Palladium complexes of *o*-xylyl-linked alkoxybenzimidazolin-2-ylidenes: interesting structural conformations and application as pre-catalysts†‡

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New $PdBr_2$-bis(*N*-heterocyclic carbene) complexes derived from 4,7-dibutoxybenzimidazole and 5,6-dibutoxybenzimidazole have been synthesized and structurally and spectroscopically characterized. The complexes show much greater solubility compared to the parent complex derived from benzimidazole, and interesting structural characteristics dependent on the position of the butoxy substituents. The complexes display high activities in the coupling of aryl iodides in the Mizoroki-Heck reaction and moderate activities in the Suzuki-Miyaura coupling of inactivated aryl bromides at low catalyst loadings, although activity differences between pre-catalysts has been observed. Structural studies suggest electronic effects within the complexes to be strongly affected by steric interactions between the hydrogen atoms of the *o*-xylyl bridges and the benzimidazole components and their substituents.

Introduction

Since the synthesis of the first *N*-heterocyclic carbene (NHC) metal complexes[1,2] a wide variety of NHC complexes have been prepared. Key work by Herrmann and co-workers has led to the widespread use of NHC complexes in catalysis.[3] As ligands, NHCs have the advantage of being strong

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σ-donors and the robust nature of the metal-NHC bonding leads to high stability, ensuring that, as catalysts, decomposition is minimized.[4-6] NHC metal complexes of palladium, ruthenium, rhodium, platinum and nickel have been shown to effectively act as pre-catalysts in many C-C and C-N cross-coupling, olefin metathesis, hydrogenation and hydrosilylation reactions.[7-12] Intense research aimed at elucidating the reasons behind high catalytic activity in NHC metal complexes has led researchers to synthesize a wide range of metal complexes bearing NHCs of different structural design, including mono-dentate, poly-dentate and chelating ligands having mixed donor groups.[10,13-15] Further study into the mechanism of many cross-coupling reactions has assisted the rational design of NHC metal complexes as pre-catalysts.[16] Increasing steric bulk around the metal centre to facilitate reductive elimination and minimise over-ligation of the metal has been shown to dramatically improve catalyst activity, while the addition of electron donating groups onto the NHC has exhibited a beneficial effect by increasing the electronic density around the metal, leading to an increased rate of oxidative addition.[17,18]

We have had extensive experience in synthesizing bidentate NHC metal complexes based on bis(imidazolin-2-ylidene) and bis(benzimidazolin-2-ylidene) ligands in which the NHC units are joined by either one or two *o*-xylyl linkers.[19-22] The azolium salts that serve as precursors to the NHC ligands are easily synthesized and adopt a rigid structure when bound to a metal. We are interested in investigating the structural and catalytic properties of a number of palladium complexes based on bridged benzimidazolin-2-ylidene ligands that incorporate butoxy groups on the arene ring. The butoxy groups serve two purposes: to potentially increase the electron density around the metal centre, and to help solubilize the complex, which has been an ongoing problem with cyclophane type complexes. To the best of our knowledge, there are no reports of similar palladium-NHC cyclophane complexes bearing electron donating alkoxy groups.

In this paper we report the synthesis of five palladium-NHC cyclophane (bis-NHCs linked by two *o*-xylyl groups) and 'open' (bis-NHCs linked by one *o*-xylyl group) complexes that are pre-catalysts in various cross-coupling reactions. It was postulated that the rigidity conferred by the cyclophane skeleton would provide a stabilising effect on the active species and hence prevent catalyst

decomposition. The stabilisation conferred by the NHC ligand occurs by way of strong σ-bonds to the palladium centre, and should prevent under-ligation of the active species, hence diminishing the possibility of forming inactive, insoluble palladium colloids. The complexes have been structurally and spectroscopically characterized and, although similar in structure, nevertheless exhibit some differences in catalytic activity that may be attributed to differences in the stability of the complexes under the reaction conditions employed. Four of the palladium complexes have been tested as pre-catalysts in the Mizoroki-Heck and Suzuki-Miyaura coupling reactions, with our study focussing on differences in structure-activity relationships rather than optimisation of reaction conditions.

Results and discussion

Synthesis of complexes

The benzimidazolium cyclophane salts **1a** and **1b** were prepared according to established procedures.[23] The non-cyclophane benzimidazolium salts **2a** and **2b** were prepared in good to excellent yields by alkylation of the corresponding 1-methylbenzimidazoles with α,α'-dibromo-*o*-xylene. The salts **1a**,**b** and **2a**,**b** show good solubility in a range of common organic solvents (*e.g.* DMSO, CH_2Cl_2, $CHCl_3$ and MeOH). Interestingly, the salts show excellent solubility in CH_3CN when the butoxy groups are in the 4,7 positions on the benzimidazole ring, but poor solubility with the butoxy groups in the 5,6 positions.

<structures 1x-4x here>

The palladium complexes **3a** and **3b** were synthesized in 72 and 51% yields respectively by the reaction of the benzimidazolium salts **1a** and **1b** and $Pd(OAc)_2$ in refluxing CH_3CN over two days. Both **3a** and **3b** are air-stable, although they demonstrate poor solubility in most solvents except DMSO, DMF and CH_2Cl_2. Despite this, the butoxy groups nevertheless serve to dramatically increase their solubility compared to the benzimidazole based cyclophane complex **5** reported previously.[22]

<structure 5 here>

Complex **4a** was obtained in 55% yield from **2a** and $Pd(OAc)_2$ in DMF at 90 °C over three days. Complexes *cis*-**4b** (*syn*) and *trans*-**4b** were obtained in yields of 43 and 7% respectively from **2b** and $Pd(OAc)_2$ in refluxing THF over five days. Complex mixtures were obtained when DMF or CH_3CN were used in place of THF. Complexes **4a**, *cis*-**4b** (*syn*), and *trans*-**4b** are soluble in CH_2Cl_2, $CHCl_3$, acetone, DMSO and DMF, with **4a** and *trans*-**4b** also exhibiting good solubility in THF. Separation of *cis*-**4b** (*syn*) and *trans*-**4b** was straightforward on account of the substantially lower solubility of the *cis* complex in THF.

NMR Spectra of the complexes

The ^1H and ^{13}C NMR spectra of the palladium complexes **3a**,**b**, **4a** and *cis*-**4b** (*syn*) are consistent with metal complexes in which the NHC units are mutually *cis* and linked by an *o*-xylyl group "folded away" from the metal centre. The ^1H NMR spectra of these systems typically show a pair of signals due to the diastereotopic (*endo* and *exo*) xylyl benzylic protons.[22] For **3a**,**b**, **4a**, these signals appeared near 5.70 and 6.90 ppm, but for *cis*-**4b** (*syn*) they appeared significantly more upfield (5.60 and 5.95 ppm), consistent with a different conformation for the NHC ligand, in this case with the xylyl ring towards the metal centre.

Interestingly, while the ^1H NMR spectra of freshly prepared solutions of *cis*-**4b** (*syn*) showed only the expected signals, a new set of signals associated with a second conformation of the complex, *cis*-**4b** (*anti*), began to emerge after about an hour at room temperature. The identification of the new conformation as *cis*-**4b** (*anti*) was determined by recording the ^1H NMR spectrum of a fresh solution of the complex derived from crystals of *cis*-**4b** (*anti*) (confirmed by an X-ray study (see below)). Over approximately twenty six days the mixture reached an equilibrium of 35:65 *cis*-**4b** (*syn*) : *cis*-**4b** (*anti*) (Fig. 1). Apparently there is a fine balance between the two forms of *cis*-**4b**, with differing interactions between the xylyl group and butoxy groups *cf.* the $PdBr_2$ moiety, resulting in differing kinetic *vs.* thermodynamic conformational preferences.

