Bridged Imidazolium Salts Used as Precursors for Chelating Carbene Complexes of Palladium in the Mizoroki–Heck Reaction[1]

Tobias Scherg, Sabine K. Schneider, Guido D. Frey, Jürgen Schwarz, Eberhardt Herdtweck, Wolfgang A. Herrmann*

Department Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Fax +49(89)28913473; E-mail: lit@arthur.anorg.chemie.tu-muenchen.de

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Dedicated to Prof. Richard Heck on the occasion of his 75th birthday

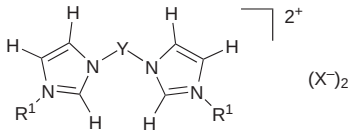
Abstract: A variety of chiral and achiral imidazolium salts is synthesized. Methylene-, ethylene-, propylene- and pyridinyl-bridged bis(imidazolium) halides are used to generate the respective free chelating carbenes. The synthesis of palladium complexes of general formula [*cis*-CH_2{NC(H)=C(H)N(R)C}$_2$$PdX_2$] with these chelating N-heterocyclic carbene ligands is reported. Structural proofs of complexes **28** and **46** are represented by X-ray diffraction studies. Catalytic applications in the Mizoroki–Heck reaction are presented.

Key words: catalysis, chelating ligands, chiral ligands, free carbenes, Mizoroki–Heck reaction, imidazolium salts, palladium

In advance of the Fischer[2,3] and prior to the Schrock[4] carbenes, N-heterocyclic carbenes (NHCs) were discovered by Wanzlick[5] and Öfele[6] in 1968. It turned out that the free species of these carbenes are poorly accessible. Their renaissance started with the work of Arduengo[7] in 1991 who discovered the free carbene 1,3-diadamantyl-imidazolin-2-ylidene. The bond between the N-heterocyclic carbene and the metal center of a complex can be described best as a dative σ-bond, as the bond length falls comfortably in the range of typical single bond lengths (X-ray diffraction).[8,9] One main feature of this type of carbene complexes is their resistance towards nucleophilic and electrophilic attacks.

Today, N-heterocyclic carbenes play a major role as ligands in organometallic chemistry. They make metal complexes suitable for a broad spectrum of catalytic applications.[10–12] For example, ruthenium complexes catalyze olefin metathesis,[13] rhodium complexes catalyze hydroformylation[14] and palladium complexes are used in the catalytic C–C bond formation[12,15,16] (e.g. Mizoroki–Heck reaction[17]). In the absence of π-acidic co-ligands, the strongly σ-donating NHCs are expected to stabilize high-oxidation state metal centers or generate highly reactive, electron-rich complexes. In this context, it seems to be of major interest to discuss the synthesis of this ligand class and to show its good accessibility. In this context, quite a few chelated complexes and their ligands are already known.[18,19] The preparation of chelating ligands of N-heterocyclic carbenes, which would provide extra air and moisture stability for palladium centers, are receiving much attention.[20,2,1] We have published palladium NHC complexes which can be used in C–C coupling reactions.[22–24] For example, some methylene-bridged bis(imidazolium) salts, in combination with $Pd(OAc)_2$, were equally efficient in Suzuki coupling with aryl chlorides as substrates,[15,25] and they even achieve the C–H activation of methane.[26]

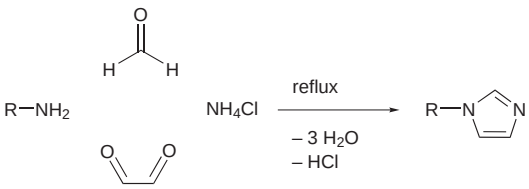
In the first part of the present article, a variety of new imidazolium salts will be presented. We will focus on the variation of the bridging group Y and the substituents R^1 (Figure 1). Additionally, the isolation of the free carbene 1,1′-dibutyl-3,3′-ethylene-diimidazolin-2,2′-diylidene (**26**) has been achieved. The ammonia method is not applicable to deprotonate the methylene-bridged salts because of the higher acidity of the bridging methylene protons in comparison to the imidazolium ring protons.[27]



R^1 = Me, *i*-Pr, *t*-Bu, Cy, Ad, Mes, 2,6-(*i*-Pr)$_2$$C_6H_3$
rac-phenylethyl, (*R*)-phenylethyl, *rac*-1'-naphthylethyl
X = Cl, Br, I
Y = CH_2, $(CH_2)_2$, pyridinyl, 2,6-lutidine, *o*-, *m*-, *p*-xylylene

Figure 1 R^1-substituted imidazolium salts with bridging groups Y

For this purpose, the weak base K[$N(SiMe_3)_2$] has been successfully used.[28] The substituted imidazole precursors are accessible via a one-pot synthesis route related to a method reported by Gridnev et al. (Scheme 1).[29]



Scheme 1 Synthesis of substituted imidazoles

The products can be purified by sublimation, extraction, recrystallization, distillation, bulb-to-bulb distillation or column chromatography.[29,30] This method of synthesis, however, is only suitable for aliphatic substituted imida-

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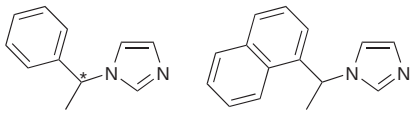
zoles. *rac*-1-(Phenylethyl)imidazole (**1a**, Figure 2), (*R*)-1-(phenylethyl)imidazole (**1b**),[30a] and the new modified *rac*-1-(1′-naphthylethyl)imidazole (**2**), could be synthesized via this procedure.[29] In the case of aromatic groups, the synthesis according to Liu et al. can be applied (Scheme 2).[30b]

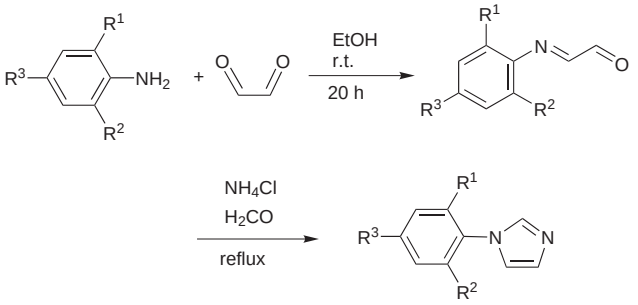


1a *rac*
1b *R*

2

Figure 2

In order to synthesize a library of bridged imidazolium salts, we used a general synthetic procedure. Two equivalents of the R-imidazole (R = alkyl, aryl) were dissolved in THF and brought into an ACE pressure tube. One equivalent of the corresponding dibromo compound was added and the resulting mixture was heated. The work-up as well as the purification of the air-stable hygroscopic colorless-to-pale-brown products[17] were achieved by filtration of the obtained solids by washing with THF, and were afterwards dried in high vacuo.[31] To the best of our knowledge these are the first bridged diimidazolium salts with the chirality next to the N-atoms reported to date. Table 1 gives an overview of the prepared 1,3-bisazolium salts.

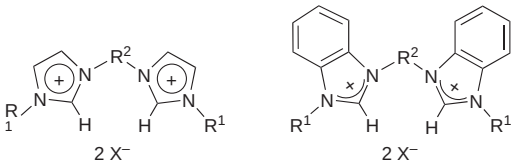


Scheme 2 Synthesis of aryl-substituted imidazoles

Free carbenes have become available on a broad basis through the ‘ammonia method’ (Scheme 3); thereby the deprotonation takes place at low temperatures in liquid ammonia with NaH as a strong base.[18] The deprotonation of the corresponding imidazolium salts is carried out in an argon atmosphere using a specially designed apparatus.[18] The corresponding 1,3-bisimidazolium salt is suspended in THF and ammonia is condensed via this special apparatus into the reaction vessel at –78 °C. After removing the cooling bath, NaH is added; an excess of NaH being recommendable, especially if the ammonia has not been dried before with potassium. After two hours a light yellow solution is formed.

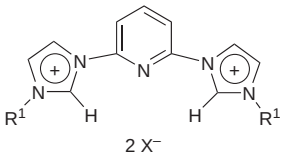
After removal of ammonia, the free carbenes can be isolated and crystallized. At the end the solvent (THF) is removed in vacuo and the free carbene is extracted with *n*-hexane. The product can be obtained in good yields at low temperatures (–30 °C or –78 °C). This method is applicable for the synthesis of sterically hindered cyclic free carbenes, for saturated and unsaturated imidazolium salts or

Table 1 Chelating Imidazolium Salts as Carbene (NHC) Precursors



3–**9**, **11**–**14**, **19**–**25**

10, **15**



16–**18**

Salt	R^1	R^2	X^-	Yield (%)
3[26]	Me	CH_2	Br	83
4	*i*-Pr	CH_2	Br	96
5[22]	*t*-Bu	CH_2	Br	79
6[32]	Cy	CH_2	I	98
7	Ad	CH_2	Br	67
8	2,6-(*i*-Pr)$_2$C$_6$H$_3$	CH_2	Br	80
9[23]	Mes	CH_2	Br	72
10	Me	CH_2	Br	68
11	CH_2(*p*-C$_6$H$_4$)CH=CH_2	CH_2	Cl	86
12	*i*-Pr	CH_2CH_2	Br	90
13	*t*-Bu	CH_2CH_2	Br	85
14	Ad	CH_2CH_2	Br	71
15	Me	CH_2CH_2	Br	90
16	*i*-Pr	–	Br	90
17	*t*-Bu	–	Br	71
18	Ad	–	Br	75
19	*rac*-CH(C$_6$H$_5$)CH$_3$	CH_2	Br	49
20	*rac*-CH(C$_6$H$_5$)CH$_3$	*o*-xylene	Br	83
21	*rac*-CH(C$_{10}$H$_7$)CH$_3$	*o*-xylene	Br	76
22	*rac*-CH(C$_6$H$_5$)CH$_3$	*m*-xylene	Br	97
23	*rac*-CH(C$_6$H$_5$)CH$_3$	*p*-xylene	Br	93
24	*rac*-CH(C$_6$H$_5$)CH$_3$	2,6-(CH$_2$)$_2$(C$_5$H$_3$N)	Br	80
25	*rac*-CH(C$_{10}$H$_7$)CH$_3$	2,6-(CH$_2$)$_2$(C$_5$H$_3$N)	Br	75

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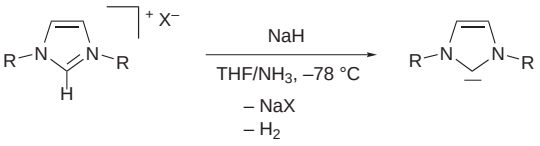


Scheme 3 Deprotonation of imidazolium salts via the 'ammonia method'

acyclic diamino carbenes, such as the bis(*N*,*N*-diisopropylamino)carbene.[31] However, as shown by Alder[33] and Herrmann,[34] the route does not work for cyclic substituted acyclic bis(*N*,*N*-dialkylamino) carbenes. The 'ammonia method' can be used to deprotonate ethylene- or higher bridged imidazolium salts, but as mentioned previously not methylene-bridged imidazolium salts.

The neutral di(carbene)palladium(II) halide complexes **27** and **28** were prepared via an adaptation of an in situ carbene-generation procedure[15] which utilized longer reaction times and milder temperatures to increase yields of the complexes, particularly when bulky alkyl substituents are present in the methylene-bridged diimidazolium salt precursors[22] (Scheme 4). The easiest way to prepare diiodide complexes **29** and **30** is via halide exchange of the dibromo complexes **32**,[35] **35**[36] with NaI (Table 2), rather than direct reaction of the diimidazolium diiodide salt precursor with $Pd(OAc)_2$ (**31**). The dihalide complexes crystallize as very fine needles and have excellent solubility in DMSO, good solubility in hot acetonitrile, are sparingly soluble in CH_2Cl_2 and THF and have no solubility in diethyl ether and hydrocarbon solvents. Complex **28** crystallizes as colorless rods suitable for X-ray structure determination (Figure 3).

