Heck reaction catalysed by palladium supported with an electron-rich benzimidazolylidene generated *in situ*: remarkable ligand electronic effects and controllable mono- and di-arylation†

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The Heck reactions of aryl bromides and chlorides are efficiently catalysed by palladium supported with benzimidazolylidenes generated *in situ* from *N*,*N*-dialkylbenzimidazolium salts in molten tetrabutylammonium bromide (TBAB) as ionic liquid reaction medium. Remarkable electronic effects from the benzimidazoliums on the catalysis have been observed. Reaction of 4-chloroacetophone with butyl acrylate catalysed by 1 mol% of the benzimidazolium–palladium catalyst systems containing 5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide **3**, *N*,*N*′-dibutylbenzimidazolium bromide **1** or 5,6-difluoro-*N*,*N*′-dibutylbenzimidazolium bromide **4**, gave 4-acetyl-*trans*-cinnamic acid ester in 93% (6 h), 79% (12 h) and 50% (12 h) yields, respectively, under otherwise identical conditions. For aryl bromides and activated aryl chlorides without steric hindrance, mono- and di-arylation of terminal olefins could be controllably effected, giving the corresponding di- and tri-substituted olefins in high yields. The electronic factors from aryl bromides are negligible in diarylation while electron-poor aryl halides react faster than the electron-rich ones in the monoarylation. Aryl halides with modest steric hindrance, such as 2,5-dimethylbromobenzene and 2-chlorobenzonitrile, react smoothly in the monoarylation of butyl acrylate with 0.1 and 1 mol% palladium loading, respectively. Mesityl bromide could also be converted to butyl mesityl-*trans*-cinnamate in 88% yield using an increased palladium loading of 1 mol%.

Introduction

The Heck reaction of aryl halides has recently been one of the most intensively studied transition-metal catalysed C–C bond forming reactions.[1] As the engine of the reaction, palladium catalysts have attracted most attention in advances of the methodology. Soluble palladiums, such as phosphine or N-heterocyclic carbene (NHC) palladium complexes and palladacycles with a covalent Pd–C bond, represent the most efficient catalysts for the Heck reaction. Although the phosphine–palladium catalysts are well established, providing excellent results in many respects, an obvious drawback of phosphine–palladium catalysts is that most phosphine ligands are expensive, toxic and unstable. The palladacycles are known to work through generating underligated palladium species that are often highly active and prone to decomposition within the catalytic cycles, though the palladacycles themselves are thermally stable.[2] N-Heterocyclic carbene palladium catalysts of imidazolylidenes and analogous ligands have recently emerged as efficient and practical catalysts for the Heck reaction.[1c–g,3] Imidazolylidenes are believed to be electronic mimics of tertiary phosphines,[4] showing stronger σ-donor ability but negligible π-accepting ability.[5] However, in contrast to phosphine complexes, imidazolylidene palladium complexes have higher stability toward heat, moisture and oxygen, and are therefore more suitable for the activation of challenging aryl halides, such as chlorides and deactivated bromides, which require elevated reaction temperature.[6] Practically, the catalytically active species could be generated *in situ* from a combination of imidazolium salts with palladium precursors.

While the N-heterocyclic carbene palladium catalysts hold promise they still lag behind phosphine catalysts in many respects. Only the N-heterocyclic carbenes derived from imidazolium salts have been extensively used as supporting ligands for palladium catalysts for the Heck reaction although a couple of types of N-heterocyclic carbenes have been reported.[4a–c] N-Heterocyclic carbenes from benzimidazoles, benzimidazolylidenes, have drawn little attention in the development of palladium catalysts until recently.[7] Fundamental thermodynamic studies have shown that benzimidazolylidenes behave intermediately between imidazolylidenes and their saturated analogues, imidazolinylidenes,[8] but possess richer chemistry with respect to electronic factors that have proven to be crucial in phosphine–palladium catalysts to activate aryl halides.[6,9]

We have recently reported that *N*,*N*′-dialkylbenzimidazolium–$PdCl_2$ catalyst systems performed well in Suzuki coupling of aryl halides and displayed sharply different N-substituent effects from the imidazolylidene systems.[10] As a part of our continuing exploration in transition-metal

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catalysed carbon–carbon bond forming reactions, we report here the Heck reaction of aryl bromides and chlorides catalysed by palladium supported with an electron-rich benzimidazolylidene generated *in situ* from 5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide for controllable mono- and di-arylation of electron-deficient olefins in molten tetrabutylammonium bromide (TBAB).

