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Syntheses and catalytic activities of Pd(II) dicarbene and hetero-dicarbene complexes

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ABSTRACT

A series of palladium(II) complexes (**1**–**6**) bearing *cis*-chelating *homo-dicarbene* ligands with varying alkyl bridges (C1-C3) and *N*-heterocyclic backbones (imidazole and benzimidazole) have been synthesized by reaction of $Pd(OAc)_2$ with the respective diazolium bromides (**A**·2HBr – **F**·2HBr) in DMSO. A comparative catalytic study employing aryl chlorides in the Mizoroki–Heck reaction revealed the superiority of methylene- and propylene-bridged dibenzimidazolin-2-ylidenes over their imidazole-derived analogues. Based on these results, two new propylene-bridged *hetero-dicarbene* complexes (**7** and **8**) were designed containing a mixed benzimidazole/imidazole-derived NHC-donor set. Notably, both complexes outperformed their homo-dicarbene analogues, which may be due to the electronic asymmetry induced by hetero-dicarbene ligands. The molecular structures of complex **6** and **8** are also presented.

1. Introduction

N-heterocyclic carbenes (NHCs) have become ubiquitous ligands in organometallic chemistry [1,2]. Among the few basic types, NHCs derived from imidazole are dominating this area, although benzimidazolin-2-ylidenes are becoming increasingly popular. The latter are slightly weaker electron-donors due to the negative inductive (*-I*) effect arising from benzannulation [3]. Nevertheless, benzimidazole-derived NHCs offer the distinct advantage of a more straightforward complexation to metals, which can be explained by the presence of only one acidic proton in their benzimidazolium precursors [4]. Imidazolium rings, on the other hand, have three competing acidic protons at C2, C4 and C5, which can lead to complicated product mixtures containing classical and mesoionic (abnormal) NHCs [5], particularly when bulky *N*-substituents are present. Palladium complexes of both types have also been reported to be highly active catalysts for the Mizoroki–Heck reaction [6,7]. Similarly, chelating ligands are believed to provide additional catalyst stability and therefore increasing the conversion under the relatively harsh conditions usually applied in the Heck protocol. Several studies have appeared that describe applications of bridged dicarbene Pd(II) complexes in such C–C couplings [8–13], but to the best of our knowledge, a detailed and combined comparison on the spacer-length and the nature of the carbene unit has not been reported yet. Herein, we report the synthesis and characterization of Pd(II) complexes bearing *cis*-chelating homo- and hetero-dicarbene ligands of C1-C3 spacers and a comparison of their catalytic activities in the Mizoroki–Heck reaction of aryl bromides and chlorides.

2. Results and discussion

2.1. Syntheses, characterizations and catalytic activities of homo-dicarbene Pd(II) complexes

The Pd(II) complexes **1**–**6** bearing *cis*-chelating symmetrical dicarbene ligands derived from imidazole and benzimidazole have been routinely synthesized by heating the respective diazolium bromides **A**·2HBr – **F**·2HBr with 1 equiv $Pd(OAc)_2$ in wet DMSO (Scheme 1). The methylene-bridged dicarbene complexes **1** and **4** [14] (85–90% yield) and their properties have been reported previously. In general, the ethylene-bridged palladium complexes **2** and **5** were obtained at lower yield (30–50%) as compared to their propylene-bridged analogues (80–90%) **3** and **6**. The difficulty of converting ethylene-bridged diazolium halides to the corresponding chelating metal–dicarbene complexes has been noted previously [8,15,16]. Propylene-bridged dicarbenes on the other hand can coordinate to metal centres with ease as we have already demonstrated with Ni(II) [16]. All Pd(II) complexes **1**–**6** have been obtained as air- and moisture-stable yellow solids. Their formation

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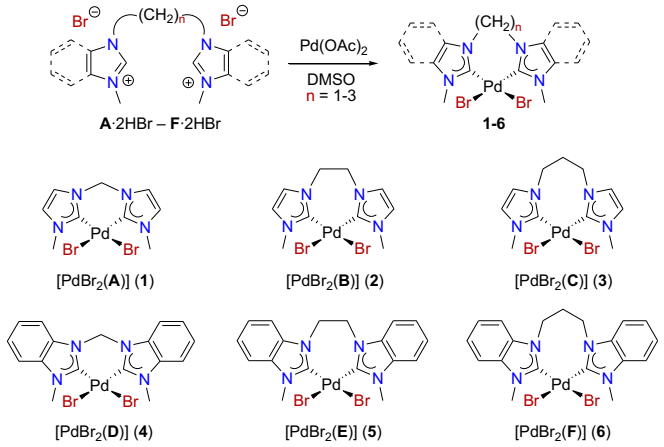


Scheme 1. Synthesis of Pd(II)-diNHC complexes **1**–**6**.

as carbene complexes is generally indicated by the absence of the downfield signal (~9–10 ppm) typical for their precursors in the ^{1}H NMR spectra. In addition, it was noted that all methylene protons of the bridges become diastereotopic as a result of ligand coordination. The observed broadening of these resonances has been attributed to the fluxionality of the seven- (**2** and **5**) or eight-membered (**3** and **6**) palladacycles. The ^{13}C signal for the carbene carbon in complex **2** was observed at 156.9 ppm, which is in the range observed for other ethylene-bridged analogues [8]. Due to the poor solubility of the other complexes (**3**, **5** and **6**), either their ^{13}C NMR spectra could not be obtained or the carbene signal could not be resolved despite prolonged acquisition time.

