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Synthesis and Characterisation of Mono- and Bidentate Alkoxybenzimidazolin-2-ylidene Palladium Complexes: Interesting Solution Behaviour and Application in Catalysis

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New mono- and bidentate N-heterocyclic carbene (NHC) silver and palladium complexes bearing benzimidazolin-2-ylidene ligands have been synthesized and structurally and spectroscopically characterised. The NHC ligands are decorated with bulky substituents on the nitrogen atoms and electron-donating butoxy groups on the benzo-fused ring, with the aim of enhancing the ability of their complexes as catalysts. The two types of palladium complexes presented, which possess either a bidentate bis(NHC) or a mixed NHC/allyl ligand system, demonstrate significantly different activities in the Mizoroki–Heck cross-coupling reactions but similar activities in the Suzuki–Miyaura and Buchwald–Hartwig reactions. Interesting behaviour of the mixed NHC/allyl palladium complexes in solution has been investigated.

Introduction

Since their initial use by Herrmann and co-workers,[1] N-heterocyclic carbene (NHC) metal complexes have become ubiquitous in the field of homogeneous catalysis, often proving more robust and of equal or greater activity than analogous phosphane-based catalysts. The drive to enhance the activity of NHC metal complexes as catalysts has led researchers to synthesize a huge library of complexes containing NHC ligands based on imidazole and benzimidazole, with variations including mono- and poly-ligating NHCs, pincer NHCs, and mixed-donor systems.[2,3] NHCs are used extensively as ligands in complexes of palladium, platinum, nickel, rhodium, and ruthenium, examples of which display high activity in promoting numerous cross-coupling reactions such as C–C and C–N bond forming reactions, olefin metathesis, and hydrosilylation reactions.[3,4] A greater knowledge of the mechanism of the catalytic cycle in specific cross-coupling reactions has facilitated the rational design of NHCs as ligands in metal complexes. By increasing the steric bulk or electron density around the metal centre, the rates of both reductive elimination and oxidative addition can often be enhanced, and understanding the effects of these structural changes has allowed more active catalysts to be devised.[5]

In this paper we report the synthesis and characterisation of some benzimidazolium salts and silver and palladium NHC complexes of the types (NHC)AgX, (NHC)(allyl)PdX, and bis(NHC)PdX_2, [where bis(NHC) refers to a bidentate ligand coordinating through two NHC groups]. The benzimidazolium salts and silver complexes were synthesized in high yields by established methods, and served as precursors to the palladium complexes. The bidentate NHCs consist of benzimidazolin-2-ylidene units that are linked by one *o*-xylyene group, and generally bind to the metal centre in a rigid fashion.[6,7] The benzimidazolin-2-ylidene units possess bulky substituents on the nitrogen atoms and electron donating butoxy groups on the arene ring, the latter which also serve to increase the solubility of the complexes in common organic solvents. We have previously reported the use of similar electron-rich benzimidazolin-2-ylidenes as ligands in a range of palladium complexes of mono- and bidentate NHC ligands possessing phosphane or pyridine ancillary ligands,[8,9] and are interested in extending this investigation by studying the differences in catalytic activity between the bis(NHC)PdX_2 and (NHC)Pd(allyl)X systems. The palladium complexes were evaluated as catalysts for the Mizoroki–Heck, Suzuki–Miyaura and Buchwald–Hartwig cross-coupling reactions.

Results and Discussion

Synthesis of Complexes

1-Benzyl- and 1-benzhydryl-5,6-dibutoxybenzimidazole (**1a** and **1b**) were prepared from 5,6-dibutoxybenzimidazole.[10] 1,3-Dibenzyl-5,6-dibutoxybenzimidazolium chloride (**2a**) was prepared in excellent yield (94%) by alkylation

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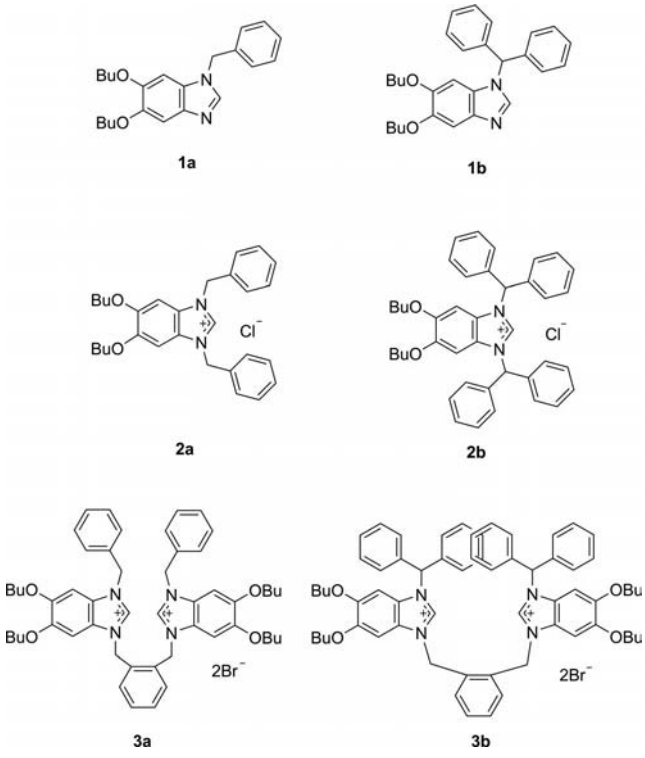
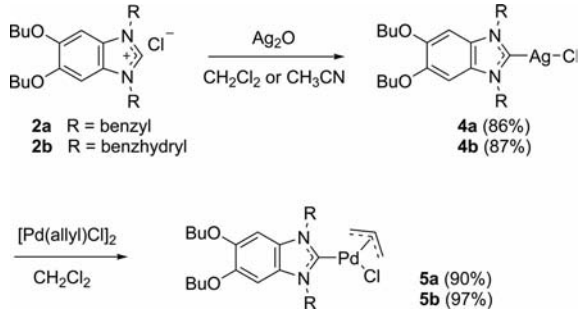
of **1a** with benzyl chloride, while 1,3-dibenzhydryl-5,6-dibutoxybenzimidazolium chloride (**2b**) was prepared in more modest yield (37%) in one pot from 5,6-dibutoxybenzimidazole, diphenylchloromethane and NaOH. The bis(benzimidazolium) salts **3a** and **3b** were prepared in high yields (78% and 83%, respectively) by the reaction of α,α′-dibromo-*o*-xylene with **1a** and **1b**, respectively. The benzimidazolium salts **2a**,**b** and **3a**,**b** are slightly hygroscopic and readily soluble in most common organic solvents (DMSO, dmf, CH_3CN, CH_2Cl_2, $CHCl_3$, EtOAc, MeOH and acetone).

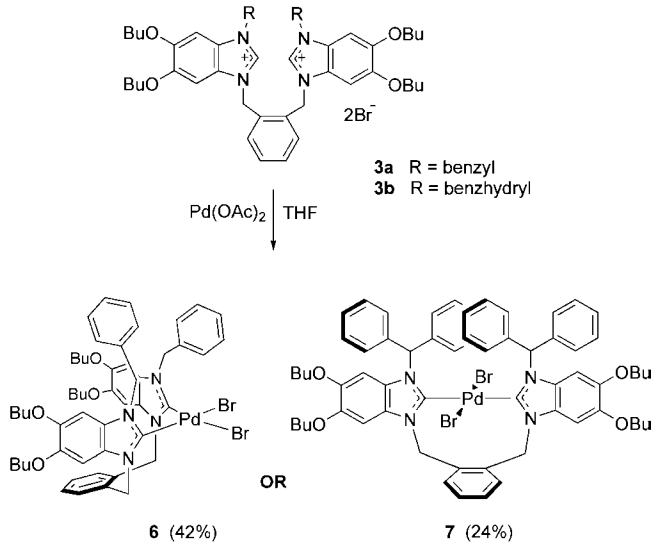


The benzimidazolium salts **2a**,**b** and **3a**,**b** were used to prepare a series of silver(I) and palladium(II) complexes, including the (NHC)AgCl complexes **4a**,**b**, the (NHC)-(allyl)PdCl complexes **5a**,**b** and the bis(NHC)$PdBr_2$ complexes **6** and **7** (Scheme 1 and Scheme 2). We were interested in comparing the catalytic activities of the bis(NHC)$PdBr_2$ complexes to those of the (NHC)(allyl)PdCl complexes, the latter being based on the extremely active systems developed by Nolan and co-workers.[11]

The silver complex **4a** was synthesized by the treatment of **2a** with Ag_2O in CH_2Cl_2 for three days at room temperature, and was subsequently isolated in an 86% yield. The silver complex **4b**, however, was prepared by the treatment of **2b** with Ag_2O in CH_3CN at 70 °C for four days, and isolated in an 87% yield after recrystallisation from acetone/diethyl ether. Many Ag–NHC complexes can be synthesized by the reaction of Ag_2O with an azolium salt in CH_2Cl_2 at room temperature, but all attempts to prepare **4b** in CH_2Cl_2 at room temperature resulted in significantly lower yields. Both **4a** and **4b** exhibit excellent solubilities in CH_2Cl_2, $CHCl_3$, CH_3CN and acetone.



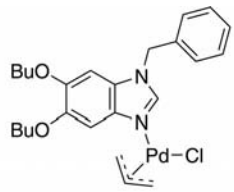
Scheme 1. Synthesis of NHC-silver (**4a**,**4b**) and NHC-palladium (**5a**,**5b**) complexes.



Scheme 2. Synthesis of bis(NHC)-palladium complexes **6** and **7**.

Following the procedure outlined by Nolan and co-workers,[11] the (NHC)(allyl)PdCl complexes **5a** and **5b** were prepared by reacting two equivalents of the appropriate silver complex (**4a**, **4b**) with $[\{Pd(\eta^3\text{-}C_3H_5)Cl(\mu\text{-}Cl)\}_2]$ in CH_2Cl_2, and were isolated in yields of 90 and 97%, respectively. Both **5a** and **5b** are air-stable in the solid state but mildly air-sensitive in solution. They are very soluble in halogenated solvents such as CH_2Cl_2 and $CHCl_3$, but also soluble, to a lesser extent, in toluene, benzene and THF.

Initial attempts to synthesize **5a** via treatment of **2a** with *t*BuOK or KH in THF (to generate the corresponding free carbene) followed by addition of $[\{Pd(\eta^3\text{-}C_3H_5)Cl(\mu\text{-}Cl)\}_2]$ were not satisfying, resulting in dark mixtures and palladium black. In these experiments, the benzimidazole-Pd-(allyl) complex **8** (formed in trace amounts) was the only identifiable product, and its structure was elucidated by single-crystal X-ray diffraction. Presumably, **2a** decomposes to **1a** and other compounds under the reaction conditions, and **1a** in turn reacts with $[\{Pd(\eta^3\text{-}C_3H_5)Cl(\mu\text{-}Cl)\}_2]$ to form **8**. This result is not surprising, as the loss of a benzyl group from *N*-benzyl azolium salts upon treatment with a strong base such as NaH has been previously reported,[12] as has the migration of a benzyl group from the nitrogen atom to the carbene carbon.[13]



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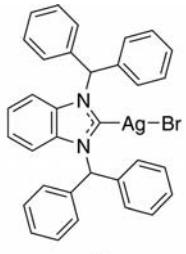
The bis(NHC)$PdBr_2$ complexes **6** and **7** were obtained as white and yellow solids in 42 and 24%, respectively, by the reaction of **3a** and **3b** with $Pd(OAc)_2$ in refluxing THF, and were purified by recrystallisation (**6**) or rapid silica-gel filtration (**7**). Complex mixtures were formed when CH_3CN or toluene were used as the reaction solvent in attempts to synthesize of **7**. Both **6** and **7** are air-stable solids, readily soluble in CH_2Cl_2, $CHCl_3$, DMSO, and dmf, and sparingly soluble in CH_3CN and acetone.

