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1,3-Diarylimidazolidin-2-ylidene (NHC) complexes of Pd(II): Electronic effects on cross-coupling reactions and thermal decompositions

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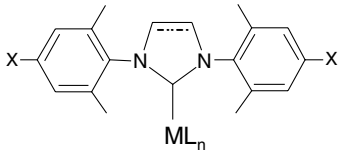
Abstract

The synthesis of 1,3-diarylimidazolidin-2-ylidene (NHC) precursor, 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride, (**3b**) has been extended to the electronically and sterically modified NHC precursors **3a** (X = H), **3c** (X = Br) and **3e** (X = Cl) in order to investigate the electronic effect of a *p*-substituent (X) on cross-coupling catalysts. Complexes of the type $PdCl_2(NHC)_2$ (**5**), $PdCl_2(NHC)(PPh_3)$ (**6**) and [RhCl(NHC)(cod)] (**7**) were prepared from **3** or **4d** (1,3-bis(2,4-dimethylphenyl)-2-trichloromethylimidazolidin). Initial decomposition temperatures of the complexes **5** and **6** were determined by TGA. In situ formed complexes from $Pd(OAc)_2$ and **3** as well as the preformed complexes **5** and **6** have been tested as catalysts in coupling of phenylboronic acid with 4-haloacetophenones. The electron donating ability of NHCs derived from **3** was assessed by measuring C–O frequencies in the respective [RhCl(NHC)$(CO)_2$] complex **8** which was prepared by replacement of cod ligand of **7** with CO. An interesting correlation between the electron-donating nature of the aryl substituent and catalytic activity and also initial decomposition temperature of the complexes **5** and **6** was observed.

Keywords: Palladium; *N*-heterocyclic carbenes; Electronic effects; Cross-coupling; Thermal gravimetric analysis

1. Introduction

Recently, *N*-heterocyclic carbene (NHC) ligands are receiving intensive attention in the fields of coordination chemistry and homogeneous catalysis because organometallic compounds containing NHC ligands exhibit high reactivities. NHCs have appeared as sterically and electronically tunable ligands which make stable coordinative bonds with transition metals [1–3]. Dramatic improvements in C–C coupling activity have been observed with complexes (**A**, M = palladium; L = ligands other than NHC; X = Me) using five-membered NHCs as ligands. Since then, a number of five-membered NHC ligands with different substituents have been studied [4,5].



A

It was found that ligands bearing two bulky Aryl groups (Ar = Mes or 2,6-di-*i*-propylphenyl) promote the reaction of unactivated aryl chlorides [6,7]. The ligands may afford coordinatively unsaturated mono- or dicarbene ligated complexes and accelerate the catalytic steps, that is, oxidative addition, transmetalation and reductive elimination [8]. The steric bulk of the ligand is believed to aid the reductive elimination of product, while electron richness of the ligand imparts a high catalytic performance via an oxidative addition step [7]. Since Hermann's discovery in 1995 [9] many structural modifications, including steric tuning

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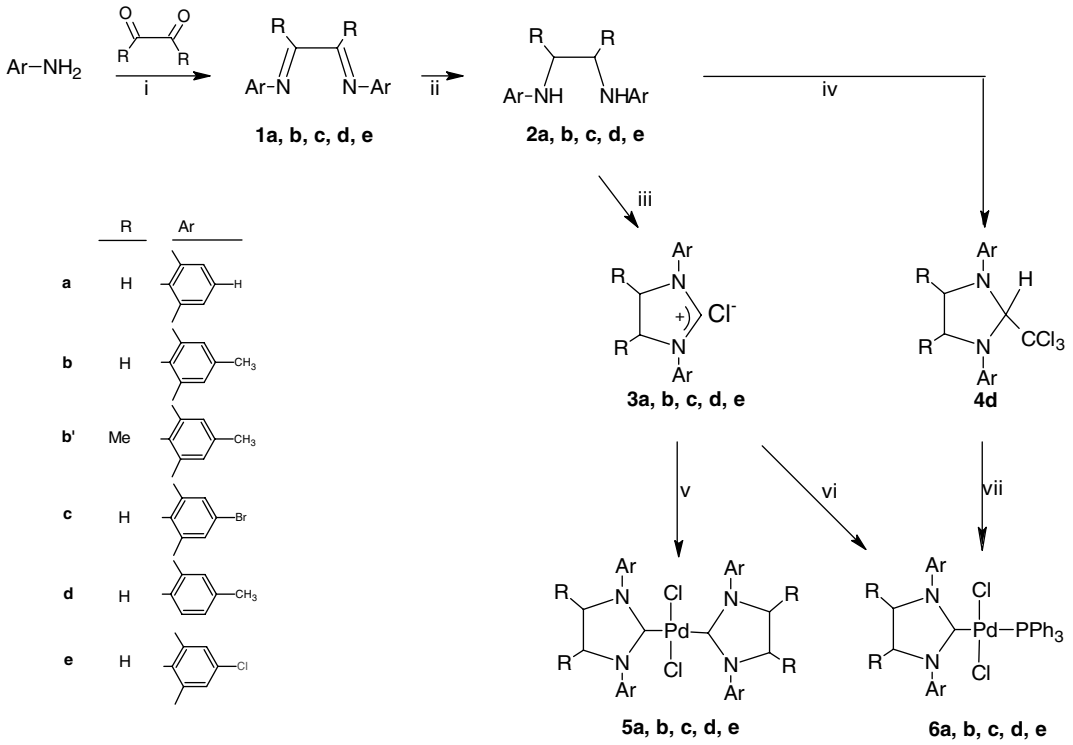
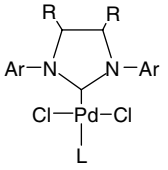


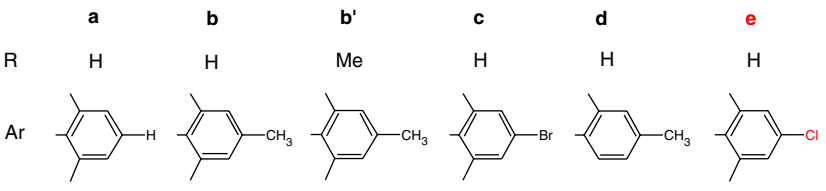
Scheme 1. (i) EtOH, 16 h, RT. (ii) THF, $NaBH_4$, 24 h, RT. (iii) $HC(OEt)_3$, NH_4Cl, 130 °C. (iv) AcOH, Cl_3CCHO, 3 h, RT. (v) DCM, Ag_2O, 24 h, RT, then $PdCl_2(MeCN)_2$, 2 days, RT. (vi) THF, NaH, 4 h, 65 °C then $PhCH_3$, $[PdCl_2(PPh_3)]_2$, 4 h, 110 °C. (vii) $PhCH_3$, $[PdCl_2(PPh_3)]_2$, 4 h, 110 °C.

