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Chiral, bridged bis(imidazolin-2-ylidene) complexes of palladium ☆

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Dedicated to Prof. Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Varieties of chiral, bridged bisimidazolium salts as well as the synthesis of palladium complexes of general formula [*bridge* $\{NC(H)=C(H)N(R^*)C\}_2PdBr_2$] with the corresponding chelating N-heterocyclic carbene ligands is reported. This is the first systematic study of chiral bis(imidazolin-2-ylidene)palladium(II) complexes bearing chiral groups on the endocyclic nitrogens. Structural proof of such a chiral palladium(II) complex is presented by way of an X-ray diffraction study of complex **3a**.

Keywords: Chelating ligands; Chiral ligands; Bisimidazolium salts; Palladium

1. Introduction

N-Heterocyclic carbenes have become universal ligands in organometallic and inorganic coordination chemistry [1,2]. The bond between the N-heterocyclic carbene and the metal centre of a complex can be best described as a dative σ-bond as the M–C distance falls comfortably in the range of typical single M–C bond lengths (X-ray diffraction) [3,4]. Metal complexes of imidazolin-2-ylidenes have attracted considerable attention as homogeneous catalysts [2]. For example, complexes of ruthenium and palladium show excellent catalytic properties for olefin metathesis and C–C coupling reactions [5]. In contrast to the corresponding phosphine complexes, ligand dissociation is not favored in NHC complexes [6]. This eliminates the need for an excess of ligand [7], and makes them possible candidates for asymmetric catalysis [8,9]. Thus, a substantial amount of work on the preparation of chiral NHC ligands has been published [10], following our report of the first chiral NHC-complex employed in homogeneous catalysis [4]. The rigidity of chelating chiral carbene ligands is expected to result in higher optical inductions in asymmetric reactions relative to two non-chelating ligands. Such ligands can be constructed, for example, by a bridged bis(imidazolin-2-ylidene) ligand, a well known framework for achiral NHC ligands [11–17]. The complexes with chelating carbene ligands are presumably highly thermal stable because of the chelating effect.

The preparation of chelating ligands of N-heterocyclic carbenes, in order to impart higher air- and moisture stability to palladium centers, is receiving nowadays much attention [18,19]. We and others have published chelated palladium NHC complexes which can be used in C–C coupling reactions [13,15,20–22]. For example, some methylene-bridged bis(imidazolium) salts, in combination with $Pd(OAc)_2$, were equally efficient as the non-bridged biscarbene complexes in the Suzuki coupling reaction with aryl chlorides as substrates [23,24] and the bridged biscarbene complexes even achieve the C–H activation of methane [25]. In the first part of the present article, a variety of

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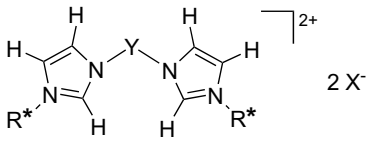


Fig. 1. R*-substituted (R* = chiral alkyl group) imidazolium salts with Y-bridging groups (Y = bridging moiety).

new bis(imidazolium) salts will be presented. We will focus on the variation of the bridging group Y and the substituents R* (Fig. 1).

2. Results and discussions

2.1. General synthesis of chiral imidazole derivatives

The substituted imidazole precursors are accessible via an one-pot synthesis route according to Gridnev and Mihaltseva (Scheme 1) [26].

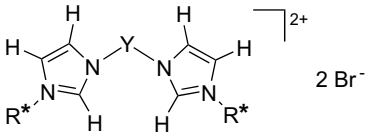
The products can be purified by extraction, recrystallization or distillation. Via this synthesis two new chirally modified imidazoles, 1-(*R*)-(phenylethyl)imidazole **1a** [27], and 1-(*R*)-(1′-naphthylethyl)imidazole **1b**, could be synthesized without racemization and with retention of the (*R*)-configuration employing commercially available chiral amines.

In order to synthesize a library of chirally modified bridged imidazolium salts, we used a general synthetic procedure. Two equivalents of the imidazole were dissolved in THF and transferred to an ACE pressure tube. One equivalent of the corresponding dibromo compound was added and the resulting mixture was heated. The purification of the air stable hygroscopic colorless to pale brown products was achieved by washing the obtained solids with THF [28]. The product was dried under high vacuum. It is remarkable that the synthesis of chiral imidazolium salts occurs without racemization of the chiral centers; the (*R*)-configuration is maintained in each case. To the best of our knowledge these are the first enantiomerically pure chiral, bridged bisimidazolium salts with the chirality introduced at the N-atoms reported to date [15]. Table 1 gives an overview of the prepared bis(1,3-azolium) salts.

