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ORIGINAL ARTICLE

Palladium complexes of *o*-xylylene-linked alkoxybenzimidazolin-2-ylidenes containing aryl *N*-substituents: examples of C–H activation and the formation of a tri-nuclear palladium complex

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Abstract Palladium complexes of new bidentate *N*-heterocyclic carbene (NHC) incorporating benzimidazolin-2-ylidene units have been synthesized and structurally and spectroscopically characterised. The NHC ligands are furnished with aryl substituents on the nitrogen atoms and electron-donating butoxy groups on the benzo-fused ring. The incorporation of these aryl substituents on the bis(NHC) ligands leads to interesting and unexpected conformations around the palladium atoms, and interesting reactivity, including cyclometallation and the formation of a tri-nuclear species. One of the complexes has been studied in an initial series of Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions but shows moderate to poor activity.

Keywords *N*-heterocyclic carbene · Palladium · C–H activation · Crystal structure · NMR · Catalysis

Dedicated to Jack Harrowfield and Jacques Vicens, two elders of supramolecular chemistry who have uncovered the world of the Lilliputian and continue to fascinate us with what they discover.

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Introduction

Initially employed in 1995 as catalysts by Herrmann and co-workers [1], *N*-heterocyclic carbene (NHC) metal complexes are now widely used to promote a range of organic transformations [2–8]. As homogeneous catalysts, NHC complexes based on imidazole are the most common, but similar systems based on benzimidazole are also emerging as highly active alternatives [9–14] Although the arene ring in the benzimidazole skeleton can be functionalised and thus provide a further site of modification, the incorporation of bulky aryl substituents on the nitrogen atoms usually involves palladium or copper catalysed C–N cross-coupling reactions, a less convenient method compared to imidazole-based systems. Functionalization of NHC ligands with bulky groups around the metal centre has been shown to aid the reductive elimination step of the catalytic cycle, while more electron-donating NHC ligands will facilitate oxidative addition. Palladium complexes bearing chelating NHC ligands are generally robust, and thus are often favoured as catalysts in reactions such as the Mizoroki–Heck reaction, which requires high temperatures to promote cross-coupling [9, 15–17].

Recently, Shi and co-workers reported the preparation of a series of bis(benzimidazolium) salts **1** (Scheme 1), via C–N coupling reactions. In this work, each benzimidazolyl unit was linked by one of its N atoms to a binaphthyl group, the other N atom possessing a substituted phenyl group [18]. These bis(benzimidazolium) salts were used to prepare a series of palladium complexes **2** (Scheme 1) in which the proximity of the phenyl group permitted cyclometallation by the palladium atom via C–H activation. The are few reports of chelating bis(NHC) ligands possessing aryl substituents on the nitrogen atoms, and there are no cases of palladium complexes of this type in which the bis(NHC) ligands are linked by an *o*-xylylene group.

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In this paper we report the synthesis and characterisation of a pair of butoxy-functionalised bis(benzimidazolium) salts that serve as precursors to three palladium NHC complexes. The bidentate NHCs consist of benzimidazolin-2-ylidene units that are linked by one *o*-xylylene group, and are furnished with phenyl and 2,4-dinitrophenyl *N*-substituents. These bis(NHC) ligands generally bind to the metal centre in a rigid fashion [19–22]. The butoxy groups serve to increase the solubility of the complexes, and also to increase the electron density at the palladium centre, which has been shown to enhance the activity of the catalysts relative to non-butoxy functionalised analogues in the Mizoroki–Heck and Suzuki–Miyaura reactions [15, 23]. The interesting, and somewhat unexpected nature of the palladium complexes was examined by single crystal X-ray diffraction studies. One of the palladium complexes has been studied in a preliminary series of Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions.

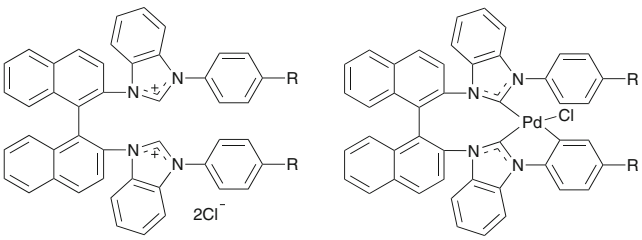
Results and discussion

Synthesis of complexes

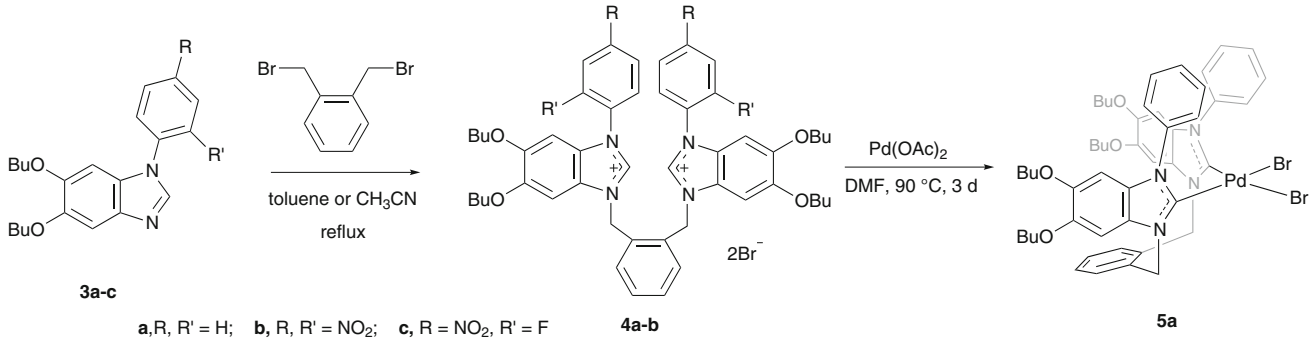
1-Phenyl-5,6-dibutoxybenzimidazole **3a** was synthesized via the copper(I)-catalysed Ullman cross-coupling reaction between 5,6-dibutoxybenzimidazole and iodobenzene in refluxing DMA, with Cs_2CO_3 as the base, following a modification of the procedure developed by You and co-workers for the preparation of functionalised azoles [24]. Compound **3a** was isolated as a waxy solid in an 87 % yield after column chromatography, although significantly lower yields were obtained when DMF was used as the reaction solvent at 150 °C, or if bromobenzene was employed as the aryl halide.

1-(2′,4′-Dinitrophenyl)-5,6-dibutoxybenzimidazole **3b** was prepared by the treatment of 5,6-dibutoxybenzimidazole with 2,4-dinitrofluorobenzene and K_2CO_3 in refluxing CH_3CN for three hours, and was isolated as an orange solid in a 92 % yield. It was found that the choice of base, solvent and reaction time greatly affected the outcome of the reaction. When the reaction was done stepwise, by deprotonation of 5,6-dibutoxybenzimidazole with NaH in THF followed by the addition of 2,4-dinitrofluorobenzene, the mixture immediately turned black, and **3b** was subsequently isolated in low yields (20 %) after heating the mixture at reflux overnight. When the reaction was repeated using K_2CO_3 in DMF for 2 days at 80 °C both **3b** and 1-(2′-fluoro-4′-nitrophenyl)-5,6-dibutoxybenzimidazole **3c** were isolated in yields of 35 and 11 % respectively, after column chromatography. Presumably the longer reaction time and increased temperature allowed nucleophilic displacement of the *o*-nitro group in **3b** by fluoride (which was initially displaced from the starting material 2,4-dinitrofluorobenzene by the benzimidazolide anion). Compound **3c** is bright yellow, and displays the expected C-F coupling in the ^{13}C NMR spectrum (e.g. $^{1}J_{C,F} = 257$ Hz).

