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ortho-Phenylene bridged palladium bis-*N*-heterocyclic carbene complexes: synthesis, structure and catalysis†

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A series of *ortho*-phenylene bridged palladium bis-NHC complexes has been synthesized. Complexes with imidazolium and benzimidazolium derived NHCs and methyl-/benzyl-wingtips are reported. Bis-(benz)imidazoles with a doubly brominated *ortho*-phenylene bridge could be obtained by an electrophilic substitution reaction. The structure of the complexes could be confirmed by three solid-state structures. All catalysts have been tested in the catalytic functionalisation of propane. The catalytic activity is highly dependent on the ligand, whereas ligand effects on the regioselectivity (*n*/*iso*) are much smaller.

Introduction

N-heterocyclic carbene ligands have been established as an alternative to phosphines in catalysis and their synthesis, properties and applications have been reviewed in detail.[1–9] Palladium(II) complexes with chelating bis-NHC ligands have been shown to be very active catalysts for many cross coupling reactions.[10–19] The selective functionalisation of saturated hydro-carbons remains an enormous challenge for chemistry and is a highly active field of research.[20–32] Due to the extraordinary stability under oxidative and acidic conditions chelated bis-NHC palladium complexes can be used for the catalytic functionalisation of methane in trifluoroacetic acid (HOTFA).[17–19,33] It has also been demonstrated that these and related amidate complexes can be used for the trifluoroacetoxylation of functionalised alkanes.[34,35]

The functionalisation of alkanes by palladium acetate ($Pd(OAc)_2$) in trifluoroacetic acid has been shown to involve the formation of palladium(0).[36–41] But in contrast to $Pd(OAc)_2$ we do not observe the formation of palladium black in the stoichiometric reaction of cyclohexane with chelated palladium bis-NHC catalysts in trifluoroacetic acid.[42] We therefore believe that the palladium(II) bis-NHC complex catalysed functionalisation of hydrocarbons does not involve the formation of palladium(0).[43] It has also been shown that chelated palladium(IV) bis-NHC complexes and palladium(II) bis-NHC alkyl complexes are stable compounds and therefore viable intermediates of a catalytic cycle.[44–47]

Much research effort has been devoted to the oxidative conversion of light alkanes to more valuable C_3 products like propene, acrylic acid, acrylonitrile or acroleine, which are important intermediates for the chemical industry.[48,49] Herein we report on the functionalisation of propane, which in contrast to methane additionally allows for the investigation of ligand effects on the chemo- and regioselectivity.

The modular structure of the chelated bis-NHC complexes essentially relies on four different building blocks. Those are the nature of the bridge (*e.g.* methylene *vs.* *ortho*-phenylene), the particular NHCs employed (*e.g.* imidazole *vs.* benzimidazole), the wingtips R on the NHC moieties (*e.g.* methyl *vs.* benzyl) and the nature of the counter ligands (Fig. 1).[12,50,51]

It has been shown that the hydrogen atoms of the methylene bridge of bis-NHC palladium(II) complexes are acidic and interact with anions present in the reaction mixture.[44] Furthermore we could show that NHC–pyrimidine complexes show significantly lower activity[18] than methylene or ethylene

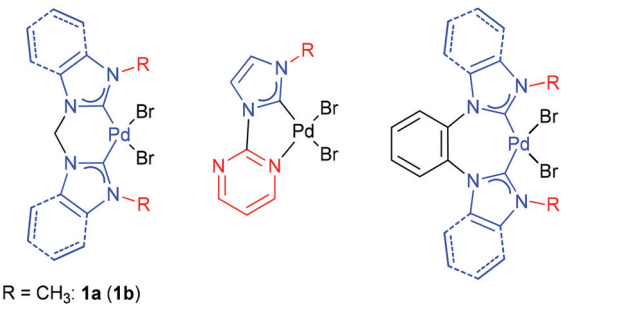

Fig. 1 Modular structure of palladium(II)–NHC complexes with chelating ligands. For complexes **1a** (R = Me, imidazole) and **1b** (R = Me, benzimidazole) also see Table 1.

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†Electronic supplementary information (ESI) available: Tables of crystal data parameters, bond lengths, bond angles, and thermal displacement parameters for **8a**, **8b** and **11a** in .cif format. CCDC 915849 (**8a**), 915850 (**8b**), and 915851 (**11a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33006k

bridged biscarbene complexes[17] in the functionalisation of methane. We therefore set out to synthesise a series of *ortho*-phenylene bridged chelated bis-NHC complexes in order to avoid potential problems induced by the methylene bridge and to systematically study the influence of electronic and steric effects of the ligand design on the overall catalytic activity in comparison to the methylene bridged analogues. The variation of the nature of the bridge connecting the two NHC building blocks mainly changes the conformational rigidity and the bite angle of the ligand.[52,53]

Electronic effects have been investigated by substituents at the aromatic ring and by substitution of imidazole- by benzimidazole-NHCs.[54,55] The variation of the wingtip substituents mainly changes steric aspects of the catalyst.[56–58] Electronic effects of the two wingtip substituents have been considered to be rather small.[59,60]

In the literature there are so far only few reports about the synthesis and especially catalytic activity of phenylene bridged bis-NHC complexes and to our knowledge no transition metal complexes with additional functionality at the aryl moiety of the ligand have been prepared.[61–70]

Results and discussion

The *ortho*-phenylene bridged bisimidazoles and bis-benzimidazoles are synthesised *via* two different routes starting from aryl bishalides (Scheme 1). Fluorides in *ortho*-position at electron deficient phenyl rings are selectively substituted under basic conditions by (benz)imidazoles following an electrophilic aromatic substitution mechanism in 66% yield for imidazole (**3a**) and in 47% for benzimidazole (**3b**). The more electron rich *ortho*-phenylene bisimidazoles **2a**[71] and **2b** are synthesized by an Ullman type coupling in the presence of copper salts in moderate yields well below 50%. Treatment of the bis(benz)imidazoles with methylbromide or benzylbromide in acetonitrile then affords the imidazolium salts **4–7** in almost quantitative yields (Scheme 1). Reaction with palladium acetate in DMSO leads to the formation of the bis-NHC palladium(II) complexes (**8–11**).