A series of selective 1D-NOESY experiments in which the diastereotopic (*exo* and *endo*) benzylic protons were irradiated provided further evidence concerning the conformations of the kinetic and thermodynamic products *cis*-**4b** (*syn*) and *cis*-**4b** (*anti*). An NOE was observed for the OCH_2 protons in *cis*-**4b** (*syn*) from both the *endo* and the *exo* benzylic protons, but corresponding NOEs were not seen for *cis*-**4b** (*anti*) (see Fig. 2 and Supporting Information). The lack of such a correlation is consistent with the *cis*-**4b** (*anti*) conformation, in which the OCH_2 protons are anchored relatively far from the benzylic CH_2 group. There was also no NOE observed between the butyl chain and the *endo* benzylic proton in *cis*-**4b** (*anti*).

The ^{1}H NMR spectra of *cis*-**4b** (*syn*), *cis*-**4b** (*anti*) and *trans*-**4b** can be seen in Figure 3. The spectra show the expected signals, but in the case of *cis*-**4b** (*anti*) there is a far larger separation in the chemical shifts of the aromatic protons of the xylyl group ($\Delta\delta \sim 0.8$ ppm) compared with that seen for the other isomers ($\Delta\delta < 0.2$ ppm). This difference for *cis*-**4b** (*anti*) is presumably a consequence of the proximity of two butoxy groups to the *o*-xylyl ring–the butoxy groups approach the mutually *trans* protons of the xylyl ring much more closely than the other two protons (see Structure determinations, below). This interaction also makes the two OCH_2 protons of the butoxy groups anisochronous. The difference in conformations of the organic framework in the three complexes also results in substantial differences in chemical shifts of the signals due to the benzylic protons.

The ^{13}C NMR spectra of **3a**,**b**, **4a**, *cis*-**4b** (*syn*) and *cis*-**4b** (*anti*) each exhibit a singlet in the range 170-175 ppm, which is characteristic of the carbene carbon of bis(NHC)Pd dihalide complexes in which the NHC groups are mutually *cis*.[24,25] The signal attributed to the carbene carbon in *trans*-**4b**, however, is seen at 182 ppm, which is typical of a palladium complex bearing NHC ligands in a mutually *trans* environment.[25] Similar trends in shifts of NHC carbons are seen in spectra of *cis vs trans* isomers of diiodobis(dimethylbenzimidazolin-2-ylidene)palladium, where the *trans* complex has a carbene signal ~6 ppm downfield *cf*. the *cis*.[25]

Structure determinations

2b·H_2O. A pair of *pseudo*-symmetrically related formula units comprise the asymmetric unit of the structure, the two cations differing in the conformations of their *n*-butyl substituent 'tails'. The components lie in sheets parallel to (101) (Fig. 4(a)). Within each cation, the two benzimidazole units are *quasi*-planar (C_7N_2/C_7N_2 interplanar dihedral angles 14.16(6), 14.46(7)º), with the central *o*-xylyl plane *quasi*-normal to them (C_6/C_7N_2 dihedrals: 81.83(8), 76.02(9) (cation 1), 80.45(9), 75.96(10)º (cation 2)), one benzimidazole unit pendant *trans* in each case ((τ $C(n1)^{Xy}$-$C(n2)^{Xy}$-C-N 177.1(2), 175.1(3)º), Xy = xylyl), the other *gauche* (τ $C(n2)^{Xy}$-$C(n1)^{Xy}$-C-N -108.7(3), -106.7(3)º) (Fig. 4(b)). Each cation forms an essentially closed cluster with a pair of bromide ions and a water molecule (Fig. 4(a)), with only limited interactions between clusters (Table 1), and with the *pseudo*-symmetry imposing/reflecting a parallelism between the sets of interactions. The water molecule environments comprise a pair of bromide ions (Br(1)···O(1)···Br(2) 97.67(6); Br(3)···O(2)···Br(4) 100.23(7)º) and a hydrogen atom from the central aromatic ring of a symmetry-related associated cation, with Br(1,3) 'chelated' by the pairs of imidazolium hydrogen atoms, supported in each case by an adjacent methyl hydrogen atom, and Br(2,4) each supported by a methylene hydrogen, with contacts to other neighbouring cations (Fig. 4(b)).

trans-**4b**·0.84$CHCl_3$. In the single molecule of the asymmetric unit, the pairs of benzimidazole moieties are similarly disposed with respect to the central xylyl ring (C_7N_2/C_7N_2 interplanar dihedral angle 18.7(2); C_6/C_7N_2 dihedrals 79.4(3), 78.1(3)º). The ligand, rather than 'chelating' a bromide anion through imidazole hydrogen atoms, as in **2b**·H_2O, now deprotonated, chelates the metal atom of a *trans*-$PdBr_2$ component through the resulting carbene carbon atoms, the C_2Br_2 'plane' of the palladium atom environment lying *quasi*-parallel to the central C_6 xylyl plane ($\chi^2(C_2Br_2)$ 2718; C_6/C_2Br_2 dihedral 23.2(2), C_2Br_2/C_7N_2 dihedrals 77.5(2), 79.4(2)º). The palladium atom lies 0.242(8), 0.234(9) Å out of the benzimidazole planes towards Br(2). The *trans* angles about the palladium atom are well-removed from linearity (Table 2), suggesting some degree of strain in the binding of the carbene components: Pd-C (1.988(8), 2.003(8) Å) are somewhat shorter than in the 'half-ligand' diiodo complexes **7**, **8** (2.032(6) 2(x2); 2.023(2), 2.017(2) Å) where the arrays are (more nearly) linear.[26] This description is

similar to that of the *trans*-dichloro palladium complex **9**,[27] in which Pd-C are 1.98(2), 2.04(2) Å, with C-Pd-C 163.6(7)º. In **9**, *trans*-**4b**, **7**, and **8** respectively, Pd-Cl are 2.286(4), 2.352(4), Pd-Br 2.4469(12), 2.4303(12), and Pd-I 2.6193(4); 2.6040(3), 2.6357(9) Å. The slight difference between the Pd-Br distances in *trans*-**4b** may be a consequence of the hydrogen-bonding interaction of the longer with the chloroform solvent molecule (Fig. 5(a)), the chloroform molecules lying in tunnels in the lattice (Fig. 5(b)).

<structures 7-9 here>

The remaining compounds, **3b**, **4a**, *cis*-**4b** (*anti*) (the latter as two different solvate forms) are all *cis* complexes, one, or in the case of **3b**, two, formula units devoid of crystallographic symmetry comprising the asymmetric unit of the structure. They provide representative complexes of three distinct ligand types; a 'closed' 4,7-substituted ligand (**1b**) in complex **3b**, and 'open' 4,7- and 5,6-substituted ligands (**2b**, **2a**) in complexes *cis*-**4b** (*anti*) and **4a**. Geometrical descriptors are presented in Table 3, notable variations being observed (a) in the C-Pd-C angles (and dependent parameters) where that in **4a** (85.7(4)º) is considerably less than those for **3b** and *cis*-**4b** (*anti*) (95.1(2) - 96.57(10)º), and the dihedral angle of the central xylyl ring plane to the coordination plane – 46.4(3)º in **4a**, *cf.* 5.6(1) - 21.1(3)º in **3b**, *cis*-**4b** (*anti*). Baseline comparators for these systems are found in previously described imidazole analogues. *cis*-$PdBr_2$ complexes of (a) a 'closed'/cyclophane unsubstituted and (b) an 'open' unsubstituted imidazole-based ligands are found in complexes **10**[22] (contaminated?) and **11**,[22] wherein C-Pd-C are 85.5(2) and 89.7(2)º, with central-C_6/C_2Br_2 interplanar dihedral angles of 25.7(2), 33.1(2) and 28.2(1)º. In **10**, these may be impacted by contaminant, and by included solvent; values for the PdI_2 analogue **12**[22] and *bis*-ligand complex **13**[22] are 82.2((1), 44.7(1)/36.8(1) and 81.35(7), 44.19(7)/23.61(7)º, suggesting the values for **10** to be toward the upper and lower limits of likely values respectively. A further *cis*-$PdBr_2$ complex of a similar 'open' ligand, compound **14**,[21] has C-M-C 91.9(2)º, (similar to that of **11**) with the C_6/C_2Br_2 interplanar dihedral angle 30.4(1)º.

