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Palladium complexes of N-heterocyclic carbenes displaying an unsymmetrical *N*-alkylfluorenyl/*N*′-aryl substitution pattern and their behaviour in Suzuki–Miyaura cross coupling†

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A series of new Pd–PEPPSI complexes containing imidazolylidene ligands with a mixed 9-alkyl-9-fluorenyl/aryl *N*,*N*′-substitution pattern have been synthesised. Single crystal X-ray diffraction studies were carried out for four complexes, which revealed that the N-heterocyclic carbene ligands display a semi-open, unsymmetrical space occupancy about the metal. Despite their particular unsymmetrical shape, the new complexes were found to perform as well in Suzuki–Miyaura cross coupling (dioxane, 80 °C) as previously reported, highly active analogues bearing two sterically protecting 9-alkylfluorenyl substituents. They were further found to be considerably more active than the standard Pd–PEPPSI complexes [$PdCl_2$IMes(pyridine)] and [$PdCl_2$IPr(pyridine)]. Surprisingly, unlike the latter, the unsymmetrical complexes of this study were practically inactive in *isopropanol* at 80 °C. Under these conditions the complexes appear to decompose with formation of non-stabilised nanoparticles.

Introduction

Transition metal complexes featuring N-heterocyclic carbenes (NHCs) play a central role in contemporary coordination chemistry and catalysis.[1] Research in this field has led to a variety of effective, new metal catalysts, striking examples including soluble complexes suitable for C–C bond forming reactions,[2] olefin metathesis[3] and asymmetric hydrogenation,[4] not to mention applications in heterogeneous catalysis.[5] Although NHC-complexes have been known since the late 1960s,[6] their chemistry really began when organic chemists found that free (N-heterocyclic) carbenes can be isolated.[7] This discovery, logically, gave rise to an explosion of interesting experimental and theoretical studies, and paradoxically also stimulated research aiming at the production of NHC complexes from precursors other than organic carbenes.[8] In the sole field of inorganic chemistry, over 3800 studies dealing with NHC-complexes have appeared in the literature since 2000. This topic has been documented in a number of reviews and books.[1b,c,9]

The chemistry of complexes containing bis-*N*,*N*′-(9-alkyl-9-fluorenyl)-substituted NHCs (noted $^{A}F_2$-NHCs hereafter) has been under investigation in our group for several years.[10] NHC ligands of this type constitute valuable monodentate ligands suitable for a meridional confinement of metal ions. Thus, for example, in PEPPSI-type complexes (PEPPSI stands for pyridine-enhanced precatalyst preparation, stabilisation and initiation) of general formula [$PdCl_2$($^{A}F_2$-NHC)(pyridine)] (Fig. 1), the presence of CH groups in the two alkyl side chains

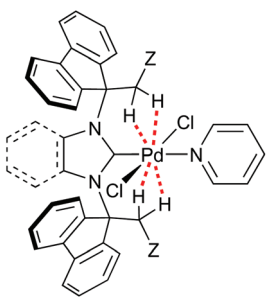

Fig. 1 General formula of previously reported [$PdCl_2$($^{A}F_2$-NHC)(pyridine)] complexes.[10]

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symmetrically located on the two sides of the metal plane gives rise to electrostatic C–H···Pd interactions, with the consequence that the NHC ligand behaves as a pseudo-tridentate ligand in which metal binding is ensured by a classical $C_{carbene}$–Pd bond and two anagostic C–H···Pd interactions (with M···H distances in the range 2.3–2.9 Å). The resulting high steric shielding provided by such ligands was found responsible for the formation of highly stable complexes.

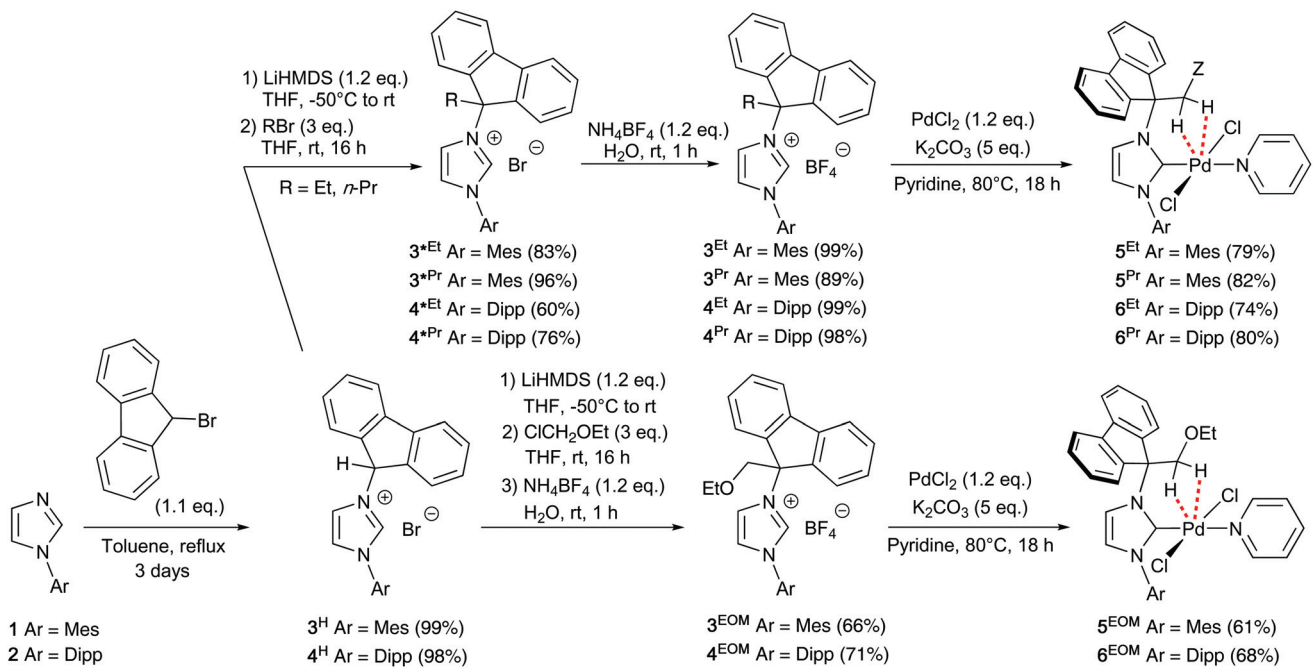
Remarkably, some of these showed *higher* activities in cross coupling catalysis than those obtained with conventional, bis-aryl substituted NHCs (notably IMes and IPr[11]).

As a continuation of our studies on 9-alkyl-fluorenyl substituted NHCs, we decided to embark on the synthesis of palladium imidazolylidene (Im) complexes having only one of the heterocyclic N atoms substituted by an ^{A}F group, with the other substituted by an *o*-substituted aryl group. To date, complexes of this kind remain unreported. The purpose of this study was three-fold: (a) to establish a convenient procedure for the preparation of Pd–PEPPSI complexes containing such unsymmetrically substituted NHCs, expecting them to possess a less crowded metal environment than that of their bis-^{A}F substituted versions; (b) to compare the performance of such complexes in Suzuki–Miyaura coupling with that of conventional bis-aryl substituted catalysts; and (c) to gain some insight into the stability of the complexes under catalytic conditions with regard to the formation of nanoparticles. The benefits of mixed alkyl/aryl-substituted NHCs for use in Suzuki Miyaura reactions were recently established in a study by Hashmi *et al.*[12] focussed on NHCs substituted by a flexible *cycloalkyl* group and a di-*ortho*-substituted aryl ring.

Results and discussion

Synthesis of Pd–PEPPSI complexes with unsymmetrical (^{A}F, Ar)-Im ligands

The unsymmetrical complexes described in this study were obtained starting either from *N*-mesitylimidazole (**1**) or *N*-2,6-diisopropyl imidazole (**2**) (Scheme 1). Both heterocycles were alkylated with 9-bromofluorene to yield quantitatively the corresponding imidazolium salts $\mathbf{3}^{H}$ and $\mathbf{4}^{H}$, respectively. Deprotonation of $\mathbf{3}^{H}$ and $\mathbf{4}^{H}$ with LiHMDS (1.2 equiv.), followed by reaction with appropriate alkyl halides (RX = EtBr, *n*-PrBr, $ClCH_2OEt$) and subsequent treatment with NH_4BF_4 resulted in six new azolium derivatives, namely $\mathbf{3}^{Et}$, $\mathbf{3}^{Pr}$, $\mathbf{3}^{EOM}$, $\mathbf{4}^{Et}$, $\mathbf{4}^{Pr}$, and $\mathbf{4}^{EOM}$ (EOM standing for CH_2OMe). This methodology for grafting alkyl side chains on the fluorenylidene unit was based on a procedure reported recently by César *et al.* for the preparation of an analogous salt. All six compounds were then reacted with $PdCl_2$ in pyridine at 80 °C in the presence of K_2CO_3, affording the expected PEPPSI-type complexes $\mathbf{5}^{Et}$, $\mathbf{5}^{Pr}$, $\mathbf{5}^{EOM}$, $\mathbf{6}^{Et}$, $\mathbf{6}^{Pr}$, $\mathbf{6}^{EOM}$, respectively (Scheme 1). It is noteworthy that the individual intermediates of the six reaction sequences were all purified chromatographically, the overall yields of these reactions being close to 50% in each case (see experimental details). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the complexes at ambient temperature are straighforwardly analysed, all showing the two different (olefinic) CH groups of the NHC ring, as well as the C*H* protons of the alkyl side chain. For each complex, the ^{1}H NMR spectrum reveals that the signal of the methylene unit attached to the fluorenylidene moiety (termed α-CH_2 group hereafter) has undergone a significant lowfield



Scheme 1 Synthesis of the Pd–PEPPSI complexes $\mathbf{5}^{R}$ and $\mathbf{6}^{R}$. The intermediates **3*** and **4*** have been fully characterised.

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shift ($1.78 < \Delta\delta < 1.95$ ppm) with respect to that of the corresponding azolium precursor. Similar differences were found in previously reported PEPPSI-type complexes based on NHCs bearing two identical ^{A}F substituents. The ^{1}J(CH) coupling constant was determined only for the α-CH_2 group of complex $\mathbf{6}^{\mathbf{Et}}$. As the observed value, 132 Hz, is typical for H atoms bound to sp^3-hybridised C atoms, no further ^{1}J(CH) values were determined. Overall, these findings are consistent with the existence of anagostic interactions[13] involving the palladium centre and the neighbouring α-CH_2 group. Single crystal X-ray diffraction studies carried out for the complexes $\mathbf{5}^{\mathbf{Et}}$, $\mathbf{5}^{\mathbf{Pr}}$, $\mathbf{6}^{\mathbf{Et}}$, and $\mathbf{6}^{\mathbf{EOM}}$ confirmed, in each case, the close proximity of the α-CH_2 group to the Pd atom (Fig. 2). As expected, the two chlorido ligands are in a relative trans position and the NHC plane is nearly perpendicular to the metal plane (Fig. 2), thereby positioning the α-CH_2 group near the metal d_{z^2} axis. The bond lengths between the palladium atom and the four atoms of the first coordination sphere are not unusual (Table 1).

The above four structural studies were useful to establish the topographic steric map[14] and buried volume[15] (V_{Bur}) of the corresponding ligands. Owing to the presence of two distinct *N*-substituents, in particular to that of a single alkyl group pointing to the d_{z^2} axis, the ligand has a markedly unsymmetrical space occupancy about the metal centre (Fig. 3).