NMR Studies

^1H and ^{13}C NMR spectra of the new complexes were consistent with the structures proposed above. A ^{13}C NMR signal for the carbene carbon in **4a** was not observed, presumably due to the labile nature of the silver-carbon bond.[14] The absence of this signal suggests that **4a** exists in rapid equilibrium with species of the type $[L_2Ag][AgCl_2]$, and similar behaviour has been identified previously for other Ag complexes of benzimidazolin-2-ylidenes.[15] The ^{13}C NMR spectrum of **4b** in $CDCl_3$ solution shows distinct signals for the carbene carbon, however, suggesting that the steric bulk associated with the benzhydryl groups prohibits the formation of $[L_2Ag][AgCl_2]$ in this case. In the ^{13}C NMR spectrum in $CDCl_3$ solution, **4b** shows two doublets near δ = 188.5 ppm attributed to Ag–C carbons, with $^1J_{Ag,C}$ values of 233 and 269 Hz for ^{107}Ag–C and ^{109}Ag–C, respectively, which are higher than previously reported silver-NHC complexes.[14,16] The chemical shift of the carbene carbon is similar to that seen for the "non-butoxy" silver bromide analogue **9** prepared by Huynh and co-workers,[17] but they did not observe any silver-carbon coupling in $CDCl_3$, reporting only a broad singlet.



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The ^1H NMR spectra of **5a** showed interesting temperature dependence that can be interpreted in terms of processes involving rotation about the Pd–$C_{carbene}$ bond and isomerisation of the allyl ligand. At 233 K, the benzylic CH_2 protons appeared as four doublets, and the two protons attached to the benzimidazolyl group appeared as two separate singlets, consistent with a situation where the Pd-allyl bonding is rigid and there is no rotation about the Pd–$C_{carbene}$ bond on the NMR timescale. Changes that occur to the signals of the benzylic protons as the sample is warmed to 328 K (Figure 1), can be interpreted in terms of rotation of the NHC ligand about the Pd–$C_{carbene}$ bond axis occurring rapidly on the NMR timescale, a process that would render the benzylic CH_2 groups equivalent and the benzimidazole protons equivalent, but maintain chemically distinct environments for the two protons within each benzylic CH_2 group. Further changes that occur to the signals of the benzylic protons, and changes that occur in the signals due to the protons of the allyl ligand, as the sample is warmed to 373 K (Figure 2) can be attributed to an isomerisation of the π-allyl ligand that occurs via a σ-allyl intermediate (Figure 3). This phenomenon has previously been described by Pörschke and co-workers in their studies of allyl Pd adducts with phosphanes,[18] and similar fluxional behaviour was recently reported for a mixed NHC/allyl palladium complex.[19] The formation of a σ-allyl intermediate bonded to Pd via C^3 (Figure 3) is consistent with the greater *trans* influence of the NHC compared to the chloride ligand. Stronger bonding between Pd and C^3 (*trans* to Cl) compared to C^1 (*trans* to the NHC) is also suggested by the shorter Pd–C^3 bond length seen in the solid state (see Structure determinations).

The ^1H NMR spectrum of a solution of **5b** in CD_2Cl_2 at room temperature shows broad signals for the aromatic and -OCH_2- groups, as well as two broad peaks at δ = 8.05 and 7.79 *ppm* corresponding to the two benzhydryl methine protons. The broadness is due in part to restricted rotation about the Pd–$C_{carbene}$ bond caused by the bulk of the two benzhydryl substituents, which renders the "top" and "bottom" of the NHC ligand chemically inequivalent.[20] The change in the chemical shift in the methine protons in **5b** (7.79, 8.05 ppm, CD_2Cl_2) relative to **2b** (δ =7.71 ppm, CD_2Cl_2) may be a consequence of short C–H···Pd distances (2.901 and 2.692 Å, see chapter Structure Determinations) that lead to agostic interactions and a subsequent downfield shift in the ^1H NMR spectrum.[21] To explore the dynamics of **5b**, a solution of the complex in $[D_8]$THF was studied by variable temperature ^1H NMR spectroscopy (Figure 4). Upon cooling of the sample to 233 K, significant sharpening of all the resonances associated with the NHC ligand occurred, and a sharp signal was present for each of the benzhydryl methine protons (*ca.* δ = 8 ppm) and each proton on the benzimidazolyl skeleton (ca. δ = 6.25 ppm). The -OCH_2- protons appeared as four distinct signals (one for each diastereotopic proton), while the signals for protons associated with the allyl group do not change upon cooling of the sample.

At elevated temperatures (ca. 333 K), the signals associated with the benzhydryl methine and benzimidazole protons were seen as broad and sharp singlets, respectively, and the –OCH_2- protons appeared as a single apparent triplet. As in the case of **5a**, as the temperature was raised, the signals for the two most upfield allyl protons (H^3 and $H^{3'}$, δ = 1.15 and 2.25 ppm at 233 K, Figure 4) were significantly broadened, but the signals for the other protons of the allyl

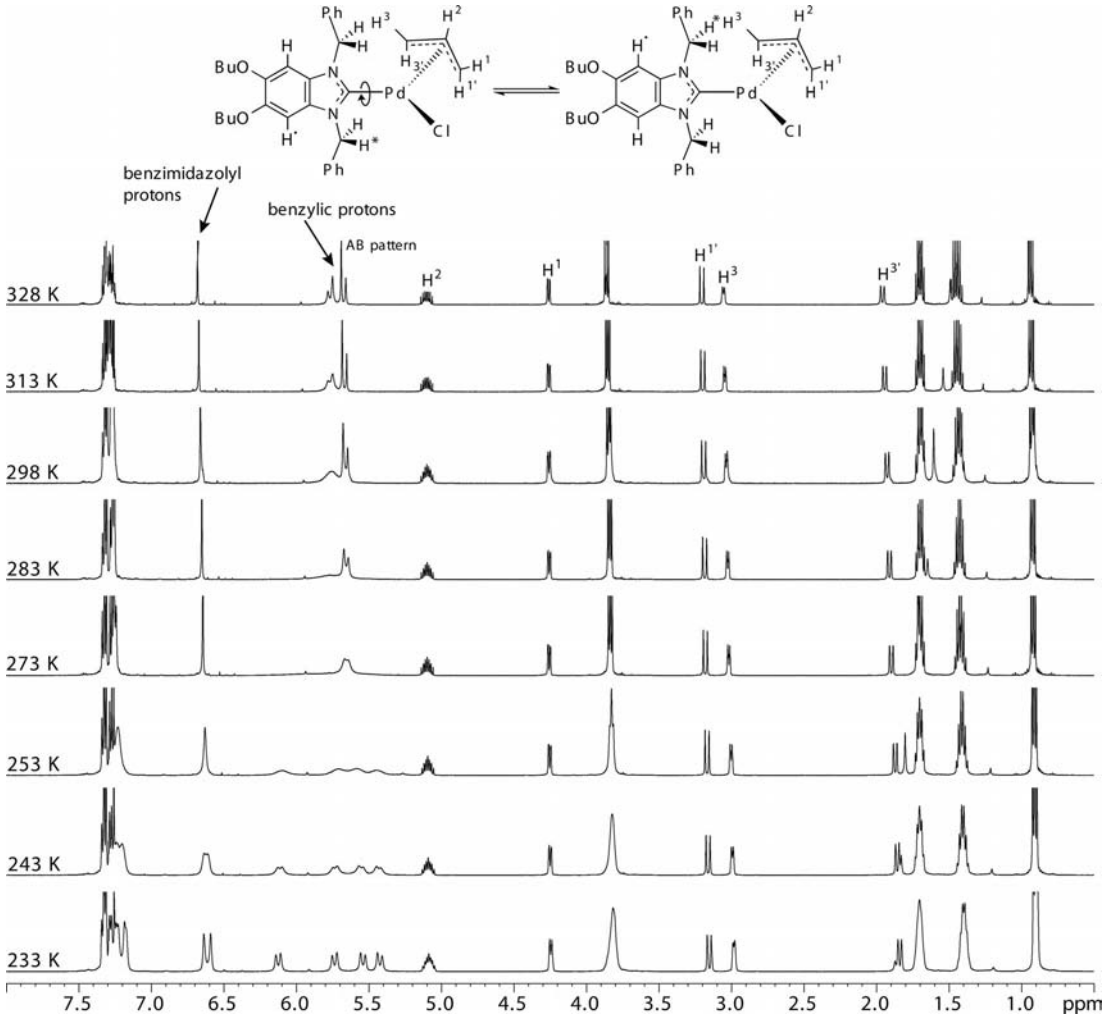


Figure 1. Variable temperature ^{1}H NMR spectrum (500.13 MHz) of **5a** in $CDCl_3$.

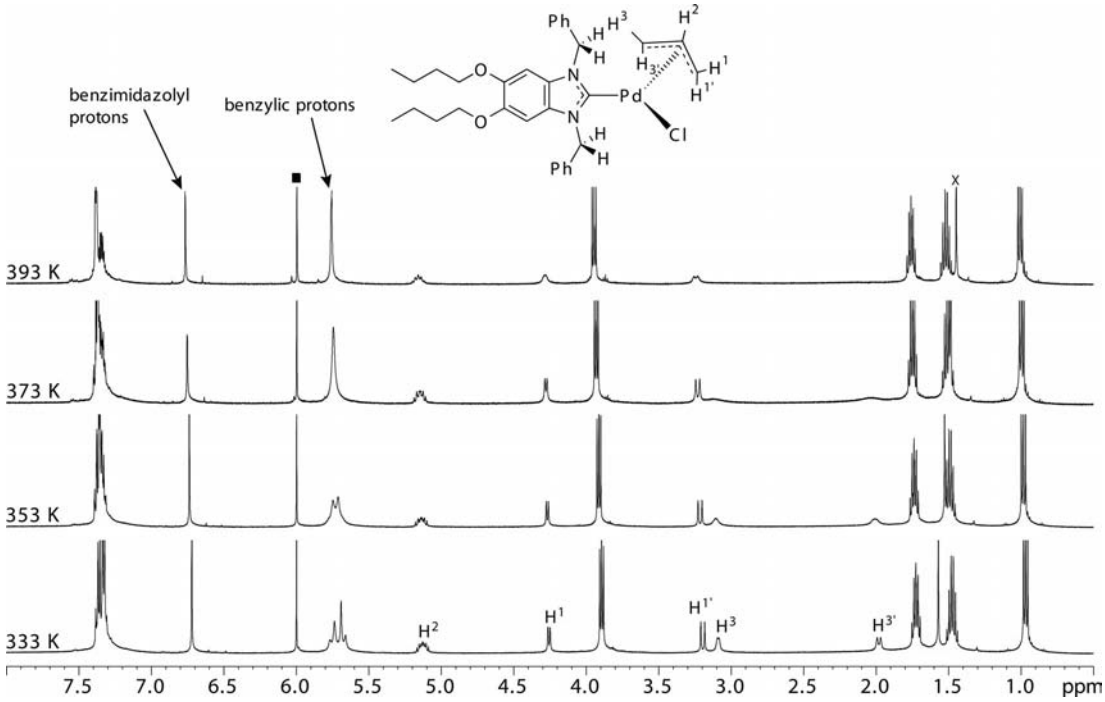


Figure 2. Variable temperature ^{1}H NMR spectrum (500.13 MHz) of **5a** in $C_2D_2Cl_4$ (× = H_2O, ■ = $C_2H_2Cl_4$).

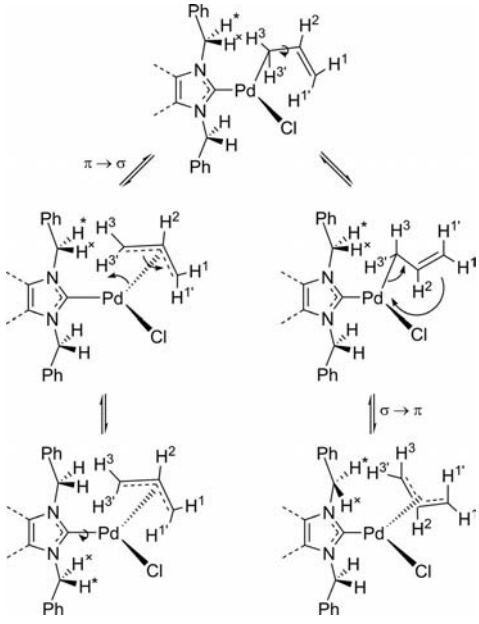
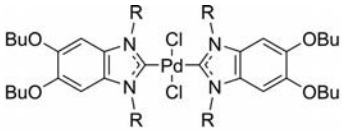


Figure 3. π-σ isomerisation and Pd–C rotation in **5a**.

group remained sharp. Again, these results are consistent with operation of a process in which the allyl group exchanges between σ- and π-bound forms, which in turn results in higher apparent symmetry for the NHC ligand.

