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Synthesis of pyrazine-bridged diimidazolium salts and their application in palladium catalyzed Heck-type coupling reactions

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ABSTRACT

Reaction of imidazole derivatives with 2,3-di(bromomethyl)pyrazine results in the formation of the new pyrazine-bridged diimidazolium salts **1**–**8**. These salts proved to be valuable precursors for dinuclear complexes with mixed NHC/pyrazine ligands. Two of the pyrazine-bridged diimidazolium salts **3**·H_2O and **8**·$2H_2O$ have been characterized by X-ray diffraction. Furthermore, the first catalytic studies with mixtures of palladium acetate and the imidazolium salts have been carried out. The in situ prepared palladium complexes derived from the diimidazolium salts **1**–**8** exhibit a modest catalytic activity in Heck-type coupling reactions between 4-bromo benzaldehyde and styrene or *n*-butyl acrylate.

1. Introduction

Initiated by the isolation of the first stable *N*-heterocyclic carbene (NHC) by Arduengo et al. in 1991,[1] a large number of stable NHC ligands has since been prepared.[2] The preparation and the properties of stable NHCs derived from imidazole, imidazolidine, triazole, and benzimidazole have been studied in detail.[2a,c] Apart from the well-known NHCs with a five-membered heterocycle,[1,3] stable NHCs with six-[4] and seven-membered heterocycles[5] have been described. Furthermore, not only the preparation and isolation of free NHC ligands, but also the synthesis of transition metal complexes with such ligands has attracted considerable interest due to the interesting coordination chemistry of the NHC ligands[2] and, especially, the potential application of the metal complexes as catalysts in a variety of catalytic transformations.[6] In spite of the application of NHC complexes as catalysts in different reactions, such as the ruthenium-catalyzed olefin metathesis,[7] the most common application for catalytically active NHC complexes are still C–C coupling reactions such as the Heck or Suzuki reaction.[8]

The advantage of complexes with NHC ligands compared to phosphine complexes emerges from the superior σ-donor properties of the NHC ligands. These result in stronger metal–ligand bonds,[2] which in turn leads to a stabilization of the metal center during a catalytic process by compensating of a charge deficit at the metal atom.[9]

Complexes with bidentate heteroatom-functionalized carbene ligands bearing additional phosphine[10] or nitrogen[11] donor function have been prepared as well as tridentate ligands with one[12] or two imidazolin-2-ylidene[13] or benzimidazolin-2-ylidene donors,[14] leading to complexes with the pincer-type topology.[15] The combination of the carbene moiety with classical donor functions allows a fine tuning of the properties of the catalytically active metal center resulting often in an increased activity of the catalytic active species.[8]

Recently a new development in the field of the heteroatom-functionalized carbenes has been presented dealing with aromatic heterocyclic bridging units between two carbene donor functions. In contrast to the pincer complexes with tridentate ligands of type (**A**)[13,14] the bridging unit in this ligand type possesses two heteroatom donor functions. This arrangement leads to preorganized bimetallic complexes.[16] Bimetallic complexes with pyradizine- (**B**)[17] and pyrazolato-bridged (**C**)[18] dicarbene ligands have been previously prepared. These ligands with the N-atoms in adjoining positions give dinuclear complexes with the metal centers in close proximity. Contrary to this, we introduce here pyrazine as the bridging unit bearing the two N-atoms in *para*-positions, and hence placing the two metal centers in more remote positions. Consequently, complexes with pyrazine-bridged dicarbene ligands of

