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Synthesis and Characterisation of (Alkoxybenzimidazolin-2-ylidene)palladium Complexes: The Effect of Ancillary Ligands on the Behaviour of Precatalysts

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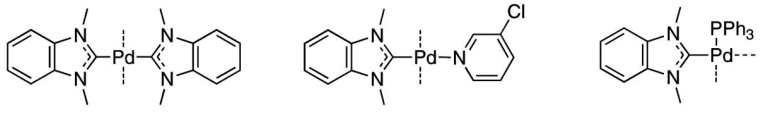
A series of new N-heterocyclic carbene (NHC)–palladium(II) complexes bearing electron-rich benzimidazolin-2-ylidene ligands are described and structurally and spectroscopically characterised. These (benzimidazolin-2-ylidene)palladium complexes bear butoxy groups to increase the solubility and perhaps influence the catalytic activity by increasing the electron density around the metal centre. The effect of varying the ancillary ligands is investigated, although these ligands do not appear to significantly alter the activity of the complexes as precatalysts. Preliminary studies indicate the complexes act as precatalysts with moderate activity in the Mizoroki–Heck and Suzuki–Miyaura coupling reactions.

Introduction

The first N-heterocyclic carbene (NHC)–metal complexes were prepared by Öfele[1] and Wanzlick,[2] but it was not until 1991 that the first free NHC was synthesized by Arduengo and co-workers.[3] The use of this class of ligands is now prevalent in homogeneous precatalyst design. The relative ease of synthesis and functionalisation of NHCs based on imidazole and benzimidazole in particular, has led to the rapid growth and optimisation of NHC–metal complexes of palladium, platinum, nickel, ruthenium and rhodium.[4] NHC complexes of these metals have been used extensively as precatalysts in a wide range of coupling reactions including C–C and C–N cross-coupling, olefin metathesis, hydrosilylation and hydrogenation reactions. The strong σ-donating properties of NHCs ensure that NHC–metal bonding is strong and confers stability to NHC-based catalysts by minimising decomposition.[5] The desire for more active precatalysts has led researchers to synthesize NHC–metal complexes that encompass a wide gamut of structural variability, including mono- and polyligated systems, pincer complexes and other mixed-donor systems. A greater understanding of the catalytic cycle of various coupling reactions has led to a more systematic approach to precatalyst design, which often involves increasing the steric bulk around the metal centre to aid the reductive elimination step, and to a lesser extent increasing the electronic density around the metal atom to facilitate oxidation addition.[6,7] The increased steric bulk may also lead to a lower coordination number around the metal centre, and thus a more facile oxidative addition step.[8] Understanding the effects of these structural changes and how they translate to catalytic activity is a question of great interest to both the academic and industrial communities.

In this paper, we report the synthesis and characterisation of a series of Pd–NHC complexes that includes examples of the types $Pd(NHC)_2$, Pd(NHC)(pyridine), and Pd(NHC)(phosphane) (Scheme 1). Our main interest is to study, which type of complex is the most favourable in terms of catalytic activity. To minimise any steric effects, NHCs that impart constant steric bulk around the metal centre have been used, so that the effect of ligand type (NHC vs. pyridine vs. phosphane) is the primary factor responsible for any observed differences in catalytic activity.



Scheme 1.

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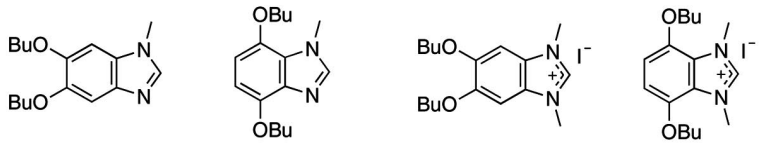


We are also interested in exploring the effects of monodentate NHCs derived from benzimidazoles that possess butoxy substituents on the arene ring. These butoxy groups increase the solubility of the complexes in common organic solvents, but may also increase the electron density at the metal centre. Although similar electron-rich benzimidazolin-2-ylidenes have previously been used as ligands for an in-situ generated catalyst,[6,9] there are few cases in which a well-defined palladium complex bearing these ligands has been employed as a precatalyst.[9] The benzimidazolium salts that serve as the ligand precursors of NHCs are readily synthesized in high yields.

The precatalysts have been designed in order to enhance our general understanding of the structure/activity relationship of NHC–palladium complexes, and hence help to elucidate which features of a potential precatalyst lead to increased catalyst activation and stability. The activities of six of the NHC–palladium complexes in the Mizoroki–Heck and Suzuki–Miyaura coupling reactions have been examined.

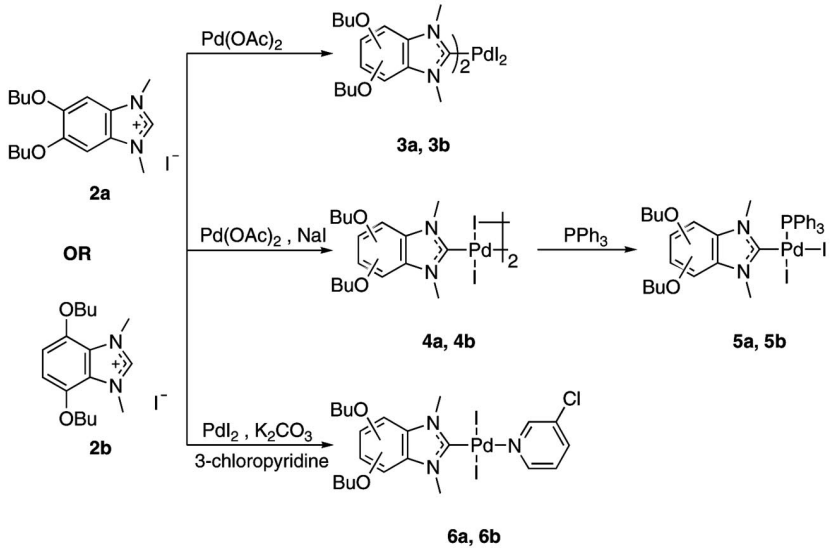
Results and Discussion

Synthesis of Complexes

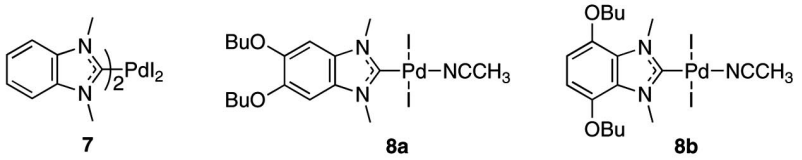
The *N*-methylbenzimidazoles **1a** and **1b** were prepared from the appropriate dibutoxybenzimidazole,[10] and were subsequently alkylated by using an excess of methyl iodide to give the benzimidazolium salts **2a** and **2b** in excellent yields. These salts, which serve as ligand precursors, were not hygroscopic and showed excellent solubility in a range of common organic solvents (e.g. dmso, dmf, CH_3CN, $CHCl_3$, CH_2Cl_2 and acetone).

The benzimidazolium salts **2a** ($L^aH{\cdot}I$) and **2b** ($L^bH{\cdot}I$) were used to prepare a series of palladium complexes, including bis(NHC) complexes **3a**,**b** [$L^x{}_2PdI_2$], iodo-bridged mono(NHC) complexes **4a**,**b** [$\{L^xIPd(\mu\text{-}I)\}_2$], and mono(NHC) "mixed-ligand" complexes **5a**,**b** [$L^x(Ph_3P)PdI_2$] and **6a**,**b** [L^x(3-Clpy)PdI_2] (3-Clpy = 3-chloropyridine) (Scheme 2). It was postulated that the differences in the structures of the Pd–NHC complexes would translate into different catalytic properties due to different rates of catalyst activation, and hence provide an additional insight into the most favourable features for catalyst precursors.

The palladium complex **3a** was synthesized by the reaction of the benzimidazolium salt **2a** with $Pd(OAc)_2$ in refluxing CH_3CN. *trans*-**3a** precipitated from the reaction mixture and was isolated in a 31% yield by filtration. *cis*-**3a** was not isolated from the reaction mixture, but crystals of *cis*-**3a** suitable for X-ray studies (see below) could be grown from solutions prepared by dissolving *trans*-**3a** in C_6D_6 or $CHCl_3$ and diffusing in hexanes. *trans*-**3a** is air-stable and is extremely soluble in halogenated solvents (and to a lesser degree in C_6H_6) but exhibits very low solubility in the polar solvents dmso, dmf and CH_3CN. In 2005 Huynh and co-workers reported the synthesis of the related palladium complex **7** bearing two dimethylbenzimidazolin-2-ylidene ligands. The *cis* and *trans* forms of **7** displayed remarkably different solubilities: *trans*-**7** was readily soluble in halogenated solvents but insoluble in more polar solvents



Scheme 2. Synthesis of NHC–palladium complexes.



