 | CHO | H | Br | **9a** | 18 | **12c**, 95 |
| 4 | H | H | Br | **9a** | 18 | **12d**, 93 |
| 5 | H | $CH_3$ | Br | **9a** | 18 | **12e**, 82 |
| 6 | H | H | I | **9a** | 18 | **12d**, 99 |
| 7 | H | H | Cl | **9a** | 18 | trace |
| 8 | $OCH_3$ | H | Br | **10b** | 18 | **12a**, 83 |
| 9 | $CH_3$ | H | Br | **10b** | 18 | **12b**, 85 |
| 10 | CHO | H | Br | **10b** | 18 | **12c**, 94 |
| 11 | H | H | Br | **10b** | 18 | **12d**, 88 |
| 12 | H | $CH_3$ | Br | **10b** | 18 | **12e**, 76 |
| 13 | H | H | I | **10b** | 18 | **12d**, 99 |
| 14 | H | H | Cl | **10b** | 18 | trace |

[a] Reactions of NHC–Pd complex **9a** or **10b** (0.1 mol-% Pd), sodium carbonate (2.0 mmol), tetrabutylammonium bromide (TBAB, 0.1 mmol), aryl halogenides (1.0 mmol), and *n*-butyl acrylate (1.5 mmol) in *N*,*N*-dimethylacetamide (DMAc, 3.0 mL) were carried out at 140 °C for 18 h. [b] Isolated yield by silica-gel column chromatography.

## Conclusions

In summary, we reported the first example of the imidazole-coordinated dinuclear monodentate NHC–Pd complexes **9a**, **9c**, and **9d** as well as *cis*-chelated bidentate NHC–metal complexes **10a** and **10b** from the novel bis(imidazolium) salts **4a**, **4c**, and **4d** and their application in the Heck reaction. These dinuclear monodentate NHC–Pd complexes possess a chiral "parallelogram" grid by coordinative self-assembly. This work may allow the further development of NHC chemistry in two important directions: (1) Novel NHC–metal catalysts can be designed on the basis of such elimination of an alkyl group from an imidazolium salt precursor to generate the in situ coordinative imidazole moiety; (2) Molecular architectures such as triangles, squares, rectangles, and helical polymer by self-assembly from NHC–metal coordination chemistry can be realized, as the design and synthesis of novel ligands have been widely used in coordinative self-assembly for the construction of molecular subunits (tectons).[16] At the same time, a novel synthetic method for such compounds bearing imidazole and imidazolin-2-one groups was developed. The application of these novel NHC–Pd$^{II}$ complexes in asymmetric catalysis as well as the design and synthesis of new bis(imidazolium) salts are currently under investigation in our laboratory.

## Experimental Section

**General Remarks:** Dichloromethane was freshly distilled from calcium hydride; thf and toluene were distilled from sodium (Na) under an argon (Ar) atmosphere. Melting points were determined with a digital melting point apparatus and temperatures are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker AM-300 or AM-400 spectrophotometer. Infrared spectra were recorded with a Perkin–Elmer PE-983 spectrometer. Flash column chromatography was performed by using 300–400 mesh silica gel. For thin-layer chromatography (TLC), silica-gel plates (Huanghai $GF_{254}$) were used. Elementary analysis was taken with a Carlo–Erba 1106 analyzer. Mass spectra were recorded by EI and ESI and were measured with a HP-5989 instrument.

**NHC–Pd$^{II}$ Complex 9a and 10a:** Compound **4a** (455.1 mg, 0.60 mmol), $Pd(OAc)_2$ (134.7 mg, 0.60 mmol), and *t*BuOK (168.3 mg, 1.50 mmol) were heated at reflux in thf (10 mL) for 24 h. The volatiles were then removed under reduced pressure, and the residue was purified by a silica-gel flash column chromatography (petroleum ether/ethyl acetate, 8:1–2:1 and 1:1–0:1, for **9a** and **10a**, respectively) to give **9a** as a yellow solid (315.5 mg, 63%) and **10a** as a yellow solid (77.7 mg, 15%). A single crystal of **9a** suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of $CH_2Cl_2$/hexane (1:4).