Table 1
Thermal analysis data for complexes **5** and **6**

Entry	Complex	TG		DTG
		Theoretical wt. loss (%)	Observed wt. loss (%)	Peak temperature (°C)
1	**5a**	80.73	82.86	393
2	**5b**	80.39	82.04	370
3	**5b′**	87.45	86.59	378
4	**5c**	83.17	83.70	315
5	**5d**	75.92	70.83	320
6	**5e**	79.64	75.12	376
6	**6a**	80.15	82.87	334, 362
7	**6b**	76.25	75.37	232, 329, 371
8	**6b′**	81.73	79.97	339, 354
9	**6c**	79.77	65.64	323, 371
10	**6d**	75.31	73.47	322, 354
11	**6e**	77.46	70.11	330, 350
12	$PdCl_2(PPh_3)_2$	70.30	69.82	330, 360, 367, 373



L : NHC (**5**), PPh_3 (**6**)



and changing the ligand backbone structure, had been pursued on NHC ligands [5]. However, an important parameter on the ligand design, the ligand electronic structure, has not been systematically investigated. Such effects have been observed in several catalytic systems [10]. While this work has been in progress, ligand electronic effects have been reported in a benzimidazol-2-ylidene palladium(II) catalytic system [11]. Despite these studies, a systematic account of electronic effects on a palladium–NHC catalyst system has yet to be reported. Here we describe the preparation, characterization, catalytic activities and thermal stabilities of two series of palladium–NHC complexes (**5** and **6**) that incorporate H, Me, Br, Cl groups at the *p*-position of N-aryl substituent of NHC ligand.

2. Results and discussion

Originally, we thought that changing the electronic nature of the *p*-substituent X on compound **A** might effect the catalytic activity of NHC complexes. This would be a purely electronic affect as changing the *p*-substituent from H, to CH_3, Br or Cl is not expected to cause a significant change in steric bulk at the metal center.

2.1. Preparation of ligand precursors and NHC complexes

Compound **3b** has been previously reported [12]; however, for a complete comparison of electronic properties, **3a**, **3c**, **3d**, **3e** and **4d** were also deemed necessary. The general route to the *p*-substituent containing ligand precursors (**3** and **4d**) to prepare Pd–NHC complexes is shown in Scheme 1. This route typically used commercially available anilines. The imidazolinium salts (**3**) prepared in Scheme 1 were subsequently palladated in a deprotonation reaction using Ag_2O or NaH; in the case of **6d**, we had to prepare the 2-trichloromethylimidazolidine (**4d**) as intermediate reagent [13–15].

In order to enlarge our set of NHC ligands and to better understand the role of the electron donating Me substituents at the 4- and 5-positions and the *ortho*-methyl substituents in the aryl of NHC complexes **5** and **6**, we have also prepared the related new salts **3b′** and **3d** (which is an isomer of **3a**).

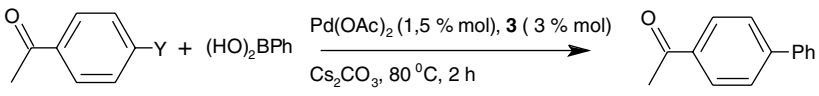
The characterization of the new compounds (**1**–**6**), except **1a**, **2a**, **3a**, has been carried out by elemental analysis, FTIR, NMR spectroscopy and, in addition, thermal gravimetric analysis (TGA) was applied to the complexes **5** and **6**.

The NMR spectra of the compounds are very diagnostic with all signals well resolved. The singlets in the spectral region between 7.86 and 10.29 ppm confirmed the presence of C_2–H in **3**. Of course, these signals are not present in the spectra of the complexes (**5** and **6**) [16].

The ^{1}H NMR spectra of **5** and **6** showed one singlet resonance due to the methyl groups at the 2,6-position of the aromatic ring at δ 1.83–2.57 along with a singlet resonance due to ring CH_2 (δ 3.65–4.04) and aromatic signals. Additionally, the signals due to the carbene carbon of the NHC ligand were observed at δ 194.9–199.4 in the $^{13}C\{^1H\}$ NMR spectra. Furthermore, $^{13}C\{^1H\}$ NMR spectra of **6** revealed doublets due to coupling of the phosphorus atom in the *trans* position, $J_{(P-C)} =$ 183.8–185.3 Hz. It is worth noting that the coupling in the analogous imidazol-2-ylidene complex has not been observed [16]. The $^{13}C\{^1H\}$ NMR signals of the carbene carbon atoms of **6** (δ 194.9–198.8) are slightly shifted to higher field as compared to their signals in the bisNHC complexes **5** (δ 196.7–199.4). These observations indicate, once more, the close similarity between saturated NHCs and tertiary phosphines [17].

In the case of **6d** *trans*-configuration has been confirmed by X-ray diffraction studies [18], and attempts to convert complex **6** into the *cis*-isomer in the presence of PPh_3 were unsuccessful.

Table 2



Entry	3	Y	Conversion (%)	Yield (%)
1	**a**	Cl	75	70
2	**a**	Br	93	92
3	**b**	Cl	79	71
4	**b**	Br	100	100
5	**b′**	Cl	81	77
6	**b′**	Br	100	98
7	**c**	Cl	70	42
8	**c**	Br	89	87
9	**d**	Cl	86	78
10	**d**	Br	93	78
11	**e**	Cl	82	28
12	**e**	Br	85	48

Reaction conditions: 1.0 mmol of phenylboronic acid, 1.5 mmol Cs_2CO_3, dioxane (3 mL). GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard.

2.2. Thermogravimetric analyses (TGA)

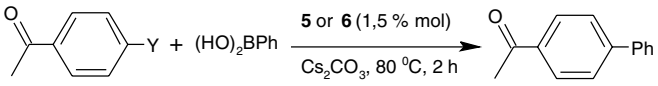
TGA has been extensively employed in the study of coordination compounds [19]. However, to the best of our knowledge no report has been published dealing with its use for the investigation of NHC complexes. In this study we employed this technique to obtain evidence for the influence of closely related ligands coordinated to the Pd atom on the initial decomposition temperatures and on the thermal decomposition steps. The steps, initial and final temperatures, partial and total weight losses for the decomposition of compounds **5** and **6** are given Table 1. The thermal behavior of Pd complexes of $PdCl_2(NHC)_2$ and their mixed-ligand complexes $PdCl_2(NHC)(PPh_3)$ was studied by TG and DTG in a dynamic N_2 atmosphere.

The thermal decompositions of **5** occur in one step whereas **6** occur in multiple steps. The residues correspond to PdCl or $PdCl_2$. The initial decomposition temperatures within the series **5** increase in the following order: **d** ∼ **c** < **b** < **e** < **a**.

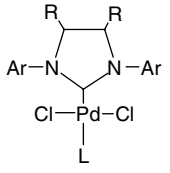
The lower thermal stability of **d** may be attributed to the unsymmetrical substitution on the aryl ring of NHC ligand. Thus, if the restriction would play an important role **5a** should be less stable than **5d**.