2.2. Synthesis of chiral bis(carbene)palladium(II) complexes

The neutral bis(carbene)palladium(II) bromide complexes **3a**–**3f** were prepared via an adaptation of our straightforward procedure, avoiding the formation of free carbenes as intermediates [13], which utilizes longer reaction times and milder temperatures to increase yields of the palladium complexes, particularly when chiral substituents are present in the bridged bis(imidazolium) salt precursors. Thereon, the bis(imidazolium) salt and $Pd(OAc)_2$ were stirred in DMSO overnight at room temperature. After this, slow heating over a period of 6 h not reaching more than 120 °C afforded the bis(carbene)palladium(II) complexes **3a**–**3f** without racemization of the chiral groups (Scheme 2). The synthesized complexes are depicted in Fig. 2.

Table 1
Chelating imidazolium salts as carbene (NHC) precursors

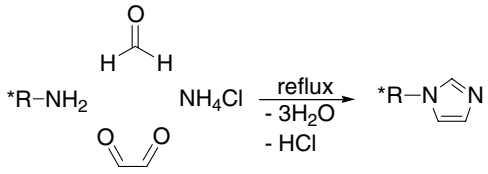


Azolium salt	R*	Y	Yield [%]
2a	(*R*)-CH(C_6H_5)CH_3	–CH_2–	49
2b	(*R*)-CH(C_6H_5)CH_3	*o*-Xylene	83
2c	(*R*)-CH($C_{10}H_7$)CH_3	*o*-Xylene	76
2d	(*R*)-CH(C_6H_5)CH_3	*m*-Xylene	97
2e	(*R*)-CH(C_6H_5)CH_3	*p*-Xylene	93
2f	(*R*)-CH(C_6H_5)CH_3	2,6(CH_2)$_2$(C_5H_3N)	80
2g	(*R*)-CH($C_{10}H_7$)CH_3	2,6(CH_2)$_2$(C_5H_3N)	75

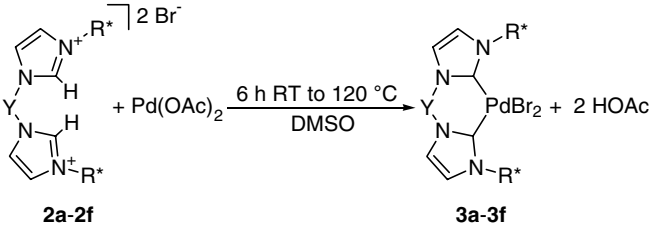
2.3. X-ray crystal structure of complex *3a*

The molecular structure of the square-planar Pd(II) complex **3a** in the solid state is shown in Fig. 3. Selected bond lengths and angles are denoted in the figure caption. The crystal structure of complex **3a** shows the biscarbene ligand chelating the palladium(II) center in a *cis*-arrangement 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.

The Pd–C distances (1.974(3), 1.992(3) Å) fall comfortably within the range found for the dicationic and neutral chelating bis(carbene)palladium(II) complexes [*cis*-CH_2



Scheme 1. Synthesis of substituted imidazoles.



Scheme 2. Synthesis of chiral bis(carbene)palladium(II) complexes.

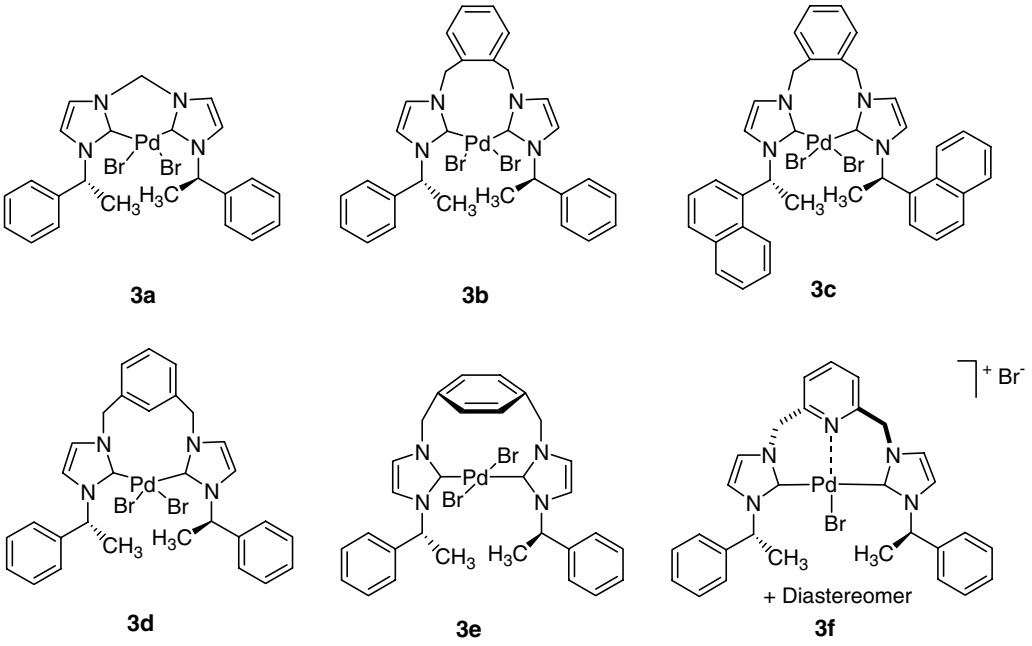


Fig. 2. Synthesized palladium(II) complexes and postulated structure configurations.