Solid-state structures of complexes **8a** (Fig. 2), **8b** (Fig. 3) and **11a** (Fig. 4) could be determined. Single crystals of **8a** were obtained by slow diffusion of diethyl ether into a saturated solution of the palladium complex in acetonitrile and for **8b** and **11a** by slow evaporation of the solvent of saturated solutions.

The palladium bis-NHC complex **8a** is structurally very similar to the bis-NHC complex **1a**.[72] The bite angle C_1–Pd_1–C_{10} in **8a** (83.45(15)°) does not differ significantly from the reported value in **1a** (83.2(2)°) and also the Pd–$C_{carbene}$ (1.965(4) Å and 1.958(3) Å for **8a** and 1.983(5) Å and 1.971(5) Å for **1a**) and Pd–Br bond lengths (2.4960(6) Å and 2.4885(8) Å *vs.* 2.4999(6) Å and 2.4942(6) Å) are very similar. The *ortho*-phenylene bridge however pushes the imidazolylidene moieties into a more perpendicular position regarding the square planar coordination geometry of the palladium atom (**8a** Br_1–Pd_1–C_1–N_2 114.0(3)°, **1a** 131.1(5)°). The solid-state structure of the benzimidazolylidene equivalent **8b** (Fig. 3) reveals a smaller bite angle C_1–Pd_1–C_{10} of 82.45(13)°, but also comparable Pd–$C_{carbene}$ bond lengths (1.957(3) Å and 1.964(3) Å).

The unit cell of compound **11a** contains two equivalent molecules of **11a** and three dichloromethane molecules. The solid-state structure indicates a considerably larger bite angle

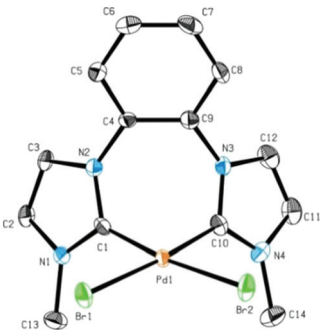
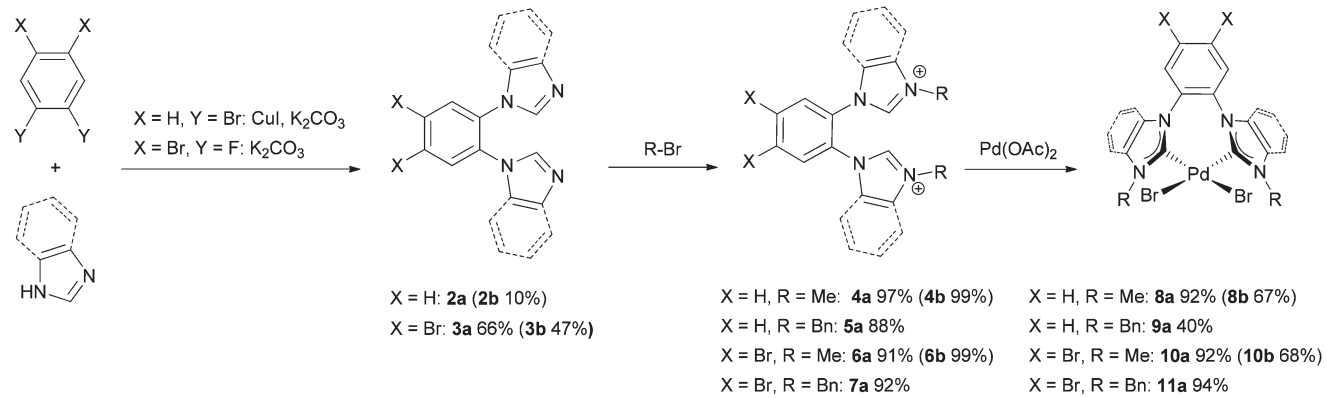


Fig. 2 Solid-state structure of **8a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles and dihedral angles (°): Pd(1)–C(1) 1.965(4), Pd(1)–C(10) 1.958(3), Pd(1)–Br(1) 2.4960(6), Pd(1)–Br(2) 2.4885(8), Br(1)–Pd(1)–Br(2) 94.10(2), Br(1)–Pd(1)–C(1) 91.65(10), C(1)–Pd(1)–C(10) 83.45(15), Br(1)–Pd(1)–C(1)–N(2) 114.0(3), Br(2)–Pd(1)–C(10)–N(3) −114.1(3).



Scheme 1 Synthesis of *ortho*-phenylene bridged bis(benz)imidazoles (**2–3**), bis(benz)imidazolium salts (**4–7**) and bis-NHC palladium complexes (**8–11**). Yields for benzimidazole derived compounds (**b**) are given in parentheses after the corresponding imidazole derived compounds (**a**).