7 8a 8b

such as dmf and dmso, whereas *cis*-**7** was found to be soluble only in dmso and dmf.[11]

The palladium complex **3b** was synthesized by the reaction of the benzimidazolium salt **2b** with $Pd(OAc)_2$ in refluxing thf. In the case of **3b**, however, a mixture of *cis*/*trans* isomers (in an approximate 30:70 ratio, as determined by NMR spectroscopy) precipitated from the reaction mixture in an overall yield of 75%. In view of our results for **3a** and those of Huynh et al. for **7**,[11] we explored the possibility of using solvents of different polarities to direct the synthesis of **3b** to yield a single isomer. However, when CH_3CN was used as the reaction solvent, *cis* and *trans* isomers again co-precipitated, although in an approximate 1:1 ratio. Nevertheless, by judicious choices of solvents, crystals of both *cis*- and *trans*-**3a** and *cis*- and *trans*-**3b** suitable for crystallographic studies could be grown selectively. Diffusion of C_6D_6 or hexanes into $CHCl_3$ solutions of **3a** or **3b** resulted in crystallisation of the *cis* isomers, whereas slow concentration of $CH_3CN/CHCl_3$ solutions gave crystals of the *trans* isomers. Interestingly, during the synthesis of **3a** and **3b**, small amounts of the complexes *trans*-**8a** and *trans*-**8b**, possessing one carbene ligand and one CH_3CN ligand were isolated in about 10 and 4% yield, respectively. The structures of *trans*-**8a** and *trans*-**8b** were confirmed by X-ray diffraction studies. These complexes may be intermediates in the formation of **3a** and **3b**.

The dimeric complexes **4a** and **4b** were synthesized by a modification of a procedure to prepare a similar bridged (benzimidazolin-2-ylidene)palladium complex, bearing an *N*-(2-acetamidocyclohexyl) group.[12] The reaction of 1 equiv. of the appropriate benzimidazolium salt, $Pd(OAc)_2$ and NaI in CH_3CN afforded **4a** and **4b** as dark red powders in 42 and 62% yields, respectively. The complexes **4a** and **4b** freely dissolved in CH_3CN, dmso, dmf, $CHCl_3$, and CH_2Cl_2. It was found that when the reaction was performed in dmf, the monomeric bis(carbene)palladium complexes **3a** and **3b** were formed together with the desired dimeric complexes **4a** and **4b** in a ratio of approximately 20:80 (**3***x*/**4***x*), as determined by ^1H NMR spectroscopy. This problem was avoided by the use of CH_3CN as the reaction solvent. Interestingly, there was no evidence to suggest that the dimeric complex could be cleaved by CH_3CN, which contrasts with earlier reports concerning similar complexes.[13]

The mixed carbene/phosphane complexes *cis*-**5a** and *cis*-**5b** were synthesized by treatment of the dimeric complexes **4a** and **4b** with PPh_3 in degassed CH_2Cl_2. Complexes tentatively assigned as *trans*-**5a** and *trans*-**5b** were detected (by NMR spectroscopy, see below) as intermediates in this reaction. Presumably, this reaction involves the formation of *trans*-**5a** and *trans*-**5b** initially, which subsequently isomerise to *cis*-**5a** and *cis*-**5b**; similar results have been reported for related systems.[14] In the case of **5a**, stirring of the reaction mixture at room temperature overnight ensured complete conversion to the *cis* isomer, whereas with **5b** a small amount of the *trans* complex was still present after this time, indicating a slower rate of isomerisation. In both cases, however, the *cis* conformation is favoured, and conversion from *cis* to *trans* does not occur, which is consistent with the literature reports for similar systems.[13] Both *cis*-**5a** and *cis*-**5b** were isolated as bright yellow crystals in yields of 91 and 93%, respectively, by simply diffusing hexanes into the reaction mixture.

Complexes **6a** and **6b** are based on the PEPPSI (Pyridine Enhanced Precatalyst Preparation Stabilisation and Initiation) family of catalysts first synthesized by Organ and coworkers,[15] and were synthesized by modifications of procedures used to prepare the PEPPSI complexes. The reaction of the appropriate benzimidazolium salt, PdI_2 and K_2CO_3 in neat 3-chloropyridine afforded **6a** and **6b** in 88 and 92% yield, respectively. The complexes **6a** and **6b** were insoluble in MeOH and CH_3CN and sparingly soluble in acetone and dmso, but demonstrated good solubility in CH_2Cl_2. Complex **6a** also shows good solubility in $CHCl_3$, whereas **6b** is sparingly soluble in this solvent. The complexes readily decomposed when heated in $CHCl_3$, acetone and dmso and even in CH_2Cl_2, presumably due to dissociation of 3-chloropyridine, but were generally stable when an excess of 3-chloropyridine is present. Interestingly, we found that the syntheses of **6a** and **6b** proceeded most smoothly when an excess of the benzimidazolium salt relative to PdI_2 was used, but when stoichiometric quantities were used the reaction mixtures rapidly darkened and afforded mixtures of difficult to separate products. It may be that under these conditions the excess benzimidazolium salt prevents the formation of $(3\text{-Clpy})_2PdI_2$ and its decomposition products.

NMR Studies

^1H and ^{13}C NMR spectra of *cis*-**3a** and *trans*-**3a** were as expected. The ^{13}C NMR spectrum of *trans*-**3a** showed a signal attributed to the carbene carbon atom at δ = 179.2 ppm in C_6D_6 and at δ = 177.2 ppm in $CDCl_3$. The analogous complex **7** (which lacks the electron-donating butoxy groups) was reported to have a carbene signal slightly downfield of this range, at δ = 181.0 ppm.[11] *trans*-**3a** was stable in C_6D_6, but in $CDCl_3$ solution isomerised over a number of days to *cis*-**3a**. *cis*-**3a** showed a signal for the carbene carbon atom at δ = 173.2 ppm, which is in the region expected for *cis*-bis(NHC)palladium complexes of this type.[9,11]

NMR spectra for **3b**–**6** were as expected. Carbene signals in the ^{13}C NMR spectra ($CDCl_3$) of *cis*-**3b** and *trans*-**3b** at δ = 175.2 and 178.8 ppm, respectively, and for **4a** and **4b** at δ = 163.0 and 164.7 ppm, respectively, are all in the ranges expected for these classes of compounds.[12,13] The signals corresponding to the carbene carbon atom in the ^{13}C NMR spectra for **5a** and **5b** are both doublets and can be seen at δ = 171.8 ($^2J_{C,P}$ = 3 Hz) and 174.5 ($^2J_{C,P}$ = 4 Hz) ppm, respectively. The ^{31}P NMR spectra show singlets at δ = 23.5, 23.3, and 16.3 ppm for *cis*-**5a**, *cis*-**5b**, and *trans*-**5b**, respectively. The chemical shifts of the carbene carbon atoms in complexes *trans*-**6a** and *trans*-**6b** (δ = 154.4 and 157.0 ppm, respectively) are similar to those of the (imidazolin-2-ylidene)palladium compounds prepared by Organ.[15]

Structure Determinations

The results of the single-crystal X-ray studies of **3**–**6** (Figures 1, 2, 3, 4, and 5; Tables 1, 2, 3, 4, and 5; Table S1) support the formulations of Scheme 2: **5a**,**b** in the *cis* form; **6a**,**b** in the *trans* form; and **3a**,**b** being isolated in both forms; **8a**,**b** are also in the *trans* form. All except *trans*-**3a**,**b**, *cis*-**5a**,**b**, *trans*-**6b** and **8a** are solvated in some manner, and all are mononuclear neutral molecules except for **4a**,**b** which

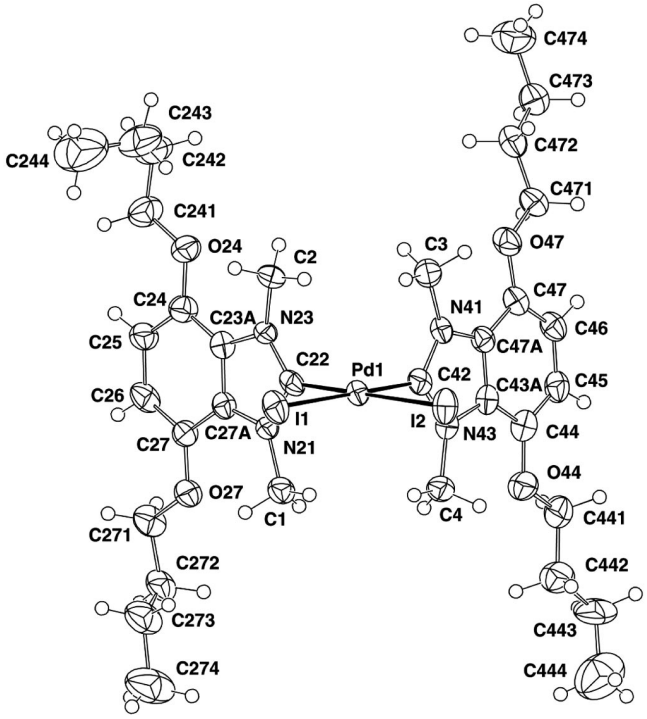


Figure 1. Projection of a single molecule of *cis*-**3b** [$L^b_2PdI_2$] (*cis*-**3a** is similar, but with crystallographic symmetry 2/*m*).

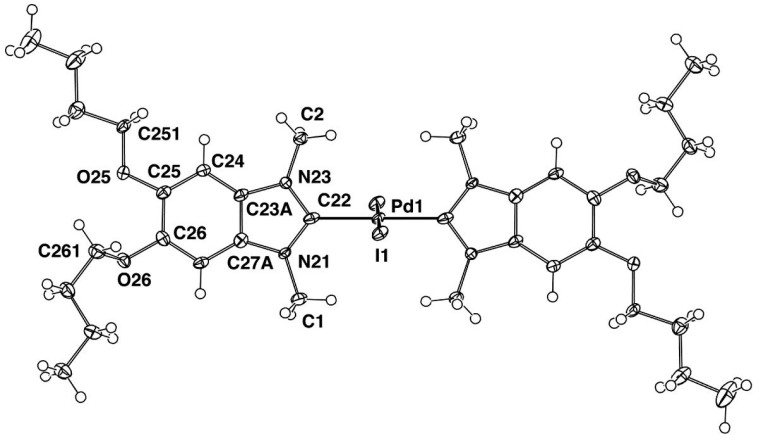


Figure 2. Projection of a single molecule of *trans*-**3a** [$L^a_2PdI_2$] (*trans*-**3b** is similar but devoid of symmetry).

