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Chiral bisimidazolium salts derived from amino acids and their palladium(II)- and platinum(II)-biscarbene complexes

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We report new chiral bisimidazolium salts synthesized from naturally occurring L-amino acids. They served as precursors for bidentate *N*-heterocyclic carbene metal complexes. The chiral imidazoles could be synthesized in good yields via a one-pot ring closing reaction, followed by esterification. The methylene bridged bisimidazolium iodide salts are accessible in moderate yields. Corresponding palladium(II)- and platinum(II)-NHC complexes could be synthesized and fully characterized, but do not show optical activity. We also report a solid state structure of one of the synthesized palladium(II) biscarbene compounds derived from alanine.

1. Introduction

N-heterocyclic carbenes are extraordinary stable ligands for homogeneous transition metal catalysis, which has been reviewed recently [1–9]. Especially bidentate or tridentate NHC-ligands have shown their potential in many applications, for example C–C coupling reactions [10–15] or CH activation [16,17]. The first chiral *N*-heterocyclic carbene structures were published by Herrmann [18] and Enders [19] in 1996. Structural concepts, known from efficient stereodirecting phosphine ligands, were applied to *N*-heterocylic carbenes together with newly developed structural motifs. Chiral NHC-complexes have been used in different asymmetric catalytic reactions, e.g. the hydrosilylation [20,21], the conjugate addition of diethylzinc [22–25], hydrogenation [26–28] and the palladium-catalyzed allylic alkylation [29,30]. A significant number of selective catalysts based on *N*-heterocyclic carbene ligands were published during the last years and quite recently reviewed [30–35].

Some main concepts for ligand design have emerged. Gade and Bellemin-Laponnaz distinguish between five families of chiral *N*-heterocyclic carbene ligands [34], based on the type of chirality. Ligands with centers of chirality within the *N*-substituents [29,36–41] (**A**) or in the backbone of the heterocycle [42] (**B**), axial [43,44] (**C**) and planar chirality [45,46] (**D**) have been published. Fragments from the chiral pool, e.g. amino acids have been used for the synthesis of chiral NHC-ligands, e.g. for oxazoline units [20,28,47–51] (**E**). Some examples from each family (**A**–**E**) are given in Scheme 1.

We wanted to use the chiral pool in a different way by converting the naturally occurring amino acids to imidazoles, followed by quaternization and deprotonation to yield new chiral metal–NHC complexes with asymmetric centers near the carbene carbon. The additional stability of bidentate ligands and their palladium(II)- and platinum(II)-biscarbene complexes was described before [17,52–62] and we therefore aimed at combining both concepts by using methylene bridged bisimidazolium salts derived from natural L-amino acids as precursors for the metal complex synthesis of palladium(II)- and platinum(II)-biscarbene complexes.

2. Results and discussion

2.1. Preparation of the chiral imidazoles *1a–j*

It was shown by Bao that chiral imidazoles can be synthesized starting from L-amino acids, which were converted to chiral ionic liquids [63]. We modified the published procedure for the preparation of the imidazoles **1a**–**j** (without previous esterification of the L-amino acid) by substituting HCl/MeOH by $SOCl_2$/ROH, which is more convenient and turned out to be superior to the one-pot imidazole synthesis [12,53] where glyoxal and paraformaldehyde react with the amino acid ester hydrochloride in methanol solution.

The synthesized chiral imidazoles **1a**–**j** and the reaction conditions are given in Scheme 2. The amino acids react with glyoxal,

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[1] X-ray analysis.

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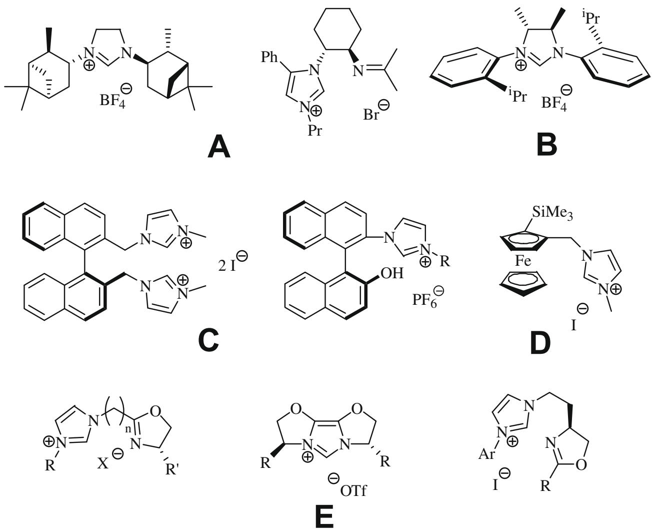
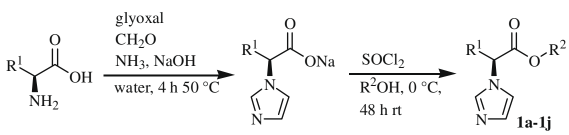