Interestingly, despite their unsymmetrical shape, the ligands of the four complexes are characterised by a similar steric bulk ($36.1 < \%V_{Bur}$[15] < 38.9), which, in fact, does not differ significantly from that of the "symmetrical" ligand $^{Et}F_2$-Im ($\%V_{Bur} = 38.8$).

Synthesis of Pd–PEPPSI complexes with symmetrical $^{A}F_2$-Im ligands

For comparative purposes (*vide infra*, catalytic study), the three PEPPSI complexes $\mathbf{9}^{\mathbf{Me}}$, $\mathbf{9}^{\mathbf{Et}}$, $\mathbf{9}^{\mathbf{Pr}}$, in which the NHC ligands bear two identical ^{A}F substituents, were also synthesised (Scheme 2). Their preparation began with that of $\mathbf{7}^{\mathbf{H}}$, which was obtained by reacting 9-aminofluorene with glyoxal and formaldehyde in acetic acid in the presence of $MgSO_4$ and $ZnCl_2$. The beneficial role of $ZnCl_2$ as additive in condensation reactions forming imidazolium salts was recently demonstrated by Mauduit *et al.*[16] To obtain the product as a tetrafluoroborate salt, the reaction mixture was treated with NH_4BF_4 after completion of the reaction. Chromatographic purification gave $\mathbf{7}^{\mathbf{H}}$ in 81% yield. The imidazolium salts $\mathbf{8}^{\mathbf{Me}}$, $\mathbf{8}^{\mathbf{Et}}$, $\mathbf{8}^{\mathbf{Pr}}$ were then obtained by alkylation of $\mathbf{7}^{\mathbf{H}}$ with the appropriate alkyl halide, applying the same methodology as that used above in the synthesis of the "unsymmetrical" salts $\mathbf{3}^{\mathbf{R}}$ and $\mathbf{4}^{\mathbf{R}}$.

The final products, $\mathbf{9}^{\mathbf{Me}}$, $\mathbf{9}^{\mathbf{Et}}$, and $\mathbf{9}^{\mathbf{Pr}}$, were synthesised from $[PdCl_2]$ applying Organ's method (Scheme 2). Unsurprisingly,

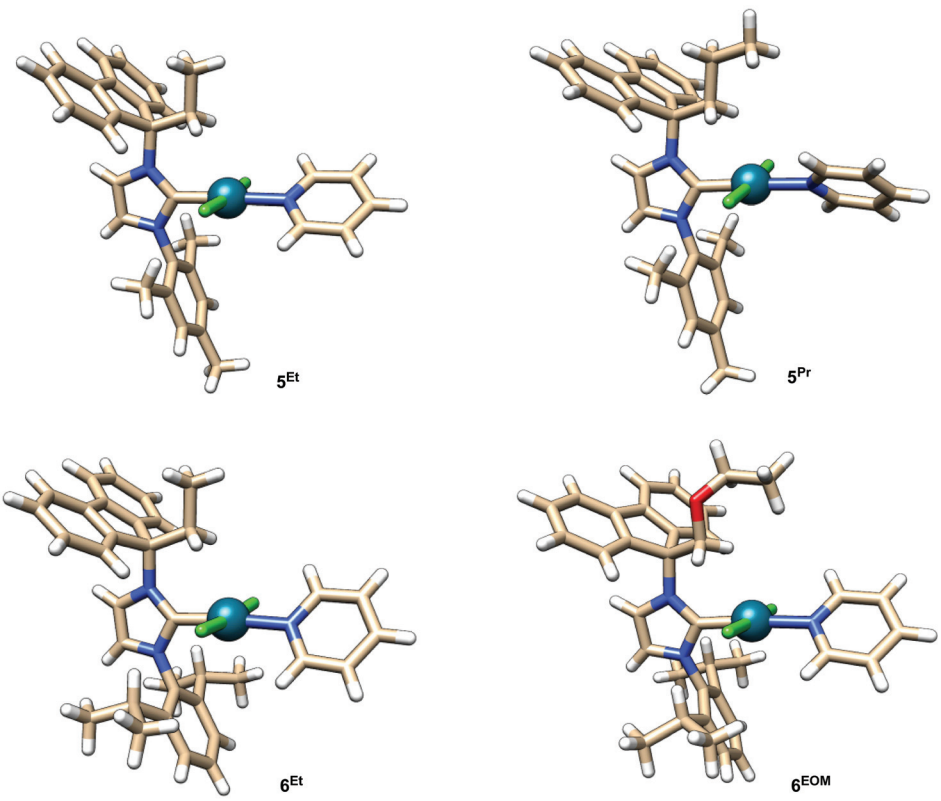

Fig. 2 Molecular structures of $\mathbf{5}^{\mathbf{Et}}$, $\mathbf{5}^{\mathbf{Pr}}$, $\mathbf{6}^{\mathbf{Et}}$ and $\mathbf{6}^{\mathbf{EOM}}$. The CH_2Cl_2 molecules in $\mathbf{6}^{\mathbf{Et}}$ and $\mathbf{6}^{\mathbf{EOM}}$ are omitted for clarity. α-CH···Pd distances (Å): 2.70, 2.81 ($\mathbf{5}^{\mathbf{Et}}$); 2.62, 2.82 ($\mathbf{5}^{\mathbf{Pr}}$); 2.68, 2.91 ($\mathbf{6}^{\mathbf{Et}}$); 2.61, 2.98 ($\mathbf{6}^{\mathbf{EOM}}$). The α-C*H*$_2$ atoms were positioned geometrically, with C–H = 0.95 (Å). Dihedral angle (°) between the coordination plane and the NHC ring plane: 87.2 ($\mathbf{5}^{\mathbf{Et}}$), 84.5 ($\mathbf{5}^{\mathbf{Pr}}$), 86.5 ($\mathbf{6}^{\mathbf{Et}}$), 83.9 ($\mathbf{6}^{\mathbf{EOM}}$).

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Table 1 Important bond lengths in 5^{Et}, 5^{Pr}, 6^{Et} and 6^{EOM}

Complex	Pd–Cl	Pd–C (carbene)	Pd–N (pyridine)
5^{Et}	2.303(1); 2.311(2)	1.975(4)	2.112(3)
5^{Pr}	2.308(2); 2.316(2)	1.970(3)	2.096(3)
6^{Et}	2.306(2); 2.315(2)	1.977(4)	2.081(3)
6^{EOM}	2.306(2); 2.312(2)	1.976(3)	2.101(3)

all three complexes exhibit a ^{1}H NMR spectrum in which the α-CH_2 proton signals appear again at considerably lower field than in the spectra of the corresponding precursors, this being, as for **5** and **6**, consistent with anagostic CH···Pd interactions. Note, the deshielding is less pronounced for the methylated complex 9^{Me} ($\Delta\delta_{\alpha\text{-CH}}$ = 1.20) than for 9^{Et} and 9^{Pr} ($\Delta\delta_{\alpha\text{-CH}}$ = *ca.* 2 ppm). This is probably for steric reasons, the alkyl groups of 9^{Et} and 9^{Pr} favouring conformations in which the two α-C–H bonds are turned towards the metal rather than towards the fluorenylidene moiety. In contrast, the three C–H bonds of the small Me group of 9^{Me} can freely adopt a variety of orientations (because of unimpeded rotation of the Me group about the $C_{9\text{-fluorenyl}}$–Me bond), thereby reducing their time-averaged proximity to the palladium atom and consequently reducing anagostic bonding.

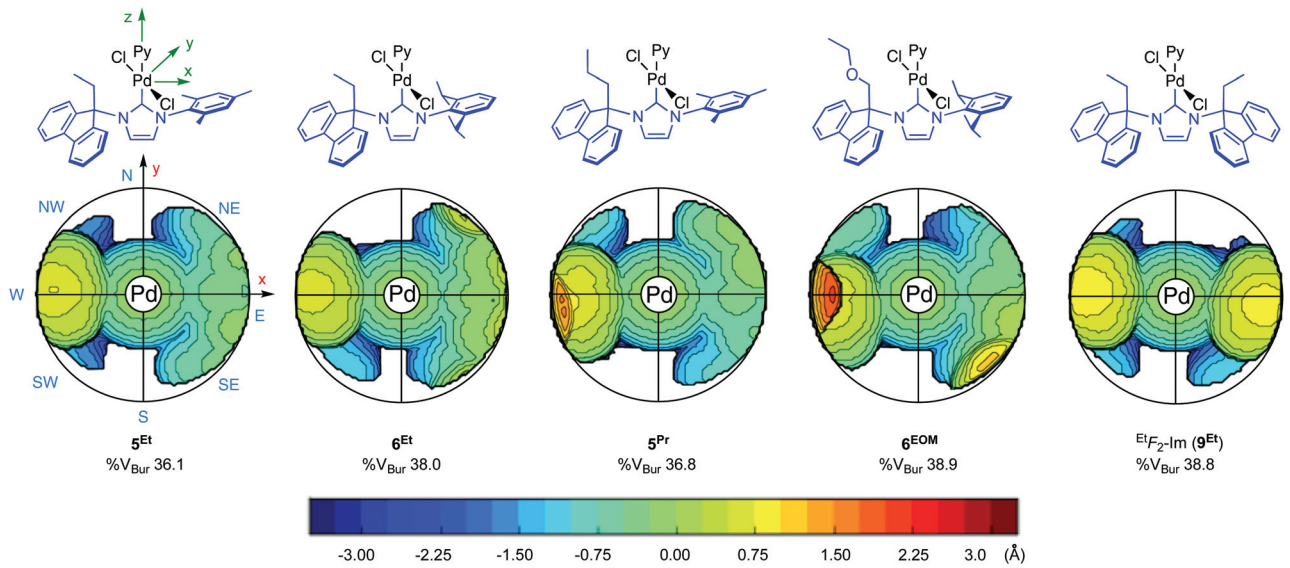
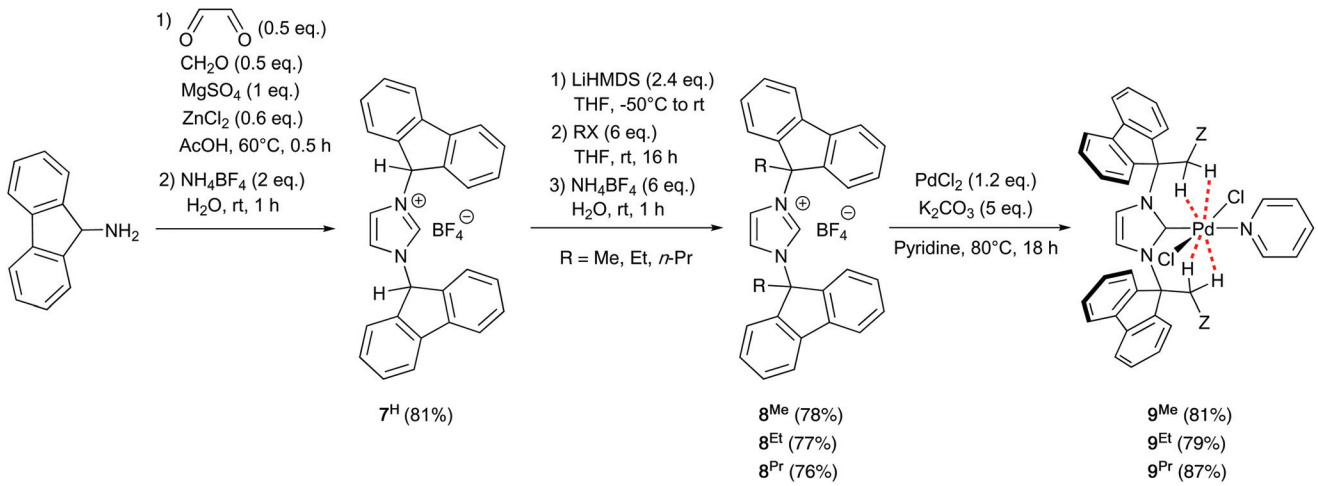


Fig. 3 Topographic steric map of the ligands of 5^{Et}, 5^{Pr}, 6^{Et}, 6^{EOM} and $^{Et}F_2$-Im (9^{Et}) with their $\%V_{Bur}$. The numbering below each steric map is that of the corresponding complex. Views have the carbene axis pointing to the observer; the domain on the left side corresponds to the alkylfluorenyl group. The distances on the coloured scale indicate the height along the z axis. The calculated buried volumes ($\%V_{Bur}$) were obtained applying a sphere radius of 3.5 Å, and taking into account the H atoms.