Single crystals suitable for X-ray diffraction analyses of complex **6** were obtained by slow diffusion of diethyl ether into a saturated DMSO solution. The asymmetric unit cell consists of two independent half molecules of the complex and a diethyl ether lying on the mirror plane. The solid state structure of only one independent molecule of **6** is depicted in Fig. 1 as a representative, which shows a square-planar Pd(II) centre coordinated by a *cis*-chelating dicarbene ligand and two terminal bromido ligands balancing the charges. The bite angle of 85.7(3)° is almost the same as that observed for methylene-bridged analogues indicating that the length of alkyl bridges cannot be used to alter the bite angle [17]. On the other hand, the bridging units affect the dihedral angle between the coordination and the carbene ring plane to a great extent. For example, small angles ranging from 39° to 54° were reported for Pd(II) complexes of dibenzimidazolin-2-ylidenes with methylene spacers [18,14] whereas that in complex **6** amounts to 76°. The Pd–C and Pd–Br bonds of 1.986(6) Å and 2.4832(8) Å, respectively, are non-exceptional and as expected slightly longer than those observed for its direct Ni(II) analogue [16].

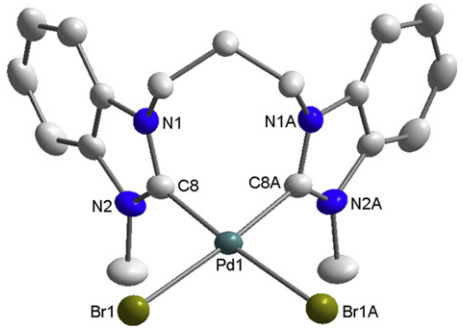


Fig. 1. Molecular structure of complex 6·0.5Et$_2$O showing 50% probability ellipsoids. Only one of two independent half molecules is shown. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1-C8 1.986(6), Pd1-Br1 2.4832(8); C8-Pd1-C8A 85.7(3), Br1-Pd1-Br1A 96.38(2), C8-Pd1-Br1 88.96(16), C8-Pd1-Br1A 174.53(17).

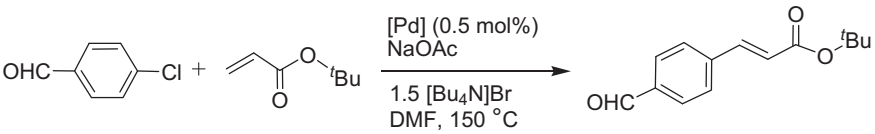
Complexes **1**–**6** have been comparatively studied for their catalytic activities to discern any influences brought across by (i) the length of the bridging unit and (ii) the nature of the NHC moiety. For this purpose, the Mizoroki–Heck coupling reaction of 4-bromobenzaldehyde with *t*-butyl acrylate at 0.5 mol% catalyst loading was initially chosen as a standard test reaction. However, this substrate turned out to be unsuitable for this study, since all 6 complexes gave quantitative conversion. The use of the more difficult substrate 4-chlorobenzaldehyde finally allowed for a comparison of the complexes, and the results are summarized in Table 1. Surprisingly imidazole- and benzimidazole-derived dicarbene complexes showed a different trend. For example, while ethylene-bridged **2** performed best among the diimidazolin-2-ylidene complexes (entry 2), its benzannulated analogue **5** gave the poorest results (entry 5). On the other hand, the propylene-bridged complex **3** was the poorest in the imidazole-derived series (entry 3), although its dibenzimidazolin-2-ylidene analogue turned out to be overall the best precatalyst (entry 6). In most cases, benzimidazole-derived diNHC complexes were superior. A possible explanation for this observation may be the absence of any acidic protons on the benzimidazole heterocycle. Imidazole-derived NHCs on the other hand contain acidic protons at C4/5, which may interfere with bases or active intermediates providing for additional catalyst decomposition pathways. Furthermore, small amounts of Pd black were only observed for ethylene-bridged complexes **2** and **5** pointing to their generally lower stability under the harsh reaction conditions (Table 2).