Scheme 1. Examples for precursors of chiral *N*-heterocyclic carbene ligands.



1a: Ala, $R^1 = CH_3$, $R^2 = CH_3$, 52%
1b: Ala, $R^1 = CH_3$, $R^2 = CH_2CH_3$, 29%
1c: Ala, $R^1 = CH_3$, $R^2 = (CH_2)_3CH_3$, 63%
1d: Val, $R^1 = CH(CH_3)_2$, $R^2 = CH_3$, 62%
1e: Val, $R^1 = CH(CH_3)_2$, $R^2 = CH_2CH_3$, 25%
1f: Leu, $R^1 = CH_2CH(CH_3)_2$, $R^2 = CH_3$, 71%
1g: Ile, $R^1 = CH(CH_3)CH_2CH_3$, $R^2 = CH_3$, 60%
1h: Phe, $R^1 = CH_2(C_6H_5)$, $R^2 = CH_3$, 36%
1i: Met, $R^1 = (CH_2)_2SCH_3$, $R^2 = CH_3$, 54%
1j: Asp, $R^1 = CH_2COOCH_3$, $R^2 = CH_3$, 31%

Scheme 2. Preparation and yields for the synthesis of imidazoles from amino acids.

formaldehyde and ammonia in water at 50 °C under basic conditions. For the necessary esterification we used thionyl chloride, which is a reliable method for the preparation of amino acid esters [64–66]. This strategy offers two possibilities to modify the product by using different amino acids (R^1) other than alanine (**1a**–**c**) and valine (**1d**–**e**) and various alcohols (R^2).

2.2. Preparation of the chiral bisimidazolium salts **2a**–**h**

As we have been worried about the stability of the chiral center we tried to keep the reaction temperatures as low as possible and therefore chose diiodomethane for the preparation of the bisimidazolium salts as the nucleophilic substitution reaction should need less activation energy compared to dibromomethane. Initially the substitution reaction was carried out in tetrahydrofuran at 100–130 °C according to known procedures [52], but the corresponding products could not be isolated. By screening different solvents at variable temperatures we found acetonitrile at temperatures of 70–80 °C to be the best choice (Scheme 3).

Reaction of imidazoles **1a**–**h** (derived from amino acids Ala, Val, Leu, Ile, Phe) with diiodomethane lead to the corresponding optically active bisimidazolium salts **2a**–**h** (Scheme 3). The analogous bisimidazolium salts derived from the imidazoles **1i** (Met) and **1j** (Asp) could not be isolated because of decomposition processes during the reaction or workup.

2.3. Preparation of the metal biscarbene complexes

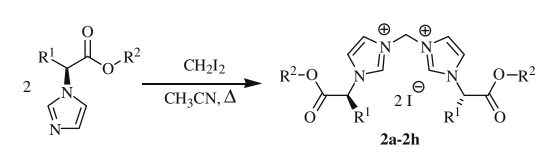
In situ deprotonation methods by palladium(II) acetate [58,67] or platinum(II) acetylacetonate [53] have proven to be reliable synthetic pathways for the synthesis of metal biscarbene complexes. The reactions are carried out in DMSO with different temperature settings. Similar to comparable systems it is necessary to increase the temperature slowly during a couple of hours to avoid decomposition of the ligand or precipitation of palladium/platinum black [53,56]. The bisimidazolium salts **2a** and **2d** were tested in these reactions (Scheme 4). Even after one week of drying under high vacuum, complexes **3a** and **3b** (Ala) could be only isolated as DMSO adducts, while the corresponding compounds **3c** and **3d** do not contain DMSO.