The bis(benzimidazolium) salts **4a** and **4b** (Scheme 2) were synthesized by the reaction of **3a** or **3b** with α,α′-dibromo-o-xylene in refluxing toluene (**4a**) or CH_3CN (**4b**), and were isolated in yields of 87 and 85 % respectively. The salts **4a** and **4b** are slightly hygroscopic white solids and show good solubility in a range of common organic solvents (e.g. DMSO, CH_2Cl_2, $CHCl_3$ and MeOH).



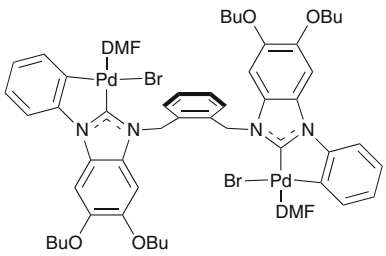
Scheme 1 Benzimidazolium salts **1** and Pd-NHC complexes **2**



Scheme 2 Synthesis of benzimidazolium salts and NHC complex **5a**

Palladium complex **5a** was synthesized by the treatment of **4a** with $Pd(OAc)_2$ in DMF at 90 °C for 3 days (Scheme 2), and was isolated in a 58 % yield as a white solid after recrystallisation from acetone. Complex **5a** is soluble in halogenated solvents but exhibit poor solubility in MeOH, DMF, and DMSO. During catalysis studies (see below), a 2 mM stock solution of complex **5a** was prepared in dry, degassed DMF. During storage of this solution in a sealed Schlenk flask over several months, **5a** underwent decomposition and crystals were deposited on the walls of the flask. An X-ray study showed the crystals to be the interesting dinuclear complex **6** (Scheme 3), which apparently arose by a sequence of reactions that included cyclometallation of each of the phenyl substitutents at a position *ortho* to the benzimidazole N atom. Presumably the proximity of the *ortho*-C–H bond to the Pd centre in **5a** facilitates the cyclometallation that leads to **6**. Related compounds such as **7** [15] and **8** [25] (Scheme 4) (which have respectively methyl and benzyl substituents instead of the phenyl substituents of **6**) show no propensity to undergo cyclometallation under similar conditions.

It was envisaged that in the same way that treatment of **4a** with $Pd(OAc)_2$ resulted in formation of **5**, treatment of **4b** with $Pd(OAc)_2$ would lead to the formation of **5b**. The reaction of **4b** with $Pd(OAc)_2$ in refluxing CH_3CN for 1 day in the presence of 3 Å molecular sieves (Scheme 5) did not, however, result in **5b**. Instead, loss of one dinitrophenyl group from each bis(NHC) ligand led to formation of the trinuclear complex **9**, which was isolated in a 20 % yield after column chromatography. This interesting complex was obtained as an orange, air-stable solid that displays good solubility in halogenated solvents but poor to moderate solubility in DMSO, DMF, CH_3CN, MeOH and acetone.



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Scheme 3 Dinuclear Pd-NHC complex **6**

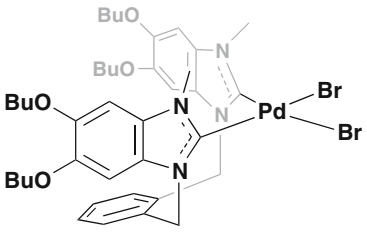
Attempts to synthesize **5b** by the reaction of **4b** with $Pd(OAc)_2$ in refluxing CH_3CN (no sieves present) or THF for 5 days, were not successful. In the case of the reaction in CH_3CN, a small amount of 2,4-dinitrophenol was isolated from the product mixture by column chromatography, but no identifiable complexes were obtained. When the reaction was repeated with dry, degassed DMF, again no identifiable complexes could be isolated. In all cases above, there were several signals near ca 9.5 ppm in the ^1H NMR spectrum, which may be due to the benzimidazolium H_2 hydrogen and/or the product of the hydrolysis of benzimidazolium cations to afford formanilides, as has previously been reported [26]. The formation of 2,4-dinitrophenol presumably occurs due to nucleophilic attack on the dinitrophenyl group by adventitious H_2O present in the solvent, or by attack of acetate or acetic acid, and subsequent hydrolysis on the column. When molecular sieves were absent, no complex could be isolated, and the majority of the material contained species that could not be identified by ^1H NMR spectroscopy. Even in the presence of molecular sieves, although they had a beneficial effect, the formation of 2,4-dinitrophenol still occurred to some extent. This attack could occur before or after the initial coordination of the carbene carbon to palladium, but either way would lead to the formation of the neutral trinuclear complex **9**.

Structure determinations

Complex 6

This complex crystallised in trace amounts from a DMF solution of **5a** that had been standing for several months. As such, only a crystallographic study was performed.

Scheme 4 Complexes **7** and **8**



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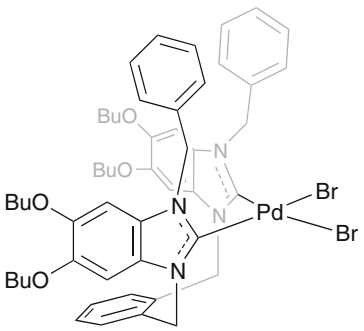

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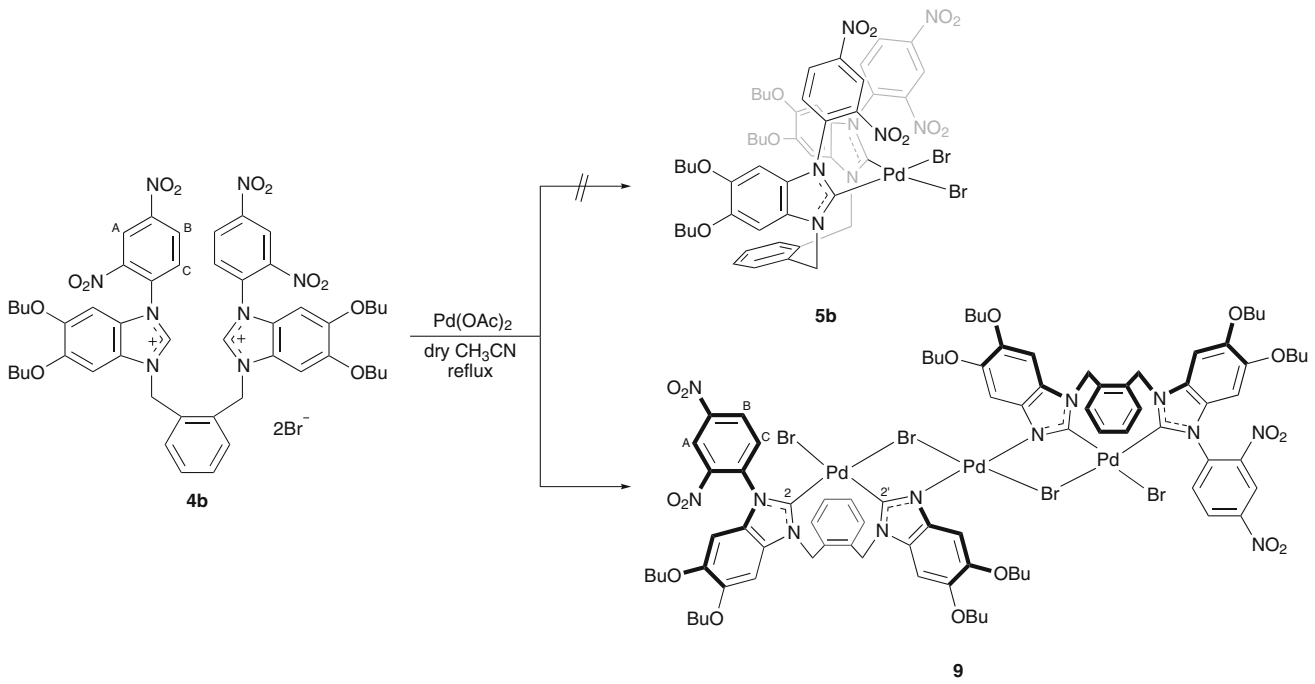