Scheme 2 Synthesis of the Pd–PEPPSI complexes 9^R.

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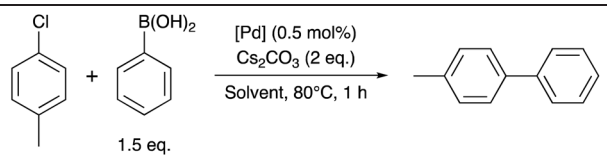
Catalytic studies

The six unsymmetrical complexes $\mathbf{5^R}$ and $\mathbf{6^R}$ (R = Et, *n*-Pr, $EtOCH_2$) were assessed in the coupling of phenylboronic acid with *p*-tolyl chloride. Catalysis was performed in dioxane at 80 °C in the presence of 0.5 mol% Pd and 2 equiv. of Cs_2CO_3. Under these conditions, all the complexes displayed high activity (Table 2, entries 3–8), significantly superior to those obtained with the standard complexes [$PdCl_2$(IMes)(pyridine)] and [$PdCl_2$(IPr)(pyridine)] (Table 2, entries 1 and 2). Interestingly, the results obtained with $\mathbf{5^R}$ and $\mathbf{6^R}$ were quite similar to those obtained with the symmetrically functionalised complexes $\mathbf{9^R}$ (entries 9–11), this showing that a single alkylfluorenyl group *per se* provides efficient catalyst stabilisation. Repeating the reactions carried out with $\mathbf{5^{Et}}$, $\mathbf{6^{Et}}$, and $\mathbf{9^{Et}}$ in the presence of added mercury kept the activity high (decrease of activity 7–15%, Table 2), this being a good indication that nanoparticle formation was marginal during these runs, and thus that these catalysts are stable in dioxane. In contrast, when adding mercury to the catalytic solution containing [$PdCl_2$(IMes)(pyridine)], the yield dropped to *ca.* 33%. Further tests were performed in isopropanol at 80 °C. Thus, the complexes $\mathbf{5^{Pr}}$ and $\mathbf{6^{Et}}$ showed nearly no activity in isopropanol (Table 2, entries 4 and 6), this markedly contrasting with the reference complex [$PdCl_2$(IMes)(pyridine)], which turned out to be twice as active in isopropanol as in dioxane despite considerable production of colloids in that case (Table 2, entry 1). It should be remembered here that nanoparticles and/or clusters can be readily formed from Pd–NHC complexes (after formation of Pd–C or Pd–H bonds followed by C-NHC or H-NHC coupling), and that these can result in azolium-stabilised species which are active in cross coupling.[17] The complexes $\mathbf{5^R}$ and $\mathbf{6^R}$ themselves are stable in isopropanol at 80 °C. However, in the presence of the reagents, they provided totally inactive species (at 80 °C). Possibly, under these conditions the carbene ligand dissociates from the metal and subsequently undergoes cleavage of the N–C(^AF) unit, leading to a neutral imidazole unable to favour the formation of active nanoparticles.

Table 2 Suzuki–Miyaura cross-coupling of $PhB(OH)_2$ with *p*-tolylchloride using palladium complexes $\mathbf{5^R}$, $\mathbf{6^R}$, $\mathbf{9^R}$ [a]



Entry	[Pd]	Yield[a] (%) in dioxane		Yield[a] (%) in i-PrOH	
		with Hg[b]		with Hg[b]	
1	[$PdCl_2$(IMes)(Py)]	47	32	83	17
2	[$PdCl_2$(IPr)(Py)]	23	—	81	—
3	$\mathbf{5^{Et}}$	71	—	—	—
4	$\mathbf{5^{Pr}}$	83	70	5	—
5	$\mathbf{5^{EOM}}$	74	—	—	—
6	$\mathbf{6^{Et}}$	81	75	3	—
7	$\mathbf{6^{Pr}}$	57	—	—	—
8	$\mathbf{6^{EOM}}$	73	—	—	—
9	$\mathbf{9^{Me}}$	64	—	—	—
10	$\mathbf{9^{Et}}$	87	81	18	—
11	$\mathbf{9^{Pr}}$	76	—	—	—

[a] *p*-Tolyl chloride (1 mmol), phenylboronic acid (1.5 mmol), Cs_2CO_3 (2 mmol), solvent (3 mL). Yields determined by ^1H NMR using 1,4-dimethoxybenzene as internal standard. Averaged over two runs. [b] Reaction performed in the presence of 50 μL of Hg (3.38 mmol, 3.4 eq.).

Conclusions

We have synthesised the first Pd–PEPPSI complexes featuring imidazolylidene ligands characterised by a mixed 9-alkyl-9-fluorenyl/aryl *N*,*N*′-substitution pattern. As revealed by several X-ray diffraction studies, the bound NHCs display a markedly unsymmetrical space occupancy about the metal, quite unlike that of doubly ^AF-substituted analogues, known to be highly active in Suzuki–Miyaura cross couplings carried out in dioxane (80 °C). Significantly, the unsymmetrical form of the new NHCs is not at all an obstacle to high catalytic activity, thus showing that the presence of a single ^AF group ensures good complex stability. Surprisingly, unlike conventional Pd–PEPPSI complexes such as [$PdCl_2$IMes(pyridine)] or [$PdCl_2$IPr(pyridine)], the new unsymmetrical complexes were practically inactive in isopropanol at 80 °C. This observation, together with that of the formation of black, colloidal solutions in this alcohol, suggests that the complexes decompose and result in organic compounds unable to stabilise concomitantly formed nanoparticles.

Experimental section

General procedures

All commercial reagents were used as supplied. The syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a FT Bruker Avance 500, 400 or 300 instrument at 25 °C. ^1H NMR shifts were referenced to residual protonated solvent ($CHCl_3$, δ 7.26; [D_6]DMSO, δ 2.50), ^{13}C chemical shifts are reported relative to deuterated solvent signals ($CDCl_3$, δ 77.16; [D_6]DMSO, δ 39.52). In the NMR data given hereafter, Cq denotes a quaternary carbon atom. Flash chromatography was performed as described by Still *et al.*,[18] employing Geduran SI (E. Merck, 0.040–0.063 mm) silica. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF254. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie (UdS-CNRS), Strasbourg. *N*-Mesityl imidazole (**1**) and *N*-(2,6-diisopropylphenyl)imid-

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azole (**2**) were prepared according to a literature procedure.[19] 9-Fluorenylamine was obtained from commercially available 9-fluorenylamine hydrochloride or following a protocol starting from fluorenone.[20] $[PdCl_2(IMes)(Py)]$[10a] and $[PdCl_2(IPr)(Py)]$[10a] were prepared as described in the literature.

Synthesis of unsymmetrical imidazolium salts 3^R and 4^R

1-(Fluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (3^H). A mixture of *N*-mesityl imidazole (**1**) (0.500 g, 2.68 mmol) and 9-bromofluorene (0.720 g, 2.95 mmol) in toluene (25 mL) was heated under reflux for 3 days. The mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 2 : 98) to afford $\mathbf{3^H}$ as a pale brown solid (1.14 g, 99%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 11.30 (1H, s, NCHN), 7.77 (2H, d, ^3J = 7.4 Hz, ArH), 7.76 (1H, s, NCH), 7.63 (2H, d, ^3J = 7.4 Hz, ArH), 7.49 (2H, dd, $^3J = {}^3J'$ = 7.4 Hz, ArH), 7.34 (2H, dd, $^3J = {}^3J'$ = 7.4 Hz, ArH), 7.07 (1H, s, NCH), 7.03 (2H, s, ArH), 6.85 (1H, s, aliph. CH), 2.35 (3H, s, CH_3), 2.14 (6H, s, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 141.6 (arom. Cq), 141.0 (arom. Cq), 140.1 (arom. Cq), 139.4 (NCHN), 134.2 (arom. Cq), 130.7 (arom. Cq), 130.6 (arom. CH), 130.1 (arom. CH), 128.8 (arom. CH), 125.7 (arom. CH), 123.4 (NCH), 120.8 (arom. CH), 120.2 (NCH), 63.2 (aliph. CH), 21.2 (CH_3), 17.8 ($2CH_3$) ppm. Found C, 67.17; H, 5.44; N, 6.14. Calcd for $C_{25}H_{23}BrN_2 \cdot 0.25\ CH_2Cl_2$ (M_r = 431.38 + 21.23): C, 67.01; H, 5.23; N, 6.19%. NMR spectroscopic data are consistent with those in the literature.[21]

1-(Fluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide (4^H). A mixture of *N*-(2,6-diisopropylphenyl)imidazole (**2**) (3.00 g, 13.1 mmol) and 9-bromofluorene (3.50 g, 14.3 mmol) in toluene (50 mL) was heated under reflux for 3 days. The mixture was cooled to room temperature and the solvent removed under reduced pressure. The crude product was washed with diethyl ether (40 mL) and then dried to afford $\mathbf{4^H}$ as a pale grey solid (6.06 g, 98%). ^{1}H NMR ([D$_6$]DMSO, 500 MHz), δ 10.15 (1H, s, NCHN), 8.18 (1H, s, NCH), 8.05 (2H, d, ^3J = 7.5 Hz, ArH), 7.85 (1H, s, NCH), 7.68–7.57 (5H, m, ArH), 7.49–7.44 (4H, m, ArH), 7.07 (1H, s, aliph. CH), 2.29 (2H, qq, $^3J = {}^3J'$ = 6.8 Hz, C*H*Me$_2$), 1.19 (6H, d, ^3J = 6.8 Hz, CH_3), 1.14 (6H, d, ^3J = 6.8 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 125 MHz), δ 145.0 (arom. Cq), 140.5 (arom. Cq), 140.1 (arom. Cq), 138.7 (NCHN), 131.5 (*para* arom. CH dipp), 130.5 (arom. Cq), 130.4 (arom. CH), 128.5 (arom. CH), 125.9 (NCH), 125.1 (arom. CH), 124.4 (arom. CH), 121.6 (NCH), 121.2 (arom. CH), 62.7 (aliph. CH), 28.2 (*C*HMe$_2$), 23.8 (CH_3), 23.7 (CH_3) ppm. Found C, 70.79; H, 6.16; N, 5.98. Calcd for $C_{28}H_{29}BrN_2$ (M_r = 473.47): C, 71.03; H, 6.17; N, 5.92%.