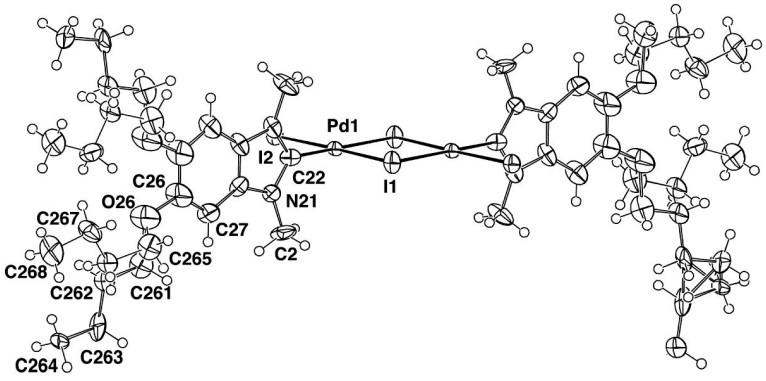


Figure 3. Projection of a single molecule of **4a** [{L^aIPd(μ-I)}$_2$] (**4b** is similar but devoid of symmetry).

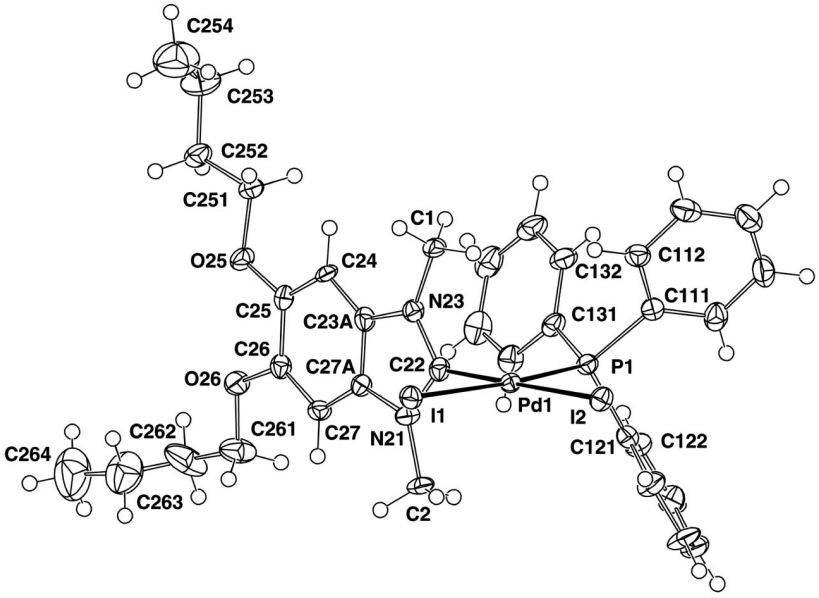


Figure 4. Projection of a single molecule of *cis*-**5a** [$L^a(Ph_3P)PdI_2$] [*cis*-**5b** (two independent molecules) is similar].

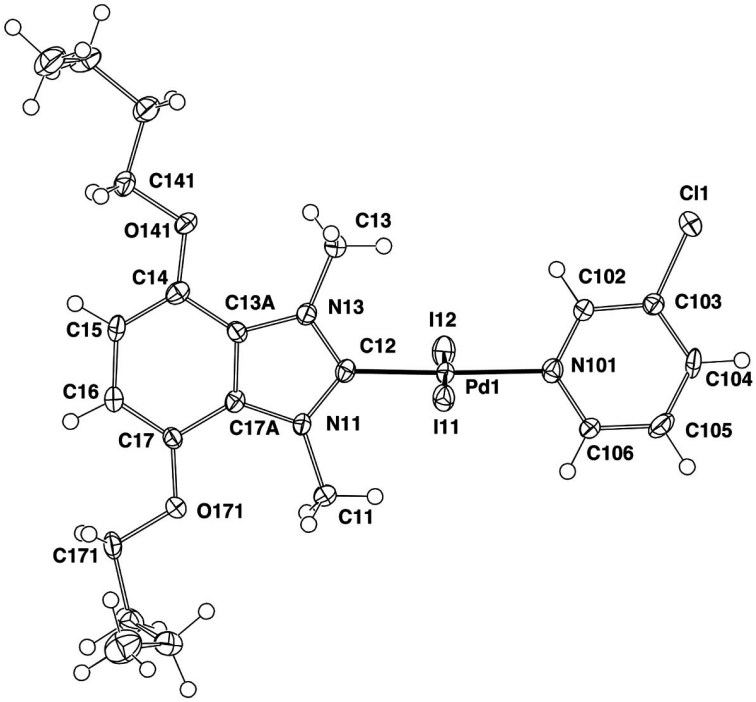


Figure 5. Projection of a single molecule of *trans*-**6b** (molecule 1; molecule 2 is similar, as are the two independent molecules of *trans*-**6a**).

are $(\mu\text{-}I)_2$-bridged neutral dimers. In all cases the palladium atom(s) may be ascribed the divalent state, consistent with its four-coordinate quasi-"square-planar" coordination environments; the aromatic components of the carbene ligands lie (quasi-)normal to the coordination planes in all cases, the combination being influential in determining crystal packing, the planes in a number of cases being disposed parallel/normal to crystallographic axes. The determinations are variable in quality (Table 6), precision in a number of cases being degraded by disorder among the solvent molecules, the ligand substituents, and even the ligands themselves (as modelled; see Variata in the Exp. Sect.), and crystal quality.

The diversity of ligands in the various coordination environments results in significant diversities in the bonding parameters associated with them. Assuming "*trans* effects" to be more predominant than "*cis* effects", the Pd–I distance of 2.60 Å in *trans*-**6a**,**b**, **8a**,**b** may be taken as a datum for

Table 1. Selected bond lengths and angles for *cis*-[$L^x_2PdI_2$] (**3a**,**b**),[a] and the parent *cis*-[L_2PdI_2].[17]

	3a	**3b**	[L_2PdI_2]
	Distances [Å]		
Pd–C(22)	2.003(6)	2.015(6)	1.987(4)
Pd–C(42)	[2.003(6)]	2.017(6)	1.989(4)
Pd–I(1)	2.6537(5)	2.6269(7)	2.6371(5)
Pd–I(2)	[2.6537(5)]	2.6255(10)	2.6805(5)
	Angles [°]		
I(1)–Pd–I(2)	94.10(2)	94.09(2)	95.79(2)
I(1)–Pd–C(22)	89.1(2)	87.6(1)	88.3(1)
I(1)–Pd–C(42)	176.8(2)	179.4(1)	175.5(1)
I(2)–Pd–C(22)	[176.8(2)]	178.3(1)	172.6(1)
I(2)–Pd–C(42)	[89.1(2)]	86.5(1)	85.1(1)
C(22)–Pd–C(42)	87.6(3)	91.7(2)	91.3(2)

[a] In **3a** the C_2I_2/C_7N_2(ar) interplanar dihedral angle is 83.5(2)°; in **3b** it is 89.7(1)°.

Table 2. Selected bond lengths and angles for *trans*-[$L^x_2PdI_2$] (**3a**,**b**).[a]

	3a	**3b**
	Distances [Å]	
Pd–C(22)	2.032(6)	2.023(2)
Pd–C(42)	[2.032(6)]	2.017(2)
Pd–I(1)(I(1′))	2.6193(4)	2.6040(3), [2.6357(9)]
Pd–I(2)	[2.6193(4)]	2.6011(2)
	Angles [°]	
I(1)–Pd–I(2)	180(–)	173.58(2), [172.13(6)]
I(1)–Pd–C(22)	91.1(2)	89.97(5), [90.55(5)]
I(1)–Pd–C(42)	[88.9(2)]	90.44(5), [89.29(5)]
I(2)–Pd–C(22)	[88.9(2)]	90.71(5)
I(2)–Pd–C(42)	[91.1(2)]	89.14(5)
C(22)–Pd–C(42)	180(–)	177.69(6)

[a] In **3a**, the C_2I_2/C_7N_2(ar) interplanar dihedral angle is 73.3(1)°; in **3b**, the two such angles are 85.15(4), 82.57(4)°. The angle between the pair of C_7N_2 planes in the latter is 2.74(5)°.

that parameter, a value which persists in those Pd–(terminal)-I distances (ca. 2.59 Å), which lie *trans* to Pd–(μ-)I in **4a**,**b**, and the associated Pd–(μ-)I distances (ca. 2.61 Å). The other Pd–I distances are all associated with *cis*-PdI_2 arrays, in which the Pd–I bonds lie *trans* to Pd–C or Pd–P, and these distances are all appreciably longer, with similar elongations associated with bonds *trans* to Pd–C, Pd–P in *cis*-**5a**,**b**. *trans*-$PdC(carbene)_2$ arrays have been reported by Huynh,[11] offering a datum value of 2.01 Å for that bond in that situation, with an interplanar dihedral angle between the two ligands of 4.50°. Here, in *cis*-**3**,**4**,**5*x***, the Pd–C bonds are all *trans* to Pd–I (terminal or bridging; there appears to be little difference, although the values for **4a**,**b** are regrettably all less precise than desirable), typically 2.00 Å. In **8a**,**b**, *trans* to N(acetonitrile), the Pd–C bonds are appreciably shorter (ca. 1.96 Å, Table S1), comparable with the values found in **6a**,**b**, *trans* to Pd–N(3-Clpy).