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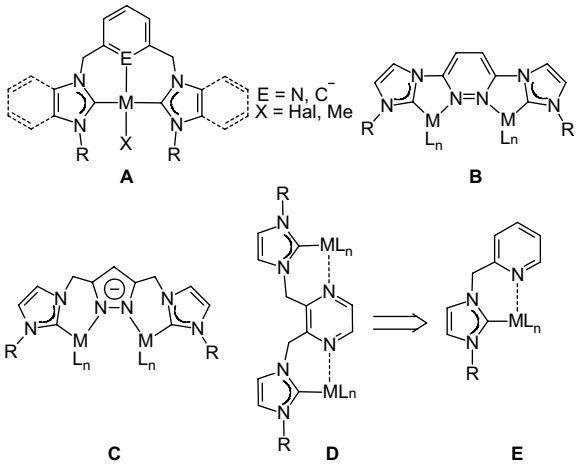
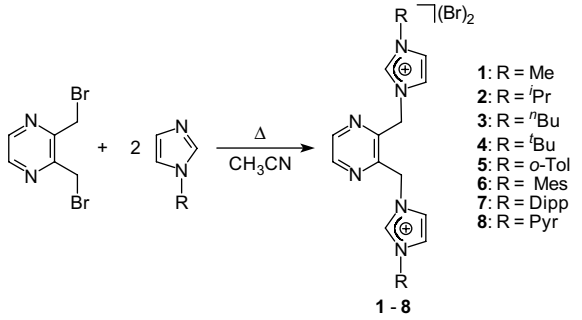


Figure 1. Differently bridged dicarbene ligands.

type **D** can formally be described as dinuclear versions of the well-known complexes of type **E** with picoline-functionalized carbene donors.[11,19] Here we describe the synthesis of pyrazine-bridged imidazolium salts together with preliminary results on the application of these azolium salts for the in situ preparation of palladium catalysts for Heck-type C–C coupling reactions (Fig. 1).

2. Results

The pyrazine-bridged diimidazolium salts were readily prepared by treatment of 2,3-di(bromomethyl)pyrazine[20] with *N*-alkylated or *N*-arylated imidazole derivatives in boiling acetonitrile (Scheme 1). The resulting imidazolium salts, including the potentially bis-tridentate ligand **8** featuring an *N*-pyridine substituted imidazolium ring, were obtained in good yields of 50–75%.



Scheme 1.

The ^{1}H NMR spectra of the diimidazolium salts **1**–**8** exhibit the signal for the NCHN proton in the range of δ 9.34–10.40 ppm. These values are typical for NCHN protons of imidazolium[2a] and benzimidazolium salts.[14,21] The resonances for the methylene protons of the bridge were observed as singlets and fall in the wide range between δ 5.94 and 6.75 ppm. The ^{13}C NMR spectra of **1**–**8** exhibit the NCN resonances between δ 136.3 and 139.5 ppm, which are also typical values previously reported for imidazolium salts.[2a]

Crystals of the imidazolium salts **3**·H_2O and **8**·$2H_2O$, which were suitable for X-ray diffraction studies could be obtained from concentrated methanol solutions of the salts through slow evaporation of the solvent. The molecular structures of the diimidazolium dication in **3**·H_2O and **8**·$2H_2O$ are depicted in Figure 2.

The eight C1/C10–N bond distances for the NCHN groups in the diimidazolium dications of **3** and **8** fall in the range between

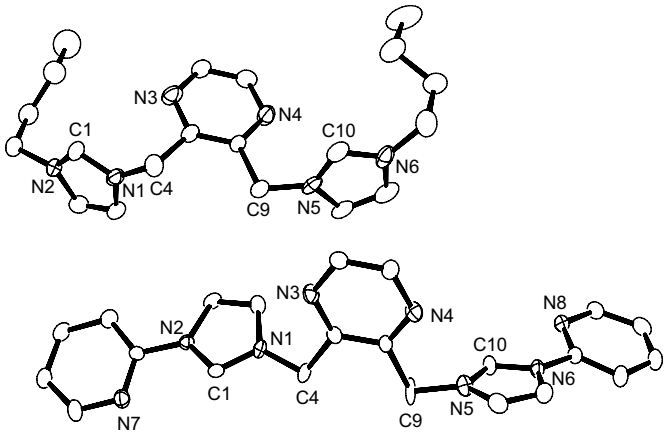
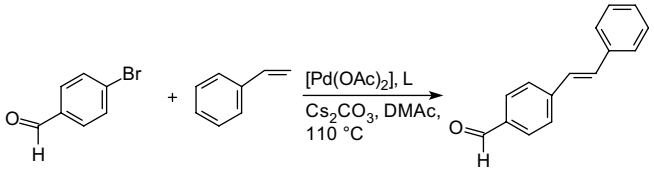