Experimental

General procedures

All reactions and manipulations were performed in air unless otherwise indicated. All the commercially available chemicals, reagents and solvents, were used as received. 4,5-Dibutoxybenzene-1,2-diamine,[11] 4,5-difluorobenzene-1,2-diamine,[12] *N*,*N*′-dibutylbenzimidazolium bromide **1** and *N*,*N*′-dibenzylbenzimidazolium chloride **2**[10] were prepared according to the previously reported procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 spectrometer using residual deuterated solvents as the internal standard. GC-MS analysis was performed using a Hewlett Packard Model HP 6890 Series with HP-5 column. Elemental analyses were performed at the Center of Analysis and Structure Determination of ECNU.

Synthesis of benzimidazolium salts and palladium complexes

5,6-Dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide 3. To a 100 mL flask charged with 4,5-dibutoxybenzene-1,2-diamine (2.52 g, 10 mmol) under nitrogen was added 20 mL HCO_2H. The resulting mixture was stirred under nitrogen at 80 °C for 3 h. After being cooled to room temperature, the mixture was poured into 100 mL water and adjusted to pH = 10 with 30% aqueous KOH. The pale white solid material was filtered off and dried *in vacuo* to provide crude 5,6-dibutoxybenzimidazole (2.4 g), which was used for the preparation of **3** without further purification.

To a 100 mL flask charged with 5,6-dibutoxybenzimidazole (2.4 g) in 30 mL DMSO was added 3–5 equiv. KOH (83%) powder (2 g) followed by 1-bromobutane (1.8 g, 13 mmol) at room temperature. The mixture was stirred at room temperature for 2 h before being poured into 100 mL water and extracted with toluene (3 × 30 mL). The toluene extracts was dried with Na_2SO_4, filtered and added to a 20 mL toluene solution of 1-bromobutane (1.8 g, 13 mmol) in a 250 mL flask. The mixture was refluxed for 12 h and slowly cooled to room temperature to precipitate out **3** as a white powder (3.5 g, 76%). Mp. 149–150 °C. Anal. Found: C, 53.39; H, 8.51; N, 5.52. $C_{23}H_{39}BrN_2O_2 \cdot 3H_2O$ requires C, 53.28; H, 8.94; N, 5.40%. ^{1}H NMR ($CDCl_3$, 25 °C), δ, ppm: 11.07 (1H, s, H-2), 7.01 (2H, s, Ar), 4.55 (4H, t, J = 7 Hz, NCH_2), 4.09 (4H, t, J = 7 Hz, OCH_2), 1.98–2.03 (4H, m, CH_2), 1.86–1.89 (4H, m, CH_2), 1.55–1.58 (4H, m, CH_2), 1.44–1.46 (4H, m, CH_2), 1.03 (6H, t, J = 7 Hz, CH_3), 0.97 (6H, t, J = 8 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C), δ, ppm: 150.64, 139.87, 125.28, 96.02, 69.96, 47.25, 31.38, 31.06, 19.78, 19.24, 13.83, 13.56.

5,6-Difluoro-*N*,*N*′-dibutylbenzimidazolium bromide 4. A similar procedure to that for the preparation of **3** was adopted employing 4,5-difluorobenzene-1,2-diamine (0.576 g, 4.0 mmol) to give 5,6-difluoro-*N*,*N*′-dibutylbenzimidazolium bromide **4** as a white powder 0.98 g (71%). Mp 178–180 °C Anal. Found: C, 52.01; H, 5.88; N, 8.59. $C_{15}H_{21}F_2N_2Br$ requires C, 51.88; H, 6.10; N, 8.07%. ^{1}H NMR ($CDCl_3$, 25 °C), δ, ppm: 11.48 (1H, s, H-2), 7.75 (2H, t, Ar), 4.68 (4H, t, J = 8 Hz, N–CH_2), 2.01–2.07 (4H, m, CH_2), 1.44–1.49 (4H, m, CH_2), 1.01–1.98 (6H, t, J = 7 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C), δ, ppm: 150.53 (dd, $^{1}J_{C-F}$ = 255.8 Hz, $^{2}J_{C-F}$ = 18.9 Hz), 144.37, 127.13 (q, $^{3}J_{C-F}$ = 6.3 Hz), 102.36 (m), 48.15, 31.30, 19.83, 13.52.