Scheme 5 Synthesis of the trinuclear Pd-NHC complex **9**

Complex **6** is binuclear, two palladium atoms being coordinated by the one ligand within a single neutral molecule, which, together with a single molecule of acetonitrile (uncoordinated), makes up the asymmetric unit of the structure. Disorder is found at the peripheries of the *n*-butyl substituents of the ligand, and for one of the methyl groups of dimethylformanide 1. Although devoid of crystallographic symmetry, the core of the complex molecule approximates quasi-2/*m* symmetry (Fig. 1a), the quasi-2 axis passing through the central aromatic ring and in its plane, the remainder of the molecular core being *quasi*-planar and normal to it. The coordination environments of the two palladium atoms are closely similar (Table 1), comprising a familiar quasi-planar four-coordinate array typical of Pd(II), *quasi*-planarity extending to encompass the associated benzimidazole and pendant coordinated aromatic ring, and the plane of a DMF molecule coordinated to/about each metal atom, and beyond, to encompass both coordination environments. The central *o*-xylylene ring of the ligand lies quasi-normal to the pendant extended benzimidazole systems to either side, the latter having interplanar dihedral angles of 86.83(14)°, 84.55(14)° to it, while the dihedral angle between the benzimidazole systems is 2.36(3)°, i.e. their planes are quasi-parallel to each other and to crystallographic *c*. Maintenance of the overall quasi-coplanarity, perhaps even rigidity, of the two sections appears to be assisted by approaches/contacts between each bromine atom and hydrogen atoms associated with (a) the methylene substituents of the central aromatic ring, and (b) the hydrogen atom of the benzimidazole ring of the other section of the molecule, the latter contacts (b) being 3.34, 3.07 Å (est.) (Br(1,2) respectively) and the former 3.50, 3.16 Å.

A single crystal X-ray study has already been recorded for **10** (Scheme 6), a 1:1 complex of palladium(II) bromide with a ligand similar to the present, but with butoxy groups at the 4- and 7-positions of the benzimidazole units rather than the 5- and 6-positions [15]. In complex **10** the $PdBr_2C_2$ coordination environment of the palladium atom is *trans*, with Pd-Br 2.4472(12), 2.4306(12) and Pd–C 1.988(8), 2.003(8) Å. A *cis* counterpart **11** (Scheme 6), devoid of substituents on the central aromatic ring, and with imidazole rather than benzimidazole C-donors, (C *trans* to Br), has Pd-Br 2.445(8), 2.4688(7) and Pd-C 1.982(5), 1.989(4) Å [22]. In the PdBrC(im)C(Ar)O(DMF) environment of the present compound **6**, Pd-Br; C(im); C(Ar); O(DMF) are 2.5562(7), 2.5684(7); 1.957(6), 1.965(5); 2.003(6), 2.015(5); 2.116(4), 2.110(4) Å, Pd-Br considerably longer than in **10** and **11**, presumably due to the strong *trans* effect caused by the anionic, σ-donating phenyl ligand mutually *trans* to the bromides in **6**. Rather similar environments with Pd-O(DMF) opposed to a Pd-C(carbene) type system are found in the $PdBr_2$(C)O-(DMF) arrays of **12** [27] and **13** [28] (Scheme 6). In **12** and **13**, Pd–C,O are 1.941(3), 2.100(2) and 1.921(2), 2.101(2) Å respectively; in the complex **6** Pd–C;O are quite similar: 1.957(6), 1.965(5); 2.116(4), 2.0110(4) Å.

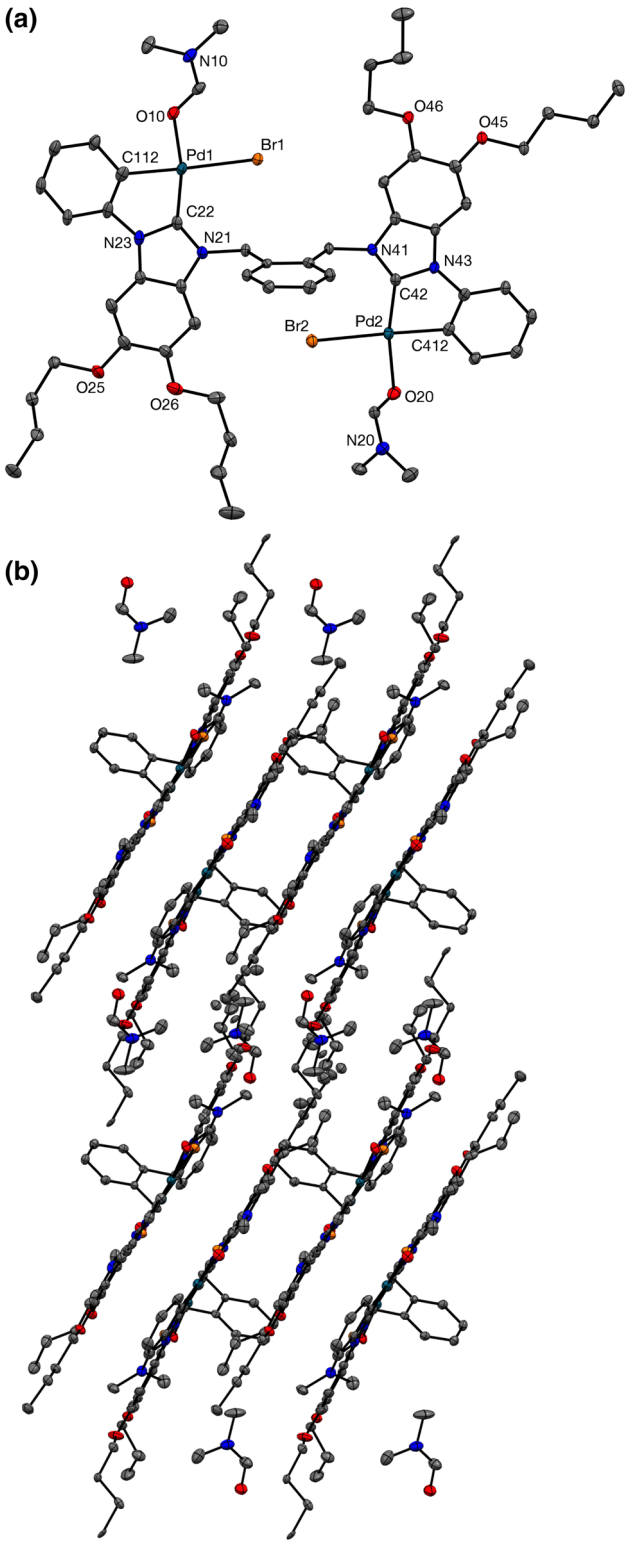


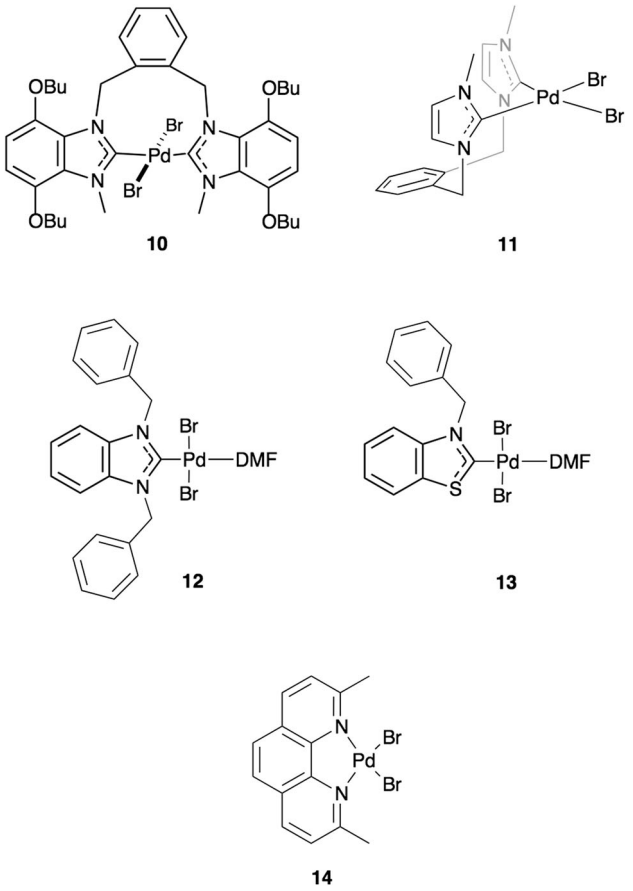
Fig. 1 **a** Projection of the molecule of **6**, **b** Unit cell contents, projected down *c*