Figure 2. Molecular structures of the pyrazine-bridged diimidazolium cations in **3**·H_2O (top) and **8**·H_2O (bottom). Hydrogen atoms, the bromide counterions, and the water molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) for **3**·H_2O: N1–C1 1.334(7), N2–C1 1.306(7), N5–C10 1.332(7), N6–C10 1.337(7); N1–C1–N2 109.2(6), N5–C10–N6. For **8**·H_2O: N1–C1 1.319(9), N2–C1 1.330(9), N5–C10 1.326(10), N6–C10 1.332(9); N1–C1–N2 108.6(6), N5–C10–N6 108.0(7).

1.306(7) and 1.337(7) Å, which are typical values for imidazolium salts.[2a] The same is true for the N–C–N bond angles within the imidazolium rings [N–C–N 107.9(6)–109.2(6)°].[2a] The bond angles at the bridging methylene carbon atoms C4 and C9 are also close to tetrahedral in both compounds.

Metal-catalyzed C–C coupling reactions between aryl halides and olefins are usually carried out homogenously in the presence of a base under an inert atmosphere.[22] It was noted that in some cases the in situ formation of the catalytically active species led to significantly better results than the use of the preformed complex.[23] We studied first the Pd-catalyzed Heck-type coupling reaction of *para*-bromo benzaldehyde and styrene using the new pyrazine-bridged diimidazolium salts **1**–**8** and palladium acetate in the ratio of one to two. The best results were obtained using 1.0 mol % of a diimidazolium salt, 2.0 mol % of [$Pd(OAc)_2$], and 2.0 mmol of Cs_2CO_3 in dimethylacetamide at 110 °C over a reaction period of 20 h. Chromatographic analysis of the reaction mixture revealed total conversions of 96.6–100% (Table 1). Catalyst stability was not monitored. It is possible that Pd-colloids, which themselves are

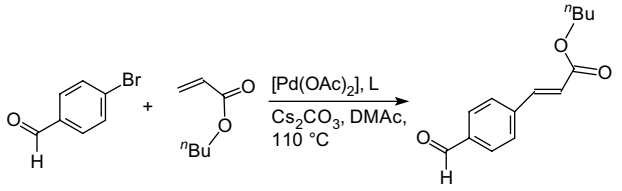
Table 1
Pd-catalyzed Heck coupling reaction of styrene with 4-bromo benzaldehyde[a]



Entry	Salt	Time (h)	Yield (%)		
			cis	trans	Total
1	**1**	20	13.5	83.0	96.6
2	**2**	20	12.7	87.3	100
3	**3**	20	15.8	83.3	99.1
4	**4**	20	5.1	94.9	100
5	**5**	20	12.7	87.3	100
6	**6**	20	14.4	85.7	100
7	**7**	20	5.9	94.1	100
8	**8**	20	11.7	88.3	100

[a] Reaction conditions: 1.0 mmol of the 4-bromo benzaldehyde, 1.4 mmol of styrene, 2.0 mmol Cs_2CO_3, 1.0 mol % of the salts **1**–**8**, 2.0 mol % of [$Pd(OAc)_2$], and 5 mL of DMAc. Yields were determined by GC–MS.