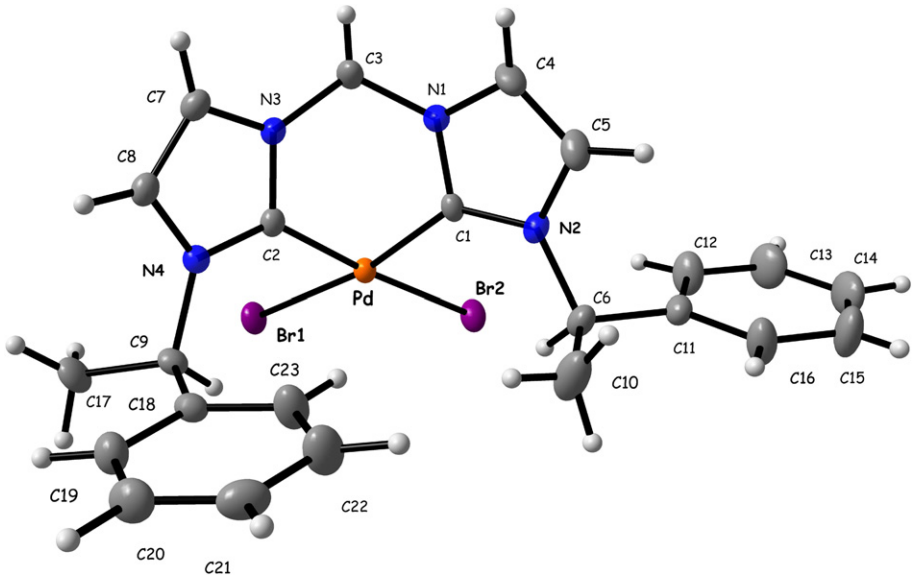


Fig. 3. ORTEP [30] style plot of compound **3a** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and bond angles [°]: Pd–Br1 2.4961(4), Pd–Br2 2.4859(4), Pd–C1 1.992(3), Pd–C2 1.974(3), N1–C1 1.357(4), N1–C3 1.457(4), N1–C4 1.389(4), N3–C2 1.359(4), N3–C3 1.454(4), N3–C7 1.390(4); Br1–Pd–Br2 93.52(1), Br1–Pd–C1 169.81(8), Br1–Pd–C2 89.59(9), Br2–Pd–C1 92.55(9), Br2–Pd–C2 175.91(8), C1–Pd–C2 84.0(1).

$\{\overline{NC(H)=C(H)N(CH_3)C}\}_2Pd(NCCH_3)_2]^{2+}[BF_4]^-_2$ (1.966(2) and 1.972(3) Å) [20] and [*cis*-$CH_2\{\overline{NC(H)=C(H)N(CH_3)C}\}_2PdI_2$] (1.990(3) and 1.997(3) Å) [5i] as well as with those reported for the related non-chelating complex [*cis*-{MeNC=CN(Me)C}$_2$PdI$_2$] (1.990(3) and 1.997(3) Å) [23,29].

This structure is further proof, that the synthesis of such chiral palladium(II) complexes is not accompanied by any racemization. If enantiomerically pure amines [or enantiomerically pure bis(imidazolium) salts] are employed the absolute configuration remains the same; in this case the absolute configuration at each chiral centre is assigned as (*R*) via anomalous X-ray dispersion (scattering factors *f*′ and *f*″), which is in accordance with the absolute configuration of the primarily employed amine. In this regard the explored crystals were unitary and their NMR spectral data were in accordance to those of the mother liquor.

2.4. Spectroscopic and structural properties of chiral bis(carbene)palladium(II) complexes

If chelating bis(imidazolin-2-ylidene)palladium(II) complexes are formed, there is the possibility of formation of

the *cis*- as well as of the *trans*-arrangement, depending on the size of the bridge. In the case of non-bridged bis-(carbene)palladium(II) complexes, in most cases the *cis*-arrangement is formed unless sterically demanding imidazolium salts are employed [15,31]. If bridged bis(imidazolium) salts are employed as ligands, the geometry of the bridging moiety determines the substitution pattern. In the case of the methylene bridge, only the *cis*-arrangement is possible which was confirmed by a single crystal X-ray analysis of complex **3a** (Fig. 3).

^{1}H and ^{13}C NMR spectra of complex **3a** are in agreement with the assigned structure. The appearance of inequivalent methylene proton resonances in the ^{1}H NMR spectrum indicate the retention of a conformationally restrained boat shaped six-membered chelate ring for the complex, and this was determined by the X-ray solid state structure. Such conformationally rigid ring systems have been noted by us and other groups. Similar complexes for examples show a fluxional behavior at room temperature [15].

