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Solvent-controlled selective synthesis of a *trans*-configured benzimidazoline-2-ylidene palladium(II) complex and investigations of its Heck-type catalytic activity

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Abstract

Reaction of *N*,*N*′-dimethylbenzimidazolyl iodide (**A**) with $Pd(OAc)_2$ in DMSO gives selectively *trans*-bis(*N*,*N*′-dimethylbenzimidazoline-2-ylidene) palladium(II) diiodide (*trans*-**2**) in 77% yield. The selective formation of the *trans*-coordination isomer and thus the *cis–trans* rearrangement is driven by the insolubility of *trans*-**2** in DMSO. X-ray single-crystal diffraction analysis and ^{13}C NMR spectroscopy confirm the *trans*-geometry of the square planar Pd(II) complex. Catalytic studies show that *cis*-**1** and *trans*-**2** are highly efficient in the Mizoroki–Heck coupling reaction of aryl bromides and activated aryl chlorides both in DMF and $[N(n\text{-}C_4H_9)_4]Br$ as ionic liquid. The catalytic activities of Pd(II) complexes with *N*-heterocyclic carbene ligands derived from benzimidazole are comparable to their imidazole-derived analogues.

Keywords: Palladium; *N*-Heterocyclic carbene; Homogeneous catalysis; Heck coupling reaction

1. Introduction

Nucleophilic *N*-heterocyclic carbenes (NHC) and their transition metal complexes have been the focus of intense research in organometallic chemistry and homogeneous catalysis since the past decade [1]. In particular, palladium(II) carbene complexes were successfully developed as highly active precatalysts for C–C coupling reactions such as Mizoroki–Heck and Suzuki–Miyaura couplings as well as CO-olefin co-polymerization. It has been shown that such complexes offer the distinctive advantage of greater stability over the classical Pd/phosphine systems as the latter suffer from sensitivity to air and moisture [2]. The majority of these precatalysts contain NHC as ancillary ligands that are derived from imidazolium salts. It has been reported that carbenes derived from benzimidazolium precursors exhibit the topology of an unsaturated *N*-heterocyclic carbene, but show spectroscopic and structural properties and the reactivity of carbenes with a saturated *N*-heterocyclic ring [3]. Previously, several examples of palladium(II) carbene complexes derived from benzimidazolium precursors with achiral [4] and chiral [5] alkyl groups or even the ferrocene moiety [6] adjacent to the nitrogen atoms have been reported. However, their potential application as phosphine free precatalysts remains relatively unexplored [7]. We herein present a solvent-controlled selective synthesis and structural characterization of a *trans*-configured palladium(II) bis(benzimidazoline-2-ylidene) complex and investigations of its catalytic activity in the Mizoroki–Heck coupling reaction.

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2. Results and discussion

2.1. Synthesis and characterization

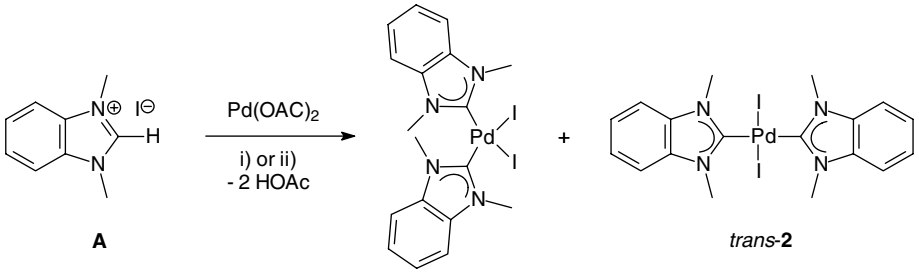
In connection with our research on carbene carboxylate complexes [8], we were interested in the complex *cis*-bis(*N*,*N*′-dimethylbenzimidazoline-2-ylidene) palladium(II) diiodide (*cis*-**1**) as a precursor. *cis*-**1** can be easily prepared by reacting two equivalents of *N*,*N*′-dimethylbenzimidazolyl iodide (**A**) with $Pd(OAc)_2$ in THF at ambient temperature as described by Hahn and Foth [4a]. However, we found that this procedure not only afforded *cis*-**1** but also the novel *trans*-isomer *trans*-**2** in substantial amount (40%) explaining the moderate yield of *cis*-**1** reported by the authors (Scheme 1). The remarkably different solubility of the two coordination isomers in organic solvents allows an easy separation step. The *trans* form, e.g., is readily soluble in halogenated solvents and insoluble in more polar solvents such as DMSO and DMF, while the *cis*-form on the contrary dissolves only in the two latter solvents and CH_3CN. The configuration of *trans*-**2** was confirmed by ^{13}C NMR spectroscopy, in which the carbene carbon resonances at 181.0 ppm and as expected downfield from the reported value of 172.1 ppm (175.1 ppm in this work) for *cis*-**1** [9]. Upon prolonged standing of a CH_2Cl_2 solution *trans*-**2** slowly converts into *cis*-**1**, which precipitates as a fine yellow powder. However, evaporation of a concentrated CH_2Cl_2 solution at ambient temperature afforded yellow cubic crystals of *trans*-**2** suitable for X-ray diffraction studies (see Section 2.2). On the other hand, the *trans*-form precipitates from a DMSO solution of the *cis*-isomer upon standing, presumably helping to drive the equilibrium towards the *trans*-isomer. Thus this isomerization process is strongly influenced by the solubility of the two isomers in different solvents. Based on this observation we could increase the yield of *trans*-**2** up to 77% by employing DMSO as the reaction media at moderate temperatures of 80 °C. Unfortunately, our attempts to monitor this rearrangement by ^1H NMR spectroscopy failed due to the different solubilities of the two isomers. It is noteworthy that a *trans–cis* rearrangement of a similar benzimidazoline-2-ylidene palladium(II) complex has recently been reported by Wang and Lin [10] based on ^1H NMR data.