Table 2
Pd-catalyzed Heck coupling reaction of *n*-butyl acrylate with 4-bromo benzaldehyde[a]



Entry	Salt	Time (h)	Yield (%)		
			cis	trans	Total
1	**1**	22	7.6	68.3	75.9
2	**2**	22	5.9	69.6	75.6
3	**3**	22	7.8	66.5	74.2
4	**4**	22	5.3	77.2	82.5
5	**5**	24	5.9	71.9	77.8
6	**6**	24	5.7	69.3	75.0
7	**7**	24	5.0	71.2	76.2
8	**8**	24	5.6	67.0	74.6

[a] Reaction conditions: 1.0 mmol of the 4-bromo benzaldehyde, 1.4 mmol of *n*-butyl acrylate, 2.0 mmol Cs_2CO_3, 1.0 mol % of the salt **1**–**8**, 2.0 mol % of $[Pd(OAc)_2]$ and 5 mL of DMAc. Yields were determined by GC–MS.

catalytically active form by reductive elimination of C2-functionalized imidazolium salts. Such salts, however, were not detected in the reaction products. In addition, no indications for the formation of Pd-black were observed.

All in situ generated catalysts have shown catalytic activity, although conversions were not outstanding. They are lower than those found for catalytic systems derived from well-defined palladium complexes with mixed carbene/phosphine or pincer-type ligand exhibiting better conversion rates even after shorter reaction times. Nevertheless, steric effects influence the cis/trans ratio of the product mixture obtained. The formation of the trans-product is favored with sterically demanding *N*-substituents at the carbene ligand.

Alternatively, *n*-butyl acrylate was also tested as olefinic substrate in the C–C coupling reaction with 4-bromo benzaldehyde. The total conversion after the selected reaction time (22–24 h) is generally lower (74.2–82.5%) when compared to other palladium catalysts. A reduced tendency for the formation of the cis-coupling product was observed (Table 2).

3. Conclusion

We have prepared a set of new pyrazine-bridged diimidazolium salts derived from 2,3-di(bromomethyl)-pyrazine and *N*-alkyl- or *N*-arylimidazoles. It was shown that the diimidazolium salts in combination with palladium acetate form an effective catalytic system for Heck-type C–C coupling reactions with an acceptable conversion rate. The tendency for the formation of the trans-product depends on the steric demand of the *N*-substituents of the imidazolium salts and also on the olefinic substrate. Further Heck-type coupling reactions with deactivated aryl bromides and aryl chlorides in addition to Suzuki-type reactions are in progress.

4. Experimental

4.1. General comments

All manipulations were performed in air. The 2,3-di(bromomethyl)pyrazine,[20] the *N*-alkylated imidazoles,[24] and the aromatic-substituted imidazole derivatives[25] have been prepared by the literature procedures. *N*-Methyl- and *N*-(*n*-butyl)imidazole were purchased from Aldrich and were used without any further purification.

4.2. General method for the preparation of imidazolium salt

A sample of the desired functionalized imidazole (2.2 mmol) and 1 equiv of 2,3-di(bromomethyl)pyrazine (1.0 mmol, 0.266 g) were dissolved in 70 mL of acetonitrile. The reaction mixture was heated under reflux for 12 h. Subsequently, the solvent was removed in vacuo. The solid residue was dissolved in a small amount of dichloromethane or methanol. This solution was added dropwise under stirring to 150 mL of diethyl ether. A precipitate of the diimidazolium salt formed, which was isolated by filtration and dried in vacuo.

4.2.1. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-methyl-1H-imidazol-3-ium) dibromide ***1***

Yield: 52.4%. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ 9.34 (s, 2H, NCHN), 8.58 (s, 2H, pyrazine–H), 7.84 (s, 2H, imidazolium–H), 7.80 (s, 2H, imidazolium–H), 5.94 (s, 4H, pyrazine–CH_2–N), 3.96 (s, 6H, N–CH_3). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ 147.6, 143.9 (pyrazine–C), 138.2 (NCN), 124.0, 123.9 (imidazolium–C), 49.8 (pyrazine–CH_2–N), 36.3 (N–CH_3). Anal. Calcd for $C_{14}H_{18}N_6Br_2$ (430.1): C, 39.01; H, 4.21; N, 19.50. Found: C, 38.75; H, 3.96; N, 20.03%. MS (MALDI-TOF): *m*/*z* 351, 349 $[M-Br]^+$.