Literature examples of related achiral *ortho*-xylene bridged palladium(II) complexes also exhibit *cis*-geometry which has been confirmed by X-ray analysis; therefore such a arrangement can also be postulated for **3b** and **3c**, as the spectroscopic data are in line with the literature examples [15,31]. The NMR data of the two *ortho*-xylene bridged complexes **3b** and **3c** are very similar to **3a**, where also a double set of signals for the carbene carbon atoms were obtained between 161 and 164 ppm. This also proves the postulated *cis*-arrangement in the complex. Our results are in agreement with the work of RajanBabu [32], where chiral chelating bis(carbene)palladium(II) complexes bearing a chiral bridging moiety were described. In this case the *cis*-complex showed a double set of NMR signals contrary to the *trans*-complex, where only a single set was obtained, due to a mirror plane in the molecule [32]. In contrast to **3a**–**3c**, complex **3d** shows broadened NMR signals, which is probably due to either rapid *cis*/*trans* isomerization, or a dynamic 'ring flipping' process in which the xylene ring may interchange between a boat and a chair type configuration. Similar behavior with achiral *meta*-xylene bridged palladium(II) complexes was discovered by Magill and Cavell [31]. As low solubility of complex **3d** in conventional NMR solvents prevented us from carrying out low temperature NMR studies of this complex, in this case the broadening could not be confirmed. Repeated attempts to crystallize **3d** were invariably unsuccessful, and at present the true geometry neither of this complex nor of *meta*-xylene bridged literature examples has been established [31]. However, given the NMR data, which also manifests as a double set of signals, the *cis*-orientation for **3d** is more likely. RajanBabu noted only a single NMR data set for chiral *trans*-complexes of this kind [32]. This is also in accordance with the NMR spectra of complex **3e**. Additionally the signals are broadened like in the spectra of **3d**, which may also arise from phenomena like *cis*/*trans* isomerization (with a strong preference of the *trans*-isomer) or restricted rotation around bonds within the molecule. A 'ring flipping' process between boat and chair type configurations can be excluded in the case of **3e**, because of the restrained *para*-configuration within the bridge.

Because of atropisomerism arising from triple coordination of the ligand to the palladium centre, it was expected to present four diastereomers of **3f** and therefore a quadruple set of NMR signals should be detected [33]. As both of the chiral centers have (*R*)-configuration the molecule is C_2-symmetric, and thus the four diastereomers are reduced to two as well as for the NMR data set. In our case only a double data set was detected for this compound. However, the gross structure proposed in Fig. 2 can be derived by comparison to a related structure of an analogous complex with achiral N-substituents, which was determined by X-ray analysis [34–36]. Additionally all complexes **3a**–**3f** showed in the FAB-MS spectrum the $[M-Br]^{+}$ fragment as well as the $[M-2Br]^{+}$ fragment.

The *ortho*-xylene bridged-complexes **3b** and **3c** exhibit excellent solubility in dichloromethane, chloroform as well as acetonitrile. In contrast, the rest of the complexes **3a**, **3d**–**3f** are only soluble in highly polar solvents like DMSO or alcohols (MeOH/EtOH) and only sparingly soluble in CH_2Cl_2 and acetonitrile. Complex **3e** is only soluble in hot DMSO which hampered the acquisition of ^{13}C NMR data. The biscarbene complexes **3a**–**3f** exhibit a very high stability towards air, moisture and high temperatures, as is typical for this class of bis(carbene)palladium(II) complexes [5i,13,14,20,21,23].

2.5. Conclusion

A variety of chiral, bridged palladium(II) complexes of the general formula $[bridge\{\overline{NC(H)=C(H)N(R^{*})C}\}_2PdBr_2]$ were synthesized according to established routes. The synthesis of all new ligands and catalysts presented in this work is simple and proceeds without any racemization of the chiral groups. Moreover, the complexes are exceedingly stable towards air, moisture and heat. The majority of chiral catalysts known in literature – mainly consisting of phosphine ligands – would not bear reaction mediums under oxidizing conditions and high temperatures. This makes these new chiral complexes potentially suitable for asymmetric catalysis under extreme reaction conditions like high temperatures or reactions in oxidizing mediums. Therefore, we expect that this class of chiral ligands and complexes will find application in enantioselective catalytic processes and should, individually, be considered as useful alternatives to classical chiral bis- or trisphosphine ligands.

3. Experimental

All experiments were carried out under dry argon using standard Schlenk techniques [37]. Solvents were dried by standard methods and distilled under nitrogen. ^{1}H 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.

NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Chemical shifts δ are given in ppm, coupling constants J are given in Hz. 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.

