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Efficient Palladium(II) Precatalysts Bearing 4,5-Dicyanoimidazol-2-ylidene for the Mizoroki–Heck Reaction

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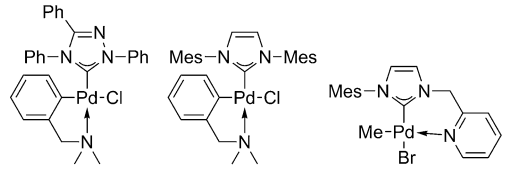
The new N-heterocyclic carbene (NHC) complex $[PdCl_2\{(CN)_2IMes\}(PPh_3)]$ (**2**) ({$(CN)_2IMes$}: 4,5-dicyano-1,3-dimesitylimidazol-2-ylidene) and the NHC palladacycle [PdCl(dmba){$(CN)_2IMes$}] (**3**) (dmba: *N*,*N*-dimethylbenzylamine) have been synthesized by thermolysis of 4,5-dicyano-1,3-dimesityl-2-(pentafluorophenyl)imidazoline (**1**) in the presence of suitable palladium(II) precursors. The acyclic complex **2** was formed by ligand exchange using the mononuclear precursor $[PdCl_2(PPh_3)_2]$ and the palladacycle **3** was formed by cleavage of the dinuclear chloro-bridged precursor $[Pd(\mu\text{-}Cl)(dmba)]_2$. The new NHC precursor 1-benzyl-4,5-dicyano-2-(pentafluorophenyl)-3-picolylimidazoline (**5**) was formed by condensation of pentafluorobenzaldehyde with *N*-benzyl-*N*′-picolyldiaminomaleonitrile (**4**). The NHC palladacycle $[PdCl_2\{(CN)_2IBzPic\}]$ (**6**) ({$(CN)_2IBzPic$}: 1-benzyl-4,5-dicyano-3-picolylimidazol-2-ylidene) was prepared by in situ thermolysis of **5** in the presence of $[PdCl_2(PhCN)_2]$. The three palladium(II) complexes were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis. In addition, the molecular structures of **2** and **3** were determined by X-ray diffraction. The π-acidity of $(CN)_2IBzPic$ was compared with $(CN)_2IMes$ and perviously reported π-acidic imidazol-2-ylidenes by NBO analysis. The Mizoroki–Heck (MH) reactions of various aryl halides with *n*-butyl acrylate were performed in the presence of complexes **2**, **3** and **6**. The new precatalysts showed high activity in the MH reactions giving good-to-excellent product yields with 0.1 mol-% precatalyst. The nature of the catalytically active species of **2**, **3** and **6** was investigated by poisoning experiments with mercury and transmission electron microscopy. It was found that palladium nanoparticles formed from the precatalysts were involved in the catalytic process.

Introduction

For the last 40 years, the Mizoroki–Heck reaction (MH reaction) has been one of the most useful preparative tools for the synthesis of pharmaceuticals, natural products and polymer building blocks,[1] leading to the Nobel Prize in chemistry in 2010. Since the early 1970s, complexes bearing tertiary phosphine ligands have been used as efficient precatalysts for the MH reaction.[2] However, their use has been limited due their expense and the intolerance of the phosphine ligands towards air and moisture. N-Heterocyclic carbenes (NHCs) offer an efficient alternative to tertiary phosphines. Since the report of the first isolated NHC in 1991, NHCs have become one of the most intensively investigated ligand families in the field of transition-metal catalysis.[3] Since the initial presentation of NHC-bearing palladium precatalysts for the Mizoroki–Heck reaction by Herrmann et al. in 1995,[4] tremendous effort has been devoted to the development of new NHCs and their metal complexes, leading to a variety of NHC ligands with a broad range of steric and electronic properties.[5] This variety has allowed the synthesis of customized NHC ligands for specific applications. In particular, strong σ-donating ligands with negligible π-accepting ability have been used to create efficient precatalysts. On the other hand, there are only a few reports of transition-metal precatalysts bearing π-acceptor NHCs.[6] The few contributions concerning transition-metal catalysis by complexes bearing π-acceptor carbenes showed that the MH reaction could be performed efficiently with these complexes.[6d] In 2005, Herrmann and co-workers presented the NHC palladacycle [PdCl(dmba)(NHC)] (dmba: *N*,*N*-dimethylbenzylamine) (**A**) bearing a 1,2,4-triazole-based NHC ligand (Scheme 1),[7a]



A — Herrmann 2005[7a] | B — Ying 2008[7b] | C — Hursthouse 2000[10]

Scheme 1. Palladacycle precatalysts bearing NHCs.

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and in 2008, Ying and co-workers synthesized the efficient precatalyst [PdCl(dmba)(IMes)] (**B**) bearing 1,3-dimesitylimidazol-2-ylidene (IMes).[7b] Both palladacycles showed good catalytic activity in the coupling of aryl bromides with terminal olefins. Under optimized conditions, even rather unreactive aryl chlorides could be used for the MH reaction.

Another example of a catalytically active complex contains a NHC bearing a chelating unit. In 2000, Hursthouse and co-workers presented the catalytically active palladium(II) complex **C** bearing a picolyl-substituted NHC (Scheme 1).[10] In the palladacycle, the carbenic carbon atom and the nitrogen atom of the picolyl substituent act as coordinating atoms. Unfortunately, these complexes only showed high reaction yields in the MH reactions of iodobenzene or strongly activated aryl bromides with methyl and *n*-butyl acrylate.

In general, palladacycles form catalytically active palladium(0) under MH conditions (e.g., high temperature).[8] The zero-valent palladium can be stabilized by a bulky ligand, thus forming the catalytically active [Pd^0(NHC)] species.[9] Otherwise palladium black formation and precipitation will occur and terminate the MH reaction.

It was our goal to prepare stable palladium(II) precatalysts for the MH reaction with π-acceptor carbenes. By using our new precatalysts, stable [Pd^0(NHC)] particles should be formed during the catalytic process by reductive elimination, and it is these particles that are expected to be the catalytically active species.