The ^{13}C NMR spectra of $CDCl_3$ solutions containing **5a** and **5b** showed signals attributed to the carbene carbon at δ = 190.5 and 193.5 ppm, respectively, which are similar to the chemical shift values reported by Nolan and co-workers for (NHC)(allyl)PdCl complexes based on imidazole.[11] After **5a** and **5b** were kept in $CDCl_3$ solution for several days, a fine black precipitate (presumably colloidal palladium) formed, and NMR spectra indicated that the complexes had undergone some decomposition. The ^{13}C NMR spectra of these solutions containing **5a** and **5b** showed new signals, including signals at δ = 179.2 and 182.4 ppm, respectively. These new signals are in the range consistent with *trans*-$(NHC)_2PdL_2$ complexes,[8,22] and are presumably due to **10a** and **10b**, which it is reasonable to expect would arise during decomposition of **5a** and **5b**.



10a R = benzyl
10b R = benzhydryl

The ^1H and ^{13}C NMR spectra of **6** and **7** are consistent with palladium complexes bearing NHC ligands linked by an *o*-xylyene group in mutually *cis* and *trans* arrangements, respectively.[9] The ^1H NMR spectra show a pair of doublets at δ = 6.30 and 7.10 ppm (**6**), and δ = 5.72 and 6.79 ppm (**7**), which are attributed to the diastereotopic xylyene benzylic protons (*endo* and *exo* environments) characteristic of *o*-xylyene-linked bis(NHC)Pd^{II} complexes.[7] The signals associated with the carbene carbons for **6** and **7** are seen at δ = 171.1 and 184.3 ppm, respectively, values which fall in the range expected for *cis*- and *trans*-bis(NHC)PdL_2 complexes of this type.[9,22,23] The symmetry of **7** dictates that the two phenyl groups in each benzhydryl substituent are diastereotopic due to their different positions relative to the

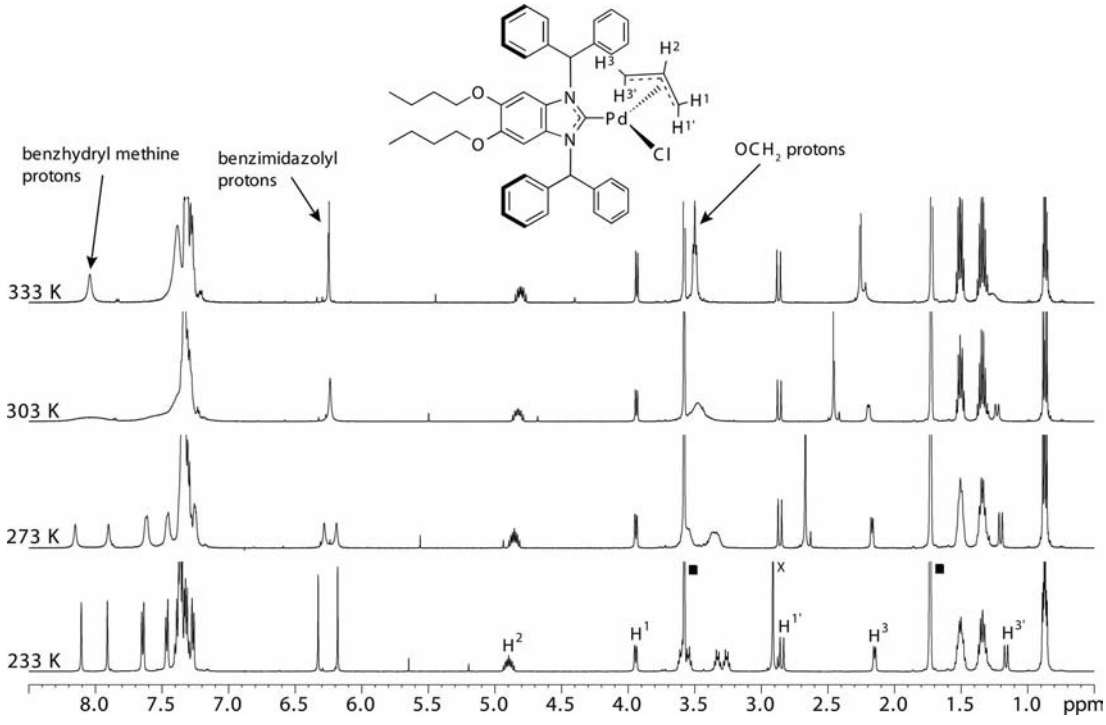


Figure 4. Variable temperature ^1H NMR spectrum (500.13 MHz) of **5b** in [D_8]THF (× = H_2O, ■ = THF).

xylyene ring. The phenyl groups therefore give rise to two sets of signals in the ^{1}H and ^{13}C NMR spectra.

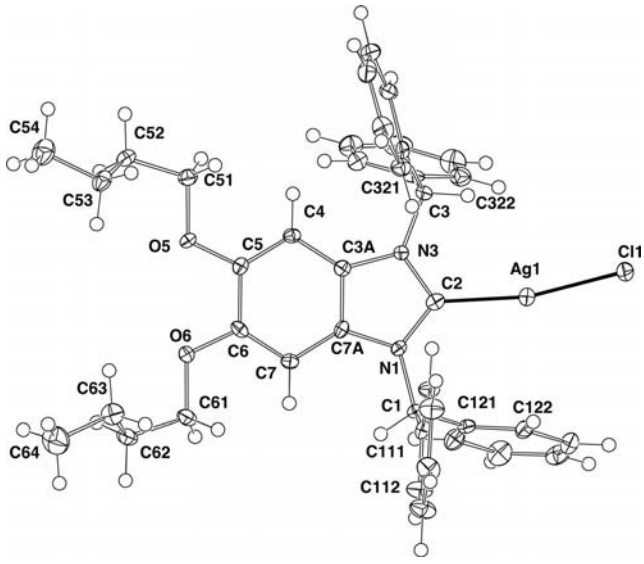


Figure 5. Projection of a molecule of **4b**, showing the *anti* conformation of the benzhydryl groups.

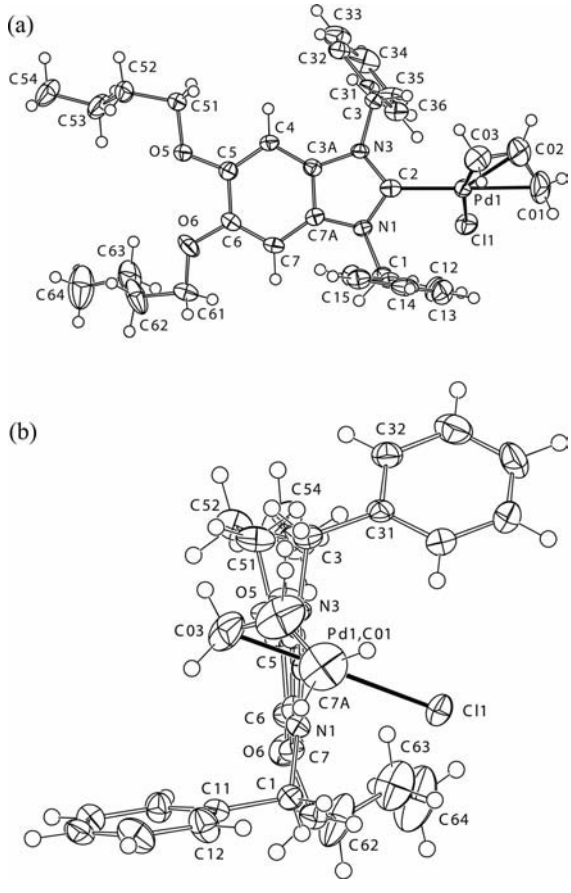


Figure 6. Projections of a molecule of **5a** (a) perpendicular to the benzimidazolyl plane (b) along the Pd–$C_{carbene}$ bond, showing the *anti* conformation of the benzyl groups. Minor components of the disordered atoms have been omitted.

Structure Determinations

The results of the single-crystal X-ray studies of **2b** (Figure S1), and **4–8** (see Figures 5, 6, 7, 8, 9, and 10; Tables 1, 2, 3, and 4) support the proposed formulations, with **2b**, **6**, **7**, and **8** solvated in some manner. Compound **2b** crystallised with one molecule of $CHCl_3$ per formula unit. The phenyl rings of the benzhydryl units point away from the butoxy substituents, presumably adopting the less sterically hindered conformation. There was no indication of hydrogen bonding interactions between H2 and the chloride ion, such interaction presumably being precluded by the bulky benzhydryl substituents.

In **4a**, the coordination around the Ag atom is almost linear (C2–Ag–Cl 179.01(10)°], with a Ag–C2 bond length of 2.081(3) Å. The benzyl groups are disposed *syn* to each other, with the rotational axes of the phenyl groups pointing approximately perpendicular to the benzimidazolyl plane. The molecules pack in approximately co-planar pairs parallel to the (101) plane in the unit cell. In **4b** the benzhydryl groups are disposed *anti* to each other (Fig-

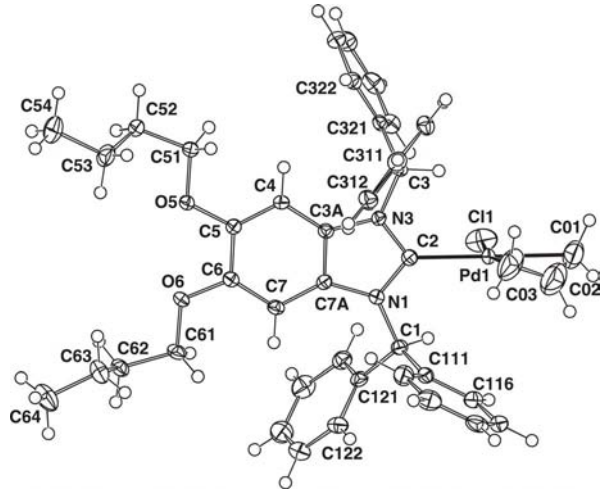


Figure 7. Projection of a molecule of **5b** perpendicular to the benzimidazolyl plane. Minor components of the disordered atoms have been omitted.

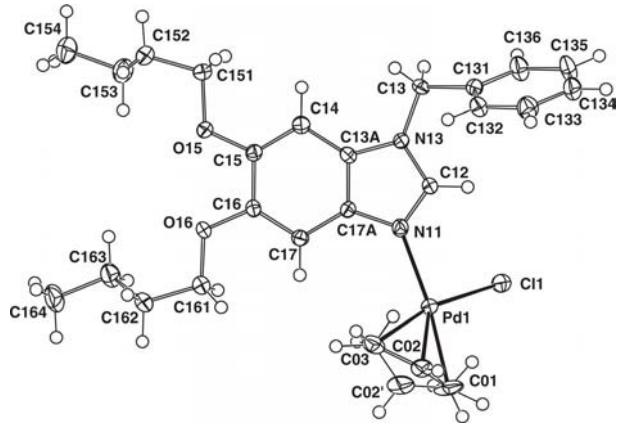


Figure 8. Projection of a molecule of **8** perpendicular to the benzimidazolyl plane.

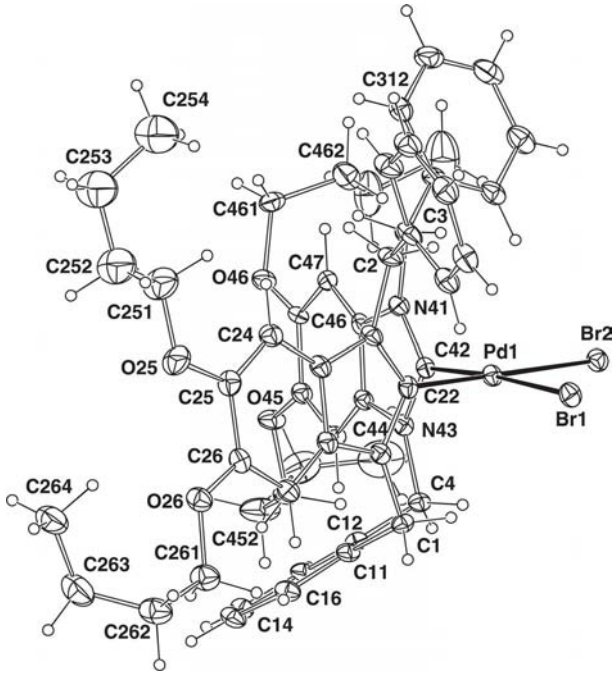


Figure 9. Projection of a molecule of **6**. Only one component of each of the disordered groups is shown.