Detailed commentary on the structures is provided in the Supporting Information.

Table 3. Selected bond lengths and angles for [{$L^xIPd(\mu\text{-}I)\}_2$] (**4a**,**b**),[a] and the related [{$L^PBrPd(\mu\text{-}Br)\}_2$][13] ($L^P$ = *N*,*N*-diisopropylbenzimidazolin-2-ylidene).

	4a	**4b**	[{$L^PBrPd(\mu\text{-}Br)\}_2$]
	Distances [Å]		
Pd(1)–C(22)	1.99(2)	1.96(2)	1.947(3)
Pd(2)–C(42)	[1.99(2)]	2.04(2)	[1.947(3)]
Pd(1)–I(3)	2.590(2)	2.576(2)	2.4182(4)
Pd(2)–I(4)	[2.590(2)]	2.587(2)	[2.4182(4)]
Pd(1)–I(1)	2.658(2)	2.674(2)	2.5281(4)
Pd(2)–I(2)	[2.658(2)]	2.671(2)	[2.5281(4)]
Pd(1)–I(2)	2.604(2)	2.610(2)	2.4183(5)
Pd(2)–I(1)	2.604(2)	2.617(2)	2.4542(5)
Pd(1)···Pd(2)	3.757(2)	3.781(3)	3.5886(4)
I(1)···I(2)	3.6860(2)	3.680(3)	3.4569(6)
	Angles [°]		
I(1)–Pd(1)–I(2)	88.91(5)	88.29(7)	87.86(1)
I(1)–Pd(2)–I(2)	[88.91(5)]	88.19(7)	[87.86(1)]
I(1)–Pd(1)–I(3)	94.55(5)	93.63(7)	95.41(1)
I(2)–Pd(2)–I(4)	[94.55(5)]	94.00(7)	[95.41(1)]
I(2)–Pd(1)–I(3)	176.53(6)	177.89(8)	176.60(2)
I(1)–Pd(2)–I(4)	[176.53(6)]	177.58(9)	[176.60(2)]
C(22)–Pd(1)–I(3)	85.4(5)	86.7(5)	87.50(9)
C(42)–Pd(2)–I(4)	[85.4(5)]	87.1(5)	[87.50(9)]
C(22)–Pd(1)–I(1)	179.9(5)	179.1(6)	176.67(9)
C(42)–Pd(2)–I(2)	[179.9(5)]	176.9(6)	[176.67(9)]
C(22)–Pd(1)–I(2)	91.1(5)	91.3(5)	89.26(9)
C(42)–Pd(2)–I(1)	[91.1(5)]	90.8(5)	[89.26(9)]
I(1)–Pd(1)–I(2)	88.91(5)	88.29(7)	87.86(2)
I(2)–Pd(2)–I(1)	[88.91(5)]	88.19(7)	[87.86(2)]
Pd(1)–I(1)–Pd(2)	91.09(5)	91.21(7)	92.14(2)
Pd(1)–I(2)–Pd(2)	[91.09(5)]	91.43(7)	[92.14(2)]

[a] In **4a**, the C_2I_2/C_7N_2 (ar) interplanar dihedral angle is 90.0(3)°; in **4b**, the C_2I_2/C_2I_2 interplanar dihedral angle is 11.12(7)°, with the individual C_2I_2/C_7N_2(ar) dihedral angles being 87.5(5), 80.2(5)°. In the entries for centrosymmetric [{$L^PBrPd(\mu\text{-}Br)\}_2$], for I read Br.

Table 4. Selected bond lengths and angles for *cis*-[$L^x(Ph_3P)PdI_2$] (**5a**,**b**),[a] and the related *cis*-[$L^P(Ph_3P)PdBr_2$].[13]

	5a	**5b** (molecules 1,2)	[$L^P(Ph_3P)PdBr_2$]
	Distances [Å]		
Pd–I(1)	2.6641(3)	2.6519(3), 2.6578(3)	2.4761(4)
Pd–I(2)	2.6656(3)	2.6507(3), 2.6620(3)	2.4815(4)
Pd–C	1.985(3)	1.998(3), 1.995(3)	1.978(3)
Pd–P	2.2973(7)	2.2762(8), 2.2686(8)	2.2624(8)
	Angles [°]		
I(1)–Pd–I(2)	94.347(9)	94.823(9), 94.811(9)	92.63(1)
I(1)–Pd–P	172.90(2)	170.42(2), 169.48(2)	175.28(2)
I(1)–Pd–C	82.86(8)	86.73(8), 88.34(8)	84.13(8)
I(2)–Pd–P	92.42(2)	89.49(2), 89.33(2)	91.50(2)
I(2)–Pd–C	176.99(8)	172.35(8), 172.16(8)	175.15(9)
P–Pd–C	90.32(8)	90.12(8), 88.81(8)	91.61(9)

[a] PdCP/PdI_2 interplanar dihedral angles are 2.43(7)° for **5a**, and 11.41(6), 12.23(6)° for molecules 1, 2, respectively, of **5b**. The C_7N_2/PdI_2 interplanar dihedral angles are 88.51(6) (**5a**), 80.28(6), 76.10(6)° (**5b**; molecules 1, 2). In the entries for centrosymmetric [{$L^P(Ph_3P)PdBr_2$], for I read Br.

Catalysis Studies

An initial series of catalysis experiments have been carried out to test the relative activities of **3a**, **3b**, **5a**, **5b**, **6a** and **6b** in the Mizoroki–Heck and Suzuki–Miyaura coup-

Table 5. Selected bond lengths and angles for *trans*-[L^x(3-Clpy)-PdI$_2$] (**6a**,**b**).[a]

	6a (molecules 1,2)	**6b** (molecules 1,2)
	Distances [Å]	
Pd–I(1)	2.5977(8), 2.5979(8)	2.5975(2), 2.6004(2)
Pd–I(2)	2.5964(8), 2.5990(8)	2.5981(2), 2.6017(2)
Pd–C	1.960(7), 1.950(6)	1.957(2), 1.961(2)
Pd–N	2.105(6), 2.101(6)	2.097(2), 2.099(2)
	Angles [°]	
I(1)–Pd–I(2)	175.63(3), 173.93(3)	177.947(7), 175.692(7)
I(1)–Pd–C	88.8(2), 88.3(2)	88.86(6), 87.58(7)
I(1)–Pd–N	91.0(2), 90.9(2)	91.09(5), 92.97(5)
I(2)–Pd–C	87.2(2), 87.0(2)	89.70(6), 88.34(7)
I(2)–Pd–N	93.0(2), 93.9(2)	90.41(5), 91.14(5)
N–Pd–C	178.5(3), 178.2(3)	177.58(8), 178.40(8)

[a] CNI_2/C_7N_2 interplanar dihedral angles are 76.1(2), 82.0(1) (**6a**; molecules 1, 2); 88.31(4), 84.17(5)° (**6b**; molecules 1, 2). C_7N_2/C_5N(3-Clpy) interplanar dihedral angles are 4.5(2), 38.7(3) (**6a**; molecules 1, 2); 11.49(7), 27.92(7)° (**6b**; molecules 1, 2). CNI_2/C_5N interplanar dihedral angles are 73.4(2), 59.4(2) (**6a**; molecules 1, 2), 76.93(6), 56.63(6)° (**6b**; molecules 1, 2).

ling reactions. We have not attempted to optimise reaction conditions, which can have a significant influence, but instead focussed on one set of conditions to try and gain an understanding of the effect of precatalyst design.

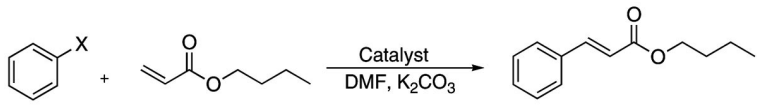
Initial tests focused on the Mizoroki–Heck coupling of iodobenzene and butyl acrylate to form butyl cinnamate by using K_2CO_3 in dmf with a reaction time of 24 h. Due to the reactivity of aryl iodide substrates, low catalyst loadings of 0.00005 and 0.0001 mol-% (maximum TON of 2000000 and 1000000) were employed, and all catalyst activities were compared to that of a standard, $Pd(OAc)_2$. The results are summarised in Table 7. All precatalysts show a high activity under these conditions, with the PEPPSI based complex **6a** achieving a TON > 1800000 at a TOF approaching 80000 h^{-1} (Entry 9). Although the precatalysts do not seem to be significantly different in their activities, they all give conversions much greater than that of the $Pd(OAc)_2$.