The crystal structure of complex **28** has shown the compound to be monomeric with the dicarbene ligand chelating the palladium(II) center in a *cis*-fashion with a boat conformation being observed for the six-membered C_3N_2Pd ring. The remaining two coordination sites of the distorted square planar coordinated palladium center are occupied by bromine anions. A summary of important bond distances and angles for complex **28** is depicted in Figure 3. The Pd–C distances [1.991(3), 1.973(3) Å] of the complex can be respectively compared with those found in the dicationic[23] and neutral chelating[15] dicarbene palladium complexes [*cis*-$CH_2\{NC(H)=C(H)N(CH_3)C\}_2Pd(NCCH_3)_2]^{2+}[BF_4]^-_2$ [1.966(2), 1.972(3) Å] (**47**, see Figure 5) and [*cis*-$CH_2\{NC(H)=C(H)N(CH_3)C\}_2PdI_2$] [1.988(7), 1.989(8) Å] (**48**), respectively, and the related non-chelating complex (**49**) [*cis*-$\{(CH_3)NC(H)=C(H)N(CH_3)C\}_2PdI_2$] with 1.990(3) and 1.997(3) Å.[37] The C–C and C–N bond distances within the imidazolin-2-ylidene based ring systems and the Pd–C bond distances in complex **28** are consistent with both contributions from σ- and π-donation to the metal center and π-stabilization of the carbene onto the adjacent nitrogen centers. Other bond angles within the molecule are unexceptional and do not require further comments.

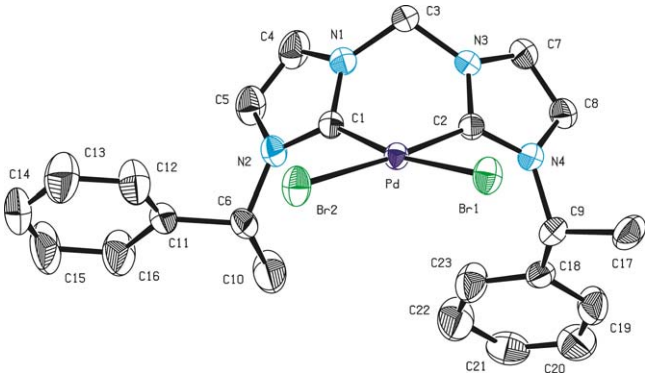
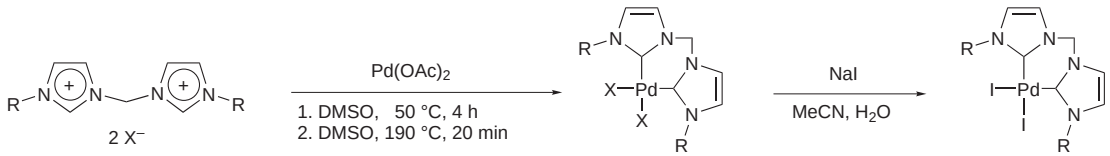


Figure 3 ORTEP-style plot of compound **28** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Pd–Br1 2.4969(4), Pd–Br2 2.4858(4), Pd–C1 1.991(3), Pd–C2 1.973(3), N1–C1 1.366(4), N1–C3 1.459(4), N1–C4 1.373(4), N3–C2 1.357(4), N3–C3 1.456(4), N3–C7 1.379(4); Br1–Pd–Br2 93.33(1), Br1–Pd–C1 170.43(8), Br1–Pd–C2 89.90(8), Br2–Pd–C1 92.08(7), Br2–Pd–C2 175.62(8), C1–Pd–C2 84.3(1).

^1H NMR and ^{13}C NMR spectra of the complexes **27**–**31** and **34**–**40** are in agreement with their assigned structures. The appearance of inequivalent methylene proton resonances for **29**, **30** and **31** indicate the retention of a conformationally restrained boat-shaped six-membered chelate ring for the complexes, as was determined by X-ray crystal structure analysis of the dibromide complex **28** and the neutral complex **46**. Such conformationally rigid ring systems have been noted by us and other groups in related complexes as examples which are fluxional at room temperature.[20j,32,40] A detailed discussion about the coalescence temperature of different biscarbene ligands and the coordinated anion of this palladium-complex-type is depicted in Table 2.

In the ^1H NMR an AB set for the protons of the NCH_2N-bridged complexes were found at room temperature



27: X = Cl, R = $CH_2(p\text{-}C_6H_4)CH=CH_2$
28: X = Br, R = $(R)\text{-}CH(C_6H_5)CH_3$

29: R = Et
30: R = Bz
31: R = Cy

Scheme 4

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Table 2 ^{1}H NMR Measurements for the [*cis*-CH_2{N(H)C=C(H)N(R)C}$_2$PdX$_2$] Complexes, in Dependence of the N-Substituents and the Anions of the Protons of the NCH_2N-Bridge

Complex	R	X	NCH_2N (25 °C) [ppm]	NCH_2N [ppm]	Coalescence temperature (°C)
33[23]	Me	Br	6.28 (s)	–	–
34[15,37]	Me	I	6.15, 6.54 (AB, $^2J_{HH}$ = 10.9 Hz)	6.41 (s)	56
32[35]	Et	Br	6.09, 6.39 (AB, $^2J_{HH}$ = 11.1 Hz)	6.35 (s)	60
29	Et	I	6.35, 6.62 (AB, $^2J_{HH}$ = 13.5 Hz)	6.31 (s)	79
35[36]	Bz	Br	6.21, 6.57 (AB, $^2J_{HH}$ = 11.9 Hz)	6.44 (s)	69
30	Bz	I	6.13, 6.46 (AB, $^2J_{HH}$ = 12.2 Hz)	6.41 (s)	84
36[21]	*i*-Pr	Br	6.28, 6.61 (AB, $^2J_{HH}$ = 12.5 Hz)	6.49 (s)	128
37[21]	*i*-Pr	I	6.19, 6.46 (AB, $^2J_{HH}$ = 12.1 Hz)	6.33 (s)	154
38[35]	Cy	Br	6.23, 6.58 (AB, $^2J_{HH}$ = 11.4 Hz)	6.39 (s)	141
31	Cy	I	6.11, 6.39 (AB, $^2J_{HH}$ = 11.8 Hz)	–	>180
39[22]	*t*-Bu	Br	6.00, 6.27 (AB, $^2J_{HH}$ = 12.9 Hz)	–	>180
40[22]	*t*-Bu	I	6.30, 6.60 (AB, $^2J_{HH}$ = 12.8 Hz)	–	>180

(Table 2). This occurs from retention of the bend-boat conformation in these complexes (see Figure 4). Therefore, fluctuation effects in solution were studied and for a choice of complex the coalescence temperature was determined. The coalescence temperature is influenced by the bulkiness of the N-substituents and the coordinated anion (Br, I). We found that a ring inversion occurs already at room temperature for R = CH_3 and bromide as the coordinated anion. In general the coalescence temperature for secondary N-substituents is between 128 °C and 154 °C, for tertiary N-substituents a temperature higher than 180 °C is necessary.

The preparation of the cationic species **42**, **43**, **44** and **46**[23] was achieved by exchange reactions involving Na[PF_6], K[PF_6] or Ag[BF_4] in cases where alkali metal salts were effective in only replacing one halide ion, and isolated as air-stable acetonitrile adducts (Scheme 5).

Crystals of complex **46** suitable for X-ray crystal structure determination were grown by vapor diffusion of diethyl ether into a concentrated acetonitrile solution of the complex. The crystal structure determination has shown the compound to be monomeric with the dicarbene ligand chelating the palladium(II) center, the remaining two coordination sites of the distorted square planar coordinated palladium center being occupied by molecules of

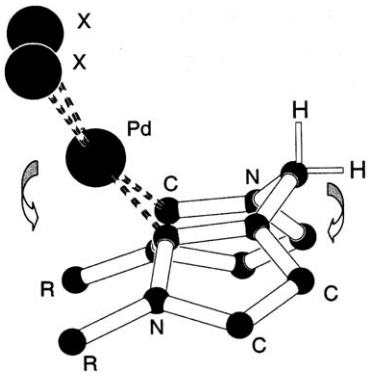
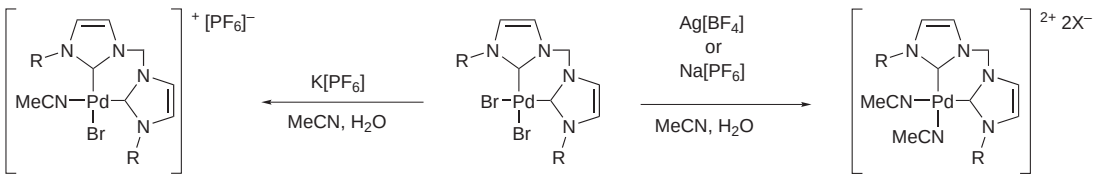


Figure 4 Solution-phase fluctuation effects in [*cis*-CH_2{N(H)C=C(H)N(R)C}$_2$PdX$_2$] complexes



42: R = *t*-Bu

28: R = (*R*)-CH(C_6H_5)CH_3
39: R = *t*-Bu
45: R = Mes

43: R = (*R*)-CH(C_6H_5)CH_3; X = BF_4^-
44: R = *t*-Bu; X = BF_4^-
46: R = Mes, X = PF_6^-

Scheme 5

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acetonitrile (Figure 6). The Pd–C distances are, with 1.9653(8) and 1.9893(5) Å, nearly the same as those in the analogous methyl complex [*cis*-$CH_2\{NC(H)=C(H)N(CH_3)C\}_2Pd(NCCH_3)_2]^{2+}[BF_4]^-_2$ (**47**) [1.966(2), 1.972(3) Å][23] or the related non-chelating [*cis*-$\{(CH_3)NC(H)=C(H)N(CH_3)C\}_2PdI_2$] complex (**49**) [1.990(3), 1.997(3) Å].[37] All complexes are, however, shortened significantly relative to the dicationic tetracarbene complex $[\{CH_2[NC(H)=C(H)N(CH_3)C]_2\}_2Pd]^{2+}2I^-$ (**50**) and the chiral dicarbene complex [*trans*-{[*syn*-Ph(Me)CH{NC(H)=C(H)N(Ph)C}$_2$]}$_2$PdI$_2$] (**51**, see Figure 5) in which the Pd–C distances measure 2.137(5), 2.049(4) Å[18,21] and 2.018(7), 2.042(7) Å,[38] respectively, in the absence of strong *trans*-effects of iodide and acetonitrile substituents.

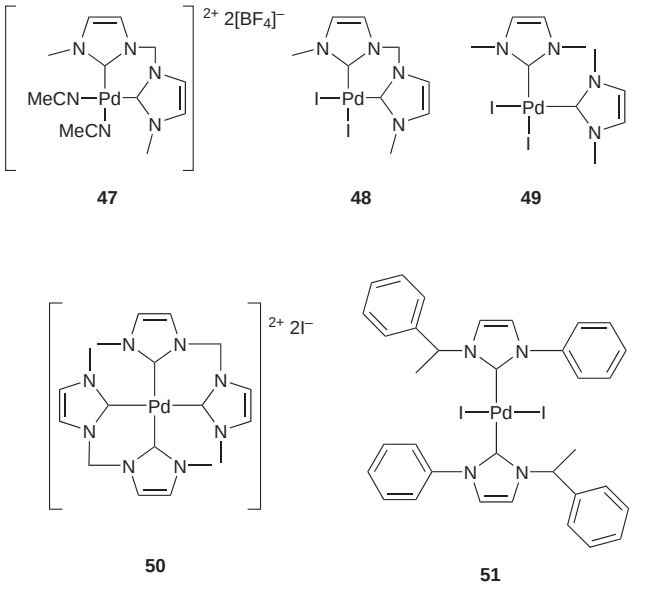

Figure 5 Known palladium complexes.