<structures 10-14 here>

The usefulness of imidazole (*cf.* benzimidazole) analogues as baseline comparators is brought into question by the observation that, in the present **4a**, where the 5,6-dibutoxy substituents are well

removed, there are close contacts (2.2_6, 2.2_8 Å) between the *trans* pair of hydrogen atoms on the central xylyl ring and the hydrogen atoms of the C_6 rings of the benzimidazole component. These interactions are compatible with the observed C_6/C_2Br_2 dihedral angle, and, if attractive, may also assist the closure of the C-Pd-C 'bite' angle. In **3b** and *cis*-**4b** (*anti*) (both solvates), by contrast, the 'bite' angles are unusually large and the C_6/C_2Br_2 inclination unusually 'shallow'. Here we find that, with the benzimidazole 4,7 hydrogen atoms now replaced by the oxygen atoms of butoxy substituents, we have very short Xy-H···O contacts (2.2_5-2.4_4 Å), suggestive of strong interactions which draw the central aromatic rings in between the pairs of oxygen atoms, with the expected impact on plane inclinations and C-Pd-C 'bite' angles; large out-of-plane deviations of the palladium atoms are also found (Table 3), with concomitant minor deviations of the carbene carbon atoms (up to 0.13 Å), both toward the adjacent bromine atom.

The above results suggest that, while variation of the substitution pattern of the butoxy components between 4,7 and 5,6 locations may impact electronically on the ligand and complex characteristics, the effect of such a change may be greatly influenced, *inter alia*, by the steric consequences described above.

Catalysis studies

The four pre-catalysts **3a**,**b**, **4a** and *cis*-**4b** (*syn*) were tested against **5** and $Pd(OAc)_2$ in an initial series of Mizoroki-Heck coupling reactions. We did not set out to optimise reaction conditions, which themselves can cause significant changes in catalytic activity, but instead focussed on any differences between pre-catalysts that might arise. The Mizoroki-Heck coupling of iodobenzene and butyl acrylate in DMF, using K_2CO_3 as the base, was studied at low pre-catalyst loadings of 5×10^{-5} and 1×10^{-4} mol % (Table 5). The results suggested that the two non-cyclophane pre-catalysts **4a** and *cis*-**4b** (*syn*) are the most active under these conditions, with 5×10^{-5} mol % **4a** catalyzing the formation of butyl cinnamate in a 92% yield, corresponding to a turnover frequency (TOF) in excess of 75,000 h^{-1} (Table 5, entry 5). Complex **5**, the non-butoxy functionalised analogue of **3a** and **3b** promoted the formation

of butylcinnamate in a 92% yield at 1 x 10^{-4} mol % pre-catalyst but was significantly less active at a loading of 5 x 10^{-5} mol%. All pre-catalysts resulted in the formation of butyl cinnamate, with yields significantly higher than achieved using $Pd(OAc)_2$. When the less reactive bromobenzene was employed as a substrate, with 1 mol % pre-catalyst loading, the yields of butyl cinnamate were greatly reduced, but were still higher than those achieved using **5** or $Pd(OAc)_2$. Complexes **3b** and **4a** facilitated the highest yields, 48 and 42% respectively (Table 5, entries 14 and 15), suggesting that they are approximately twice as active as **3a** and *cis*-**4b** (*syn*) under these reaction conditions. The activity of the complexes towards aryl chlorides was tested using 4-chlorobenzaldehyde, NaOAc as the base and tetrabutylammonium bromide (TBAB) in DMA at 165 °C (Table 6), following the protocol developed by Crabtree and co-workers.[28] The two non-cyclophane palladium complexes **4a** and *cis*-**4b** (*syn*) were the most active under these conditions, catalyzing the formation of butyl *p*-formylcinnamate in yields of 18 and 14% yield (Table 6, entries 3 and 4). There was no reaction observed using $Pd(OAc)_2$ under these conditions, while complex **5** led to butyl *p*-formylcinnamate in 9% yield.

The four pre-catalysts were also tested against **5** and $Pd(OAc)_2$ in the Suzuki-Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid, using K_2CO_3 in DMF at pre-catalyst loadings of 0.002 and 0.02 mol % (Table 7). There is very little difference in the activities of the pre-catalysts **3a**, **4a** and *cis*-**4b** (*syn*), with all complexes promoting the formation of 4-methylbiphenyl in 57-62% at loadings of 0.02 mol % pre-catalyst (Entries 2, 6 and 8). However, complex **3b**, the cyclophane complex with the butoxy groups in the 4,7 positions, was significantly less active under the reaction conditions employed. The diminished activity of **3b** compared to the other pre-catalysts may be attributed to the strained nature of the complex, which may result in catalyst decomposition. Complex **5** at 0.02 mol% promoted the formation of 4-methylbiphenyl in a 47% yield, but only gave trace amounts of product at a loading of 0.002 mol% pre-catalyst. Tests were also performed using 4-bromoanisole (typically considered to be a deactivated substrate for Suzuki-Miyaura couplings) as the aryl halide. In this case, complexes **3a**, **4a** and *cis*-**4b** (*syn*) again exhibit similar activities, promoting the formation of 4-methoxybiphenyl in a 52-57% yield with 0.02 mol % pre-catalyst loading (Entries

12, 16 and 18). Complex **3b** at 0.02 mol % was again less active than **3a**, **4a** and *cis*-**4b** (*syn*), promoting the formation of 4-bromoanisole in only 42% yield, although it was slightly more active than **4a** at a loading of 0.002 mol %. Complex **5** at 0.002 and 0.02 mol% catalysed the formation of 4-methoxybiphenyl in a 28 and 30% yield respectively. Although complexes **3a**, **4a** and *cis*-**4b** (*syn*) show relatively high activity under the conditions employed, all attempts using 4-chlorotoluene or 4-chlorobenzaldehyde as substrates with 1 mol % pre-catalyst did not lead to any product being formed.

Conclusion

We have synthesized two benzimidazolium salts that serve as ligand precursors for a series of five cyclophane and non-cyclophane palladium NHC complexes. The ligands were functionalised with butoxy groups, which may serve to increase electron density around the palladium centre and also to solubilize the complexes in common organic solvents. The position of the butoxy groups on the arene ring had a significant impact on the structural properties of the complexes. Apparently as a consequence of the steric bulk associated with the butoxy groups in the 4,7-positions in *cis*-**4b**, the *o*-xylyl linker in this complex can occupy a position under the metal centre or under the NHC units, resulting in an equilibrium between *syn* and *anti* conformations in solution. Another consequence of the steric bulk associated with butoxy groups in the 4,7-positions in the bis(benzimidazolium) structures is the formation of an NHC complex with a *trans*-spanning bis(NHC) ligand, *trans*-**4b**, a rare example of an *o*-xylyl linked bis(NHC) coordinated mutually *trans* about the palladium centre. The complexes **3a**, **4a** and *cis*-**4b** (*syn*) all demonstrate excellent activity in the Mizoroki-Heck coupling of aryl iodides, moderate activity with aryl bromides, and even some modest activity with aryl chlorides. They show moderate activity in the Suzuki-Miyaura coupling of inactivated aryl bromides at low catalyst loadings, but are inactive towards aryl chloride substrates. The 4,7-dibutoxy cyclophane complex **3b** exhibited the lowest activity of the four complexes tested, presumably due to relatively poor stability associated with internal steric strain that cannot be relieved by "splaying apart" of the NHC groups. The butoxy functionalised complexes were generally more active than the non-

butoxy analogue **5** in the Mizoroki-Heck and Suzuki-Miyaura coupling reactions, further emphasizing the beneficial nature of an electron-rich metal centre during the catalytic cycle.