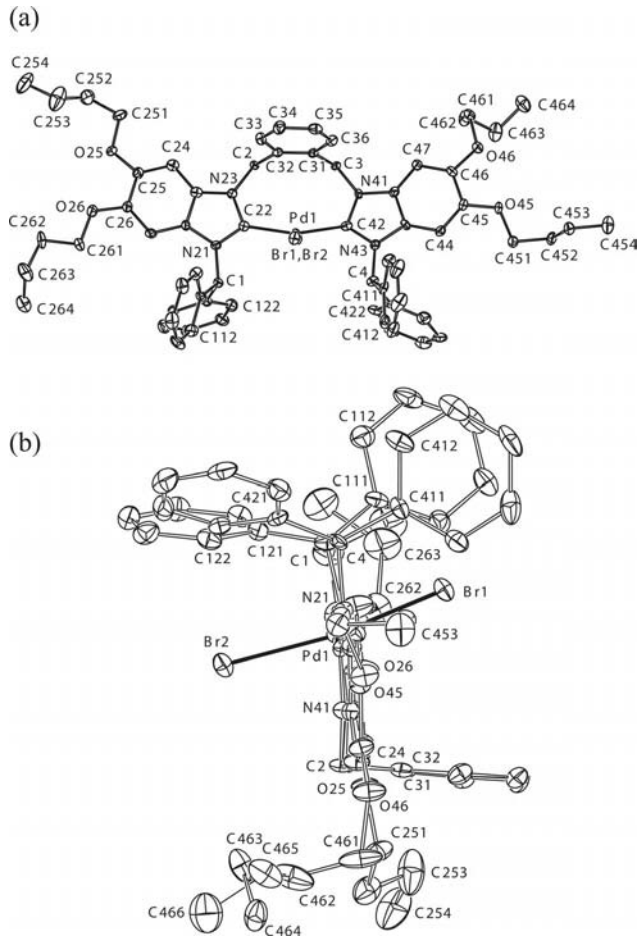


Figure 10. Projections of a molecule of **7** (a) perpendicular to the benzimidazolyl plane (b) down the benzimidazolyl plane (hydrogen atoms omitted for clarity).

Table 1. Selected bond lengths and angles for **5a**, **5b** and **8**.

	5a	**5b**	**8**
Distances [Å]			
Pd–C(2)	2.025(2)	2.025(2)	–
Pd–N(11)	–	–	2.109(2)
Pd–Cl(1)	2.3679(6)	2.3689(9)	2.3774(7)
Pd–C(01)	2.186(3)	2.176(3)	2.113(3)
Pd–C(02)	2.132(4)	2.110(4)	2.078(4)
Pd–C(03)	2.092(3)	2.090(4)	2.123(3)
Angles [°]			
C(2)–Pd–C(01)	168.75(12)	170.82(13)	–
C(2)–Pd–C(03)	101.10(11)	100.68(12)	–
C(2)–Pd–Cl(1)	92.21(6)	90.74(6)	–
N(11)–Pd–C(01)	–	–	168.81(11)
N(11)–Pd–C(03)	–	–	100.73(10)
N(11)–Pd–Cl(1)	–	–	91.93(6)
Interplanar dihedral angles			
C_3Cl/C_7N_2	69.53(6)	79.00(6)	–
C_2NCl/C_7N_2	–	–	44.28(6)

Table 2. Selected bond lengths and angles for **6** and **11**.[9]

	6	**11**
Distances [Å]		
Pd–C(22)	1.969(5)	1.972(9)
Pd–C(42)	1.982(5)	1.943(10)
Pd–Br(1)	2.4889(7)	2.4840(13)
Pd–Br(2)	2.4946(7)	2.4772(13)
H(13)···H(44), H(16)···H(27)	2.16, 2.21	2.27, 2.26
Angles [°]		
C(22)–Pd–C(42)	91.0(2)	85.7(4)
C(22)–Pd–Br(1)	86.13(15)	88.4(3)
C(42)–Pd–Br(1)	175.23(15)	173.0(3)
C(22)–Pd–Br(2)	179.23(17)	175.6(3)
C(42)–Pd–Br(2)	88.25(15)	90.1(3)
Br(1)–Pd–Br(2)	94.64(2)	95.94(5)
Interplanar dihedral angles		
C_2Br_2/C_7N_2	83.7(1), 88.7(1)	80.9(2), 82.6(2)
C_2Br_2/C_6	29.7(2)	46.5(3)

Table 3. Selected bond lengths and angles for **7**, **12**[9] and **13**.[24] For **7** and **12**, X = Br, for **13** X = Cl.

	7	**12**	**13**
Distances [Å]			
Pd–C(22)	2.008(4)	1.988(8)	1.976(17)
Pd–C(42)	1.997(5)	2.003(8)	2.043(17)
Pd–X(1)	2.4585(5)	2.4472(12)	2.286(4)
Pd–X(2)	2.4457(5)	2.4306(12)	2.352(4)
Angles [°]			
C(22)–Pd–C(42)	163.37(17)	163.4(3)	163.6(7)
C(22)–Pd–X(1)	89.79(11)	91.3(2)	90.1(4)
C(42)–Pd–X(1)	91.52(12)	91.8(2)	89.3(4)
C(22)–Pd–X(2)	90.86(11)	89.2(2)	90.6(4)
C(42)–Pd–X(2)	90.18(12)	89.5(2)	90.8(4)
X(1)–Pd–X(2)	171.87(2)	173.81(5)	176.85(16)
Interplanar dihedral angles			
C_2X_2/C_7N_2	75.70(9), 73.35(9)	77.5(2), 79.4(2)	75.6(6), 73.9(5)
C_2X_2/C_6	23.0(1)	23.2(2)	30.3(5)

Table 4. Crystal data and refinement details.

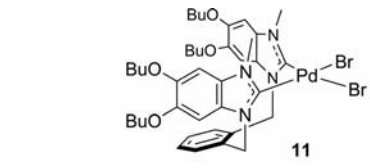
	2b	**4a**	**4b**	**5a**
Formula	$C_{42}H_{44}Cl_4N_2O_2$	$C_{29}H_{34}AgClN_2O_2$	$C_{41}H_{42}AgClN_2O_2$	$C_{32}H_{39}ClN_2O_2Pd$
M_r/[Da]	750.6	585.9	738.1	625.5
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	Cc	Pn	$P2_12_12_1$
a [Å]	10.5256(3)	13.5671(6)	11.9672(3)	9.8548(4)
b [Å]	24.5173(12)	19.6249(4)	10.4827(2)	12.4971(3)
c [Å]	15.3179(8)	10.2032(3)	14.2554(3)	24.2395(7)
α [°]				
β [°]	96.195(4)	103.686(3)	93.848(2)	
γ [°]				
V [Å^3]	3929.8(3)	2639.50(15)	1784.29(7)	2985.25(17)
ρ_c [g cm^{-3}]	1.269	1.474	1.374	1.392
Z	4	4	2	4
μ [mm^{-1}]	0.34	0.89	0.68	0.74
Specimen [mm]	0.28, 0.24, 0.17	0.23, 0.12, 0.12	0.36, 0.15, 0.07	0.26, 0.12, 0.09
Absorption (min./max.)	0.98	0.94	0.97	0.93
$2\theta_{max}$ [°]	58	70	64	65
Reflections collected	44267	50134	24841	38471
Unique reflections (R_{int})	10442 (0.053)	11575 (0.152)	10721 (0.045)	10115 (0.044)
Reflections [$I > 2\sigma(I)$]	6218	8909	8418	6977
$R1$ [$I > 2\sigma(I)$]	0.057	0.058	0.038	0.035
$wR2$ (all data)	0.146	0.103	0.062	0.071
	5b	**6**	**7**	**8**
Formula	$C_{44}H_{47}ClN_2O_2Pd$	$C_{52}H_{62}Br_2N_4O_4Pd\cdot(DMSO/H_2O)$	$C_{64}H_{70}Br_2N_4O_4Pd\cdot$(acetone)	$C_{25}H_{33}ClN_2O_2Pd\cdot CHCl_3$
M_r/[Da]	777.7	1169.4	1283.5	654.7
Crystal system	monoclinic	rhombohedral	monoclinic	triclinic
Space group	$P2_1/n$	$R\bar{3}$	Cc	$P\bar{1}$
a [Å]	15.5225(3)	33.5801(7)	32.0671(9)	8.0831(3)
b [Å]	15.7312(3)	33.5801(7)	11.9073(3)	11.0948(3)
c [Å]	16.0734(4)	25.6310(3)	15.8798(3)	16.0976(8)
α [°]				100.847(3)
β [°]	104.814(2)		91.779(2)	90.638(3)
γ [°]		120		96.203(2)
V [Å^3]	3794.46(14)	25030.0(8)	6060.5(3)	1408.81(10)
ρ_c [g cm^{-3}]	1.361	1.396	1.407	1.543
Z	4	18	4	2
μ [mm^{-1}]	0.60	5.12	1.68	1.06
Specimen [mm]	0.35, 0.29, 0.15	0.25, 0.03, 0.02	0.51, 0.09, 0.08	0.21, 0.10, 0.05
Absorption (min./max.)	0.98	0.87	0.90	0.92
$2\theta_{max}$ [°]	64	134	65	71
Reflections collected	45019	47606	38712	27474
Unique reflections (R_{int})	12691 (0.042)	9777 (0.070)	17649 (0.062)	11843 (0.056)
Reflections [$I > 2\sigma(I)$]	8179	6911	11809	7040
$R1$ [$I > 2\sigma(I)$]	0.050	0.058	0.041	0.046
$wR2$ (all data)	0.122	0.176	0.110	0.121

ure 5), one with its methine proton oriented towards the Ag centre, the other with the two phenyl groups oriented towards the Ag centre. A similar orientation has been observed in the non-butoxy-functionalised silver bromide analogue **9**.[17] The Ag–Cl unit is bent away from the closest phenyl group, resulting in a C2–Ag–Cl angle of 166.08(7)° (cf. 170.81(13)° for **9**). The Ag–C2 bond lengths for **4b** and **9** are indistinguishable (2.081(3) and 2.081(5) Å, respectively).

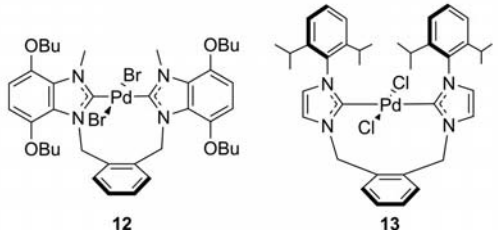
In **5a**, the phenyl rings of the benzyl units are disposed *anti* to one another (Figure 6), with the rotational axes of the phenyl groups oriented approximately perpendicular to the plane of the benzimidazolyl skeleton. The dihedral angle between the coordination plane and the benzimidazolyl ring plane is 69.53(6)°, significantly deviated from the perpendicular, and may be due to the minimisation of steric effects between the benzyl and η^3-allyl groups. In **5b**, the benzhydryl groups are orientated so that the methine hydrogen atoms point approximately toward the palladium centre, thus minimising steric effects with the η^3-allyl group (Figure 7). This geometry causes relatively short contacts of 2.903 and 2.691 Å between the benzhydryl methine protons and the palladium centre, which may lead to agostic interactions, as suggested by ^{1}H NMR studies. The angle between the Pd coordination plane and the benzimidazolyl units is in **5b** is 79.00(6)°, again presumably due to minimisation of

steric effects between the benzyl and η^3-allyl groups. In the Pd-allyl moiety, the Pd–C(03) bond lengths (**5a**, 2.092(3) Å; **5b**, 2.090(4) Å] are shorter than Pd–C(01) (**5a**, 2.186(3) Å; **5b**, 2.176(3) Å], presumably due to the stronger *trans* effect of the NHC compared to Cl. In complex **8**, the palladium is bound to the nitrogen atom of the benzimidazole ring with a Pd–N bond length of 2.109(2) Å (Figure 8). The Pd–C(01) and Pd–C(03) bond length are 2.113(3) and 2.123(3) Å, respectively, which suggests a smaller *trans* influence of the *N*-bound benzimidazolyl ligand cf. the NHCs in **5a** and **5b**. The angle between the coordination plane containing Cl1, N11, C1 and C3 and the plane of the benzimidazole ligand is 44.28(6)°.