4.2.2. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-iso-propyl-1H-imidazol-3-ium) dibromide ***2***

Yield: 60.1%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 10.02 (s, 2H, NCHN), 8.31 (s, 2H, pyrazine–H), 7.99 (s, 2H, imidazolium–H), 7.48 (s, 2H, imidazolium–H), 6.37 (s, 4H, pyrazine–CH_2–N), 4.72 (sept, 2H, ^3J=6.7 Hz, N–C*H*$(CH_3)_2$), 1.57 (d, 12H, ^3J=6.7 Hz, N–CH(CH_3)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.0, 143.5 (pyrazine–C), 136.3 (NCN), 124.8, 119.4 (imidazolium–C), 53.4 (N–*C*H$(CH_3)_2$), 51.5 (pyrazine–CH_2–N), 23.1 (N–CH(CH_3)$_2$). Anal. Calcd for $C_{18}H_{26}N_6Br_2$ (486.2): C, 44.46; H, 5.39; N, 17.28. Found: C, 45.03; H, 5.64; N, 17.01%. MS (MALDI-TOF): *m*/*z* 407, 405 $[M-Br]^+$.

4.2.3. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(n-butyl)-1H-imidazol-3-ium) dibromide ***3***

Yield: 65.3%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 9.96 (s, 2H, NCHN), 8.31 (s, 2H, pyrazine–H), 7.96 (s, 2H, imidazolium–H), 7.19 (s, 2H, imidazolium–H), 6.45 (s, 4H, pyrazine–CH_2–N), 4.19 (t, 4H, ^3J=7.3 Hz, N–C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.86 (quint, 4H, ^3J=7.3 Hz, N–CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.34 (sext, 4H, ^3J=7.3 Hz, N–CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.92 (t, 6H, ^3J=7.3 Hz, N–CH$_2$CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.4, 143.9 (pyrazine–C), 137.8 (NCN), 125.2, 121.5 (imidazolium–C), 51.0 (pyrazine–CH_2–N), 50.4 (N–*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.4 (N–CH$_2$CH$_2$CH$_2$CH$_3$), 19.9 (N–CH$_2$CH$_2$CH$_2$CH$_3$), 13.9 (N–CH$_2$CH$_2$CH$_2$CH$_3$). Anal. Calcd for $C_{20}H_{30}N_6Br_2$ (514.3): C, 46.71; H, 5.88; N, 16.34. Found: C, 46.43; H, 5.83; N, 15.97%. MS (MALDI-TOF): *m*/*z* 435, 433 $[M-Br]^+$.

4.2.4. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(tert-butyl)-1H-imidazol-3-ium) dibromide ***4***

Yield: 66.4%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 10.10 (s, 2H, NCHN), 8.30 (s, 2H, pyrazine–H), 7.96 (s, 2H, imidazolium–H), 7.34 (s, 2H, imidazolium–H), 6.40 (s, 4H, pyrazine–CH_2–N), 1.66 (s, 18H, N–C(CH_3)$_3$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.5, 143.7 (pyrazine–C), 136.5 (NCN), 125.5, 118.8 (imidazolium–C), 60.7 (N–*C*(CH_3)$_3$), 50.9 (pyrazine–CH_2–N), 30.5 (N–C(*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{30}N_6Br_2$ (514.3): C, 46.71; H, 5.88; N, 16.34. Found: C, 46.34; H, 5.94; N, 15.99%. MS (MALDI-TOF): *m*/*z* 435, 433 $[M-Br]^+$.

4.2.5. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(2-methylphenyl)-1H-imidazol-3-ium) dibromide ***5***

Yield: 61.5%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 10.49 (s, 2H, NCHN), 8.31 (s, 2H, pyrazine–H), 7.73 (s, 2H, imidazolium–H), 7.47–7.41 (m, 2H, Ar–H), 7.39–7.30 (m, 6H, Ar–H), 7.27 (s, 2H, imidazolium–H), 6.31 (s, 4H, pyrazine–CH_2–N), 2.21 (s, 6H, *o*-CH_3–Ph). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 145.7, 143.6 (pyrazine–C), 138.6 (NCN), 133.8, 133.4, 132.2, 131.2, 127.8, 126.2 (Ar–C), 124.5, 122.4 (imidazolium–C), 50.9 (pyrazine–CH_2–N), 17.8 (*o*-CH_3–Ph). Anal. Calcd for $C_{26}H_{26}N_6Br_2$ (582.3): C, 53.63; H, 4.50; N, 14.43. Found: C, 53.46; H, 4.27; N, 14.21%. MS (MALDI-TOF): *m*/*z* 503, 501 $[M-Br]^+$.