Bis(*N*,*N*′-dibutylbenzimidazolylidene)palladium(II) dichloride 5. A mixture of 0.311 g (1.0 mmol) *N*,*N*′-dibutylbenzimidazolium bromide **2** and 0.46 g (2.0 mmol) Ag_2O was suspended in 20 ml of CH_2Cl_2. The mixture was stirred for 12 h at room temperature. Then excess Ag_2O was filtered off and a slight yellow solution was obtained, to which was added $Pd(CH_3CN)_2Cl_2$ (130 mg, 0.5 mmol) in 10 ml CH_2Cl_2. After the mixture was stirred for 5 h at room temperature, the precipitate was filtered off and the solvents were removed *in vacuo* to give a yellow power (0.19 g 30%). Mp >250 °C. Anal. Found: C, 54.61; H, 6.75; N, 8.49. $C_{30}H_{44}Cl_2N_4Pd \cdot H_2O$ requires C, 54.92; H, 7.07; N, 8.54%. ^{1}H NMR for *trans*/*cis* isomers ($CDCl_3$, 25 °C), δ, ppm: 7.38–7.40 (4H, m, Ar), 7.25–7.28 (4H, m, Ar), 4.81–4.89 (8H, m, NCH_2), 2.21–2.27 (8H, m, CH_2), 1.54–1.63 (8H, m, CH_2), 1.04–1.07 (12H, t, J = 7 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C), δ, ppm, *trans* (*cis*) isomers: 181.41, 134.64 (134.52), 122.72 (122.68), 110.52 (110.50), 48.30 (48.17), 32.32 (32.13), 20.76, 14.06.

Crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution affording yellow cubes. *Crystal data* for **5**: $C_{30}H_{44}Cl_2N_4Pd$, M = 637.99, λ = 0.71073 Å, monoclinic, space group $P2_1/c$, a = 14.0750(13), b = 8.8410(8), c = 14.3377(13) Å, β = 119.0520(10)°, V = 1559.7(2) Å^3, Z = 2, D_c = 1.359 g cm^{-3}, $R1$ = 0.0719, $wR2$ = 0.2101 ($I > 2\sigma(I)$), $R1$ = 0.0886, $wR2$ = 0.2252 (all data). Selected bond lengths and angles are compiled in Table 1.

CCDC reference number 600971.

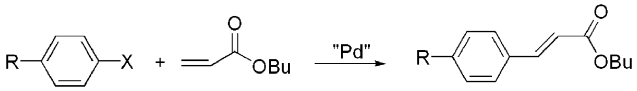
For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601833e

Bis(5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolylidene)palladium(II) dichloride 6. A similar procedure to that for the preparation of **5** was adopted employing 5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide **3** (0.455 g, 1.0 mmol) to provide **6** as a pale yellow solid (0.26 g, 28%). Mp >250 °C. Anal. Found: C, 57.85; H, 7.92; N, 5.97. $C_{46}H_{76}Cl_2N_4O_4Pd \cdot 0.5CH_2Cl_2$ requires C, 57.59; H, 7.94; N, 5.77%. ^{1}H NMR for *trans*/*cis* isomers ($CDCl_3$, 25 °C), δ, ppm: 6.83 (2H, s, Ar–H), 4.76–4.71 (4H, m, OCH_2), 4.01–3.98 (4H, t, J = 7 Hz, N–CH_2), 2.14–2.18 (4H, m, CH_2), 1.77–1.83 (4H, m, CH_2), 1.49–1.57 (8H, m, CH_2), 1.02 (6H, t, J = 7 Hz, CH_3), 0.98 (6H, t, J = 7 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 25 °C), δ, ppm, *trans* (*cis*)

Table 1 Selected bond lengths (Å) and angles (°) for **5**

Pd–C(1)	2.020(6)	C(1)–Pd–Cl	89.19(11)
Pd–Cl	2.3455(13)	N(1)–C(1)–N(2)	106.4(5)
N(1)–C(1)	1.370(7)	N(1)–C(1)–Pd	127.5(4)
N(1)–C(2)	1.377(7)	N(2)–C(1)–Pd	126.0(4)
N(2)–C(1)	1.327(6)	C(1)–N(1)–C(8)	125.2(5)
N(2)–C(7)	1.386(6)	C(1)–N(2)–C(12)	124.8(5)