**NHC–Pd$^{II}$ Complex 9a:** Yellow solid. M.p. >250 °C. $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ = 1.88 (t, $J$ = 7.2 Hz, 6 H, $CH_3$), 2.60 (s, 6 H, $OCH_3$), 2.83 (s, 6 H, $OCH_3$), 4.83–4.95 (m, 2 H, $CH_2$), 5.51–5.63 (m, 2 H, $CH_2$), 6.72 (d, $J$ = 8.1 Hz, 2 H, ArH), 6.83 (d, $J$ = 8.4 Hz, 2 H, ArH), 7.00 (d, $J$ = 7.8 Hz, 2 H, ArH), 7.09 (d, $J$ = 6.9 Hz, 2 H, ArH), 7.12–7.48 (m, 20 H, ArH), 8.44 (d, $J$ = 7.8 Hz, 2 H, ArH), 9.67 (s, 2 H, CH) ppm. IR (KBr, neat): $\tilde{\nu}$ = 3075, 2925, 2853, 1732, 1680, 1587, 1503, 1465, 1435, 1398, 1344, 1313, 1260, 1161, 1084, 1014, 847, 792, 742, 722, 699, 656 $cm^{-1}$. MS (ESI): $m/z$ (%) = 1694.8 (18.3) $[M]^+$, 1670.8 (43.5) $[M]^+$, 1543.0 (13.3) $[M]^+$, 1317.2 (12.2) $[M]^+$, 803.6 (100) $[M]^+$, 721.1 (58.6) $[M]^+$, 519.2 (73.1) $[M]^+$. HRMS (Micromass LCT): calcd. for $C_{60}H_{53}I_4N_8O_4Pd_2$ 1668.8438; found 1668.8477.

**NHC–Pd$^{II}$ Complex 10a:** Yellow solid. M.p. >250 °C. $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ = 1.22 (t, $J$ = 7.2 Hz, 6 H, $CH_3$), 2.86 (s, 6 H, $OCH_3$), 4.04–4.12 (m, 2 H, $CH_2$), 5.43–5.50 (m, 2 H, $CH_2$), 6.52 (d, $J$ = 7.8 Hz, 2 H, ArH), 6.91 (d, $J$ = 7.5 Hz, 2 H, ArH), 7.16–7.27 (m, 5 H, ArH), 7.28–7.45 (m, 5 H, ArH) ppm. IR (KBr, neat): $\tilde{\nu}$ = 3032, 2926, 2853, 1678, 1579, 1468, 1437, 1343, 1265, 1118, 1083, 1060, 1013, 801, 779, 742 $cm^{-1}$. MS (ESI): $m/z$ (%) = 739.0 (23.5) $[M]^+$, 735.0 (100) $[M]^+$. HRMS (Micromass LCT): calcd. for $C_{32}H_{30}IN_4O_2Pd$ 735.0448; found 735.0472.

**Typical Procedure for the Heck Reaction:** NHC–Pd complex **9a** (8.3 mg, 0.005 mmol), sodium carbonate (212.0 mg, 2.0 mmol), tetrabutylammonium bromide (TBAB; 32.2 mg, 0.10 mmol), 1-bromobenzene (157.0 mg, 1.0 mmol), *n*-butyl acrylate (192.3 mg, 1.50 mmol), and *N*,*N*-dimethylacetamide (DMAc; 3.0 mL) were introduced into an Schlenk tube. The mixture was stirred at 140 °C for 18 h. The reaction mixture was diluted with $H_2O$ (15 mL) and ethyl acetate (15 mL), followed by extraction with ethyl acetate (2×). The combined organic layer was dried with $MgSO_4$, filtered, and evaporated under reduced pressure to give the crude product. The pure product was isolated by column chromatography (hexane/ethyl acetate, 15:1) on silica gel to give 4-acetylbiphenyl **12d** (190.0 mg, 93%) as a yellow oil, which was analyzed by $^1H$ NMR spectroscopy.

**X-ray Crystal Structure Determinations:** CCDC-675585 (**9a**) and -686012 (**10b**) 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/datarequest/cif.

**Supporting Information** (see footnote on the first page of this article): Experimental procedures and characterization data for **4**, **6**, **7**, **8**, **9**, **10**, **11**, and **12**.

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