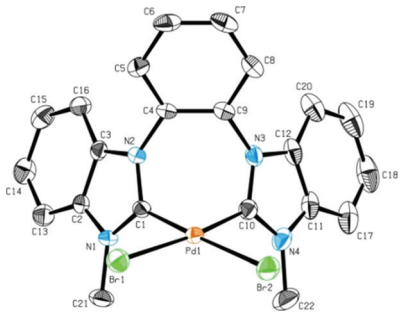


Fig. 3 Solid-state structure of **8b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and occluded acetonitrile molecules have been omitted for clarity. Selected bond lengths (Å), angles and dihedral angles (°): Pd(1)–C(1) 1.957(3), Pd(1)–C(10) 1.964(3), Pd(1)–Br(1) 2.4705(6), Pd(1)–Br(2) 2.4924(6), Br(1)–Pd(1)–Br(2) 94.52(2), Br(1)–Pd(1)–C(1) 90.53(9), C(1)–Pd(1)–C(10) 82.45(13), Br(1)–Pd(1)–C(1)–N(2) 114.1(3), Br(2)–Pd(1)–C(10)–N(3) −117.0(2).

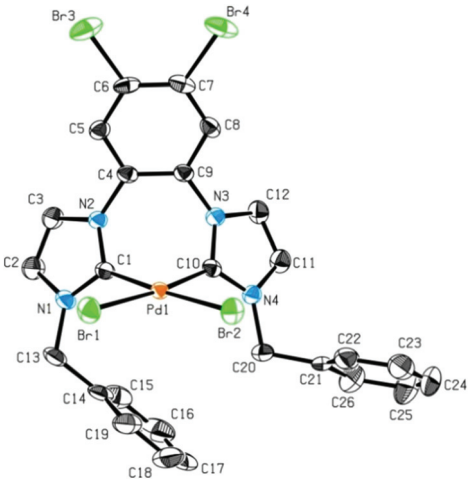


Fig. 4 Solid-state structure of **11a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and occluded dichloromethane molecules have been omitted for clarity. Selected bond lengths (Å), angles and dihedral angles (°): Pd(1)–C(1) 1.961(3), Pd(1)–C(10) 1.975(3), Br(1)–Pd(1)–Br(2) 92.12(2), Br(1)–Pd(1)–C(1) 90.59(10), C(1)–Pd(1)–C(10) 85.39(13), Br(1)–Pd(1)–C(1)–N(2) 113.3(3), Br(2)–Pd(1)–C(10)–N(3) −116.0(3), C(10)–N(4)–C(20)–C(21) −136.7(3), C(1)–N(1)–C(13)–C(14) 63.4(4).

C_1–Pd_1–C_{10} of 85.39(13)°. One of the two benzyl groups is bent away from the palladium centre (C_{10}–N_4–C_{20}–C_{21}).

The catalytic activity of complexes **8–11** was compared in the catalytic functionalisation of propane in trifluoroacetic acid with the oxidant peroxodisulfate. A reaction time of 12 h, which lies well below the time of maximum turnover, and a reaction temperature of 60 °C have been chosen in order to guarantee comparability between the different catalysts and in order to suppress theoretically possible competing radical pathways.[73,74] No signs of decomposition of the bis-NHC catalysts were observed during the course of the reaction.

Independent of the complex used we found *iso*-selectivity of 90% with the concomitant formation of *n*-product, allyl

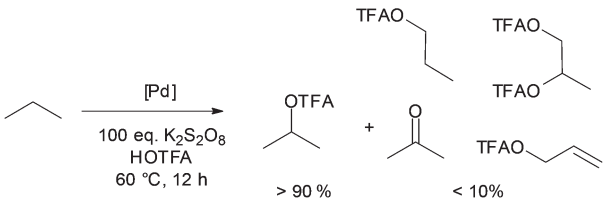


Fig. 5 Regio- and chemoselectivity of the functionalisation of propane in trifluoroacetic acid catalysed by palladium bis-NHC catalysts.

Table 1 Comparison of catalytic activity of palladium catalysts in the functionalisation of propane

Entry	Catalyst	TON
1	**8a**	30
2	**8b**	18
3	**9a**	3
4	**10a**	6
5	**10b**	Traces
6	**11a**	Traces
7	**1a**	28
8	**1b**	18
9	None	0
10	$Pd(OAc)_2$	6

trifluoroacetate, 1,2-ditrifluoroacetoxypropane and traces of acetone in a combined yield of about 10% (Fig. 5).

It has been reported that palladium(II) diphosphines react with hexane to preferentially form the internally functionalised thermodynamic products (*i.e.* 2- and 3- instead of 1-hexyl derivatives).[75] Similarly, it has been shown that under acidic conditions the functionalization of the higher substituted carbon atom is favoured in the case of palladium diimine catalysts and palladium acetate in trifluoroacetic acid.[40,76,77] Nevertheless there is also much precedence for the preferential functionalisation of the terminal methyl group of hydrocarbons,[77–83] which renders a further discussion of the regioselectivity challenging.