The complexes **5** and **6** exhibit very high thermal stability and degradation of PPh_3 complexes follow a complicated process. In the case of biscarbene complexes (**5**) both NHC ligands are simultaneously lost. Whereas in the case of mixed complexes (**6**), first PPh_3, and then the NHC is lost. Thus, once more it was observed that the Pd–NHC

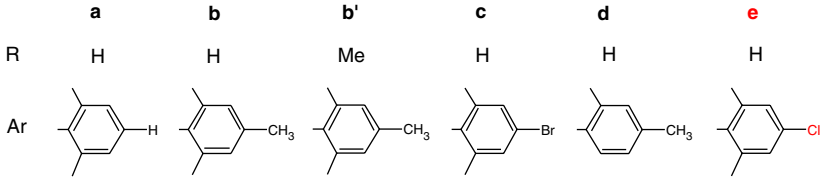
Table 3



Entry	Catalyst	Y	Conversion (%)	Yield (%)
1	**5a**	Cl	43	28
2	**5a**	Br	95	69
3	**5b**	Cl	48	35
4	**5b**	Br	97	89
5	**5b′**	Cl	50	43
6	**5b′**	Br	80	60
7	**5c**	Cl	99	3
8	**5c**	Br	89	39
9	**5d**	Cl	97	40
10	**5d**	Br	67	41
11	**5e**	Cl	19	0
12	**5e**	Br	28	20
13	**6a**	Cl	83	78
14	**6a**	Br	99	90
15	**6b**	Cl	100	88
16	**6b**	Br	100	92
17	**6b′**	Cl	97	93
18	**6b′**	Br	95	92
19	**6c**	Cl	94	23
20	**6c**	Br	95	89
21	**6d**	Cl	97	8
22	**6d**	Br	93	33
23	**6e**	Cl	90	7
24	**6e**	Br	87	43



L : NHC (**5**), PPh_3 (**6**)



Reaction conditions: 1.0 mmol of phenylboronic acid, 1.5 mmol Cs_2CO_3, 1.5 mol % **5** or **6**, dioxane (3 mL). GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard.

bond is stronger than the Pd–PR_3 bond. In the case of $[PdCl_2(PPh_3)]_2$, the loss of one PPh_3 was followed by partial loss of PPh_3. These data indicate that NHC complexes are thermally stable above 300 °C and the initial decomposition temperature is sufficiently sensitive to reflect a *p*-substituent effect within a series of NHC complexes. These observations further confirm that the electron-donating nature of the peripheral substituent has a marked influence on the metal–ligand interactions which subsequently determines the catalyst life.

2.3. Catalytic cross-coupling reactions

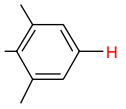
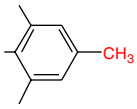
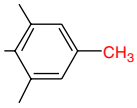
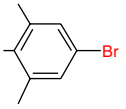
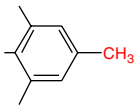
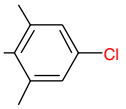
The aim of this research was to gain a preliminary insight into the effects of *p*-substituents on the aryl group of the NHC ligand on the cross-coupling reaction. It is well known that the activities of NHC complexes are influenced by the steric bulk and electronegativities of *ortho*-substituents and the way the catalyst is prepared [7,8,20].

The coupling of 4-bromoacetophenone with phenylboronic acid (in dioxane at 80 °C, Cs_2CO_3 as base) was used as the model reaction in order to highlight the influence of *para* substituents (H, Me, Br and Cl) on the catalytic activity and the protocol was also applied to 4-chloroacetophenone. The reactivity of in situ generated catalysts and preformed complexes **5** and **6** were compared and the relevant results are reported in Tables 2 and 3.

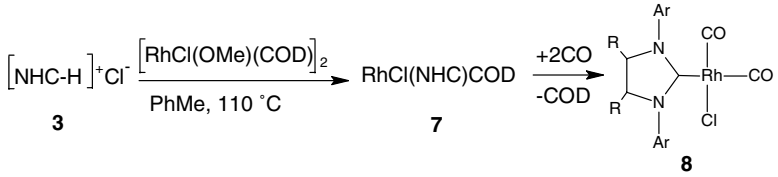
The results indicate that the highest yield can be achieved with the in situ formed complexes prepared from **3** and $Pd(OAc)_2$ (in a 2:1 ratio) with 4-bromoacetophenone (entries 2, 4, 8). As expected [20], under the same conditions, the yield is significantly lower with 4-chloroacetophenone (entries 1, 3, 7). These results also indicate that among the salts used, **3b** and **3b′** could be the most effective catalyst precursors. As the electron-donating property of the *p*-substituent increased (Cl < Br < H < Me), the catalytic activity increased. In order to rule out the possibility of intervention of *p*-bromo substituents in the Suzuki coupling, the reaction between $PhB(OH)_2$ and **5c/6c** was carried out under the same catalytic reaction conditions and the starting palladium complexes **5c/6c** were recovered and remain unchanged. It is worth noting that the catalyst derived from **3d**, the isomer of **3a**, is very effective for 4-chloroacetophenone. Whether this efficiency is due to the different topology imparted by 2,4-dimethylphenyl groups (compared to the 2,6-dimethylphenyl) remains unclear at this point.

The catalytic activity is also influenced by the nature of the π-ligands (NHC vs. PPh_3) on the palladium center, as indicated by the significant increase in the reaction rate on going from **5** to **6** (Table 3, compare entries 1–12 to 13–24) and a similar trend is found. These observations are in agreement with earlier findings [8,20]. The complexes **5e** and **6e** derived from the substituted *p*-chloroaniline showed almost no catalytic activity against the aryl chloride (entries 11 and 23, respectively). In contrast to benzimidazol-2-ylidene system [11], 1,3-dimesityl-4,5-dimethylimidazolidin-2-ylidene complexes (**5b′** and **6b′**) are not significantly better than their bare analogous (**5b** and **6b**; of Table 3, entries 3–6 and 15–18, respectively).

Table 4
Carbonyl stretching wavenumbers (cm^{-1}) of **8**[a]

	R	Ar	(CO)/sym.	(CO)/asym.
8a	H		2078	1996
8b	H		2074	1958
8b′	Me		2072	1953
8c	H		2092	1994
8d	H		2080	1997
8e	H		2103	1999

[a] Recorded in CH_2Cl_2.



Scheme 2.

In order to rationalize the observed differences in catalytic activity, we measured IR stretching frequencies in [RhCl(NHC)$(CO)_2$] complexes which were prepared according to Scheme 2. The full characterization of **7** and **8** will be reported in due course. The C–O stretching frequencies of carbonyl complexes **8**, recorded in CH_2Cl_2 solution (Table 4), indicate that the basicity increases in the order: **e** < **d** < **c** < **a** < **b** ≈ **b′**. The data also show that the symmetrical *ν*(CO) in the respective [RhCl(NHC)$(CO)_2$] complexes does correlate with the catalytic activity of in situ formed Pd–NHC complexes as well as preformed **5** and **6** (Tables 2 and 3, respectively) [21,22].

3. Conclusion

The structurally and sterically similar 1,3-bis(2,6-dimethylphenyl)imidazolinium salts with H, CH_3, Br and Cl substituents at the *p*-position of the aryl ring were used to prepare two series of palladium–NHC complexes **5** and **6**. In this way *o*-substituents of NHC's were held constant and only the nature of the *p*-substituent was varied. In both cases the efficiency increased with the electron donating nature of the *p*-substituent (Cl < Br < H < Me). To better understand from a chemical view point the reasons behind the difference in activity we studied their TG analyses which indicated that the initial decomposition temperatures are relatively sensitive to the *p*-substituents of the aryl ring.

The in situ prepared catalysts and the preformed complexes allowed us to evaluate simultaneously subtle electronic influence of H, Me, Br and Cl without possible complications due to steric effects. The C–O stretching frequencies in [RhCl(NHC)$(CO)_2$] complexes which derived from **3** are sensitive to *p*-substituents. The data indicate clearly the superiority of the complex with the most electron donating NHC **5b** and **6b**. Hence, the electron donating capability of the complexes, as well as the steric bulk, appears to play a role in the complex's catalytic activity [7,8]. In contrast to the substituents at the 4-position of the aryl ring, the oxidative addition step is less sensitive to the methyl substituents in the 4,5-positions of the imidazolidine ring. These results indicate that NHC ligand design should focus on creating electron-rich carbene with a carefully selected steric environment.