4.2.6. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(2,4,6-trimethylphenyl)-1H-imidazol-3-ium) dibromide ***6***

Yield: 64.9%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 9.68 (s, 2H, NCHN), 8.29 (s, 2H, pyrazine–H), 8.24 (s, 2H, imidazolium–H), 7.20 (s, 2H, imidazolium–H), 6.96 (s, 4H, Ar–H), 6.76 (s, 4H, pyrazine–CH_2–N), 2.29 (s, 6H, Ar–CH_3), 2.05 (s, 12H, Ar–CH_3). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=147.5, 143.4 (pyrazine–C), 141.7 (Ar–C), 138.9 (NCN), 134.8, 130.2, 129.8 (Ar–C), 126.4, 122.5 (imidazolium–C), 51.2 (pyrazine–CH_2–N), 21.6 (Ar–CH_3), 14.7 (Ar–CH_3). Anal. Calcd for $C_{30}H_{34}N_6Br_2$ (638.4): C, 56.44; H, 5.37; N, 13.16. Found: C, 55.98; H, 5.58; N, 12.66%. MS (MALDI-TOF): *m*/*z* 559, 557 $[M-Br]^+$.

4.2.7. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(2,6-diisopropylphenyl)-1H-imidazol-3-ium) dibromide ***7***

Yield: 72.3%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 9.64 (s, 2H, NCHN), 8.50 (s, 2H, pyrazine–H), 7.96 (s, 2H, imidazolium–H), 7.19 (s, 2H, imidazolium–H), 7.49 (t, 2H, ^3J=7.8 Hz, Ar–H), 7.26 (d, 4H, ^3J=7.8 Hz, Ar–H), 6.75 (s, 4H, pyrazine–CH_2–N), 2.42 (sept, 4H, ^3J=7.0 Hz, Ar–C*H*(CH_3)$_2$), 1.16, 1.14 (d, 12H, ^3J=7.0 Hz, Ar–CH(C*H*$_3$)$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 147.6 (pyrazine–C), 145.9 (Ar–C), 143.3 (pyrazine–C), 139.5 (NCN), 132.2, 130.6, 126.3 (Ar–C), 125.0, 123.5 (imidazolium–C), 51.2 (pyrazine–CH_2–N), 29.0 (Ar–*C*H(CH_3)$_2$), 24.9, 24.6 (Ar–CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{36}H_{46}N_6Br_2$ (722.6): C, 59.84; H, 6.42; N, 11.63. Found: C, 59.46; H, 6.23; N, 11.41%. MS (MALDI-TOF): *m*/*z* 643, 641 $[M-Br]^+$, 281 $[M-2Br]^{2+}$.

4.2.8. 1,1′-(Pyrazine-2,3-diyldimethanediyl)bis(3-(2-pyridine)-1H-imidazol-3-ium) dibromide ***8***

Yield: 58.7%. ^{1}H NMR (400.1 MHz, DMSO-d_6): δ 10.40 (s, 2H, NCHN), 8.71–8.66 (m, 4H, pyrazine–H and pyridine–H), 8.64 (s, 2H, imidazolium–H), 8.29–8.23 (m, 2H, pyridine–H), 8.21 (s, 2H, imidazolium–H), 8.17–8.13 (m, 2H, pyridine–H), 7.71–7.66 (m, 2H, pyridine–H), 6.15 (s, 4H, pyrazine–CH_2–N). ^{13}C NMR (100.6 MHz, DMSO-d_6): δ=149.7 (pyridine–C), 147.4 (pyrazine–C), 146.6 (pyridine–C), 144.2 (pyrazine–C), 141.1 (pyridine–C), 136.7 (NCN), 125.8, 125.3 (imidazolium–C), 119.5, 114.7 (pyridine–C), 50.3 (pyrazine–CH_2–N). Anal. Calcd for $C_{22}H_{20}N_8Br_2$ (556.3): C, 47.50; H, 3.62; N, 20.14. Found: C, 47.41; H, 3.23; N, 19.49%. MS (MALDI-TOF): *m*/*z* 477, 475 $[M-Br]^+$.