Unfortunately the complexes do not show any optical activity in dimethylsulfoxide or dimethylformamide solution. We suspect that the basic conditions and the relatively high temperature are responsible for the racemisation. We also tried other synthetic routes and conditions to avoid the racemization, like the transmetallation by Ag_2O [68] or other deprotonation reagents, which did not lead to optically active palladium or platinum compounds. Attempts to synthesize the free carbene were not successful; they lead to decomposition of the imidazolium salt.

2.4. NMR-analysis of the metal complexes

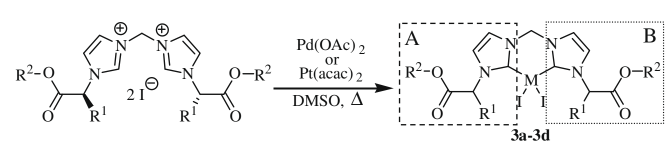
We thoroughly studied the NMR spectra of the metal–NHC biscarbene complexes, which are relatively complex due to the different stereoisomers. Although (*R,R*) and (*S,S*) configuration can not be distinguished in the NMR spectra they do show different signal sets for the "dashed" (A) and the "dotted" (B) fragments of the molecule (cf. Scheme 4). One example might be the $C_{carbene}$ shifts, which were found at 150.80 and 152.36 ppm (**3b**) and at 150.80 and 151.62 ppm (**3d**).

For all metal complexes we observe different ^1H- and ^{13}C-signals for all atoms of the substituents at the nitrogen atoms and for the imidazole core. For the methylene bridge of the platinum(II) compounds **3b** and **3d**, a doublet of doublets is detected in the ^1H NMR spectrum, an effect well known from other platinum(II) biscarbene complexes [52,53]. For the palladium(II) biscarbene complexes **3a** and **3c** a singlet is observed for both hydrogen atoms of the methylene bridge. The ^{13}C NMR spectra of all complexes (**3a**–**d**) show only one signal for the methylene bridge.



2a: Ala, $R^1 = CH_3$, $R^2 = CH_3$, 42%
2b: Ala, $R^1 = CH_3$, $R^2 = CH_2CH_3$, 50%
2c: Ala, $R^1 = CH_3$, $R^2 = (CH_2)_3CH_3$, 56%
2d: Val, $R^1 = CH(CH_3)_2$, $R^2 = CH_3$, 44%
2e: Val, $R^1 = CH(CH_3)_2$, $R^2 = CH_2CH_3$, 32%
2f: Leu, $R^1 = CH_2CH(CH_3)_2$, $R^2 = CH_3$, 26%
2g: Ile, $R^1 = CH(CH_3)CH_2CH_3$, $R^2 = CH_3$, 34%
2h: Phe, $R^1 = CH_2(C_6H_5)$, $R^2 = CH_3$, 26%

Scheme 3. Preparation and yields of the bisimidazolium salts.



3a: Ala, M = Pd, $R^1 = CH_3$, $R^2 = CH_3$, 39%
3b: Ala, M = Pt, $R^1 = CH_3$, $R^2 = CH_3$, 45%
3c: Val, M = Pd, $R^1 = CH(CH_3)_2$, $R^2 = CH_3$, 82%
3d: Val, M = Pt, $R^1 = CH(CH_3)_2$, $R^2 = CH_3$, 30%

Scheme 4. Preparation of the metal carbene complexes.

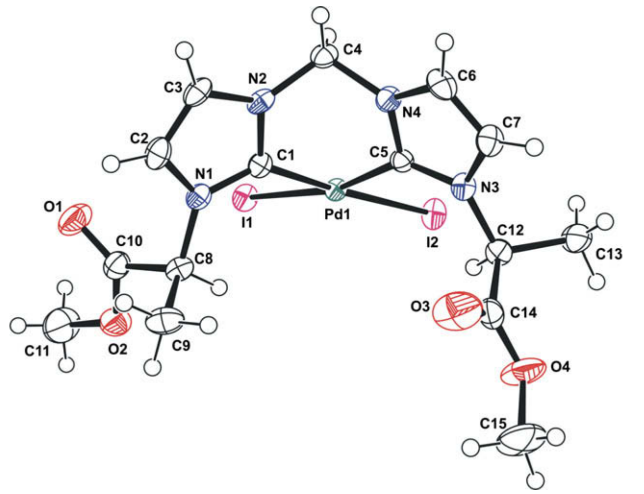


Fig. 1. ORTEP plot of the solid state structure of compound **3a**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are plotted as balls of arbitrary radii.