Experimental

General comments

All reactions were performed under atmospheres of nitrogen using standard Schlenk techniques, unless otherwise stated. Workups were carried out in air. All solvents were re-distilled (under the laboratory atmosphere) prior to use, and, if used in the preparation of air-sensitive compounds, were deoxygenated by three freeze-pump-thaw cycles. Anhydrous solvents were obtained by distillation from the appropriate drying agent.[29] Chromatographic separations were performed using BDH silica gel (40-63 μm) with the eluants indicated. Nuclear magnetic resonance spectra were recorded at room temperature using Bruker ARX600, ARX500 or ARX300 spectrometers. ^{1}H and ^{13}C NMR chemical shifts were referenced to solvent resonances. Coupling reactions were analysed using a HP 5890 Series II gas chromatograph. Yields were estimated using pre-determined response factors of pure samples of the desired products relative to an internal standard. Microanalyses were performed by the Microanalytical Laboratory at the Research School of Chemistry, Australian National University, Canberra. 1-Methyl-5,6-dibutoxybenzimidazole, 1-methyl-4,7-dibutoxybenzimidazole, 1,2-bis(5',6'-dibutoxybenzimidazol-1'-ylmethyl)benzene, 1,2-bis(4',7'-dibutoxybenzimidazol-1'-ylmethyl)benzene, the 5,6-dibutoxy cyclophane salt **1a** and the 4,7-dibutoxy cyclophane salt **1b** were synthesized according to literature methods.[23,26]

Preparation of benzimidazolium salts

The 5,6-dibutoxybenzimidazolium salt 2a. A solution of 1-methyl-5,6-dibutoxybenzimidazole (1.14 g, 4.13 mmol) and α,α'-dibromo-*o*-xylene (0.51 g, 1.93 mmol) in THF (40 mL) was stirred at room

temperature for 1 h then heated at reflux for 20 h. The resulting precipitate was filtered off, washed three times with hexanes and air-dried to give **2a** (1.17 g, 75%) as a white solid (Found: C, 55.82; H, 6.51; N, 6.18. $C_{40}H_{56}N_4O_4Br_2 \cdot (2.25H_2O)$ requires 56.04; H, 7.11; N, 6.54%); δ_H(500.13 MHz, DMSO-d_6): 8.95 (s, 2H, NC*H*N), 7.65 (m, 2H, xylyl Ar C*H*), 7.60 (m, 2H, xylyl Ar C*H*), 7.45 (s, 2H, benzim Ar C*H*), 7.40 (s, 2H, benzim Ar C*H*), 5.85 (s, 4H, benzylic CH_2), 4.10 (t, 4H, $^3J_{HH}$ = 6.5 Hz, OCH_2), 3.95 (t, 4H, $^3J_{HH}$ = 6.5 Hz, OCH_2), 3.85 (s, 6H, NCH_3), 1.75-1.85 (m, 8H, $CH_2CH_2CH_2$), 1.45-1.55 (m, 8H, $CH_2CH_2CH_3$), 0.95-1.05 (t, 12H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3); δ_C(75.47 MHz, DMSO-d_6): 149.0, 149.3 (Ar *C*O), 139.0 (N*C*HN), 132.3 (xylyl Ar *C*), 130.3, 131.5 (xylyl Ar *C*H), 124.5, 125.2 (benzim Ar *C*), 95.9, 96.0 (benzim Ar *C*H), 68.8, 68.9 (OCH_2), 47.6 (benzylic CH_2), 33.2 (NCH_3), 30.6, 30.7 ($CH_2CH_2CH_3$), 18.7, 18.8 (CH_2CH_3), 13.8 (CH_2CH_3).

The 4,7-dibutoxybenzimidazolium salt 2b. This compound was synthesized as described for **2a** from 1-methyl-4,7-dibutoxybenzimidazole (0.50 g, 1.81 mmol), and was obtained as a white solid (0.66 g, 92%). (Found: C, 57.03; H, 6.88; N, 6.65. $C_{40}H_{56}N_4O_4Br_2 \cdot (1.2H_2O)$ requires 57.31; H, 7.02; N, 6.68%); δ_H(500.13 MHz, DMSO-d_6): 9.25 (s, 2H, NC*H*N), 7.60 (m, 2H, xylyl Ar C*H*), 7.45 (m, 2H, xylyl Ar C*H*), 7.10 (d, 2H, $^3J_{HH}$ = 8.9 Hz, benzim Ar C*H*), 7.10 (d, 2H, $^3J_{HH}$ = 8.9 Hz, benzim Ar C*H*), 5.90 (s, 4H, benzylic CH_2), 4.15 (t, 4H, $^3J_{HH}$ = 6.5 Hz, OCH_2), 4.10 (s, 6H, NCH_3), 4.00 (t, 4H, $^3J_{HH}$ = 6.5 Hz, OCH_2) 1.80-1.90 (m, 8H, $CH_2CH_2CH_2$), 1.50-1.60 (m, 8H, $CH_2CH_2CH_3$, $CH_2CH_2CH_2$), 1.20-1.30 (m, 4H, $CH_2CH_2CH_3$), 0.95-1.05 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3), 0.80-0.90 (t, 6H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3); δ_C(75.47 MHz, DMSO-d_6): 142.5 (N*C*HN), 141.3, 142.5 (Ar *C*O), 132.6 (xylyl Ar *C*), 129.9, 130.2 (xylyl Ar *C*H), 122.2, 122.9 (benzim Ar *C*), 108.7, 108.9 (benzim Ar *C*H), 68.9, 69.0 (OCH_2), 49.6 (benzylic CH_2), 33.2 (NCH_3), 30.6, 30.7 ($CH_2CH_2CH_3$), 18.6, 18.9 (CH_2CH_3), 13.7 (CH_2CH_3). Crystals suitable for the X-ray study were obtained by diffusion of EtOAc into an CH_3CN solution of the salt.

Preparation of palladium complexes

Palladium complex 3a. Palladium(II) acetate (123 mg, 0.55 mmol) was added to a suspension of **1a** (0.49 g, 0.55 mmol) in degassed CH_3CN (90 mL) and the mixture heated at reflux for 2 d. The resulting precipitate was filtered off, washed three times with cold CH_3CN and air-dried to give **3a** (390 mg, 72%) as a white powder (Found: C, 55.26; H, 5.44; N, 5.48. $C_{46}H_{56}N_4O_4Br_2Pd$ requires C, 55.52; H, 5.67; N, 5.63%); δ_H(500.13 MHz, DMSO-d_6): 8.15 (m, 4H, xylyl Ar C*H*), 7.70 (s, 4H, benzim Ar C*H*), 7.45 (m, 4H, xylyl Ar C*H*), 6.95 (d, 4H, $^2J_{HH}$ = 14.7 Hz, benzylic CH*H*), 5.70 (d, 4H, $^2J_{HH}$ = 14.7 Hz, benzylic C*H*H), 4.05-4.20 (m, 8H, OCH_2), 1.70-1.80 (m, 8H, $CH_2CH_2CH_2$), 1.45-1.65 (m, 8H, $CH_2CH_2CH_3$), 0.95 (t, 12H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3); δ_C(125.76 MHz, DMSO-d_6): 171.0 (N*C*HN), 146.4 (Ar *C*O), 134.8 (xylyl Ar *C*), 129.1, 133.9 (xylyl Ar *C*H), 127.3 (benzim Ar *C*), 98.2 (benzim Ar *C*H), 69.0 (O*C*H_2), 49.8 (benzylic *C*H_2), 30.4 ($CH_2CH_2CH_2$), 18.7 ($CH_2CH_2CH_3$), 13.6 (CH_2CH_3).