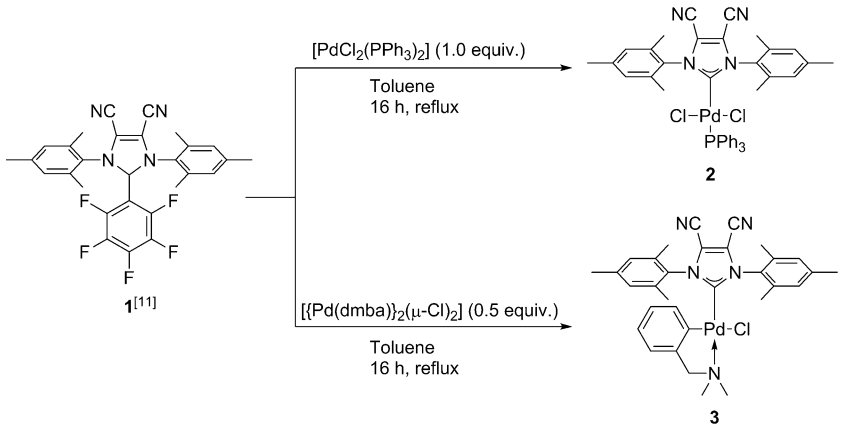
In this contribution we present the acyclic palladium(II) complex [$PdCl_2${$(CN)_2$IMes}(PPh_3)] (**2**) ({$(CN)_2$IMes}: 4,5-dicyano-1,3-dimesitylimidazol-2-ylidene) and the palladacycle [PdCl(dmba){$(CN)_2$IMes}] (**3**) (see Scheme 2). 4,5-Dicyano-1,3-dimesitylimidazol-2-ylidene is a strong π-acceptor, as indicated by the high Tolman electronic parameter (TEP) of 2060 cm^{-1}.[11] The NHC $(CN)_2$IMes was formed in situ by thermolysis of imidazoline **1** and reacted with suitable palladium(II) sources to give the palladium precatalysts **2** and **3**. Because the stability of the [Pd^0(NHC)] species, which is formed in the catalytic process, should be enhanced, we prepared 1-benzyl-4,5-dicyano-2-(pentafluorophenyl)-3-picolylimidazoline (**5**), which is the precursor for the chelating NHC ligand $(CN)_2$IBzPic ({$(CN)_2$IBzPic}: 1-benzyl-4,5-dicyano-3-picolylimidazol-2-ylidene; see Scheme 3). The complex [$PdCl_2${$(CN)_2$IBzPic}] (**6**) was prepared by thermolysis of **5** in the presence of [$PdCl_2(PhCN)_2$]. The three complexes **2**, **3** and **6** were used as precatalysts in the MH reactions of various aryl halides with *n*-butyl acrylate. They showed good catalytic activity, with the precatalysts **3** and **6** showing superior catalytic activity than their analogues **B** and **C**, respectively.[7b,10]

Results and Discussion

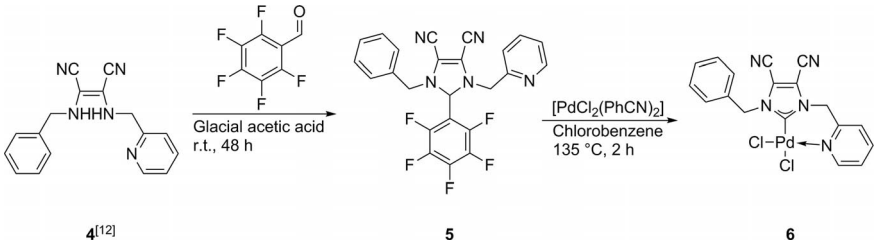
Syntheses

The NHC palladium(II) complexes **2** and **3** were prepared by heating the NHC precursor **1**, recently presented by our group,[11] in the presence of [$PdCl_2(PPh_3)_2$] or [Pd(μ-Cl)(dmba)]$_2$, respectively, in toluene at reflux for 16 h (Scheme 2). After work-up, including chromatographic purification on silica with dichloromethane as eluent, complexes **2** and **3** were obtained in good yields (**2**: 64%; **3**: 72%).

The new NHC precursor 1-benzyl-4,5-dicyano-2-(pentafluorophenyl)-3-picolylimidazoline (**5**) was prepared in a facile five-step synthesis. We started with the formation of the known *N*-benzyl-*N*′-picolyldiaminomaleonitrile (**4**)[12] and the synthetic procedure was concluded with the condensation of **4** with pentafluorobenzaldehyde in glacial acetic acid to obtain **5** in a yield of 67% (Scheme 3). Thermogravimetric analysis (TGA-MS) and differential thermoanalysis (DTA) were used to investigate the thermal decomposition and carbene formation of imidazoline **5** (Figure 1). A loss of mass of 34% was observed between 132 and 191 °C, which correlates with the theoretical loss of pentafluorobenzene (36 wt.-%) and the formation of the NHC $(CN)_2$IBzPic. An exothermic peak in the DTA at an onset temperature of 132 °C, accompanied by a mass peak at *m*/*z*



Scheme 2. Preparation of NHC palladium(II) complexes **2** and **3**.



Scheme 3. Preparation of imidazoline **5** and NHC palladium(II) complex **6**.

= 168 for pentafluorobenzene with a maximum at 160 °C, was observed by TGA-MS.

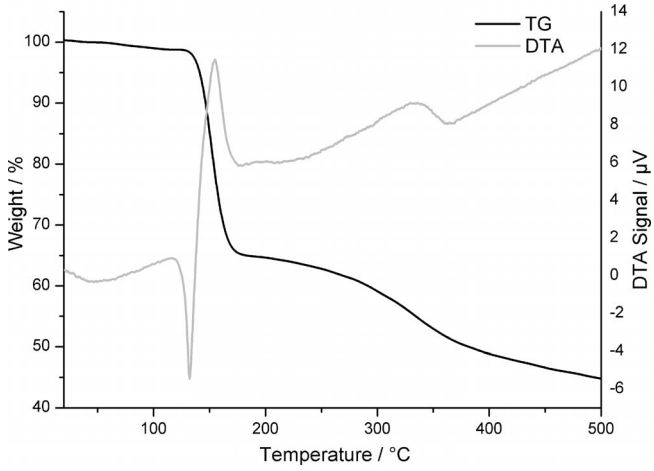


Figure 1. Thermogravimetric analysis (black line) and differential thermoanalysis (grey line) of 1-benzyl-4,5-dicyano-2-(pentafluorophenyl)-3-picolylimidazoline (**5**).

The new palladium(II) complex $[PdCl_2\{(CN)_2IBzPic\}]$ (**6**) was prepared by slow dropwise addition of a chlorobenzene solution containing $[PdCl_2(PhCN)_2]$ to a solution of **5** in chlorobenzene at an oil-bath temperature of 135 °C. Filtration of the reaction mixture after cooling to room temperature gave crude **6**, which was washed with chloroform, dissolved in dimethyl sulfoxide, precipitated with water and finally washed with chloroform and diethyl ether to obtain **6** in 27% yield. Higher reaction temperatures did not lead to the desired product due to the decomposition of $[PdCl_2(PhCN)_2]$ (Scheme 3).

Compounds **2**, **3**, **5** and **6** are stable towards air and moisture, and were satisfactorily characterized by NMR and IR spectroscopy as well as by mass spectrometry and elemental analysis (C, H, N). The melting points of the compounds could not be determined due to the slow decomposition of the compounds while heating.