Table 2 Monoarylation of butyl acrylate with aryl halides catalysed by benzimidazolylidene–palladium catalysts[a]



Entry	R	X	Base	Solvent	Pd/benzimidazolium (mol%)[b]	T^c/°C	Time/h	Yield[d] (%)
1	CH_3CO	Cl	NEt_3	DMF	1% $PdCl_2$, 2% **1** or **2**	150	12	Trace
2	CH_3CO	Cl	NEt_3	DMF	1% $PdCl_2$, 2% **1**, 20% TBAB	150	12	30
3	CH_3CO	Cl	NEt_3	TBAB	1% $PdCl_2$, 2% **1**	150	12	42
4	CH_3CO	Cl	NBu^n_3	TBAB	1% $PdCl_2$, 2% **1**	150	12	40
5	CH_3CO	Cl	$Ba(OH)_2$	TBAB	1% $PdCl_2$, 2% **1**	150	12	32
6	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2$, 2% **1**	150	12	75
7	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2$, 2% **1**	120	12	77
8	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2$, 2% **2**	120	12	65
9	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2$	120	12	53
10	CH_3CO	Cl	NaOAc	TBAB	1% $Pd(OAc)_2$, 2% **1**	120	12	51
11	CH_3CO	Cl	NaOAc	TBAB	1% $Pd_2(dba)_3$, 2% **1**	120	12	37
12	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2(MeCN)_2$, 2% **1**	120	12	79
13	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2(MeCN)_2$, 2% **3**	120	6	93
14	CH_3CO	Cl	NaOAc	TBAB	1% $PdCl_2(MeCN)_2$, 2% **4**	120	12	50
15	CH_3O	Br	NaOAc	TBAB	0.1% $PdCl_2(MeCN)_2$, 0.2% **1**	120	12	81
16	CH_3O	Br	NaOAc	TBAB	0.1% $PdCl_2(MeCN)_2$, 0.2% **3**	120	8	95
17	CH_3O	Br	NaOAc	TBAB	0.1% $PdCl_2(MeCN)_2$, 0.2% **4**	120	12	67
18	CH_3CO	Cl	NaOAc	TBAB	1% **5**, 20% HCO_2NH_4	120	12	80
19	CH_3CO	Cl	NaOAc	TBAB	1% **6**, 20% HCO_2NH_4	120	12	93

[a] 1.2 equiv. olefin used. [b] With respect to aryl halide. [c] Bath temperature. [d] Isolated yield.

isomers: 178.37 (178.35), 147.00 (146.98), 128.77 (128.64), 97.10 (97.06), 70.28 (70.25), 48.09 (47.96), 32.31 (32.12), 31.93 (31.41), 20.68, 19.28, 14.04, 13.90.

General procedure for the Heck reaction catalysed by $PdCl_2$–benzimidazolium–NaOAc in TBAB

Monoarylation of olefins. To a 10 mL Schlenk flask charged with the $PdCl_2$ or $PdCl_2(MeCN)_2$ (0.1 mol% for bromides or 1 mol% for chlorides), benzimidazolium salts (2 equiv. to palladium), NaOAc (3 equiv. to aryl halides) and tetrabutylammonium bromide (TBAB) (3 g) were added. The reaction mixture was degassed and refilled with nitrogen. The aryl halide (3.0 mmol) and the olefin (3.5 mmol, excess) were then added. The reaction mixture was heated in an oil-bath at 120–130 °C (bath temperature). The progress of the reaction was monitored by TLC or GC. After being cooled to room temperature, the mixture was poured into water, extracted with diethyl ether and dried with anhydrous sodium sulfate. Removal of solvents gave the crude products, which were purified either by flash chromatography or recrystallization.