The formation of the six-membered chelate ring of dicarbene complex **46** distorts the coordination geometry of the palladium only slightly, with the C–Pd–C bite angle being reduced to 85.05(3)°. The *cis*- and *trans*-N–Pd–C angles are also effected by the chelate ring formation with 91.17, 95.95(7), 173.87(4) and 175.04(3)°, respectively, whereas the N–Pd–N angle, being free from such distortion, is close to ideal with 87.41(3)°. Summaries of selected bond distances and angles appear in Figure 6.

We have demonstrated the general synthetic applicability of this procedure by preparing analogous examples based on triazolin-2-ylidene (**52**) and benzimidazolin-2-ylidene (**53**) heterocyclic ring systems in addition to the examples based on the imidazolin-2-ylidene heterocyclic ring system (Figure 7), using the dibromo precursors.[39,40] All complexes have excellent solubility in DMSO, acetonitrile and nitromethane, have good solubility in methanol and are insoluble in diethyl ether, CH_2Cl_2, THF and hydrocarbons.

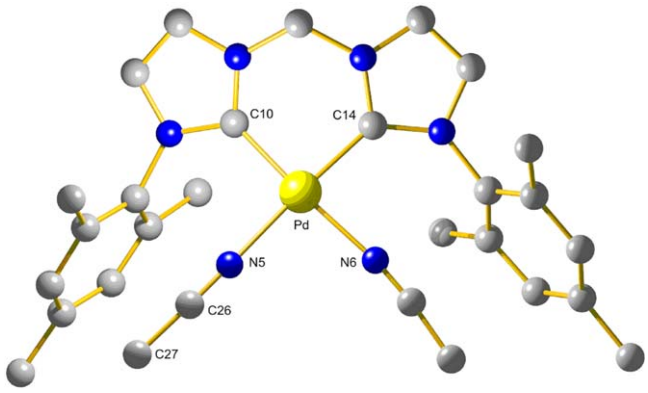

Figure 6 HyperChem[41] model of complex **46** based on the data of a single-crystal X-ray experiment. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg] are taken from ref.[42]: Pd–N5 2.0664(2), Pd–N6 2.0589(4), Pd–C10 1.9893(5), Pd–C14 1.9653(8), N5–C26 1.1394(3), C26–C27 1.4557(3); N5–Pd–N6 87.41(3), N5–Pd–C10 95.95(7), N5–Pd–C14 175.04(3), N6–Pd–C10 173.87(4), C10–Pd–C14 85.05(3).

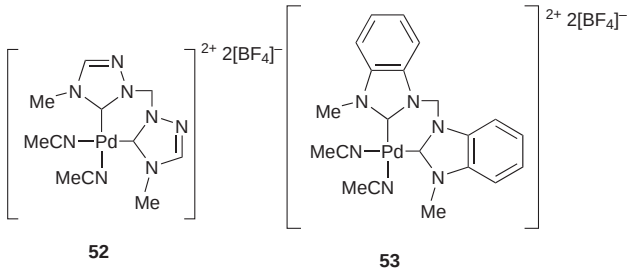

Figure 7

All described dicarbene-substituted complexes **27**–**53** are air- and moisture-stable for periods of months in the solid state and in solution, and the yields of the reactions are not reduced by using wet solvents/reactants at any point. The complexes display high thermal stability, decomposing only much higher than 215 °C in the solid state, and are stable in refluxing DMSO for varying periods. The ^{1}H NMR and ^{13}C NMR spectra of the complexes **42**–**46**, **52**, **53** are in agreement with their assigned structures. The appearance of inequivalent methylene proton resonances for the complexes **42**–**44** indicate the retention of the same conformationally restrained boat-shaped six-membered chelate ring structure discussed for complexes **29**–**40** (Table 2). Unfortunately, we could not find an AB set for the complexes **46**,[23] **52**, **53** in DMSO-d_6 for the bridged methylene protons.

The palladium-catalyzed arylation of olefins has found wide application in organic synthesis. In this reaction, homogeneous catalytic systems are highly efficient. The N-heterocyclic dicarbene complexes of type **27**–**40** have been shown excellent catalysts for the arylation of olefins, such as styrene or *n*-butyl acrylate, with aryl bromides. In the past, the catalytic activity of these complexes was investigated in detail with activated, non- and deactivated aryl halides.

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The catalytic performance of complex **27** was tested in the Heck coupling reaction of a variety of aryl halides with styrene or *n*-butyl acrylate. Full conversion was obtained for the coupling of *p*-bromoacetophenone with styrene or *n*-butyl acrylate after four hours with 0.15 mol% of the catalyst (entry 1 and 2, Table 3). The reaction of bromobenzene with both olefins gave still yields over 90% of the desired products (entry 3, 4; Table 3). Even the less reactive deactivated *p*-methoxybromobenzene gave yields around 90% (entry 5, 6; Table 3). A significant decrease in yield was observed by changing the bromoaryl compound to the chloro derivatives. In these cases, yields between 29–50% for activated chloro precursors (*p*-nitrochlorobenzene and *p*-chloroacetophenone) were observed, by using 0.15 mol% of catalyst **27** (entry 7–10; Table 3).

Under Mizoroki–Heck conditions complex **27** shows the possibility to form a C–C coupling product at the vinyl group (Scheme 6). We obtained after a 12-hour reaction period of catalyst **27** with *p*-bromoacetophenone a mixture of complex **41** and the analogous complexes, where the chloro ligand is substituted by a bromo or an acetate ligand. To obtain only one defined complex, anion exchange was performed on the mixture of products giving **41** in 78% yield.

In this manuscript a large variety of bridged imidazolium salts and their easy synthetic access has been presented. These salts are useful chelating ligands for a wide variety of complexes. The catalyst **27** has shown activity in the Mizoroki–Heck reaction. It showed self-coupling characteristics at the vinyl group to form a C–C coupling product (**41**). Furthermore fluctuation effects and the coalescence temperature in solution were studied at palladium complexes. Herein the influence of bulky N-substituents and the coordinated anion have been shown.

All experiments were carried out under dry argon using standard Schlenk or dry-box techniques. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMX-GX 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. Coupling constants *J* are given in Hz. GC-MS spectra were measured on a Hewlett Packard gas chromatograph GC 5890 A equipped with a mass selective detector MS 5970 B. Quantitative analyses were performed on a Hewlett Packard GC 5890 A equipped with a flame ionization detector (GC/FID). Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 Spectrometer using the CI or FAB technique. ESI mass spectra were performed on a Thermo Electron LCQ Classic spectrometer. IR spectra were recorded using a Jasco FT-IR 460, FTS 575C BIO-RAD or a Perkin-Elmer 1650 spectrometer. Optical rotations were measured with a Perkin Elmer 341 digital polarimeter (*c*, 1.00). Melting points were measured with a Büchi melting point apparatus system (Dr. Tottoli). The achiral imidazoles were already described in the literature and were synthesized according to literature procedures.[29,30,43] Spectroscopic data for complex **46** are presented in the literature.[23]

***rac*-1-(Phenylethyl)imidazole (1a)**

12.1 g (0.1 mol) of *rac*-1-phenylethylamine were dissolved in 100 mL H_2O and H^3PO_4 (85%) was added until a pH of 2 was reached. After addition of 3.0 g of paraformaldehyde (0.10 mol) and 11.5 mL of glyoxal (40% in H_2O, 0.1 mol), the reaction mixture was heated to 100 °C and a sat. NH_4Cl solution (5.35 g, 0.10 mol, 20 mL H_2O) was added dropwise over a period of 1 h. After stirring for another 1 h at 100 °C, the reaction mixture was cooled to 0 °C and NaOH was added until a pH higher than 12 was observed. The product was extracted three times with CH_2Cl_2 (100 mL), dried over $MgSO_4$ and afterwards the solvent was removed in vacuo. The crude product was purified by vacuum distillation to obtain a colorless oil as a racemic product mixture.[30c]

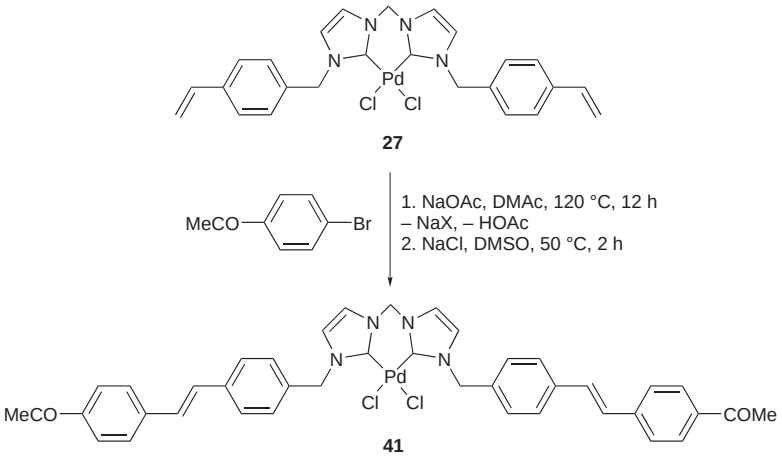
Yield: 5.81 g (34%); bp 102 °C/1 mbar.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.52 (s, 1 H, NC*H*N), 7.28–7.22 (m, 3 H, CH_{arom}), 7.13 (m, 2 H, CH_{arom}), 7.09 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, NC*H*=), 7.02 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, NC*H*), 5.27 [q, 1 H, $^3J_{HH}$ = 6.9 Hz, C*H*(C_6H_5)CH_3], 1.78 (d, 3 H, $^3J_{HH}$ = 7.2 Hz, CH_3).

^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 142.4 (N*C*HN), 136.5, 130.2, 129.4, 128.9, 126.1 (Ar), 118.1 (N*C*H=), 56.6 [*C*H(C_6H_5)CH_3], 21.9 (*C*H_3).

GC-MS: *m/z* (%) = 173 (73) [MH^+].