X-ray Analysis

Single crystals of the palladium(II) complexes **2** and **3** suitable for X-ray analysis were obtained by slow diffusion of pentane steam into saturated chloroform (**2**) or dichloromethane (**3**) solutions of the complexes at room temperature (Figures 2 and 3).

The Pd–$C_{carbene}$ distance of **2** is 2.0351(19) Å and the Pd–P distance is 2.2964(5) Å. The latter is in the range of

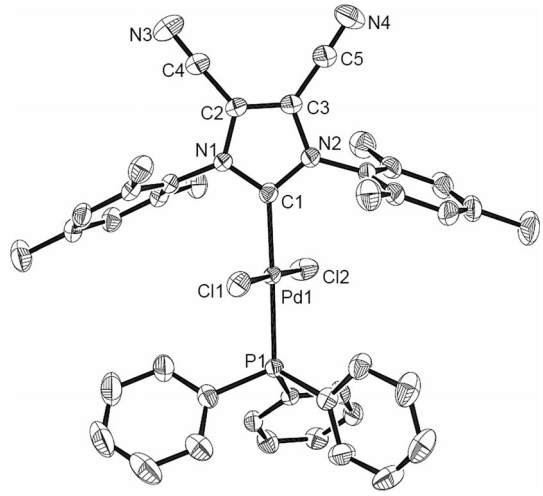


Figure 2. ORTEP structure of **2**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.358(2), C1–N2 1.360(2), C2–N1 1.386(2), C3–N2 1.388(3), C1–Pd1 2.0351(19), P1–Pd1 2.2964(5), Cl1–Pd1 2.2918(6), Cl2–Pd1 2.3051(5), C1–Pd1–P1 177.20(5), C1–Pd1–Cl1 90.81(5), C1–Pd1–Cl2 90.47(5), Cl1–Pd1–Cl2 178.56(2), N1–C1–N2 105.43(16). Hydrogen atoms have been omitted for clarity.

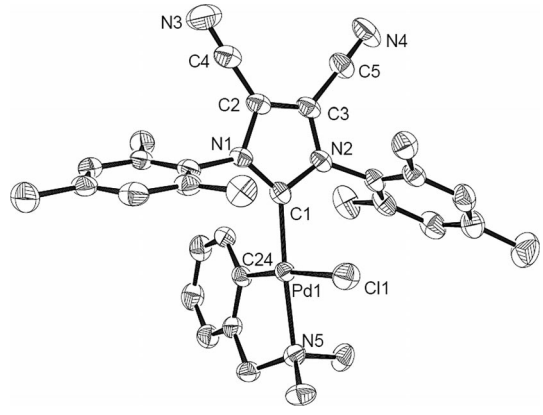


Figure 3. ORTEP structure of **3**. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.371(3), C1–N2 1.373(3), C2–N1 1.374(3), C3–N2 1.397(3), C1–Pd1 1.963(3), N5–Pd1 2.124(2), Cl1–Pd1 2.3853(7), C24–Pd1 2.007(2), C1–Pd1–N5 172.24(8), C1–Pd1–Cl1 92.50(6), C1–Pd1–C24 93.67(9), Cl1–Pd1–C24 172.83(7), C24–Pd1–N5 82.44(9), N5–Pd1–Cl1 91.00(6), N1–C1–N2 103.9(2), C24–C25–C26–N5 –27.9(3). Hydrogen atoms have been omitted for clarity.

the Pd–P distance in the precursor $[PdCl_2(PPh_3)_2]$.[13] The square-planar coordination geometry is slightly distorted with a Cl–Pd–Cl angle of 178.56(2)° and a $C_{carbene}$–Pd–P angle of 177.20(5)°. The Pd–$C_{carbene}$ distance in **3** is 1.963(3) Å, which is slightly shorter than the Pd–$C_{carbene}$ distance of 1.980(2) Å found in the analogous complex **B**.[7b] The phenylidene moiety of the chelating co-ligand dmba in palladacycle **3** is coordinated in the *cis* position and the amino unit in the *trans* position with respect to the NHC ligand. This is the same coordination pattern as found in the analogous complex **B**.[7b]

The four angles C1–Pd1–Cl1 [92.50(6)°], C1–Pd1–C24 [93.67(9)°], C24–Pd1–N5 [82.44(9)°] and Cl1–Pd1–N5 [91.00(6)°] around the palladium centre of **3** are in the range of those of the analogous complex **B**.[7b] The torsion angle between the phenylidene unit and the methyleneamino group (C24–C25–C26–N5) is –27.9(3)°, which is higher than the same torsion angle in **B** [26.3(3)/27.0(3)°]. The Pd–$C_{carbene}$ distance in complex **3** [1.963(3) Å] is slightly shorter than that in **2** [2.0351(19) Å] due to the higher π-acceptor strength of the *trans*-coordinating tertiary triphenylphosphine in complex **2** compared with the coordinated amino unit in complex **3**.

DFT Calculations

The Tolman electronic parameter, as a measure of the π-acceptor strength, of $(CN)_2$IMes has already been determined by our group.[11] As it was not possible to determine the Tolman electronic parameter of the ylidene $(CN)_2$IBzPic, we performed a natural bond orbital (NBO) analysis on $(CN)_2$IBzPic and $(CN)_2$IMes and calculated the energies of the σ-donor (E_σ) and π-acceptor (E_π) orbitals as comparative values. The σ-donor is a lone electron pair located in the sp^2-hybridized orbital and the π-acceptor is the empty p-orbital of the $C_{carbene}$ atom.

Therefore, by comparison of the calculated values of E_σ and E_π, we were able to compare the π-acceptor strengths of $(CN)_2$IBzPic with $(CN)_2$IMes and the previously reported imidazole-based NHCs 1,3-bis(diisopropylphenyl)imidazol-2-ylidene (IPr), 1,3-bis(2,4-dinitrophenyl)imidazol-2-ylidene (IDNP) and 1-(2,4-dinitrophenyl)-3-methylimidazol-2-ylidene (IMeDNP; Table 1).[14] The E_σ and E_π values of the two 4,5-dicyanoimidazol-2-ylidenes $(CN)_2$IMes (E_σ: –8.37 eV; E_π: –2.10 eV) and $(CN)_2$IBzPic (E_σ: –8.37 eV; E_π: –2.01 eV) are lower in energy than those of IPr (E_σ: –7.64 eV; E_π: –1.38 eV)[14] and IMeDNP (E_σ: –8.30 eV; E_π: –1.86 eV),[14] which implies a decrease in the σ-donor strength of the 4,5-dicyanoimidazol-2-ylidenes compared with IPr and IMeDNP. The decrease in E_π results in an increase in the π-acceptor strength of the dicyanocarbenes $(CN)_2$IMes and $(CN)_2$IBzPic compared with IPr and IMeDNP. IDNP (E_σ: –8.89 eV; E_π: –2.57 eV)[14] is the weakest σ-donor, but the strongest π-acceptor of the five NHCs. These data correlate with the TEP ranking of IPr (2052 cm^{-1}),[15] IMeDNP (2058 cm^{-1}),[14] $(CN)_2$IMes (2060 cm^{-1})[11] and IDNP (2063 cm^{-1}).[14] Based on these results, we expect $(CN)_2$-IBzPic to show a similar π-accepting behaviour to $(CN)_2$-IMes.