Palladium complex 3b. This complex was synthesized as described for **3a** from **1b** (0.40 g, 0.45 mmol), and was obtained as a white solid (160 mg, 51%). (Found C, 55.30; H, 5.69; N, 5.45. $C_{46}H_{56}N_4O_4Br_2Pd$ requires 55.52; H, 5.67; N, 5.63%); δ_H(300.13 MHz, DMSO-d_6): 8.00 (m, 4H, xylyl Ar C*H*), 7.20 (m, 4H, xylyl Ar C*H*), 7.10 (s, 4H, benzim Ar C*H*), 6.90 (d, 4H, $^2J_{HH}$ = 14.2 Hz, benzylic CH*H*), 6.00 (d, 4H, $^2J_{HH}$ = 14.7 Hz, benzylic C*H*H), 4.20-4.45 (m, 8H, OCH_2), 1.85-2.00 (m, 8H, $CH_2CH_2CH_2$), 1.45-1.65 (m, 8H, $CH_2CH_2CH_3$), 1.00 (t, 12H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3); δ_C(75.47 MHz, CD_2Cl_2): 175.7 (N*C*HN), 140.1 (Ar *C*O), 135.8 (xylyl Ar *C*), 129.2, 132.4 (xylyl Ar *C*H), 125.6 (benzim Ar *C*), 106.5 (benzim Ar *C*H), 69.5 (O*C*H_2), 50.1 (benzylic *C*H_2), 31.6 ($CH_2CH_2CH_2$), 19.9 ($CH_2CH_2CH_3$), 14.0 (CH_2CH_3). Crystals suitable for the X-ray study were obtained by diffusion of benzene into an CH_3CN solution of the complex.

Palladium complex 4a. Palladium(II) acetate (67 mg, 0.30 mmol) was added to a degassed solution of **2a** (0.26 g, 0.31 mmol) in DMF (15 mL) and the mixture was stirred at room temperature for 2 h, then

heated at 90 °C for 3 d. The solvent was removed *in vacuo* and the residue recrystallised from CH_2Cl_2/hexanes to give **4a** (150 mg, 55%) as a white powder (Found C, 51.03; H, 5.73; N, 5.66. $C_{40}H_{54}N_4O_4Br_2Pd\cdot(0.3CH_2Cl_2)$ requires C, 51.13; H, 5.81; N, 5.92%); δ_H(300.13 MHz, DMSO-d_6): 8.15 (m, 2H, xylyl Ar C*H*), 7.80 (s, 2H, benzim Ar C*H*), 7.45 (m, 2H, xylyl Ar C*H*), 7.30 (s, 2H, benzim Ar C*H*), 6.90 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic CH*H*), 5.70 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic C*H*H), 4.25 (s, 6H, NCH_3), 3.95-4.20 (m, 8H, OCH_2), 1.65-1.85 (m, 8H, $CH_2CH_2CH_2$), 1.40-1.60 (m, 8H, $CH_2CH_2CH_3$), 0.95 (m, 12H, CH_2CH_3). δ_C(75.47 MHz, DMSO-d_6): 170.2 (N*C*HN), 146.1, 146.8 (Ar *C*O), 135.1 (xylyl Ar *C*), 129.0, 133.5 (xylyl Ar *C*H), 127.0 (benzim Ar *C*), 96.7, 98.3 (benzim Ar *C*H), 68.9, 69.2 (O*C*H_2), 49.3 (benzylic *C*H_2), 35.6 (N*C*H_3), 30.7 ($CH_2CH_2CH_2$), 18.9 ($CH_2CH_2CH_3$), 13.7 (CH_2CH_3). Crystals suitable for the X-ray study were obtained by the slow evaporation of a DMSO solution of the complex.

Palladium complexes *cis*-4b and *trans*-4b. Palladium(II) acetate (74 mg, 0.33 mmol) was added to a suspension of **2b** (0.25 g, 0.31 mmol) in THF (15 mL) and the mixture was heated at reflux for 5 d. The resulting precipitate was filtered off, washed three times with hexanes and air dried to give *cis*-**4b** (*syn*) (120 mg, 43%) as a white solid (Found C, 51.88; H, 5.91; N, 5.91. $C_{40}H_{54}N_4O_4Br_2Pd$ requires C, 52.16; H, 5.91; N, 6.08%); δ_H(500.13 MHz, $CDCl_3$): 7.65 (m, 2H, xylyl Ar C*H*), 7.55 (m, 2H, xylyl Ar C*H*), 6.57 (d, 2H, $^3J_{HH}$ = 8.8 Hz, benzim Ar C*H*), 6.54 (d, 2H, $^3J_{HH}$ = 8.8 Hz, benzim Ar C*H*), 5.95 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic CH*H*), 5.60 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic C*H*H), 4.50 (s, 6H, NCH_3), 4.06 (m, 4H, OCH_2), 3.96 (m, 4H, OCH_2), 1.75-1.85 (m, 8H, $CH_2CH_2CH_2$), 1.44-1.54 (m, 8H, $CH_2CH_2CH_3$), 0.96 (t, 12H, $^3J_{HH}$ = 7.4 Hz, CH_2CH_3); δ_C(75.47 MHz, $CDCl_3$): 171.7 (N*C*HN), 140.4, 140.6 (Ar *C*O), 135.1 (xylyl Ar *C*), 130.2, 133.7 (xylyl Ar *C*H), 126.2, 126.4 (benzim Ar *C*), 105.6, 105.8 (benzim Ar *C*H), 68.9, 69.1 (O*C*H_2), 51.7 (benzylic *C*H_2), 40.6 (N*C*H_3), 31.3 ($CH_2CH_2CH_2$), 19.5 ($CH_2CH_2CH_3$), 13.9 (CH_2CH_3). Attempted recrystallisation of *cis*-**4b** (*syn*) by diffusion of benzene into a $CHCl_3$ solution of the complex or by slow evaporation of a DMSO/$CHCl_3$ solution of

the complex gave two different solvate forms of crystals of *cis*-**4b** (*anti*) which were suitable for X-ray studies.

The initial reaction filtrate (*i.e.*, the THF solution from above) was subjected to rapid silica-gel filtration (eluting with CH_2Cl_2) to give *trans*-**4b** (20 mg, 7%) as a yellow solid (Found C, 49.03; H, 6.11; N, 5.33. $C_{40}H_{54}N_4O_4Br_2Pd{\cdot}CH_2Cl_2$ requires C, 48.95; H, 5.61; N, 5.57%); δ_H(500.13 MHz, $CDCl_3$): 7.34 (m, 2H, xylyl Ar C*H*), 7.15 (m, 2H, xylyl Ar C*H*), 6.80 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic CH*H*), 6.64 (d, 2H, $^3J_{HH}$ = 8.6 Hz, benzim Ar C*H*), 6.54 (d, 2H, $^3J_{HH}$ = 8.6 Hz, benzim Ar C*H*), 6.44 (d, 2H, $^2J_{HH}$ = 14.7 Hz, benzylic C*H*H), 4.25 (s, 6H, NCH_3), 4.15 (m, 4H, OCH_2), 4.00 (m, 4H, OCH_2), 1.75-1.91 (m, 8H, $CH_2CH_2CH_2$), 1.45-1.55 (m, 8H, $CH_2CH_2CH_3$), 0.98 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3), 0.97 (t, 6H, $^3J_{HH}$ = 7.1 Hz, CH_2CH_3); δ_C(75.47 MHz, $CDCl_3$): 182.0 (N*C*HN), 141.2, 140.0 (Ar *C*O), 137.5 (xylyl Ar *C*), 130.8, 128.4 (xylyl Ar *C*H), 127.1, 126.1 (benzim Ar *C*), 105.2, 104.6 (benzim Ar *C*H), 68.7 (O*C*H_2), 48.6 (benzylic *C*H_2), 38.4 (N*C*H_3), 31.4 ($CH_2CH_2CH_2$), 19.5 ($CH_2CH_2CH_3$), 13.9 (CH_2CH_3). Crystals of *trans*-**4b** suitable for the X-ray study were obtained by diffusion of hexanes into a $CHCl_3$ solution of the complex.