By using (*R*)-1-phenylethylamine, (*R*)-1-(phenylethyl)imidazole (**1b**) was obtained according to the literature.[30a]



Scheme 6

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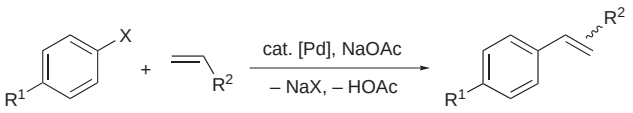
Table 3 Homogeneous Heck Coupling Catalysis with Complex **27** as the Catalyst[a]



R^1 = OMe, H, COMe, NO_2
R^2 = Ph, CO_2-*n*-Bu
X = Cl, Br

Entry	Aryl halide	Alkene	Time (h)	Temp (°C)	Conv.[b] (%)	Yield (%)[c]	TON[d]
1	4-$MeCOC_6H_4Br$	CH_2=C(H)Ph	4	150	100	96	640
2	4-$MeCOC_6H_4Br$	CH_2=C(H)COO*n*-Bu	4	150	100	100	667
3	C_6H_5Br	CH_2=C(H)Ph	20	150	92	92	613
4	C_6H_5Br	CH_2=C(H)COO*n*-Bu	44	150	90	90	600
5	4-$MeOC_6H_4Br$	CH_2=C(H)Ph	20	150	88	81	587
6	4-$MeOC_6H_4Br$	CH_2=C(H)COO*n*-Bu	44	150	100	100	667
7	4-$O_2NC_6H_4Cl$	CH_2=C(H)Ph	42	150	50	50	333
8	4-$O_2NC_6H_4Cl$	CH_2=C(H)COO*n*-Bu	42	150	29	29	193
9	4-$MeCOC_6H_4Cl$	CH_2=C(H)Ph	43	150	33	33	220
10	4-$MeCOC_6H_4Cl$	CH_2=C(H)COO*n*-Bu	43	150	30	30	200

[a] Reactions were performed in sealed pressure tubes without the exclusion of oxygen/moisture and with non-dried solvents. Yields and product identification were determined by GC-MS. Typical reaction conditions: a molar ration of 1:1.25:1.5 was used for the aryl halide (10 mmol)/alkene/base (NaOAc anhyd). In each reaction 0.15 mol% of catalyst **27** and DMAc (10 mL) as solvent was used.
[b] Conversion of the aryl halide with diethylene glycol-*n*-butyl ether as internal standard.
[c] GC yield of the *trans*-isomer based on the aryl halide.
[d] TON = [moles of coupling product (all isomers)]/(moles of Pd).

***rac*-1-(1′-Naphthylethyl)imidazole (2)**

rac-1-(1-Naphthylethyl)imidazole was synthesized similar to **1a** from *rac*-1-naphthylethylamine (5.00 g, 29.0 mmol). For purification, the crude racemic product was extracted with Et_2O to obtain a yellow oil.

Yield: 2.10 g (33%).

^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.90–7.79 (m, 2 H, CH_{arom}), 7.61 (s, 1 H, NC*H*N), 7.55–7.20 (m, 5 H, CH_{arom}), 7.08 (s, 1 H, NC*H*), 6.96 (s, 1 H, NC*H*), 6.24 [q, 1 H, *J* = 6.8 Hz, C*H* (naphthylethyl)], 2.00 [d, 3 H, *J* = 7.1 Hz, CH_3 (naphthylethyl)].

^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 136.6 (N*C*N), 129.1, 118.6 (N*C*), 136.3, 134.0, 130.4, 129.3, 127.0, 126.1, 125.5, 123.4, 122.2, 120.0 (Ar), 53.2 [*C*H (naphthylethyl)], 22.0 [(*C*H_3 (naphthylethyl)].

GC-MS: *m/z* = 222 [M^+], 155 [M^+ – imidazole], 128 [naphthyl$^+$].

General Synthesis of Methylene-Bridged Imidazolium Salts

To a solution of the *R*-imidazole (12.2 mmol) in 5 mL THF in an ACE pressure tube 1.18 g (0.94 mL, 6.1 mmol) of CH_2Br_2 was added. A colorless precipitate formed after the solution was heated for 72 h at 130 °C. The precipitate was filtered and washed three times with THF (5 mL). A colorless powder was obtained, after the product was dried in vacuo.

1,1′-Dimethyl-3,3′-methylenediimidazolium Dibromide (3)

Yield: 1.77 g (83%); mp >280 °C (dec.).

IR (KBr): 3149, 3130, 3043, 1785, 1698, 1670, 1583, 1561, 1546, 1454, 1440, 1395, 1331, 1164, 1085, 900, 865, 781, 765, 731, 682, 625, 614, 432 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ = 9.28 (s, 2 H, NC*H*N), 7.83 (s, 2 H, NC*H*C*H*N), 7.63 (s, 2 H, NC*H*C*H*N), 6.76 (s, 2 H, NCH_2N), 4.01 (s, 6 H, NCH_3).

^{13}C NMR (100.5 MHz, D_2O): δ = 136.8 (N*C*HN), 124.8 (NCH*C*HN), 122.6 (NCH*C*HN), 58.7 (NCH_2N), 35.8 (NCH_3).

MS-FAB: *m/z* = 256.9 [M^+], 177.0 [M^{2+}].

Anal. Calcd for $C_9H_{14}N_4Br_2$ (338.04): C, 31.98; H, 4.17; N, 16.57. Found: C, 31.92; H, 3.77; N, 16.25.

1,1′-Diisopropyl-3,3′-methylenediimidazolium Dibromide (4)

Yield: 2.3 g (96%); mp >280 °C (dec.).

IR (KBr): 3134, 3120, 3066, 2957, 2848, 2242, 1758, 1711, 1638, 1573, 1546, 1474, 1434, 1397, 1376, 1334, 1298, 1267, 1181, 1159, 1135, 1111, 941, 858, 759, 728, 654, 630, 614, 598, 466 cm^{-1}.

^{1}H NMR (400 MHz, D_2O): δ = 8.96 (s, 2 H, NC*H*N), 7.71 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, NC*H*CH), 7.66 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, CHC*H*N), 4.70 (s, 2 H, NCH_2N), 4.63 [m, 2 H, C*H*(CH_3)$_2$], 1.49 [s, 12 H, CH(CH_3)$_2$].

^{13}C NMR (100.5 MHz, D_2O): δ = 152.3 (N*C*HN), 122.7 (N*C*HCH), 120.6 (CH*C*HN), 58.9 (NCH_2N), 53.7 [N*C*H(CH$_3$)$_2$], 21.8 [NCH(*C*H$_3$)$_2$].

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MS-FAB: *m/z* (%) = 313 (26) [M^+], 233 (100) [M^{2+}].

Anal. Calcd for $C_{13}H_{22}N_4Br_2$ (394.15): C, 39.61; H, 5.63; N, 14.21. Found: C, 39.38; H, 5.39; N, 14.00.

1,1′-Di-*tert*-butyl-3,3′-methylenediimidazolium Dibromide (5)
Yield: 2.03 g (79%); mp >300 °C.

IR (KBr): 3051, 2952, 2881, 2851, 2781, 2459, 2422, 2237, 1754, 1711, 1628, 1565, 1541, 1481, 1464, 1433, 1408, 1377, 1301, 1240, 1207, 1132, 1051, 996, 944, 858, 820, 752, 724, 660, 623, 614, 572, 486, 404 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 8.72 (s, 2 H, NC*H*N), 7.62 (s, 2 H, NC*H*CH), 7.41 (s, 2 H, CHC*H*N), 6.57 (s, 2 H, NCH_2N), 1.43 [s, 18 H, NC(CH_3)$_3$].

^{13}C NMR (100.5 MHz, D_2O): δ = 135.3 (N*C*HN), 122.4 (N*C*HCH), 120.1 (CH*C*HN), 58.1 (N*C*H_2N), 48.7 [N*C*(CH$_3$)$_3$], 28.8 [NC(*C*H$_3$)$_3$].

MS-FAB: *m/z* (%) = 341 (47) [M^+], 261 (100) [M^{2+}].

Anal. Calcd for $C_{15}H_{26}N_4Br_2$ (422.20): C, 42.67; H, 6.21; N, 13.27. Found: C, 42.44; H, 5.70; N, 13.34.

1,1′-Dicyclohexyl-3,3′-methylenediimidazolium Diiodide (6)
Yield: 3.38 g (98%); mp >281 °C (dec.).

IR (KBr): 3126, 3065, 3030, 2927, 2854, 1757, 1713, 1633, 1572, 1547, 1464, 1445, 1434, 1376, 1350, 1296, 1271, 1241, 1189, 1168, 1121, 1051, 987, 897, 853, 815, 758, 707, 626, 610, 509, 462 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.79 (s, 2 H, NC*H*N), 7.27 (s, 2 H, NC*HCH*N), 7.23 (s, 2 H, NC*HCH*N), 5.86 (s, 2 H, NCH_2N), 3.58 (sept, 2 H, CH_{cy}), 1.34, 1.07, 0.91, 0.64, 0.45 (m, 20 H, C$H_{2,cy}$).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 136.3 (s, N*C*HN), 122.2, 121.5 (s, NCH*C*HN), 59.0 (s, N*C*H_2N), 32.0 (s, *C*H$_{cy}$), 24.2 (s, CH$_{2,cy}$).

MS-FAB: *m/z* (%) = 441 (31) [M^+], 313 (100) [M^{2+}].

Anal. Calcd for $C_{19}H_{30}N_4I_2$ (568.28): C, 40.16; H, 5.32; N, 9.86. Found: C, 39.49; H, 4.83; N, 9.95.

1,1′-Diadamantyl-3,3′-methylenediimidazolium Dibromide (7)
Yield: 2.36 g (67%); mp >320 °C.

IR (KBr): 3186, 3004, 2802, 2688, 2654, 2601, 2570, 2512, 2462, 2417, 2006, 1991, 1949, 1879, 1597, 1576, 1491, 1476, 1452, 1437, 1375, 1364, 1347, 1312, 1287, 1204, 1199, 1196, 1163, 1114, 1083, 1021, 970, 959, 925, 911, 811, 645, 542, 457, 420, 404 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 8.77 (s, 2 H, NC*H*N), 7.15 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, CHC*H*N), 6.90 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, NC*H*CH), 4.59 (s, 2 H, NCH_2N), 2.17 (d, 12 H, $^3J_{HH}$ = 2.5 Hz, NCCH_2), 1.68 (m, 12 H, CH_2), 1.47 (m, 6 H, C*H*).

^{13}C NMR (100.5 MHz, D_2O): δ = 134.1 (N*C*HN), 122.1 (CH*C*HN), 120.1 (N*C*HCH), 58.9 (N*C*H_2N), 29.9 (*C*H), 55.6 (N*C*), 43.1 (NC*C*H$_2$), 36.1 (*C*H$_2$).

1,1′-Di(2,6-diisopropylphenyl)-3,3′-methylenediimidazolium Dibromide (8)
Yield: 3.07 g (80%); mp 284 °C (dec.).

IR (KBr): 3125, 3069, 2963, 2929, 2870, 1590, 1555, 1536, 1464, 1408, 1388, 1367, 1337, 1308, 1266, 1243, 1187, 1117, 1069, 1016, 956, 936, 866, 808, 760, 742, 699, 675, 619, 555, 460 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.61 (s, 2 H, NC*H*N), 7.46 (t, 2 H, $^3J_{HH}$ = 7.7 Hz, CHC*H*CH), 7.38 (s, 2 H, NCHC*H*), 7.28 (d, 2 H, $^3J_{HH}$ = 7.7 Hz, CHC*H*CH), 6.85 (s, 2 H, NC*H*CH), 4.54 (s, 2 H, NCH_2N), 2.27 [sept, 4 H, $^3J_{HH}$ = 5.9 Hz, C*H*(CH$_3$)$_2$], 1.12 [d, 24 H, $^3J_{HH}$ = 5.9 Hz, CH(CH_3)$_2$].

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 144.2 [*C*CH(CH$_3$)$_2$], 138.4 (N*C*HN), 131.1 (N*C*), 129.5 (*C*H, Ar), 125.1 (*C*H, Ar), 123.9 (CH*C*HN), 122.6 (N*C*HCH), 58.2 (N*C*H_2N), 27.3 [*C*H(CH$_3$)$_2$], 23.1 [CH(*C*H$_3$)$_2$].

MS-FAB: *m/z* (%) = 585 (6) [$MH^+ - CH(CH_3)_2$], 551 (4) [M^+], 469 (100) [M^{2+}; and $MH^+ - C_6H_3CH(CH_3)_2$].