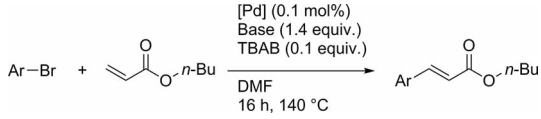
Table 1. NBO energies of the σ-donor (E_σ) and π-acceptor (E_π) orbitals of $(CN)_2$IMes, $(CN)_2$IBzPic and previously reported imidazol-2-ylidenes.

NHC	E_σ [eV]	E_π [eV]
$(CN)_2$IMes	–8.37	–2.10
$(CN)_2$IBzPic	–8.37	–2.01
IPr[a]	–7.64	–1.38
IMeDNP[a]	–8.30	–1.86
IDNP[a]	–8.98	–2.57

[a] See ref.[14].

Catalytic Studies

Initial experiments showed that the MH reaction of bromobenzene with *n*-butyl acrylate gave high yields in the presence of the three palladium(II) precatalysts **2**, **3** and **6** (Scheme 4). The first goal was to improve the reaction conditions by varying the solvent, base, reaction time and temperature. To conclude the optimization experiments, the influence of the additive tetra-*n*-butylammonium bromide (TBAB) was tested.



Scheme 4. Reaction scheme for MH reactions of monocyclic aryl bromides.

The initial precatalyst loading of 0.1 mol-% (relative to the aryl bromide) was deployed for all further experiments. The best results for the MH reaction of bromobenzene with *n*-butyl acrylate were achieved with *N*,*N*-dimethylformamide (dmf) as solvent; especially in the reaction with precatalyst **3**, the yield of the desired *n*-butyl cinnamate dropped massively when another solvent was deployed (Table 2, entries 1 and 2). After 8 h, almost 90% yield was achieved with all three precatalysts (Table 2, entry 3). After 16 h, the reactions were complete with almost quantitative yields of the desired product (entry 6). A decrease in the

Table 2. Results for the solvent optimization of the conditions for the MH reaction of bromobenzene with *n*-butyl acrylate.[a]

Entry	Solvent	*t* [h]	*T* [°C]	Yield [%][b]		
				2	**3**	**6**
1	nmp	16	140	96	13	76
2	dma	16	140	84	6	81
3	dmf	8	140	88	89	88
4	dmf	16	100	8	9	14
5	dmf[c]	16	140	89	90	90
6	dmf	16	140	100	100	98

[a] Reagents and conditions: bromobenzene (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), sodium carbonate (1.4 equiv.), TBAB (0.1 equiv.), 1,3,5-trimethoxybenzene (0.1 equiv.) and precatalyst (0.1 mol-%), solvent (0.5 mL), 16 h, 140 °C (oil bath). [b] GC yield: average yield of two independent runs, 1,3,5-trimethoxybenzene as internal standard. [c] Without TBAB.

temperature to 100 °C resulted in a massive decrease in the product yield (Table 2, entry 4). The use of TBAB as co-catalyst seems a prerequisite for the precatalysts reported herein; the average product yield dropped by 10% when no co-catalyst was used (entry 5).

Sodium carbonate proved to be the most suitable base for the MH reaction using precatalysts **2**, **3** and **6** (Table 3). Low product yields were obtained with organic bases due to their low boiling points, whereas the stronger caesium carbonate led to unidentified decomposition products, which could be seen as additional peaks in the gas chromatograms. Therefore we decided to use a reaction time of 16 h and a temperature of 140 °C for further catalytic experiments (Table 2, entry 6) with sodium carbonate as base and TBAB as additive in the reaction mixture.

Table 3. Optimization of the base for the MH reaction of bromobenzene with *n*-butyl acrylate.[a]

Entry	Base	Yield [%][b]		
		2	**3**	**6**
1	sodium carbonate	100	100	98
2	sodium acetate	33	45	27
3	caesium carbonate	40	34	19
4	calcium hydroxide	n.d.	trace	n.d.
5	piperidine	16	18	12
6	diisopropylethylamine	30	32	25

[a] Reagents and conditions: bromobenzene (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), base (1.4 equiv.), TBAB (0.1 equiv.), 1,3,5-trimethoxybenzene (0.1 equiv.), precatalyst (0.1 mol-%), *N*,*N*-dimethylformamide (0.5 mL), 16 h, 140 °C (oil bath). [b] GC yield: average yield of two independent runs, using 1,3,5-trimethoxybenzene as internal standard; n.d.: not determined.

The MH reactions of various aryl halides with *n*-butyl acrylate were performed under the optimized reaction conditions to prepare *n*-butyl cinnamate and a variety of its derivatives (Table 4). The three precatalysts **2**, **3** and **6** are suitable for use in MH reactions with electronically deactivated aryl bromides such as 4-bromoanisole (Table 4, entry 6), resulting in excellent yields. Although the precatalysts **2** and **6** achieved good yields only with sterically less demanding aryl bromides, precatalyst **3** showed excellent overall catalytic activity, giving moderate yields of 30 and 28% in the reactions of the electronically deactivated and sterically hindered bromomesitylene and 1-bromo-2,4,6-triisopropylbenzene, respectively (Table 4, entries 22 and 26). With precatalyst **6**, the yields of *ortho*-substituted butyl cinnamates were especially low, which indicates that the *cis* coordination of the chelating $(CN)_2$IBzPic is not favoured in the reactions of bulky aryl bromides. The three precatalysts showed tolerance against functional groups such as amino (Table 4, entry 18) or hydroxy groups (Table 4, entries 19–21), and also the N-heterocycle 3-bromopyridine (Table 4, entry 25) reacted to give the desired product in moderate-to-good yields. As precatalyst **3** proved to be the most efficient of the three precatalysts presented herein, we prepared the analogous complex **B**[7b] and deployed it as precatalyst to compare their precatalyst activities under the optimized conditions. Most of the reactions were catalysed efficiently by both precatalysts. However, the yields of the reactions catalysed by **B** were significantly lower than those catalysed by **3** when electronically deactivated substrates were used, especially phenols, which reacted in good-to-excellent yields with **3** but did not undergo any conversion with **B** (Table 4, entries 19–21). Chlorobenzene (Table 4, entry 1) and chloroanisole (Table 4, entry 2) gave only trace amounts of the cinnamates, whereas chloroacetophenone reacted well with all the tested precatalysts to give moderate yields of the product (Table 4, entry 3).