1-(9-Ethylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide ($3^{\star Et}$). LiHMDS (0.55 mL, 0.55 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide ($\mathbf{3^H}$) (0.200 g, 0.46 mmol) in THF (6 mL) cooled to −50 °C. After 1 h (at −50 °C), the reaction mixture was allowed to reach room temperature and ethyl bromide (0.150 g, 1.37 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (1 mL) was added to quench any further reaction. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 2 : 98) to afford $\mathbf{3^{\star Et}}$ as a tan solid (0.175 g, 83%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 10.76 (1H, s, NCHN), 7.78 (2H, d, ^3J = 7.5 Hz, ArH), 7.74 (2H, d, ^3J = 7.5 Hz, ArH), 7.51 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.41 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.26 (1H, s, NCH), 7.18 (1H, s, NCH), 6.97 (2H, s, ArH), 3.24 (2H, q, ^3J = 6.9 Hz, CH_2), 2.30 (3H, s, CH_3), 2.10 (6H, s, CH_3), 0.53 (3H, t, ^3J = 6.9 Hz, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 142.9 (arom. Cq), 141.0 (arom. Cq), 140.3 (arom. Cq), 137.6 (NCHN), 134.1 (arom. Cq), 130.8 (arom. Cq), 130.6 (arom. CH), 129.7 (arom. CH), 129.2 (arom. CH), 124.2 (arom. CH), 123.7 (NCH), 121.4 (NCH), 120.8 (arom. CH), 75.4 (Cq), 30.4 (CH_2), 21.1 (CH_3), 17.8 ($2CH_3$), 7.8 (CH_2CH_3) ppm. Found C, 68.25; H, 6.01; N, 5.91. Calcd for $C_{27}H_{27}BrN_2 \cdot 0.21\ CH_2Cl_2$ (M_r = 459.43 + 17.83): C, 68.48; H, 5.79; N, 5.87%.

1-(9-Ethylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (3^{Et}). To a solution of imidazolium bromide $\mathbf{3^{\star Et}}$ (0.400 g, 0.87 mmol) in CH_2Cl_2 (20 mL) was added a solution of ammonium tetrafluoroborate (0.110 g, 1.04 mmol) in water (20 mL). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The imidazolium tetrafluoroborate $\mathbf{3^{Et}}$ (0.401 g, 99%) was obtained as a tan solid. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.16 (1H, s, NCHN), 7.79 (2H, d, ^3J = 7.5 Hz, ArH), 7.57–7.49 (4H, m, ArH), 7.40 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.24 (1H, s, NCH), 7.19 (1H, s, NCH), 6.96 (2H, s, ArH), 2.95 (2H, q, ^3J = 7.2 Hz, CH_2), 2.29 (3H, s, CH_3), 2.02 (6H, s, CH_3), 0.52 (3H, t, ^3J = 7.2 Hz, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 142.9 (arom. Cq), 141.2 (arom. Cq), 140.3 (arom. Cq), 135.4 (NCHN), 134.2 (arom. Cq), 130.8 (overlapped signals, arom. Cq and arom. CH), 129.8 (arom. CH), 129.4 (arom. CH), 124.4 (NCH), 123.7 (arom. CH), 121.8 (NCH), 121.0 (arom. CH), 75.1 (Cq), 29.3 (CH_2), 21.1 (CH_3), 17.2 ($2CH_3$), 7.8 (CH_2CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.77 (br s, ^{19}F–^{10}B), −152.83 (q, $^1J(^{19}F–^{11}B)$ = 1.1 Hz) ppm. Found C, 69.30; H, 5.93; N, 6.12. Calcd for $C_{27}H_{27}BF_4N_2$ (M_r = 466.33): C, 69.54; H, 5.84; N, 6.01%.

1-(9-Ethylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide ($4^{\star Et}$). LiHMDS (2.53 mL, 2.53 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide ($\mathbf{4^H}$) (1.00 g, 2.11 mmol) in THF (40 mL) cooled at −50 °C. After 1 h, the reaction mixture was allowed to reach room temperature and ethyl bromide (0.70 g, 6.4 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added to quench any further reaction. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 4 : 96) to afford $\mathbf{4^{\star Et}}$ as a white solid (0.64 g, 60%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 10.25 (1H, s, NCHN), 7.86 (1H, s, NCH), 7.78 (2H, d, ^3J = 7.5 Hz, ArH), 7.76 (2H, d, ^3J = 7.5 Hz, ArH), 7.52 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.48 (1H, t, ^3J = 7.8 Hz, ArH), 7.42 (2H,

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dd, $^3J = {}^3J' = 7.5$ Hz, ArH), 7.34 (1H, s, NCH), 7.26 (2H, d, $^3J = 7.8$ Hz, ArH), 3.25 (2H, q, $^3J = 7.2$ Hz, CH_2), 2.18 (2H, qq, $^3J = {}^3J' = 6.9$ Hz, C*H*Me$_2$), 1.19 (6H, d, $^3J = 6.9$ Hz, CH_3), 1.11 (6H, d, $^3J = 6.9$ Hz, CH_3), 0.57 (3H, t, $^3J = 7.2$ Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 145.0 (arom. Cq), 142.8 (arom. Cq), 140.2 (arom. Cq), 137.3 (NCHN), 131.8 (*para* arom. CH dipp), 130.7 (arom. CH), 130.2 (arom. Cq), 129.3 (arom. CH), 124.8 (NCH), 124.6 (arom. CH), 124.1 (arom. CH), 122.3 (NCH), 121.0 (arom. CH), 75.5 (Cq), 30.4 (CH_2), 28.8 (*C*HMe$_2$), 24.4 (CH_3), 23.9 (CH_3), 7.9 (CH_2CH_3) ppm. Found C, 71.83; H, 6.61; N, 5.70. Calcd for $C_{30}H_{33}BrN_2$ (M_r = 501.51): C, 71.85; H, 6.63; N, 5.59%.

1-(9-Ethylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium tetrafluoroborate (4^{Et}). To a solution of imidazolium bromide 4^{*Et} (0.508 g, 1.01 mmol) in CH_2Cl_2 (20 mL) was added a solution of ammonium tetrafluoroborate (0.127 g, 1.21 mmol) in water (20 mL). The mixture was stirred vigorously at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The imidazolium tetrafluoroborate 4^{Et} (0.510 g, 99%) was obtained as a light pink solid. ^1H NMR ($CDCl_3$, 500 MHz), δ 8.96 (1H, s, NCHN), 7.80 (2H, d, $^3J = 7.5$ Hz, ArH), 7.57–7.46 (6H, m, ArH), 7.42 (2H, dd, $^3J = {}^3J' = 7.5$ Hz, ArH), 7.33 (1H, s, NCH), 7.26 (2H, d, $^3J = 7.7$ Hz, ArH), 2.95 (2H, q, $^3J = 7.2$ Hz, CH_2), 2.17 (2H, qq, $^3J = {}^3J' = 6.8$ Hz, C*H*Me$_2$), 1.12 (6H, d, $^3J = 6.9$ Hz, CH_3) 1.11 (6H, d, $^3J = 6.9$ Hz, CH_3), 0.55 (3H, t, $^3J = 7.2$ Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 145.1 (arom. Cq), 142.7 (arom. Cq), 140.3 (arom. Cq), 135.6 (NCHN), 131.9 (*para* arom. CH dipp), 130.9 (arom. CH), 130.2 (arom. Cq), 129.4 (arom. CH), 125.3 (NCH), 124.6 (arom. CH), 123.6 (arom. CH), 121.9 (NCH), 121.1 (arom. CH), 75.2 (Cq), 29.3 (CH_2), 28.8 (*C*HMe$_2$), 24.0 (CH_3), 23.9 (CH_3), 7.8 (CH_2CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.70 (br s, ^{19}F–^{10}B), −152.76 (q, $^1J(^{19}F$–$^{11}B) = 1.1$ Hz) ppm. Found C, 70.98; H, 6.62; N, 5.58. Calcd for $C_{30}H_{33}BF_4N_2$ (M_r = 508.41): C, 70.87; H, 6.54; N, 5.51%.

1-(9-Propylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (3^{*Pr}). LiHMDS (1.70 mL, 1.70 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (3^H) (0.600 g, 1.40 mmol) in THF (20 mL) cooled at −50 °C. After stirring for 1 h (temperature being maintained at −50 °C), the reaction mixture was allowed to reach room temperature and *n*-propyl bromide (0.52 g, 4.22 mmol) was added. The mixture was stirred overnight at room temperature, then MeOH (2 mL) was added. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 3 : 97) to afford 3^{*Pr} as a tan solid (0.64 g, 96%). ^1H NMR ($CDCl_3$, 500 MHz), δ 10.74 (1H, s, NCHN), 7.77 (2H, d, $^3J = 7.6$ Hz, ArH), 7.75 (2H, d, $^3J = 7.6$ Hz, ArH), 7.50 (2H, dd, $^3J = {}^3J' = 7.6$ Hz, ArH), 7.40 (2H, dd, $^3J = {}^3J' = 7.6$ Hz, ArH), 7.28 (1H, s, NCH), 7.15 (1H, s, NCH), 6.97 (2H, s, ArH), 3.20–3.15 (2H, m, $CqCH_2$), 2.29 (3H, s, CH_3), 2.10 (6H, s, CH_3), 0.86–0.80 (5H, m, CH_2CH_3 and CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 143.3 (arom. Cq), 141.0 (arom. Cq), 140.1 (arom. Cq), 137.5 (NCHN), 134.0 (arom. Cq), 130.7 (arom. Cq), 130.5 (arom. CH), 129.7 (arom. CH), 129.2 (arom. CH), 124.1 (arom. CH), 123.8 (NCH), 121.3 (NCH), 120.8 (arom. CH), 74.8 (Cq), 38.8 ($CqCH_2$), 21.1 (CH_3), 17.8 ($2CH_3$), 17.0 (CH_2CH_3), 13.6 (CH_2CH_3) ppm. Found C, 69.99; H, 6.13; N, 5.86. Calcd for $C_{28}H_{29}BrN_2$ (M_r = 473.46): C, 71.03; H, 6.17; N, 5.92%.

1-(9-Propylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate (3^{Pr}). To a solution of imidazolium bromide 3^{*Pr} (0.556 g, 1.17 mmol) in CH_2Cl_2 (20 mL) was added water (20 mL) and ammonium tetrafluoroborate (0.148 g, 1.40 mmol). The mixture was stirred vigorously at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The imidazolium tetrafluoroborate 3^{Pr} (0.502 g, 89%) was obtained as a tan solid. ^1H NMR ($CDCl_3$, 500 MHz), δ 9.09 (1H, s, NCHN), 7.79 (2H, d, $^3J = 7.5$ Hz, ArH), 7.56 (2H, d, $^3J = 7.5$ Hz, ArH), 7.52 (2H, dd, $^3J = {}^3J' = 7.5$ Hz, ArH), 7.40 (2H, dd, $^3J = {}^3J' = 7.5$ Hz, ArH), 7.26 (1H, s, NCH), 7.19 (1H, s, NCH), 6.97 (2H, s, ArH), 2.90–2.84 (2H, m, $CqCH_2$), 2.29 (3H, s, CH_3), 2.02 (6H, s, CH_3), 0.83–0.77 (5H, m, CH_2CH_3 and CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 143.2 (arom. Cq), 141.1 (arom. Cq), 140.1 (arom. Cq), 135.1 (NCHN), 134.2 (arom. Cq), 130.7 (overlapped signals, arom. Cq and arom. CH), 129.7 (arom. CH), 129.4 (arom. CH), 124.4 (NCH), 123.7 (arom. CH), 121.7 (NCH), 121.0 (arom. CH), 74.4 (Cq), 37.8 ($CqCH_2$), 21.3 (CH_3), 17.2 ($2CH_3$), 16.9 (CH_2CH_3), 13.4 (CH_2CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.43 (br s, ^{19}F–^{10}B), −152.49 (q, $^1J(^{19}F$–$^{11}B) = 1.1$ Hz) ppm. Found C, 70.09; H, 6.16; N, 5.82. Calcd for $C_{28}H_{29}BF_4N_2$ (M_r = 480.36): C, 70.01; H, 6.09; N, 5.83%.