Diarylation of olefins. A similar procedure to that for the monoarylation was adopted employing $PdCl_2(MeCN)_2$ (0.2 or 1 mol% to olefins for bromides or chlorides, respectively), benzimidazolium **3** (2 equiv. to palladium), TBAB (3 g), NaOAc (12 mmol, 6 equiv. to olefin) and aryl halide (4.5 mmol, excess) and the olefin (2.0 mmol). For the characterization of the Heck reaction products see ESI.†

Results and discussion

Monoarylation of olefins

The reaction of *p*-chloroacetophone with butyl acrylate was used as a model to evaluate the performance of the *N*,*N*′-dialkylbenzimidazolium–palladium catalyst system and optimize the reaction conditions. Since the *N*,*N*′-dialkylbenzimidazolium–palladium system was previously found to display higher activities in Suzuki coupling of aryl bromides and chlorides in DMF–H_2O than many other solvents, we initially carried out the model reaction with a combination of 2 mol% *N*,*N*′-dialkylbenzimidazolium bromide (butyl, **1**) or chloride (benzyl, **2**) and 1 mol% palladium chloride in the presence of 3 equiv. NEt_3 as base in DMF at 150 °C. Unfortunately, palladium black was observed on the wall of the flask at a very early stage of the reaction (within 10 min) and only a trace amount of *p*-chloroacetophone was converted to 4-acetyl *trans*-cinnamate in 12 h with both benzimidazoliums **1** and **2** (Table 2, entry 1). The beneficial effects of tetrabutylammonium salts as additive or solvent on the Heck reaction have been known for a long time although the precise mechanism is still under debate.[13] In fact, when tetrabutylammonium bromide (TBAB, 0.2 equiv.) was added to the reaction solution, the yield of 4-acetyl *trans*-cinnamate increased to 30%. A further slight improvement (42%) was obtained when the reaction was carried out in ionic medium molten (TBAB) with NEt_3 or $(n\text{-Bu})_3N$ (Table 2, entries 2–4). Anhydrous sodium acetate proved to be the best choice of base for the reaction in molten TBAB, from which 4-acetyl *trans*-cinnamate was isolated in 75% yield under the otherwise identical conditions to those used for tertiary amines (Table 2, entry 6). Due to the decomposition of TBAB at 150 °C, the reaction was better carried out at 120 °C. The catalysis of benzimidazolylidene–palladium was established by comparing with the control experiment without benzimidazolium salts (Table 2, entry 9). The rationale for the improved performance of the benzimidazolylidene–palladium catalyst for the Heck reaction in molten TBAB possibly lies in the formation of anionic palladium(0) intermediates, $[(NHC)_{1-2}Pd^0Br^-_m]^{m-}$ (m = 1–3),

which have been identified through electrochemical techniques by Amatore and Jutand to play a crucial role in palladium-catalysed Heck and cross-coupling reactions.[14]

Palladium chloride, $PdCl_2$, or $PdCl_2(CH_3CN)_2$ performed better than the other tested palladium sources, such as $Pd(OAc)_2$ and $Pd_2(dba)_3$, for the benzimidazolium–palladium–NaOAc catalyst system. *N*,*N*′-Dibenzylbenzimidazolium chloride **2** showed comparatively lower activity than **1** in the Heck reaction albeit the latter performed slightly better in the corresponding Suzuki coupling. Remarkable electronic effects of benzimidazoliums were observed on the catalytic activity of the benzimidazolium–palladium–NaOAc system. With the electron-rich benzimidazolium, 5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide **3**, the isolated yield of 4-acetyl-*trans*-cinnamate increased to 93% in 6 h while the yield decreased to 50% in 12 h with electron-poor 5,6-difluoro-*N*,*N*′-dibutylbenzimidazolium bromide **4** from 79% with the electron-neutral analogue **1** (Table 2, entries 12–14). A similar trend was also observed for the reaction of 4-bromoanisole (Table 2, entries 15–17).

To further confirm the catalytic species, benzimidazolylidene–palladium, bis(*N*,*N*′-dibutylbenzimidazolylidene)palladium dichloride **5** and bis(*N*,*N*′-dibutyl-5,6-dibutoxybenzimidazolylidene)palladium dichloride **6** were separately prepared and structurally characterized (Scheme 1).

^1H and ^{13}C NMR spectra of **5** and **6** indicated that they existed as *trans*/*cis* isomers in $CDCl_3$ solution, with the *trans* isomer being favoured. The equilibrium between *trans*/*cis* isomers of bis(*N*,*N*′-dialkylbenzimidazolylidene)palladium halides has been found to thermodynamically favour the *cis* isomer for those with small alkyl groups (alkyl = Me, Et),[15] which was attributed to the strong *trans*-effect of NHC ligand, while the steric hindrance between the bulky alkyl groups from the *N*,*N*′-dialkylbenzimidazolylidene ligands could switch the *trans*/*cis* selectivity to favour the *trans* isomer.[16] X-Ray crystal structure analysis revealed a symmetric structure for the bis(*N*,*N*′-dibutylbenzimidazolylidene)palladium dichloride **5** with the palladium atom located at the inversion center similar to the reported decyl analogue,[17] confirming that the *trans* isomer is favored (Fig. 1).