When bromobenzene was used as the substrate with 1 mol-% precatalyst, however, the conversion to butyl cinnamate was greatly decreased, with a maximum yield of

Table 6. Crystal data and refinement details.

	cis-**3a**·$CHCl_3$	*cis*-**3b**·$CHCl_3$	*trans*-**3a**	*trans*-**3b**	**4a**·C_6H_6	**4b**·$2C_6H_6$
Empirical formula	$C_{35}H_{53}Cl_3I_2N_4O_4Pd$	$C_{35}H_{53}Cl_3I_2N_4O_4Pd$	$C_{34}H_{52}I_2N_4O_4Pd$	$C_{34}H_{52}I_2N_4O_4Pd$	$C_{40}H_{58}I_4N_4O_4Pd_2$	$C_{46}H_{64}I_4N_4O_4Pd_2$
M_r [Da]	1060.4	1060.4	941.0	941.0	1379.3	1457.4
Crystal system	orthorhombic	triclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	*Cmcm*	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*C*2/*m*	$P\bar{1}$
a [Å]	10.4476(3)	12.327(3)	20.192(1)	11.0677(3)	11.2165(5)	11.651(5)
b [Å]	13.5008(8)	12.377(3)	12.1879(8)	12.2605(5)	10.8991(5)	12.333(5)
c [Å]	29.3680(10)	16.208(2)	7.7561(7)	16.4893(5)	19.5180(10)	20.098(5)
α [°]		101.090(10)		111.417(3)		92.274(5)
β [°]		111.930(10)	97.608(6)	90.392(2)	95.541(5)	98.696(5)
γ [°]		102.94(2)		112.221(3)		105.608(6)
V [Å^3]	4142	2129	1892	1901	2375	2740
$\rho_{calcd.}$ [g cm^{-3}]	1.70_0	1.65_4	1.65_2	1.64_4	1.92_9	1.76_7
Z	4	2	2	2	2	2
μ [mm]$^{-1}$	2.2	2.1	2.2	2.2	3.4	3.0
Specimen [mm]	0.24×0.18×0.03	0.23×0.17×0.05	0.20×0.18×0.02	0.26×0.13×0.03	0.28×0.26×0.12	0.22×0.20×0.10
$T'_{min/max}$	0.79	0.66	0.84	0.94	0.31	0.62
$2\theta_{max}$ [°]	63	60	66	69	50	50
N_t	29507	67617	22974	36735	12478	25183
N (R_{int})	3604 (0.051)	12413 (0.087)	6682 (0.080)	15136 (0.026)	2224 (0.071)	9562 (0.084)
N_o	2266	6028	4193	10796	1793	3461
*R*1	0.044	0.059	0.067	0.030	0.079	0.12
*wR*2 [*a* (*b*)]	0.12 (0.065)	0.14 (0.063)	0.18 (0.105)	0.066 (0.033)	0.19 (0.082,87)	0.41 (0.20)
	cis-**5a**	*cis*-**5b**	*trans*-**6a**·$0.19CHCl_3$	*trans*-**6b**	*trans*-**8a**	*trans*-**8b**·C_2H_3N
Empirical formula	$C_{35}H_{41}I_2N_2O_2PPd$	$C_{35}H_{41}I_2N_2O_2PPd$	$C_{22.19}H_{30.19}Cl_{1.57}I_2N_3O_2Pd$	$C_{22}H_{30}ClI_2N_3O_2Pd$	$C_{19}H_{29}I_2N_3O_2Pd$	$C_{21}H_{32}I_2N_4O_2Pd$
M_r [Da]	912.9	912.9	786.8	764.1	691.7	732.7
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	*Pc*	*C*2/*c*	$P2_1/c$
a [Å]	15.8613(6)	19.1167(5)	12.8865(8)	14.6302(2)	37.1708(8)	14.6556(4)
b [Å]	15.0466(7)	14.4469(3)	13.015(3)	11.4364(1)	10.3423(2)	8.3806(5)
c [Å]	16.5031(5)	25.5160(10)	18.765(2)	17.2249(2)	13.4347(3)	21.8851(5)
α [°]			78.020(10)			
β [°]	117.263(4)	90.203(3)	89.855(7)	108.777(1)	110.936(2)	92.812(2)
γ [°]			69.190(10)			
V [Å^3]	3501	7047	2869	2729	4824	2685
$\rho_{calcd.}$ [g cm^{-3}]	1.73_2	1.72_1	1.82_2	1.86_0	1.90_5	1.81_3
Z	4	8	4	4	8	4
μ [mm^{-1}]	2.4	2.4	3.0	3.1	3.3	3.0
Specimen [mm]	0.23×0.21×0.06	0.35×0.15×0.10	0.21×0.12×0.08	0.44×0.18×0.04	0.34×0.30×0.11	0.26×0.12×0.10
$T'_{min/max}$	0.76	0.82	0.88	0.62	0.47	0.76
$2\theta_{max}$ [°]	68	75	55	62	74	50
N_t	64217	295014	31292	76493	43506	23078
N (R_{int})	13855 (0.039)	35651 (0.072)	13130 (0.042)	16704 (0.042)	11739 (0.032)	4717 (0.18)
N_o	8648	15970	8075	12738	9174	2910
*R*1	0.038	0.036	0.051	0.033	0.031	0.089
*wR*2 [*a* (*b*)]	0.11 (0.059)	0.075 (0.021)	0.14 (0.068)	0.079 (0.046)	0.093 (0.059, 13.7)	0.27 (0.157, 1.48)

Table 7. 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	79	1540000	64300
2	**3a**	0.0001	iodobenzene	24	120	90	886000	36900
3	**3b**	0.00005	iodobenzene	24	120	85	1675000	69800
4	**3b**	0.0001	iodobenzene	24	120	96	939000	39100
5	**5a**	0.00005	iodobenzene	24	120	87	1713000	71400
6	**5a**	0.0001	iodobenzene	24	120	91	890000	37100
7	**5b**	0.00005	iodobenzene	24	120	75	1475000	61400
8	**5b**	0.0001	iodobenzene	24	120	82	807000	33600
9	**6a**	0.00005	iodobenzene	24	120	94	1837000	76500
10	**6a**	0.0001	iodobenzene	24	120	94	918000	38200
11	**6b**	0.00005	iodobenzene	24	120	85	1670000	69600
12	**6b**	0.0001	iodobenzene	24	120	89	877000	36500
13	$Pd(OAc)_2$	0.00005	iodobenzene	24	120	19	367000	15300
14	$Pd(OAc)_2$	0.0001	iodobenzene	24	120	26	253000	10500
15	**3a**	1	bromobenzene	24	120	15	15	0.6
16	**3b**	1	bromobenzene	24	120	13	13	0.5
17	**5a**	1	bromobenzene	24	120	23	23	1
18	**5b**	1	bromobenzene	24	120	13	13	0.5
19	**6a**	1	bromobenzene	24	120	9	9	0.4
20	**6b**	1	bromobenzene	24	120	7	7	0.3
21	$Pd(OAc)_2$	1	bromobenzene	24	120	3	3	0.1

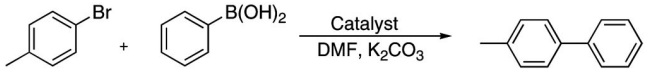
[a] 1 mmol aryl halide, 1.2 mmol butyl acrylate, 1.5 mmol K_2CO_3, 0.5 mL dmf. [b] GC yield determined using bis(ethylene glycol) dibutyl ether as the internal standard.

23% achieved by using the mixed carbene/phosphane complex **5a** (Entry 17). Despite the lack of activity displayed, all precatalysts gave a higher conversion than $Pd(OAc)_2$, presumably due to the increased stability of the catalytic species and a decreased tendency to form large, unreactive palladium colloids.

The precatalysts were also tested in the Suzuki–Miyaura coupling reaction of 4-bromotoluene and phenylboronic acid to produce 4-methylbiphenyl (Table 8). Again, low catalyst loadings of 0.002 and 0.02 mol-% (maximum TONs of 50000 and 5000, respectively) were employed. The results show that the monomeric bis(ligated) complexes **3a**,**b** and the mixed carbene/phosphane complexes **5a**,**b** have an activity significantly higher than that of $Pd(OAc)_2$. Interestingly, the two PEPPSI-based complexes **6a** and **6b**, although exhibiting a higher activity than $Pd(OAc)_2$, show an activity significantly lower than **3a**,**b** and **5a**,**b**.

These preliminary catalysis studies indicate that there is no significant difference between the activities of the precatalysts under the conditions examined. The precatalysts are significantly more active than $Pd(OAc)_2$, but are less active than the PEPPSI catalysts. These results, although unsurprising, nevertheless serve to highlight the importance of steric effects in precatalyst design, suggesting that the increased rate of reductive elimination aided by steric bulk around the metal centre is of greater importance than having two monodentate NHCs or a mixed NHC/phosphane, NHC/pyridine system. Although the value of the "throw-away"-type ligand is of no question (as seen in the precatalysts designed by Organ and co-workers),[15] they must be used in conjunction with NHCs that impart steric bulk around the metal atom to ensure high activity and minimal catalyst decomposition.

Table 8. Suzuki–Miyaura reaction catalyzed by palladium complexes and $Pd(OAc)_2$.[a]



Entry	Catalyst	Mol-% cat.	*t* [h]	*T* [°C]	% yield[b]	TON	TOF
1	**3a**	0.002	24	80	23	11700	490
2	**3a**	0.02	24	80	31	1540	65
3	**3b**	0.002	24	80	27	13700	570
4	**3b**	0.02	24	80	42	2100	90
5	**5a**	0.002	24	80	37	18300	760
6	**5a**	0.02	24	80	39	1960	80
7	**5b**	0.002	24	80	35	17400	720
8	**5b**	0.02	24	80	43	2160	90
9	**6a**	0.002	24	80	10	4930	205
10	**6a**	0.02	24	80	20	1000	40
11	**6b**	0.002	24	80	4	2210	90
12	**6b**	0.02	24	80	20	1020	40
13	$Pd(OAc)_2$	0.002	24	80	3	1630	68
14	$Pd(OAc)_2$	0.02	24	80	6	320	14

[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.