2.2. Molecular structures of salt *A* and complex *trans*-*2*

Single crystals of *trans*-**2** suitable for X-ray diffraction studies were obtained by evaporation of a saturated CH_2Cl_2 solution at ambient temperature. For the purpose of a comparison, we have also carried out the X-ray crystal structure analysis of the benzimidazolium salt **A**. Crystallographic data are listed in Table 1. The molecular structures of the salt **A** and *trans*-**2** are depicted in Fig. 1 and selected bond lengths and angles are listed in Table 2.

Compound *trans*-**2** crystallizes as a mononuclear complex with half a molecule in the asymmetric unit. The palladium center is coordinated by two carbene and two iodo ligands in a square-planar fashion. As found by ^{13}C NMR spectroscopy in solution, the two carbene ligands are arranged *trans* to each other with an ideal angle of 180° due to symmetry. Both carbene ring planes are oriented almost perpendicular to the PdC_2I_2 plane with a torsion angle of 88.09(21)°. Significantly smaller torsion angles were found in the *cis* isomer [4a] with values of 83.06(10)° and 79.84(13)°. Compared to its benzimidazolium salt precursor **A**, the $C_{carbene}$–N1/2 bonds of the heterocyclic ligand in both isomers have become elongated by $\Delta d = 0.03$ Å. This bond elongation is furthermore accompanied by a decrease of the N–C–N angle from 110.6(3)° in **A** to about 106° in both isomers. Other structural parameters remain largely unchanged indicating that the coordination to the Pd-center is only affecting the carbene carbon and the two neighboring nitrogen atoms.

More importantly, a comparison of the mean Pd–$C_{carbene}$ bond lengths in both isomers (2.010(2) Å for



i) THF, RT: *cis*-**1**, 54% vs. *trans*-**2**, 40%
ii) DMSO, 80°C: *cis*-**1**, 20% vs. *trans*-**2**, 77%

Scheme 1. Preparation of *cis*-**1** and *trans*-**2**.

Table 1
Selected crystal data, data collection and refinement parameters for salt **A** · H_2O and complex *trans*-**2**

	A · H_2O	*trans*-**2**
Formula	$C_9H_{11}IN_2 \cdot H_2O$	$C_{18}H_{20}I_2N_4Pd$
Formula weight	292.11	652.58
Color, habit	Colorless, block	Yellow, block
Crystal size (mm)	$0.36 \times 0.14 \times 0.14$	$0.44 \times 0.24 \times 0.18$
T (K)	223(2)	223(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	8.8666(10)	8.2797(5)
b (Å)	7.0570(8)	16.2675(10)
c (Å)	17.5218(19)	7.6549(5)
α (°)	90	90
β (°)	101.107(2)	99.6000(10)
γ (°)	90	90
V (Å^3)	1075.8(2)	1016.60(11)
Z	4	2
D_{calc} (g cm^{-3})	1.804	2.132
Radiation used	Mo Kα	Mo Kα
μ (mm^{-1})	2.942	3.958
θ Range (°)	2.37–24.99	2.49–27.50
Number of unique reflections measured	5870	6897
Maximum and minimum transmission	0.6835 and 0.4173	0.5360 and 0.2748
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0234$, $wR_2 = 0.0652$	$R_1 = 0.0206$, $wR_2 = 0.0508$
R indices (all data)	$R_1 = 0.0250$, $wR_2 = 0.0664$	$R_1 = 0.0223$, $wR_2 = 0.0516$
Goodness-of-fit on F^2	1.093	1.108
Large difference in peak and hole (eÅ^{-3})	0.908 and −0.411	0.727 and −0.312