1-(9-Propylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide (4^{*Pr}). LiHMDS (2.53 mL, 2.53 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide (4^H) (1.00 g, 2.11 mmol) in THF (40 mL) cooled at −50 °C. After stirring for 1 h, the reaction mixture was allowed to reach room temperature and *n*-propyl bromide (0.78 g, 6.30 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (SiO_2; MeOH/CH_2Cl_2, 3 : 97) to afford 4^{*Pr} as a light pink solid (0.82 g, 76%). ^1H NMR ($CDCl_3$, 400 MHz), δ 10.22 (1H, s, NCHN), 7.83–7.73 (5H, m, ArH), 7.55–7.38 (6H, m, ArH), 7.25 (2H, d, $^3J = 7.7$ Hz, ArH), 3.21–3.14 (2H, m, $CqCH_2$), 2.19 (2H, qq, $^3J = {}^3J' = 6.9$ Hz, C*H*Me$_2$), 1.18 (6H, d, $^3J = 6.9$ Hz, CH_3), 1.11 (6H, d, $^3J = 6.9$ Hz, CH_3), 0.93–0.82 (5H, m, CH_2CH_3 and CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 144.8 (arom. Cq), 143.0 (arom. Cq), 139.9 (arom. Cq), 136.9 (NCHN), 131.6 (*para* arom. CH dipp), 130.6 (arom. CH), 130.1 (arom. Cq), 129.1 (arom. CH), 124.9 (NCH), 124.4 (arom. CH), 124.0 (arom. CH), 122.0 (NCH), 120.9 (arom. CH), 74.5 (Cq), 38.6 ($CqCH_2$), 28.6 (*C*HMe$_2$), 24.3 (CH_3), 23.7 (CH_3), 16.9 (CH_2CH_3), 13.5 (CH_2CH_3) ppm. Found C, 72.33; H, 6.79;

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N, 5.53. Calcd for $C_{31}H_{35}BrN_2$ (M_r = 515.54): C, 72.22; H, 6.84; N, 5.43%.

1-(9-Propylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium tetrafluoroborate (4^{Pr}). To a solution of imidazolium bromide 4^{*Pr} (0.778 g, 1.50 mmol) in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (0.189 g, 1.80 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The imidazolium tetrafluoroborate 4^{Pr} (0.770 g, 98%) was obtained as a light pink solid. ^{1}H NMR ($CDCl_3$, 500 MHz), δ 8.93 (1H, s, NCHN), 7.79 (2H, d, ^3J = 7.5 Hz, ArH), 7.57 (2H, d, ^3J = 7.5 Hz, ArH), 7.53 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.50–7.46 (2H, m, ArH and NCH), 7.41 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.36 (1H, s, NCH), 7.26 (2H, d, ^3J = 7.8 Hz, ArH), 2.92–2.84 (2H, m, $CqCH_2$), 2.17 (2H, qq, ^3J = $^3J'$ = 6.8 Hz, C*H*Me$_2$), 1.12 (6H, d, ^3J = 6.8 Hz, CH_3), 1.11 (6H, d, ^3J = 6.8 Hz, CH_3), 0.87–0.79 (5H, m, C*H*$_2$CH$_3$ and CH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 145.1 (arom. Cq), 143.1 (arom. Cq), 140.1 (arom. Cq), 135.4 (NCHN), 131.9 (*para* arom. CH dipp), 130.9 (arom. CH), 130.2 (arom. Cq), 129.3 (arom. CH), 125.4 (NCH), 125.5 (arom. CH), 123.6 (arom. CH), 121.8 (NCH), 121.1 (arom. CH), 74.5 (Cq), 37.8 (Cq*C*H$_2$), 28.7 (*C*HMe$_2$), 24.0 (overlapped signals 2CH$_3$), 16.9 (*C*H$_2$CH$_3$), 13.4 (CH$_2$*C*H$_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.45 (br s, ^{19}F–^{10}B), −152.50 (q, ^1J(^{19}F–^{11}B) = 1.1 Hz) ppm. Found C, 71.36; H, 6.87; N, 5.38. Calcd for $C_{31}H_{35}BF_4N_2$ (M_r = 522.44): C, 71.27; H, 6.75; N, 5.36%.

1-(9-(Ethoxymethyl)fluoren-9-yl)-3-(2,4,6-trimethylphenyl) imidazolium tetrafluoroborate (3^{EOM}). LiHMDS (2.78 mL, 2.78 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (3^H) (1.00 g, 2.32 mmol) in THF (30 mL) cooled at −50 °C. After stirring the cold solution for 1 h, the reaction mixture was allowed to reach room temperature and chlormethyl ethyl ether (0.660 g, 6.96 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added. The solvent was removed under reduced pressure and water (20 mL) was added. The product was extracted with CH_2Cl_2 (3 × 20 mL), the organic layers were combined and the solvent was removed under reduced pressure. To the crude mixture dissolved in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (0.295 g, 2.81 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; EtOAc/petroleum ether, 70 : 30) to afford 3^{EOM} as a tan solid (0.760 g, 66%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.22 (1H, s, NCHN), 7.81 (2H, d, ^3J = 7.5 Hz, ArH), 7.73 (2H, d, ^3J = 7.5 Hz, ArH), 7.54 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.38 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.20 (1H, s, NCH), 6.98 (2H, s, ArH), 6.96 (1H, s, NCH), 4.25 (2H, s, CqCH_2), 3.64 (2H, q, ^3J = 6.9 Hz, OC*H*$_2$CH$_3$), 2.29 (3H, s, CH$_3$), 2.07 (6H, s, CH$_3$), 1.19 (3H, t, ^3J = 6.9 Hz, OCH$_2$C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 141.7 (arom. Cq), 141.1 (arom. Cq), 139.8 (arom. Cq), 137.3 (NCHN), 134.3 (arom. Cq), 131.0 (arom. CH), 130.8 (arom. Cq), 129.8 (arom. CH), 129.1 (arom. CH), 125.6 (arom. CH), 123.7 (NCH), 121.7 (NCH), 120.9 (arom. CH), 73.1 (Cq), 71.5 (Cq*C*H$_2$), 66.9 (O*C*H$_2$CH$_3$), 21.1 (CH$_3$), 17.2 (2CH$_3$), 15.1 (OCH$_2$*C*H$_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.49 (br s, ^{19}F–^{10}B), −152.54 (br s, ^{19}F–^{11}B) ppm. Found C, 67.33; H, 5.84; N, 5.67. Calcd for $C_{28}H_{29}BF_4N_2O{\cdot}0.04\ CH_2Cl_2$ (M_r = 496.36 + 3.40): C, 67.39; H, 5.87; N, 5.61%.

1-(9-(Ethoxymethyl)fluoren-9-yl)-3-(2,6-diisopropylphenyl) imidazolium tetrafluoroborate (4^{EOM}). LiHMDS (2.55 mL, 2.55 mmol, 1 M in THF) was added dropwise to a stirred suspension of 1-(fluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazolium bromide (4^H) (1.00 g, 2.11 mmol) in THF (40 mL) cooled at −50 °C. After stirring the cold solution for 1 h, the reaction mixture was allowed to reach room temperature and chlormethyl ethyl ether (0.600 g, 6.33 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added. The solvent was removed under reduced pressure and water (20 mL) was added. The product was extracted with CH_2Cl_2 (3 × 20 mL), the organic layers were combined and the solvent was removed under reduced pressure. To the crude mixture dissolved in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (0.265 g, 2.53 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; EtOAc/CH_2Cl_2, 3 : 97) to afford 4^{EOM} as a pale brown solid (0.810 g, 71%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.20 (1H, s, NCHN), 7.82 (2H, d, ^3J = 7.6 Hz, ArH), 7.74 (2H, d, ^3J = 7.6 Hz, ArH), 7.56 (2H, dd, ^3J = $^3J'$ = 7.6 Hz, ArH), 7.51 (1H, t, ^3J = 7.8 Hz, ArH), 7.40 (2H, dd, ^3J = $^3J'$ = 7.6 Hz, ArH), 7.29 (2H, d, ^3J = 7.8 Hz, ArH), 7.28 (1H, s, NCH), 7.12 (1H, s, NCH), 4.28 (2H, s, CqCH_2), 3.65 (2H, q, ^3J = 7.0 Hz, OC*H*$_2$CH$_3$), 2.31 (2H, qq, ^3J = $^3J'$ = 6.8 Hz, C*H*Me$_2$), 1.22 (6H, d, ^3J = 6.8 Hz, CH$_3$), 1.19 (3H, t, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 1.14 (6H, d, ^3J = 6.8 Hz, CH$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz), δ 145.3 (arom. Cq), 141.6 (arom. Cq), 139.9 (arom. Cq), 137.3 (NCHN), 131.8 (*para* arom. CH dipp), 131.1 (arom. CH), 130.3 (arom. Cq), 129.1 (arom. CH), 125.5 (arom. CH), 124.7 (NCH), 124.6 (arom. CH), 121.8 (NCH), 121.0 (arom. CH), 73.2 (Cq), 71.5 (Cq*C*H$_2$), 67.0 (O*C*H$_2$CH$_3$), 28.7 (*C*HMe$_2$), 24.1 (CH$_3$), 24.0 (CH$_3$), 15.0 (OCH$_2$*C*H$_3$) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −152.30 (br s, ^{19}F–^{10}B), −152.35 (q, ^1J(^{19}F–^{11}B) = 1.1 Hz) ppm. Found C, 69.24; H, 6.60; N, 5.24. Calcd for $C_{31}H_{35}BF_4N_2O$ (M_r = 538.44): C, 69.15; H, 6.55; N, 5.20%.

Synthesis of palladium complexes 5^R and 6^R

***trans*-[1-(9-Ethylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (5^{Et}).** A suspen-

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sion of imidazolium salt $\mathbf{3}^{\mathbf{Et}}$ (0.350 g, 0.750 mmol), finely crushed K_2CO_3 (0.520 g, 3.75 mmol), and $PdCl_2$ (0.159 g, 0.90 mmol) in pyridine (6 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford $\mathbf{5}^{\mathbf{Et}}$ as a yellow solid (0.377 g, 79%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 8.77–8.73 (2H, m, *o*-NC_5H_5), 7.77 (2H, d, ^3J = 7.5 Hz, ArH), 7.74 (2H, d, ^3J = 7.5 Hz, ArH), 7.68 (1H, tt, ^3J = 7.7 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.44 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.37 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.27–7.23 (2H, m, *m*-NC_5H_5), 7.05 (2H, s, ArH), 6.67 (1H, d, ^3J = 2.1 Hz, NCH), 6.27 (1H, d, ^3J = 2.1 Hz, NCH), 4.73 (2H, q, ^3J = 7.3 Hz, CH_2), 2.34 (3H, s, CH_3), 2.29 (6H, s, CH_3), 0.46 (3H, t, ^3J = 7.3 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.7 (arom. CH *o*-Py), 148.7 (NCN), 147.4 (arom. Cq), 140.2 (arom. Cq), 139.2 (arom. Cq), 137.8 (arom. CH *p*-Py), 137.0 (arom. Cq), 136.0 (arom. Cq), 129.4 (arom. CH), 129.3 (arom. CH), 129.1 (arom. CH), 124.8 (arom. CH), 124.4 (arom. CH), 123.9 (NCH Imid.), 123.2 (NCH Imid.), 120.1 (arom. CH), 75.7 (Cq), 32.8 (CH_2), 21.3 (CH_3), 19.3 ($2CH_3$), 8.7 (CH_2CH_3) ppm. Found C, 58.10; H, 4.72; N, 6.32. Calcd for $C_{32}H_{31}Cl_2N_3Pd{\cdot}0.4\ CH_2Cl_2$ (M_r = 634.94 + 33.97): C, 58.18; H, 4.79; N, 6.28%.