Conclusions

We have synthesized two benzimidazolium salts, bearing electron-donating butoxy groups, which serve as ligand precursors for a series of electron-rich NHC–palladium complexes bearing different ancillary ligands. The butoxy groups also serve to increase the solubility of these complexes in many common organic solvents. All of the complexes prepared have been characterised by single-crystal X-ray diffraction studies. The palladium complexes have been tested in an initial series of Mizoroki–Heck and Suzuki–Miyaura coupling reactions, displaying high activity when using aryl iodides but only modest conversions when the less reactive aryl bromides are employed. The significant electronic differences between L^a and L^b do not seem to be reflected in the activity of the precatalysts. Despite this, the complexes bearing two NHCs or an NHC/phosphane seem to be more active as precatalysts than the mixed NHC/pyridine complexes, particularly in the Suzuki–Miyaura coupling reaction. Efforts are underway to synthesize similar electron-rich palladium complexes with increased steric bulk around the metal centre, which should increase the activity of the precatalyst by facilitating the reductive elimination step of the catalytic cycle.

Experimental Section

General Comments: All experiments were performed under nitrogen by using standard Schlenk techniques, unless otherwise stated. Subsequent manipulations were carried out in air. All solvents were redistilled (under the laboratory atmosphere) prior to use, and, if used in the preparation of air-sensitive compounds, were deoxygenated. Anhydrous solvents were obtained by distillation from the appropriate drying agent. Chromatographic separations were performed by using BDH silica gel (40–63 μm) with the eluants indicated. Nuclear magnetic resonance spectra were recorded at room temperature with Bruker ARX500 or Bruker ARX300 spectrometers. ^{1}H and ^{13}C NMR chemical shifts were referenced to solvent resonances, and ^{31}P chemical shifts were referenced to an external 85% H_3PO_4 solution. Coupling reactions were analysed with an HP 5890 Series II gas chromatograph. Yields were estimated by 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.

Preparation of 1-Methylbenzimidazoles

5,6-Dibutoxy-1-methylbenzimidazole (1a): 5,6-Dibutoxybenzimidazole[10] (3.5 g, 13 mmol) was added to a suspension of NaH (0.38 g, 16 mmol) in thf (80 mL), and the mixture was stirred for 1 h. Methyl iodide (0.85 mL, 13 mmol) was added dropwise, and the mixture was stirred at room temperature for 1 h, then heated at 40 °C for 20 h. The mixture was filtered through Celite, and the filtrate was concentrated in vacuo. The residue was dissolved in diethyl ether and washed with water (3 × 30 mL), then dried ($MgSO_4$). The diethyl ether extract was concentrated in vacuo, and the residue was purified by rapid silica gel filtration (by elution with diethyl ether, followed by methanol). The methanol fractions were combined, the solvent was removed in vacuo, and the residue was recrystallised from hexanes to give **1a** as a pale pink powder. Yield: 1.94 g (54%). ^{1}H NMR (500.13 MHz, [D$_6$]acetone): δ = 7.81 (s, 1 H, NC*H*N), 7.17 (s, 1 H, Ar C*H*), 7.09 (s, 1 H, Ar C*H*), 4.05 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, OCH_2), 4.01 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, OCH_2), 3.83 (s, 3 H, NCH_3), 1.77 (m, 4 H, 2× OCH$_2$CH_2), 1.55 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, [D$_6$]acetone): δ = 148.5 (Ar *C*O), 147.4 (Ar *C*O), 143.4 (N*C*N), 138.6 (Ar *C*), 130.0 (Ar *C*), 105.7 (Ar *C*H), 96.1 (Ar *C*H), 70.0, 70.1 (O*C*H$_2$CH$_2$), 32.3, 32.4 (*C*H$_2$CH$_2$CH$_3$), 31.1 (N*C*H$_3$), 20.0 (*C*H$_2$CH$_3$), 14.2 (CH$_2$*C*H$_3$) ppm. $C_{16}H_{24}N_2O_2$ (276.38): calcd. C 69.53, H 8.75, N 10.14; found C 69.25, H 8.72, N 9.93.

4,7-Dibutoxy-1-methylbenzimidazole (1b): 4,7-Dibutoxy-1-methylbenzimidazole was synthesized as described for **1a** from 4,7-dibutoxybenzimidazole (3.5 g, 13 mmol), but the rapid silica gel filtration step was omitted. The compound was recrystallised from hexanes. Yield: 2.5 g (68%). ^{1}H NMR (500.13 MHz, [D$_6$]acetone): δ = 7.95 (s, 1 H, NC*H*N), 6.60 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar C*H*), 6.55 (d, $^3J_{H,H}$ = 8.5 Hz, 1 H, Ar C*H*), 4.15 (t, $^3J_{H,H}$ = 6.5 Hz, 2 H, OCH_2), 4.05 (t, $^3J_{H,H}$ = 6.5 Hz, 2 H, OCH_2), 3.95 (s, 3 H, NCH_3), 1.70 (m, 4 H, 2× OCH$_2$CH_2), 1.50 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, [D$_6$]acetone): δ = 144.7 (Ar *C*O), 143.5 (N*C*N), 141.0 (Ar *C*O), 135.8 (Ar *C*), 125.5 (Ar *C*), 104.2 (Ar *C*H), 68.0, 68.2 (O*C*H$_2$CH$_2$), 33.3 (N*C*H$_3$), 30.9, 31.1 (*C*H$_2$CH$_2$CH$_3$), 18.8, 19 (*C*H$_2$CH$_3$), 13.8 (CH$_2$*C*H$_3$) ppm. $C_{16}H_{24}N_2O_2$ (276.38): calcd. C 69.53, H 8.75, N 10.14; found C 69.36, H 8.87, N 9.90.

Preparation of Benzimidazolium Salts

5,6-Dibutoxy-1,3-dimethylbenzimidazolium Iodide (2a, L^aH·I): A solution of **1a** (0.93 g, 3.37 mmol) and methyl iodide (0.75 mL, 12 mmol) in thf (35 mL) was heated at 40 °C for 20 h. The resulting white precipitate was filtered off, washed three times with hexanes, and air-dried to give **2a**. Yield: 1.31 g (93%). ^{1}H NMR (500.13 MHz, [D$_6$]dmso): δ = 9.40 (s, 1 H, NC*H*N), 7.60 (s, 2 H, 2× Ar C*H*), 4.15 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, 2× OCH_2), 4.02 (s, 6 H, 2× NCH_3), 1.80 (m, 4 H, 2× OCH$_2$CH_2), 1.50 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, [D$_6$]dmso): δ = 149.1 (Ar *C*O), 140.3 (N*C*HN), 125.6 (Ar *C*), 96.5 (Ar *C*H), 68.9 (O*C*H$_2$CH$_2$), 33.2 (N*C*H$_3$), 30.6 (*C*H$_2$CH$_2$CH$_3$), 18.8 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$) ppm. $C_{17}H_{27}IN_2O_2$ (418.32): calcd. C 48.81, H 6.51, N 6.70; found C 48.62, H 6.40, N 6.45.

4,7-Dibutoxy-1,3-dimethylbenzimidazolium Iodide (2b, L^bH·I): 4,7-Dibutoxy-1,3-dimethylbenzimidazolium iodide was synthesized as described for **2a** from **1b** (1 g, 3.62 mmol). Yield: 1.40 g (92%). ^{1}H NMR (500.13 MHz, [D$_6$]dmso): δ = 9.45 (s, 1 H, NC*H*N), 7.10 (s, 2 H, 2× Ar C*H*), 4.15 (t, $^3J_{H,H}$ = 8.6 Hz, 4 H, 2× OCH_2), 4.12 (s, 6 H, 2× NCH_3), 1.80 (m, 4 H, 2× OCH$_2$CH_2), 1.50 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, [D$_6$]dmso): δ = 143.1 (N*C*HN), 141.2 (Ar *C*O), 123.1 (Ar *C*), 108.5 (Ar *C*H), 68.8 (O*C*H$_2$CH$_2$), 36.2 (N*C*H$_3$), 30.5 (*C*H$_2$CH$_2$CH$_3$), 18.8 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$) ppm. $C_{17}H_{27}IN_2O_2$·H_2O (436.33): calcd. C 46.80, H 6.70, N 6.42; found C 46.93, H 6.75, N 6.15.