Anal. Calcd for $C_{31}H_{42}N_4Br_2$ (630.50): C, 59.05; H, 6.71; N, 8.89. Found: C, 59.93; H, 6.78; N, 8.92.

1,1′-Dimesityl-3,3′-methylenediimidazolium Dibromide (9)
Yield: 2.38 g (72%); mp >318 °C (dec.).

IR (KBr): 3142, 3040, 2961, 2765, 1630, 1608, 1547, 1486, 1442, 1419, 1379, 1319, 1298, 1265, 1211, 1158, 1110, 1066, 1028, 969, 936, 857, 846, 822, 808, 763, 734, 658, 610, 580, 551, 438 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 10.56 (s, 2 H, NC*H*N), 8.96 (d, 2 H, NC*HCH*N), 8.54 (d, 2 H, NC*HCH*N), 7.61 (s, 4 H, C$H_{mesityl.}$), 7.41 (s, 2 H, NCH_2N), 3.79 [d, 6 H, C(CH_3)], 2.78 [s, 6 H, C(CH_3)], 2.49 [s, 6 H, C(CH_3)].

$^{13}C\{^1H\}$-NMR (100.5 MHz, DMSO-d_6): δ = 140.6 [s, *C*C(CH$_3$)$_{arom}$], 134.6 (*ipso*-*C*$_{mesityl}$), 134.2 (*o*-*C*$_{mesityl}$), 129.7 (*m*-*C*$_{mesityl}$), 129.4 (*p*-*C*$_{mesityl}$), 122.8 (N*C*HCHN), 58.9 (N*C*H_2N), 17.4 (*p*-*C*H$_3$), 17.0 (*o*-*C*H$_3$).

MS-FAB: *m/z* (%) = 467 (3) [M^+], 385 (100) [M^{2+}].

Anal. Calcd for $C_{25}H_{30}N_4Br_2$ (546.34): C, 45.96; H, 5.53; N, 10.25. Found: C, 45.56; H, 5.41; N, 10.57.

1,1′-Dimethyl-3,3′-methylenedibenzimidazolium Dibromide (10)
Yield: 1.83 g (68%); mp 255 °C (dec.).

IR (KBr): 3098, 3027, 2938, 1613, 1562, 1487, 1454, 1436, 1390, 1334, 1269, 1213, 1136, 1109, 1033, 1019, 830, 794, 784, 766, 697, 639, 590, 568, 549, 522, 435, 421, 396, 388, 379, 362, 357 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.46 (s, 2 H, NC*H*N), 6.91 (s, 2 H, CH_{arom}), 6.75 (s, 2 H, CH_{arom}), 5.53 (s, 2 H, NCH_2N), 4.35 (s, 6 H, NCH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 134.2 (N*C*HN), 129.4, 128.9, 123.5, 122.8 (s, *C*H$_{arom}$), 58.7 (N*C*H_2N), 52.7 (N*C*H$_3$).

MS-FAB: *m/z* (%) = 357 (21) [M^+], 277 (100) [M^{2+}].

1,1′-Di(4-vinylbenzyl)-3,3′-methylenediimidazolium Dichloride (11)
N,*N*-Diimidazolylmethane (1.50 g, 10.6 mmol) and 4-vinylbenzyl chloride (9.70 g, 63.4 mmol) are dissolved in *i*-PrOH (9 mL) in an ACE pressure tube and heated for 40 h at 100 °C. The solvent was removed in vacuo and the precipitate was washed four times with THF (15 mL) and dried in vacuo.

Yield: 4.13 g (86%); mp >300 °C.

^1H NMR (400 MHz, DMSO-d_6): δ = 10.12 (s, 2 H, NC*H*N), 8.37 (s, 2 H, NC*H*), 7.96 (s, 2 H, NC*H*), 7.54–7.47 (m, 8 H, CH_{arom}), 6.91 (s, 2 H, NCH_2N), 6.75 (dd, 2 H, $^3J_{HH}$ = 17.6 Hz, $^3J_{HH}$ = 11.0 Hz, H_2C=C*H*), 5.88 (d, 2 H, $^3J_{HH}$ = 17.6 Hz, *H*$_2$C=C), 5.53 (s, 4 H, NCH_2Ph), 5.31 (d, $^3J_{HH}$ = 11.0 Hz, *H*$_2$C=C).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 138.5 (H*C*$_{vinyl}$), 138.2 (N*C*HN), 136.4, 134.2, 129.6, 127.1 (Ar), 123.4 (N*C*H), 115.9 (H_2C_{vinyl}), 58.5 (N*C*H_2N), 52.5 (N*C*H_2Ph).

Anal. Calcd for $C_{25}H_{26}N_4Cl_2$ (453.41): C, 66.22; H, 5.78; N, 12.36. Found: C, 66.10; H, 5.94; N, 11.80.

General Synthesis of Ethylene-Bridged Imidazolium Salts
To a solution of the *R*-imidazole (50 mmol) in THF (5 mL) in an ACE pressure tube, 4.69 g (3.51 mL, 25 mmol) of CH_2Br_2 was added. A light yellow precipitate was observed after the solution was

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heated for 48 h at 130 °C. The precipitate was filtered and washed three times with THF (5 mL). A beige highly hygroscopic powder was isolated after the product was dried in high vacuum.

1,1′-Diisopropyl-3,3′-ethylenediimidazolium Dibromide (12)
Yield: 9.18 g (90%).

IR (KBr): 3048, 2975, 2877, 2427, 1762, 1638, 1565, 1542, 1470, 1428, 1406, 1376, 1307, 1293, 1240, 1202, 1165, 1133, 881, 849, 819, 766, 730, 656, 613, 570, 486, 418, 407, 384, 366, 352 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 9.08 (s, 2 H, NC*H*N), 7.83 (m, 2 H, NC*H*CH), 7.61 (m, 2 H, CHC*H*N), 4.93 (s, 4 H, NCH_2CH_2N), 4.81 [m, 2 H, $CH(CH_3)_2$], 1.68 [s, 12 H, $CH(CH_3)_2$].

^{13}C NMR (100.5 MHz, D_2O): δ = 156.3 (NCHN), 123.1 (NCHCH), 121.6 (CHCHN), 53.9 (NCH_2CH_2N), 48.8 [$NCH(CH_3)_2$], 21.9 [$NCH(CH_3)_2$].

MS-FAB: *m/z* (%) = 327 (64) [M^+], 247 (100) [M^{2+}].

Anal. Calcd for $C_{14}H_{24}N_4Br_2$ (408.18): C, 41.20; H, 5.93; N, 13.73. Found: C, 40.71; H, 6.10; N, 13.58.

1,1′-Di-*tert*-butyl-3,3′-ethylenediimidazolium Dibromide (13)
Yield: 9.26 g (85%); mp 262 °C (dec.).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.51 (s, 2 H, NC*H*N), 7.12 (s, 2 H, NC*H*C*H*N), 6.75 (s, 2 H, NC*H*C*H*N), 3.84 (s, 4 H, NCH_2CH_2N), 1.59 [s, 18 H, $NC(CH_3)_3$].

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 135.3 (NCHN), 122.8, 120.5 (NCHCHN), 59.8 (NCH_2CH_2N), 48.4 [$NC(CH_3)_3$], 28.9 [$NC(CH_3)_3$].

MS-FAB: *m/z* = 355.3 [M^+], 275.3 [M^{2+}].

Anal. Calcd for $C_{16}H_{28}N_4Br_2$ (436.23): C, 44.05; H, 6.47; N, 12.84. Found: C, 43.81; H, 6.45; N, 12.69.

1,1′-Diadamantyl-3,3′-ethylenediimidazolium Dibromide (14)
Yield: 10.53 g (71%); mp >330 °C.

IR (KBr): 2912, 2852, 2586, 2523, 2472, 2051, 1956, 1896, 1604, 1499, 1477, 1453, 1438, 1365, 1348, 1312, 1301, 1200, 1113, 1084, 972, 960, 912, 811, 645, 543, 458, 422 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 9.48 (s, 2 H, NC*H*N), 7.25 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, CHC*H*N), 7.01 (d, 1 H, $^3J_{HH}$ = 2.0 Hz, NC*H*CH), 4.51 (s, 4 H, NCH_2CH_2N), 2.22 (d, 12 H, $^3J_{HH}$ = 2.5 Hz, $NCCH_2$), 1.65 (m, 12 H, CH_2), 1.42 (m, 6 H, C*H*).

^{13}C NMR (100.5 MHz, D_2O): δ = 134.6 (NCHN), 121.7 (CHCHN), 120.4 (NCHCH), 59.2 (NCH_2CH_2N), 55.9 (N*C*), 42.9 ($NCCH_2$), 36.6 (CH_2), 29.1 (*C*H).

MS-FAB: *m/z* (%) = 380.4 (2) [M^+ – (Br + Ad)], 339.3 (100), 329.4 (22).

Anal. Calcd for $C_{28}H_{40}N_4Br_2$ (592.45): C, 56.76; H, 6.81; N, 9.46. Found: C, 57.39; H, 6.49; N, 8.91.

1,1′-Dimethyl-3,3′-ethylenedibenzimidazolium Dibromide (15)
Yield: 10.2 g (90%).

IR (KBr): 2980, 2914, 2825, 2782, 1611, 1567, 1452, 1385, 1337, 1227, 1184, 851, 824, 610, 437, 395 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 11.72 (s, 2 H, NC*H*N), 9.86 (s, 4 H, CH_{arom}), 7.28 (s, 4 H, CH_{arom}), 6.25 (s, 2 H, NCH_2CH_2N), 5.84 (s, 2 H, NCH_2CH_2N), 3.28 (s, 6 H, NCH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 155.9 (CH_{arom}), 139.3 (CH_{arom}), 135.6 (NCHN), 128.8, 128.5 (s, NCHCHN), 113.8 (s, NCH_2CH_2N), 19.9 (s, NCH_3).

MS-FAB: *m/z* (%) = 293 (2) [M^{2+}], 147 (100) [$C_9H_{10}N_2$].

Anal. Calcd for $C_{18}H_{20}N_4Br_2$ (452.19): C, 47.81; H, 4.46; N, 12.39. Found: C, 47.52; H, 4.32; N, 12.21.

General Synthesis of Pyridinyl-Bridged Imidazolium Salts
To a solution of the *R*-imidazol (25 mmol) in 3 mL THF in an ACE pressure tube, 2.96 g (12.5 mmol) of 2,6-dibromopyridine was added. The solution was heated for 48 h at 130 °C and a colorless precipitate was observed. The precipitate was filtered and washed three times with THF (3 mL). A colorless powder was isolated after the product was dried in vacuo.

1,1′-Diisopropyl-3,3′-pyridinyldiimidazolium Dibromide (16)
Yield: 5.14 g (90%); mp 271 °C (dec.).

IR (KBr): 3051, 1928, 1741, 1665, 1628, 1613, 1591, 1572, 1532, 1466, 1425, 1392, 1377, 1335, 1308, 1265, 1253, 1223, 1136, 1116, 1092, 1000, 942, 872, 822, 772, 763, 657, 626, 586, 530, 437, 406 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 8.42 (t, 1 H, $^3J_{HH}$ = 8.4 Hz, CHC*H*CH), 8.32 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, NC*H*CHN), 7.99 (d, 2 H, $^3J_{HH}$ = 8.4 Hz, C*H*CHC*H*), 7.85 (d, 2 H, $^3J_{HH}$ = 2.4 Hz, NCHC*H*N), 4.82 [m, 2 H, $CH(CH_3)_2$], 1.65 [d, 12 H, $^3J_{HH}$ = 6.8 Hz, $CH(CH_3)_2$].