4. Experimental

All manipulations were performed by using Schlenk-type flasks under dry argon and standard high vacuum-line techniques. The solvents were analytical grade and distilled under argon from sodium benzophenone (toluene, diethyl ether), sodium–potassium (pentane), P_2O_5 (dichloromethane), Mg/I_2 (methanol). NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR spectrometer at 400 MHz (^{1}H), 100,56 MHz (^{13}C). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Strumentazione Model 1106 apparatus. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained using a Perkin–Elmer Pyris 6 analyzer in the range 50–950 °C in alumina crucibles under nitrogen (flux rate: 20 cm^3 min^{-1}) at a heating rate of 20 °C min^{-1} using alumina as reference. FTIR spectra were recorded on a Perkin–Elmer Spectrum 100 Series.

4.1. Preparation of N,N′-bis(2,6-dimethylphenyl)imine (*1a*)

To a solution of 2,6-dimethylphenylamine (1.21 g, 10 mmol) in 100 mL ethanol was added at 25 °C a mixture of a 40% aqueous solution of glyoxal (0.72 g, 5 mmol). The mixture was stirred for 16 h at 25 °C. The resulting yellow precipitate was collected by filtration and dried in vacuum. Yield: 2.13 g, 85%; m.p = 154–155 °C. Anal. Calc. for $C_{18}H_{20}N_2$; C, 81.78; H, 7.63; N, 10.60. Found: C, 81.70; H, 7.72; N, 9.89%. ^{1}H NMR ($CDCl_3$): $\delta = 2.19$ (s, 12H, *ortho*-CH_3), 6.93 (t, 2H $J = 7.7$ Hz, *para*-CH), 7.07 (d, 4H, $J = 7.6$ Hz, *meta*-CH), 8.13 (s, 2H, HC=N); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.20$ (*ortho*-CH_3), 125.5, 126.5, 128.9, 148.4 (Ar), 163.2 (HC=N). The synthesis of **1b**, **2b** and **3b** were carried out using literature methods [12].

4.2. Preparation of N,N′-bis(2,4,6-trimethylphenyl)-1,2-bis(methyl)ethanediimine (*1b′*)

Compound **1b′** was prepared in the same way as **1a** from 2,4,6-trimethylphenylamine (1.88 g, 13.9 mmol) and 2,3-butadione (0.60 g, 6.95 mmol) to give yellow crystals of **1b′**. Yield: 1.85 g, 83%; m.p = 53–55 °C. Anal. Calc. for $C_{22}H_{28}N_2$; C, 82,45; H, 8.81; N, 8.74. Found: C, 82.17; H, 8.99; N, 8.98%.

^{1}H NMR ($CDCl_3$): $\delta = 2.26$ (s, 6H, *para*-CH_3), 2.30 (s, 6H, *ortho*-CH_3), 2.38 (s, 6H, *ortho*-CH_3), 3.18 (s, 6H, N=CCH_3), 7.19 (s, 2H, *meta*-CH), 7.22 (s, 2H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.5$ (s, *para*-CH_3), 19.2 (*ortho*-CH_3), 20.1 (*ortho*-CH_3), 25.5 (N=C–CH_3), 128.9, 130.4, 130.5, 134.8, 136.3, 140.3 (Ar), 162.65 (s, N=C).

4.3. Preparation of N,N′-bis(4-bromo-2,6-dimethylphenyl)imine (*1c*)

Compound **1c** was prepared in the same way as **1a** from 4-bromo-2,6-dimethyl phenylamine (2.00 g, 10 mmol) and glyoxal (0.72 g, 5 mmol) to give yellow crystals of **1c**. Yield: 1.47 g, 70%; m.p = 198–200 °C. Anal. Calc. for $C_{18}H_{18}N_2Br_2$; C, 51.21; H, 4.30; N, 6.64. Found: C, 51.32; H, 4.41; N, 6.58%.

^{1}H NMR ($CDCl_3$): $\delta = 2.15$ (s, 12H, *ortho*-CH_3), 7.22 (s, 4H, *meta*-CH), 8.05 (s, 2H, HC=N); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.3$ (*ortho*-CH_3); 118.7, 128.7, 131.2, 148.8 (Ar), 163.6 (s, HC=N).

4.4. Preparation of N,N′-bis(2,4-dimethylphenyl)imine (*1d*)

Compound **1d** was prepared in the same way as **1a** from 2,4-dimethylphenylamine (1, 21, 10 mmol) in 100 mL

ethanol and glyoxal (0.72 g, 5 mmol) to give yellow crystals of **1d**. Yield: 2.27 g, 86%; m.p = 147–149 °C. Anal. Calc. for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.78; H, 7.10; N, 10.36%.

^{1}H NMR ($CDCl_3$): $\delta = 2.24$ (s, 6H, *para*-CH_3), 2.28 (s, 6H, *ortho*-CH_3), 6.85 (d, 2H, $J = 7.9$ Hz, *ortho*-CH), 6.93 (d, 2H, $J = 7.9$ Hz, *meta*-CH), 6.97 (s, 2H, *meta*-CH), 8.22 (s, 2H, HC=N); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.2$ (*para*-CH_3), 21.4 (*ortho*-CH_3), 117.5, 127.8, 131.8,133.5, 137.7, 147.4 (Ar), 159.3 (HC=N).

4.5. Preparation of *N,N′*-bis(4-chloro-2,6-dimethylphenyl)imine (**1e**)

Compound **1e** was prepared in the same way as **1a** from 4-chloro-2,6-dimethyl phenylamine (1.55 g, 10 mmol) and glyoxal (0.72 g, 5 mmol) to give yellow crystals of **1e**. Yield: 2.76 g 83%; m.p = 201–202 °C. Anal. Calc. for $C_{18}H_{18}N_2Cl_2$: C, 64.87; H, 5.44; N, 8.41. Found: C, 64.91; H, 5.67; N, 8.33%.

^{1}H NMR ($CDCl_3$): $\delta = 2.16$ (s, 12H, *ortho*-CH_3), 7.08 (s, 4H, *meta*-CH), 8.07 (s, 2H, HC=N); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.4$ (*ortho*-CH_3); 128.3, 128.5, 130.1, 148.4 (Ar), 163.8 (HC=N).

4.6. Preparation of *N,N′*-bis(2,6-dimethylphenyl)ethylenediamine (**2a**)

A suspension of *N,N′*-bis(2,6-dimethylphenyl)imine (2.64 g, 10 mmol) **1a** in 40 mL THF was treated at 0 °C with sodium borohydride (1.60 g, 41 mmol) in portions of 1 g over a period of 1 h. The mixture was stirred for 24 h at RT and heated subsequently for 2 h under reflux. To the mixture was added 50 mL of 20% NaCl and 50 mL of ice-water. A colorless solid precipitated and was collected by filtration and dried under vacuum. Yield: 2.38 g, 89%; m.p = 39–40 °C. Anal. Calc. for $C_{20}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 81.01; H, 9.11; N, 10.03%.

^{1}H NMR ($CDCl_3$): $\delta = 2.18$ (s, 12H, *ortho*-CH_3), 3.35 (s, 4H, NCH_2), 7.12 (d, 4H, $J = 7.6$ Hz, *meta*-CH), 7.51 (t, 2H, $J = 7.7$ Hz, *para*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.6$ (*ortho*-CH_3), 46.9 (NCH_2), 115.8, 130.6, 130.9, 143.8 (Ar).