***trans*-[1-(9-Ethylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride ($\mathbf{6}^{\mathbf{Et}}$).** A suspension of imidazolium salt $\mathbf{4}^{\mathbf{Et}}$ (0.500 g, 0.983 mmol), finely crushed K_2CO_3 (0.700 g, 5.06 mmol), and $PdCl_2$ (0.208 g, 1.17 mmol) in pyridine (14 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 25 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford $\mathbf{6}^{\mathbf{Et}}$ as a yellow solid (0.495 g, 74%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 8.79–8.74 (2H, m, *o*-NC_5H_5), 7.83 (2H, d, ^3J = 7.5 Hz, ArH), 7.77 (2H, d, ^3J = 7.5 Hz, ArH), 7.67 (1H, tt, ^3J = 7.7 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.52 (1H, t, ^3J = 7.7 Hz, ArH), 7.47 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.43–7.35 (4H, m, ArH), 7.27–7.22 (2H, m, *m*-NC_5H_5), 6.76 (1H, d, ^3J = 2.0 Hz, NCH), 6.28 (1H, d, ^3J = 2.0 Hz, NCH), 4.78 (2H, q, ^3J = 7.3 Hz, CH_2), 3.00 (2H, qq, ^3J = $^3J'$ = 6.8 Hz, $CHMe_2$), 1.49 (6H, d, ^3J = 6.8 Hz, CH_3), 0.97 (6H, d, ^3J = 6.8 Hz, CH_3), 0.47 (3H, t, ^3J = 7.3 Hz, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.5 (arom. CH *o*-Py), 149.7 (NCN), 147.5 (arom. Cq), 147.4 (arom. Cq), 140.1 (arom. Cq), 137.7 (arom. CH *p*-Py), 135.7 (arom. Cq), 130.3 (arom. CH), 129.3 (arom. CH), 129.0 (arom. CH), 125.7 (arom. CH), 124.8 (arom. CH), 124.4 (arom. CH), 123.9 (arom. CH), 122.2 (arom. CH), 120.0 (arom. CH), 75.8 (Cq), 32.7 (CH_2), 28.7 ($CHMe_2$), 26.8 (CH_3), 23.2 (CH_3), 8.7 (CH_2CH_3) ppm. Found C, 62.24; H, 5.49; N, 6.18. Calcd for $C_{35}H_{37}Cl_2N_3Pd$ (M_r = 677.02): C, 62.09; H, 5.51; N, 6.21%.

***trans*-[1-(9-Propylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride ($\mathbf{5}^{\mathbf{Pr}}$).** A suspension of imidazolium salt $\mathbf{3}^{\mathbf{Pr}}$ (0.400 g, 0.830 mmol), finely crushed K_2CO_3 (0.575 g, 4.15 mmol), and $PdCl_2$ (0.176 g, 0.996 mmol) in pyridine (7 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the collected solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford $\mathbf{5}^{\mathbf{Pr}}$ as a yellow solid (0.443 g, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 8.76–8.71 (2H, m, *o*-NC_5H_5), 7.80 (2H, d, ^3J = 7.5 Hz, ArH), 7.75 (2H, d, ^3J = 7.5 Hz, ArH), 7.68 (1H, tt, ^3J = 7.7 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.45 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.37 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.28–7.23 (2H, m, *m*-NC_5H_5), 7.07 (2H, s, ArH), 6.66 (1H, d, ^3J = 2.2 Hz, NCH), 6.26 (1H, d, ^3J = 2.2 Hz, NCH), 4.83–4.75 (2H, m, $CqCH_2$), 2.39 (3H, s, CH_3), 2.30 (6H, s, CH_3), 0.95 (3H, t, ^3J = 7.3 Hz, CH_2CH_3), 0.75–0.66 (2H, m, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.6 (arom. CH *o*-Py), 148.9 (NCN), 147.8 (arom. Cq), 139.9 (arom. Cq), 139.1 (arom. Cq), 137.7 (arom. CH *p*-Py), 136.9 (arom. Cq), 136.0 (arom. Cq), 129.3 (arom. CH), 129.2 (arom. CH), 129.1 (arom. CH), 124.7 (arom. CH), 124.4 (arom. CH), 123.8 (NCH Imid.), 122.9 (NCH Imid.), 120.1 (arom. CH), 74.9 (Cq), 42.3 ($CqCH_2$), 21.3 (CH_3), 19.3 ($2CH_3$), 17.6 (CH_2CH_3), 14.4 (CH_2CH_3) ppm. Found C, 61.03; H, 5.11; N, 6.49. Calcd for $C_{33}H_{33}Cl_2N_3Pd$ (M_r = 648.97): C, 61.08; H, 5.15; N, 6.48%.

***trans*-[1-(9-Propylfluoren-9-yl)-3-(2,6-diisopropylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride ($\mathbf{6}^{\mathbf{Pr}}$).** A suspension of imidazolium salt $\mathbf{4}^{\mathbf{Pr}}$ (0.639 g, 1.22 mmol), finely crushed K_2CO_3 (0.850 g, 6.15 mmol), and $PdCl_2$ (0.259 g, 1.46 mmol) in pyridine (18 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 25 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford $\mathbf{6}^{\mathbf{Pr}}$ as a yellow solid (0.673 g, 80%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ 8.77–8.73 (2H, m, *o*-NC_5H_5), 7.85 (2H, d, ^3J = 7.5 Hz, ArH), 7.77 (2H, d, ^3J = 7.5 Hz, ArH), 7.67 (1H, tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.53 (1H, t, ^3J = 7.8 Hz, ArH), 7.47 (2H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.43–7.36 (4H, m, ArH), 7.27–7.22 (2H, m, *m*-NC_5H_5), 6.75 (1H, d, ^3J = 1.9 Hz, NCH), 6.27 (1H, d, ^3J = 1.9 Hz, NCH), 4.88–4.79 (2H, m, $CqCH_2$), 3.02 (2H, qq, ^3J = $^3J'$ = 6.8 Hz, $CHMe_2$), 1.50 (6H, d, ^3J = 6.8 Hz, CH_3), 0.98 (6H, d, ^3J = 6.8 Hz, CH_3), 0.96 (3H, t, ^3J = 7.3 Hz, CH_2CH_3), 0.78–0.66 (2H, m, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.4 (arom. CH *o*-Py), 150.1 (NCN), 147.8 (arom. Cq), 147.5 (arom. Cq), 139.9 (arom. Cq), 137.7 (arom. CH *p*-Py), 135.7 (arom. Cq), 130.3 (arom. CH), 129.3 (arom. CH), 129.0 (arom. CH), 125.7 (arom. CH), 124.8 (arom. CH), 124.4 (arom. CH), 123.9 (arom. CH), 121.9 (arom. CH), 120.0 (arom. CH), 75.0 (Cq), 42.2 ($CqCH_2$), 28.7 ($CHMe_2$), 26.7 (CH_3), 23.2 (CH_3), 17.5 (CH_2CH_3), 14.4 (CH_2CH_3) ppm. Found C, 62.84; H, 5.73; N, 6.00. Calcd for $C_{36}H_{39}Cl_2N_3Pd$ (M_r = 691.05): C, 62.57; H, 5.69; N, 6.08%.

***trans*-[1-(9-Ethoxymethylfluoren-9-yl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene](pyridine)palladium(II) dichloride ($\mathbf{5}^{\mathbf{EOM}}$).** A suspension of imidazolium salt $\mathbf{3}^{\mathbf{EOM}}$ (0.641 g, 1.29 mmol), finely crushed K_2CO_3 (0.900 g, 6.51 mmol), and $PdCl_2$ (0.276 g,

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1.56 mmol) in pyridine (20 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 30 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; EtOAc/CH_2Cl_2, 1.5 : 98.5) to afford $\mathbf{5^{EOM}}$ as a yellow solid (0.521 g, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ 8.64–8.60 (2H, m, *o*-NC_5H_5), 7.83 (2H, d, ^3J = 7.5 Hz, ArH), 7.74 (2H, d, ^3J = 7.5 Hz, ArH), 7.63 (1H, tt, ^3J = 7.8 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.44 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.35 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.23–7.16 (2H, m, *m*-NC_5H_5), 7.03 (2H, s, ArH), 6.72 (1H, d, ^3J = 1.9 Hz, NCH), 6.64 (1H, d, ^3J = 1.9 Hz, NCH), 6.05 (2H, s, $CqCH_2$), 3.42 (2H, q, ^3J = 7.0 Hz, OCH_2CH_3), 2.36 (3H, s, CH_3), 2.27 (6H, s, CH_3), 0.95 (3H, t, ^3J = 7.0 Hz, OCH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.4 (arom. CH *o*-Py), 149.4 (NCN), 146.3 (arom. Cq), 140.7 (arom. Cq), 139.1 (arom. Cq), 137.7 (arom. CH *p*-Py), 136.8 (arom. Cq), 135.7 (arom. Cq), 129.4 (arom. CH), 129.2 (arom. CH), 128.4 (arom. CH), 125.2 (arom. CH), 124.3 (arom. CH), 123.7 (NCH Imid.), 123.0 (NCH Imid.), 120.1 (arom. CH), 74.9 ($CqCH_2$), 73.5 (Cq), 67.7 (OCH_2CH_3), 21.2 (CH_3), 19.2 ($2CH_3$), 14.9 (OCH_2CH_3) ppm. Found C, 58.59; H, 4.82; N, 6.19. Calcd for $C_{33}H_{33}Cl_2N_3OPd$ (M_r = 664.97): C, 59.61; H, 5.00; N, 6.32%.