3.1. 1-(*R*)-(Phenylethyl)imidazole **1a**

1-(*R*)-phenylethylamine (12.1 g, 0.1 mol) was dissolved in 100 mL H_2O and phosphoric acid (85%) was added until a pH of approximately 2 was reached. After addition of 3.0 g of paraformaldehyde (0.1 mol) and 11.5 mL of glyoxal (40% in water, 0.1 mol), the reaction mixture was heated to 100 °C and a saturated ammonium chloride solution (5.4 g, 0.1 mol, 20 mL H_2O) was added drop wise over a period of 60 min. After stirring for another 1 h at 100 °C, the reaction mixture was cooled to 0 °C and sodium hydroxide was added until a pH higher than 12 was observed. The product was extracted three times with 100 mL methylene chloride, 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 [27].

Yield: 5.81 g (34%); bp: 102 °C/1 mbar. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.52$ (s, 1H, NC*H*N), 7.28–7.22 (m, 3H, CH_{arom}), 7.13 (m, 2H, CH_{arom}), 7.09 (d, 1H, $^3J_{HH} = 2.0$ Hz, NC*H*=), 7.02 (d, 1H, $^3J_{HH} = 2.0$ Hz, NC*H*), 5.27 (q, 1H, $^3J_{HH} = 6.9$ Hz, C*H*(C_6H_5)CH_3), 1.78 (d, 3H, $^3J_{HH} = 7.2$ Hz, CH_3). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): $\delta = 142.4$ (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^+]).

3.2. 1-(*R*)-(1′-Naphthylethyl)imidazole **1b**

1-(*R*)-(1-Naphthylethyl)imidazole was synthesized analogously to **1a** from (*R*)-1-naphthylethylamine (5.0 g, 29.0 mmol). The crude product was purified by extracting with diethyl ether to obtain a yellow oil.

Yield: 2.10 g (33%). ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 7.90$–7.79 (m, 2H, CH_{arom}), 7.61 (s, 1H, NC*H*N), 7.55–7.20 (m, 5H, CH_{arom}), 7.08 (s, 1H, NC*H*), 6.96 (s, 1H, NC*H*), 6.24 (q, 1H, $J = 6.8$ Hz, C*H* (naphthylethyl)), 2.00 (d, 3H, $J = 7.1$ Hz, CH_3 (naphthylethyl)). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): $\delta = 136.6$ (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$^+$].

3.3. General synthesis of chiral bisimidazolium salts

(*R*)-Imidazole (5.0 mmol) was dissolved in 5 mL THF in an ACE pressure tube and 2.5 mmol of dibromomethane, α,α′-dibromo-*o*-, -*m*-, -*p*-xylylene or 2,6-di(bromomethyl)pyridine 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 (**2a**, **2d**), or recrystallized from dichloromethane/diethyl ether (**2b**, **2c**, **2e**, **2f**), and dried in high vacuum to obtain a highly hygroscopic colorless powder.

3.3.1. 1,1′-Di((*R*)-1″-phenylethyl)-3,3′-methylene-diimidazolium dibromide **2a**

Yield: 635 mg (49%). Mp >300 °C. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 10.11$ (s, 2H, NC*H*N), 8.80 (s, 2H, NC*H*), 8.02 (s, 2H, NC*H*), 7.52–7.35 (m, 10H, CH_{arom}), 6.82 (s, 2H, NCH_2N), 5.93 (q, 2H, $^3J_{HH} = 7.4$ Hz, NC*H*), 1.86 (d, 6H, $^3J_{HH} = 7.4$ Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): $\delta = 139.5$ (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, N*C*H_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. Calc. for $C_{23}H_{26}Br_2N_4$ (518.19): C, 53.30; H, 5.06; N, 10.81. Found: C, 53.73; H, 5.37; N, 10.62%.

3.3.2. 1,1′-Di((*R*)-1″-phenylethyl)-3,3′-*o*-xylylene-diimidazolium dibromide **2b**

Yield: 1.26 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.39$ (s, 2H, NC*H*N), 7.69 (s, 2H, NC*H*), 7.49–7.20 (m, 14H, Ar), 7.09 (s, 2H, NC*H*), 6.15 (d, 2H, $J_{HH} = 16.0$ Hz, CH_2), 5.93 (d, 2H, $J_{HH} = 12.0$ Hz, CH_2), 5.82 (q, 2H, $J = 8.0$ Hz, C*H*(phenylethyl)), 1.96 (d, 6H, $^3J_{HH} = 7.6$ Hz, CH_3 (phenylethyl)). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): $\delta = 137.9$ (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. Calc. 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%.