4.7. Preparation of *N,N′*-bis(4-bromo-2,6-dimethylphenyl)ethylenediamine (**2c**)

Compound **2c** was prepared in the same way as **2a** from *N,N′*-bis(4-bromo-2,6-dimethylphenyl)imine **1b** (4.22 g, 10 mmol) and sodium borohydride (1.60 g, 41 mmol) to give colorless solid of **2c**. Yield: 3.62 g, 85%; m.p = 97–99 °C. Anal. Calc. for $C_{18}H_{22}N_2Br_2$: C, 50.73; H, 5.20; N, 6.57. Found: C, 51.01; H, 5.19; N, 6.64%.

^{1}H NMR ($CDCl_3$): $\delta = 2.17$ (s, 12H, *ortho*-CH_3), 3.05 (s, 4H, NCH_2), 7.04 (s, 4H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.6$ (*ortho*-CH_3), 48.9 (NCH_2), 114.7, 131.2, 132.0, 145.7 (Ar).

4.8. Preparation of *N,N′*-bis(2,4-dimethylphenyl)ethylenediamine (**2d**)

Compound **2d** was prepared in the same way as **2a** from *N,N′*-bis(2,4-dimethylphenyl)imine **1d** (2.64 g, 10 mmol) and sodium borohydride (1.60 g, 41 mmol) to give a colorless solid of **2d**. Yield: 3.62 g, 85%; m.p = 67 °C. Anal. Calc. for $C_{18}H_{24}N_2$: C, 80.55; H, 9.01; N, 10.44. Found: C, 80.50; H, 7.87; N, 10.19%.

^{1}H NMR ($CDCl_3$): $\delta = 2.01$ (s, 6H, *ortho*-CH_3), 2.15 (s, 6H, *ortho*-CH_3), 3.35 (s, 4H, NCH_2), 6.50 (d, 2H, $J = 8.0$ Hz, *ortho*-CH), 6.81 (s, 2H, *meta*-CH), 6.85 (d, 2H, $J = 8.03$ Hz, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 17.9$ (*ortho*-CH_3), 20.7 (*para*-CH_3); 43.9 (NCH_2), 110.7, 123.0, 127.1, 127.8, 145.7 (Ar).

4.9. Preparation of *N,N′*-bis(4-chloro-2,6-dimethylphenyl)ethylenediamine (**2e**)

Compound **2e** was prepared in the same way as **2a** from *N,N′*-bis(4-bromo-2,6-dimethylphenyl)imine **1b** (3.33 g, 10 mmol) and sodium borohydride (1.60 g, 41 mmol) to give colorless solid of **2c**. Yield: 2.76 g, 82%; m.p = 96–98 °C. Anal. Calc. for $C_{18}H_{22}N_2Cl_2$: C, 64.10; H, 6.57; N, 8.31. Found: C, 64.32; H, 6.83; N, 8.12%.

^{1}H NMR ($CDCl_3$): $\delta = 2.27$ (s, 12H, *ortho*-CH_3), 3.15 (s, 4H, NCH_2), 6.99 (s, 4H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.7$ (*ortho*-CH_3), 49.0 (NCH_2), 127.0, 128.7, 131.6, 144.6 (Ar).

4.10. Preparation of 1,3-bis(2,6-dimethylphenyl)imidazolinium chloride (**3a**)

A mixture of *N,N′*-bis(2,6-dimethylphenyl)ethylenediamine (**2a**) (2.68 g, 10 mmol), triethyl orthoformate 10 mL and ammonium chloride (0.54 g, 10.2 mmol) was heated in a distillation apparatus until the ethanol distillation ceased. The temperature of the reaction mixture reached 130 °C. After cooling to RT, to the reaction mixture was added 30 mL of ether. A colorless solid precipitated which was collected by filtration. Purification was achieved by repeated recrystallizations from ethanol/ether. Yield: 2.51 g, 80%; m.p = 364–365 °C. Anal. Calc. for $C_{18}H_{23}N_2Cl$: C, 72.48; H, 7.36; N, 8.90. Found: C, 72.45; H, 7.35; N, 9.15%.

^{1}H NMR ($CDCl_3$): $\delta = 2.51$ (s, 12H, *ortho*-CH_3), 4.70 (s, 4H, Im-$H^{4,5}$), 7.21 (d, 4H, $J = 7.60$ Hz, *meta*-CH), 7.31 (t, 2H, $J = 7.60$ Hz, *para*-CH), 9.38 (s, 1H, Im-H^2); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.4$ (*ortho*-CH_3), 52.1 (Im-$C^{4,5}$), 130.4, 131.3, 134.0, 136.6 (Ar), 161.3 (Im-C^2).

4.11. Preparation of 1,3-bis(2,4,6-trimethylphenyl)-4,5-bis(methyl)imidazolinium chloride (**3b′**)

A suspension of **1b′** (4 g, 12.5 mmol) in MeOH (50 mL) was treated at room temperature under argon with $NaCNBH_3$ (3.92 g, 62.5 mmol) in portions of 1 g over a period

of 20 min. To the mixture was added bromo cresole green and until a color change from green to yellow occurred, 0.1 N HCl was added. The solution was stirred for 20 h and heated subsequently for 4 h under reflux. It was cooled to room temperature and 0.1 N (10 mL) KOH solution, (100 mL) H_2O and (50 mL) CH_2Cl_2 were added. The water phase was washed with CH_2Cl_2 for a few more times. After the washing steps all of the CH_2Cl_2 phases were combined and dried with $MgSO_4$. $Et_2O \cdot HCl$ was added to the CH_2Cl_2 solution. The obtained colorless solid was filtered off and recrystallized from methanol (10 mL)/diethyl ether (20 mL). Triethyl orthoformate (10 mL) was added without isolation of the latter compound. The mixture was stirred for 6 h in an oil bath at 140 °C under an argon atmosphere. Meanwhile EtOH, formed as a by product, is removed from the medium via distillation. It was then cooled to room temperature and Et_2O (15 mL) was added. The resulting colorless solid was filtered off and was crystallized from methanol (5 mL)/diethyl ether (15 mL). Yield: 3.98 g, 86%; m.p = 278–280 °C. Anal. Calc. for $C_{23}H_{31}N_2Cl$: C, 74.47; H, 8.42; N, 7.55. Found: C, 74.91; H, 8.02; N, 7.83%.

^{1}H NMR ($CDCl_3$): $\delta = 1.40$ (d, 6H, $J = 1{,}4$ Hz $Im-CH_3^{4,5}$), 2.23 (s, 6H, *ortho*-CH_3), 2.29 (s, 6H, *ortho*-CH_3), 2.33 (s, 6H, *para*-CH_3), 4.34 (m, 2H, Im-$H^{4,5}$), 6.88 (s, 2H, *meta*-CH), 6.90 (s, 2H, *meta*-CH), 10.29 (s, 1H, Im-H^2); ^{13}C{H} NMR ($CDCl_3$): $\delta = 17.9$ ($Im-CH_3^{4,5}$); 18.5 (*ortho*-CH_3), 19.2 (*ortho*-CH_3), 21.2 (*para*-CH_3), 66.9 (Im-$C^{4,5}$), 128.9, 130.4, 130.5, 134.8, 136.3, 140.3 (Ar), 160.6 (Im-C^2).