2.2. Syntheses, characterizations and catalytic activities of hetero-dicarbene Pd(II) complexes

Having identified the propylene-bridged dibenzimidazolin-2-ylidene complex **6** as the best homo-dicarbene Pd(II) precatalyst, we turned our attention to *hetero-dicarbenes* with propylene spacers as new ligand systems that contain two different NHC units. An obvious choice would be to combine imidazole- and benzimidazole-derived NHCs in one diNHC ligand. Previously, we have already reported a new methodology for the preparation of *hetero-bis(carbene)* Pd(II) complexes, which contain two different monodentate NHCs [3]. These complexes have been used as probes for the donor strength determination of various carbenes and are also catalyst precursors in their own right [19]. In this work, however, we focus on *cis*-chelating bidentate ligands containing two different carbene units. The electronic asymmetry induced by such hetero-dicarbenes through their two electronically different donors may lead to complexes of interesting properties and catalytic activities.

The preparation of the hetero-dicarbene complexes **7** and **8** and their hetero-diazolium salt precursors is summarized in Scheme 1. The reaction of methyl- or benzylbenzimidazole with neat dibromopropane afforded the bromopropyl-benzimidazolium bromides **H** and **G** in yields of 80 and 72%, respectively. Both salts are soluble in dichloromethane, and thus can be easily separated from small amounts of the respective propylene-bridged dibenzimidazolium salts that may form as by-products. The formation of **H** and **G** is supported by base peaks in their ESI mass spectra at $m/z = 254$ and 330 for their molecular cations $[M–Br]^+$. Furthermore, their ^{1}H NMR spectra show downfield signals at 10.05 and 9.92 ppm characteristic for the NCHN protons in azolium salts and the expected multiplets assignable to the inequivalent methylene groups of the bromopropylene *N*-substituents (Scheme 2).

Table 1
Mizoroki–Heck Coupling reactions catalyzed by complexes **1**–**6**.[a]



Entry	Catalyst	*t* [h]	Yield [%][b]	TON
1	**1**	18	39	78
2	**2**	18	46	92
3	**3**	18	33	66
4	**4**	18	77	154
5	**5**	18	25	50
6	**6**	18	90	180

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs.

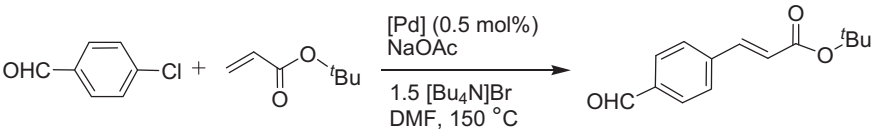
The desired hetero-diazolium salts **I**·2HBr and **J**·2HBr were furnished by nucleophilic substitution reactions of **H** and **G** with methylimidazole and benzylimidazole, respectively. As expected, the solubilities of both hetero-diazolium bromides decrease further compared to those of their precursors making them only soluble in highly polar solvents like water, alcohols, DMF and DMSO. Evidence for their formation can be found in their ESI mass spectra, which shows strong peaks at $m/z = 335$ for the $[M-Br]^+$ monocation of **I**·2HBr and at $m/z = 204$ for the $[M-2Br]^{2+}$ dication for **J**·2HBr. Their NMR spectra also show the presence of both imidazolium and benzimidazolium units in a 1:1 ratio with two very downfield signals in the ^{1}H NMR spectrum for the acidic NCHN protons. The lowest field signal was assigned to the more acidic benzimidazolium C2-proton.

Palladation occurs straightforwardly with $Pd(OAc)_2$ in DMSO at elevated temperatures affording the first hetero-dicarbene Pd(II) complexes **7** and **8** as pale yellow or off-white solids. Like their homo-dicarbene analogues, they are only soluble in more polar organic solvents such as DMF, DMSO and sparingly soluble in CH_3CN. Complex **8** is also sparingly soluble in chlorinated solvents. ESI mass spectrometry supports their formation by isotopic patterns at $m/z = 482$ for $[M-Br + CH_3CN]^+$ and $m/z = 593$ for $[M-Br]^+$ for complex fragments of **7** and **8**, respectively. The absence of downfield signals in their ^{1}H NMR spectra characteristic for their ligand precursors **I**·2HBr and **J**·2HBr also indicates the formation of carbene complexes. Furthermore, all methylene protons become diastereotopic upon coordination indicating a rigid structure with restricted movement of the propylene bridges. As expected, two carbene signals are observed for each complex at 174.3 and 159.6 ppm (**7**) and 175.0 and 160.2 ppm (**8**), respectively. The more downfield resonances are assigned to the benzimidazolin-2-ylidene donor.

Single crystals of **8** suitable for X-ray diffraction were obtained as the solvate **8**·0.5CH_3CN by slow evaporation of a mixed acetonitrile/ethyl acetate solution. The molecular structure depicted in Fig. 2 confirms its identity as a square-planar dibromido-hetero-dicarbene Pd(II) complex. The bite angle of the *cis*-chelating hetero-dicarbene ligand is with 85.66(18)° essentially the same as in the homo-dicarbene complex **6**. The dihedral angles between both imidazole- and benzimidazole-derived carbene planes and the PdC_2Br_2 coordination planes are with values of 77° and 79° likewise very similar to those found in **6**. The Pd–$C_{carbene}$ bond distances of 1.977(7) and 1.967(4) Å are indistinguishable within 3σ. The Pd–Br distances, on the other hand, are significantly different. Notably, the Pd–Br bond *trans* to the imidazolin-2-ylidene is with 2.4855(9) Å markedly longer than that *trans* to the benzannulated NHC [2.4783(6) Å], perhaps indicating a stronger *trans* influence of imidazole-derived NHCs.