The obtained TONs turned out to be highly related to the particular catalyst employed (Table 1). We determined the highest TON for the *ortho*-phenylene bridged imidazole derived complex **8a** and a comparable activity for the methylene bridged complex **1a** (entries 1, 7). The benzimidazole derived catalysts **8b**, **10b** and **1b** show only about half of the activity of their imidazole counterparts (entries 2, 5, 8). The sterically more demanding benzyl group as the wingtip substituent leads to a drop in yield compared to the methyl substituent (entries 3, 6 *vs.* 1, 4). The bromine substituents at the central phenyl ring did not lead to a higher catalytic activity (entries 4, 5, 6). It is interesting to note that the structurally very similar catalysts **1a** and **8a** (and also **1b** and **8b**) both lead to high turnover numbers, whereas the benzyl substituted analogues **9a** and **11a** are significantly less active. In a test reaction without the addition of a palladium catalyst, no reaction products were observed (entry 9). To put the performance of the bis-NHC complexes into perspective they were also compared

to palladium acetate, which shows moderate activity of about one-fifth of the complexes **8a** or **1a** (entries 1, 10).

Sterically demanding wingtips of the *ortho*-phenylene bridged complexes (benzyl groups) seem to impede the activity of the catalysts without a significant effect on the regioselectivity. Likewise a reduction of electron density *via* a larger π-system or electron withdrawing groups (benzimidazole,[84] bromide) seems to decrease the activity of the catalyst. In contrast, the observed influence of the ligand design on the overall activity underlines that chelating bis-NHC ligands are important for an efficient reaction.

Conclusion

A series of *ortho*-phenylene bridged imidazolium and benzimidazolium derived palladium bis-NHC complexes has been synthesized. Three of the palladium(II) complexes could be characterised by single crystal X-ray structures. The catalytic activity of all synthesised catalysts has been tested in the oxidative trifluoroacetoxylation of propane in trifluoroacetic acid. The determined catalytic activity of the different catalysts is highly dependent on the ligand design, while the regio- and chemoselectivity of the reaction is significantly less affected. Further work is aiming at rationalising the observed ligand effects by mechanistic investigations.

Experimental details

General

Solvents of at least 99.5% purity were used throughout this study. DMF, MeCN and NMP have been dried by standard procedures prior to use. All other chemicals used were obtained from commercial suppliers and used without further purification.

The NMR spectra were recorded with a Bruker AC 300 P, Bruker DRX 500 P or Bruker Avance III 600 spectrometer and referenced internally to the solvent signals. Elemental analyses were measured by the analytical laboratory of the department using a Eurovektor Hekatech EA-3000 elemental analyzer. Melting points were determined using a Wagner and Munz PolythermA system. Slaughter reported deviating elemental analyses for similar *ortho*-phenylene bridged bis-NHC palladium complexes and imidazolium salts which are most probably due to insufficient combustion and which might as well be responsible for small deviations of the elemental analyses reported herein for compound **8b**.[66]

Positive mode ESI-MS spectra for the synthesised compounds were recorded on a Bruker Esquire MS with an Ion Trap Detector on samples dissolved in NH_4OAc buffered methanol, which has been reported to exchange the bromide ligand by acetate.

Catalyses were run in 10 mL crimp vials with *PTFE* faced butyl rubber septa. 8.4 μmol of palladium catalyst and 0.84 mmol of $K_2S_2O_8$ have been suspended in 5 mL of HOTFA. In cases where the catalyst amount was less than 5 mg, stock solutions of the catalyst in HOTFA have been freshly prepared. Subsequently propane was bubbled through the suspension for 60 seconds. The vials were sealed immediately and it was stirred vigorously at 60 °C for 12 h. The reaction mixture was analysed by gas chromatography with an Agilent 6850 Series II Networked GC equipped with a flame ionisation detector (FID) and a Macherey-Nagel Optima-210 0.25 μm column (30 m × 0.25 mm).

Quantification of the yield of the reaction products was done by adding 25 μL of C_6F_5Cl as the standard to 1.00 mL of the reaction mixture after the reaction and injection of this mixture into the GC. Reported TONs are based on *iso*-propyl trifluoroacetate only. The identity of the reaction products was confirmed by comparison to the retention time of defined samples and NMR spectra of the reaction mixtures in an NMR tube which contained a capillary filled with DMSO-d_6 to provide a lock signal. All GC measurements were repeated four times and catalysed twice. Given values are averaged over all measurements.

3,3′-Bis(methyl)-[(1,1′-diimidazolin-2,2′-diylidene) 1,1′-methylene] palladium(II) dibromide (1a). 1a was prepared as reported previously.[85]

3,3′-Bis(methyl)-[(1,1′-diibenzmidazolin-2,2′-diylidene) 1,1′-methylene] palladium(II) dibromide (1b). 1b was prepared as reported previously.[86] For single crystal X-ray structure determination, see the ESI.†[87–97]

General procedure for the synthesis of the bis(benz)imidazoles 2, 3

The given amount of benzene, (benz)imidazole, K_2CO_3 and in the case of **2b** copper iodide and phenanthroline were stirred in the solvent for the given time at the given temperature under argon. At the end of the reaction the mixture was diluted with dichloromethane, filtered and washed twice with brine (**2b**: a saturated solution of NH_3). After removal of the solvent *in vacuo* the crude products were subjected to column chromatography (dichloromethane : methanol = 9 : 1, silica gel KG60) and recrystallized at 3 °C from dichloromethane/diethyl ether (**2b**) or dichloromethane (**3b**) and dried *in vacuo* to afford the colourless compounds.