4.3. General procedure for the Heck coupling reaction

Heck coupling reactions were carried out using 4-bromo benzaldehyde (1.0 mmol), an olefinic substrate (1.4 mmol), and cesium carbonate as base (0.65 g, 2.0 mmol) dissolved in 5 mL of *N*,*N*-dimethylacetamide (DMAc). An appropriate amount of one of the diimidazolium salts **1**–**8** (1.0 mol %), palladium acetate (2.0 mol %), and di-(ethylene glycol) *n*-butyl ether as internal standard were added to this mixture. The reaction mixture was heated to 110 °C for the selected reaction time. Coupling product yields were calculated from GC data relative to the residual aryl halide. The product identity was confirmed by GC–MS.

4.4. X-ray structure determination of 3·H$_2$O and 8·2H$_2$O

4.4.1. X-ray structure determination of compounds ***3***·H_2O *and* ***8***·$2H_2O$

Diffraction data for **3**·H_2O were obtained on a Bruker SMART diffractometer equipped with a rotating anode using Cu Kα radiation (λ=1.54184 Å). Data for compound **8**·$2H_2O$ were collected on a Bruker AXS APEX CCD diffractometer equipped with a rotating anode using graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The diffraction data were measured at 153(2) K in the range $6.5\leq 2\Theta\leq 144.8°$ for **3**·H_2O and $3.3\leq 2\Theta\leq 53.0°$ for **8**·$2H_2O$. Structure solution[26] and refinement[27] were achieved with standard Patterson and Fourier techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure models on calculated positions.

4.4.2. Selected crystallographic details for ***3***·H_2O

$C_{20}H_{32}N_6Br_2O$, M=532.34, colorless crystal, 0.32×0.15×0.08 mm^3, triclinic, space group *P*-1, a=8.4588(3), b=10.8379(4), c=13.5766(5) Å, α=95.392(3), β=92.054(3), γ=95.207(3)°, V=1232.79(8) Å^3, ρ_{calcd}=1.434 g cm^{-3}, μ=4.342 mm^{-1}, empirical absorption correction ($0.3372\leq T\leq 0.7227$), Z=2, 7049 intensities collected ($\pm h$, $\pm k$, $\pm l$), 4165 independent intensities (R_{int}=0.0659), refinement of 264 parameters against all unique $|F^2|$, R=0.0659, wR=0.1590 for 2791 contributing intensities [$I\geq 2\sigma(I)$].

4.4.3. Selected crystallographic details for ***8***·$2H_2O$

$C_{22}H_{22}N_8Br_2O_2$, M=590.30, colorless crystal, 0.08×0.04×0.02 mm^3, monoclinic, space group $P2_1/n$, a=14.983(3), b=10.100(2), c=16.163(3) Å, β=105.566(2)°, V=2356.2(7) Å^3, ρ_{calcd}=1.664 g cm^{-3}, μ=3.478 mm^{-1}, empirical absorption correction ($0.7683\leq T\leq 0.9337$), Z=4, 21,019 intensities collected ($\pm h$, $\pm k$, $\pm l$), 4892 independent intensities (R_{int}=0.0654), refinement of 307 parameters against all unique $|F^2|$, R=0.0752, wR=0.1910 for 3740 contributing intensities [$I\geq 2\sigma(I)$].

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC-702780 for **3**·H_2O and CCDC-702781 for **8**·$2H_2O$. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data.request/cif.

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