Table 4. Substrate scope of the Mizoroki–Heck reaction of *n*-butyl acrylate vwith arious aryl halides using precatalysts **2**, **3**, **6** and **B**.[a]

Entry	Aryl bromide	Yield [%][b]			
		2	**3**	**6**	**B**
1	chlorobenzene	0	2	0	1
3	4-chloroanisole	0	1	0	1
3	4-chloroacetophenone	55	56	57	61
4	bromobenzene	100	100	98	99
5	4-bromoacetophenone	98	95	89	96
6	4-bromoanisole	94	98	80	86
7	3-bromoanisole	76	77	40	43
8	2-bromoanisole	54	83	55	49
9	4-bromobenzaldehyde	99	100	98	99
10	4-bromotoluene	81	98	73	65
11	4-bromofluorobenzene	97	89	91	88
12	2-bromofluorobenzene	78	82	85	39
13	4-bromo-*N*,*N*-diethylaniline	96	94	99	61
14	4-bromonitrobenzene	99	99	89	100
15	2-bromo-5-nitroanisole	91	99	63	90
16	methyl 4-bromobenzoate	87	84	84	80
17	4-bromobenzonitrile	92	100	87	100
18	4-bromoaniline	64	84	75	44
19	4-bromophenol	95	100	67	0
20	3-bromophenol	52	72	48	0
21	2-bromophenol	44	57	33	0
22	bromomesitylene	17	30	15	15
23	1,4-dibromobenzene	82	79	62	70
24	2-bromobiphenyl	92	91	87	76
25	3-bromopyridine	73	58	49	45
26	1-bromo-2,4,6-triisopropylbenzene	11	28	5	12
27	1-bromo-3,4,5-trimethoxybenzene	46	66	58	53
28	1-bromonaphthalene	98	92	72	70
29	9-bromoanthracene	64	88	70	66

[a] Reagents and conditions: aryl halide (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), sodium carbonate (1.4 equiv.), TBAB (0.1 equiv.), 1,3,5-trimethoxybenzene (0.1 equiv.), precatalyst (0.1 mol-%), *N*,*N*-dimethylformamide (0.5 mL), 16 h, 140 °C (oil bath); reaction scale: 126 µmol aryl bromide. [b] GC yield: average yield of two independent runs, using 1,3,5-trimethoxybenzene as internal standard.

The long-term stabilities of the precatalysts **2**, **3** and **6** were investigated by performing the MH reaction of bromobenzene with *n*-butyl acrylate using decreased precatalyst loadings of 0.01, 0.001 and 0.0001 mol-% over a reaction time of 64 h at 140 °C. The experiments showed that the MH reaction occurred even with reduced precatalyst loadings. Complex **3** proved to be more efficient than **2** and **6**. A maximum turnover number (TON) of 150000 was obtained by using 0.0001 mol-% of complex **3** (Table 5).

Mechanistic Investigations

The formation of palladium black was not observed during the reaction when the palladacycles **3** and **6** were used.

Table 5. Long-term stability experiments performed by using reduced catalyst loadings.[a]

Entry	Precatalyst loading [mol-%]	Yield [%][b] 2	3	6
1	0.01	85	91	81
2	0.001	22	33	33
3	0.0001	7	15	12

[a] Reagents and conditions: bromobenzene (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), sodium carbonate (1.4 equiv.), TBAB (0.1 equiv.), 1,3,5-trimethoxybenzene (0.1 equiv.), precatalyst (0.1 mol-%), *N*,*N*-dimethylformamide (0.5 mL), 64 h, 140 °C (oil bath). [b] GC yield: average yield of two independent runs, using 1,3,5-trimethoxybenzene as internal standard.

Hydrolysis with 1 N hydrochloric acid in the work-up procedure led to palladium black formation, which could be observed in the separation funnel. In the case of acyclic complex **2**, the formation of palladium black could be observed in the reaction vessel. For further insights into the nature of the catalytically active species, poisoning experiments were performed. In the Mizoroki–Heck reaction of bromobenzene with *n*-butyl acrylate under the optimized conditions, a large excess of elemental mercury (1000 equiv., based on the precatalyst) was added at the start of the reactions. In all cases, the reaction was quenched by the mercury and only traces of *n*-butyl cinnamate could be detected by gas chromatography. In another experiment using precatalyst **3**, mercury was added 4 h after the start of the reaction. At the same time, a sample of the reaction mixture was removed and the yield of *n*-butyl cinnamate was determined to be 44% by GC-FID. Further samples were taken 1, 2 and 3 h after the addition of mercury, but no increase in yield could be determined. This indicates the formation of nanoparticles during the catalytic process and their participation in the catalytic reaction. To confirm the formation of palladium nanoparticles, dynamic light scattering (DLS) measurements were performed on freshly prepared reaction mixtures three times for each of the precatalysts, but the presence of nanoparticles could not be confirmed. As the DLS experiments did not prove the presence of nanoparticles, transmission electronic microscopy (TEM) was conducted on the same samples. Figure 4 shows a representative TEM image taken from a reaction mixture containing **3**. In all cases, nanoparticles as well as larger agglomerations of palladium are visible and the results of the poisoning experiments could be confirmed. Presumably the palladium nanoparticles formed during the catalytic reaction are the leading actors in the MH reactions performed with the precatalysts **2**, **3** and **6**.[16]

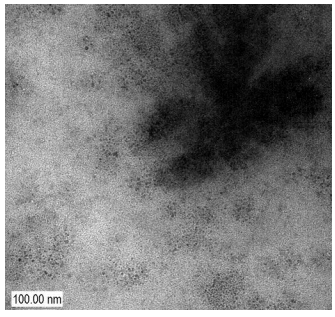


Figure 4. TEM image of a colloidal solution containing palladium particles created from **3** (×130k, 100 nm scale bar is shown).