Using complexes **5** and **6** as pre-catalysts for the model reaction of *p*-chloroacetophone with butyl acrylate, comparable results to the combination of *N*,*N*′-dibutylbenzimidazoliums **1** and **3** with $PdCl_2(CH_3CN)_2$ were obtained in the presence of HCO_2NH_4 under similar reaction conditions (Table 2, entries 18 and 19). Surprisingly, no reaction was observed within 12 h in the absence of reducing reagent HCO_2NH_4, indicating that the bis(*N*,*N*′-dibutylbenzimidazolylidene)]palladium(II) halides are too stable to be reduced to

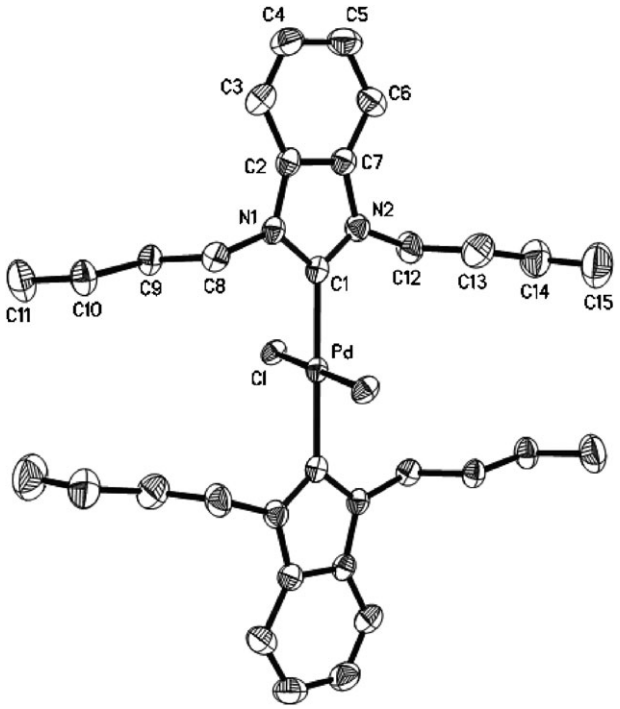
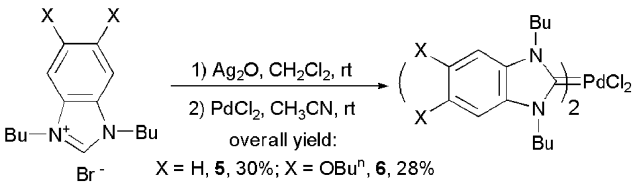


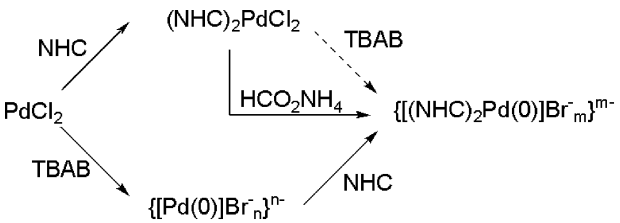
Fig. 1 ORTEP plot showing 30% probability ellipsoids of the X-ray crystal structure of bis(*N*,*N*′-dibutylbenzimidazolylidene)palladium dichloride **5**.

palladium(0) species. This result suggests a process of formation of the catalytically active NHC–palladium species of benzimidazolium–palladium(II) catalyst systems. The lack of catalytic activity of **5** and **6** without HCO_2NH_4 indicated the catalytic species of the $PdCl_2$–**3**–NaOAc system should not consist in pre-formation of the bis(N-heterocyclic carbene)-palladium(II) complex. Instead, it seems that reduction of an underligated or ligandless palladium(II) dichloride to palladium(0), which could be initially stabilised by the bromide anion of TBAB, occurred initially, followed by coordination of the NHC ligand to generate the true and more stable catalytic species of bis(benzimidazolylidene)]palladium(0) (Scheme 2).[13c,h,14]