Table 1
Selected geometrical parameters of the solid state structure of **3a**.

3a[a]	
Pd(1)–C(1)	1.991(4)
Pd(1)–C(5)	1.998(4)
Pd(1)–I(1)	2.6649(4)
Pd(1)–I(2)	2.6516(5)
N(2)–C(4)–N(4)	108.9(3)
C(1)–Pd(1)–C(5)	83.98(17)
C(1)–Pd(1)–I(1)	88.90(12)
I(1)–Pd(1)–I(2)	93.35(14)
N(1)–C(1)–Pd(1)–I(1)	56.96(1)
Pd(1)–C(1)–N(2)–C(4)	−8.89(4)

[a] Distances in angstroms (Å) and angles in degrees (°).

2.5. X-ray crystal structure of complex 3a

The solid state structure of the palladium complex **3a** is given in Fig. 1. The crystals were obtained by slow diffusion of methanol into a DMSO solution of compound **3a**. The substituents at the imidazole have only a small effect on the geometry (Table 1) which is in good agreement with the published solid state structure of 1,1′-dimethyl-3,3′-methylenediimidazoline-2,2′-diylidenepalladium(II) diiodide [69]. The major difference is the asymmetry of **3a**, which can e.g. be found in the bond lengths of the Pd–I bonds (Table 1). The central six-membered ring of **3a** shows the expected boat conformation, which has already been observed for many other palladium(II)- and platinum(II)-NHC bishalogene complexes [12,52,53].

3. Conclusion

Although we had been aware of the potential lability of the chiral center we intended to create the chiral center as close as possible to the metal atom. A variety of natural L-amino acids could be converted successfully to chiral imidazoles and the corresponding chiral bisimidazolium salts. The new synthetic route offers the possibility for variation of the side chain R^1 through the amino acid and R^2 by choice of the alcohol during the esterification. After optimization of the temperature program we succeeded in the synthesis of palladium(II)- and platinum(II) *N*-heterocyclic biscarbene complexes. Unfortunately, our initial concerns were confirmed as the metal complexes did not show any optical activity. Additionally we report the solid state structure of 1,1′-bis-[(1*S*)-1-methoxycarbonyl-ethyl]-3,3′-methylenediimidazoline-2,2′-diylidenepalladium(II) diiodide **3a**. Different reaction conditions were tested, but the chiral bisimidazolium salts could not be converted into chiral metal complexes. Attempts to reduce the acidity of the proton at the asymmetric carbon atom are under way and seem to be necessary to succeed in making chiral complexes.

4. Experimental

4.1. General experimental methods

Platinum(II) acetylacetonate and palladium(II) acetate were purchased from ACROS. All other chemicals and solvents were obtained from common suppliers and used without further purification. Melting points were measured with an Electrothermal IA9100 and were uncorrected. A Perkin Elmer polarimeter (model 341) was used to prove the optical activity. Elemental analysis, mass spectrometry as well as NMR spectrometry were performed by our departmental analytical laboratory. Elemental analyses were measured with an Eurovektor Hekatech EA-3000 Elemental Analyzer. The mass spectra were recorded with a Bruker Esquire mass spectrometer, which is equipped with an ion trap detector. The NMR spectra were measured with a Bruker AC 300 P NMR-spectrometer. ^1H NMR spectra were recorded at 300.13 MHz and the ^{13}C NMR spectra at 75.475 MHz. The solvent was used as internal reference. The imidazoles **1a**–**j** were prepared with some modifications according to known procedures [63,66].

4.2. Synthesis of the imidazoles

4.2.1. (S)-2-(1-Imidazolyl)-propionicacidmethylester 1a

A mixture of formaldehyde (37% solution in water, 17.12 mL, 0.22 mol formaldehyde) and glyoxal (40% solution in water, 25.13 mL, 0.22 mol glyoxal) was heated to 50 °C. Meanwhile L-alanine (20 g, 0.22 mol), sodium hydroxide (8.8 g, 0.22 mol) and ammonia (25% solution in water, 16.47 mL, 0.22 mol ammonia) were put together and water was added until all components were dissolved. This solution was added dropwise to the formaldehyde glyoxal mixture over 0.5 h. The reaction was stirred at 50 °C for 4 h. Afterwards the solvent was removed in vacuo.