Conclusions

The new acyclic NHC palladium(II) complex $[PdCl_2\{(CN)_2IMes\}(PPh_3)]$ (**2**) and the palladacycle $[PdCl(dmba)\{(CN)_2IMes\}]$ (**3**) have been synthesized in satisfactory yields by using the NHC precursor 4,5-dicyano-1,3-dimesityl-2-(pentafluorophenyl)imidazoline (**1**) and their crystal structures determined. The new NHC precursor 1-benzyl-4,5-dicyano-2-(pentafluorophenyl)-3-picolylimidazoline (**5**) was synthesized as precursor of the chelating NHC $(CN)_2$IBzPic and used for the formation of precatalyst $[PdCl_2\{(CN)_2IBzPic\}]$ (**6**). The π-acceptor strength of the new $(CN)_2$IBzPic were compared with $(CN)_2$IMes and other π-acidic NHCs by NBO analysis. The three complexes **2**, **3** and **6** and the previously reported analogous precatalyst **B** were tested as precatalysts for the Mizoroki–Heck reactions between various aryl bromides and *n*-butyl acrylate at low catalyst loadings. Precatalyst **3** showed the best overall catalytic performance and facilitated the MH reaction even with sterically hindered and electronically deactivated substrates to give moderate yields of the products. In addition, complex **3** gave higher yields than the analogous complex **B**. Poisoning experiments with mercury showed that palladium nanoparticles play a leading role in the catalytic process in all three cases. The formation of palladium nanoparticles was confirmed by TEM analysis of the MH reaction mixtures.

Experimental Section

General: All synthetic manipulations were performed under argon or nitrogen using standard Schlenk techniques. For all manipulations, solvents were dried according to literature procedures.[17] Compounds **1**,[11] **4**,[12] $[PdCl_2(PPh_3)_2]$,[18a] $[Pd(\mu\text{-}Cl)(dmba)]_2$[18b] and $[PdCl_2(PhCN)_2]$[18c] were synthesized as described in the literature. Other chemicals were purchased from commercial sources and used in the reactions as received. TGA-MS and DTA analyses were performed with a Linseis STA PT-1600 thermoscale coupled with a Pfeiffer MS Thermostar mass spectrometer. Elemental analyses (C, H, N) were performed with an Elementar Vario EL elemental analyser. NMR spectra were recorded with a Bruker Avance 300 or 500 spectrometer. Resonances for NMR spectra are reported relative to Me_4Si (δ = 0.0 ppm) and calibrated based on the solvent signal for ^1H and ^{13}C.[19] Spectra are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) and integration. Mass spectra were recorded with a Micromass Q-TOFmicro (ESI) or Thermo Quest SSQ 710 (70 eV, EI) spectrometer. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR spectrometer in a KBr disk between 400 and 4000 cm^{-1} using a resolution of 4 cm^{-1}. A background measurement was performed before recording spectra of the samples using a bare KBr disc. The DLS measurements were performed with a Malvern Zetasizer Nano ZS instrument at 25 °C using freshly prepared reaction mixtures. Each measurement consisted of a minimum of 50 runs. TEM images were recorded

with a Philips CM100 electron microscope at 80 kV using freshly prepared reaction mixtures on a 400 nm copper grid coated with carbon. Single-crystal X-ray diffraction data were collected with a STOE IPDS 2 diffractometer at 293 K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The crystal structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 by using SHELX-97.[20] Non-hydrogen atoms were refined by using anisotropic temperature factors. The deposited atom data (CIF) as well as the data in Table 6 reflect only the known cell content.

Table 6. Crystallographic data for NHC palladium(II) complexes **2** and **3**.

	2	**3**
Formula	$C_{41}H_{37}Cl_2N_4PPd$	$C_{32}H_{34}ClN_5Pd$
M [g mol^{-1}]	794.02	630.49
Crystal size [mm^3]	1.5 × 0.93 × 0.42	0.36 × 0.22 × 0.13
T [K]	210(2)	210(2)
Radiation	Mo-K_α	Mo-K_α
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
a [Å]	12.3413(5)	9.3510(12)
b [Å]	21.8296(7)	13.5202(17)
c [Å]	14.2030(6)	13.5656(15)
α [°]	90.00	74.508(9)
β [°]	99.703(4)	72.639(9)
γ [°]	90.00	69.875(10)
V [Å^3]	3771.6(3)	1510.9(3)
Z	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.398	1.386
μ [mm^{-1}]	0.710	0.731
Reflns. measured	24078	9804
Unique reflections	6621	4993
Unique reflns. with $I_0 > 2\sigma(I)$	6317	4512
R_{int}	0.0746	0.0314
$2\theta_{max}$	50.00	50.00
$R1$, $wR2$ [$I_0 > 2\sigma(I)$]	0.0258, 0.0682	0.0278, 0.0742
$R1$, $wR2$ (all data)	0.0271, 0.0691	0.0312, 0.0756
Goodness of fit	1.086	1.034
Difference density min./max.	–0.471/0.607	–0.590/0.555

CCDC-985751 (for **2**) and -985752 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT calculations were performed at the M06[21]/cc-pVTZ[22] level of theory using the Gaussian 09 package of programs.[23] NBO analysis was carried out by using the NBO version 3.1 program.[24]

Synthetic Procedures

[PdCl$_2${(CN)$_2$IMes}(PPh$_3$)] (2): [PdCl$_2$(PPh$_3$)$_2$] (200 mg, 284.9 mmol) and **1** (149 mg, 284.9 mmol; 1.0 equiv.) were added to toluene (20 mL) under argon in a 50 mL round-bottomed flask fitted with a reflux condenser and magnetic stirrer. The mixture was heated at reflux for 16 h under vigorous stirring and then cooled to room temperature. The solvent was removed in a rotary evaporator and the product was isolated by column chromatography on silica (height: 30 cm; diameter 3 cm) with dichloromethane as eluent. The product was obtained as a yellow crystalline solid in 64% yield (145 mg). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.44–7.36 (m, 3 H), 7.32–7.23 (m, 12 H), 7.19 (s, 4 H, $H_{Mes\text{-}Aryl}$), 2.50 (s, 6 H, $H_{Mes\text{-}p\text{-}Methyl}$), 2.32 (s, 12 H, $H_{Mes\text{-}o\text{-}methyl}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.0, 141.8, 136.7, 135.4, 135.2, 132.2, 130.8, 130.7, 130.2, 129.5, 128.2, 128.1, 117.4 (CN), 106.6 (CCN), 21.6, 19.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 3060, 2974, 2954, 2916, 2857, 2248, 2236, 1605, 1480, 1436, 1383, 1338, 1300, 1207, 1187, 1161, 1099, 1069, 1029, 1001, 867, 856, 749, 741, 713, 691, 561, 530, 514, 495, 459 cm^{-1}. HRMS: calcd. for $C_{41}H_{37}Cl_2N_4Pd$ 794.0682 [M]$^+$; found 757.1519 [M – Cl]$^+$. $C_{41}H_{37}Cl_2N_4PPd$ (794.07): calcd. C 62.02, H 4.70, N 7.06; found C 61.86, H 4.57, N 6.91.