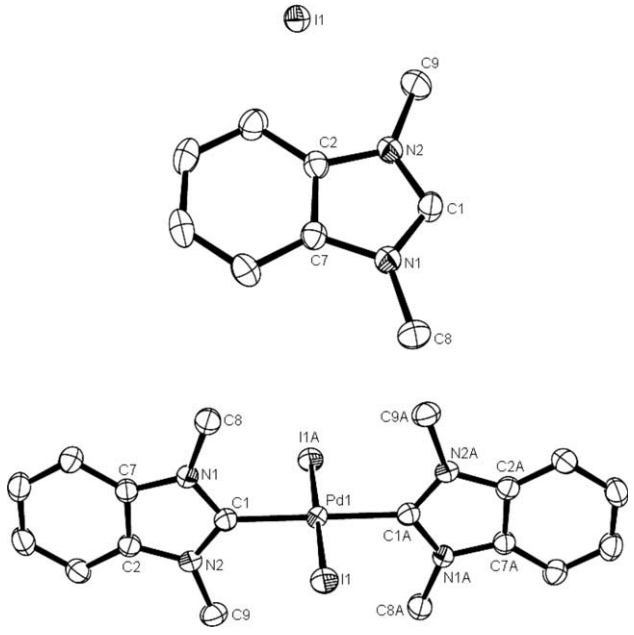


Fig. 1. Molecular structure of benzimidazolium salt **A** (upper, the disordered water molecule is not depicted) and complex *trans*-**2** (lower).

Table 2
Selected bond lengths (Å) and bond angles (°) for the salt **A** · H_2O and complex *trans*-**2**

	A · H_2O	*trans*-**2**
Pd1–I1	–	2.5969(2)
Pd1–C1	–	2.010(2)
N1–C1	1.320(4)	1.353(3)
N1–C7	1.384(4)	1.397(3)
N1–C8	1.471(4)	1.459(3)
N2–C1	1.320(4)	1.353(3)
N2–C2	1.394(4)	1.390(3)
N2–C9	1.463(4)	1.452(3)
C2–C7	1.388(4)	1.396(3)
C1–Pd1–I1	–	89.11(11)
C1–Pd1–I1A	–	90.89(7)
C1–Pd1–C1A	–	180.0(2)
I1–Pd1–I1A	–	180.000(6)
N1–C1–N2	110.6(3)	106.4(2)

trans-**2** vs. 1.988(4) Å for *cis*-**1**) reveals that the carbene ligands are more strongly bound to the Pd-center in the *cis*-form. In addition, the longer Pd–I bond lengths in *cis*-**1** (2.6371(5) and 2.6805(5) Å) as compared to those in *trans*-**2** (2.5969(2) Å) reflects the strong *trans*-effect of the benzimidazoline-2-ylidene ligand. These findings strongly support the view that a *cis* arrangement is generally more favorable for *N*-heterocyclic carbene complexes [10].

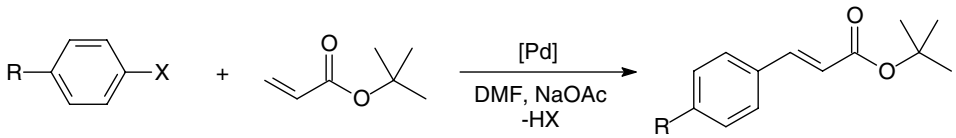
2.3. Catalysis

Palladium complexes of NHC derived from imidazolium and imidazolinium salts are highly active catalysts for a wide range of C–C coupling reactions [1]. Complexes derived from benzimidazolium precursors on the other hand have scarcely been investigated for their

catalytic activities [7]. This prompted us to start a preliminary study on the catalytic activities of the benzimidazoline-2-ylidene complexes *cis*-**1** and *trans*-**2** for the Mizoroki–Heck coupling reaction of aryl halides with *t*-butyl acrylate to give the corresponding cinnamates. Since the coupling of aryl iodides is in general common and facile, we focused on the coupling of the less reactive aryl bromides and chlorides. Our results, summarized in Table 3, indicate that both isomers are highly efficient in the coupling of aryl bromides. For example, both *cis*-**1** and *trans*-**2** (1 mol%) can couple 4-bromobenzaldehyde (entry 1) and bromobenzene (entry 2) with the acrylate in quantitative yield at 120 °C.