Table 1 Palladium atom environments, **6**

Section (n)	1	2
Distances (Å)		
Pd(n)-O(n)	2.116 (4)	2.110 (4)
Pd(n)-C_{ar}(n)	2.003 (6)	2.015 (5)
Pd(n)-C_{im}(n)	1.957 (6)	1.965 (5)
Pd(n)-Br(n)	2.5562 (7)	2.5864 (7)
Angles (degrees)		
O(n)-Pd(n)-C_{ar}(n)	89.1 (2)	89.3 (2)
O(n)-Pd(n)-C_{im}(n)	166.5 (2)	167.0 (2)
O(n)-Pd(n)-Br(n)	90.13 (11)	88.06 (11)
C_{ar}(n)-Pd(n)-C_{im}(n)	78.9 (2)	78.9 (2)
C_{ar}(n)-Pd(n)-Br(n)	177.0 (2)	176.1 (2)
C_{im}(n)-Pd(n)-Br(n)	102.2 (2)	104.0 (2)

Complex ***9***

The structure of **9**, although more symmetrical crystallographically than that of **6**, is more complex (Table 2). Here the symmetry and coordinating capability of the ligand is diminished by replacement of one of the N-substituting aromatic groups by a 2,4-dinitro-Ar component, blocking the possibility of it C-coordinating, and removing the other completely, so that the imidazole-N can now coordinate. Which it does, two such N-donors lying *trans* about a planar four-coordinate central metal atom (Pd(2)) of a centrosymmetric trinuclear form, this metal atom being located on a crystallographic inversion centre (Fig. 2a); its other pair of coordination sites, *trans* in a planar four-coordinate environment, are occupied by a pair of symmetry-related halogen atoms, X(2) (x2), completing a *trans*-PdX_2N_2 array. The remainders of the pair of ligands so involved constitute a pair of bidentate NHC ligands, the two donors of which chelate peripheral palladium (Pd(1)) atoms, *cis* in their coordination spheres, again planar four-coordinate. One of the remaining pair of *cis*-coordination sites of each of these is occupied by the above-mentioned X(2), now bridging (Pd-X-Pd 83.5(2)°), while the other site is occupied about each Pd(1) by a terminally bound halogen atom X(1) (x2). The Pd-X(1,2) distances are very similar (2.4719(7), 2.4871(6) Å, regardless of bridging (2) or terminal (1) disposition; the equivalent *trans* Pd-′Br′ distances about the central palladium atom are appreciably shorter (2.4290(2) Å). Representative values in structurally characterized *trans*-$PdBr_2$(*im-N*-monodentate donor)$_2$ are 2.3842(10)–2.4389(3) (Pd-Br) and 1.990(11)–2.103(2) Å,



Scheme 6 Pd complexes **10–14**

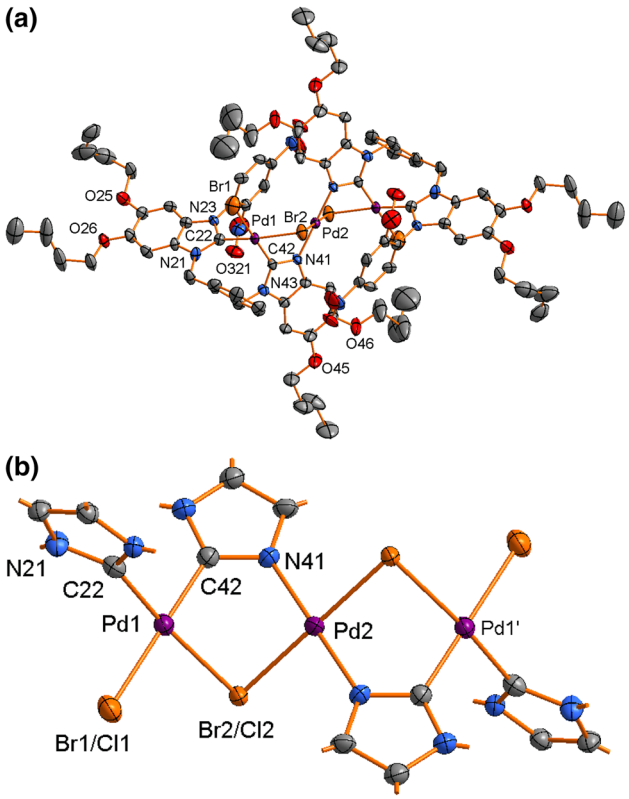


Fig. 2 **a** Projection of the centrosymmetric molecule of **9** normal to the N-Pd(central)-N line, **b** The molecular core of **9**; interplanar dihedral angles are presented in Table 3

Table 2 Palladium atom environments, **9**

Pd(2)		Pd(1)	
Distances (Å)			
Pd(2)-′Br(2)′	2.4290 (5)	Pd(1)-′Br(2)′	2.4871 (6)
Pd(2)-N(41)	2.002 (3)	Pd(1)-′Br(1))′	2.4719 (7)
		Pd(1)-C(22)	1.951 (4)
		Pd(1)-C(42)	1.974 (4)
Angles (degrees)			
′Br(2)′-Pd(2)-Br(2′)	180 (−)	′Br(2)′-Pc(1)-C(22)	171.84 (12)
Br(2)-Pd(2)-N(41)	87.55 (9)	′Br(2)′-Pd(1)-Br(1)	93.20 (2)
N(41)-Pd(2)-*N41*)	180 (−)	′Br(2)′-Pd(1)-C(42)	86.98 (11)
		′Br(1)′-Pd(1)-C(22)	88.01 (11)
		′Br(1)′-Pd(1)-C42)	178.97 (12)
		C(22)-Pd(1)-C(42)	91.67 (16)

[b-d] indicating the Pd-X distances in **9** to be long (see below). The unit cell of **9** is occupied by a single trinuclear molecule, one half of which comprises the asymmetric unit of the structure, together with residues modelled as 2 × 2 disordered dmso molecules, uncoordinated, despite the precedent of the binding of dmso augmenting the rather similar four-coordinate *cis*-$PdBr_2$(ar-*N*)$_2$ environment of **14** (Scheme 6) [29].

The halogen component of the complex molecule presents some cause for conjecture, the most sensible model being in terms of one-half of a bromine and one-half of a chlorine atom, the latter presumed to originate in chlorinated crystallization solvent; the occupancies of 0.5 (or close to it), consequent upon refinement on common sites for all halogen components, are interesting, refinement with separated sites being inauspicious, while trial

Table 3 Interplanar dihedral angles (degrees) and palladium atom deviations (Å), **9**

	B	C	D	E	F	δPd(1)	δPd(2)
A	73.24 (5)	49.95 (7)	66.00 (8)	33.01 (14)	60.15 (13)		0.000 (−)
B		44.60 (10)	88.82 (10)	88.10 (14)	16.29 (12)	0.086 (2)	
C			73.90 (9)	67.70 (15)	33.96 (14)	0.337 (4)	0.100 (5)
D				76.62 (55)	77.15 (13)	0.377 (4)	
E					81.26 (17)		

Planes A, B are the planes defined by the four coordinating atoms about Pd(2,1) respectively. Planes C, D are the C_7N_2 planes of the benzimidazole forms (C) bridging Pd(1,2) and (D) with the 2,4-dinitrophenyl pendant; in the latter, the CNO_2 dihedral angles to the pendant C_6 aromatic ring plane are 22.2(2), 8.9(2)°. E is the C_6 plane of the bridging phenylene group and F the pendant C_6 of the 2,4-dinitrophenyl group

replacement of half-chlorine by oxygen atoms from coordinated dmso (cf. **6**) presents problems of charge balance, as well as the absence of any plausible associated other residues, notably sulfur, the maximum difference density in the vicinity being 1.37 eÅ^{-3}.