Preparation of Palladium Complexes

Bis(5,6-dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)palladium(II) Diiodide (3a, [L^a_2PdI$_2$]): Palladium(II) acetate (77 mg, 0.34 mmol) was added to a degassed solution of **2a** (260 mg, 0.62 mmol) in

CH_3CN (20 mL) and the mixture stirred at room temperature for 2 h, then heated at reflux for 4 d. The mixture was filtered, and the solid was washed with cold CH_3CN to give *trans*-**3a** as a yellow powder. Yield: 90 mg (31%). Crystals of *cis*-**3a** suitable for the X-ray study were obtained by diffusion of hexanes into a $C_6D_6/CHCl_3$ solution of the complex. Crystals of *trans*-**3a** suitable for the X-ray study were obtained by slow concentration of a $CH_3CN/CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, C_6D_6): *trans* isomer: δ = 6.45 (s, 4 H, 4× Ar C*H*), 4.05 (s, 12 H, 4× NCH_3), 3.75 (t, $^3J_{H,H}$ = 6.3 Hz, 8 H, 4× OCH_2), 1.75 (m, 8 H, 4× OCH$_2$CH_2), 1.55 (m, 8 H, 4× CH$_2$CH_2CH$_3$), 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, 4× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, C_6D_6): *trans* isomer: δ = 179.2 (C-Pd), 147.5 (Ar *C*O), 129.7 (Ar *C*), 96.4 (Ar *C*H), 69.8 (O*C*H$_2$), 35.1 (N*C*H$_3$), 31.9 (*C*H$_2$CH$_2$CH$_3$), 19.8 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$) ppm. $C_{34}H_{52}I_2N_4O_4Pd$ (941.04): calcd. C 43.40, H 5.57, N 5.95; found C 43.23, H 5.52, N 5.51.

1,2-Bis(4,7-dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)palladium(II) Diiodide (3b, [L$^b_2$PdI$_2$]): Palladium(II) acetate (67 mg, 0.30 mmol) was added to a suspension of **2b** (250 mg, 0.60 mmol) in thf (15 mL) and the mixture stirred at room temperature for 2 h, then heated at reflux for 3 d. The resulting solid was collected, washed three times with hexanes and air-dried to give **3b** as a mixture of *trans*/*cis* isomers in an approximate ratio of 70:30. Yield: 210 mg (75%). Crystals of *cis*-**3b** suitable for the X-ray study were obtained by diffusion of hexanes into a $CHCl_3$ solution of the complex. Crystals of *trans*-**3b** suitable for the X-ray study were obtained by slow concentration of a $CH_3CN/CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, $CDCl_3$): *trans* isomer: δ = 6.45 (s, 4 H, 4× Ar C*H*), 4.40 (s, 12 H, 4× NCH_3), 4.00 (t, $^3J_{H,H}$ = 6.2 Hz, 8 H, 4× OCH_2), 1.75 (m, 8 H, 4× OCH$_2$CH_2), 1.50 (m, 8 H, 4× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, 4× CH$_2$CH_3) ppm; *cis* isomer: δ = 6.50 (s, 4 H, 4× Ar C*H*), 4.45 (s, 12 H, 4× NCH_3), 3.95 (t, $^3J_{H,H}$ = 6.2 Hz, 8 H, 4× OCH_2), 1.75 (m, 8 H, 4× OCH$_2$CH_2), 1.45 (m, 8 H, 4× CH$_2$CH_2CH$_3$), 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, 4× CH$_2$CH_3) ppm; some coupling constants could not be determined due to overlap of isomer signals. ^{13}C NMR (75.47 MHz, $CDCl_3$): *trans* isomer: δ = 178.8 (C-Pd), 140.7 (Ar *C*O), 127.0 (Ar *C*), 105.3 (Ar *C*H), 68.8 (O*C*H$_2$), 39.5 (N*C*H$_3$), 31.5 (*C*H$_2$CH$_2$CH$_3$), 19.6 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm; *cis* isomer: δ = 175.2 (N*C*HN), 140.5 (Ar *C*O), 126.6 (Ar *C*), 104.6 (Ar *C*H), 68.6 (O*C*H$_2$), 38.4 (N*C*H$_3$), 31.4 (*C*H$_2$CH$_2$CH$_3$), 19.5 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$) ppm. $C_{34}H_{52}I_2N_4O_4Pd$ (941.04): calcd. C 43.40, H 5.57, N 5.95; found C 43.57, H 5.48, N 5.90.

Di-μ-iodidobis[(5,6-dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)iodidopalladium(II)] (4a, [{L^{a}IPd(μ-I)}$_2$]): Palladium(II) acetate (151 mg, 0.67 mmol) and NaI (93 mg, 0.62 mmol) were added to a solution of **2a** (260 mg, 0.62 mmol) in degassed CH_3CN (15 mL), and the mixture was heated at reflux for 5 d. The mixture was filtered through Celite, and the solvent was removed in vacuo. The resulting residue was recrystallised from CH_2Cl_2/hexanes to give **4a** as a dark red powder. Yield: 170 mg (42%). Crystals suitable for the X-ray study were obtained by slow concentration of a solution of the complex in C_6H_6. ^{1}H NMR (500.13 MHz, C_6D_6): δ = 6.20 (s, 4 H, 4× Ar C*H*), 3.75 (s, 12 H, 4× NCH_3), 3.65 (t, $^3J_{H,H}$ = 6.2 Hz, 8 H, 4× OCH_2), 1.70 (m, 8 H, 4× OCH$_2$CH_2), 1.50 (m, 8 H, 4× CH$_2$CH_2CH$_3$), 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, 4× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, C_6D_6): δ = 163.0 (C-Pd), 147.7 (Ar *C*O), 129.3 (Ar *C*), 95.8 (Ar *C*H), 69.5 (O*C*H$_2$), 35.4 (N*C*H$_3$), 31.7 (*C*H$_2$CH$_2$CH$_3$), 19.7 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{34}H_{52}I_4N_4O_4Pd_2$ (1301.27): calcd. C 31.38, H 4.03, N 4.31; found C 31.03, H 3.95, N 4.18.

Di-μ-iodidobis[(4,7-dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)iodidopalladium(II)] (4b, [{L^{b}IPd(μ-I)}$_2$]): This compound was synthesized as described for **4a**, from **2b** (380 mg, 0.92 mmol). Yield: 370 mg (62%). Crystals suitable for the X-ray study were obtained by the slow diffusion of C_6H_6 into a $CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 6.50 (s, 4 H, 4× Ar C*H*), 4.45 (s, 12 H, 4× NCH_3), 4.00 (t, $^3J_{H,H}$ = 6.3 Hz, 8 H, 4× OCH_2), 1.80 (m, 8 H, 4× OCH$_2$CH_2), 1.55 (m, 8 H, 4× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, 4× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 164.7 (C-Pd), 140.5 (Ar *C*O), 126.8 (Ar *C*), 105.3 (Ar *C*H), 68.8 (O*C*H$_2$), 39.0 (N*C*H$_3$), 31.4 (*C*H$_2$CH$_2$CH$_3$), 19.5 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{34}H_{52}I_4N_4O_4Pd_2$ (1301.27): calcd. C 31.38, H 4.03, N 4.31; found C 31.43, H 4.08, N 4.18.

***cis*-(5,6-Dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)(triphenylphosphane)palladium(II) Diiodide (5a, [L^a(Ph$_3$P)PdI$_2$]):** Triphenylphosphane (66 mg, 0.25 mmol) was added to a solution of **4a** (150 mg, 0.12 mmol) in degassed CH_2Cl_2 (7 mL), and the mixture was stirred at room temperature for 20 h. The solution was transferred to a sample vial, and vapour diffusion of hexanes into the solution resulted in crystallisation of **5a** as large yellow prisms, suitable for the X-ray study. Yield: 190 mg (91%). ^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 7.60 (m, 6 H, 6× Ar C*H*), 7.35 (m, 3 H, 3× Ar C*H*), 7.25 (m, 6 H, 6× Ar C*H*), 6.60 (s, 2 H, 2× benzim Ar C*H*), 3.95 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, 2× OCH_2), 3.67 (s, 6 H, 2× NCH_3), 1.80 (m, 4 H, 2× OCH$_2$CH_2), 1.50 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, CD_2Cl_2): δ = 171.8 (d, $^2J_{C,P}$ = 3 Hz, C-Pd), 147.6 (Ar *C*O), 134.8 (d, $^3J_{C,P}$ = 11 Hz, Ar *C*H), 131.6 (d, $^1J_{C,P}$ = 50 Hz, Ar *C*), 131.4 (d, $^5J_{C,P}$ = 3 Hz, Ar *C*H), 129.6 (benzim Ar *C*), 128.7 (d, $^4J_{C,P}$ = 11 Hz, Ar *C*H), 96.1 (benzim Ar *C*H), 70.4 (O*C*H$_2$), 35.1 (N*C*H$_3$), 31.8 (*C*H$_2$CH$_2$CH$_3$), 19.8 (*C*H$_2$CH$_3$), 14.2 (CH$_2$*C*H$_3$) ppm. ^{31}P NMR (121.50 MHz, CD_2Cl_2): δ = 23.5 (s, PPh$_3$) ppm. $C_{35}H_{41}I_2N_2O_2PPd$ (912.93): calcd. C 46.05, H 4.53, N 3.07; found C 45.72, H 4.54, N 2.99.