***trans*-[1-(9-Ethoxymethylfluoren-9-yl)-3-(2,6-diisopropylphenyl) imidazol-2-ylidene](pyridine)palladium(II) dichloride ($\mathbf{6^{EOM}}$).** A suspension of imidazolium salt $\mathbf{4^{EOM}}$ (0.500 g, 0.928 mmol), finely crushed K_2CO_3 (0.642 g, 4.64 mmol), and $PdCl_2$ (0.197 g, 1.11 mmol) in pyridine (15 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 20 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2) to afford $\mathbf{6^{EOM}}$ as a yellow solid (0.444 g, 68%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 8.68–8.64 (2H, m, *o*-NC_5H_5), 7.90 (2H, d, ^3J = 7.5 Hz, ArH), 7.78 (2H, d, ^3J = 7.5 Hz, ArH), 7.65 (1H, tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.53 (1H, t, ^3J = 7.7 Hz, ArH), 7.48 (2H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.43–7.35 (4H, m, ArH), 7.25–7.19 (2H, m, *m*-NC_5H_5), 6.83 (1H, d, ^3J = 1.9 Hz, NCH), 6.62 (1H, d, ^3J = 1.9 Hz, NCH), 6.18 (2H, s, $CqCH_2$), 3.43 (2H, q, ^3J = 7.0 Hz, OCH_2CH_3), 2.98 (2H, qq, $^3J = {}^3J'$ = 6.7 Hz, $CHMe_2$), 1.47 (6H, d, ^3J = 6.7 Hz, CH_3), 0.99 (6H, d, ^3J = 6.7 Hz, CH_3), 0.97 (3H, t, ^3J = 7.0 Hz, OCH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.3 (arom. CH *o*-Py), 150.5 (NCN), 147.4 (arom. Cq), 146.4 (arom. Cq), 140.8 (arom. Cq), 137.7 (arom. CH *p*-Py), 135.4 (arom. Cq), 130.3 (arom. CH), 129.4 (arom. CH), 128.4 (arom. CH), 125.6 (arom. CH), 125.3 (arom. CH), 124.3 (arom. CH), 123.9 (arom. CH), 122.1 (arom. CH), 120.1 (arom. CH), 74.9 ($CqCH_2$), 73.7 (Cq), 67.7 (OCH_2CH_3), 28.6 ($CHMe_2$), 26.7 (CH_3), 23.1 (CH_3), 14.8 (OCH_2CH_3) ppm. Found C, 61.19; H, 5.52; N, 5.90. Calcd for $C_{36}H_{39}Cl_2N_3OPd$ (M_r = 707.05): C, 61.16; H, 5.56; N, 5.94%.

Synthesis of symmetrical imidazolium salts 7^R and 8^R

1,3-Bis(fluoren-9-yl)imidazolium tetrafluoroborate ($\mathbf{7^H}$). The following procedure follows that applied by Mauduit *et al.* for the synthesis of *unsymmetrical* imidazolium salts.[16] A mixture of 9-fluorenylamine (1.66 g, 9.16 mmol) and acetic acid (1.18 mL, 1.24 g, 20.6 mmol) was heated at 60 °C for 5 min, then $MgSO_4$ (1.10 g, 9.16 mmol) was added. This gave mixture A. In another flask, a mixture of glyoxal (0.525 mL, 0.664 g, 4.58 mmol, 40 wt% in water), formaldehyde (0.343 mL, 0.371 g, 4.58 mmol, 37 wt% in water) and acetic acid (1.18 mL, 1.24 g, 20.6 mmol) was heated at 60 °C for 5 min, then $ZnCl_2$ (0.750 g, 5.50 mmol) was added. This gave mixture B. Mixture B was then added to mixture A at 60 °C. After stirring for 25 min, the solution was cooled to room temperature. CH_2Cl_2 (50 mL) and a 3 M aqueous solution of HCl (90 mL) were added and the resulting mixture was stirred for 1 h at room temperature. The organic layer was separated, water (40 mL) and ammonium tetrafluoroborate (1.92 g, 18.3 mmol) were added and the mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous layer treated with CH_2Cl_2 (2 × 25 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was washed with EtOAc (25 mL) then with diethyl ether (25 mL). After drying, product $\mathbf{7^H}$ was obtained as a white solid (1.79 g, 81%). ^{1}H NMR ([D_6]DMSO, 500 MHz), δ 9.73 (1H, t, ^4J = 1.5 Hz, NCHN), 8.03 (4H, d, ^3J = 7.5 Hz, ArH), 7.65 (4H, d, ^3J = 7.5 Hz, ArH), 7.59 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.53 (2H, d, ^4J = 1.5 Hz, NCH), 7.45 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 6.83 (2H, s, aliph. CH) ppm. $^{13}C\{^1H\}$ NMR ([D_6]DMSO, 125 MHz), δ 140.4 (arom. Cq), 140.0 (arom. Cq), 137.1 (NCHN), 130.3 (arom. CH), 128.5 (arom. CH), 125.5 (arom. CH), 121.9 (NCH), 121.0 (arom. CH), 62.7 (aliph. CH) ppm. ^{19}F NMR ([D_6]DMSO, 282 MHz), −148.19 (br s, ^{19}F–^{10}B), −148.24 (q, $^1J(^{19}F$–$^{11}B)$ = 1.1 Hz) ppm. Found C, 71.42; H, 4.43; N, 5.90. Calcd for $C_{29}H_{21}BF_4N_2 \cdot 0.05\ CH_2Cl_2$ (M_r = 484.30 + 4.25): C, 71.42; H, 4.35; N, 5.73%.

1,3-Bis(9-methylfluoren-9-yl)imidazolium tetrafluoroborate ($\mathbf{8^{Me}}$). LiHMDS (4.43 mL, 4.43 mmol, 1 M in THF) was added dropwise to a stirred suspension of imidazolium tetrafluoroborate $\mathbf{7^H}$ (0.895 g, 1.85 mmol) in THF (25 mL) cooled at −50 °C. After stirring for 1 h, the reaction mixture was allowed to reach room temperature, then CH_3I (0.700 mL, 1.57 g, 11.1 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added. The solvent was removed under reduced pressure and water (20 mL) was added. The product was extracted with CH_2Cl_2 (3 × 20 mL), the organic layers were combined and the solvent was removed under reduced pressure. To the crude mixture dissolved in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (1.16 g, 11.1 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was treated with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; EtOAc/CH_2Cl_2, 5 : 95) to afford $\mathbf{8^{Me}}$ as a white solid (0.740 g, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ 9.87 (1H, t, ^4J = 1.3 Hz, NCHN), 7.69 (4H, d, ^3J = 7.5 Hz, ArH), 7.72 (4H, d, ^3J = 7.5 Hz, ArH), 7.44 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.38 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 6.38 (2H, d, ^4J = 1.3 Hz, NCH), 2.51 (6H,

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s, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 145.3 (arom. Cq), 139.0 (arom. Cq), 134.6 (NCHN), 130.4 (arom. CH), 129.4 (arom. CH), 124.4 (arom. CH), 120.8 (arom. CH), 120.6 (arom. CH), 71.6 (Cq), 23.4 (CH_3) ppm. ^{19}F NMR ($CDCl_3$, 470 MHz), δ −149.15 (br s, ^{19}F–^{10}B), −149.20 (br s, ^{19}F–^{11}B) ppm. Found C, 72.14; H, 5.12; N, 5.23. Calcd for $C_{31}H_{25}BF_4N_2 \cdot 0.15\ H_2O$ (M_r = 512.36 + 2.70): C, 72.29; H, 4.95; N, 5.44%.

1,3-Bis(9-ethylfluoren-9-yl)imidazolium tetrafluoroborate (8^{Et}). LiHMDS (7.92 mL, 7.92 mmol, 1 M in THF) was added dropwise to a stirred suspension of imidazolium tetrafluoroborate 7^H (1.59 g, 3.30 mmol) in THF (50 mL) cooled at −50 °C. After stirring for 1 h (with the temperature maintained at −50 °C), the reaction mixture was allowed to reach room temperature, then EtBr (1.50 mL, 2.15 g, 19.8 mmol) was added. The mixture was stirred overnight at room temperature, then MeOH (3 mL) was added to quench any further reaction. The solvent was removed under reduced pressure and water (30 mL) was added. The product was extracted with CH_2Cl_2 (3 × 30 mL), the organic layers were combined and the solvent was removed under reduced pressure. To the crude mixture dissolved in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (2.07 g, 19.8 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was treated with CH_2Cl_2 (2 × 30 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; EtOAc/CH_2Cl_2, 7 : 93) to afford 8^{Et} as a white solid (1.38 g, 77%). ^1H NMR ($CDCl_3$, 500 MHz), δ 9.60 (1H, s, NCHN), 7.70 (4H, d, ^3J = 7.5 Hz, ArH), 7.60 (4H, d, ^3J = 7.5 Hz, ArH), 7.46 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.38 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.61 (2H, s, NCH), 3.08 (4H, q, ^3J = 7.2 Hz, CH_2), 0.49 (6H, t, ^3J = 7.2 Hz, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 142.9 (arom. Cq), 140.3 (arom. Cq), 133.5 (NCHN), 130.6 (arom. CH), 129.4 (arom. CH), 124.2 (arom. CH), 120.9 (arom. CH), 120.7 (arom. CH), 75.3 (Cq), 29.1 (CH_2), 7.9 (CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), δ −151.54 (br s, ^{19}F–^{10}B), −151.56 to −151.62 (m, ^{19}F–^{11}B) ppm. Found C, 73.28; H, 5.43; N, 5.26. Calcd for $C_{33}H_{29}BF_4N_2$ (M_r = 540.41): C, 73.34; H, 5.41; N, 5.18%.

1,3-Bis(9-propylfluoren-9-yl)imidazolium tetrafluoroborate (8^{Pr}). LiHMDS (4.90 mL, 4.90 mmol, 1 M in THF) was added dropwise to a stirred suspension of imidazolium tetrafluoroborate 7^H (0.987 g, 2.04 mmol) in THF (25 mL) cooled at −50 °C. After stirring the cold solution for 1 h, the reaction mixture was allowed to reach room temperature and *n*-PrBr (1.10 mL, 1.50 g, 12.2 mmol) was added. The mixture was stirred overnight at room temperature and MeOH (2 mL) was added. The solvent was removed under reduced pressure before water (20 mL) was added. The product was extracted with CH_2Cl_2 (3 × 20 mL), the organic layers were combined and the solvent was removed under reduced pressure. To the crude mixture dissolved in CH_2Cl_2 (30 mL) was added water (30 mL) and ammonium tetrafluoroborate (1.28 g, 12.2 mmol). The mixture was vigorously stirred at room temperature for 1 h. The organic layer was separated and the aqueous phase was treated with CH_2Cl_2 (2 × 20 mL). The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (SiO_2; EtOAc/CH_2Cl_2, 5 : 95) to afford 8^{Pr} as a white solid (0.888 g, 76%). ^1H NMR ($CDCl_3$, 500 MHz), δ 9.65 (1H, t, ^4J = 1.4 Hz, NCHN), 7.70 (4H, d, ^3J = 7.5 Hz, ArH), 7.61 (4H, d, ^3J = 7.5 Hz, ArH), 7.45 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.37 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 6.59 (2H, d, ^4J = 1.4 Hz, NCH), 3.03–2.97 (4H, m, $CqCH_2$), 0.85 (6H, t, ^3J = 7.1 Hz, CH_3), 0.80–0.71 (4H, m, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 140.2 (arom. Cq), 140.3 (arom. Cq), 133.4 (NCHN), 130.5 (arom. CH), 129.3 (arom. CH), 124.1 (arom. CH), 120.8 (arom. CH), 120.7 (arom. CH), 74.6 (Cq), 37.7 ($CqCH_2$), 16.9 (CH_2CH_3), 13.5 (CH_2CH_3) ppm. ^{19}F NMR ($CDCl_3$, 282 MHz), −151.95 (br s, ^{19}F–^{10}B), −150.98 to −151.02 (m, ^{19}F–^{11}B) ppm. Found C, 73.73; H, 5.91; N, 4.86. Calcd for $C_{35}H_{33}BF_4N_2$ (M_r = 568.47): C, 73.95; H, 5.85; N, 4.93%.