The molecular core of **9** is shown in Fig. 2b, with the interplanar dihedral angles between the various components presented in Table 3. The dihedral angle between the coordination planes of the two independent palladium atoms is 73.24(5)°, rather steeply inclined, with the plane of the benzimidazole group which bridges them, being similarly pitched at 49.95(7)°, 44.60(10)°, and, together with one of the halide components, forming a five-membered ring, a pair of which, inversion-related, comprises the core of trinuclear array.

NMR studies

The ^{1}H NMR spectrum of a solution of **5a** in $CDCl_3$ contains two sharp doublets due to the *endo* and *exo* benzylic protons ($^2J_{H,H}$ = 15.2 Hz), consistent with a complex in which the Pd-NHC bonding is rigid on the NMR timescale. The chemical shifts for the signals associated with the xylylene protons suggest a conformation where the xylylene ring is 'folded away' from the metal centre [15, 25], as is common for *o*-xylylene-linked Pd(II)-NHC complexes of this type [15, 21, 22]. In the ^{13}C NMR spectrum of **5a**, the signal attributed to the carbene carbons is seen at 170.8 ppm, which is characteristic of the carbene carbons of bis(NHC)-Pd(II) dihalide complexes in which the NHC groups are mutually *cis* [14, 30].

The ^{1}H and ^{13}C NMR spectra of solutions of **9** are consistent with the coordination seen in the solid state persisting in solution. For example, the ^{1}H NMR spectrum contains four distinct doublets at 4.59, 5.17, 5.45, and 5.94 ppm, due to the benzylic protons; the presence of four benzylic signals is consistent with the two ligands being chemically equivalent, related by an inversion centre. Examination of the integrals for the dinitrophenyl signals indicates only one such group is present per NHC ligand, thus giving rise to the unsymmetrical nature of the complex. There is no signal associated with an NH group, which further suggests the loss of the dinitrophenyl group and subsequent furnishing of the benzimidazolyl nitrogen with a lone pair of electrons as the probable outcome of the reaction. The ^{13}C NMR spectrum contains two signals associated with C2 and C2′ carbene carbons, at 169.4 and 163.8 ppm respectively, which fall in the region expected for Pd-bound carbene centres trans to Br.

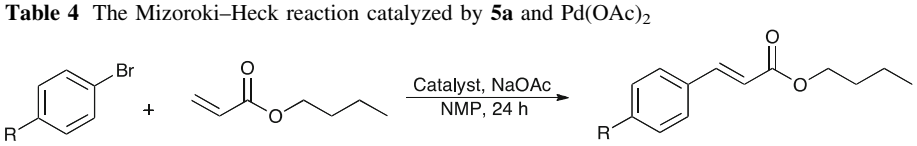
Catalysis studies

The Pd(II)-NHC complex **5a** was tested in a preliminary series of Mizoroki–Heck cross-coupling reactions between bromobenzene or 4-bromoanisole and butyl cinnamate, with NaOAc as the base in NMP at 120 °C and 0.1 and 1 mol% catalyst (Table 4). Complex **5a** promoted the formation of butyl cinnamate and butyl 4-methoxycinnamate in yields of 12 and 13 % respectively (0.1 mol% **5a**), and 29 and 24 % respectively (1 mol% **5a**), and was slightly more active than $Pd(OAc)_2$. In the coupling of bromobenzene and butyl cinnamate at 80 °C there was no product formation observed. In comparison to **5a**, complexes **7** [15] and **8** [25] (Scheme 4), which have respectively methyl or benzyl groups instead of the phenyl substituents, both showed superior catalytic activity. The difference in activities may be a consequence of the propensity of **5a** to undergo degradation by cyclometallation, to form species such as **6**.

Complex **5a** was also in the Suzuki–Miyaura cross-coupling reaction of 4-bromotoluene or 4-bromoanisole and phenylboronic acid using K_2CO_3 as the base in DMF at 80 °C with 0.002 and 0.02 mol% catalyst (Table 5). At a catalyst loading of 0.02 mol%, complex **5a** promoted the formation of 4-methylbiphenyl and 4-methoxybiphenyl in yields of 46 and 39 % respectively, which were greater than when $Pd(OAc)_2$ was employed as the catalyst. The catalytic activities obtained using **5a** are modest but similar to those obtained previously with **7** [15] and **8** [25].

Complex **5a** was also tested against $Pd(OAc)_2$ in the Buchwald-Hartwig reaction of bromobenzene and morpholine using KO^{t}Bu in refluxing toluene for 24 h with a

Table 4 The Mizoroki–Heck reaction catalyzed by **5a** and $Pd(OAc)_2$

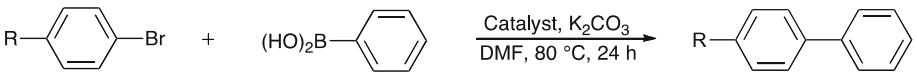


Entry	Catalyst	Mol% cat	R	T (°C)	Yield (%)[a]	TON	TOF
1	**3**	0.1	H	120	12	120	5
2	**3**	1	H	120	29	29	1.2
3	**3**	1	H	80	0	0	0
4	$Pd(OAc)_2$	0.1	H	120	3	30	1.2
5	$Pd(OAc)_2$	1	H	120	6	6	0.2
6	$Pd(OAc)_2$	1	H	80	0	0	0
7	**3**	0.1	OMe	120	13	130	5.4
8	**3**	1	OMe	120	24	24	1
9	$Pd(OAc)_2$	0.1	OMe	120	3	30	1.2
10	$Pd(OAc)_2$	1	OMe	120	8	8	0.3

Conditions: 1 mmol aryl halide, 1.2 mmol butyl acrylate, 1.5 mmol NaOAc, 0.5 mL NMP

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

Table 5 The Suzuki–Miyaura reaction catalyzed by **5a** and $Pd(OAc)_2$



Entry	Catalyst	Mol% cat	R	Yield (%)[a]	TON	TOF
1	**3**	0.002	H	34	17,000	710
2	**3**	0.02	H	46	2300	96
3	$Pd(OAc)_2$	0.002	H	3	1500	63
4	$Pd(OAc)_2$	0.02	H	6	300	13
5	**3**	0.002	OMe	29	15,000	630
6	**3**	0.02	OMe	39	2000	83
7	$Pd(OAc)_2$	0.002	OMe	0	0	0
8	$Pd(OAc)_2$	0.02	OMe	20	1000	42

Conditions: 1 mmol aryl halide, 1.2 mmol phenylboronic acid, 1.2 mmol K_2CO_3, 0.5 mL DMF

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

catalyst loading of 1 mol%. Under these conditions, **5a** promoted the formation of *N*-phenyl morpholine in a 37 % yield, compared to 13 % using $Pd(OAc)_2$.