The scope of the monoarylation reaction of olefins catalysed by the $PdCl_2$–**3**–NaOAc system was explored under optimal conditions (Table 3). For aryl bromides, the system showed very high activity. The electron-poor aryl bromide 4-bromoacetophone reacted completely in 2 h at 120 °C with 0.1 mol% palladium loading. At the lower palladium loading of 0.01 mol%, the reaction still proceeded smoothly providing

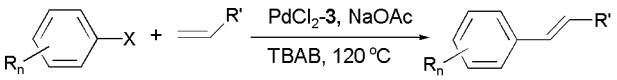


Scheme 1 Synthesis of bis(*N*,*N*′-dibutylbenzimidazolylidene)palladium dichlorides **5** and **6**.



Scheme 2 A probable path for the *in situ* generation of the catalytically active NHC–palladium species.

Table 3 Monoarylation of olefins catalysed by $PdCl_2$–**3**–NaOAc in TBAB[a]



Entry	R_n	X	R′	Pd loading[b]	Time/h	Yield[c] (%)
1	4-CH_3CO	Br	COOBu	0.1%	2	93
2	4-CH_3CO	Br	COOBu	0.01%	12	89
3	H	Br	COOBu	0.1%	5	96
4	4-CH_3	Br	COOBu	0.1%	7	92
5	4-CH_3O	Br	COOBu	0.1%	12	93
6	2,5-$(CH_3)_2$	Br	COOBu	0.1%	12	92
7	2,4,6-$(CH_3)_3$	Br	COOBu	0.1%	24	27
8	2,4,6-$(CH_3)_3$	Br	COOBu	0.5%	12	44
9	2,4,6-$(CH_3)_3$	Br	COOBu	1%	12	88
10	2,5-$(CH_3)_2$-4-Br	Br	COOBu	0.2%	12	90[d]
11	H	Br	C_6H_5	0.1%	5	85
12	4-CH_3O	Br	C_6H_5	0.1%	10	83
13	4-CH_3CO	Br	C_6H_5	0.1%	3	87
14	H	Br	$CONMe_2$	0.1%	5	89
15	4-CH_3CO	Cl	COOBu	1%	6	93
16	2-CN	Cl	COOBu	1%	12	87
17	4-CH_3	Cl	COOBu	3%	24	35

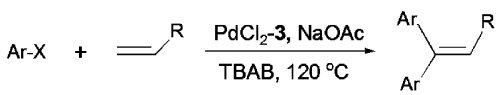
[a] 1.2 equiv. olefin used with Pd : **3** = 1 : 2. [b] With respect to aryl halide (mol%). [c] Isolated yield. [d] 2.5 equiv. butyl acrylate used and 1,4-di(2-butoxycarbonyl-*trans*-vinyl)-*p*-xylene as product.

4-acetyl *trans*-cinnamate in 89% yield in 12 h (Table 3, entries 1 and 2). The reaction of electron-neutral and electron-rich aryl bromides, such as bromobenzene, 4-bromotoluene and 4-bromoanisole, required elongated reaction times to achieve good yields (Table 3, entries 3–5). For an aryl bromide with modest steric hindrance, 2,5-dimethylbromobenzene, the reaction still went well giving the desired monoarylation product in 92% yield (Table 3, entry 6). Even the sterically demanding di-*ortho*-substituted aryl bromide, bromomesitylene, also reacted smoothly with a higher loading of palladium (1 mol%) (Table 3, entries 7–9). Styrene and *N*,*N*-dimethylacrylamide also reacted smoothly with aryl bromides providing the corresponding cinnamamide and stilbenes in 89 and 83–87% yields, respectively (Table 3, entries 11–14). The $PdCl_2$–**3**–NaOAc catalyst system also showed satisfactory activity for activated aryl chlorides, such as 4-chloroacetophone and 2-chlorobenzonitrile, while unactivated aryl chlorides were quite inert even with 3% loading of palladium (Table 3, entries 15–17).

Diarylation of olefins

Diarylation of olefins *via* the Heck reaction has scarcely been investigated.[18,19] Recently, a benzothiazol-2-ylidene palladium complex and an oxime-derived palladacycle have been reported to effect diarylation of acrylates *via* Heck reaction.[18a,20] During our investigation of the Heck reaction of aryl bromides with butyl acrylates catalysed by the $PdCl_2$–**3**–NaOAc system in TBAB, we noticed that β,β-diaryl acrylates appeared after butyl acrylate was consumed if an excess of aryl bromide was used, implying a possibility for diarylation of olefins.