The structure of **6** provides a further insight into the geometry of *o*-xylyene-linked bis(NHC)-Pd^{II} complexes possessing butoxy groups on the benzimidazolyl skeleton, a class of compounds that we have reported previously.[9] In **6**, the bulk of the benzyl groups results in a relatively large NHC-Pd-NHC "bite" angle of 91.0(2)°, which allows space for the linking xylyene ring to "move up", giving a relatively small dihedral angle between the coordination and xylyene ring planes 29.7(2)° (Figure 9). This relatively "shallow" dihedral angle in **6** leads to close contacts (2.16, 2.21 Å) between the benzimidazolyl hydrogen atoms (H27, H44) and the *trans*-disposed xylyene hydrogen atoms H(13) and H(16). The notion that the N-substituents (i.e. benzyl in **6**) are largely responsible for this geometry is supported by examination of the analogous complex **11**, in which the benzyl groups have now been replaced by methyl substituents.[9] In **11**, the small methyl groups allow the NHC units to chelate the palladium atoms with a smaller "bite" angle of 85.7(4)°, which forces the xylyene ring to "move down" relative to **6**, and is reflected by a C_2Br_2/C_6 dihedral angle of 46.5(3)°[9] (Table 2). This greater dihedral angle leads to slightly longer contacts (2.27, 2.26 Å) between H7 and H(Xy), compared to **6**. Complex **6**, which crystallised with one molecule each of H_2O and DMSO, displays hydrogen bonding from the water molecule hydrogen atoms to Br2 and also to O1 of the DMSO molecule.



11



12 13

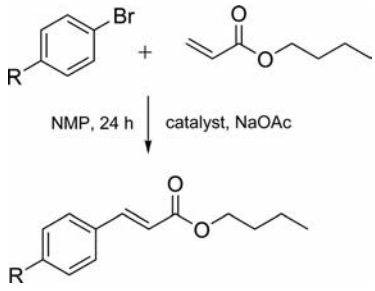
In **7**, the NHC units are disposed mutually *trans* around the palladium atom (Figure 10), which has been reported previously (**12**[9] and **13**[24]) for some *o*-xylyene-linked bis(NHC)-Pd^{II} complexes having intramolecular steric interactions. While steric interactions between the xylyene ring and the 4,7-butoxy groups force the *trans* geometry in **12**, both **7** and **13** adopt the *trans* geometry due to the bulk of the N-substituents, which prevent the NHCs adopting a mutually *cis* coordination at the palladium atom. Complex **7** displays distorted square-planar geometry around the palladium atom, tending towards tetrahedral, with C(22)–Pd–C(42) *trans* angles (ca. 163.4(2)°] that are far from linearity. This result suggests strain in the Pd-NHC bonding, a consequence of the *o*-xylyene group not being sufficiently "long" to link the two fully-*trans*-disposed NHC units. The bond lengths and angles in **7** are consistent with those in **12** and **13** (Table 3). The C_2Br_2/C_7N_2 dihedral angles in **7** (75.70(9), 73.35(9)°] deviate significantly from the perpendicular, which can be ascribed to steric repulsion between one of the bromide atoms and the xylyene ring linking the NHC units. This tilt in the coordination place, which is also observed in **12** and **13**, renders one bromide atom distinctly bent away from the plane of the arene ring, while the other bromide is free to point down. The C_6/C_2Br_2 interplanar dihedral angle in **7** is 23.0(1)°, which is consistent with **12** but considerably lower than that of **13** (30.47°).

Catalysis Studies

Complexes **5a**, **5b**, **6**, and **7** were initially tested against $Pd(OAc)_2$ as catalysts in the Mizoroki–Heck cross-coupling reaction of bromobenzene and *n*-butyl acrylate using NaOAc in NMP at 1 mol-% loading (Table 5). We have shown previously that butoxy-functionalised complexes are more active than their non-butoxy analogues, presumably due to the electron donating properties of the butoxy groups.[9] It was found that the complexes **6** and **7**, possessing the chelating bis(NHC) ligands, were the most active at 120 °C, promoting the formation of butyl cinnamate in yields of 59 and 51%, respectively (entries 6 and 8), compared to 10 and 12% for **5a** and **5b**. When the experiments were conducted at 80 °C, however, activity was greatly diminished for all complexes, with **6** and **7** promoting formation of butyl cinnamate in yields of only 35 and 2%, respectively. The relative activities of **6** vs. **7** are consistent with previous observations that complexes possessing two strong donor in a mutually *trans* arrangement are generally poor catalysts in the Mizoroki–Heck reaction, compared to similar *cis* complexes.[22,25] While **7** presumably isomerises or decomposes at 120 °C to an active species, the retention of the *trans* geometry at 80 °C likely inhibits the reductive elimination step of the catalytic cycle, leading to poor catalytic turnover. All complexes were more active than $Pd(OAc)_2$ under the conditions employed. When the deactivated aryl halide 4-bromoanisole was used as the substrate for the Mizoroki–Heck reaction, **6** and **7** were again the most active complexes, promoting the formation of butyl 4-methoxycinnamate in a 46 and 44% yield, respectively. Although there is some literature regarding the use of (NHC)(allyl)Pd complexes to promote the Mizoroki–Heck reaction, those studies generally involved aryl iodides or activated aryl bro-

mides at high temperatures.[26] The most active NHC-based catalysts in the Mizoroki–Heck coupling reaction are generally chelating or pincer-type complexes, although high temperatures are also required with those systems.[27]

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



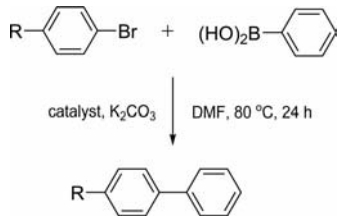
Entry	Catalyst	R	*T* [°C]	% Yield[b]	TON	TOF
1	**5a**	H	80	1	1	0.04
2	**5a**	H	120	10	10	0.4
3	**5b**	H	80	2	2	0.1
4	**5b**	H	120	12	12	0.5
5	**6**	H	80	35	35	1.5
6	**6**	H	120	59	59	2.5
7	**7**	H	80	2	2	0.1
8	**7**	H	120	51	51	2.1
9	$Pd(OAc)_2$	H	80	0	0	0
10	$Pd(OAc)_2$	H	120	6	6	0.2
11	**5a**	OMe	120	6	6	0.2
12	**5b**	OMe	120	7	7	0.3
13	**6**	OMe	120	46	46	1.9
14	**7**	OMe	120	44	44	1.8
15	$Pd(OAc)_2$	OMe	120	8	8	0.3

[a] 1 mmol aryl halide, 1.2 mmol butyl acrylate, 1.5 mmol NaOAc, 1 mol-% catalyst, 0.5 mL NMP, 24 h. [b] GC-yield determined using bis(ethylene glycol) dibutyl ether as the internal standard.

The complexes were also tested in the Suzuki–Miyaura cross-coupling reaction of 4-bromotoluene and phenylboronic acid using K_2CO_3 as the base in DMF at 80 °C (Table 6). At a loading of 0.002 mol-%, **6** was again the most active, catalysing the formation of 4-methylbiphenyl in a 52% yield, corresponding to a TON of 26,000 (entry 5). In this case, the (NHC)(allyl)PdCl complexes did show reasonable activity, with 0.02 mol-% **5a** promoting the formation of 4-methylbiphenyl in a 56% yield (entry 2). When 4-bromoanisole was used as the aryl halide, complexes **5a** and **6** were the most active, with 0.02% loadings resulting in 4-methoxybiphenyl in yields of 52 and 53%, respectively. All complexes were significantly more active than $Pd(OAc)_2$. In experiments conducted under similar conditions (but in water or dioxane, at 60–100 °C) Yuan and Huynh also noted good catalytic activity at low catalyst loadings in Suzuki–Miyaura reactions promoted by Pd^{II}-NHC complexes, where the NHC ligand was a (mono)-benzimidazolin-2-ylidene bearing a pendant thiolato group.[28]

As complex **6** was the most active of the four tested, this complex was tested in all subsequent reactions in an attempt to optimize the solvent and the base in the Suzuki–Miyaura cross-coupling reaction (see Tables 7 and 8). Initial studies aimed at optimizing the solvent in the coupling of

Table 6. The Suzuki–Miyaura reaction catalyzed by palladium complexes and $Pd(OAc)_2$.[a]



Entry	Catalyst	mol-% cat.	R	% Yield[b]	TON	TOF
1	**5a**	0.002	Me	39	19,000	790
2	**5a**	0.02	Me	56	2,800	120
3	**5b**	0.002	Me	21	10,000	420
4	**5b**	0.02	Me	48	2,400	100
5	**6**	0.002	Me	52	26,000	1,100
6	**6**	0.02	Me	61	3,000	120
7	**7**	0.002	Me	23	11,000	460
8	**7**	0.02	Me	52	2,600	110
9	$Pd(OAc)_2$	0.002	Me	3	1,500	60
10	$Pd(OAc)_2$	0.02	Me	6	300	12
11	**5a**	0.002	OMe	34	17,000	710
12	**5a**	0.02	OMe	52	2,600	110
13	**5b**	0.002	OMe	23	11,000	460
14	**5b**	0.02	OMe	46	2,300	96
15	**6**	0.002	OMe	18	9,000	370
16	**6**	0.02	OMe	53	2,600	110
17	**7**	0.002	OMe	11	5,500	230
18	**7**	0.02	OMe	46	2,300	96
19	$Pd(OAc)_2$	0.002	OMe	0	0	0
20	$Pd(OAc)_2$	0.02	OMe	20	1,000	42

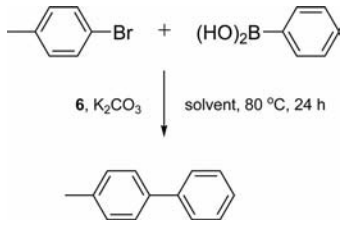
[a] 1 mmol aryl halide, 1.2 mmol phenylboronic acid, 1.2 mmol K_2CO_3, 0.5 mL DMF. 80 °C, 24 h. [b] GC-yield determined using 1-methylnaphthalene as the internal standard.

4-bromotoluene and phenylboronic acid (Table 7). It was found that a 75% yield of 4-methylbiphenyl was achieved when CH_3CN/H_2O (1:1) was used as the solvent, and a slightly lower yield (69%) was obtained using a 3:1 mixture of ethylene glycol monomethyl ether/H_2O as solvent, following the protocol developed by Del Zotto and coworkers.[29] Interestingly, when the solvent was neat H_2O, a 60% yield of 4-methylbiphenyl was achieved (entry 7).

As the solvent system of CH_3CN/H_2O (1:1) was found to give the highest yields of cross-coupling product, a variety of bases were tested using this system in the coupling of 4-bromotoluene and phenylboronic acid (Table 9). Significant variation in activity was observed between bases, highlighting the importance of the choice of base, with the inorganic bases consistently leading to higher yields than the organic bases. The highest yields of 4-methylbiphenyl, 88 and 80%, respectively, were achieved using $K_3PO_4 \cdot H_2O$ or Cs_2CO_3 as the base (entries 1 and 3). When 4-bromoanisole was used as the aryl halide with $K_3PO_4 \cdot H_2O$ in CH_3CN/H_2O (1:1), the yield of the coupling product dropped to 69% (entry 10). Unfortunately, this catalyst system was not active towards 4-chlorobenzaldehyde even at 1 mol-% **6**, with no 4-formylbiphenyl observed.

These catalysis studies indicate that there are significant differences in the activities of the complexes in the Mizoroki–Heck cross-coupling reaction, with the chelating

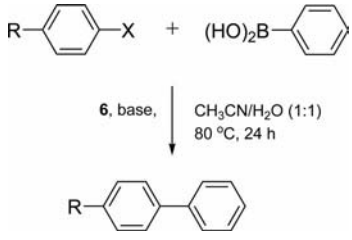
Table 7. The effect of different solvents in the Suzuki–Miyaura reaction catalyzed by **6**.[a]



Entry	Solvent	% Yield[b]	TON	TOF
1	dioxane	37	1,800	75
2	toluene	32	1,600	67
3	DMA	41	2,000	83
4	*i*PrOH	51	2,500	100
5	EtOH	49	2,400	100
6	CH_3CN	30	1,500	62
7	H_2O	60	3,000	120
8	CH_3CN/H_2O (1:1)	75	3,700	150
9	NMP	53	2,600	110
10	toluene/H_2O (1:1)	53	2,600	110
11	pyridine	5	250	10
12	EGME/H_2O (3:1)	69	3,400	140

[a] 1 mmol 4-bromotoluene, 1.2 mmol phenylboronic acid, 1.2 mmol K_2CO_3, 0.02 mol-% **6**, 0.5 mL solvent, 80 °C, 24 h. [b] GC-yield determined using 1-methylnaphthalene as the internal standard.