4.12. Preparation of 1,3-bis(4-bromo-2,6-dimethylphenyl)imidazolinium chloride (3c)

Compound **3c** was prepared in the same way as **3a** from *N*,*N*′-bis(4-bromo-2,6-dimethylphenyl)ethylenediamine (**2c**) (4.26 g, 10 mmol), 10 mL of triethyl orthoformate and ammonium chloride (0.54 g, 10.2 mmol) to give white crystals of **3c**. Yield: 4.11 g, 87%; mp = 358–360 °C. Anal. Calc. for $C_{18}H_{22}N_2Br_2Cl$: C, 48.28; H, 4.48; N, 5.93. Found: C, 49.40; H, 4.35; N, 6.01%.

^{1}H NMR ($CDCl_3$): $\delta = 2.46$ (s, 12H, *ortho*-CH_3), 4.55 (s, 4H, Im-$H^{4,5}$), 7.60 (s, 4H, *meta*-CH), 9.31 (s, 1H, Im-H^2); ^{13}C{H} NMR ($CDCl_3$): $\delta = 17.8$ (*ortho*-CH_3), 51.4 (Im-$C^{4,5}$), 123.6, 132.1, 133.5, 139.3 (Ar), 161.1 (Im-C^2).

4.13. Preparation of 1,3-bis(2,4-dimethylphenyl)imidazolinium chloride (3d)

Compound **3d** was prepared in the same way as **3a** from *N*,*N*′-bis(2,4-dimethyl phenyl)ethylenediamine (**2d**) (2.68 g, 10 mmol), 10 mL of triethyl orthoformate and ammonium chloride (0.54 g, 10.2 mmol) to give white crystals of **3d**. Yield: 2.91 g, 93%; m.p = 290–292 °C. Anal. Calc. for $C_{18}H_{23}N_2Cl$: C, 72.48; H, 7.36; N, 8.90. Found: C, 70.53; H, 6.25; N, 8.52%.

^{1}H NMR ($CDCl_3$): $\delta = 2.34$ (s, 6H, *para*-CH_3), 2.43 (s, 6H, *ortho*-CH_3), 4.68 (s, 4H, Im-$H^{4,5}$), 7.07 (d, 2H $J = 7.60$ Hz, *ortho*-CH), 7.28 (s, 2H, *meta*-CH), 7.75 (d, 2H, $J = 7.85$ Hz *meta*-CH), 8.54 (s, 1H, Im-H^2); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.4$ (*ortho*-CH_3), 21.4 (*para*-CH_3), 53.3 (Im-$C^{4,5}$), 126.6, 128.4, 132.3, 132.5, 132.5, 140.2 (Ar), 157.9 (Im-C^2).

4.14. Preparation of 1,3-bis(4-chloro-2,6-dimethylphenyl)imidazolinium chloride (3e)

Compound **3e** was prepared in the same way as **3a** from *N*,*N*′-bis(4-chloro-2,6-dimethyl phenyl)ethylenediamine (**2e**) (3.37 g, 10 mmol), 10 mL of triethyl orthoformate and ammonium chloride (0.54 g, 10.2 mmol) to give white crystals of **3e**. Yield: 3.26 g, 85%; mp = 345–346 °C. Anal. Calc. for $C_{19}H_{21}N_2Cl_3$: C, 59.47; H, 5.52; N, 7.30. Found: C, 59.45; H, 5.73; N, 7.49%.

^{1}H NMR ($CDCl_3$): $\delta = 2.14$ (s, 12H, *ortho*-CH_3), 3.70 (s, 4H, Im-$H^{4,5}$), 7.07 (s, 4H, *meta*-CH), 7.86 (s, 1H, Im-H^2); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.7$ (*ortho*-CH_3), 43.9 (Im-$C^{4,5}$), 129.2, 134.4, 137.0, 138.7 (Ar), 163.6 (Im-C^2).

4.15. Preparation of 1,3-bis(2,4-dimethylphenyl)-2-(trichloromethyl)imidazolidine (4d)

A 50 mL Schlenk tube was charged with **2d** (1.21 g, 4.51 mmol) and 5 mL CH_3COOH. The solution was treated with Cl_3CCHO (1.00 mL, 10.17 mmol) and was left to stand for 3 h at room temperature. The solid formed was filtered and was recrystallized in CH_2Cl_2/hexane. Yield: 1.33 g, 74%; m.p. = 144–145 °C. Anal. Calc. for $C_{20}H_{23}Cl_3N_2$: C, 60.39; H, 5.83; N, 7.04. Found: C, 60.54; H, 5.48; N, 6.83%.

^{1}H NMR ($CDCl_3$): $\delta = 2.23$ (s, 6H, *para*-CH_3), 2.30 (s, 6H, *ortho*-CH_3), 3.08 (s, 2H, NCH_2), 3.82 (s, 2H, NCH_2), 5.68 (s, H, $NCHCCl_3N$), 6.72 (s, 2H, *meta*-CH), 6.96 (dd, 2H, $J = 3.6$ Hz, *ortho*-CH), 7.20 (d, 2H, $J = 3.61$, Ar-CH); ^{13}C NMR ($CDCl_3$): $\delta = 18.9$ (*para*-CH_3), 21.2 (*ortho*-CH_3), 55.3 (NCH_2), 92.4 ($NCHCCl_3N$), 108.1 ($NCHCCl_3N$), 122.8, 127.8, 132.4, 134.5, 135.5, 147.2 (Ar).

4.16. trans-Bis[1,3-bis(2,6-dimethylphenylimidazolidin-2-ylidene)]dichloropalladium(II) (5a)

Imidazolinium salt **3a** (0.31 g, 10 mmol) was dissolved in 50 mL CH_2Cl_2 and Ag_2O (0.12 g, 5 mmol) added. The resulting black suspension was protected from light and stirred for 24 h at RT until only a voluminous light grey precipitate remained, followed by addition of $PdCl_2(NCCH_3)_2$ (0.13 g, 5 mmol). The yellow color faded after several minutes, and after a further two days the reaction was filtered. The CH_2Cl_2 removed in vacuo, and the residue was washed with Et_2O. The crude product was recrystallized from CH_2Cl_2/Et_2O. Yield: 0.44 g, 60%; m.p = 304–306 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal.

Calc. for $C_{38}H_{44}N_2Cl_2Pd$: C, 62.17; H, 6.04; N, 7.63. Found: C, 62.14; H, 6.35; N, 7.89%.

^{1}H NMR ($CDCl_3$): $\delta = 2.13$ (s, 24H, *ortho*-CH_3), 3.67 (s, 8H, Im-$H^{4,5}$), 7.06 (d, 8H, $J = 2.0$ Hz, *meta*-CH), 7.23 (t, 4H, $J = 2.0$ Hz, *para*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.3$ (*ortho*-CH_3), 51.1 (Im-$C^{4,5}$), 127.6, 128.8, 137.4, 138.6 (Ar), 198.7 (C–Pd).

4.17. trans-Bis[1,3-bis(2,4,6-trimethylphenylimidazolidin-2-ylidene)]dichloropalladium(II) (**5b**)

The product was obtained in a similar fashion to **5a** as yellow crystals. Yield: 0.49 g, 62%; m.p = 348–350 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1456. Anal. Calc. for $C_{42}H_{52}N_4Cl_2Pd$: C, 63.84; H, 6.63; N, 7.09. Found: C, 63.51; H, 6.94; N, 7.55%.

^{1}H NMR ($CDCl_3$): $\delta = 2.10$ (s, 24H, *ortho*-CH_3), 2.43 (s, 12H, *para*-CH_3), 3.65 (s, 8H, Im-$H^{4,5}$), 6.86 (s, 8H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.2$ (*ortho*-CH_3), 21.4 (*para*-CH_3), 51.2 (Im-$C^{4,5}$), 129.4, 136.1, 136.8, 137.1 (Ar), 199.0 (C–Pd).