A more detailed kinetic study on the coupling of the electron-withdrawing 4-bromobenzaldehyde employing 1 mol% catalyst revealed that both isomers showed different catalytic behavior. In the case of *trans*-**2**, the conversion is already complete within 90 min (Fig. 2). Furthermore, the concentration/time diagram indicates an induction period for this reaction of about

Table 3
Mizoroki–Heck coupling reactions[a] catalyzed by *cis*-**1** and *trans*-**2**



X = Br, Cl
R = CHO, H, CH_3CO, CH_3O

Entry	Catalyst	Catalyst load (mol%)	Aryl halide	*t* (h)	*T* (°C)	Yield (%)
1	*cis*-**1**, *trans*-**2**	1	4-Bromobenzaldehyde	2	120	100[b]
2	*cis*-**1**, *trans*-**2**	1	Bromobenzene	20	120	100[b]
3	*trans*-**2**	0.1	Bromobenzene	20	120	100[b]
4	*trans*-**2**	0.02	Bromobenzene	65	120	72[c]
5	*trans*-**2**	0.002	Bromobenzene	65	140	59[c]
6	*trans*-**2**	1	4-Bromoanisole	18	120	90[b]
7[d]	*trans*-**2**	1	4-Chlorobenzaldehyde	20	140	86[b]
8[d]	*trans*-**2**	1	4-Chloroacetophenone	24	140	63[b]
9[d]	*trans*-**2**	1	Chlorobenzene	20	140	20[c]
10[e]	*trans*-**2**	1	4-Bromobenzaldehyde	4	120	0
11[e]	*trans*-**2**	1	4-Bromobenzaldehyde	18	120	100[b]
12[e,f]	*trans*-**2**	1	4-Bromobenzaldehyde	2	120	100[b]

[a] Reaction conditions generally not optimized.
[b] Yields were determined by ^1H NMR spectroscopy.
[c] Isolated yields.
[d] With addition of 1.5 equivalents of $[N(n\text{-}C_4H_9)_4]Br$.
[e] Coupling reaction was carried out in neat $[N(n\text{-}C_4H_9)_4]Br$ as ionic liquid.
[f] With addition of NaO_2CH as reducing agent.

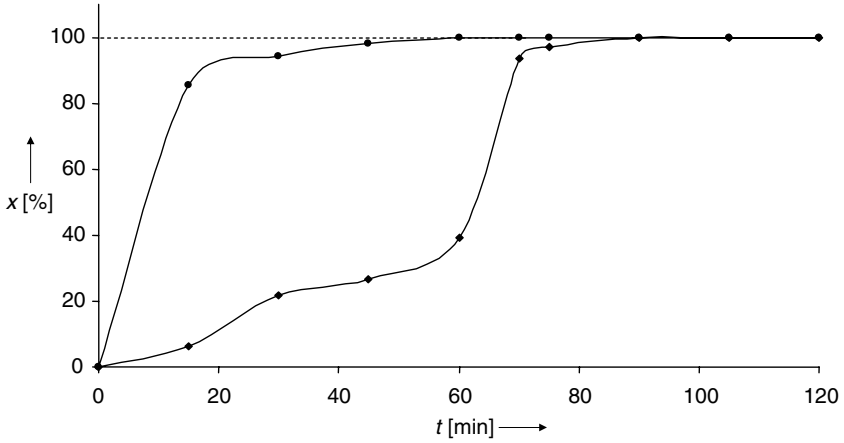
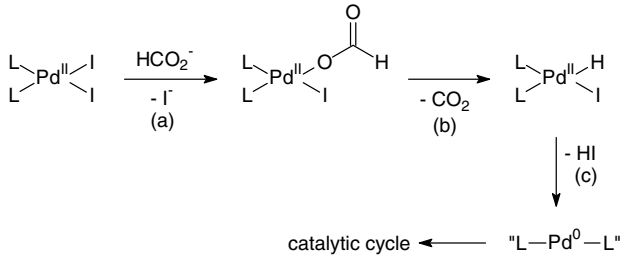


Fig. 2. Concentration/time diagram (amount of substance *x* (%), time *t* (min)) for the Mizoroki–Heck olefination of 4-bromobenzaldehyde with *t*-butyl acrylate to form *t*-butyl (*E*)-4-formylcinnamate catalyzed by *cis*-**1** (•) and *trans*-**2** (♦).