[PdCl{(CN)$_2$IMes}(dmba)] (3): [Pd(μ-Cl)(dmba)]$_2$ (100 mg, 181.1 mmol) and **1** (189 mg, 362.2 mmol; 2.0 equiv.) were added to toluene (20 mL) under argon in a 50 mL round-bottomed flask fitted with a reflux condenser and magnetic stirrer, . The mixture was heated at reflux for 16 h under vigorous stirring and then cooled to room temperature. The solvent was removed in a rotary evaporator and the crude product was isolated by column chromatography on silica (height: 30 cm; diameter 3 cm) with dichloromethane as eluent. The product was obtained as a colourless crystalline solid in 72% yield (164 mg). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.08 (s, 2 H), 6.92 (s, 2 H), 6.87 (dd, J = 7.1, 1.2 Hz, 1 H), 6.82 (dd, J = 7.3, 1.5, 1 H), 6.78–6.72 (m, 1 H), 6.51 (dd, J = 7.5, 0.9 Hz, 1 H) 3.54 (s, 2 H), 2.41 (s, 12 H), 2.34 (s, 6 H), 2.23 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.6, 149.1, 148.1, 141.3, 138.2, 137.7, 134.7, 133.0, 130.4, 128.8, 124.8, 124.3, 122.2, 117.2, 107.0, 72.9, 50.5, 21.3, 20.2, 20.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 3050, 2995, 2963, 2914, 2885, 2854, 2238, 1606, 1582, 1477, 1452, 1371, 1318, 1295, 1285, 1070, 1025, 992, 972, 856, 742, 713 cm^{-1}. HRMS: calcd. for $C_{32}H_{34}ClN_5Pd$ 629.1532 [M]$^+$; found 629.1521 [M]$^+$. $C_{32}H_{34}ClN_5Pd$ (629.15): calcd. C 60.96, H 5.44, N 11.11; found C 60.89, H 5.52, N 11.22.

1-Benzyl-4,5-dicyano-3-picolyl-2-(pentafluorophenyl)imidazoline (5): Compound **4** (700 mg, 2.42 mmol) was suspended in glacial acetic acid (0.4 mL) in a 2 mL Schlenk flask fitted with a magnetic stirrer, and the Schlenk flask was then sealed with a septum and flushed with argon. Pentafluorobenzaldehyde (712 mg, 448 μL, 3.63 mmol; 1.5 equiv.) was added in one portion through a syringe and the mixture was stirred for 48 h in the dark. After the reaction, crude **5** was filtered and washed with water (20 mL) and ice-cold methanol (5 mL) and dried in vacuo to afford 754 mg of **5** as a pale-yellow solid (67% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.46 (d, J = 4.2 Hz, 1 H), 7.60 (td, J = 7.7, 1.7 Hz, 1 H), 7.24–7.18 (m, 4 H), 7.10–7.06 (m, 3 H), 6.16 (s, 1 H), 4.21 (d, J = 15.0 Hz, 1 H), 4.15 (d, J = 15.0 Hz, 1 H), 4.03 (t, J = 15.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.2, 149.8, 137.0, 133.6, 128.9, 128.8, 128.7, 123.3, 123.0, 114.3 (CN), 113.8 (CN), 110.8 (CCN), 110.7 (CCN), 78.0, 54.4, 53.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 3085, 3065, 3032, 3010, 2935, 2873, 2215, 1734, 1717, 1700, 1684, 1655, 1594, 1523, 1511, 1454, 1439, 1393, 1371, 1305, 1297, 1262, 1204, 1130, 1082, 1050, 960, 911, 837, 818, 750, 741, 702, 678, 655, 643, 586, 575, 560, 508, 482 cm^{-1}. HRMS: calcd. for $C_{24}H_{14}F_5N_5$ 467.1250 [M]$^+$; found 468.1242 [M + H]$^+$.

[PdCl$_2${(CN)$_2$IBzPic}] (6): Imidazoline **5** (200 mg, 427.9 μmol) was dissolved in chlorobenzene (60 mL) in a 250 mL two-necked flask fitted with a magnetic stirrer, dropping funnel and reflux condenser, and the dropping funnel was filled with a solution of [PdCl$_2$-(PhCN)$_2$] (156 mg, 427.9 μmol; 1.0 equiv.) in chlorobenzene (60 mL). The apparatus was evacuated and subsequently flushed with argon three times and the flask heated in an oil bath to 135 °C. After stirring at this temperature for 5 min, the solution of [PdCl$_2$(PhCN)$_2$] was added dropwise over a period of 120 min to the imidazoline solution. The mixture was stirred at 135 °C for an additional 120 min and the mixture cooled to 0 °C. The resulting bright solid was filtered through a glass frit and washed with chloroform (3× 20 mL), dissolved in dimethyl sulfoxide (2 mL) and precipitated by the addition of water (20 mL). The solid was filtered through a glass frit and washed three times with chloroform

(3 × 10 mL) and three times with diethyl ether (3 × 10 mL) to obtain 53 mg of **6** (27% yield) as a colourless solid. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.99 (d, J = 5.2 Hz, 2 H), 8.15 (dt, J = 7.6, 1.5 Hz, 1 H), 8.05 (d, J = 7.0 Hz, 1 H), 7.65–7.58 (m, 1 H), 7.49–7.34 (m, 5 H), 6.22 (d, J = 15.6 Hz, 1 H), 6.05 (d, J = 15.7 Hz, 1 H), 5.81 (d, J = 15.5 Hz, 1 H), 5.68 (d, J = 15.8 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 162.2, 154.2, 151.2, 140.4, 134.3, 128.7, 128.6, 127.9, 126.2, 125.3, 117.0 (CN), 114.3 (CN), 106.8 (CCN), 106.7 (CCN), 55.4, 53.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 3367, 3322, 3014, 2980, 2944, 2922, 2861, 2735, 2206 (CN), 1742, 1602, 1484, 1457, 1448, 1437, 1352, 1227, 1158, 1038, 1010, 891, 857, 822, 777, 706, 564, 502, 419 cm^{-1}. HRMS: calcd. for $C_{18}H_{13}Cl_2N_5Pd$ 474.9583 [M]$^+$; found 439.9992 [M – Cl]$^+$. $C_{18}H_{13}Cl_2N_5Pd$ (474.96): calcd. C 45.36, H 2.75, N 14.69; found C 45.07, H 2.87, N 14.85.