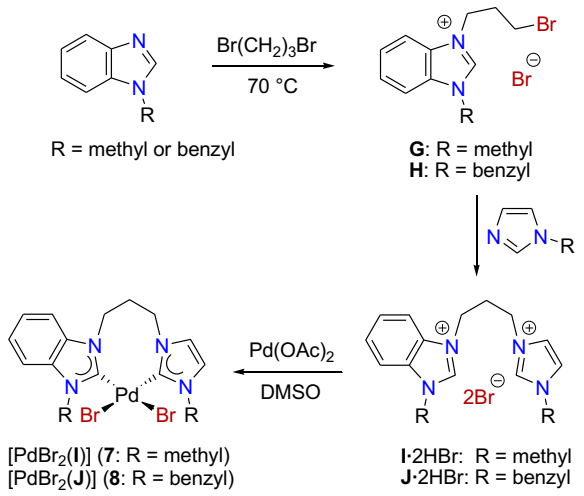
With the two hetero-dicarbene complexes **7** and **8** in hand, their catalytic activities have been tested and compared to those of the homo-dicarbene complexes **1**–**6**. Under identical reaction conditions, it was found that both **7** and **8** gave rise to better precatalysts resulting in quantitative yields of the Mizoroki–Heck product. When the reaction time was shorten to 12 h there was no drop in yield (entries 1 and 2). Further shortening of the time to 6 h finally revealed the superiority of complex **7** over **8**. The former still gave near-quantitative yield (entry 3), while the latter afforded only 43%

Table 2
Mizoroki–Heck Coupling reactions catalyzed by complexes **7** and **8**.[a]



Entry	Catalyst	*t* (h)	Yield (%)[b]	TON
1	**7**	12	>99	200
2	**8**	12	>99	200
3	**7**	6	98	196
4	**8**	6	43	86
5	**7**	3	78	156

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs.



Scheme 2. Syntheses of Pd(II) *hetero-dicarbene* complexes **7** and **8**.

(entry 4). Even after 3 h, a good yield of 78% could be obtained with complex **7** (entry 5). It is interesting to note that complex **8** with bulkier *N*-benzyl groups is inferior to its analogue **7** with *N*-methyl groups. Again, the presence of rather acidic benzylic protons may lead to a non-innocent behaviour of benzyl-substituted ligands causing catalyst decomposition particularly under the harsh reaction conditions employed. A cleavage of the benzylic C–N bond is also feasible.

To study the scope and limitations of the most active and stable catalyst precursor **7**, it was subjected to a range of substrates (Table 3). 9-Bromoanthracene and 2,6-dibromopyridine could be coupled quantitatively giving the desired mono- and disubstituted products (entries 1 and 2). Activated aryl chlorides with nitro and cyano substituents also gave near-quantitative yields (entries 3 and 4). Surprisingly, chloroacetophenone gave only a moderate yield of 47% (entry 5), which is comparable to that of the parent chlorobenzene (entry 6). Finally, the lowest yield of 22% was obtained with the difficult substrate chloropyridine revealing the limitation of complex **7**.

3. Conclusion

Six *homo-dicarbene* Pd(II) complexes bearing imidazole- (**1**–**3**) and benzimidazole-derived carbenes (**4**–**6**) with C1-C3 alkyl bridges have been synthesized. Comparison of their catalytic activities in the Mizoroki–Heck reaction revealed that C1 and C3 bridged-dicarbenes gave generally better Pd-catalysts. Furthermore, benzimidazolin-2-ylidenes were found to be superior to their imidazolin-2-ylidenes possibly due to the absence of any interfering acidic protons on the heterocycle. Based on these results, two Pd(II) complexes (**7** and **8**) of new propylene-bridged *hetero-dicarbenes* containing both imidazole- and benzimidazole-derived NHCs have been synthesized. Their catalytic activities turned out to be superior to that of homo-dicarbene complexes, which may be traced back to an electronic asymmetry induced by the unusual hetero-dicarbene ligands. Research is currently underway to expand the scope of new hetero-dicarbenes as *cis*-chelating ligands for other transition metal and to explore their use in catalysis.