4.18. trans-Bis[1,3-bis(2,4,6-trimethylphenyl)-4,5-bis(methyl)imidazolidin-2-ylidene]dichloro palladium(II) (**5b′**)

The product was obtained in a similar fashion to **5a** as cream crystals. Yield: 0.62 g, 73%; m.p = >318 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1449. Anal. Calc. for $C_{46}H_{60}N_4Cl_2Pd$: C, 65.28; H, 7.15; N, 6.62. Found: C, 65.22; H, 7.30; N, 6.91%.

^{1}H NMR ($CDCl_3$): $\delta = 1.01$ (d, 24H $J = 1.5$ Hz, Im − $CH_3{}^{4,5}$), 1.83 (s, 12H, *ortho*-CH_3) 1.86 (s, 12H, *ortho*-CH_3), 2.43 (s, 12H, *para*-CH_3), 3.62 (m, 4H, Im-$H^{4,5}$), 6.85 (s, 4H, *meta*-CH); 6.87 (s, 4H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.5$ (Im − $CH_3{}^{4,5}$), 20.0 (*ortho*-CH_3), 20.1 (*ortho*-CH_3), 21.4 (*para*-CH_3), 65.8 (Im-$C^{4,5}$), 129.2, 130.0, 134.8, 136.5, 137.2, 138.2 (Ar), 196.7 (C–Pd).

4.19. trans-Bis[1,3-bis(4-bromo-2,6-dimethylphenylimidazolidin-2- ylidene)]dichloropalladium(II) (**5c**)

The product was obtained in a similar fashion to **5a** as yellow crystals. Yield: 0.77 g 74%; m.p = >320 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal. Calc. for $C_{38}H_{40}N_4Br_4Cl_2Pd$: C, 43.48; H, 3.84; N, 5.34. Found: C, 43.51; H, 4.35; N, 5.64%.

^{1}H NMR ($CDCl_3$): $\delta = 2.12$ (s, 24H, *ortho*-CH_3), 3.69 (s, 8H, Im-$H^{4,5}$), 7.24 (s, 8H, *meta*-CH), ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.1$ (*ortho*-CH_3), 50.8 (Im-$C^{4,5}$), 121.6, 131.6, 137.1, 139.6 (Ar), 199.4 (C–Pd).

4.20. trans-Bis[1,3-bis(2,4-dimethylphenylimidazolidin-2-ylidene)]dichloropalladium(II) (**5d**)

The product was obtained in a similar fashion to **5a** as yellow crystals. Yield: 0.44 g, 60%; m.p = 185–186 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1456. Anal. Calc. for $C_{38}H_{46}N_4Cl_2Pd \cdot 2H_2O$: C, 59.26; H, 6.28; N, 7.27. Found: C, 60.01; H, 6.32; N, 7.40%.

^{1}H NMR ($CDCl_3$): $\delta = 2.10$ (s, 12H, *ortho*-CH_3), 2.44 (s, 12H, *para*-CH_3), 3.67 (s, 8H, Im-$H^{4,5}$), 6.80 (d, 4H, $J = 1.9$ Hz, *ortho*-CH), 6.93 (s, 4H, *meta*-CH), 7.16 (d, 4H, $J = 1.9$ Hz, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 18.3$ (*ortho*-CH_3), 21.6 (*para*-CH_3), 52.9 (Im-$C^{4,5}$), 127.3, 129.9, 131.6, 135.8, 136.7, 137.5 (Ar), 199.2 (C–Pd).

4.21. trans-Bis[1,3-bis(4-chloro-2,6-dimethylphenylimidazolidin-2-ylidene)]dichloropalladium(II) (**5e**)

The product was obtained in a similar fashion to **5a** as yellow crystals. Yield: 0.61 g 70%; m.p = >323 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal. Calc. for $C_{38}H_{42}N_4Cl_6Pd \cdot 4H_2O$: C, 48.35; H, 5.13; N, 5.94. Found: C, 48.38; H, 5.28; N, 5.82%.

^{1}H NMR ($CDCl_3$): $\delta = 2.14$ (s, 24H, *ortho*-CH_3), 3.68 (s, 8H, Im-$H^{4,5}$), 7.07 (s, 8H, *meta*-CH); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.2$ (*ortho*-CH_3), 50.9 (Im-$C^{4,5}$), 128.6, 133.1, 136.7, 139.4 (Ar), 199.4 (C–Pd).

4.22. trans-[1,3-Bis(2,6-dimethylphenyl)imidazolidin-2-ylidene]dichlorotriphenylphosphine palladium(II) (**6a**)

A suspension of the salt **3a** (0.16 g, 0.5 mmol) and sodium hydride (0.17 g, 0.75 mmol) in THF (10 mL) was heated under reflux for 4 h. The mixture was cooled to 25 °C, and volatiles were removed. The residue was charged with $[PdCl_2(PPh_3)]_2$ (0.22 g, 0.25 mmol) and toluene (5 mL). The mixture was heated under reflux for 4 h, after which it was cooled to room temperature and hexane (10 mL) was added. The resulting cream precipitate was filtered off and recrystallized from CH_2Cl_2/Et_2O. Yield: 0.11 g, 63%; m.p. = 275–277 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1456. Anal. Calc. for $C_{37}H_{38}Cl_2N_2PPd$: C, 61.90; H, 5.19; N, 3,90. Found: C, 61.77; H, 4,55; N, 4.77%.

^{1}H NMR ($CDCl_3$): $\delta = 2.57$ (s, 12H, *ortho*-CH_3), 4.04 (s, 4H, Im-$H^{4,5}$), 7.31–7.17 (m, 21H, Ar, PPh_3); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.6$ (*ortho*-CH_3), 51.2 (Im-$C^{4,5}$), 127.8 (d, $J_{C-P} = 9.9$ Hz, *m*-C PC_6H_5), 129.9 (d, $J_{C-P} = 2.3$ Hz, *p*-C PC_6H_5), 130.6 (d, $J_{C-P} = 44.2$ Hz, *ipso*-C PC_6H_5), 128.6, 128.7, 132.3, 138.0 (Ar), 135.1 (d, $J_{C-P} =$ 10.7 Hz, *o*-C PC_6H_5), 197.5 (d, $^2J_{C-P} = 184.5$ Hz, C–Pd); ^{31}P{H} NMR ($CDCl_3$): $\delta = 21.27$.

4.23. trans-[1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene]dichlorotriphenylphosphine palladium(II) (**6b**)

The product was obtained in a similar fashion to **6a** as yellow crystals. Yield: 0.30 g, 75%; m.p = 272–274 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal. Calc. for $C_{39}H_{41}Cl_2N_2PPd$: C, 62.79; H, 5.54; N, 3,75. Found: C, 61.63; H, 5,55; N, 3.75%. ^{1}H NMR ($CDCl_3$): $\delta = 2.41$ (s, 12H, *ortho*-CH_3), 2.53 (s, 6H, *para*-CH_3), 4.00 (s, 4H, Im-$H^{4,5}$), 7.30–7.16 (m, 19H, Ar, PPH_3); ^{13}C{H} NMR ($CDCl_3$): $\delta = 19.5$ (*ortho*-CH_3), 21.4 (*para*-CH_3), 51.45 (Im-$C^{4,5}$), 127.7 (d, $J_{C-P} = 9.9$ Hz, *m*-C PC_6H_5), 129.4 (Ar), 129.9 (d, $J_{C-P} =$

2.3 Hz, *p*-C PC_6H_5), 130.7 (d, $J_{C-P} = 43.5$ Hz, *ipso*-C PC_6H_5), 135.2 (d, $J_{C-P} = 10.7$ Hz, *o*-C PC_6H_5), 135.6, 137.6, 138.0 (Ar), 197.2 (d, $^2J_{C-P} = 185.3$ Hz, C–Pd); $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = 20.88$.