(1,2-Phenylene)bisimidazole (2a). 2a was prepared as reported previously.[62]

(1,2-Phenylene)bisbenzimidazole (2b). Reagents: 4.29 g (18.2 mmol) 1,2-dibromobenzene, 707 mg (3.6 mmol) CuI, 7.52 g (63.7 mmol) benzimidazole, 8.80 g (63.7 mmol) K_2CO_3, 40 mL NMP, 24 h at 160 °C and 48 h at 185 °C.

Yield: 540 mg (10%). M.p. 202 °C. Anal. Calc. for $C_{20}H_{14}N_4$: C, 77.40; H, 4.55; N, 18.05%. Found: C, 77.36; H, 4.50; N, 18.00%. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ/ppm: 8.23 (2*H*, m, NC*H*N). 7.85 (4*H*, m), 7.55 (1*H*, m), 7.52 (1*H*, m), 7.10 (6*H*, m). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 143.6 (N*C*HN), 142.7 (C_{ipso}), 133.5 (C_{ipso}), 131.7 (C_{ipso}), 130.5 (*C*H), 129.1 (*C*H), 123.3 (*C*H), 122.3 (*C*H), 119.6 (*C*H), 109.9 (*C*H).

(3,4-Dibromo-1,2-phenylene)bisimidazole (3a). Reagents: 200 mg (0.74 mmol) 1,2-dibromo-3,4-difluorobenzene, 150 mg

(2.21 mmol) imidazole, 610 mg (4.42 mmol) K_2CO_3, 5 mL DMF, 48 h at 110 °C.

Yield: 179 mg (66%). M.p. 183 °C. Anal. Calc. for $C_{12}H_8N_4Br_2$: C, 39.16; H, 2.19; N, 15.22%. Found: C, 39.04; H, 2.00; N, 14.98%. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ/ppm: 7.77 (2*H*, s, C*H*); 7.41 (2*H*, bs, C*H*); 7.14 (2*H*, bs, C*H*); 6.73 (2*H*, t, J = 1.3 Hz, C*H*). ^{13}C NMR (74.475 MHz, $CDCl_3$, 25 °C) δ/ppm: 136.4 (*C*H); 131.8 (C_{ipso}); 131.4 (*C*H); 131.2 (*C*H); 125.6 (C_{ipso}); 119.0 (*C*H).

(3,4-Dibromo-1,2-phenylene)bisbenzimidazole (3b). Reagents: 3.00 g (11.0 mmol) 1,2-dibromobenzene, 2.61 g benzimidazole, 3.81 g (27.6 mmol) K_2CO_3, 40 mL NMP, 24 h at 160 °C and 48 h at 185 °C.

Yield: 2.45 g (47%).

M.p.: 224 °C. Anal. Calc. for $C_{20}H_{12}N_4Br_2$: C, 51.31; H, 2.58; N, 11.97%. Found: C, 51.57; H, 2.44; N, 11.99%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 8.1 (2*H*, s, NC*H*N), 7.75 (2*H*, d, NCCC*H*), 7.50 (2*H*, BrCC*H*), 7.24 (6*H*, m, benzimidazole). ^{13}C NMR (74.475 MHz, $CDCl_3$, 25 °C) δ/ppm: 143.3 (C_{ipso}), 141.1 (N*C*HN), 133.2 (C_{ipso}), 132.8 (*C*H), 131.6 (C_{ipso}), 126.1 (C_{ipso}), 124.6 (*C*H), 123.6 (*C*H), 121.1 (*C*H), 109.1 (*C*H).

General procedure for the synthesis of the bis(benz)-imidazolium salts 4–7

The given amount of bromomethane or benzyl bromide was added to a solution of the bisimidazole in acetonitrile in an ACE pressure tube at −78 °C (benzyl bromide: room temperature). The mixtures were then stirred for the indicated time at the given temperature, during which a colourless precipitate formed. The solids were filtered off at room temperature, washed with the given solvent and dried *in vacuo* to afford the products as colourless hygroscopic compounds. In the case of benzylation the crude products were precipitated by the addition of diethyl ether at 3 °C.

3,3′-Bis(methyl)-[(1,2-diimidazolium)phenylene] dibromide (4a). Reagents: 130 μL (4.90 mmol) MeBr, 450 mg (2.14 mmol) of **2a** in 7 mL of MeCN, 24 h, 90 °C, washed with 10 mL DCM.

Yield: 830 mg (97%). M.p.: 260 °C. Anal. Calc. for $C_{14}H_{14}N_4Br_2$: C, 42.03; H, 4.03; N, 14.00%. Found: C, 41.78; H, 3.87; N, 13.87%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 9.54 (2*H*, s, NC*H*N), 7.93 (2*H*, s, C*H*), 7.87 (2*H*, bs, NC*H*), 7.77 (2*H*, bs, NC*H*), 3.93 (6*H*, s, CH_3).

^{13}C NMR (75.47 MHz, DMSO-d_6, 25 °C) δ/ppm: 138.6 (CH), 132.1 (CH), 126.7 (C_{ipso}), 128.2 (*C*H), 124.3 (*C*H), 122.9 (*C*H), 36.0 (*C*H_3).

3,3′-Bis(methyl)-[(1,2-dibenzimidazolium)phenylene] dibromide (4b). Reagents: 66 μL (2.78 mmol) MeBr, 430 mg (1.39 mmol) of **2b** in 10 mL of MeCN, 24 h, 120 °C, washed twice with 10 mL THF.