Table 4 Diarylation of olefins catalysed by $PdCl_2$–**3**–NaOAc in TBAB[a]



Entry	Ar	X	R	Pd loading[b]	Time/h	Yield[c] (%)
1	*p*-FC_6H_4	Br	COOBu	0.2%	8	94
2	C_6H_5	Br	COOBu	0.2%	10	91
3	C_6H_5	Br	$CONMe_2$	0.2%	10	86
4	C_6H_5	Br	C_6H_5	0.2%	24	75
5	*p*-MeC_6H_4	Br	COOBu	0.2%	12	96
6	*o*-MeC_6H_4	Br	COOBu	0.2%	24	14[d]
7	*p*-$MeOC_6H_4$	Br	COOBu	0.2%	12	90
8	*p*-$CH_3COC_6H_4$	Br	COOBu	0.2%	10	92
9	*p*-$CH_3COC_6H_4$	Cl	COOBu	1%	16	87
10	*o*-C_6H_4CN	Cl	COOBu	1%	24	8[d]

[a] 2.5 equiv. aryl halide used with Pd : **3** = 1 : 2. [b] With respect to olefin (mol%). [c] Isolated yield. [d] By GC-MS.

Therefore, the diarylation of olefins catalysed by the $PdCl_2$–**3**–NaOAc catalyst system with 0.2 mol% palladium loading was investigated (Table 4).

In sharp contrast to the monoarylation, electronic factors from the aryl bromides showed few effects on the diarylation of olefins catalysed by the $PdCl_2$–**3**–NaOAc system. Both electron-rich and -poor aryl bromides reacted similarly giving diarylation products in high yields (Table 4, entries 1, 5, 7 and 8), indicating that oxidative addition of aryl bromides to palladium(0) species was no longer the rate-determining step in the catalytic cycle. The activated aryl chloride, 4-chloroacetophone, also reacted smoothly (Table 4, entry 9). However, steric hindrance from aryl halides affected the diarylation markedly. Only a trace amount of diarylation product was detected by GC-MS for the reactions of 2-bromotoluene and 2-chlorobenzonitrile with butyl acrylate (Table 4, entries 6 and 10). The major products of these reactions consisted of monoarylation products, *trans*-cinnamates, as the major component along with some aryls and biaryls from dehalogenation and homocoupling of aryl halides, respectively. Diarylation of styrene and *N*,*N*-dimethyl acrylamide with bromobenzene also proceeded smoothly giving trisubstituted olefins in good yields (Table 4, entries 3 and 4). It is noteworthy that almost no diarylation was observed before the terminal olefins, such as acrylate, were consumed in all cases. Thus the mono- and di-arylation of terminal olefins catalysed by the $PdCl_2$–**3**–NaOAc system is well controlled by simply changing the substrate ratio. These results implied that the insertion of the C–C double bond of 1,2-disubstituted olefins, such as cinnamate, to the Pd–C_{Ar} bond should determine the rate of the diarylation reaction.

Conclusions

In summary, the Heck reaction of aryl bromides and activated aryl chlorides is efficiently catalysed by (benzimidazolylidene)-palladium generated *in situ* from benzimidazolium and $PdCl_2$ in TBAB. Remarkable electronic effects from the benzimidazolylidene were observed, leading to the development of a highly active benzimidazolium–palladium–NaOAc catalyst system based on the electron-rich benzimidazolium, 5,6-dibutoxy-*N*,*N*′-dibutylbenzimidazolium bromide, for the Heck reaction of aryl bromides and activated aryl chlorides. The mono- and di-arylation of terminal olefins could be controllably effected for aryl bromides and activated aryl chlorides without steric hindrance. The electronic factors from aryl bromides showed negligible influence on diarylation under catalysis of the benzimidazolium–palladium–NaOAc system in TBAB while electron-poor aryl halides reacted faster than electron-rich ones in the monoarylation. Although only aryl halides without steric hindrance reacted in the diarylation, providing trisubstituted olefins, steric hindrance from aryl halides could be overcome by increasing the loading of palladium in the monoarylation. Further applications of the electron-rich benzimidazolium–palladium catalyst systems in other palladium-catalysed organic reactions are in progress in our laboratory.

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