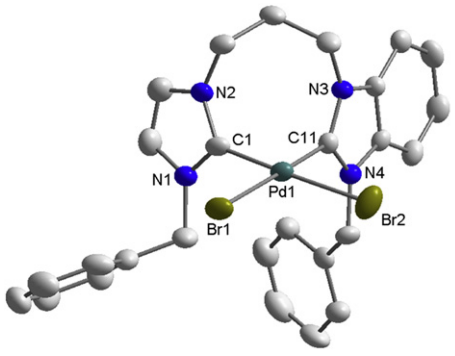


Fig. 2. Molecular structure of complex $8\cdot0.5CH_3CN$ showing 50% probability ellipsoids. Hydrogen atoms and the solvent molecule have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Pd1-C1 1.977(7), Pd1-C11 1.967(4), Pd1-Br1 2.4783(6), Pd1-Br2 2.4855(9); C1-Pd1-C11 85.66(18), Br1-Pd1-Br2 94.4(2), C1-Pd1-Br1 91.44(13), C11-Pd1-Br2 88.45(13), C1-Pd1-Br2 173.91(13), C11-Pd1-Br1 176.73(14).

4. Experimental section

4.1. General considerations

All manipulations were carried out without taking precautions to exclude air and moisture unless otherwise stated. All solvents were used as received. The preparation of dicarbene salt precursors **A**·2HBr [10], **B**·2HBr [8], **C**·2HBr [20], **D**·2HBr [10,14], **E**·2HBr [10], **F**·2HBr [16] and the dicarbene complexes **1** [21] and **4** [14] have been reported elsewhere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 or AMX 500 spectrometer. The chemical shifts were internally referenced to the residual protio solvent signals relative to tetramethylsilane. ESI mass spectra were obtained using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

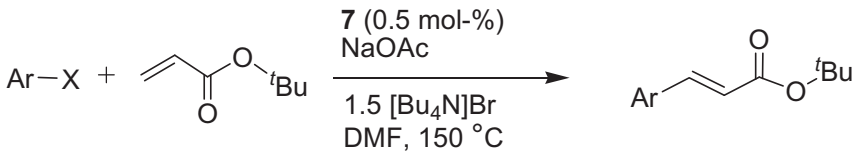
4.1.1. 1-(3-bromopropyl)-3-methylbenzimidazolium bromide (*G*)

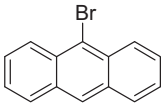
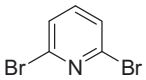
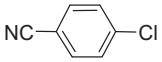
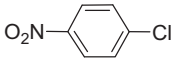
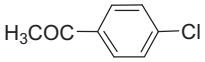
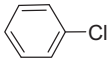
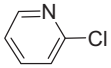
1-methylbenzimidazole (0.581 g, 4.4 mmol) was added to 1,3-dibromopropane (6 mL), and the resulting mixture was stirred for 12 h at 70 °C. The reaction mixture was added dropwise into a flask containing diethyl ether (50 mL) under stirring, and the resulting suspension was filtered through a sintered funnel. The solid product was washed with diethyl ether and dried under vacuum. Compound **G** (1.17 g, 3.52 mmol, 80%) was isolated as a white powder. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.81 (s, 1 H, NCHN), 8.10 (dd, 1 H, Ar-H), 8.04 (dd, 1 H, Ar-H), 7.71 (m, 2 H, Ar-H), 4.62 (t, 2 H, ^3J(H,H) = 6.9 Hz, NCH_2), 4.08 (s, 3 H, NCH_3), 3.62 (t, 2 H, ^3J(H,H) = 6.7 Hz, CH_2Br), 2.46 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): 143.0 (NCN), 131.9, 130.9, 126.5, 126.4, 113.6, 113.4 (Ar-C), 45.2 (NCH_2), 33.2 (NCH_3), 31.5 (CH_2Br), 30.7 (CH_2). MS (ESI): m/z = 254 $[M-Br]^+$.

4.1.2. 1-(3-bromopropyl)-3-benzylbenzimidazolium bromide (*H*)

1,3-dibromopropane (5 mL) was added to benzylbenzimidazole (0.625 g, 3 mmol) and stirred for 12 h at 70 °C. After cooling to room temperature, the reaction mixture was added dropwise into a flask containing diethyl ether (50 mL) under stirring. The resulting suspension was filtered through a sintered funnel, and the residue was subsequently washed with ethyl acetate and dried under reduced pressure to afford compound **H** (0.885 g, 2.16 mmol, 72%) as a white powder. ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.05 (s, 1 H, NCHN), 8.13 (d, 1 H, Ar-H), 7.96 (d, 1 H, Ar-H), 7.67 (m, 2 H, Ar-H), 7.54 (d, 2 H, Ar-H), 7.41 (m, 3 H, Ar-H), 5.79 (s, 2 H, NCH_2Ph), 4.66 (t, 2 H, ^3J(H,H) = 6.95 Hz, NCH_2), 3.66 (t, 2 H, ^3J(H,H) = 6.3 Hz, CH_2Br), 2.51 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR (125.77 MHz, DMSO-d_6): 142.8 (NCN), 133.9, 131.3, 130.9, 128.9, 128.7, 128.3, 126.7, 113.9, 113.7 (Ar–C), 49.9 (NCH_2Ph), 45.5 (NCH_2), 31.3 (CH_2Br), 30.8 (CH_2). MS (ESI): m/z = 330 $[M-Br]^+$.