Yield: 688 mg (99%). M.p.: 273 °C. Anal. Calc. for $C_{22}H_{20}N_4Br_2$: C, 52.82; H, 4.02; N, 11.20%. Found: C, 52.71; H, 4.11; N, 11.17%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 10.16 (2*H*, s, NC*H*N), 8.14 (2*H*, bs), 8.02 (2*H*, bs), 7.99 (2*H*, bs), 7.66 (4*H*, m), 7.53 (2*H*, m), 4.07 (6*H*, s, CH_3). ^{13}C NMR (75.47 MHz, DMSO-d_6, 25 °C) δ/ppm: 143.9 (N*C*HN), 132.9 (*C*H), 131.2 (C_{ipso}), 129.8 (*C*H), 128.9 (C_{ipso}), 127.3 (*C*H), 126.9 (*C*H), 113.8 (*C*H), 112.4 (*C*H), 33.6 (*C*H_3), one C_{ipso} not detected presumably due to superposition.

3,3′-Bis(benzyl)-[(1,2-dimidazolium)phenylene] dibromide (5a). Reagents: 240 μL (2.02 mmol) BnBr, 200 mg (0.95 mmol) of **3a** in 15 mL of MeCN, 96 h, 105 °C, product precipitated with 20 mL of diethyl ether at 3 °C.

Yield: 462 mg (88%). M.p.: 248 °C. Anal. Calc. for $C_{26}H_{24}N_4Br_2$: C, 56.54; H, 4.38; N, 10.14%. Found: C, 56.29; H, 4.15; N, 10.26%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 9.73 (2*H*, s, NC*H*N), 7.98 (4*H*, m, Ar), 7.91 (2*H*, bs, NC*H*), 7.83 (2*H*, bs, NC*H*), 7.41 (10*H*, m, Ar), 5.47 (4*H*, s, CH_2). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 138.2 (*C*H), 134.1 (C_{ipso}), 132.2 (*C*H), 129.8 (C_{ipso}), 129.0 (*C*H), 128.9 (*C*H), 128.4 (*C*H), 128.3 (*C*H), 123.7 (*C*H), 123.1 (*C*H), 52.4 (*C*H_2).

3,3′-Bis(methyl)-[3,4-dibromo-(1,2-diimidazolium)phenylene] dibromide (6a). Reagents: 50 μL (2.10 mmol) MeBr, 240 mg (0.65 mmol) of **3a** in 5 mL of MeCN, 24 h, 90 °C, washed with 10 mL of ethyl acetate.

Yield: 330 mg (91%). M.p.: 334 °C. Anal. Calc. for $C_{14}H_{12}N_4Br_4$: C, 30.14; H, 2.53; N, 10.04%. Found: C, 30.09; H, 2.53; N, 9.94%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 9.53 (2*H*, s, NC*H*N), 8.46 (2*H*, s, phenyl-C*H*), 7.85 (2*H*, bs, NC*H*), 7.72 (2*H*, bs, NC*H*), 3.92 (6*H*, s, CH_3). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 139.0 (*C*H), 132.6 (*C*H), 129.6 (C_{ipso}), 127.0 (C_{ipso}), 124.3 (*C*H), 122.6 (*C*H), 36.4 (*C*H_3).

3,3′-Bis(methyl)-[3,4-dibromo-(1,2-dibenzimidazolium)phenylene] dibromide (6b). Reagents: 71 μL (1.50 mmol) MeBr, 350 mg (0.75 mmol) of **3b** in 40 mL of MeCN, 48 h, 120 °C, washed with 10 mL MeCN.

Yield: 490 mg (99%). M.p.: >350 °C. Anal. Calc. for $C_{22}H_{18}N_4Br_4$: C, 40.16; H, 2.76; N, 8.51%. Found: C, 39.96; H, 2.60; N, 8.17%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 10.11 (2*H*, s, NC*H*N), 8.64 (2*H*, s, phenyl-C*H*), 7.99 (2*H*, bs, benzimidazole), 7.82 (2*H*, bs, benzimidazole), 7.64 (4*H*, m, benzimidazole), 7.55 (2*H*, m, benzimidazole), 4.08 (6*H*, s, CH_3). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 144.3 (N*C*HN), 134.6 (*C*H), 131.1 (C_{ipso}), 129.2 (C_{ipso}), 128.4 (C_{ipso}), 127.7 (*C*H), 127.2 (*C*H), 114.1 (*C*H), 112.8 (*C*H), 33.9 (*C*H_3), one C_{ipso} not detected presumably due to superposition.

3,3′-Bis(benzyl)-[3,4-dibromo-(1,2-diimidazolium)phenylene] dibromide (7a). Reagents: 150 μL (2.02 mmol) BnBr, 220 mg (0.60 mmol) of **3a** in 7 mL of MeCN, 72 h, 100 °C, product precipitated with 50 mL of diethyl ether at 3 °C and washed three times with 10 mL of ethyl acetate.

Yield: 390 mg (92%). M.p.: >350 °C. Anal. Calc. for $C_{26}H_{22}N_4Br_4$: C, 43.98; H, 3.12; N, 7.89%. Found: C, 43.61; H, 2.69; N, 7.78%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 9.74 (2*H*, s, NC*H*N), 8.56 (2*H*, s, Ar), 7.91 (2*H*, bs, NC*H*), 7.79 (2*H*, bs, NC*H*), 7.43 (10*H*, m, Ar), 5.48 (4*H*, s, CH_2). ^{13}C NMR (75.47 MHz, DMSO-d_6, 25 °C) δ/ppm: 138.5 (*C*H), 133.9 (C_{ipso}), 132.7 (*C*H), 129.7 (C_{ipso}), 129.0 (*C*H), 128.9 (*C*H), 128.5 (*C*H), 127.1 (C_{ipso}), 123.5 (*C*H), 123.2 (*C*H), 52.5 (*C*H_2).