3.3.3. 1,1′-Di((*R*)-1″-naphthylethyl)-3,3′-*o*-xylylene-diimidazolium dibromide **2c**

Yield: 1.35 g (76 %). Mp >300 °C. ^{1}H NMR (270 MHz, $CDCl_3$): $\delta = 10.50$ (s, 2H, NC*H*N), 8.20–6.81 (m, 22H, CH_{arom} (14 naphthyl, 4 *o*-Tol, 4 imidazole)), 6.62 (q, 2H, $^3J_{HH} = 7.5$ Hz, C*H* (naphthylethyl)), 6.21 (d, 2H, $J = 13.5$ Hz, CH_2), 5.91 (d, 2H, $^3J_{HH} = 16.2$ Hz, CH_2), 2.13 (d, 6H, $^3J_{HH} = 7.3$ Hz, CH_3 (naphthylethyl)). ^{13}C{^{1}H} NMR (67.5 MHz, $CDCl_3$): $\delta = 136.6$, (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. Calc. 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%.

3.3.4. 1,1′-Di((*R*)-1″-phenylethyl)-3,3′-*m*-xylylene-diimidazolium dibromide **2d**

Yield: 1.48 g (97%). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.67$ (s, 2H, NC*H*N), 7.87–7.41 (m, 14H, CH_{arom} (10

phenyl + 4 imidazole)), 5.45 (m, 4H, CH_2), 5.81 (q, 2H, $^3J_{HH}$ = 8.0 Hz, CH (phenylethyl)), 1.88 (d, 6H, $^3J_{HH}$ = 7.6 Hz, CH_3 (phenylethyl)). $^{13}C\{^1H\}$ NMR (100.5 MHz, DMSO-d_6): δ = 139.3 (NCN), 136.0, 135.9, 130.4, 129.7, 129.4, 129.3, 128.5, 127.2 (Ar), 123.4, 122.1 (NC), 59.2 (CH (phenylethyl)), 52.2 (CH_2), 20.9 (CH_3 (phenylethyl)). MS (FAB): m/z (%) = 527 (100, [M^+]). Anal. Calc. 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%.

3.3.5. 1,1′-Di((R)-1″-phenylethyl)-3,3′-p-xylylene-diimidazolium dibromide **2e**

Yield: 1.41 g (93%). Mp >300 °C. ^1H NMR (400 MHz, DMSO-d_6): δ = 9.79 (s, 2H, NCHN), 7.94 (s, 2H, NCH), 7.90 (s, 2H, NCH), 7.53–7.30 (m, 14H, CH_{arom}), 5.86 (m, 2H, CH (phenylethyl)), 5.49 (s, 4H, CH_2), 1.88 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH_3 (phenylethyl)). $^{13}C\{^1H\}$ NMR (100.5 MHz, DMSO-d_6): δ = 140.0 (NCN), 136.2, 135.9, 129.7, 129.4, 127.2, 123.5 (Ar), 123.3, 122.2 (NC), 59.3 (CH (phenylethyl)), 51.9 (CH_2), 21.0 (CH_3 (phenylethyl)). MS (FAB): m/z (%) = 527 (100, [M^+]). Anal. Calc. 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%.

3.3.6. 1,1′-Di((R)-1″-phenylethyl)-2,6-lutidine-diimidazolium dibromide **2f**

Yield: 1.22 g (80%). ^1H NMR (400 MHz, $CDCl_3$): δ = 10.86 (s, 2H, NCHN), 8.02–7.00 (m, 17H, CH_{arom} (10 phenyl + 3 pyridyl + 4 imidazole)), 6.06 (q, 2H, $^3J_{HH}$ = 5.6 Hz, CH (phenylethyl)), 5.79 (d, 2H, J = 14.8 Hz, CH_2), 5.67 (d, 2H, J = 14.0 Hz, CH_2), 1.99 (d, 6H, $^3J_{HH}$ = 6.0 Hz, CH_3 (phenylethyl)). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_3CN): δ = 153.3 (lutidineNC), 138.9 (NCN), 138.9, 136.3, 129.2, 129.1, 127.0, 123.0 (Ar), 123.6, 122.3 (NC), 59.5 (CH (phenylethyl)), 53.4 (CH_2), 20.3 (CH_3 (phenylethyl)). MS (FAB): m/z (%) = 528 (100, [M^+]). Anal. Calc. 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%.

3.4. General procedure for chiral bisimidazolin-2-ylidene palladium(II) complexes

0.445 mmol of the chiral bisimidazolium salt and $Pd(OAc)_2$ (100 mg, 0.445 mmol) were dissolved in 5 mL DMSO and stirred at room temperature for 20 h, afterwards the mixture was heated for 3 h at 50 °C and later 1 h at 100 °C. The volatile compounds were removed *in vacuo* and the precipitate was washed twice with 5 mL THF. The complexes were recrystallized by slow condensation of diethyl ether/*n*-pentane (**3b**, **3c**) or ethanol/methanol (**3a**, **3d**, **3e**, **3f**) into a saturated DCM (**3b**, **3c**) or DMSO (**3a**, **3d**, **3e**, **3f**) solution.