Table 8. The effect of different bases in the Suzuki–Miyaura reaction catalyzed by **6**.[a]

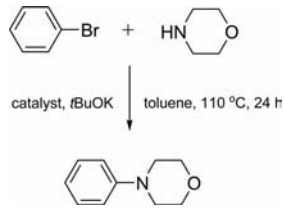


Entry	R	X	Base	% Yield[b]	TON	TOF
1	Me	Br	$K_3PO_4 \cdot H_2O$	88	4,400	180
2	Me	Br	NaOH	73	3,600	150
3	Me	Br	Cs_2CO_3	80	4,000	170
4	Me	Br	NaOAc	26	1,300	54
5	Me	Br	KF	41	2,000	83
6	Me	Br	Na_2CO_3	73	3,600	150
7	Me	Br	Et_3N	10	500	21
8	Me	Br	Me_2NBu	7	350	15
9	Me	Br	$EtN(iPr)_2$	38	1,900	79
10	OMe	Br	$K_3PO_4 \cdot H_2O$	69	3,400	140
11[c]	CHO	Cl	$K_3PO_4 \cdot H_2O$	0	0	0

[a] 1 mmol aryl halide, 1.2 mmol phenylboronic acid, 1.2 mmol base, 0.02 mol-% **6**, 0.5 mL CH_3CN/H_2O (1:1), 80 °C, 24 h. [b] GC-yield determined using 1-methylnaphthalene as the internal standard. [c] 1 mol-% **6**.

bis(NHC)Pd complexes more active than the (NHC)-(allyl)PdCl complexes. This result is presumably due to decomposition and formation of palladium black at elevated temperatures for complexes **5a** and **5b**, whereas the chelate complexes **6** and **7** are more stable under these conditions.

Table 9. The Buchwald–Hartwig reaction catalyzed by palladium complexes and $Pd(OAc)_2$.[a]



Entry	Catalyst	% Yield[b]	TON	TOF
1	**5a**	22	22	0.90
2	**5b**	15	15	0.60
3	**6**	21	21	0.90
4	**7**	28	28	1.2
5	$Pd(OAc)_2$	13	13	0.50

[a] 1 mmol bromobenzene, 1.1 morpholine, 1.2 mmol *t*BuOK, 1 mol-% catalyst, 0.5 mL toluene, 110 °C, 24 h. [b] GC-yield determined using 1-methylnaphthalene as the internal standard.

In the Suzuki–Miyaura cross-coupling reaction, a reaction where (NHC)(allyl)PdCl complexes have previously excelled,[30] the differences in activities between different types of complexes (chelating bis(NHC)PdX_2 cf. (NHC)(allyl)-PdX) is less marked.

The complexes were also tested for their ability to promote the Buchwald–Hartwig cross-coupling of bromobenzene and morpholine, using *t*BuOK in refluxing toluene at 1 mol-% loadings (Table 9). Complex **7** was the most active, leading to the formation of *N*-phenylmorpholine in a 28% yield (entry 4). While **5a** and **6** were of comparable activity (resulting in yields of *N*-phenylmorpholine of 22 and 21%, respectively), **5b** was the least active under these conditions, with a yield of *N*-phenylmorpholine (15%), similar to that achieved using $Pd(OAc)_2$.

Conclusions

We have synthesized two mono- and two bis(alkoxybenzimidazolium) salts, which were used as precursors for a series of silver and palladium NHC complexes of the types (NHC)AgCl, bis(NHC)$PdBr_2$ and (NHC)(allyl)PdCl. The complexes possess butoxy groups to increase the electron density around the metal centre and to enhance their solubility, and also carry benzyl or bulkier benzhydryl groups on the nitrogen atoms. ^{1}H NMR studies of the (NHC)-(allyl)PdCl complexes **5a** and **5b** provided evidence for restricted rotation about the Pd–$C_{carbene}$ bond and a process involving σ/π-isomerisation of the binding of the allyl ligand. The bulky benzhydryl N-substituents in **7** force the NHC ligands to adopt a mutually *trans* coordination around the palladium atom, which is relatively uncommon for *o*-xylyene linked bis(NHC)PdX_2 complexes. This complex possessed a distorted linear geometry of the NHC ligands about the palladium atom, and also a considerable tilt in the coordination plane relative to the NHC ring planes. The bis(NHC)$PdBr_2$ complexes **6** and **7** demonstrated modest activity in the Mizoroki–Heck cross-coupling reac-

tion using aryl bromides, and were significantly more active than the (NHC)(allyl)PdCl complexes **5a** and **5b**, which were prone to decomposition. All the complexes displayed similar activities in the Suzuki–Miyaura cross-coupling reactions, with **6** slightly more active than the others, and therefore chosen to study the effect of different bases and solvents on the yield of coupling product. It was found that when an aqueous solvent was used (CH_3CN or a 3:1 mixture of ethylene glycol monomethyl ether/H_2O), the highest yield of 4-bromotoluene were obtained, perhaps in part due to the increased solubility of the inorganic base using this system. The complexes also promoted the Buchwald–Hartwig coupling of bromobenzene and morpholine in modest yields, although **5b** was the least active of the complexes tested. Efforts are underway to synthesize similar complexes that combine the robustness of the chelating bis(NHC) palladium complexes with the enhanced activation and reactivity of the (NHC)(allyl) palladium complexes.

Experimental Section

General Comments: All experiments were performed under nitrogen using standard Schlenk techniques, unless otherwise stated. Subsequent manipulations were carried out in air. All solvents were distilled (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.[31] Chromatographic separations were performed using BDH silica gel (40–63 μm) with the eluants indicated. Nuclear magnetic resonance spectra were recorded at room temperature using Bruker ARX600 or Bruker ARX500 spectrometers. ^1H and ^{13}C NMR chemical shifts were referenced to solvent resonances. Coupling reactions were analysed using a HP 5890 Series II gas chromatograph; yields were estimated using pre-determined response factors of pure samples of the desired products relative to an internal standard. Microanalyses were performed by the Microanalytical Laboratory at the Research School of Chemistry, Australian National University, Canberra. 5,6-Dibutoxybenzimidazole[10] and $[\{Pd(\eta^3\text{-}C_3H_5)Cl(\mu\text{-}Cl)\}_2]$[32] were prepared according to established procedures.

Preparation of 1-Alkylbenzimidazoles

1-Benzyl-5,6-dibutoxybenzimidazole (1a): A 60% dispersion of NaH in mineral oil (0.64 g, 0.16 mol) was washed with hexanes and suspended in dry THF (60 mL). 5,6-Dibutoxybenzimidazole (3.5 g, 0.013 mol) was added portionwise to the mixture it was then stirred for 1 h. A solution of benzyl bromide (1.58 mL, 0.013 mol) in THF (20 mL) was added dropwise to the refluxing mixture, which was then stirred overnight at reflux. The mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was dissolved in diethyl ether and washed with water (2 × 30 mL) then dried with $MgSO_4$. The solution was concentrated in vacuo and the residue was recrystallised from hexanes to give **1a** as a white powder; yield 3.78 g (81%). ^1H NMR (500.13 MHz, [D$_6$]DMSO): δ = 8.19 (s, 1 H, NC*H*N), 7.28–7.39 (m, 5 H, Ar C*H*), 7.21 (s, 1 H, benzimidazolyl Ar C*H*), 7.11 (s, 1 H, benzimidazolyl Ar C*H*), 5.45 (s, 2 H, benzylic CH_2), 3.97 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, OCH_2), 3.95 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, OCH_2), 1.67–1.76 (m, 4 H, 2 × OCH$_2$CH_2), 1.44–1.54 (m, 4 H, 2 × CH_2CH$_3$), 0.94–1.00 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.76 MHz, [D$_6$]DMSO): δ = 146.6 (benzimidazolyl Ar *C*O), 145.9 (benzimidazolyl Ar *C*O), 142.6 (N*C*N), 137.2 (benzimidazolyl Ar *C*), 137.2 (Ar *C*), 128.6 (Ar *C*H), 127.8 (benzimidazolyl Ar *C*), 127.6 (Ar *C*H), 127.4 (Ar *C*H), 104.3 (benzimidazolyl Ar *C*H), 96.1 (benzimidazolyl Ar *C*H), 68.8 (O*C*H$_2$CH$_2$), 47.5 (benzylic *C*H$_2$), 30.8, 31.0 (OCH$_2$*C*H$_2$), 18.78, 18.82 (*C*H$_2$CH$_3$), 13.7 (CH$_2$*C*H$_3$) ppm. $C_{22}H_{28}N_2O_2$ (352.49): calcd. C 74.97, H 8.01, N 7.95; found C 75.06, H 8.29, N 7.84.

1-Benzhydryl-5,6-dibutoxybenzimidazole (1b): A mixture of 5,6-dibutoxybenzimidazole (0.5 g, 1.91 mmol) and NaOH (97 mg, 2.42 mmol) in CH_3CN (10 mL) were heated at reflux for 2 h. A solution of chlorodiphenylmethane (0.34 mL, 1.91 mmol) in CH_3CN (10 mL) was added dropwise to the refluxing mixture and the resulting mixture was heated at reflux for 2 d. The solution was concentrated in vacuo and the residue was purified by column chromatography (gradient elution with EtOAc/hexanes) to give **1b** as a white solid; yield 0.42 g (51%). ^1H NMR (500.13 MHz, $CDCl_3$): δ = 7.45 (s, 1 H, NC*H*N), 7.34–7.38 (m, 6 H, Ar C*H*), 7.27 (s, 1 H, benzimidazolyl Ar C*H*), 7.13–7.16 (m, 4 H, Ar C*H*), 6.64 (s, 1 H, NC*H*Ph$_2$), 6.50 (s, 1 H, benzimidazolyl Ar C*H*), 4.03 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, OCH_2), 3.82 (t, $^3J_{H,H}$ = 6.6 Hz, 2 H, OCH_2), 1.77–1.84 (m, 2 H, OCH$_2$CH_2), 1.65–1.74 (m, 2 H, OCH$_2$CH_2), 1.46–1.54 (m, 2 H, CH_2CH$_3$), 1.38–1.46 (m, 2 H, CH$_2$CH_2CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH$_2$CH_3), 0.91 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.76 MHz, $CDCl_3$): δ = 147.3 (benzimidazolyl Ar *C*O), 147.2 (benzimidazolyl Ar *C*O), 141.4 (N*C*N), 138.3 (Ar *C*), 138.0 (benzimidazolyl Ar *C*), 129.1 (Ar *C*H), 128.6 (Ar *C*H), 128.4 (Ar *C*H), 128.2 (benzimidazolyl Ar *C*), 104.6 (benzimidazolyl Ar *C*H), 96.6 (benzimidazolyl Ar *C*H), 69.5, 69.8 (O*C*H$_2$CH$_2$), 63.8 (N*C*HPh$_2$), 31.3, 31.5 (OCH$_2$*C*H$_2$), 19.3, 19.4 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{28}H_{32}N_2O_2$ (428.58): calcd. C 78.47, H 7.53, N 6.54; found C 78.67, H 7.60, N 6.54.

Preparation of Benzimidazolium Salts

Benzimidazolium Salt 2a: Benzyl chloride (0.80 mL, 6.95 mmol) was added, with stirring, to a solution of **1a** (0.70 g, 1.99 mmol) in toluene (15 mL) and the mixture was heated at reflux under nitrogen for 2 d. An additional amount of benzyl chloride (0.80 mL, 6.95 mmol) was added and heating was continued for a further 3 d. The resulting solid was collected, washed with hexanes and air-dried to give **2a** as a white powder; yield 0.90 g (94%). ^1H NMR (500.13 MHz, [D$_6$]DMSO): δ = 9.90 (s, 1 H, NC*H*N), 7.60 (s, 2 H, benzimidazolyl Ar C*H*), 7.39–7.55 (m, 10 H, Ar C*H*), 5.75 (s, 4 H, benzylic CH_2), 4.06 (t, $^3J_{H,H}$ = 6.3 Hz, 2 H, OCH_2), 1.68–1.76 (m, 4 H, OCH$_2$CH_2), 1.40–1.50 (m, 4 H, CH_2CH$_3$), 0.95 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 149.3 (benzimidazolyl Ar *C*O), 139.8 (N*C*N), 134.4 (Ar *C*), 129.0 (Ar *C*H), 128.7 (Ar *C*H), 128.2 (Ar *C*H), 125.1 (benzimidazolyl Ar *C*), 97.0 (benzimidazolyl Ar *C*H), 68.9 (O*C*H$_2$), 49.6 (benzylic *C*H$_2$), 30.3 (OCH$_2$*C*H$_2$), 18.7 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$) ppm. $C_{29}H_{35}ClN_2O_2$ (479.12): calcd. C 72.71, H 7.36, N 5.85; found C 72.93, H 7.64, N 5.60.