Synthesis of palladium complexes 9

***trans*-[1,3-Bis(9-methylfluoren-9-yl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (9^{Me}).** A suspension of imidazolium salt 8^{Me} (0.367 g, 0.716 mmol), finely crushed K_2CO_3 (0.500 g, 3.61 mmol), and $PdCl_2$ (0.153 g, 0.862 mmol) in pyridine (10 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 25 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford 9^{Me} as a yellow solid (0.393 g, 81%). ^1H NMR ($CDCl_3$, 500 MHz), δ 9.15 (2H, d, ^3J = 5.2 Hz, *o*-NC_5H_5), 7.88–7.79 (5H, m, 4ArH and *p*-NC_5H_5), 7.70 (4H, d, ^3J = 7.5 Hz, ArH), 7.44–7.36 (6H, m, 4ArH and *m*-NC_5H_5), 7.33 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 5.85 (2H, s, NCH), 3.71 (6H, s, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.7 (arom. CH *o*-Py), 149.7 (NCN), 144.9 (arom. Cq), 138.4 (arom. Cq), 138.1 (arom. CH), 129.1 (arom. CH), 128.9 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 122.5 (arom. CH), 120.2 (arom. CH), 71.0 (Cq), 28.8 (CH_3) ppm. Found C, 63.56; H, 4.26; N, 6.14. Calcd for $C_{33}H_{29}Cl_2N_3Pd$ (M_r = 680.97): C, 63.50; H, 4.29; N, 6.17%.

***trans*-[1,3-Bis(9-methylfluoren-9-yl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (9^{Et}).** A suspension of imidazolium salt 8^{Et} (0.600 g, 1.11 mmol), finely crushed K_2CO_3 (0.767 g, 5.54 mmol), and $PdCl_2$ (0.236 g, 1.33 mmol) in pyridine (18 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 25 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford 9^{Et} as a yellow solid (0.623 g, 79%). ^1H NMR ($CDCl_3$, 400 MHz), δ 9.15–9.11 (2H, m, *o*-NC_5H_5), 7.82 (1H, tt, ^3J = 7.6 Hz, ^4J = 1.6 Hz, *p*-NC_5H_5), 7.76 (4H, d, ^3J = 7.5 Hz, ArH), 7.66 (4H, d, ^3J = 7.5 Hz, ArH), 7.45–7.40 (2H, m, *m*-NC_5H_5), 7.37 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 7.32 (4H, dd, ^3J = $^3J'$ = 7.5 Hz, ArH), 5.85 (2H, s, NCH), 4.99 (4H, q, ^3J = 7.3 Hz, CH_2), 0.47 (6H, t, ^3J = 7.3 Hz, CH_3) ppm. NMR data are consistent with those given in the literature.[10e]

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***trans*-[1,3-Bis(9-propylfluoren-9-yl)imidazol-2-ylidene](pyridine)palladium(II) dichloride (9^{Pr}).** A suspension of imidazolium salt 8^{Pr} (0.542 g, 0.953 mmol), finely crushed K_2CO_3 (0.656 g, 4.75 mmol), and $PdCl_2$ (0.202 g, 1.14 mmol) in pyridine (15 mL) was heated at 80 °C for 18 h under vigorous stirring. The mixture was cooled to room temperature, filtered through Celite and the retained solid washed with CH_2Cl_2 (*ca.* 25 mL). The filtrate was evaporated to dryness and the residue purified by flash chromatography (SiO_2; CH_2Cl_2/petroleum ether, 50 : 50) to afford 9^{Pr} as a yellow solid (0.611 g, 87%). ^{1}H NMR ($CDCl_3$, 500 MHz), δ 9.12 (2H, d, ^3J = 5.3 Hz, *o*-NC_5H_5), 7.82 (1H, t, ^3J = 7.6 Hz, *p*-NC_5H_5), 7.78 (4H, d, ^3J = 7.5 Hz, ArH), 7.66 (4H, d, ^3J = 7.5 Hz, ArH), 7.44–7.40 (2H, m, *m*-NC_5H_5), 7.37 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 7.32 (4H, dd, $^3J = {}^3J'$ = 7.5 Hz, ArH), 5.81 (2H, s, NCH), 5.08–4.98 (4H, m, $CqCH_2$), 0.98 (6H, t, ^3J = 7.3 Hz, CH_3), 0.75–0.65 (4H, m, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz), δ 151.7 (arom. CH *o*-Py), 144.3 (NCN), 144.9 (arom. Cq), 139.8 (arom. Cq), 138.0 (arom. CH), 129.1 (arom. CH), 128.9 (arom. CH), 124.9 (arom. CH), 124.8 (arom. CH), 122.4 (arom. CH), 119.9 (arom. CH), 74.9 (Cq), 42.5 ($CqCH_2$), 17.7 (CH_2CH_3), 14.5 (CH_2CH_3) ppm. Found C, 65.13; H, 4.97; N, 5.67. Calcd for $C_{40}H_{37}Cl_2N_3Pd$ (M_r = 737.08): C, 65.18; H, 5.06; N, 5.70%.

General procedure for palladium-catalysed Suzuki–Miyaura cross-coupling reactions

A mixture of palladium complex (0.01 mmol), phenylboronic acid (0.183 g, 1.50 mmol), Cs_2CO_3 (0.652 g, 2.00 mmol) and, for the specific runs carried out in the presence of mercury, Hg (50 μl, 0.677 g, 3.38 mol), was suspended in dioxane (3 mL). After addition of *p*-tolyl chloride (0.126 g, 1.00 mmol), the mixture was vigorously stirred at 80 °C for a given period of time. The hot mixture was filtered through Celite. 1,4-Dimethoxybenzene (0.069 g, 0.5 mmol; internal standard) was then added to the filtrate. The solvent was removed under reduced pressure, and the crude mixture was analysed by ^{1}H NMR spectroscopy. The yields were determined by comparing the intensity of the methyl signal of the product [δ(Me) = 2.41 ppm] with that of the internal reference [δ(Me) = 3.78 ppm]. In some experiments the product was isolated chromatographically. The isolated yield turned out to be very close (deviation less than 5%) to that determined by using the internal reference.

X-ray crystallography

Crystal data for complex 5^{Et}. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. Crystal data: $C_{32}H_{31}Cl_2N_3Pd$, M_r = 634.90 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 10.7007(4) Å, b = 14.7879(7) Å, c = 17.9151(7) Å, $\alpha = \beta = \gamma$ = 90°, V = 2834.9(2) Å^3, Z = 4, D = 1.488 g cm^{-3}, μ = 0.869 mm^{-1}, F(000) = 1296, T = 173(2) K. The sample was studied on a Kappa APEX II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 60.4°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: h – 15,9 k – 20,20 l – 25,25) gave 65 424 reflections. The structure was solved using SHELXS-2013,[22] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found using a Fourier difference map. The structure was refined using SHELXL-2013[23] by the full-matrix least-squares technique (use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N and Pd atoms; x, y, z in riding mode for H atoms); 347 variables and 7970 observations with $I > 2.0\sigma(I)$; calcd w = 1/[$\sigma^2(F_o^2)$ + (0.0098P)^2 + 3.8829P] where $P = (F_o^2 + 2F_c^2)/3$, with the resulting R = 0.0326, R_W = 0.0703 and S_W = 1.172, $\Delta\rho$ < 1.317 e Å^{-3}. CCDC 1897858.†

Crystal data for complex 6^{Et}. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. Crystal data: $C_{35}H_{37}Cl_2N_3Pd{\cdot}CH_2Cl_2$, M_r = 761.90 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 22.6496(4) Å, b = 10.2717(2) Å, c = 16.0422(2) Å, α = 90°, β = 104.4740(10)°, γ = 90°, V = 3613.76 (11) Å^3, Z = 4, D = 1.400 g cm^{-3}, μ = 0.838 mm^{-1}, F(000) = 1560, T = 173(2) K. The sample was studied on a Kappa CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 55.0°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: h – 29,29 k – 13,13 l – 20,20) gave 59 152 reflections. The structure was solved using SIR-92,[24] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found using a Fourier difference map. The structure was refined using SHELXL-2014[23] by the full-matrix least-squares technique (use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N and Pd atoms; x, y, z in riding mode for H atoms); 402 variables and 6731 observations with $I > 2.0\sigma(I)$; calcd w = 1/[$\sigma^2(F_o^2)$ + (0.0705P)^2 + 8.7427P] where $P = (F_o^2 + 2F_c^2)/3$, with the resulting R = 0.0551, R_W = 0.1507 and S_W = 1.102, $\Delta\rho$ < 3.267 e Å^{-3}. CCDC 1897859.†

Crystal data for complex 5^{Pr}. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. Crystal data: $C_{33}H_{33}Cl_2N_3Pd$, M_r = 648.92 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 10.7502(2) Å, b = 24.8309(5) Å, c = 11.05370(10) Å, α = 90°, β = 93.3620(10), γ = 90°, V = 2945.57(9) Å^3, Z = 4, D = 1.463 g cm^{-3}, μ = 0.839 mm^{-1}, F(000) = 1328, T = 173(2) K. The sample was studied on a Kappa CCD diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 54.9°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: h – 13,13 k – 31,32 l – 14,14) gave 45 352 reflections. The structure was solved using SIR-92,[24] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found using a Fourier difference map. The structure was refined using SHELXL-2014[23] by the full-matrix least-squares technique (use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N and Pd atoms; x, y, z in riding mode for H atoms); 356 variables and 5502 observations with $I > 2.0\sigma(I)$; calcd w = 1/[$\sigma^2(F_o^2)$ + (0.0260P)^2 + 5.9879P] where $P = (F_o^2 + 2F_c^2)/3$, with the resulting R = 0.0468, R_W = 0.1028 and S_W = 1.085, $\Delta\rho$ < 0.576 e Å^{-3}. CCDC 1897856.†

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Crystal data for complex 6^{EOM}. Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a dichloromethane solution of the complex. Crystal data: $C_{36}H_{39}Cl_2N_3OPd.CH_2Cl_2$, M_r = 791.93 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 12.1594(2) Å, b = 19.9702(3) Å, c = 15.1796(3) Å, α = 90°, β = 99.3060(10)°, γ = 90°, V = 3637.48(11) Å^3, Z = 4, D = 1.446 g cm^{-3}, μ = 0.837 mm^{-1}, $F(000)$ = 1624, T = 173(2) K. The sample was studied on a Kappa CCD diffractometer (graphite monochromated Mo-K$_\alpha$ radiation, λ = 0.71073 Å). The data collection ($2\theta_{max}$ = 54.9.0°, omega scan frames by using 0.7° omega rotation and 30 s per frame, range *hkl*: h – 15,15 k – 25,25 l – 19,19) gave 59 394 reflections. The structure was solved using SHELXS-2014,[22] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, all of the hydrogen atoms were found using a Fourier difference map. The structure was refined using SHELXL-2014[23] by the full-matrix least-squares technique (use of F^2 magnitude; x, y, z, β_{ij} for C, Cl, N, O and Pd atoms; x, y, z in riding mode for H atoms); 427 variables and 6730 observations with $I > 2.0\sigma(I)$; calcd w = $1/[\sigma^2(F_o^2) + (0.0589P)^2 + 2.0747P]$ where $P = (F_o^2 + 2F_c^2)/3$, with the resulting R = 0.0426, R_W = 0.1218 and S_W = 1.161, $\Delta\rho$ < 0.736 e Å^{-3}. CCDC 1897857.†

Conflicts of interest

There are no conflicts of interest to declare.

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