^{13}C NMR (100.5 MHz, D_2O): δ = 156.3 (NCHN), 145.7 (CHCHCH), 144.6 (CHCHCN), 121.8 (NCNCH), 119.1 (NCHCH), 114.6 (CHCHN), 54.2 [$NCH(CH_3)_2$], 21.8 [$NCH(CH_3)_2$].

MS-FAB: *m/z* (%) = 376 (21) [M^+], 296 (100) [M^{2+}].

Anal. Calcd for $C_{17}H_{23}N_5Br_2$ (457.21): C, 44.66; H, 5.07; N, 15.32. Found: C, 44.77; H, 5.12; N, 15.21.

1,1′-Di-*tert*-butyl-3,3′-pyridinyldiimidazolium Dibromide (17)
Yield: 4.31 g (71%); mp >320 °C.

IR (KBr): 3069, 2961, 1934, 1861, 1753, 1654, 1615, 1593, 1558, 1522, 1463, 1405, 1377, 1348, 1316, 1273, 1231, 1210, 1127, 1109, 1089, 1048, 1002, 944, 932, 863, 820, 762, 746, 649, 616, 590, 478, 451 cm^{-1}.

^1H NMR (270 MHz, D_2O): δ = 8.43 (t, 1 H, $^3J_{HH}$ = 5.4 Hz, CHC*H*CH), 8.36 (s, 2 H, NC*H*CH), 8.01 (d, 2 H, $^3J_{HH}$ = 5.4 Hz, C*H*CHC*H*), 7.96 (m, 2 H, CHC*H*N), 1.75 [s, 18 H, $NC(CH_3)_3$].

^{13}C NMR (67.9 MHz, DMSO-d_6): δ = 156.4 (NCHN), 145.8 (CHCHCH), 121.3 (CHCHCN), 119.7 (NCNCH), 115.1 (NCHCH), 114.9 (CHCHN), 61.2 [$NC(CH_3)_3$], 28.4 [$NC(CH_3)_3$].

MS-FAB: *m/z* (%) = 404 (28) [M^+], 324 (100) [M^{2+}].

Anal. Calcd for $C_{19}H_{27}N_5Br_2$ (485.26): C, 47.03; H, 5.61; N, 14.43. Found: C, 47.00; H, 5.32; N, 14.57.

1,1′-Diadamantyl-3,3′-pyridinyldiimidazolium Dibromide (18)
Yield: 16.1 g (75%); mp >290 °C.

^1H NMR (400 MHz, D_2O): δ = 8.91–7.65 (m, 7 H, C*H*C*H*CH, NC*H*C*H*N), 2.11 (m, 12 H, $NCCH_2$), 1.78 (m, 12 H, CH_2), 1.35 (m, 6 H, C*H*).

^{13}C NMR (100.5 MHz, D_2O): δ = 158.2 (NCHN), 147.7 (CHCHCN), 130.9 (CHCHCN), 123.8 (NCNCH), 122.3 (CHCHN), 111.4 (NCHCH), 63.3 (N*C*), 41.7 ($NCCH_2$), 33.7 (CH_2), 31.1 (*C*H).

1,1′-Di[(*R*)-1″-phenylethyl]-3,3′-methylenediimidazolium Dibromide (19)
(*R*)-(1-Phenylethyl)imidazole (860 mg, 5.0 mmol) was dissolved in 10 mL toluene in an ACE pressure tube and 3.0 mmol of CH_2Br_2 was added. The solution was heated for 48 h at 140 °C and a colorless precipitate was obtained. The precipitate was filtered off and washed twice with 20 mL THF to obtain a colorless solid.

Yield: 635 mg (49%); mp >300 °C; $[\alpha]_D^{20}$ +2.0 (DMSO).

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IR (KBr): 3116, 2917, 1903, 1818, 1667, 1628, 1562, 1544, 1495, 1455, 1385, 1355, 1333, 1300, 1286, 1234, 1202, 1152, 1108, 1081, 1030, 1012, 915, 844, 765, 704, 651, 614, 538 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 10.11 (s, 2 H, NC*H*N), 8.80 (s, 2 H, NC*H*), 8.02 (s, 2 H, NC*H*), 7.52–7.35 (m, 10 H, CH_{arom}), 6.82 (s, 2 H, NCH_2N), 5.93 (d, $^3J_{HH}$ = 7.4 Hz, NC*H*), 1.86 (d, 6 H, $^3J_{HH}$ = 7.4 Hz, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 139.5 (N*C*HN), 137.7, 129.4, 129.3, 127.3 (*C*H_{arom}), 123.1 (N*C*H), 122.4 (NCH=), 59.6 (N*C*H), 58.6 (s, NCH_2*C*H_2N), 21.1 (N*C*H_3).

MS-FAB: *m/z* (%) = 437 (13) [M^+], 357 (57) [M^{2+}], 253 (70) [$C_{15}H_{17}N_4$], 186 (8) [$C_{12}H_{14}N_2$], 173 (100) [$C_{11}H_{12}N_2$].

Anal. Calcd for $C_{23}H_{26}N_4Br_2$ (518.19): C, 53.30; H, 5.06; N, 10.81. Found: C, 53.73; H, 5.37; N, 10.62.

General Synthesis of *o*-, *m*-, *p*-Xylylene-Bridged Imidazolium Salts

A *rac*-imidazole derivative (5 mmol) was dissolved in 5 mL *i*-PrOH (**20**) or THF (**21**–**25**) in an ACE pressure tube and 2.5 mmol of α,α′-dibromo-*o*-, -*m*-, -*p*-xylylene were added. The solution was heated for 24 h at 80 °C and a colorless precipitate was obtained. The precipitate was filtered off and washed three times with 10 mL THF (**22**, **25**), or recrystallized from CH_2Cl_2–Et_2O (**20**–**24**) and dried under high vacuum to obtain a highly hygroscopic colorless powder.

1,1′-Di(*rac*-1″-phenylethyl)-3,3′-*o*-xylylenediimidazolium Dibromide (20)

Yield: 1.26g (83%).

IR (KBr): 3117, 3047, 2975, 2869, 1763, 1626, 1603, 1550, 1495, 1455, 1422, 1383, 1356, 1327, 1312, 1281, 1262, 1202, 1184, 1150, 1013, 971, 843, 763, 738, 707, 650, 628, 533, 459 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.39 (s, 2 H, NC*H*N), 7.69 (s, 2 H, NC*H*), 7.49–7.20 (m, 14 H, Ar), 7.09 (s, 2 H, NC*H*), 6.15 (d, 2 H, J_{HH} = 16.0 Hz, CH_2), 5.93 (d, 2 H, J_{HH} = 12.0 Hz, CH_2), 5.82 [q, 2 H, *J* = 8.0 Hz, C*H* (phenylethyl)], 1.96 [d, 6 H, $^3J_{HH}$ = 7.6 Hz, CH_3 (phenylethyl)].

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 137.9 (N*C*N), 136.1, 132.3, 130.4, 130.2, 129.5, 129.5, 127.1 (Ar), 123.1, 121.0 (N*C*), 60.4 [*C*H (phenylethyl)], 50.5 (*C*H_2), 21.1 [*C*H_3 (phenylethyl)].

MS-FAB: *m/z* (%) = 527 (100) [M^+].

Anal. Calcd for $C_{30}H_{32}Br_2N_4$ (608.41): C, 59.22; H, 5.30; N, 9.21. Found: C, 59.45; H, 5.39; N, 9.13.

1,1′-Di(*rac*-1″-naphthylethyl)-3,3′-*o*-xylylenediimidazolium Dibromide (21)

Yield: 1.35 g (76%); mp >300 °C.

IR (KBr): 3120, 3049, 2978, 1623, 1597, 1550, 1510, 1453, 1418, 1398, 1381, 1360, 1318, 1243, 1215, 1147, 1106, 1021, 967, 807, 781, 738, 630, 441, 419 cm^{-1}.

^1H NMR (270 MHz, $CDCl_3$): δ = 10.50 (s, 2 H, NC*H*N), 8.20–6.81 [m, 22 H, CH_{arom} (14 naphthyl, 4 *o*-Tol, 4 imidazole)], 6.62 [q, 2 H, $^3J_{HH}$ = 7.5 Hz, C*H*(naphthylethyl)], 6.21 (d, 2 H, *J* = 13.5 Hz, CH_2), 5.91 (d, 2 H, $^3J_{HH}$ = 16.2 Hz, CH_2), 2.13 [d, 6 H, $^3J_{HH}$ = 7.3 Hz, CH_3 (naphthylethyl)].

^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 136.6 (N*C*N), 134.0, 133.2, 132.3, 132.0, 131.1, 130.3, 129.3, 127.9, 126.6, 125.6, 124.7, 122.4, 122.3 (Ar), 122.9, 121.1 (N*C*), 56.5 [*C*H (naphthylethyl)], 50.8 (*C*H_2), 21.4 [*C*H_3 (naphthylethyl)].

MS-FAB: *m/z* (%) = 627 (100) [M^+].

Anal. Calcd for $C_{38}H_{36}Br_2N_4$ (708.53): C, 64.42; H, 5.12; N, 7.91. Found: C, 64.53; H, 5.17; N, 7.85.

1,1′-Di(*rac*-1″-phenylethyl)-3,3′-*m*-xylylenediimidazolium Dibromide (22)

Yield: 1.48 g (97%).

IR (KBr): 3120, 3073, 3019, 2977, 2055, 1760, 1613, 1554, 1494, 1454, 1382, 1355, 1322, 1311, 1262, 1201, 1149, 1084, 1013, 973, 827, 754, 731, 707, 650, 533, 432 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.67 (s, 2 H, NC*H*N), 7.87–7.41 [m, 18 H, CH_{arom} (10 phenyl + 4 imidazole)], 5.45 (m, 4 H, CH_2), 5.81 [q, 2 H, $^3J_{HH}$ = 8.0 Hz, C*H* (phenylethyl)], 1.88 [d, 6 H, $^3J_{HH}$ = 7.6 Hz, CH_3 (phenylethyl)].

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 139.3 (N*C*N), 136.0, 135.9, 130.4, 129.7, 129.4, 129.3, 128.5, 127.2 (Ar), 123.4, 122.1 (N*C*), 59.2 [*C*H (phenylethyl)], 52.2 (*C*H_2), 20.9 [*C*H_3 (phenylethyl)].

MS-FAB: *m/z* (%) = 527 (100) [M^+].

Anal. Calcd for $C_{30}H_{32}Br_2N_4$ (608.41): C, 59.22; H, 5.30; N, 9.21. Found: C, 59.34; H, 5.41; N, 9.11.

1,1′-Di(*rac*-1″-phenylethyl)-3,3′-*p*-xylylenediimidazolium Dibromide (23)

Yield: 1.41 g (93%); mp >300 °C.

IR (KBr): 3069, 2973, 2847, 2063, 1968, 1756, 1619, 1557, 1518, 1495, 1454, 1430, 1358, 1324, 1310, 1280, 1260, 1201, 1152, 1080, 1015, 972, 864, 768, 728, 708, 652, 629, 521 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 9.79 (s, 2 H, NC*H*N), 7.94 (s, 2 H, NCH), 7.90 (s, 2 H, NC*H*), 7.53–7.30 (m, 14 H, CH_{arom}), 5.86 [m, 2 H, C*H* (phenylethyl)], 5.49 (s, 4 H, CH_2), 1.88 [d, 6 H, $^3J_{HH}$ = 6.0 Hz, CH_3 (phenylethyl)].