Benzimidazolium Salt 2b: A solution of chlorodiphenylmethane (0.68 mL, 3.81 mmol) in CH_3CN (20 mL) was added dropwise to a refluxing solution of 5,6-dibutoxybenzimidazole (1.00 g, 3.81 mmol) and NaOH (168 mg, 4.19 mmol) in CH_3CN (20 mL) and the resulting mixture was stirred at reflux overnight. An additional amount of chlorodiphenylmethane (0.80 mL, 4.50 mmol) was added and heating was continued for a further 5 d. The mixture was filtered, and the filtrate was concentrated in vacuo. The residue was subjected to column chromatography (gradient elution with EtOAc/MeOH), followed by recrystallisation from CH_2Cl_2/hexanes to give **2b** as a white powder; yield 0.90 g (37%). ^1H NMR

(500.13 MHz, [D$_6$]DMSO): δ = 9.21 (s, 1 H, NC*H*N), 7.62 (s, 2 H, NC*H*Ph$_2$), 7.40–7.53 (m, 20 H, Ar C*H*), 7.10 (s, 2 H, benzimidazolyl Ar C*H*), 3.86 (t, $^3J_{H,H}$ = 6.4 Hz, 4 H, OC*H*$_2$), 1.58–1.65 (m, 4 H, OCH$_2$C*H*$_2$), 1.34–1.44 (m, 4 H, C*H*$_2$CH$_3$), 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 149.0 (benzimidazolyl Ar *C*O), 139.2 (N*C*N), 136.2 (Ar *C*), 129.2 (Ar *C*H), 129.0 (Ar *C*H), 128.3 (Ar *C*H), 125.5 (benzimidazolyl Ar *C*), 97.5 (benzimidazolyl Ar *C*H), 68.6 (O*C*H$_2$), 64.4 (N*C*HPh$_2$), 30.0 (OCH$_2$*C*H$_2$), 18.6 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$) ppm. $C_{41}H_{43}ClN_2O_2{\cdot}1.5H_2O$ (658.28): calcd. C 74.81, H 7.04, N 4.26; found C 74.86, H 6.93, N 4.13. Crystals suitable for X-ray diffraction were grown by the diffusion of vapours between hexanes and a solution of the complex in chloroform.

Benzimidazolium Salt 3a: A solution of **1a** (0.46 g, 1.31 mmol) and α,α′-dibromo-*o*-xylene (0.17 g, 0.64 mmol) in THF (15 mL) was stirred at reflux under nitrogen for 7 d. The solution was concentrated in vacuo and the residue was triturated with hexanes (3× 10 mL) and dried under vacuum to yield **3a** as a white powder; yield 0.48 g (78%). ^{1}H NMR (500.13 MHz, [D$_6$]DMSO): δ = 9.45 (s, 2 H, NC*H*N), 7.38–7.60 (m, 18 H, Ar C*H*, xylyene Ar C*H*, benzimidazolyl Ar C*H*), 5.97 (s, 4 H, benzylic C*H*$_2$), 5.68 (s, 4 H, benzylic C*H*$_2$), 4.07 (t, $^3J_{H,H}$ = 6.4 Hz, 4 H, OC*H*$_2$), 3.95 (t, $^3J_{H,H}$ = 6.4 Hz, 4 H, OC*H*$_2$), 1.69–1.78 (m, 8 H, OCH$_2$C*H*$_2$), 1.40–1.57 (m, 8 H, C*H*$_2$CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 12 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 149.3 (benzimidazolyl Ar *C*O), 149.2 (benzimidazolyl Ar *C*O), 139.3 (N*C*N), 134.3 (Ar *C*), 132.3 (xylyene Ar *C*), 130.3 (xylyene Ar *C*H), 129.9 (xylyene Ar *C*H), 128.9 (Ar *C*H), 128.6 (Ar *C*H), 128.0 (Ar *C*H), 125.1 (benzimidazolyl Ar *C*), 124.6 (benzimidazolyl Ar *C*), 96.4, 96.7 (benzimidazolyl Ar *C*H), 68.9 (O*C*H$_2$), 47.7, 49.5 (benzylic *C*H$_2$), 30.4, 30.5 (OCH$_2$*C*H$_2$), 18.6, 18.7 (*C*H$_2$CH$_3$), 13.6, 13.7 (CH$_2$*C*H$_3$) ppm. $C_{52}H_{64}Br_2N_4O_4{\cdot}H_2O$ (986.93): calcd. C 63.28, H 6.74, N 5.68; found C 62.94, H 6.69, N 5.32.

Benzimidazolium Salt 3b: A mixture of **1b** (120 mg, 0.28 mmol), α,α′-dibromo-*o*-xylene (36 mg, 0.14 mmol) and NaI (0.9 mg, 0.006 mmol) in CH$_3$CN (10 mL) was stirred at reflux for 6 d. The solvent was removed in vacuo and the residue was subjected to column chromatography (gradient elution with EtOAc/MeOH). The combined fractions were concentrated in vacuo, and the residue was dissolved in CH$_2$Cl$_2$ and passed through a 0.2 μm nylon filter. The solvent was removed in vacuo to give **3b** as a white powder; yield 130 mg (83%). ^{1}H NMR (500.13 MHz, [D$_6$]DMSO): δ = 9.48 (s, 2 H, NC*H*N), 7.64 (s, 2 H, NC*H*Ph$_2$), 7.47–7.52 (m, 12 H, Ar C*H*), 7.40–7.50 (m, 10 H, Ar C*H*, xylyene Ar C*H*), 7.38 (s, 2 H, benzimidazolyl Ar C*H*), 7.32 (s, 2 H, benzimidazolyl Ar C*H*), 7.08 (m, 2 H, xylyene Ar C*H*), 5.96 (s, 4 H, benzylic C*H*$_2$), 3.94 (apparent t, $^3J_{H,H}$ = 6.4 Hz, 8 H, OC*H*$_2$), 1.62–1.70 (m, 8 H, OCH$_2$C*H*$_2$), 1.36–1.46 (m, 8 H, CH$_2$C*H*$_2$CH$_3$), 0.94 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH$_2$C*H*$_3$), 0.90 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 149.4 (benzimidazolyl Ar *C*O), 149.3 (benzimidazolyl Ar *C*O), 139.9 (N*C*N), 136.2 (Ar *C*), 132.3 (xylyene Ar *C*), 129.3 (Ar *C*H), 129.1 (Ar *C*H), 128.9 (xylyene Ar *C*H), 128.3 (Ar *C*H), 127.4 (xylyene Ar *C*H), 125.6 (benzimidazolyl Ar *C*), 124.5 (benzimidazolyl Ar *C*), 97.2, 97.3 (benzimidazolyl Ar *C*H), 68.7, 68.9 (O*C*H$_2$), 64.0 (N*C*HPh$_2$), 47.9 (benzylic *C*H$_2$), 30.1, 30.2 (OCH$_2$*C*H$_2$), 18.6, 18.6 (*C*H$_2$CH$_3$), 13.6, 13.6 (CH$_2$*C*H$_3$) ppm. $C_{64}H_{72}Br_2N_4O_4{\cdot}H_2O$ (1139.12): calcd. C 67.48, H 6.55, N 4.92; found C 67.39, H 6.85, N 4.55.

Preparation of Silver Complexes

Silver Complex 4a: Silver oxide (49 mg, 0.21 mmol) was added to a solution of **2a** (200 mg, 0.42 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture was stirred in darkness at room temperature for 3 d. The mixture was filtered through Celite and the filtrate was concentrated in vacuo. The resulting solid was recrystallised by layering hexanes onto a CHCl$_3$ solution of the complex to give **4a** as a clear crystalline solid; yield 209 mg (86%). ^{1}H NMR (500.13 MHz, CDCl$_3$): δ = 7.23–7.36 (m, 10 H, Ar C*H*), 6.70 (s, 2 H, benzimidazolyl Ar C*H*), 5.55 (s, 4 H, benzylic C*H*$_2$), 3.85 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, OC*H*$_2$), 1.68–1.74 (m, 4 H, OCH$_2$C*H*$_2$), 1.40–1.57 (m, 4 H, C*H*$_2$CH$_3$), 0.94 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$): δ = 148.3 (benzimidazolyl Ar *C*O), 135.0 (Ar *C*), 129.3 (Ar *C*H), 128.7 (Ar *C*H), 128.0 (benzimidazolyl Ar *C*), 127.2 (Ar *C*H), 97.0 (benzimidazolyl Ar *C*H), 69.7 (O*C*H$_2$), 53.7 (benzylic *C*H$_2$), 31.1 (OCH$_2$*C*H$_2$), 19.3 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$) ppm (carbene carbon signal not detected). $C_{29}H_{34}AgClN_2O_2{\cdot}0.15CH_2Cl_2$ (598.66): calcd. C 58.48, H 5.78, N 4.68; found C 58.82, H 5.79, N 4.21.

Silver Complex 4b: Silver oxide (73 mg, 0.32 mmol) was added to a solution of **2b** (400 mg, 0.63 mmol) in CH$_3$CN (15 mL) and the mixture was heated at 70 °C in darkness for 4 d. The mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was recrystallised by the diffusion of vapours between diethyl ether and a solution of the complex in acetone to give **4b** as a colourless crystalline solid (405 mg, 87%). ^{1}H NMR (500.13 MHz, CDCl$_3$: δ = 7.35–7.41 (m, 12 H, Ar C*H*), 7.16–7.24 (m, 8 H, Ar C*H*), 7.21 (s, 2 H, NC*H*Ph$_2$), 6.40 (s, 2 H, benzimidazolyl Ar C*H*), 3.63 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, OC*H*$_2$), 1.55–1.64 (m, 4 H, OCH$_2$C*H*$_2$), 1.32–1.40 (m, 4 H, C*H*$_2$CH$_3$), 0.88 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$: δ = 188.5 (d, $^1J_{109Ag,C}$ = 269 Hz, $^1J_{107Ag,C}$ = 233 Hz, N*C*N), 148.4 (benzimidazolyl Ar *C*O), 139.0 (Ar *C*), 130.2 (Ar *C*H), 129.9 (Ar *C*H), 129.4 (Ar *C*H), 129.2 (benzimidazolyl Ar *C*), 98.7 (benzimidazolyl Ar *C*H), 69.7 (O*C*H$_2$), 68.2 (N*C*HPh$_2$), 31.7 (OCH$_2$*C*H$_2$), 19.8 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{41}H_{42}AgClN_2O_2$ (738.12): calcd. C 66.72, H 5.74, N 3.80; found C 66.88, H 6.01, N 3.95. Crystals suitable for X-ray diffraction were grown by the diffusion of vapours between diethyl ether and a solution of the complex in acetone.

Preparation of Palladium Complexes

Palladium Complex 5a: Silver complex **4a** (400 mg, 0.68 mmol) was added to a solution of [{Pd(η^3-C$_3$H$_5$)Cl(μ-Cl)}$_2$] (125 mg, 0.34 mmol) in CH$_2$Cl$_2$ (20 mL) and the mixture was stirred in darkness for 5 d. The mixture was filtered through Celite and the filtrate was concentrated in vacuo to give **5a** as a white solid; yield 384 mg (90%). ^{1}H NMR (500.13 MHz, CDCl$_3$: δ = 7.30–7.35 (m, 4 H, Ar C*H*), 7.25–7.30 (m, 6 H, Ar C*H*), 6.66 (s, 2 H, benzimidazolyl Ar C*H*), 5.63–5.85 (m, 4 H, benzylic C*H*$_2$), 5.10 (m, 1 H, allyl C*H*), 4.26 (m, 1 H, allyl C*H*), 3.85 (t, $^3J_{H,H}$ = 6.6 Hz, 4 H, OC*H*$_2$), 3.19 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, allyl C*H*), 3.03 (m, 1 H, allyl C*H*), 1.93 (d, $^2J_{H,H}$ = 12.0 Hz, 1 H, allyl C*H*), 1.68–1.75 (m, 4 H, OCH$_2$C*H*$_2$), 1.43–1.49 (m, 4 H, C*H*$_2$CH$_3$), 0.93 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$C*H*$_3$) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 190.5 (N*C*N), 147.2 (benzimidazolyl Ar *C*O), 136.4 (Ar *C*), 129.1 (benzimidazolyl Ar *C*), 129.0 (Ar *C*H), 128.0 (Ar *C*H), 127.3 (Ar *C*H), 115.5 (allyl *C*H), 97.0 (benzimidazolyl Ar *C*H), 73.6 (allyl *C*H$_2$), 69.9 (O*C*H$_2$), 52.4 (benzylic *C*H$_2$), 49.3 (allyl *C*H$_2$), 31.2 (OCH$_2$*C*H$_2$), 19.3 (*C*H$_2$CH$_3$), 14.0 (CH$_2$*C*H$_3$) ppm. $C_{32}H_{39}ClN_2O_2Pd$ (625.50): calcd. C 61.44, H 6.28, N 4.48; found C 61.58, H 6.46, N 4.45. Crystals suitable for X-ray diffraction were grown by the slow evaporation of a CH$_2$Cl$_2$/hexanes solution of the complex.