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

Yield: 235 mg (85%). Mp 299 °C. $[\alpha]_D^{20} = +182°$ (DMSO). ^1H NMR (400 MHz, DMSO-d_6): δ = 7.63–7.33 (m, 10H, Ar), 6.92 (s, 2H, NCH), 6.79 (s, 2H, NCH), 6.35 (br, 2H, NCH_2N), 5.91 (br, 2H, NCH), 2.06 (br, 6H, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, DMSO-d_6): δ = 172.2 (NCN), 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 (NCH), 63.2 (NCH$_2$), 58.9, 57.0 (NCH), 21.3, 21.0 (CH_3). MS (FAB): m/z (%) = 623 (36, [MH^+]), 543 (100, [M^+]), 461 (45, [M^{2+}]). Anal. Calc. for $C_{23}H_{24}Br_2N_4Pd$ (622.68): C, 44.36; H, 3.88; N, 9.00. Found: C, 44.36; H, 3.96; N, 8.95%.

3.4.2. Dibromo{1,1′-di[(R)-1″-phenylethyl]-3,3′-o-xylylenediimidazolin-2,2′-diylidene}palladium(II) **3b**

Yield: 281 mg (88%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.05 (m, 19H, Ar (14 × phenyl + 4 × NCH, 1 × CH_2)), 6.95 (d, 1H, $^3J_{HH}$ = 14.0 Hz, CH_2), 6.80 (q, 1H, $^3J_{HH}$ = 6.0 Hz, CH(PhEt)), 5.99 (q, 1H, $^3J_{HH}$ = 6.0 Hz, CH(PhEt)), 5.04 (d, 1H, $^3J_{HH}$ = 15.2 Hz, CH_2), 4.98 (d, 1H, $^3J_{HH}$ = 14.8 Hz, CH$_2$), 1.92 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CH_3(PhEt)), 0.61 (d, 3H, $^3J_{HH}$ = 9.6 Hz, CH_3(PhEt)). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 163.8 (NCN), 161.1 (NCN), 141.0, 139.3, 135.4, 134.9, 132.1, 131.8, 130.0, 129.9, 129.1, 28.4, 128.1, 127.8, 127.4, 125.9 (Ar), 122.7, 121.8, 120.7, 119.7 (NC), 67.8, 60.6, 59.2 (CH(PhEt)), 51.3 (CH_2), 25.6, 24.8 (CH_3(PhEt)). MS (FAB): m/z = 712 [M^+], 632 [M^+−Br], 551 [M^+−2Br]. Anal. Calc. for $C_{30}H_{30}N_4Br_2Pd$ (712.82): C, 50.55; H, 4.24; N, 7.86. Found: C, 50.14; H, 4.14; N, 8.00%.

3.4.3. Dibromo{1,1′-di[(R)-1″-naphthylethyl]-3,3′-o-xylylenediimidazolin-2,2′-diylidene}palladium(II) **3c**

Yield: 273 mg (75%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10–7.08 (m, 22H, Ar (18 × naphthyl + 4 × NCH)), 7.20 (d, 1H, $^3J_{HH}$ = 16.4 Hz, CH_2), 6.68 (d, 1H, $^3J_{HH}$ = 16.3 Hz, CH_2), 5.59 (m, 3H, (2 × CH_2 + CH(PhEt))), 5.29 (q, 1H, $^3J_{HH}$ = 7.0 Hz, CH(naphthEt)), 2.01 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CH_3(naphthEt)), 0.91 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3(napthEt)). $^{13}C\{^1H\}$ NMR (100.5 MHz, $CDCl_3$): δ = 163.9 (NCN), 161.6 (NCN), 136.9, 136.5, 135.2, 134.9, 134.3, 134.0, 133.6, 133.4, 133.2, 132.0, 130.4, 130.2, 129.9, 129.1, 128.9, 128.5, 128.3, 127.8, 127.3, 126.4, 126.3, 125.5, 125.3, 124.8, 123.9, 123.6 (Ar), 123.2, 122.6, 121.9, 121.1 (NC), 58.7, 57.3 (CH(naphthEt)), 56.4, 56.2 (CH_2), 25.0, 20.8 (CH_3(naphthEt)). MS (FAB): m/z = 731 [M^+−Br]. Anal. Calc. for $C_{38}H_{34}N_4Br_2Pd$ (812.93): C, 56.14; H, 4.22; N, 6.89. Found: C, 56.27; H, 4.28; N, 7.19%.