Table 3
Mizoroki–Heck Coupling reactions catalyzed by complex **7**.[a]



Entry	Aryl halide	*t* [h]	Yield [%][b]	TON
1		18	>99	200
2[c]		18	>99	200
3		18	97	194
4		18	95	190
5		18	47	94
6		48	41	82
7		48	22	44

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^{1}H NMR spectroscopy for an average of two runs.
[c] The yield refers to the doubly coupled product.

*4.1.3. Hetero-diazolium salt (**I**·2HBr)*

Compound **G** (0.27 g, 0.81 mmol) was added to 1-methylimidazole (3 mL) and the resulting mixture was stirred at 90 °C for 12 h. After cooling to room temperature, the reaction mixture was added to a flask containing diethyl ether under stirring, and the resulting suspension was filtered through a sintered funnel. The residue was subsequently washed with diethyl ether. Upon drying the residue under reduced pressure, compound **I**·2HBr (0.32 g, 0.77 mmol, 95%) was isolated as an off-white powder. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.92 (s, 1 H, NCH_{bimi}N), 9.26 (s, 1 H, NCH_{imi}N), 8.12 (dd, 1 H, Ar-H), 8.05 (dd, 1 H, Ar-H), 7.84 (s, 1 H, Ar-H), 7.83–7.70 (m, 3 H, Ar-H), 4.60 (t, 2 H, N$_{bimi}$CH_2), 4.37 (t, 2 H, N$_{imi}$CH_2), 4.12 (s, 3 H, N$_{bimi}$CH_3), 3.85 (s, 3 H, N$_{imi}$CH_3), 2.52 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 142.9 (NC$_{bimi}$N), 136.8 (NC$_{imi}$N), 131.8, 130.8, 126.5, 126.4, 123.7, 122.1, 113.6, 113.5 (Ar-C), 45.8 (N$_{bimi}$CH_2), 43.6 (N$_{imi}$CH_2), 35.8 (N$_{bimi}$CH_3), 33.3 (N$_{imi}$CH_3), 28.8 (CH_2). MS (ESI): m/z = 335 [M–Br]$^+$.

*4.1.4. Hetero-diazolium salt (**J**·2HBr)*

Compound **H** (0.41 g, 1 mmol) was added to a CH_3CN solution of benzylimidazole (0.316 g, 2 mmol) and stirred for 12 h at 80 °C. The solvent of the reaction mixture was removed under reduced pressure and the resulting residue was washed with diethyl ether and CH_2Cl_2. Upon drying the residue under vacuum, compound **I**·2HBr (0.517 g, 0.9 mmol, 91%) was isolated as a white powder. ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.14 (s, 1 H, NCH_{bimi}N), 9.47 (s, 1 H, NCH_{imi}N), 8.14 (dd, 1 H, Ar-H), 7.98 (m, 1 H, Ar-H), 7.91 (t, 1 H, Ar-H), 7.85 (t, 1 H, Ar-H), 7.68 (m, 2 H, Ar-H), 7.55 (m, 2 H, Ar-H), 7.44–7.40 (m, 8 H, Ar-H), 5.82 (s, 2 H, N$_{bimi}$CH_2Ph), 5.46 (s, 2 H, N$_{imi}$CH_2Ph), 4.63 (t, 2 H, ^3J(H,H) = 7.05 Hz, N$_{bimi}$CH_2), 4.41 (t, 2 H, ^3J(H,H) = 7.05 Hz, N$_{imi}$CH_2), 2.56 (m, 2 H, CH_2). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 142.6 (NC$_{bimi}$N), 136.4 (NC$_{imi}$N), 134.7, 133.9, 131.3, 130.9, 129.0, 128.9, 128.7, 128.4, 126.7, 126.6, 122.8, 122.6, 114.0, 113.9 (Ar-C), 51.9 (N$_{bimi}$CH_2Ph), 49.9 (N$_{imi}$CH_2Ph), 46.2 (N$_{bimi}$CH_2), 44.0 (N$_{imi}$CH_2), 28.7 (CH_2). MS (ESI): m/z = 204 [M–2Br]$^{2+}$.

*4.1.5. Dibromido-(1,1′-dimethyl-3,3′-ethylenediimidazolin-2,2′-diylidene)palladium(II) (**2**)*

A mixture of **B**·2HBr (352 mg, 1.0 mmol) and Pd(OAc)$_2$ (225 mg, 1.0 mmol) was stirred in DMSO (10 mL) at 70 °C for 24 h. The solution was then filtered through a small column of Celite, and the solvent was removed completely by vacuum distillation. The residue was washed with water, ethanol, hexane and diethyl ether. Drying under vacuum gave a yellow solid (150 mg, 0.33 mmol, 33%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.38 (s, 2H, CH), 7.34 (s, 2H, CH), 5.19 (m, 2H, C*H*H), 4.50 (m, 2H, CH*H*), 3.87 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (75.47 MHz, DMSO-d_6): 156.9 (NCN), 123.7 (CH), 122.5 (CH), 46.7 (CH_2), 35.8 (CH_3). MS (ESI): m/z = 376 [M–Br]$^+$.