Catalysis studies

Stock solutions of $Pd(OAc)_2$, **3a**, **3b**, **4a** and *cis*-**4b** (*syn*) in degassed DMF were prepared at concentrations of 0.025 mM, 0.5 mM and 5 mM. Stock solutions of **5** were prepared at 0.002 mM, 0.04 mM and 0.4 mM due to the extremely low solubility of the complex. The $Pd(OAc)_2$ solutions were used within 20 h (aged solutions deposited colloidal material and exhibited noticeably higher catalytic activities than fresh solutions), while solutions of the NHC complexes (which showed no apparent changes on storage) were used within one month.

General procedure for the Mizoroki-Heck reaction of iodo- and bromo-benzene

A flask equipped with a magnetic stirrer bar was charged with iodobenzene (112 μL, 1 mmol), butyl acrylate (172 μL, 1.2 mmol), K_2CO_3 (207 mg, 1.5 mmol) and di(ethylene glycol) dibutyl ether (200 μL, 0.81 mmol). The flask was evacuated and backfilled with nitrogen three times. DMF (0.5 mL) and the required amount of the appropriate complex (5×10^{-5} mol %, 20 μL from 0.25 mM solution) were added and the solution was heated at 120 °C for 24 h. After cooling, the reaction mixture was diluted with $CHCl_3$ (9 mL), washed with water (3 mL) and dried over $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was diluted with EtOAc (1.5 mL) and analysed by GC.

General procedure for the Mizoroki-Heck reaction of 4-chlorobenzaldehyde

A flask equipped with a magnetic stirrer bar was charged with 4-chlorobenzaldehyde (141 mg, 1 mmol), butyl acrylate (172 μL, 1.2 mmol), NaOAc (123 mg, 1.5 mmol), tetrabutylammonium bromide (64 mg, 0.2 mmol) and di(ethylene glycol) dibutyl ether (200 μL, 0.81 mmol). The flask was evacuated and backfilled with nitrogen three times. DMA (0.5 mL) and the required amount of the appropriate complex (1 mol %) were added and the solution was heated at 165 °C for 24 h. After cooling, the reaction mixture was diluted with $CHCl_3$ (9 mL), washed with water (3 mL) and dried over $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was diluted with EtOAc (1.5 mL) and analysed by GC.

General procedure for the Suzuki-Miyaura reaction

A flask equipped with a magnetic stirrer bar was charged with *p*-bromotoluene (171 mg, 1 mmol), phenylboronic acid (134 mg, 1.1 mmol), K_2CO_3 (166 mg, 1.2 mmol) and 1-methylnaphthalene (150 μL, 1.056 mmol). The flask was evacuated and backfilled with nitrogen three times. DMF (0.5 mL) and the required amount of the appropriate complex (0.002 mol %, 40 μL from 0.5 mM solution) were added and the solution was heated at 80 °C for 24 h. After cooling, the reaction mixture was diluted with $CHCl_3$ (9 mL), washed with water (3 mL) and dried over $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was diluted with EtOAc (1.5 mL) and analysed by GC.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured [monochromatic Mo Kα (λ = 0.7107_3 Å) or Cu Kα (λ = 1.5418_4 Å) radiation (the two solvates of *cis*-**4b**), ω-scans; recorded at *T ca.* 100 K except where noted below], yielding $N_{t(otal)}$ reflections, these merging to N independent (R_{int} cited) after 'empirical'/multiscan absorption correction (proprietary software); N_o with $F > 4\sigma(F)$ were considered 'observed'. All independent reflections were used in the full matrix least squares refinement on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Reflection weights were $(\sigma^2(F_o^2) + (aP)^2 (+ bP))^{-1}$ ($P = (F_o^2 + 2F_c^2)/3$). Neutral atom complex scattering factors were employed within the SHELXL-97 program.[30] Pertinent results are presented above and in the Tables and Figures, the latter showing 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

Variata

[All samples were 'difficult', by virtue of ready loss of solvent, disorder, etc.] **2b·H_2O:** Difference map residues were modelled as water molecule oxygen atoms, no associated hydrogen atoms being located. **3b·CH_3CN·2½C_6H_6:** One of the *n*-butyl strings was modelled as disordered over sets of sites with occupancies set at 0.5 and idealized geometries. **4a:** One of the substituent *n*-butyl chains was modelled as disordered over two sets of sites, occupancies 0.5, carbon atom displacement parameter forms isotropic. ***cis*-4b (*anti*)·2½C_6H_6:** The terminal CH_2CH_3 components of each of the *n*-butyl chains was modelled as disordered over two sets of sites, site occupancy factors 0.5, carbon atom displacement parameter forms isotropic and idealized geometries. After modelling of the solvent residues in terms of C_6H_6 (one molecule partially included, one disposed about an inversion centre), further residues insusceptible of meaningful modelling were suppressed with the program SQUEEZE.[31] *T* was 200 K. ***cis*-4b**

(*anti*)·2DMSO·$CHCl_3$: The substrate molecule was modelled as disordered about a *pseudo*-2-axis through the palladium atom, bisecting the C_2PdBr_2 array; the bridging xylyl ring components were assigned occupancies of 0.5, and the methyl and methylene components were also modelled as disordered. Residual electron density in these regions was modelled in terms of a pair of DMSO solvent components, all components of disorder being refined with isotropic displacement parameter forms and idealized geometries. Other solvent components were modelled in terms of the chloroform and DMSO (disordered sulfur). ***trans*-4b·0.84$CHCl_3$:** One of the *n*-butyl substituent 'tails' was modelled as disordered over a pair of sites, occupancies set at 0.5 after trial refinement (isotropic displacement parameter forms). The site occupancy of the chloroform molecule of solvation refined to 0.843(15); its location in tunnels through the structure, loosely hydrogen-bonded to Br(1) of the substrate molecule (Br(1)···H(01) 2.7_5 Å) and with high displacement parameters, suggest some loss of solvent from full unit occupancy, perhaps consequent on a need to acquire data at room-temperature in this case, the crystals degrading at lower temperatures.