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 140.0 (N*C*N), 136.2, 135.9, 129.7, 129.4, 127.2, 123.5 (Ar), 123.3, 122.2 (N*C*), 59.3 [*C*H (phenylethyl)], 51.9 (*C*H_2), 21.0 [*C*H_3 (phenylethyl)].

MS-FAB: *m/z* (%) = 527 (100) [M^+].

Anal. Calcd for $C_{30}H_{32}Br_2N_4$ (608.41): C, 59.22; H, 5.30; N, 9.21. Found: C, 59.24; H, 5.27; N, 9.17.

General Synthesis of 2,6-Lutidine-Bridged Imidazolium Salts

A *rac*-imidazol derivative (50 mmol) was dissolved in THF (5 mL) in an ACE pressure tube and 25 mmol of 2,6-di(bromomethyl)pyridine were added. The solution was heated for 24 h at 80 °C and a colorless precipitate could be observed. The precipitate was filtered off, recrystallized from CH_2Cl_2–Et_2O and dried under high vacuum. A colorless hygroscopic powder was isolated.

1,1′-Di(*rac*-1″-phenylethyl)(2,6-lutidine)diimidazolium Dibromide (24)

Yield: 1.22 g (80%).

^1H NMR (400 MHz, $CDCl_3$): δ = 10.86 (s, 2 H, NC*H*N), 8.02–7.00 [m, 17 H, CH_{arom} (10 phenyl + 3 pyridyl + 4 imidazole)], 6.06 [q, 2 H, $^3J_{HH}$ = 5.6 Hz, CH (phenylethyl)], 5.79 (d, 2 H, *J* = 14.8 Hz, CH_2), 5.67 (d, 2 H, *J* = 14.0 Hz, CH_2), 1.99 [d, 6 H, $^3J_{HH}$ = 6.0 Hz, CH_3 (phenylethyl)].

^{13}C NMR (100.5 MHz, CD_3CN): δ = 153.3 (lutidineN*C*), 138.9 (N*C*N), 138.9, 136.3, 129.2, 129.1, 127.0, 123.0 (Ar), 123.6, 122.3 (N*C*), 59.5 [*C*H (phenylethyl)], 53.4 (*C*H_2), 20.3 [*C*H_3 (phenylethyl)].

MS-FAB: *m/z* (%) = 528 (100) [M^+].

Anal. Calcd for $C_{29}H_{31}Br_2N_5$ (609.40): C, 57.16; H, 5.13; N, 11.49. Found: C, 57.25; H, 5.23; N, 11.53.

1,1′-Di(*rac*-1″-naphthylethyl)(2,6-lutidine)diimidazolium Dibromide (25)

Yield: 1.33 g (75%).

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^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.85 (s, 2 H, NC*H*N), 8.15–7.35 [m, 17 H, CH_{arom} (14 phenyl + 3 lutidine)], 7.24 (s, 2 H, NC*H*), 6.92 (s, 2 H, NC*H*), 6.87 [q, 2 H, *J* = 7.6 Hz, C*H* (naphthylethyl)], 5.74 (d, 2 H, *J* = 14.8 Hz, CH_2), 5.56 (d, 2 H, *J* = 14.4 Hz, CH_2), 2.08 [d, 6 H, *J* = 7.2 Hz, CH_3 (naphthylethyl)].

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 153.0 (lutidineN*C*), 139.0 (N*C*N), 137.2, 134.0, 133.0, 130.4, 129.2, 127.7, 126.6, 125.5, 124.6, 123.8, 123.6 (C_{arom}), 122.5, 120.2 (N*C*), 55.9 [*C*H (naphthylethyl)], 53.6 (CH_2), 20.8 [CH_3 (naphthylethyl)].

MS-FAB: *m/z* (%) = 628 (100) [M^+].

Anal. Calcd for $C_{37}H_{35}Br_2N_5$ (709.52): C, 62.63; H, 4.97; N, 9.87. Found: C, 62.84; H, 5.13; N, 9.72.

Deprotonation of the Imidazolium Salts

The deprotonation of the corresponding imidazolium salts was performed under argon in a specially designed apparatus.[27] Then, 10.0 mmol of the corresponding bridged 1,3-di-(*R*)-imidazolium salt was suspended in 20 mL THF. NH_3 (100 mL) was condensed into the vessel at –78 °C. After removing the cold bath, NaH (520 mg, 21.6 mmol) was added; an excess of NaH is advantageous. After 2 h a light yellow solution was formed. After the NH_3 was removed, the free carbene was isolated and crystallized. Therefore, THF was removed completely under high vacuum, and the free carbene was extracted three times with *n*-hexane.

1,1′-Dibutyl-3,3′-ethylenediimidazolin-2,2′-diylidene (26)

Yield: 1.27 g (47%).

^{1}H NMR (400 MHz, C_6D_6): δ = 7.21 (s, 4 H, NC*H*C*H*N), 4.24 (s, 4 H, NCH_2CH_2N), 2.14 (s, 6 H, NCH_2), 1.31 (6 H, CH_3), 1.25 (6 H, CH_2).

^{13}C NMR (100.5 MHz, C_6D_6): δ = 218.0 (N*C*N), 123.4, 120.0 (N*C*H*C*HN), 49.8 (N*C*H_2*C*H_2N), 35.2 (N*C*H_2), 19.2 (*C*H_2), 12.2 (*C*H_3).

General Procedure for Dicarbene Complexes of Type [*cis*-CH_2{NC(H)=C(H)N(*R*)C}$_2$PdX$_2$]

1,1′-Di-(*R*)-3,3′-methylenediimidazoliumdihalogen salt (1.00 mmol) and $Pd(OAc)_2$ (225 mg, 1.00 mmol) were dissolved in DMSO (10 mL) and heated for 4 h at 50 °C. Afterwards the solution was refluxed for 20 min at 190 °C, were a clear yellow solution was formed. The volatile compounds were removed in vacuo and the precipitate was washed twice with THF (5 mL). The complex was recrystallized by slow condensation of Et_2O, EtOH or MeOH into a sat. DMSO solution of the desired complex.

Dichloro[1,1′-di(4-vinylbenzyl)-3,3′-methylenediimidazolin-2,2′-diylidene]palladium(II) (27)

Yield: 491 mg (88%); mp: 273 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.60 (s, 2 H, NC*H*), 7.30 (s, 2 H, NC*H*), 7.39–7.28 (m, 8 H, aryl), 6.69 (dd, 2 H, $^3J_{HH,trans}$ = 17.6 Hz, $^3J_{HH,cis}$ = 11.0 Hz, H_2CH), 6.34 (br, 2 H, NCH_2N), 6.17 (d, 2 H, $^2J_{HH}$ = 14.6 Hz, NCH_2Ph), 5.81 (d, 2 H, $^3J_{HH,trans}$ = 17.6 Hz, CH_2=CH), 5.29 (d, 2 H, $^2J_{HH,trans}$ = 14.6 Hz, NCH_2Ph), 5.27 (d, 2 H, $^3J_{HH,cis}$ = 11.0 Hz, CH_2=CH).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 156.4 (N*C*N), 136.7, 136.3, 136.0, 128.2, 126.4, 114.6 (2 C_{vinyl}, 4 C_{aryl}), 122.3 (N*C*H), 121.9 (N*C*H), 67.9 (*C*H_2), 52.5 (N*C*H_2Ph).

MS-FAB: *m/z* (%) = 522 (44) [M^+], 487 (100) [M^{2+}].

Anal. Calcd for $C_{25}H_{24}N_4Cl_2Pd$ (557.81): C, 53.83; H, 4.34; N, 10.04. Found: C, 53.93; H, 4.79; N, 8.97.

Dibromo{1,1′-di[(*R*)-1″-phenylethyl]-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) (28)

Yield: 529 mg (85%); mp 299 °C; $[\alpha]_D^{20}$ +182 (DMSO).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.63–7.33 (m, 10 H, Ar), 6.92 (s, 2 H, NC*H*), 6.79 (s, 2 H, NC*H*), 6.35 (br, 2 H, NCH_2N), 5.91 (br, 2 H, NC*H*), 2.06 (br, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 172.2 (N*C*N), 140.2, 137.3, 129.5, 129.1, 128.8, 128.2, 127.3, 126.7 (Ar), 123.6, 123.2, 122.8, 122.6 (N*C*H), 63.2 (N*C*H_2), 58.9, 57.0 (N*C*H), 21.3, 21.0 (*C*H_3).

MS-FAB: *m/z* (%) = 623 (36) [MH^+], 543 (100) [M^+], 461 (45) [M^{2+}].

Anal. Calcd for $C_{23}H_{24}N_4Br_2Pd$ (622.68): C, 44.36; H, 3.88; N, 9.00. Found: C, 44.36; H, 3.96; N, 8.95.

Crystal structure analysis of compound **28**: $C_{23}H_{24}Br_2N_4Pd$, M_r = 622.68, colorless fragment (0.25 × 0.41 × 0.48 mm^3), orthorhombic, $P2_12_12_1$ (No.: 19), *a* = 11.1056(5), *b* = 14.1269(7), *c* = 14.6360(8) Å, *V* = 2296.2(2) Å^3, *Z* = 4, d_{calc} = 1.801 g cm^{-3}, F_{000} = 1224, μ = 4.306 mm^{-1}. Preliminary examination and data collection were carried out on a IPDS device (Stoe & Cie) at the window of a rotating anode (NONIUS FR591) with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 293 K within the κ range of 2.72° < κ < 30.16°. A total of 26891 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging (R_{int} = 0.081), 6751 [5915: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 273 parameters. The structure was solved by a combination of direct methods and difference-Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and refined using a riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ and converged with R_1 = 0.0269 [$I_o > 2\sigma(I_o)$], wR_2 = 0.0585 [all data], GOF = 0.991, and shift/error < 0.001. The choice of the correct enantiomer is proved by Flack's parameter × = 0.004(5). The final difference-Fourier map shows no striking features ($\Delta e_{min/max}$ = +0.66/–0.66 eÅ^{-3}).[44]

Diiodo(1,1′-diethyl-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II) (29)

Yield: 502 mg (89%); mp 252 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.25 (s, 2 H, NC*H*), 7.16 (s, 2 H, NC*H*), 6.62, 6.28 (AB, 2 H, $^2J_{HH}$ = 13.5 Hz, NCH_2N), 4.18 (br, 4 H, CH_2CH$_3$), 1.19 (br, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 169.7 (N*C*N), 123.4 (N*C*H), 122.9 (N*C*H), 62.4 (*C*H_2), 46.7 (*C*H_2CH$_3$), 19.8 (*C*H_3).

MS-FAB: *m/z* (%) = 565 (9) [MH^+], 434 (100) [M^+].

Anal. Calcd for $C_{11}H_{16}N_4I_2Pd$ (564.50): C, 23.40; H, 2.86; N, 9.93. Found: C, 23.37; H, 2.78; N, 9.62.

Diiodo(1,1′-dibenzyl-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II) (30)

Yield: 544 mg (79%); mp 283 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.35 (s, 2 H, NC*H*), 7.02 (s, 2 H, NC*H*), 7.78–7.32 (m, 10 H, Ar), 6.52, 6.26 (AB, 2 H, $^2J_{HH}$ = 11.2 Hz, NCH_2N), 6.46, 6.13 (AB, 4 H, $^2J_{HH}$ = 12.2 Hz, NCH_2Ph).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 165.4 (N*C*N), 136.8, 129.3, 128.7, 128.1 (Ar), 122.0 (N*C*H), 121.9 (N*C*H), 63.7 (*C*H_2), 54.9 (N*C*H_2Ph).