Conclusion

We have synthesized two butoxy-functionalised bis(benzimidazolium) salts that serve as precursors for palladium complexes bearing chelating bis(NHC) ligands. The NHC moieties are furnished with phenyl or 2,4-dinitrophenyl substituents, and are also linked by an *o*-xylylene group. Complex **5a** possesses NHC ligands that adopt the traditional *cis* geometry around the metal centre, a conformation that is common to *o*-xylylene linked bis(NHC) palladium complexes of this type. Extended storage of a DMF solution of **5a** led to the formation of **6** in trace amounts, a crystal of which was characterised by an X-ray diffraction study. It seems that the proximity of the phenyl substituents to the metal centre in **5a** promotes the formation of **6**, albeit extremely slowly in DMF, via C–H activation of the *ortho* position of the phenyl group. The treatment of the dinitrophenyl-functionalised bis(benzimidazolium) salt **4b** with $Pd(OAc)_2$ in dry CH_3CN led to the loss of one dinitrophenyl group from each bis(NHC) ligand and the subsequent formation of the tri-nuclear complex **9**. This interesting complex involves the peripheral palladium atoms bound through the carbene carbons, while the central palladium is coordinated by the benzimidazolyl

nitrogen atoms that originally carried the dinitrophenyl substituents.

Experimental

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. Chromatographic separations were performed using BDH silica gel (40–63 μm) with the eluents 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 predetermined 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. 5,6-Dibutoxybenzimidazole was prepared according to literature procedures [31].

1-Phenyl-5,6-dibutoxybenzimidazole 3a

A mixture of bromobenzene (0.14 mL, 1.36 mmol), 5,6-dibutoxybenzimidazole (0.5 g, 1.91 mmol), CuI (52 mg, 0.27 mmol) and Cs_2CO_3 (0.89 g, 2.72 mmol) in DMA (3 mL) was heated at 140 °C for 5 days. The mixture was diluted with EtOAc (3 mL) and passed through a plug of silica, eluting with EtOAc until the eluent was colourless. The solution was concentrated in vacuo and the residue was purified by column chromatography (gradient elution with EtOAc/hexanes). The resulting oil was dissolved in CH_2Cl_2 and the solution washed with H_2O (4 × 10 mL) then dried over $MgSO_4$. Concentration of the solution in vacuo gave **3a** as a slightly yellow oil (0.40 g, 87 %), which solidified on standing. Found: C, 74.35; H, 7.47; N, 8.19. $C_{21}H_{26}N_2O_2$ requires C, 74.53; H, 7.74; N, 8.28 %; δ_H (500.13 MHz, $CDCl_3$): 8.02 (s, 1H, NCHN), 7.45–7.60 (m, 5H, Ar CH), 7.34 (s, 1H, benzimidazolyl Ar CH), 6.99 (s, 1H, benzimidazolyl Ar CH), 4.07 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 3.98 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 1.78-1.89 (m, 4H, 2 × OCH_2CH_2), 1.46–1.59 (m, 4H, 2 × CH_2CH_3) 0.95–1.01 (t, 6H, $^{3}J_{H,H} = 7.4$ Hz, 2 × CH_2CH_3); δ_C (125.77 MHz, DMSO-d_6): 147.7, 148.4 (benzimidazolyl Ar CO), 140.5 (NCHN), 137.2 (benzimidazolyl Ar C), 136.6 (Ar C), 128.2, 130.3 (Ar CH), 127.6 (benzimidazolyl Ar C), 124.0 (Ar CH), 95.9, 104.4 (benzimidazolyl Ar CH), 69.6, 70.0 (OCH_2), 31.4, 31.5 (OCH_2CH_2), 19.4, 19.4 (CH_2CH_3), 14.0, 14.0 (CH_3).

1-(2′,4′-Dinitrophenyl)-5,6-dibutoxybenzimidazole 3b and 1-(2′-fluoro-4′-nitrophenyl)-5,6-dibutoxybenzimidazole 3c

Method 1: A mixture of 5,6-dibutoxybenzimidazole (0.5 g, 1.91 mmol), 2,4-dinitrofluorobenzene (0.35 g, 1.91 mmol) and K_2CO_3 (0.4 g, 2.86 mmol) in DMF (30 mL) was heated at 80 °C, in darkness, for 2 d. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2. The solution was washed with water (3 × 20 mL) then dried over $MgSO_4$ and concentrated in vacuo. The residue was purified via column chromatography (gradient elution with EtOAc/hexanes) to give **3b** (0.29 g, 35 %) and **3c** (81 mg, 11 %) as orange and yellow solids respectively. **3b**: Found C, 58.72; H, 5.66; N, 12.94. $C_{21}H_{24}N_4O_6$ requires C, 58.87; H, 5.65; N, 13.08 %; δ_H (600.13 MHz, $CDCl_3$): 8.96 (d, 1H, $^{4}J_{3',5'} = 2.5$ Hz, H3′), 8.65 (dd, 1H, $^{3}J_{5',6'} = 8.7$ Hz, $^{4}J_{3',5'} = 2.5$ Hz, H5′), 7.86 (s, 1H, NCHN), 7.75 (d, 1H, $^{3}J_{5',6'} = 8.7$ Hz, H6′), 7.36 (s, 1H, benzimidazolyl Ar CH), 6.81 (s, 1H, benzimidazolyl Ar CH), 4.07 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 3.98 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 1.78–1.89 (m, 4H, 2 × OCH_2-CH_2), 1.47-1.58 (m, 4H, 2 × CH_2CH_3), 0.95-1.02 (t, 6H, $^{3}J_{H,H} = 7.4$ Hz, 2 × CH_2CH_3); δ_C (125.77 MHz, $CDCl_3$): 148.2, 149.0 (benzimidazolyl Ar CO), 145.0, 146.9 (C2′ and C4′), 140.0 (NCHN), 137.6 (benzimidazolyl Ar C), 135.0 (C1′), 130.0 (C6′), 128.7 (C5′), 127.3 (benzimidazolyl Ar C), 122.0 (C3′), 94.3, 105.2 (benzimidazolyl Ar CH), 69.6, 69.8 (OCH_2), 31.3, 31.4 (OCH_2CH_2), 19.4, 19.4 (CH_2CH_3), 14.0, 14.0 (CH_3). **3c**: Found C, 62.83; H, 5.97; N, 10.21. $C_{21}H_{24}N_3O_4F$ requires C, 62.83; H, 6.03; N, 10.47 %; δ_H (500.13 MHz, $CDCl_3$): 8.27 (m, 1H, H5′), 8.26 (m, 1H, H3′), 8.00 (s, 1H, NCHN), 7.83 (m, 1H, H6′), 7.34 (s, 1H, benzimidazolyl Ar CH), 6.52 (s, 1H, benzimidazolyl Ar CH), 4.06 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 3.91 (t, 2H, $^{3}J_{H,H} = 6.5$ Hz, OCH_2), 1.77–1.86 (m, 4H, 2 × OCH_2CH_2), 1.45–1.58 (m, 4H, 2 × CH_2CH_3), 0.95–1.01 (t, 6H, $^{3}J_{H,H} = 7.4$ Hz, 2 × CH_2CH_3); δ_C (125.77 MHz, $CDCl_3$): 155.2 (d, $^{1}J_{C,F} = 257$ Hz, C2′), 148.0, 148.7 (benzimidazolyl Ar CO), 147.1 (d, $^{3}J_{C,F} = 8$ Hz, C4′), 140.8 (NCHN), 137.7 (benzimidazolyl Ar C), 130.5 (d, $^{2}J_{C,F} = 12$ Hz, C1′), 127.0 (benzimidazolyl Ar C), 126.6 (C5′), 120.9 (d, $^{3}J_{C,F} = 4$ Hz, C6′), 113.9 (d, $^{2}J_{C,F} = 25$ Hz, C3′), 95.8, 104.9 (benzimidazolyl Ar CH), 69.6, 70.0 (OCH_2), 31.4, 31.5 (OCH_2CH_2), 19.4, 19.4 (CH_2CH_3), 14.0, 14.0 (CH_3). Method 2: A mixture of 5,6-dibutoxybenzimidazole (0.5 g, 1.91 mmol), 2,4-dinitrofluorobenzene (0.35 g, 1.91 mmol) and K_2CO_3 (0.4 g, 2.86 mmol) in CH_3CN (25 mL) was heated at reflux, in darkness, for 3 h. The mixture was filtered and the solvent

was removed in vacuo. The residue was dissolved in CH_2Cl_2 and **3b** was precipitated with hexanes, collected, washed with hexanes, and air-dried (0.76 g, 92 %). ^{1}H and ^{13}C NMR resonances as above.