Scheme 2. Feasible formation pathway of the active Pd(0) species.

40 min, after which the concentration of the product increases exponentially. Similar induction periods were observed for palladium carbene complexes derived from imidazolium salts and it was proposed that during this period catalytically active palladium(0) species are formed [2].

The coupling with *cis*-**1**, however, is remarkably faster and the reaction profile does not show an induction period in the observed time intervals (Fig. 2). This surprising result is worthy of comment and suggests that reduction of Pd(II) to Pd(0) and thus formation of the catalytically active species occurs faster in the *cis*-isomer. This reductive process can already be accomplished by traces of formic acid in DMF [11]. Scheme 2 depicts a feasible pathway which includes ligand substitution (a), CO_2 elimination (b) and reductive elimination (c) affording the active Pd(0) species, which subsequently enters the catalytic cycle. A facile dissociation of the iodo ligand as a possible introductory step is favored in the *cis*-isomer, in which the strong *trans*-effect of the carbene ligand weakens the Pd–I bond. On the other hand, such a Pd–I bond cleavage is less favored in *trans*-**2** and may account for the observed induction period, in which a *trans–cis* isomerization might occur to facilitate Pd–I bond cleavage prior to the reduction step.

To investigate the effect of the catalyst loading on the conversion rate, we examined the coupling of bromobenzene with the acrylate. On lowering the amount of catalyst from 0.1 mol% (entry 3) to 0.02 mol% (entry 4) and further to 0.002 mol% (entry 5), we could still observe high to moderate isolated yields of 72% (TON 3600) and 59% (TON 29,500), respectively. Not surprisingly, prolonged reaction times and higher temperatures were required to achieve a high TON of 29,500. It is expected, that much higher TONs can be achieved for the coupling of activated aryl iodides and electron-poor aryl bromides. Electron-donating substituents on the aryl halide are deactivating and thus electron-rich aryl bromides like 4-bromoanisole are usually more difficult to couple. However, the conversion of 4-bromoanisole proceeded smoothly with 1 mol% of *trans*-**2** giving an excellent yield of 90% (entry 6). The coupling of aryl chlorides was far more difficult and yielded only poor results. However, with addition of [N(*n*-C_4H_9)$_4$]Br and an elevated reaction temperature of 140 °C electron-poor aryl chlorides like 4-chlorobenzaldehyde (entry 7) and 4-chloroacetophenone (entry 8) couple with *t*-butyl acrylate affording good to high yields. This positive salt-effect has been described by other researchers and it has been suggested that quaternary salts like [N(*n*-C_4H_9)$_4$]Br can react as reducing agent to generate active Pd(0) species [2,9]. To test this statement, we investigated the coupling of 4-bromobenzaldehyde in neat [N(*n*-C_4H_9)$_4$]Br as ionic liquid at 120 °C. Surprisingly, no conversion was observed even after 4 h (entry 10) indicating that no active Pd(0) species were formed during this time in neat [N(*n*-C_4H_9)$_4$]Br. However, extension of the reaction time to 18 h yielded complete conversion (entry 11) corroborating that the ionic liquid can indeed react as a reducing agent. Nevertheless, the formation of active Pd(0) species with [N(*n*-C_4H_9)$_4$]Br is a very slow process that requires prolong reaction times. On addition of stronger reducing agents like formic acid or sodium formate to the ionic liquid, however, we could achieve quantitative conversions in 2 h (entry 12). Based on these results, we believe that the reducing properties of [N(*n*-C_4H_9)$_4$]Br play only a minor role in promoting the Mizoroki–Heck reaction. It is more likely that the addition of such salts helps in stabilizing intermediates by coordination or formation of ion-pairs in the catalytic cycle [11]. However, further investigations are needed to gain better understanding of the cause for the promoting effects of quaternary ammonium salts in Heck-type reactions. Finally, we note that the more difficult coupling of inactivated chlorobenzene afforded only a low isolated yield of 20% (entry 9) even in the presence of [N(*n*-C_4H_9)$_4$]Br.

The results of this preliminary catalytic study clearly demonstrates that benzannulated *N*-heterocyclic carbene ligands derived from benzimidazole are as versatile and excellent ligands for catalysis as their well-investigated imidazole-derived analogues. Work is currently underway to expand the scope of benzimidazoline-2-ylidene complexes in catalysis.