3.4.4. Dibromo{1,1′-di[(R)-1″-phenylethyl]-3,3′-m-xylylenediimidazolin-2,2′-diylidene}palladium(II) **3d**

Yield: 234 mg (73%). ^1H NMR (400 MHz, DMSO-d_6): δ = 7.70–7.00 (m, 18H, ArH (14 × ArH + 4 × NCH)), 6.81 (br, 1H, CH(PhEt)), 5.90–5.10 (m, 5H, CH(PhEt) + CH_2), 1.80 (m, 6H, CH_3(PhEt)). $^{13}C\{^1H\}$ NMR (100.5 MHz, DMSO-d_6): δ = 168.9 (NCN), 168.7 (NCN), 140.9, 140.3, 136.1, 135.0, 129.6, 129.3, 129.0, 128.9, 128.5, 128.4, 128.1, 127.9, 127.1, 126.8 (Ar), 122.1, 120.6, 120.3, 119.5 (NC), 59.4, 58.8 (CH(PhEt)), 58.9,

53.6 (CH_2), 20.6, 20.2 (CH_3(PhEt)). MS (FAB): $m/z = 551$ [M^+−2Br]. Anal. Calc. for $C_{30}H_{30}N_4Br_2Pd$ (712.82): C, 50.55; H, 4.24; N, 7.86. Found: C, 51.23; H, 5.01; N, 7.21%.

3.4.5. Dibromo{1,1′-di[(R)-1″-phenylethyl]-3,3′-p-xylylenediimidazolin-2,2′diylidene}palladium(II) 3e

Yield: 291 mg (91%). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.95$–7.03 (m, 18H, 14 × ArH + 4 × NC*H*), 5.78 (m, 2H, C*H*(PhEt)), 5.40 (m, 4H, CH_2), 1.85 (br s, CH_3(PhEt)). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ = carbene carbon was not detected, 136.1, 129.6, 129.3, 129.0, 128.8, 128.1, 127.1 (Ar), 123.5, 122.2 (N*C*), 59.4 (C*H*(PhEt)), 53.7 (CH_2), 21.0 (CH_3(PhEt)). MS (FAB): $m/z = 712$ [M^+], 632 [M^+−Br], 551 [M^+−2Br]. Anal. Calc. for $C_{30}H_{30}N_4Br_2Pd$ (712.81): C, 50.55; H, 4.24; N, 7.86. Found: C, 49.90; H, 4.22; N, 7.86%.

3.4.6. Dibromo{1,1′-di[(R)-1″-phenylethyl]-2,6-lutidine-diimidazolin-2,2′diylidene}palladium(II) 3f

Yield: 238 mg (75%). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.94$–6.97 (m, 17H, 13 × Ar*H* + 4 × NC*H*), 5.40 (br, 1H, CH_2), 6.59 (m, 1H, C*H*(PhEt)), 5.87 (br, 1H, CH_2), 5.61 (br, 1H, CH_2), 5.57 (m, 1H, C*H*(PhEt)), 5.32 (br, 1H, CH_2), 1.68 (br, 6H, CH_3(PhEt)). ^{13}C{^{1}H} NMR (100.5 MHz, DMSO-d_6): δ = carbene carbon was not detected, 156.1, 155.9 (lutidineNC), 140.3, 139.4, 139.0, 136.8, 129.5, 129.3, 129.0, 128.7, 128.2, 127.0 (Ar), 124.2, 121.9 (NC), 59.4, 53.8 (*C*H(PhEt)), 55.9, 52.3 (CH_2), 21.2, 20.4 (CH_3(PhEt)). MS (FAB): $m/z = 633$ [M^+−Br]. Anal. Calc. for $C_{29}H_{29}N_5Br_2Pd$ (713.80): C, 48.80; H, 4.10; N, 9.81. Found: C, 48.00; H, 3.64; N, 10.24%.

3.5. Single crystal X-ray structure determination of compound 3a

Crystal structure analysis of compound **3a**: $C_{23}H_{24}Br_2N_4Pd$, $M_r = 622.68$, colorless prism ($0.15 \times 0.20 \times 0.25$ mm^3), orthorhombic, $P2_12_12_1$ (No. 19), $a = 11.0749(2)$, $b = 13.9462(3)$, $c = 14.6204(3)$ Å, $V = 2258.16(8)$ Å^3, $Z = 4$, $d_{calc} = 1.832$ g cm^{-3}, $F_{000} = 1224$, $\mu = 4.378$ mm^{-1}. Preliminary examination and data collection were carried out on an area detecting system (Nonius, Mach3, κ-CCD) at the window of a rotating anode (Nonius, FR591) and graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection was performed at 173 K within the θ-range of $4.20° < \theta < 30.03°$. A total of 11 895 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.050$), 6173 [5971: $I_o > 2\sigma(I_o)$] independent reflections remained and all were used to refine 367 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 found in the final difference Fourier maps and were allowed to refine freely. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ and converged with $R_1 = 0.0271$ [$I_o > 2\sigma(I_o)$], $wR_2 = 0.0670$ [all data], GOF = 1.038, and shift/error <0.001. The choice of the correct enantiomer is proved by Flack's parameter $\varepsilon = 0.015(6)$. The final difference Fourier map shows no striking features ($\Delta e_{min/max} = +0.40/-0.77$ e Å^{-3}) [30].

4. Supplementary material

CCDC 640944 contains the supplementary crystallographic data for **3a**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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