Benzimidazolium salt 4a

A solution of **3a** (0.35 g, 1.02 mmol) and 1,2-bis(bromomethyl)benzene (0.13 g, 0.50 mmol) in toluene (17 mL) was stirred at reflux under nitrogen for 4 d. The solution was concentrated to ~5 mL then **4a** was precipitated with hexanes, collected, washed with hexanes, and dried under vacuum to yield a white powder (0.41 g, 87 %). Found C, 61.69; H, 6.44; N, 5.26. $C_{50}H_{60}N_4O_4Br_2{\cdot}(2H_2O)$ requires C, 61.48; H, 6.60; N, 5.73 %; δ_H (600.13 MHz, d_6-DMSO): 9.66 (s, 2H, NCHN), 7.55–7.70 (m, 16H, Ar H, xylylene Ar H, benzimidazolyl Ar CH), 7.14 (s, 2H, benzimidazolyl Ar CH), 6.08 (s, 4H, benzylic CH_2), 4.06 (t, 4H, $^3J_{H,H} = 6.4$ Hz, OCH_2), 4.03 (t, 4H, $^3J_{H,H} = 6.4$ Hz, OCH_2), 1.72–1.78 (2 × m, 8H, 2 × OCH_2CH_2), 1.46–1.53 (2 × m, 8H, 2 × CH_2CH_3), 0.99 (t, 6H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3), 0.98 (t, 6H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3); δ_C (125.77 MHz, DMSO-d_6): 149.4, 149.9 (benzimidazolyl Ar CO), 140.0 (NCHN), 132.9 (Ar C), 131.8 (xylylene Ar C), 130.0, 130.2, 130.3, 130.8 (Ar CH), 125.1 (benzimidazolyl Ar C), 124.8 (Ar CH), 124.6 (benzimidazolyl Ar C), 96.0, 96.7 (benzimidazolyl Ar CH), 68.9, 69.0 (OCH_2), 48.0 (benzylic CH_2), 30.4, 30.5 (OCH_2CH_2), 18.7, 18.7 (CH_2CH_3), 13.7, 13.8 (CH_3).

Benzimidazolium salt 4b

A solution of **3b** (0.14 g, 0.33 mmol) and 1,2-bis(bromomethyl)benzene (0.04 g, 0.16 mmol) in CH_3CN (15 mL) was stirred at reflux under nitrogen overnight. The solvent was removed in vacuo and the residue was purified via column chromatography (gradient elution with MeOH/EtOAc) to give **4b** as an orange solid (0.15 g, 85 %). Found C, 52.69; H, 5.03; N, 9.30. $C_{50}H_{56}N_8O_{12}Br_2{\cdot}(1.5H_2O)$ requires C, 52.32; H, 5.18; N, 9.76 %; δ_H (500.13 MHz, DMSO-d_6): 9.98 (s, 2H, NCHN), 9.21 (d, 2H, $^4J_{3',5'} = 2.6$ Hz, H3′), 9.00 (dd, 2H, $^3J_{5',6'} = 8.7$ Hz, $^4J_{3',5'} = 2.6$ Hz, H5′), 8.47 (br d, 2H, $^3J_{B,C} = 8.7$ Hz, H6′), 7.77 (s, 2H, benzimidazolyl Ar CH), 7.50-7.55 (m, 2H, xylylene Ar H), 7.28–7.33 (m, 2H, xylylene Ar H), 7.30 (s, 2H, benzimidazolyl Ar CH), 6.28 (br s, 4H, benzylic CH_2), 4.09 (br s, 4H, OCH_2), 3.96 (br s, 4H, OCH_2), 1.68–1.77 (2 × m, 8H, 2 × OCH_2CH_2), 1.41–1.52 (2 × m, 8H, 2 × CH_2CH_3), 0.96 (t, 12H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3), 0.95 (t, 6H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3); δ_C (125.77 MHz, DMSO-d_6): 149.6, 150.4 (benzimidazolyl Ar CO), 144.9, 149.0 (C2′ and C4′), 140.9 (NCHN), 133.2 (C6′), 131.7 (xylylene Ar C), 130.8 (C1′), 130.1 (C5′), 128.4, 129.6 (xylylene Ar CH), 124.6, 126.6 (benzimidazolyl Ar C), 122.0 (C3′), 96.3, 97.5 (benzimidazolyl Ar CH), 69.0, 69.2 (OCH_2), 48.1 (benzylic CH_2), 30.4, 30.4 (OCH_2CH_2), 18.66, 18.69 (CH_2CH_3), 13.6 (CH_3).

Palladium complex 5a

Palladium(II) acetate (26 mg, 0.12 mmol) was added, with stirring, to a solution of **4a** (100 mg, 0.11 mmol) in DMF (10 mL) and the mixture was heated at 90 °C for 3 d. The solvent was removed in vacuo and the residue was recrystallised from acetone/hexanes to yield the product as a white powder (64 mg, 58 %). Found C, 57.28; H, 5.58; N, 5.14. $C_{50}H_{58}N_4O_4Br_2Pd$ requires C, 57.46; H, 5.59; N, 5.36 %; δ_H (500.13 MHz, $CDCl_3$): 7.96 (m, 2H, xylylene Ar H), 7.78 (4H, Ar H), 7.77 (d, 2H, $^2J_{H,H} = 15.2$ Hz, benzylic C*H*H), 7.57 (m, 2H, xylylene Ar H), 7.36 (s, 2H, benzimidazolyl Ar CH), 7.20–7.25 (m, 6H, Ar H), 6.54 (s, 2H, benzimidazolyl Ar CH), 5.43 (d, 2H, $^2J_{H,H} = 15.2$ Hz, benzylic C*H*H), 4.07 (m, 4H, OCH_2), 3.76 (m, 4H, OCH_2), 1.85 (m, 4H, OCH_2CH_2), 1.67 (m, 4H, OCH_2CH_2), 1.54 (m, 4H, CH_2CH_3), 1.40 (m, 4H, CH_2CH_3), 1.00 (t, 6H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3), 0.90 (t, 6H, $^3J_{H,H} = 7.4$ Hz, CH_2CH_3); δ_C (125.77 MHz, DMSO-d_6): 170.8 (NCN), 147.6, 147.9 (benzimidazolyl Ar CO), 136.1 (Ar C), 135.3 (xylylene Ar C), 133.9 (xylylene Ar CH), 130.4 (benzimidazolyl Ar C), 129.8 (Ar CH), 129.7 (xylylene Ar CH), 129.0 (Ar CH), 128.4 (benzimidazolyl Ar C), 126.4 (Ar CH), 97.7, 98.1 (benzimidazolyl Ar CH), 69.9, 70.1 (OCH_2), 52.1 (benzylic CH_2), 31.2, 31.4 (OCH_2CH_2), 19.2, 19.4 (CH_2CH_3), 13.9, 14.0 (CH_3).