Representative Procedure for the Mizoroki–Heck Reaction: Sodium carbonate (18.7 mg, 176 μmol; 1.4 equiv.) and TBAB (4.1 mg, 12.6 μmol; 0.1 equiv.) were added to a 2 mL Schlenk tube fitted with a magnetic stirrer. A solution of precatalyst **2** (100 μg, 126 nmol; 0.001 equiv.) and 1,3,5-trimethoxybenzene (2.11 mg, 12.6 μmol; 0.1 equiv.) in *N*,*N*-dimethylformamide (0.5 mL) was added and the mixture was stirred. Bromobenzene (19.8 mg, 13.2 μL; 126 μmol) and *n*-butyl acrylate (32.3 mg, 35.9 μL, 252 μmol; 2.0 equiv.) were added through a syringe and the tube was sealed and then secured by evacuating three times and subsequently flushing with argon. The flask was then placed in a preheated oil bath at 140 °C and stirred for 16 h. After completion of the reaction, the flask was immediately cooled to 0 °C in an ice bath. The cold mixture was hydrolysed with 1 N hydrochloric acid (2 mL) and chloroform (2 mL) was then added. The mixture was poured into water (20 mL) and the aqueous phase extracted three times with chloroform (2 mL).

For the catalytic screening, the crude product was dissolved in chloroform (1.5 mL; GC grade from Merck) and the GC yield determined by using a Perkin–Elmer Clarus 580 instrument equipped with a Perkin–Elmer Elite 5 MS column (length: 30 m, diameter: 0.25 mm). Signals were detected by using an FID detector. 1,3,5-Trimethoxybenzene was used as internal standard to determine GC yields.

To calibrate the GC, the MH products were isolated by flash chromatography on silica (height: 460 mm, diameter: 15 mm) with hexane/ethyl acetate mixtures as eluent and afterwards analysed by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The spectroscopic data of already known products were in agreement with literature data.[25]

n-Butyl (*E*)-3-(4′-Diethylaminophenyl)acrylate (Table 5, entry 13) and *n*-butyl (*E*)-3-(2′-Methoxy-4′-nitrophenyl)acrylate (Table 5, entry 15) were prepared for the first time.

***n*-Butyl (*E*)-3-(4′-Diethylaminophenyl)acrylate:** ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.61 (d, J = 15.9 Hz, 1 H), 7.39 (d, J = 9.0 Hz, 2 H), 6.62 (d, J = 9.0 Hz, 2 H), 6.19 (d, J = 15.9 Hz, 1 H), 4.18 (t, J = 12.0 Hz, 2 H), 3.39 (q, J = 7.2 Hz, 4 H), 1.73–1.63 (m, 2 H), 1.50–1.37 (m, 2 H), 1.18 (t, J = 7.2 Hz, 6 H), 0.96 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 168.5, 149.7, 145.5, 130.4, 121.9, 112.4, 111.6, 64.3, 44.8, 31.3, 19.4, 14.2, 13.0 ppm. HRMS: calcd. for $C_{17}H_{25}NO_2$ 275.1885 [M]$^+$; found 275.1892 [M]$^+$.

***n*-Butyl (*E*)-3-(2′-Methoxy-4′-nitrophenyl)acrylate:** ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.96 (d, J = 16.2 Hz, 1 H), 7.86 (dd, J = 8.4, 2.1 Hz, 1 H), 7.78 (d, J = 2.1 Hz, 2 H), 7.66 (d, J = 8.4 Hz, 1 H), 6.65 (d, J = 16.2 Hz, 1 H), 4.25 (t, J = 6.9 Hz, 2 H), 4.02 (s, 3 H), 1.77–1.67 (m, 2 H), 1.52–1.40 (m, 2 H), 0.99 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 175.4, 158.7, 137.9, 130.2, 129.4, 123.2, 116.2, 109.1.3, 106.6, 65.1, 56.6, 31.1, 19.6, 14.09 ppm. HRMS: calcd. for $C_{14}H_{17}NO_5$ 279.1107 [M]$^+$; found 279.1102 [M]$^+$.

The analytical data for literature-known, but not further described *n*-butyl (*E*)-3-(3′-Hydroxyphenyl)acrylate (Table 5, entry 20)[26a] and *n*-butyl (*E*)-3-(9′-anthryl)acrylate (Table 5, entry 29),[25e,26b] are also presented.

***n*-Butyl (*E*)-3-(3′-Hydroxyphenyl)acrylate:** ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.66 (d, J = 15.9 Hz, 1 H), 7.25 (t, J = 7.8 Hz, 1 H), 7.18 (s, 1 H), 7.10–7.06 (m, 2 H), 7.07–7.03 (m, 1 H), 6.43 (d, J = 16.2 Hz, 1 H), 4.25 (t, J = 6.6 Hz, 2 H), 1.76–1.66 (m, 2 H), 1.51–1.38 (m, 2 H), 0.97 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 168.1, 156.5, 145.2, 135.7, 130.0, 120.6, 118.1, 117.8, 114.7, 65.0, 30.7, 19.2, 13.7 ppm. HRMS: calcd. for $C_{13}H_{16}O_3$ 220.1099 [M]$^+$; found 220.1095 [M]$^+$.

***n*-Butyl (*E*)-3-(9′-Anthryl)acrylate:** ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.65 (d, J = 16.2 Hz, 1 H), 8.45 (s, 1 H), 8.30–8.21 (m, 2 H), 8.06–7.97 (m, 2 H), 7.55–7.44 (m, 4 H), 6.45 (d, J = 16.2 Hz, 1 H), 4.32 (t, J = 6.6 Hz, 2 H), 1.83–1.73 (m, 2 H), 1.57–1.44 (m, 2 H), 1.02 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 166.6, 141.9, 131.3, 129.3, 128.8, 128.2, 127.3, 126.3, 125.4, 125.2, 64.8, 30.8, 19.3, 13.8 ppm. HRMS: calcd. for $C_{21}H_{20}O_2$ 303.1463 [M]$^+$; found 303.1460 [M]$^+$.

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Mizoroki–Heck Reaction

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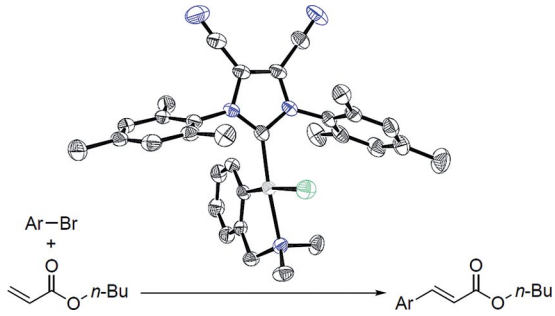

The new precatalysts [$PdCl_2${$(CN)_2$IMes}], [PdCl(dmba){$(CN)_2$IMes}] and [$PdCl_2$-{$(CN)_2$IBzPic}] have been prepared as candidates for the Mizoroki–Heck reaction and used in catalytic screening for reactions between *n*-butyl acrylate and 27 aryl bromides.