***cis*-(4,7-Dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)(triphenylphosphane)palladium(II) Diiodide (5b, [L^b(Ph$_3$P)PdI$_2$]):** This compound was synthesized as described for **5a**, from **4b** (100 mg, 0.077 mmol). Yield: 130 mg (93%). Crystals suitable for the X-ray study were obtained from diffusion of hexanes into a $CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, CD_2Cl_2): δ = 7.60 (m, 6 H, 6× Ar C*H*), 7.35 (m, 3 H, 3× Ar C*H*), 7.25 (m, 6 H, 6× Ar C*H*), 6.45 (s, 2 H, 2× benzim Ar C*H*), 3.95 (s, 6 H, 2× NCH_3), 3.90 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, 2× OCH_2), 1.80 (m, 4 H, 2× OCH$_2$CH_2), 1.50 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm; note that a small amount of the *trans* isomer was also detected. ^{13}C NMR (75.47 MHz, CD_2Cl_2): δ = 174.5 (d, $^2J_{C,P}$ = 4 Hz, C-Pd), 140.7 (Ar *C*O), 134.8 (d, $^3J_{C,P}$ = 11 Hz, Ar *C*H), 131.5 (d, $^1J_{C,P}$ = 50 Hz, Ar *C*), 131.4 (d, $^5J_{C,P}$ = 3 Hz, Ar *C*H), 128.6 (d, $^4J_{C,P}$ = 11 Hz, Ar *C*H), 127.0 (benzim Ar *C*), 105.5 (benzim Ar *C*H), 69.2 (O*C*H$_2$), 38.4 (N*C*H$_3$), 31.7 (*C*H$_2$CH$_2$CH$_3$), 19.9 (*C*H$_2$CH$_3$), 14.1 (CH$_2$*C*H$_3$) ppm; note that a small amount of the *trans* isomer was also detected. ^{31}P NMR (121.50 MHz, CD_2Cl_2): δ = 23.3 (s, PPh$_3$) ppm; a small peak due to the *trans* isomer was also detected at δ = 16.3 ppm. $C_{35}H_{41}I_2N_2O_2PPd$ (912.93): calcd. C 46.05, H 4.53, N 3.07; found C 45.99, H 4.57, N 2.93.

(5,6-Dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)(3-chloropyridine)palladium(II) Diiodide (6a, [L^a(3-Clpy)PdI$_2$]): A suspension of **2a** (120 mg, 0.29 mmol), palladium(II) iodide (94 mg, 0.26 mmol) and K_2CO_3 (198 mg, 1.43 mmol) in 3-chloropyridine (5 mL) was heated in a screw-cap Schlenk flask at 80 °C, with vigorous stirring,

for 2 d. After cooling, the mixture was diluted with CH_2Cl_2 and passed through a pad of silica gel covered with Celite, eluting with CH_2Cl_2 until the eluent was colourless. The solvent was removed in vacuo, and excess 3-chloropyridine was removed by distillation under vacuum. The residue was triturated with pentane (3 × 10 mL), and the resulting solid was dried under vacuum to give **6a** as a yellow powder. Yield: 175 mg (88%). Crystals suitable for the X-ray study were obtained by diffusion of hexanes into a $CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 9.12 (d, ^4J = 2.3 Hz, 1 H, pyr C*H*), 9.00 (dd, ^4J = 1.3, ^3J = 5.4 Hz, 1 H, pyr C*H*), 7.75 (m, ^4J = 2.3, ^3J = 8.2 Hz, 1 H, pyr C*H*), 7.30 (dd, ^3J = 5.4, ^3J = 8.2 Hz, 1 H, pyr C*H*), 6.85 (s, 2 H, 2× benzim Ar C*H*), 4.10 (s, 6 H, 2× NCH_3), 4.00 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, 2× OCH_2), 1.85 (m, 4 H, 2× OCH$_2$CH_2), 1.55 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 154.4 (C-Pd), 152.9 (pyr *C*H), 151.9 (pyr *C*H), 147.2 (Ar *C*O), 138.0 (pyr *C*H), 132.6 (pyr *C*), 129.4 (benzim Ar *C*), 125.0 (pyr *C*H), 96.0 (benzim Ar *C*H), 70.1 (O*C*H$_2$), 35.9 (N*C*H$_3$), 31.4 (*C*H$_2$CH$_2$CH$_3$), 19.4 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{22}H_{30}ClI_2N_3O_2Pd$ (764.18): calcd. C 34.58, H 3.96, N 5.50; found C 34.55, H 3.94, N 5.33.

(4,7-Dibutoxy-1,3-dimethylbenzimidazolin-2-ylidene)(3-chloropyridine)palladium(II) Diiodide (6b, [L^b(3-Clpy)PdI$_2$]): This compound was synthesized as described for **6a**, from **2b** (180 mg, 0.43 mmol). Yield: 288 mg (92%). Crystals suitable for the X-ray study were obtained by diffusion of hexanes into a $CHCl_3$ solution of the complex. ^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 9.12 (d, ^4J = 2.3 Hz, 1 H, pyr C*H*), 9.00 (dd, ^4J = 1.1, ^3J = 5.4 Hz, 1 H, pyr C*H*), 7.75 (m, ^4J = 2.3, ^3J = 8.0 Hz, 1 H, pyr C*H*), 7.30 (dd, ^3J = 5.4, ^3J = 8.0 Hz, 1 H, pyr C*H*), 6.50 (s, 2 H, 2× benzim Ar C*H*), 4.40 (s, 6 H, 2× NCH_3), 4.00 (t, $^3J_{H,H}$ = 6.3 Hz, 4 H, 2× OCH_2), 1.85 (m, 4 H, 2× OCH$_2$CH_2), 1.55 (m, 4 H, 2× CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, 2× CH$_2$CH_3) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 157.0 (C-Pd), 153.0 (pyr *C*H), 152.0 (pyr *C*H), 140.4 (Ar *C*O), 137.9 (pyr *C*H), 132.6 (pyr *C*), 126.8 (benzim Ar *C*), 124.9 (pyr *C*H), 104.9 (benzim Ar *C*H), 68.7 (O*C*H$_2$), 39.1 (N*C*H$_3$), 31.4 (*C*H$_2$CH$_2$CH$_3$), 19.5 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{22}H_{30}ClI_2N_3O_2Pd$ (764.18): calcd. C 34.58, H 3.96, N 5.50; found C 34.94, H 4.00, N 5.38.

Catalysis Studies: Stock solutions of complexes **3a**, **3b**, **5a**, **5b**, **6a**, and **6b** in dmf at 0.025 mM, 0.5 mM and 5 mM concentrations were prepared. Solutions of palladium(II) acetate in dmf at the above concentrations were prepared 20 h before use.

General Procedure for the Mizoroki–Heck Reaction: 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 bis(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 (0.00005 mol-%, 20 μL from a 0.25 mM solution) was added. The solution was heated at 120 °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 with $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was removed, 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 to the mixture. The 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 with $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was removed, diluted with EtOAc (1.5 mL), and analysed by GC.

Structure Determinations: Full spheres of CCD area-detector diffractometer data were measured (monochromatic Mo-K_α radiation; λ = 0.7107$_3$ Å, ω-scans; $T \approx 100$ K), yielding $N_{t(otal)}$ reflections, these merging to N independent (R_{int} cited) after "empirical"/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ being considered "observed". All 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.[16] Pertinent results are presented 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. Individual diversions in procedure are noted below under "Variata". CCDC-682587 (for *cis*-**3a**), -682588 (for *cis*-**3b**), -685568 (for *trans*-**3a**), -685569 (for *trans*-**3b**), -682590 (for **4a**), -682589 (for **4b**), -682591 (for *cis*-**5a**), -682592 (for *cis*-**5b**), -682593 (for *trans*-**6a**), -682594 (for *trans*-**6b**), -711286 (for *trans*-**8a**), and -711285 (for *trans*-**8b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Variata. ***cis*-3a:** The $CHCl_3$ molecule of solvation is disposed about a site of *mm* symmetry, the carbon atom being disordered to either side of one of the mirror planes. The C_2PdI_2 array lies in the x = 0.5 mirror plane (Pd on a site of *mm* symmetry), with the aromatic plane of the ligand lying at an angle of 83.5(2)° to it, generating a pair of components, occupancy 0.5, close to, but disordered about, the other mirror plane. The terminal methyl group of one of the butoxy substituents is further disordered over a pair of sites, occupancies 0.25. Attempts to model the structure in terms of lower-symmetry space groups were unsuccessful. ***cis*-3b:** Data were measured at 200 K, the crystals degrading at a lower temperature. ***trans*-3b:** One of the iodine atoms [I(1)] was modeled as disordered over a pair of sites 0.647(3) Å apart; disorder was not resolvable in other nearby atoms. Disorder (seemingly concerted) was also resolved in the periphery of one butyl chain, site occupancies refining to 0.822(2) (major component) and complement. **4a:** The molecule is disposed about a site of symmetry 2/*m*; the *n*Bu group is disordered over two sets of sites, occupancies set at 0.5 after trial refinement. The solvent molecule was modeled as a pair of superimposed components disposed about a 2/*m* site, occupancies 0.5. **4b:** Data were acquired at 300 K, the sample degrading at lower temperatures; even so, the material diffracted poorly, data supporting meaningful anisotropic displacement parameter refinement for Pd, I only. ***cis*-5a:** Displacement parameters at the peripheries of the butoxy substituents were large, but disordered components could not be resolved. ***trans*-6a:** Displacement parameters on one of the butoxy substituents of molecule 1 were elevated, but no disorder was resolvable. Solvation was modelled in terms of $CHCl_3$, disordered about an inversion centre, site occupancy refining to 0.393(8). ***trans*-6b:** x_{abs} refined to 0.002(7).

Supporting Information (see footnote on the first page of this article): Discussion and figures for structures of *cis*-**3a**, *cis*-**3b**, *trans*-**3a**, *trans*-**3b**, **4a**, **4b**, *cis*-**5a**, *cis*-**5b**, *trans*-**6a**, *trans*-**6b**, *trans*-**8a**, and *trans*-**8b** and table of selected structural parameters for *trans*-**8a** and *trans*-**8b**.

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