MS-FAB: *m/z* (%) = 689 (21) [MH^+], 562 (100) [M^+], 435 (71) [M^{2+}].

Anal. Calcd for $C_{21}H_{20}N_4I_2Pd$ (688.64): C, 36.63; H, 2.93; N, 8.14. Found: C, 36.93; H, 2.49; N, 8.61.

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Diiodo{1,1′-dicyclohexyl-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) (31)
Yield: 525 mg (78%); mp 268 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.62 (s, 2 H, NC*H*), 7.52 (s, 2 H, NC*H*), 6.39, 6.11 (AB, 2 H, $^2J_{HH}$ = 11.8 Hz, NCH_2N), 5.09 (br, 2 H, C$H_{,cy}$), 2.15–1.50 (m, 20 H, C$H_{2,cy}$).

^{13}C NMR (100.5 MHz, DMSO-d_6): impossible because of its solubility.

MS-FAB: *m/z* (%) = 673 (23) [MH^+], 545 (100) [M^+].

Anal. Calcd for $C_{19}H_{28}N_4I_2Pd$ (672.69): C, 33.92; H, 4.20; N, 8.33. Found: C, 33.94; H, 4.45; N, 8.49.

Dichloro{1,1′-di[*p*-acetophenone(4-*trans*-vinylbenzyl)]-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) (41)
A solution of dichloro[1,1′-di(4-vinylbenzyl)-3,3′-methylenediimidazolin-2,2'-diylidene]palladium(II) (**27**, 279 mg, 0.50 mmol), *p*-bromoacetophenone (398 mg, 2.00 mmol) and NaOAc (246 mg, 3.00 mmol) in DMAc was heated for 2 h at 120 °C. The volatile compounds were removed in vacuo and the precipitate was washed twice with MeOH (10 mL) and THF (10 mL). Afterwards the precipitate was dissolved in DMSO (10 mL) and NaCl (120 mg, 2.05 mmol) was added and heated for 1 h at 50 °C. The solvent was removed in vacuo and the desired complex was recrystallized from an MeCN–MeOH solution.

Yield: 310 mg (78%); mp 236 °C.

IR (KBr): 1716.1 (CO) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.89–7.28 (br, 20 H, 4 NC*H* + 16 C_{aryl}), 6.56 (br, 4 H, C*H*), 6.21 (br, 2 H, NCH_2N), 5.93 (br, 4 H, NCH_2Ph), 2.62 (s, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 196.3 (CO), 162.4 (N*C*N), 136.3, 136.1, 135.3, 135.0, 134.1, 133.8, 132.5, 129.5, 128.5, 127.5 (8 C_{aryl} + 2 C=C), 122.4 (N*C*H), 121.3 (N*C*H), 67.7 (N*C*H_2N), 52.5 (*C*H_2), 22.1 (*C*H_3).

Anal. Calcd for $C_{41}H_{36}N_4Cl_2O_2Pd$ (794.08): C, 62.01; H, 4.57; N, 7.06. Found: C, 62.21; H, 4.22; N, 7.57.

Acetonitrile[bromo(1,1′-di-*tert*-butyl-3,3′-methylenediimidazolin-2,2′-diylidene)]palladium(II) Hexafluorophosphate (42)
A solution of dibromo[1,1′-di(*tert*-butyl)-3,3′-methylenediimidazolin-2,2′-diylidene]palladium(II)[22] (**39**, 303 mg, 0.45 mmol) and K[PF_6] (1.50 g, 8.15 mmol) in MeCN–H_2O (20:15 mL) was refluxed for 5 h. Afterwards the solvent was removed in vacuo and the colorless product was washed with H_2O (10 mL). The complex was recrystallized from an MeCN–Et_2O solution.

Yield: 231 mg (81%); mp 252 °C.

IR (KBr): 2317.4 (C≡N) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.39 (br, 2 H, NC*H*), 7.15 (br, 2 H, NC*H*), 6.84 (AB, 1 H, $^2J_{HH}$ = 12.9 Hz, CH_2), 6.45 (AB, 1 H, $^2J_{HH}$ = 12.9 Hz, CH_2), 1.99 (s, 3 H, NCCH_3), 1.91 (s, 6 H, CH_3), 1.84 (s, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 144.6 (N*C*N), 142.4 (N*C*N), 123.6 (N*C*H), 122.9 (N*C*H), 122.3 (N*C*H), 119.5 (N*C*H), 118.5 (N*C*CH_3), 63.6 (*C*H_2), 61.0 [*C*(CH_3)$_3$], 60.3 [*C*(CH_3)$_3$], 39.8 (*C*H_3), 30.2 (*C*H_3), 1.0 (NC*C*H_3).

Anal. Calcd for $C_{17}H_{27}N_5BrF_6PPd$ (632.72): C, 32.27; H, 4.30; N, 11.07. Found: C, 33.62; H, 4.67; N, 11.63.

Bisacetonitrile{1,1′-di[(*R*)-1″-phenylethyl]-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) Ditetrafluoroborate (43)
A solution of dibromo{1,1′-di[(*R*)-1″-phenylethyl]-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) (**28**, 300 mg, 0.48 mmol) and Ag[BF_4] (187 mg, 0.96 mmol) in MeCN (15 mL) was heated for 12 h at 60 °C. Afterwards the formed AgBr was removed by filtration and the solvent was removed in vacuo. The colorless product was recrystallized from an MeCN–Et_2O solution.

Yield: 317 mg (92%); mp 231 °C.

IR (KBr): 2321.7 (C≡N), 2304.1 (C≡N) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.82–7.29 (m, 14 H), 6.62, 6.34 (AB, 2 H, $^2J_{HH}$ = 12.9 Hz, CH_2), 5.94 (br, 2 H, NC*H*Ph), 2.06 (br, 6 H, CH_3), 1.74 (s, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 147.0 (N*C*N), 142.0, 140.2, 129.4, 128.9, 128.4, 127.0, 126.7, 126.0 (aryl), 123.9, 123.7, 120.6, 120.3 (N*C*H), 118.6 (N*C*CH_3), 62.9 (*C*H_2), 58.8, 57.9 (N*C*HPh), 22.6 (*C*H_3), 20.0 (*C*H_3), 1.5 (NC*C*H_3).

Anal. Calcd for $C_{27}H_{30}N_6B_2F_8Pd$ (718.60): C, 45.13; H, 4.21; N, 11.70. Found: C, 44.83; H, 3.99; N, 11.39.

Bisacetonitrile(1,1′-di-*tert*-butyl-3,3′-methylenediimidazolin-2,2′-diylidene)palladium(II) Ditetrafluoroborate (44)
A solution of dibromo[1,1′-di(*tert*-butyl)-3,3′-methylenediimidazolin-2,2′-diylidene]palladium(II) (**39**, 193 mg, 0.47 mmol) and Ag[BF_4] (143 mg, 0.95 mmol) in MeCN (15 mL) was heated for 12 h at 60 °C. Afterwards the formed AgBr was removed by filtration and the solvent was removed in vacuo. The colorless product was recrystallized from an MeCN–Et_2O solution.

Yield: 246 mg (84%); mp 262 °C.

IR (KBr): 2323.2 (C≡N), 2304.7 (C≡N) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.81 (br, 2 H, NC*H*), 7.72 (br, 2 H, NC*H*), 6.90, 6.45 (AB, 2 H, $^2J_{HH}$ = 12.9 Hz, CH_2), 2.06 (s, 6 H, NCCH_3), 1.62 (s, 18 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 143.8 (N*C*N), 123.3 (N*C*H), 122.0 (N*C*H), 118.0 (N*C*CH_3), 63.8 (*C*H_2), 60.1 [*C*(CH_3)$_3$], 30.9 (*C*H_3), 1.6 (NC*C*H_3).

Anal. Calcd for $C_{19}H_{30}N_6B_2F_8Pd$ (622.51): C, 36.66; H, 4.86; N, 13.50. Found: C, 36.42; H, 4.92; N, 13.28.

Bisacetonitrile(4,4′-dimethyl-2,2′-methyleneditriazolin-3,3′-diylidene)palladium(II) Ditetrafluoroborate (52)
A solution of dibromo(4,4′-dimethyl-2,2′-methyleneditriazolin-3,3′-diylidene)palladium(II)[41] (303 mg, 0.68 mmol) and Ag[BF_4] (265 mg, 1.36 mmol) in MeCN (15 mL) was heated for 12 h at 60 °C. Afterwards the formed AgBr was removed by filtration and the solvent was removed in vacuo. The colorless product was recrystallized from an MeCN–Et_2O solution.

Yield: 314 mg (84%); mp 248 °C.

IR (KBr): 2320.0 (C≡N), 2301.5 (C≡N) cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.81 (s, 2 H, NC*H*), 6.68 (s, 2 H, CH_2), 4.35 (s, 6 H, NCH_3), 2.23 (s, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 146.8 (N*C*N), 126.7 (N*C*H), 118.9 (N*C*CH_3), 63.0 (*C*H_2), 30.0 (*C*H_3), 2.0 (NC*C*H_3).

Anal. Calcd for $C_{11}H_{16}N_8B_2F_8Pd$ (540.33): C, 24.45; H, 2.98; N, 20.74. Found: C, 24.42; H, 2.92; N, 20.28.

Bisacetonitrile(1,1′-dimethyl-3,3′-methylenedibenzimidazolin-2,2′-diylidene)palladium(II) Ditetrafluoroborate (53)
A solution of dibromo(1,1′-dimethyl-3,3′-methylenedibenzimidazolin-2,2′-diylidene)palladium(II)[40] (0.68 mmol) and Ag[BF_4] (265 mg, 1.36 mmol) in MeCN (15 mL) was heated for 12 h at 60 °C. Afterwards the formed AgBr was removed by filtration and the solvent was removed in vacuo. The colorless product was recrystallized from an MeCN–Et_2O solution.

Yield: 364 mg (84%); mp 221 °C.

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IR (KBr): 2322.1 (C≡N), 2304.5 (C≡N) cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 7.98–6.99 (m, 8 H, aryl), 6.76 (s, 2 H, CH_2), 4.98 (s, 6 H, NCH_3), 2.23 (s, 6 H, CH_3).

^{13}C NMR (100.5 MHz, DMSO-d_6): δ = 146.8 (*N*CN), 137.0, 135.8, 134.8, 129.0, 128.6, 119.9 (*NCCH*$_3$), 64.1 (*C*H_2), 31.0 (*C*H_3), 1.8 (NC*C*H_3).

Anal. Calcd for $C_{21}H_{22}N_6B_2F_8Pd$ (638.47): C, 39.50; H, 3.47; N, 13.16. Found: C, 40.43; H, 2.99; N, 13.35.

General Procedure for the Heck Catalysis

The reaction for Heck coupling studies were typically conducted as follows: The aryl halide (1.0 equiv, 10 mmol), alkene (1.2 equiv, 12 mmol), base (1.5 equiv, 15 mmol), internal standard (100 mg diethyl glycol-*n*-butyl ether) and the catalyst were added to a thick-walled 17 cm ACE pressure tube; the solvent (10 mL) and a magnetic stir bar were added. The tube was sealed with an o-ringed Teflon cap and heated to the appropriate temperature of the experiment. The reaction progress was monitored by the removal of a small aliquot of the reaction mixture, which was analyzed by GC-MS. The pressure tubes were then cooled to r.t.; a small aliquot of the reaction mixture was taken for GC-MS analysis of the reaction. Products were identified by comparison with authentic samples.

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