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Tables

Table 1 Hydrogen interactions, **2b**·H_2O (Br···H < 3 Å)

Atoms	Distance (Å)	Atoms	Distance (Å)
O(1)···H(33^{i})	2.3_3	O(2)···H(73^{ii})	2.3_9
Br(1)	3.419(2)	Br(3)	3.404(2)
Br(2)	3.275(2)	Br(4)	3.255(2)
Br(1)···H(22)	2.5_8	Br(3)···H(62^{iii})	2.5_2
H(42)	2.8_5	H(82^{iii})	2.8_4
H(4A)	2.8_4	H(8A^{iii})	2.7_5
Br(2)···H(3A)	2.7_5	Br(4)···H(7A^{iii})`	2.8_0
H(46^{iii})	2.8_9	H(86^{iv})	2.8_2
H(47A^{iii})	2.8_7	H(87B^{iv})`	2.9_2
		H(87G^{iv})	2.9_9
H(1C^{i})	2.9_7		
H(65^{ii})	2.9_4	H(25^{i})	2.6_6
H(66^{ii})	3.0_2		

Coordinate transformations: i *x*, ½–*y*, *z*–½ ii 1–*x*, *y*–½, 1½–*z*

iii 1–*x*, 1–*y*, 1–*z* iv *x*–1, *y*–1, *z*

Table 2 Molecular core geometry, (*trans*-**4b**)

Atoms	Parameter
Distances/Å	
Pd-Br(1)	2.4472(12)
Pd-Br(2)	2.4306(12)
Pd-C(22)	1.988(8)
Pd-C(42)	2.003(8)
Angles/º	
Br(1)-Pd-Br(2)	173.81(5)
C(22)-Pd-C(42)	163.4(3)
Br(1)-Pd-C(22)	91.3(2)
Br(1)-Pd-C(42)	91.8(2)
Br(2)-Pd-C(22)	89.2(2)
Br(2)-Pd-C(42)	89.5(2)

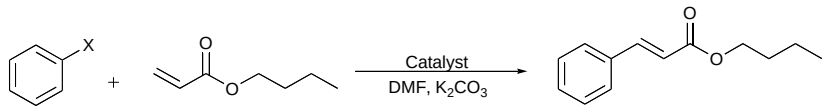
Table 3 Molecular core geometries, **3b**, **4a**, *cis*-**4b** (*anti*)

Complex/mol.	**3b**/1;2	**4a**	*cis*-**4b** (C_6H_6)	*cis*-**4b** (DMSO)
Distances/Å				
Pd-Br(1)	2.478(2); 2.470(1)	2.484(1)	2.4719(8)	2.4719(3)
Pd-Br(2)	2.478(2); 2.475(2)	2.477(1)	2.4712(8)	2.4664(3)
Pd-C(22)	1.969(12); 1.983(9)	1.967(9)	2.010(6)	2.003(3)
Pd-C(42)	1.950(11); 1.982(10)	1.941(10)	2.054(6)	1.994(2)
H(Xy)···O(Bu)	2.4_0; 2.3_6	-	2.2_5	2.4_1
	2.5_6; 2.4_4	-	2.3_8	2.3_7
Angles/º				
Br(1)-Pd-Br(2)	94.04(5); 93.85(5)	95.95(5)	92.60(3)	93.522(12)
Br(1)-Pd-C(22)	86.5(3); 84.1(3)	88.4(3)	86.09(16)	84.21(6)
Br(1)-Pd-C(42)	177.1(3); 179.3(3)	172.9 (3)	178.24(18)	179.20(7)
Br(2)-Pd-C(22)	177.6(3); 177.6(3)	175.6(3)	178.55(17)	177.16(6)
Br(2)-Pd-C(42)	83.4(3); 86.5(3)	90.1(3)	86.16(16)	85.69(8)
C(22)-Pd-C(42)	96.0(4); 95.6(4)	85.7(4)	95.1(2)	96.57(10)
Interplanar dihedral angles (º) and palladium atom deviations (δPd Å)				
C_7N_2/C_7N_2	54.8(2); 54.1(2)	77.4(2)	63.2 (1)	57.00(5)
C_7N_2/C_2Br_2	87.3(3); 86.7(3)	81.0(2)	88.7(2)	86.73(6)
	82.6(3); 86.1(2)	82.6(2)	87.4(1)	88.29(6)
C_6/C_2Br_2	21.1(3); 19.3(3)	46.5(3)	16.0(2)	5.6(1)
	8.7(3); 15.0(3)	-	-	15.4(1)
δPd/(C_7N_2)	0.537(10); 0.667(10)	0.016(10)	0.401(6)	0.609(3)
	0.604(10); 0.516(10)	0.291(10)	0.387(5)	0.373(3)

Table 4 Crystal/refinement data

Complex	**2b**·H_2O	**3b**·CH_3CN·2½C_6H_6	**4a**	*cis*-**4b**·2½C_6H_6	*cis*-**4b**·2DMSO·$CHCl_3$	*trans*-**4b**·0.84$CHCl_3$
Formula	$C_{40}H_{58}Br_2N_4O_5$	$C_{63}H_{74}Br_2N_5O_4Pd$	$C_{40}H_{54}Br_2N_4O_4Pd$	$C_{55}H_{69}Br_2N_4O_4Pd$	$C_{45}H_{67}Br_2Cl_3N_4O_6PdS_2$	$C_{40.84}H_{54.84}Br_2Cl_{2.53}N_4O_4Pd$
M_r/Da	834.7	1231.5	921.1	1116.4	1196.7	1021.7
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (# 14)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)	$C2/c$ (# 15)	$P\bar{1}$ (# 2)	$P2/c$ (# 13)
a/Å	30.686(3)	17.652(5)	17.3106(9)	27.2399(9)	12.1456(7)	20.4781(5)
b/Å	15.0391(6)	18.280(5)	19.9122(8)	20.8844(4)	14.5636(6)	9.9160(2)
c/Å	18.3270(10)	18.705(5)	12.1672(7)	20.5822(4)	16.8254(10)	25.6217(7)
α/°		82.53(2)			68.016(4)	
β/°	102.091(7)	80.84(2)	107.964(6)	90.149(2)	86.629(8)	113.190(3)
γ/°		73.94(2)			72.488(4)	
V/Å^3	8270(1)	5703(3)	3989.5(3)	11708.9(5)	2627.0(2)	4782.4(2)
D_c/g cm^{-3}	1.34_1	1.43_4	1.53_4	1.26_7	1.51_3	1.41_9
Z	8	4	4	8	2	4
μ_{Mo}/mm^{-1}	2.0	1.78	2.5	4.5 (μ_{Cu})	7.2 (μ_{Cu})	2.2
specimen/mm^3	0.21,0.17,0.10	0.43,0.08,0.07	0.10,0.095,0.03	0.15,0.07,0.05	0.26,0.05,0.02	0.30,0.095,0.085
'T'$_{min/max}$	0.77	0.67	0.86	0.83	0.51	0.89
2θ$_{max}$/°	65	64	50	135	135	56
N_t	99530	152638	33059	67877	32223	44053
N (R_{int})	28124 (0.070)	35791 (0.11)	7017 (0.14)	10449 (0.11)	9288 (0.062)	10634 (0.051)
N_o	12625	16905	3209	3743	6622	5718
$R1$	0.063	0.12	0.077	0.073	0.063	0.069
$wR2$ (a(,b))	0.24 (0.12)	0.38(0.20,62)	0.15 (0.043)	0.21 (0.103)	0.19 (0.124,0.32)	0.22 (0.071,21)
S	1.00	1.02	1.00	0.89	1.03	1.13

Table 5 The Mizoroki-Heck reaction catalyzed by palladium complexes and $Pd(OAc)_2$[a]