3. Experimental

3.1. General procedures

Unless otherwise noted all manipulations were performed in air. All solvents were used as received. *N*,*N*′-Dimethylbenzimidazolyl iodide (**A**) was prepared according to the literature procedures [12]. $Pd(OAc)_2$ was purchased from Avocado® and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer using Me_4Si as internal standard. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

3.2. Synthesis of cis and trans-bis(N,N′-dimethylbenzimidazoline-2-ylidene)palladium(II) diiodide (cis-**1** and trans-**2**)

A mixture of *N*,*N*′-dimethylbenzimidazolyl iodide (**A**) (274 mg, 1.00 mmol) and $Pd(OAc)_2$ (112.0 mg, 0.5 mmol) was suspended in THF (15 mL) and stirred overnight at ambient temperature. The orange suspension first turned dark brown and lightened up to pale brown after a few hours. The volatiles were removed in vacuo and the residue was washed with CH_2Cl_2 several times. Slow evaporation of the combined CH_2Cl_2 solutions afforded yellow cubic crystals of *trans*-**2** (130 mg, 0.2 mmol, 40%) suitable for X-ray diffraction studies. The residue, insoluble in CH_2Cl_2, was recrystallized from CH_3CN to yield an orange powder of *cis*-**1** (176 mg, 0.27 mmol, 54%). Anal. Calc. for $C_{18}H_{20}N_4I_2Pd$: C, 33.13; H, 3.09; N, 8.59. Found: C, 33.19; H, 3.12; N, 8.54%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.64 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 3.3 Hz, 4 H, Ar–H), 7.35 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 2.7 Hz, 4 H, Ar–H), 4.19 (s, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (75.48 MHz, DMSO-d_6): 175.1 (s, N–C–N), 134.5, 123.2, 110.9 (s, Ar–C), 35.8 (s, CH_3).

3.3. Improved synthesis of trans-bis(N,N′-dimethylbenzimidazoline-2-ylidene) palladium(II) diiodide (trans-**2**)

A sample of *N*,*N*′-dimethylbenzimidazolyl iodide (**A**) (1.117 g, 4.08 mmol) and $Pd(OAc)_2$ (456 mg, 2.03 mmol) was dissolved in wet DMSO (10 mL) and stirred overnight at 80 °C. The yellow precipitate obtained was filtered off and washed with small portions of DMSO and diethyl ether. It was then dried to give the product as a yellow powder of *trans*-**2** (927 mg, 1.42 mmol, 70%). Upon standing of the DMSO-filtrate a second crop of 7% can be obtained giving a total yield of 77%. Anal. Calc. for $C_{18}H_{20}N_4I_2Pd$: C, 33.13; H, 3.09; N, 8.59. Found: C, 33.15; H, 3.15; N, 8.62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 3.5 Hz, 4 H, Ar–H), 7.30 (dd, ^3J(H,H) = 6 Hz, ^4J(H,H) = 3.2 Hz, 4 H, Ar–H), 4.20 (s, 12 H, CH_3). $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$): 181.0 (s, N–C–N), 135.4, 122.7, 109.9 (s, Ar–C), 35.1 (s, CH_3).

3.4. General procedure for the Mizoroki–Heck coupling

In a typical run, a Schlenk-tube was charged with a mixture of aryl halide (1.0 mmol), anhydrous sodium acetate (1.5 mmol), *t*-butyl acrylate (1.4 mmol). 3 mL DMF was added and the mixture degassed under vacuum and filled with nitrogen. The reaction mixture was vigorously stirred at the appropriate temperature before a catalyst solution in DMF was injected. After the desired reaction time, the solution was allowed to cool. 5 mL of dichloromethane was added to the reaction mixture and the organic layer was repeatedly washed with water (5×10 mL) and dried over $MgSO_4$. The solvent and any volatiles were removed completely under high vacuum to give a crude product which was either subjected to column chromatography or analyzed by ^{1}H NMR spectroscopy.

3.5. Structure determinations

Single crystals of **A** and *trans*-**2** were obtained by slow evaporation of CH_2Cl_2 solutions of the corresponding compounds. Suitable crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo Kα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects with the SMART suite programs [13] and for absorption effects with SADABS [14]. Structure solution and refinement were carried out with the SHELXTL suite of programs [15]. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. The data collection and processing parameters are given in Table 3.

4. Supplementary material

CCDC 260776 (complex *trans*-**2**) and CCDC 260777 (compound **A**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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