3,3′-Bis(methyl)-[(1,1′-diimidazolin-2,2′-diylidene)-1,2-phenylene] palladium(II) dibromide (8a). 168 mg (0.75 mmol) of palladium acetate were stirred with 300 mg (0.75 mmol) of the bisimidazolium salt **4a** in 5 mL of DMSO for 72 h at room

temperature. After stirring for another 3 h at 120 °C, it was cooled down to room temperature and then filtered over celite. The solvent was removed *in vacuo* at 60 °C and the residue was washed with 10 mL of methanol, acetonitrile and dichloromethane to afford 350 mg (92%) of a pale yellow compound. Crystals suitable for X-ray diffraction were obtained by slowly condensing diethyl ether into a saturated solution of **8a** in acetonitrile.

M.p.: 324 °C (decomposition). Anal. Calc. for $C_{14}H_{14}N_4Br_2Pd$: C, 33.33; H, 2.80; N, 11.11%. Found: C, 33.68; H, 2.97; N, 10.72%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 7.81 (6*H*, m, C*H*); 7.64 (2*H*, s, NC*H*), 3.98 (6*H*, s, CH_3) ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 160.7 (N*C*N), 132.3 (N*C*C), 130.1 (*C*H), 126.8 (*C*H), 124.9 (*C*H), 123.3 (*C*H), 38.3 (*C*H_3). *m*/*z* 403.1 [PdL(OAc)]$^+$.

3,3′-Bis(methyl)-[(1,1′-dibenzimidazolin-2,2′-diylidene)-1,2-phenylene] palladium(II) dibromide (8b). 135 mg (0.60 mmol) of palladium acetate were stirred with 300 mg (0.60 mmol) of the bisbenzimidazolium salt **4b** in 15 mL of DMSO for 24 h at 30 °C. The mixture was slowly heated up to 130 °C and stirred for another 2 h. It was filtered over celite and the solvent was removed *in vacuo* at 60 °C. It was washed with 10 mL of water, 5 mL of methanol, 5 mL of acetonitrile and 5 mL of dichloromethane, recrystallized from 400 mL boiling dichloromethane and dried *in vacuo* to yield 244 mg (67%) of a pale yellow compound. Crystals suitable for X-ray diffraction were obtained by slowly evaporating a saturated solution of **8b** in acetonitrile.

M.p.: >350 °C. Anal. Calc. for $C_{22}H_{18}N_4Br_2Pd$: C, 43.70; H, 3.00; N, 9.27%. Found: C, 43.21; H, 2.85; N, 9.10%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 8.18 (2*H*, m, C*H*), 7.97 (2*H*, m, C*H*), 7.80 (2*H*, d, *J* = 7.6 Hz, C*H*), 7.54 (2*H*, d, *J* = 7.9 Hz, C*H*), 7.42 (4*H*, m, C*H*), 4.22 (6H, s, CH_3). ^{13}C NMR (125.76 MHz, DMSO-d_6, 25 °C) δ/ppm: 173.1 (N*C*N), 134.5 (C_{ipso}), 133.2 (C_{ipso}), 130.9 (C_{ipso}), 130.8 (*C*H), 128.1 (*C*H), 124.5 (*C*H), 124.4 (*C*H), 111.8 (*C*H), 111.2 (*C*H), 35.4 (*C*H_3). *m*/*z* 403.1 [PdL(OAc)]$^+$.

3,3′-Bis(benzyl)-[(1,1′-diimidazolin-2,2′-diylidene)-1,2-phenylene] palladium(II) dibromide (9a). 94 mg (0.45 mmol) of palladium acetate were stirred with 250 mg (0.45 mmol) of the bisimidazolium salt **5a** in 8 mL of DMSO for 24 h at room temperature. The mixture was then filtered over celite after stirring for another 1 h at 60 °C. The solvent was removed *in vacuo* at 60 °C and the residue was dissolved in 50 mL of dichloromethane. The crude product was precipitated by the addition of 100 mL of diethyl ether, dissolved in 20 mL of acetonitrile and again precipitated with 100 mL of diethyl ether to afford 120 mg (40%) of a pale yellow compound.

M.p.: >350 °C. Anal. Calc. for $C_{26}H_{24}N_4Br_2Pd$: C, 47.55; H, 3.38; N, 8.53%. Found: C, 47.42; H, 3.21; N, 8.71%. ^{1}H NMR (600.13 MHz, $CDCl_3$, 25 °C) δ/ppm: 7.66 (2*H*, m, *Ar*); 7.60 (2*H*, m, *Ar*), 7.38 (6*H*, m, *Ar*), 7.32 (4*H*, m, *Ar*), 7.20 (2*H*, d, N*CH*), 6.89 (2*H*, *J* = 1.9 Hz, NC*H*), 5.75 (2*H*, d, *J* = 14.7, CH_2), 5.31 (2*H*, d, *J* = 14.7 Hz, CH_2). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 135.0 (C_{ipso}), 132.9 (C_{ipso}), 130.4 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 126.8 (*C*H), 122.7 (*C*H), 122.5 (*C*H), 54.9 (*C*H_2), carbene signal not detected. *m*/*z* 555.3 [PdL(OAc)]$^+$; 577.1 [PdLBr]$^+$.