4.24. trans-[1,3-Bis(2,4,6-trimethylphenyl)-4,5-bis(methyl)imidazolidin-2-ylidene]dichloro triphenylphosphine palladium(II) (6b′)

The product was obtained in a similar fashion to **6a** as yellow crystals. Yield: 0.60 g, 78%; m.p = 230–232 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1449. Anal. Calc. for $C_{41}H_{45}Cl_2N_2PPd$: C, 63.61; H, 3.62; N, 5.86. Found: C, 63.97; H, 3,70; N, 5.75%. ^1H NMR ($CDCl_3$): $\delta = 1,29$ (d, $J = 1.2$ Hz, Im – $CH_3^{4,5}$), 2.41 (s, 6H, *ortho*-CH_3), 2.44 (s, 6H, *ortho*-CH_3), 2.63 (s, 6H, *para*-CH_3), 4.01 (m, 2H, Im-$H^{4,5}$), 6.94 (s, 2H, *meta*-CH), 7.07 (s, 2H, *meta*-CH), 7.26–7.31 (m, 15H, PPh_3); $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 19.6$ (s, Im – $CH_3^{4,5}$), 19.9 (*ortho*-CH_3), 20.1 (*ortho*-CH_3), 21.4 (*para*-CH_3), 63.2 (Im-$C^{4,5}$), 127.9 (d, $J_{C-P} = 9.9$ Hz, *m*-C PC_6H_5), 129.4 (d, $J_{C-P} = 2.3$ Hz, *p*-C PC_6H_5), 129.6 (Ar), 130.6 (d, $J_{C-P} = 43.5$ Hz, *ipso*-C PC_6H_5), 134.6 (d, $J_{C-P} = 10.7$ Hz, *o*-C PC_6H_5), 137.6, 137.7, 137.8, 138.1,138.7 (Ar), 194.9 (d, $^2J_{C-P} = 185.3$ Hz, C–Pd); $^{31}P\{H\}$ NMR (δ, $CDCl_3$): $\delta = 21.01$.

4.25. trans-[1,3-Bis(4-bromo-2,6-dimethylphenyl)imidazolidin-2-ylidene]dichlorotriphenyl phosphinepalladium(II) (6c)

The product was obtained in a similar fashion to **6a** as yellow crystals. Yield: 0.34 g, 77%; m.p = 267 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal. Calc. for $C_{37}H_{35}Cl_2Br_2N_2PPd$: C, 50.74; H, 4.03; N, 3,20. Found: C, 51.33; H, 4,25; N, 3.25%. ^1H NMR ($CDCl_3$): $\delta = 2.52$ (s,12H, *ortho*-CH_3), 3.99 (s, 4H, Im-$H^{4,5}$), 7.24–7.36 (m, 19H, Ar, PPH_3); $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 19.5$ (*ortho*-CH_3), 51.2 (Im-$C^{4,5}$), 127.7 (d, $J_{C-P} = 9.9$ Hz, *m*-C PC_6H_5), 129.4 (Ar), 129.9 (d, $J_{C-P} = 2.3$ Hz, *p*-C PC_6H_5), 130.7 (d, $J_{C-P} = 43.5$ Hz, *ipso*-C PC_6H_5), 135.1 (d, $J_{C-P} = 10.7$ Hz, *o*-C PC_6H_5), 135.6, 137.6, 138.0 (Ar), 198.7 (d, $^2J_{C-P} = 183.8$ Hz, CPd); $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = 21.50$.

4.26. trans-[1,3-Bis(2,4-dimethylphenyl)imidazolidin-2-ylidene]dichlorotriphenylphosphine palladium(II) (6d)

A 50 mL Schlenk tube was charged with **4d** (0.20 g, 0.5 mmol), $[PdCl_2(PPh_3)]_2$ (0.22 g, 0.25 mmol) and 5 mL toluene. The mixture was heated under reflux for 4 h. The solution was cooled to room temperature and then hexane 10 mL was added. The orange precipitate formed was filtered off and recrystallized from CH_2Cl_2/Et_2O. Yield: 0.12 g 65%; m.p. = 273 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1449. Anal. Calc. for $C_{37}H_{37}Cl_2N_2PPd$: C, 61.89; H, 5.19; N, 3,90. Found: C, 61.52; H, 5.30; N, 4.06%.

^1H NMR ($CDCl_3$): $\delta = 2.44$ (s, 6H, *ortho*-CH_3). 2.46 (s, 6H, *para*-CH_3), 4.09 (s, 4H, Im-$H^{4,5}$), 7.31–7.15 (m, 19H, Ar, PPh_3), 7.88 (d, $J = 1.9$ Hz, 2H, Ar); $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 18.0$ (*ortho*-CH_3), 20.8 (*para*-CH_3), 51.9 (Im-$C^{4,5}$), 127.2 (d, $J_{C-P} = 10.0$ Hz, *m*-C PC_6H_5), 129.8 (d, $J_{C-P} = 42.4$ Hz, *ipso*-C PC_6H_5), 126.6, 129.4, 129.9, 131.3 (Ar, *p*-C PC_6H_5), 134.4 (d, $J_{C-P} = 11.3$ Hz, *o*-C PC_6H_5), 135.3, 136.4, 137.5 (Ar), 196.8 (d, $^2J_{C-P} = 180.8$ Hz, C–Pd), $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = 19.46$.

4.27. trans-[1,3-Bis(4-chloro-2,6-dimethylphenyl)imidazolidin-2-ylidene]dichlorotriphenyl phosphinepalladium(II) (6e)

The product was obtained in a similar fashion to **6a** as yellow crystals. Yield: 0.26 g, 68%; m.p = 270 °C; $\upsilon_{(NCN)}$ (cm^{-1}) = 1457. Anal. Calc. for $C_{37}H_{35}Cl_4N_2PPd$: C, 56.47; H, 4.48; N, 3,56. Found: C, 56.53; H, 4,50; N, 3.80%. ^1H NMR ($CDCl_3$): $\delta = 2.53$ (s, 12H, *ortho*-CH_3), 3.99 (s, 4H, Im-$H^{4,5}$), 7.19–7.33 (m, 19H, Ar, PPH_3); $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 19.6$ (*ortho*-CH_3), 51.3 (Im-$C^{4,5}$), 127.8 (d, $J_{C-P} = 10.6$ Hz, *m*-C PC_6H_5), 129.4 (Ar), 129.9 (d, $J_{C-P} = 2.3$ Hz, *p*-C PC_6H_5), 130.3 (d, $J_{C-P} = 44.3$ Hz, *ipso*-C PC_6H_5), 135.0 (d, $J_{C-P} = 11.4$ Hz, *o*-C PC_6H_5), 133.9, 136.6, 139.4 (Ar), 198.3 (d, $^2J_{C-P} = 184.5$ Hz, CPd); $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = 21.50$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.020.

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