Palladium Complex 5b: Silver complex **4b** (145 mg, 0.20 mmol) was added to a solution of [{Pd(η^3-C$_3$H$_5$)Cl(μ-Cl)}$_2$] (36 mg, 0.098 mmol) in CH$_2$Cl$_2$ (10 mL) and the mixture was stirred in

darkness for 20 h. The mixture was filtered through Celite and the filtrate was concentrated in vacuo to give **5b** as a white solid; yield 148 mg (97%). ^{1}H NMR (500.13 MHz, CD_2Cl_2: δ = 8.05 (br. s, 1 H, NC*H*Ph$_2$), 7.79 (br. s, 1 H, NC*H*Ph$_2$), 7.10–7.55 (m, 20 H, Ar C*H*), 6.15 (s, 2 H, benzimidazolyl Ar C*H*), 4.88 (m, 1 H, allyl C*H*), 4.09 (m, 1 H, allyl C*H*), 3.33–3.62 (m, 4 H, OCH_2), 2.98 (d, $^2J_{H,H}$ = 13.6 Hz, 1 H, allyl C*H*), 2.26 (m, 1 H, allyl C*H*), 1.45–1.55 (m, 4 H, OCH$_2$CH_2), 1.27–1.36 (m, 4 H, CH_2CH$_3$), 1.30 (m, 1 H, allyl C*H*), 0.85 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.77 MHz, CD_2Cl_2: δ = 193.7 (N*C*N), 146.2 (benzimidazolyl Ar *C*O), 138.8 (Ar *C*), 129.4 (Ar *C*H), 129.1 (benzimidazolyl Ar *C*), 129.0 (Ar *C*H), 128.8 (Ar *C*H), 115.6 (allyl *C*H), 98.7 (benzimidazolyl Ar *C*H), 71.8 (allyl *C*H), 69.4 (O*C*H$_2$), 68.3 (N*C*HPh$_2$), 49.3 (allyl *C*H$_2$), 31.2 (OCH$_2$*C*H$_2$), 19.4 (*C*H$_2$CH$_3$), 13.9 (CH$_2$*C*H$_3$) ppm. $C_{44}H_{47}ClN_2O_2Pd{\cdot}0.25CH_2Cl_2$ (798.98): calcd. C 66.52, H 5.99, N 3.50; found C 66.89, H 6.24, N 3.10. Crystals suitable for X-ray diffraction were grown by the diffusion of vapours between pentane and a solution of the complex in CH_2Cl_2.

Palladium Complex 6: Palladium(II) acetate (93 mg, 0.41 mmol) was added, with stirring, to a solution of **3a** (0.40 g, 0.41 mmol) in THF (20 mL) and the resulting mixture was heated at reflux for 5 d. The solvent was removed in vacuo and the residue was recrystallised from acetone to give **6** as a white powder; yield 186 mg (42%). ^{1}H NMR (500.13 MHz, [D$_6$]DMSO): δ = 8.25 (m, 2 H, xylyene Ar C*H*), 7.75 (s, 2 H, benzimidazolyl Ar C*H*), 7.57 (m, 2 H, xylyene Ar C*H*), 7.18–7.37 (m, 10 H, Ar C*H*), 7.10 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, benzylic C*H*H), 6.37 (s, 2 H, benzimidazolyl Ar C*H*), 6.30 (d, $^2J_{H,H}$ = 15.6 Hz, 2 H, benzylic CH*H*), 5.75 (d, $^2J_{H,H}$ = 14.7 Hz, 2 H, benzylic C*H*H), 5.20 (d, $^2J_{H,H}$ = 14.7 Hz, 2 H, benzylic CH*H*), 4.05–4.25 (m, 4 H, OCH_2), 3.60–3.75 (m, 4 H, OCH_2), 1.73–1.80 (m, 4 H, OCH$_2$CH_2), 1.45–1.55 (m, 8 H, OCH$_2$CH_2, CH_2CH$_3$), 1.27–1.36 (m, 4 H, CH$_2$CH_2CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3), 0.85 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]DMSO): δ = 171.1 (N*C*N), 146.3 (benzimidazolyl Ar *C*O), 145.9 (Ar *C*O), 135.1 (Ar *C*), 135.0 (xylyene Ar *C*), 133.9 (xylyene Ar *C*H), 129.2 (xylyene Ar *C*H), 128.5 (Ar *C*H), 127.9 (benzimidazolyl Ar *C*), 127.8 (Ar *C*H), 127.4 (Ar *C*H), 127.4 (benzimidazolyl Ar *C*), 97.9, 98.2 (benzimidazolyl Ar *C*H), 68.7, 68.9 (O*C*H$_2$), 50.1, 52.1 (benzylic *C*H$_2$), 30.1, 30.5 (OCH$_2$*C*H$_2$), 18.5, 18.8 (*C*H$_2$CH$_3$), 13.5, 13.7 (CH$_2$*C*H$_3$) ppm. $C_{52}H_{62}Br_2N_4O_4Pd{\cdot}0.5(CH_3)_2SO$ (1112.38): calcd. C 57.23, H 5.89, N 5.04; found C 57.25, H 6.11, N 4.87. Crystals suitable for X-ray diffraction were grown by the diffusion of vapours between H_2O and a solution of the complex in DMSO.

Palladium Complex 7: Palladium(II) acetate (0.17 g, 0.78 mmol) was added, with stirring, to a solution of **3b** (0.82 g, 0.73 mmol) in THF (65 mL) and the resulting mixture was heated at reflux for 6 d. The mixture was filtered through Celite and the filtrate was concentrated in vacuo. The residue was purified by rapid silica gel filtration (eluting with CH_2Cl_2) to give the product as a yellow powder (0.22 g, 24%). ^{1}H NMR (500.13 MHz, [D$_6$]acetone): δ = 7.74 (s, 2 H, benzimidazolyl Ar C*H*), 7.69 (s, 2 H, NC*H*Ph$_2$), 7.53 (d, $^3J_{H,H}$ = 13.8 Hz, 4 H, Ar C*H*), 7.26–7.45 (m, 16 H, Ar C*H*), 7.26 (m, 2 H, xylyene Ar C*H*), 7.16 (m, 2 H, xylyene Ar C*H*), 6.79 (d, $^2J_{H,H}$ = 14.9 Hz, 2 H, benzylic C*H*H), 6.32 (s, 2 H, benzimidazolyl Ar C*H*), 5.72 (d, $^2J_{H,H}$ = 14.9 Hz, 2 H, benzylic CH*H*), 4.10–4.20 (m, 4 H, OCH_2), 3.67–3.74 (m, 2 H, OCH_2), 3.55–3.60 (m, 2 H, OCH_2), 1.76–1.83 (m, 4 H, OCH$_2$CH_2), 1.50–1.60 (m, 8 H, OCH$_2$CH_2, CH_2CH$_3$), 1.36–1.44 (m, 4 H, CH_2CH$_3$), 0.97 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3), 0.90 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH$_2$CH_3) ppm. ^{13}C NMR (125.77 MHz, [D$_6$]acetone): δ = 184.3 (N*C*N), 148.3 (benzimidazolyl Ar *C*O), 146.8 (benzimidazolyl Ar *C*O), 139.4 (Ar *C*), 138.8 (Ar *C*), 137.8 (xylyene Ar *C*), 132.0 (benzimidazolyl Ar *C*), 131.6 (xylyene Ar *C*H), 130.3 (Ar *C*H), 129.8 (Ar *C*H), 129.4 (xylyene Ar *C*H), 128.7, 128.8, 129.0, 129.3 (Ar *C*H), 127.2 (benzimidazolyl Ar *C*), 96.8, 100.2 (benzimidazolyl Ar *C*H), 70.0, 70.1 (O*C*H$_2$), 68.7 (N*C*HPh$_2$), 47.7 (benzylic *C*H$_2$), 31.7, 32.2 (OCH$_2$*C*H$_2$), 19.8, 20.0 (*C*H$_2$CH$_3$), 14.0, 14.1 (CH$_2$*C*H$_3$) ppm. $C_{64}H_{70}Br_2N_4O_4Pd{\cdot}2(CH_3)_2CO$ (1341.67): calcd. C 62.67, H 6.16, N 4.18; found C 62.32, H 5.93, N 4.26. Crystals suitable for X-ray diffraction were grown by the slow evaporation of a [D$_6$]acetone solution of the complex.

Catalysis Studies: Stock solutions of Pd(OAc)$_2$, **5a**, **5b**, **6** and **7** in degassed DMF were prepared at concentrations of 2 mM. The solutions containing **5a** and **5b** were used immediately. 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 containing **6** and **7** (which showed no apparent changes on storage) were used within one 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 bis(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 counter-current of nitrogen and the resulting 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 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 counter-current 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 with $MgSO_4$. 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), *t*BuOK (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 counter-current 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 with $MgSO_4$. A 20 μL aliquot of the $CHCl_3$ solution was diluted with EtOAc (1.5 mL) and analysed by GC.

Structure Determinations: The crystal data for **2b**, **4a**, **4b**, **5a**, **5b**, **6**, **7**, **8** are summarized in Table 4 with the structures depicted in Figures 5, 6, 7, 8, 9, and 10 where ellipsoids have been drawn at the 50% (20% for **6**) probability level. Selected coordination geometries are shown in Tables 1, 2, and 3. Crystallographic data for the structures were collected at 100(2) K on an Oxford Diffraction

Xcalibur (**2b**, **4a**, **4b**, **5b**, **7**) or Gemini (**5a**, **6**, **8**) diffractometer fitted with Mo-K_α radiation (Cu-K_α radiation for **6**). Following multi-scan or face-indexed absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.[33]

For **5a** the central atom of the allyl group, the terminal two atoms C53, C54 of one OBu chains and the four carbon atoms of the other chain, C61–C64, are each disordered over two sites. The site occupancies of pairs of disordered atoms on chain 5n and those of the allyl group were constrained to be identical at 0.711(5) and its complement after trial refinement showed them to have similar values. The occupancies for the disordered atoms of chain 6n were refined to 0.583(5) and its complement. Geometries of the atoms of the disordered atoms of both chains were restrained to ideal values. For **5b**, significant electron density located close to the Pd atom was modelled as disorder of the Pd, Cl and allyl group atoms. Site occupancy factors refined to 0.9435(5) and its complement for the major and minor components. Geometries of the minor component were restrained to those of the major component. For **6**, one butyl group (25n) was modelled as being disordered over two sites from the second carbon atom of the chain with site occupancy factors constrained to 0.5 after trial refinement. The terminal methyl groups of two other butyl groups (26n and 45n) were also disordered over two sites, each with occupancies also constrained to 0.5. Their geometries were restrained to ideal values. Water molecule hydrogen atoms were included at observed positions and refined with restrained geometries. For **7**, the terminal three atoms of chain 26n and the terminal two atoms of chain 46n were each disordered over two sets of sites with site occupancy factors constrained to 0.5 after trial refinement of the site occupancy factors showed insignificant deviation from 0.5. The C–C bond lengths of the disordered atoms were restrained to ideal values. For **8**, the solvent $CHCl_3$ molecule was modelled as being disordered over two sites with occupancy factors refined to 0.837(3) and 1–0.837(3), the geometries of the minor component being restrained to ideal values and with non-H atoms refined with isotropic displacement parameters. The central carbon atom of the allyl group was also found to be disordered over two sites, C02 and C02′, with occupancies refined to 0.652(9) and its complement.

CCDC-803878 (for **2b**), -803876 (for **4a**), -803879 (for **4b**), -803877 (for **5a**), -803881 (for **5b**), -803874 (for **6**), -803880 (for **7**), and -803875 (for **8**) 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.

Supporting Information (see footnote on the first page of this article): Figure of variable temperature ^{1}H NMR spectra of **5b**, projection of the cation of **2b**.

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