*4.1.6. Dibromido-(1,1′-dimethyl-3,3′-propylenediimidazolin-2,2′-diylidene)palladium(II) (**3**)*

Complex **3** was synthesized in analogy to compound **2** from **C**·2HBr (183 mg, 0.5 mmol) and Pd(OAc)$_2$ (113 mg, 0.5 mmol) and isolated as a yellow solid (204 mg, 0.403 mmol, 86.8%). ^{1}H NMR

(300 MHz, DMSO-d_6): δ 7.31 (s, 2H, CH), 7.27 (s, 2H, CH), 4.84 (m, 2H, NC*H*H), 4.34 (m, 2H, NCH*H*), 3.91 (s, 6H, CH_3), 2.33 (m, 1H, C*H*H), 1.73 (m, 1H, NCH*H*). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): 123.0 (CH), 122.8 (CH), 51.3 (NCH_2), 37.5 (CH_3), 30.6 (CH_2). The carbene signal of **3** could not be detected due to poor solubility. MS (ESI): $m/z = 390$ $[M-Br]^+$.

4.1.7. Dibromido-(1,1′-dimethyl-3,3′-ethylenedibenzimidazolin-2,2′-diylidene)palladium(II) (**5**)

Complex **5** was synthesized in analogy to compound 2 from E·2HBr (226 mg, 0.5 mmol) and $Pd(OAc)_2$ (113 mg, 0.5 mmol) and isolated as a yellow solid (131 mg, 0.24 mmol, 47%). ^1H NMR (300 MHz, DMSO-d_6): δ 7.69 (m, 4H, Ar-H), 7.39 (m, 4H, Ar-H), 5.62 (br s, 2H, CH*H*), 5.07 (br s, 2H, CH*H*), 4.14 (s, 6H, CH_3). The ^{13}C NMR spectrum of **5** could not be obtained due to poor solubility. MS (ESI): $m/z = 476$ $[M-Br]^+$.

4.1.8. Dibromido-(1,1′-dimethyl-3,3′-propylenedibenzimidazolin-2,2′-diylidene)palladium(II) (**6**)

Complex **6** was synthesized in analogy to compound **2** from **F**·2HBr (233 mg, 0.5 mmol) and $Pd(OAc)_2$ (113 mg, 0.5 mmol) and isolated as a yellow solid (246 mg, 0.43 mmol, 86%). ^1H NMR (300 MHz, DMSO-d_6): δ 7.71 (m, 2H, Ar-H), 7.60 (m, 2H, Ar-H), 7.31 (m, 4H, Ar-H), 5.23 (m, 2H, NC*H*H), 4.90 (m, 2H, NCH*H*), 4.23 (s, 6H, CH_3), 2.73 (m, 1H, C*H*H), 2.27 (m, 1H, CH*H*). The ^{13}C NMR spectrum of **6** could not be obtained due to poor solubility. MS (ESI): $m/z = 491$ $[M-Br]^+$.

4.1.9. Pd(II) hetero-dicarbene complex (**7**)

$Pd(OAc)_2$ (0.15 g, 0.67 mmol) was added to a DMSO solution of compound **I**·2HBr (0.333 g, 0.8 mmol). The orange solution was stirred for 12 h at 90 °C. The reaction mixture was filtered over Celite, and the solvent of the filtrate was removed by vacuum distillation. The resulting residue was washed with water and subsequently with ethanol. Upon drying the residue under vacuum, complex **7** (0.275 g, 0.53 mmol, 79%) was isolated as a pale yellow powder. ^1H NMR (300 MHz, DMSO-d_6): δ 7.74 (m, 1 H, Ar-H), 7.62 (m, 1 H, Ar-H), 7.37–7.25 (m, 4 H, Ar-H), 5.16 (m, 1 H, NC*H*H), 4.89 (m, 2 H, NCH*H*), 4.41 (m, 1 H, NC*H*H), 4.20 (s, 3 H, $N_{bimi}CH_3$), 3.94 (s, 3 H, $N_{imi}CH_3$), 2.44 (m, 1 H, C*H*H), 1.82 (m, 1 H, CH*H*). $^{13}C\{^1H\}$ NMR (75.47 MHz, DMSO-d_6): 174.3 ($NC_{bimi}N$), 159.6 ($NC_{imi}N$), 133.9, 133.4, 123.4, 123.3, 123.1, 111.0, 110.4 (Ar-C), 51.6 ($N_{bimi}CH_2$), 48.4 ($N_{imi}CH_2$), 37.6 ($N_{bimi}CH_3$), 35.0 ($N_{imi}CH_3$), 30.2 (CH_2). MS (ESI): m/z 482 $[M-Br + CH_3CN]^+$.