Palladium complex 9

Palladium(II) acetate (42 mg, 0.19 mmol) and 3 Å molecular sieves were added, with stirring, to a solution of **4b** (150 mg, 0.13 mmol) in CH_3CN (10 mL) and the mixture was heated at reflux for 20 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 and crude **9** was precipitated with hexanes, collected, and purified by column chromatography on neutral alumina (eluting with CH_2Cl_2) to give **9** as an orange powder (30 mg, 20 %). Found C, 46.70; H, 4.66; N, 7.35. $(C_{88}H_{102}N_{12}O_{16}Br_4Pd_3){\cdot}(0.5CH_2Cl_2)$ requires C, 46.93; H, 4.58; N, 7.42 %; δ_H (500.13 MHz, CD_2Cl_2): 9.34 (br d, 2H, $^3J_{B,C} = 8.7$ Hz, H_C), 8.62 (d, 2H, $^4J_{A,B} = 2.6$ Hz, H_A), 8.13 (dd, 2H, $^3J_{B,C} = 8.7$ Hz, $^4J_{A,B} = 2.6$ Hz, H_B), 7.71 (d, 2H, $^3J_{H,H} = 7.1$ Hz, xylylene Ar H), 7.61-7.65 (m, 2H, xylylene Ar H), 7.54-7.58 (m, 2H, xylylene Ar H), 7.45 (s, 2H, benzimidazolyl Ar CH), 7.20 (s, 2H, benzimidazolyl Ar CH), 7.10 (d, 2H, $^3J_{H,H} = 7.8$ Hz, xylylene Ar H), 6.85 (s, 2H, benzimidazolyl Ar CH), 6.35 (s, 2H, benzimidazolyl Ar CH), 5.94 (d, 2H, $^2J_{H,H} = 14.3$ Hz, benzylic CH*H*), 5.45 (d, 2H, $^2J_{H,H} = 14.3$ Hz, benzylic C*H*H), 5.17

(d, 2H, $^2J_{H,H}$ = 13.9 Hz, benzylic CH*H*), 4.59 (d, 2H, $^2J_{H,H}$ = 13.9 Hz, benzylic C*H*H), 3.74–4.25 (m, 16H, 4 × OCH_2), 1.63–1.90 (4 × m, 16H, 4 × OCH_2CH_2), 1.36–1.58 (4 × m, 16H, 4 × CH_2CH_3), 1.01 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3), 0.98 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3), 0.94 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3), 0.90 (t, 6H, $^3J_{H,H}$ = 7.4 Hz, CH_2CH_3); δ_C (150.90 MHz, CD_2Cl_2): 169.4 (C2), 163.8 (C2′), 149.2 (benzimidazolyl Ar CO), 148.8 (Ar CNO_2), 146.7, 147.2, 148.7 (benzimidazolyl Ar CO), 144.9 (Ar CNO_2), 139.2 (xylylene Ar C), 136.4 (Ar C), 135.8 (Ar CH_C), 134.8 (benzimidazolyl Ar C), 131.1, 131.3, 134.3 (xylylene Ar CH), 130.1 (benzimidazolyl Ar C), 129.3 (xylylene Ar C), 129.2 (Ar CH_B), 129.0 (xylylene Ar CH), 128.5, 128.6 (benzimidazolyl Ar C), 122.7 (Ar CH_A), 94.5, 95.0, 96.8, 103.7 (benzimidazolyl Ar CH), 70.0, 70.1, 70.5, 72.3 (OCH_2), 45.7, 52.0 (benzylic CH_2), 31.3, 31.6, 31.9, 31.9 (OCH_2CH_2), 19.4, 19.6, 19.7, 19.9 (CH_2CH_3), 13.8, 14.0, 14.1, 14.3 (CH_3). Crystals suitable for the X-ray diffraction study were grown by the slow evaporation of a DMSO/CH_2Cl_2 solution of the complex.

Structure determinations

The general procedure is given in a preceding paper [32].

Pertinent results are given below and in the text, Tables 1–3, 6 and Figures, the latter showing non-hydrogen atom displacement envelopes at the 50 % probability amplitude level. In **9**, some exchange of the putative halide ions (bromide) appears to have occurred with halide (chloride) from the (crystallization) solvent, occupancies being set at equivalence after trial refinement; in **6**, one is completely displaced by *O*-DMF. Full cif. depositions for both structures reside with the Cambridge Crystallographic Data Centre, CCDC: 1039098 (**9**), 1039099 (**6**).

Table 6 Crystal/refinement data (**6**,**9**)

Compound	**6**	**9**
Formula	$C_{56}H_{70}Br_2N_6O_6Pd_2$·DMF	$C_{88}H_{102}$(Br/Cl)$_{(2|2)}N_{12}O_{16}Pd_3$·4dmso
M_r	1368.9 Da	2446.2 Da
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (C_i^1, no. 2)	$P2_1/c$ (C_{2h}^5, No. 14)
Unit cell	8.3151 (6) Å	a = 14.6917 (10) Å
	18.2803 (13) Å	b = 24.1582 (11) Å
	19.7303 (13) Å	c = 16.7819 (12) Å
	α = 79.472 (6)°	α = 90°
	β = 82.253 (5)°	β = 114.975(8)°
	γ = 89.294 (6)°	γ = 90°
V	2921.4 (4) Å^3	5399.4(7) Å^3
Density (Z)	1.556 g cm^{-3} (2)	1.505 g cm^{-3} (2)
λ	λ_{Cu} 1.54178 Å	λ_{Mo} 0.71073 Å
μ	μ_{Cu} 7.0 mm^{-1}	μ_{Mo} 1.43 mm^{-1}
Specimen	0.23 × 0.06 × 0.02 mm^3	0.45 × 0.11 × 0.08 mm^3
$'T'_{min,max}$	0.594, 0.875	0.675, 0.908
$2\theta_{max}$	135°	62°
N_t	28,092	71,652
N (R_{int})	10,325 (0.056)	15,774 (0.096)
N_o	7426	7220
R_1	0.044	0.052
wR_2 (a, b)	0.138 (0.073, 3.6)	0.117 (0.49)
S	1.04	0.85
$\|\Delta\rho\|_{max}$	1.37 eÅ^{-3}	1.29 eÅ^{-3}

Catalysis studies

Stock solutions of $Pd(OAc)_2$ and **5a** in degassed DMF were prepared at concentrations of 2 mM. 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 **5a** were used within 1 month.

General procedure for the Mizoroki–Heck reaction

A flask equipped with a magnetic stirrer bar was charged with aryl halide (1 mmol), butyl acrylate (172 μL, 1.2 mmol), NaOAc (123 mg, 1.5 mmol) and di(ethylene glycol) dibutyl ether (200 μL, 0.81 mmol). The flask was evacuated and backfilled with nitrogen and the evacuation/backfill cycle was repeated twice. NMP (0.5 mL) and the required amount of the appropriate complex (0.1 or 1 mol%) were added under a positive pressure of nitrogen 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 Suzuki–Miyaura reaction

A flask equipped with a magnetic stirrer bar was charged with aryl halide (1 mmol), phenylboronic acid (134 mg, 1.1 mmol), base (1.2 mmol) and 1-methylnaphthalene (150 μL, 1.056 mmol). The flask was evacuated and backfilled with nitrogen and the evacuation/backfill cycle was repeated twice. Solvent (0.5 mL) and the required amount of the stock solution of the appropriate complex (0.002 mol%, 10 μL from 2 mM solution) were added under a positive pressure of nitrogen and the resulting solution was heated at 80 °C for 24 h in a Radley parallel synthesizer. 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 Buchwald–Hartwig reaction

A flask equipped with a magnetic stirrer bar was charged with bromobenzene (105 μL, 1 mmol), morpholine (96 μL, 1.1 mmol), KO^{t}Bu (135 mg, 1.2 mmol) and 1-methylnaphthalene (150 μL, 1.056 mmol). The flask was evacuated and backfilled with nitrogen and the evacuation/backfill cycle was repeated twice. Toluene (0.5 mL) and the required amount of the stock solution of the appropriate complex (1 mol%) were added under a positive pressure of nitrogen and the resulting solution was heated at 110 °C for 24 h in a Radley parallel synthesizer. 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.

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Conflict of interest The authors declare that they have no conflict of interest.

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