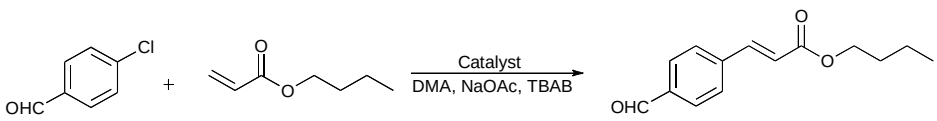
X = I, Br

Entry	Catalyst	Mol % cat	Aryl halide	t (h)	T (°C)	Yield (%)[b]	TON	TOF
1	**3a**	0.00005	Iodobenzene	24	120	48	960,000	40,000
2	**3a**	0.0001	Iodobenzene	24	120	73	730,000	30,000
3	**3b**	0.00005	Iodobenzene	24	120	72	1,400,000	58,000
4	**3b**	0.0001	Iodobenzene	24	120	78	780,000	32,000
5	**4a**	0.00005	Iodobenzene	24	120	92	1,800,000	75,000
6	**4a**	0.0001	Iodobenzene	24	120	99	990,000	41,000
7	*cis*-**4b** (*syn*)	0.00005	Iodobenzene	24	120	74	1,500,000	62,000
8	*cis*-**4b** (*syn*)	0.0001	Iodobenzene	24	120	87	870,000	36,000
9	**5**	0.00005	Iodobenzene	24	120	49	980,000	41,000
10	**5**	0.0001	Iodobenzene	24	120	92	920,000	38,000
11	$Pd(OAc)_2$	0.00005	Iodobenzene	24	120	19	380,000	16,000
12	$Pd(OAc)_2$	0.0001	Iodobenzene	24	120	26	260,000	11,000
13	**3a**	1	Bromobenzene	24	120	22	22	1
14	**3b**	1	Bromobenzene	24	120	48	48	2
15	**4a**	1	Bromobenzene	24	120	42	42	2
16	*cis*-**4b** (*syn*)	1	Bromobenzene	24	120	21	21	1
17	**5**	1	Bromobenzene	24	120	13	13	0.5
18	$Pd(OAc)_2$	1	Bromobenzene	24	120	3	3	0.1

[a] 1 mmol aryl halide, 1.2 mmol butyl acrylate, 1.5 mmol K_2CO_3, 0.5 mL DMF.

[b] GC-yield determined using di(ethylene glycol) dibutyl ether as the internal standard.

Table 6 The Mizoroki-Heck reaction of 4-chlorobenzaldehyde catalyzed by palladium complexes and $Pd(OAc)_2$[a]

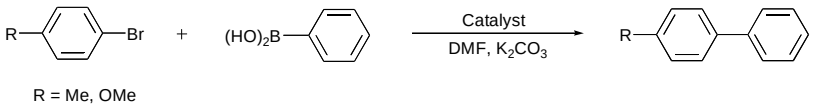


Entry	Catalyst	Mol % cat	Aryl halide	t (h)	T (°C)	Yield (%)[b]	TON	TOF
1	**3a**	1	4-chlorobenzaldehyde	24	165	10	10	0.4
2	**3b**	1	4-chlorobenzaldehyde	24	165	8	8	0.3
3	**4a**	1	4-chlorobenzaldehyde	24	165	18	18	0.7
4	*cis*-**4b** (*syn*)	1	4-chlorobenzaldehyde	24	165	14	14	0.6
5	**5**	1	4-chlorobenzaldehyde	24	165	9	9	0.4
6	$Pd(OAc)_2$	1	4-chlorobenzaldehyde	24	165	0	0	0

[a] 1 mmol 4-chlorobenzaldehyde, 1.2 mmol butyl acrylate, 1.5 mmol NaOAc, 0.2 mmol tetrabutylammonium bromide, 0.5 mL DMA.

[b] GC-yield determined using di(ethylene glycol) dibutyl ether as the internal standard.

Table 7 The Suzuki-Miyaura reaction catalyzed by palladium complexes and $Pd(OAc)_2$[a]



Entry	Catalyst	Mol % cat	Aryl halide	t (h)	T (°C)	Yield (%)[b]	TON	TOF
1	**3a**	0.002	4-Bromotoluene	24	80	52	26,000	1,100
2	**3a**	0.02	4-Bromotoluene	24	80	57	2,800	120
3	**3b**	0.002	4-Bromotoluene	24	80	19	9,500	400
4	**3b**	0.02	4-Bromotoluene	24	80	38	1,900	79
5	**4a**	0.002	4-Bromotoluene	24	80	43	21,000	870
6	**4a**	0.02	4-Bromotoluene	24	80	62	3,100	130
7	*cis*-**4b** (*syn*)	0.002	4-Bromotoluene	24	80	52	26,000	1,100
8	*cis*-**4b** (*syn*)	0.02	4-Bromotoluene	24	80	59	2,900	120
9	**5**	0.002	4-Bromotoluene	24	80	1	500	21
10	**5**	0.02	4-Bromotoluene	24	80	47	2,300	96
11	$Pd(OAc)_2$	0.002	4-Bromotoluene	24	80	3	1,500	62
12	$Pd(OAc)_2$	0.02	4-Bromotoluene	24	80	6	300	12
13	**3a**	0.002	4-Bromoanisole	24	80	41	20,000	830
14	**3a**	0.02	4-Bromoanisole	24	80	52	2,600	110
15	**3b**	0.002	4-Bromoanisole	24	80	24	12,000	500
16	**3b**	0.02	4-Bromoanisole	24	80	42	2,100	87
17	**4a**	0.002	4-Bromoanisole	24	80	19	9,500	400
18	**4a**	0.02	4-Bromoanisole	24	80	53	2,600	110
19	*cis*-**4b** (*syn*)	0.002	4-Bromoanisole	24	80	28	14,000	580
20	*cis*-**4b** (*syn*)	0.02	4-Bromoanisole	24	80	57	2,800	120
21	**5**	0.002	4-Bromoanisole	24	80	28	14,000	580
22	**5**	0.02	4-Bromoanisole	24	80	30	1,500	62

23	$Pd(OAc)_2$	0.002	4-Bromoanisole	24	80	0	0	0
24	$Pd(OAc)_2$	0.02	4-Bromoanisole	24	80	20	1,000	42

[a] 1 mmol aryl halide, 1.2 mmol phenylboronic acid, 1.2 mmol K_2CO_3, 0.5 mL DMF.

[b] GC-yield determined using 1-methylnaphthalene as the internal standard.

Figure Captions:

Fig. 1 ^{1}H NMR spectrum (500.13 MHz) of *cis*-**4b** (*syn*) in $CDCl_3$ over several days, showing the formation of *cis*-**4b** (*anti*). For clarity only the downfield region is shown. Note that the relative intensity of signals due to *cis*-**4b** (*syn*) has been kept constant by scaling the individual spectra, to highlight the early appearance of *cis*-**4b** (*anti*).

Fig. 2 Strong (solid lines) and weak (dashed lines) NOE enhancements seen in NOESY experiments for the two conformers of *cis*-**4b**.

Fig. 3 Comparison of the ^{1}H NMR spectra (500.13 MHz) of *cis*-**4b** (*anti*), *cis*-**4b** (*syn*) and *trans*-**4b** in $CDCl_3$ (× = impurities (solvents), ∗ = xylyl protons, ν = benzylic protons).

Fig. 4 (a) Unit cell contents of **2b**·H_2O, projected down *b*, showing the pseudo-symmetry and the arrangement of cation pairs into sheets parallel to (101).

(b) One of the cation/anion/solvent aggregates.

Fig. 5 (a) Projection of a molecule of *trans*-**4b**, showing its hydrogen-bonding interaction with solvent chloroform.

(b) Unit cell contents projected down *b*, showing the tunnels in the lattice in which the

chloroform molecules reside.

Fig. 6 Projection of a molecule of **4a**, showing the interaction of the benzimidazole hydrogen atoms with those of the bridging xylyl ring. An alternative projection is provided in the supporting information.

Fig. 7 Projection of molecule 1 of **3b**, showing the disposition of the bridging xylyl rings. An alternative projection is provided in the supporting information.

Fig. 8 Projection of a molecule of *cis*-**4b** (DMSO/$CHCl_3$ solvate (that of the C_6H_6 solvate is similar), showing the disposition of the bridging xylyl ring. An alternative projection is provided in the supporting information.