4.1.10. Pd(II) hetero-dicarbene complex (**8**)

A mixture of salt **J**·2HBr (0.341 g, 0.6 mmol) and $Pd(OAc)_2$ (0.112 g, 0.5 mmol) in DMSO (8 mL) was stirred at 85 °C for 12 h. The reaction mixture was filtered over Celite and the solvent from the filtrate was removed by vacuum distillation. The resulting residue was washed with water and ethanol. Upon drying under reduced pressure, complex **2** (0.289 g, 0.43 mmol, 86%) was obtained as an off-white powder. ^1H NMR (500 MHz, DMSO-d_6): δ 7.77 (d, 1 H, Ar-H), 7.37–7.30 (br m, 8 H, Ar-H), 7.18 (m, 5 H, Ar-H), 6.97 (d, 1 H, Ar-H), 6.91 (s, 1 H, Ar-H), 6.25 (d, 1 H, NC*H*HPh), 5.88 (d, 1 H, NCH*H*Ph), 5.34 (t, 1 H, NC*H*H), 5.25 (d, 1 H, NC*H*HPh), 5.05 (t, 1 H, NC*H*H), 4.93 (dd, 1 H, NCH*H*), 4.70 (d, 1 H, NCH*H*Ph), 4.48 (dd, 1 H, NCH_2), 2.54 (m, 1 H, C*H*H), 2.00 (m, 1 H, CH*H*). $^{13}C\{^1H\}$ NMR (125.77 MHz, DMSO-d_6): 175.0 ($NC_{bimi}N$), 160.2 ($NC_{imi}N$), 136.0, 135.1, 133.9, 132.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.3, 124.3, 123.5, 123.3, 121.3, 111.8, 110.9 (Ar-C), 52.8 ($N_{bimi}CH_2Ph$), 51.8 ($N_{bimi}CH_2$), 51.6 ($N_{imi}CH_2Ph$), 48.6 ($N_{imi}CH_2$), 30.1 (CH_2). MS (ESI): $m/z = 593$ $[M-Br]^+$.

4.2. General procedure for the Mizoroki–Heck reaction

In a typical run, a test tube was charged with a mixture of aryl halide or dihalide (1.0 mmol), *tert*-butyl acrylate (1.5 mmol or 3.0 mmol for dihalides), anhydrous sodium acetate (1.5 mmol), catalyst (0.005 mmol), and $[Bu_4N]Br$ (1.5 mmol). To the mixture was then added DMF (3 mL). The reaction mixture was vigorously stirred at 150 °C. After the desired reaction time, the solution was allowed to cool. Dichloromethane (10 mL) was added to the reaction mixture, and the organic phase was washed with water (6 × 5 mL) and dried over $MgSO_4$. The solvent was removed by evaporation to give a crude product, which was analyzed by ^1H NMR spectroscopy.

Table 4
Selected X-ray crystallographic data for complexes **6** and **8**.

	6·0.5Et_2O	**8**·0.5CH_3CN
Formula	$C_{21}H_{25}Br_2N_4O_{0.5}Pd$	$C_{28}H_{27.5}Br_2N_{4.5}Pd$
Formula weight	607.67	693.27
Colour	Yellow	Colourless
Temperature (K)	223(2)	223(2)
Crystal size (mm)	0.40 × 0.30 × 0.06	0.54 × 0.12 × 0.06
Crystal system	Orthorhombic	Monoclinic
Space group	$Pmn2_1$	$C2/c$
a (Å)	17.2475(9)	32.294(2)
b (Å)	8.2837(4)	9.1189(6)
c (Å)	15.1503(8)	20.7260(14)
α (°)	90	90
β (°)	90	116.8280(10)
γ (°)	90	90
V (Å3)	2164.57(19)	5446.5(6)
Z	4	8
D_c (g cm^{-3})	1.865	1.691
θ range (°)	1.79 to 27.49	2.01 to 27.50
Unique data	14782	18981
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0384$, $wR_2 = 0.1029$	$R_1 = 0.0505$, $wR_2 = 0.1123$

4.3. X-ray diffraction studies

Suitable single crystals were mounted on glass fibres. X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo K_α radiation, with the SMART suite of programs [22]. Data was processed and corrected for Lorentz and polarization effects with SAINT [23], and for absorption effect with SADABS [24]. Structural solution and refinement were carried out with the SHELXTL suite of programs [25]. The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were put at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. A summary of the most important crystallographic data is given in Table 4.

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Appendix A. Supplementary material

CCDC 825978 (for **6**·0.5Et2O) and 825979 (for **8**·0.5CH_3CN); contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2011.07.018. These

data include MOL files and InChiKeys of the most important compounds described in this article.

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