3,3′-Bis(methyl)-[3,4-dibromo-(1,1′-diimidazolin-2,2′-diylidene)-1,2-phenylene] palladium(II) dibromide (10a). 81 mg (0.36 mmol) of palladium acetate were stirred with 200 mg (0.36 mmol) of the bisimidazolium salt **6a** in 15 mL of DMSO for 72 h at room temperature. The solvent was removed *in vacuo* at 60 °C and the residue was washed with 10 mL of methanol, acetonitrile and dichloromethane to afford 210 mg (92%) of a pale yellow compound.

M.p.: >350 °C. Anal. Calc. for $C_{14}H_{22}N_4Br_4Pd$: C, 25.39; H, 1.83; N, 8.46%. Found: C, 25.22; H, 1.79; N, 8.16%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 8.35 (2*H*, s, BrCC*H*); 7.83 (2*H*, s, NC*H*); 7.64 (2*H*, s, NC*H*), 3.97 (6H, s, CH_3). ^{13}C NMR (150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 161.2 (N*C*N), 132.5 (N*C*C), 131.4 (*C*H), 125.2 (C_{ipso}), 124.9 (C_{ipso}), 123.6 (*C*H), 38.4 (*C*H_3). *m*/*z* 560.9 [PdL(OAc)]$^+$.

3,3′-Bis(methyl)-[3,4-dibromo-(1,1′-dibenzimidazolin-2,2′-diylidene)-1,2-phenylene] palladium(II) dibromide (10b). 82 mg (0.36 mmol) of palladium acetate were stirred with 240 mg (0.36 mmol) of the bisbenzimidazolium salt **6b** in 10 mL of DMSO for 24 h at room temperature. The mixture was stirred for another 3 h at 60 °C. The solvent was reduced to 1 mL and the crude product was precipitated by the addition of 10 mL of ethyl acetate and 40 mL of diethyl ether. The residue was washed with 5 mL of methanol, 0.5 mL of acetonitrile and 5 mL of dichloromethane, recrystallized from acetonitrile and dried *in vacuo* to afford 189 mg (68%) of a colourless compound.

M.p.: >350 °C. Anal. Calc. for $C_{22}H_{16}N_4Br_4Pd$: C, 34.66; H, 2.12; N, 7.35%. Found: C, 34.30; H, 1.99; N, 6.90%. ^{1}H NMR (300.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 8.73 (2*H*, s, BrCC*H*), 7.78 (2*H*, d, *J* = 7.8 Hz, benzimidazole), 7.60 (2*H*, d, *J* = 7.9 Hz, benzimidazole), 7.43 (4*H*, m, benzimidazole), 4.20 (6*H*, s, CH_3) ppm. ^{13}C NMR (75.47 MHz, DMSO-d_6, 25 °C) δ/ppm: 134.4 (C_{ipso}), 133.2 (C_{ipso}), 132.4 (*C*H), 131.3 (C_{ipso}), 126.0 (C_{ipso}), 124.6 (*C*H), 124.5 (*C*H), 111.6 (*C*H), 111.5 (*C*H), 35.4 (*C*H_3), carbene signal not detected. *m*/*z* 661.0 [PdL(OAc)]$^+$.

3,3′-Bis(benzyl)-[3,4-dibromo-(1,1′-diimidazolin-2,2′-diylidene) 1,2-phenylene] palladium(II) dibromide (11a). 79 mg (0.35 mmol) of palladium acetate were stirred with 250 mg (0.35 mmol) of the imidazolium salt **7a** in 13 mL of DMSO for 24 h at room temperature. The mixture was stirred for 24 h at 40 °C. The solvent was removed *in vacuo* at 60 °C and the residue was extracted with 400 mL of boiling dichloromethane. The solution was reduced to 15 mL and the crude product was precipitated by the addition of 60 mL diethyl ether. It was washed with 5 mL of diethyl ether and dried *in vacuo* to yield 268 mg (94%) of a pale yellow compound. Crystals suitable for X-ray diffraction were obtained by slowly evaporating the solvent of a saturated solution of **11a** in dichloromethane.

M.p.: >350 °C. Anal. Calc. for $C_{26}H_{22}N_4Br_4Pd$: C, 38.34; H, 2.47; N, 6.88%. Found: C, 38.04; H, 2.54; N, 6.45%. ^{1}H NMR (600.13 MHz, DMSO-d_6, 25 °C) δ/ppm: 8.41 (2*H*, s, C*H*); 7.86 (2*H*, bs, NC*H*), 7.42 (8*H*, m), 7.29 (2*H*, m, *Ar*), 5.57 (2*H*, d, *J* = 14.7, CH_2), 4.93 (2*H*, d, *J* = 14.7 Hz, CH_2). ^{13}C NMR

(150.91 MHz, DMSO-d_6, 25 °C) δ/ppm: 135.0 (C_{ipso}), 132.9 (C_{ipso}), 130.4 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 126.8 (*C*H), 122.7 (*C*H), 122.5 (*C*H), 54.9 (CH_2), one *C*H signal not detected, presumably due to superposition. *m*/*z* 713.2 $[PdL(OAc)]^+$; 752.0 $[PdLBr]^+$.

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