The obtained solid was dissolved in methanol and cooled to 0 °C. Thionyl chloride (3.26 mL, 0.44 mol) was added slowly over a period of 2 h, the mixture was then warmed up to room temperature and stirred for 48 h. Removal of the solvent under reduced pressure lead to an oily substance, which was treated with a saturated sodium carbonate water solution to adjust the pH (8–9). The product was extracted with ethyl acetate, the organic layer dried with sodium sulfate and the solvent evaporated in vacuo. The product was purified by column chromatography (ethyl acetate/petroleum ether 4:1, silica gel 60G) to obtain an orange solid. Yield: 17.46 g (52%). m.p. = 33 °C. $[\alpha]_D^{25}$ = +8.3 (*c* = 0.09 mol/L, methanol). ^1H NMR (DMSO-d_6): δ 1.64 (d, *J* = 7.4 Hz, 3H, C*H*$_3$), 3.68 (s, 3H, OC*H*$_3$), 5.25 (q, *J* = 7.4 Hz, 1H, C*H*), 6.91 (s, 1H, NC*H*CHN), 7.24 (s, 1H, NCHC*H*N), 7.72 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 17.95 (*C*H$_3$), 52.49 (O*C*H$_3$), 53.85 (*C*H), 118.52 (N*C*HCHN), 128.22 (NCH*C*HN), 136.88 (N*C*HN), 171.05 (*C*O) ppm. $C_7H_{10}N_2O_2$ (154.17): Calc.: C, 54.54; H, 6.54; N, 17.87. Found: C, 54.23; H, 6.54; N, 17.87%. MS (ESI): *m*/*z* = 154.9 [M$^+$]. IR 3110, 3027, 2964, 1728, 1246, 1073, 751, 661 cm^{-1}.

4.2.2. (S)-2-(1-Imidazolyl)-propionicacidethylester 1b

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.045 mol L-alanine (4 g) and ethanol in the esterification step. The product was obtained as a yellow oil. Yield: 2.22 g (29%). $[\alpha]_D^{25}$ = +12.5 (*c* = 0.09 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 1.18 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 1.64 (d, *J* = 7.3 Hz, 3H, CH_3), 4.13 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 5.21 (q, *J* = 7.3 Hz, 1H, C*H*), 6.90 (s, 1H, NC*H*CHN), 7.23 (s, 1H, NCHC*H*N), 7.71 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.89 (CH_2CH_3), 17.96 ($CHCH_3$), 53.91 (*C*H), 61.23 (OCH_2), 118.49 (N*C*HCHN), 128.15 (NCH*C*HN), 136.83 (N*C*HN), 170.52 (*C*O) ppm. $C_8H_{12}N_2O_2$ (168.20): Calc.: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.22; H, 7.28; N, 16.76%. MS (ESI): *m*/*z* = 168 [M$^+$]. IR 2986, 1736, 1192, 1089, 1017, 662 cm^{-1}.

4.2.3. (S)-2-(1-Imidazolyl)-propionicacidbutylester **1c**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.056 mol L-alanine (5 g) and butanol in the esterification step. The product was obtained as a yellow oil. Yield: 6.94 g (63%). $[\alpha]_D^{25}$ = +7.4 (*c* = 0.07 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.86 (t, *J* = 7.4 Hz, 3H, $O(CH_2)_3CH_3$), 1.21–1.33 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.49–1.58 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.64 (d, *J* = 7.3 Hz, 3H, CH_3), 4.08 (t, *J* = 6.5 Hz, 2H, OCH_2), 5.12 (q, *J* = 7.3 Hz, 1H, C*H*), 6.89 (s, 1H, NC*H*CHN), 7.22 (s, 1H, NCHC*H*N), 7.70 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.46 (CH_2CH_3), 17.89 ($CHCH_3$), 18.41 (CH_2), 29.96 (CH_2), 53.92 (*C*H), 64.80 (OCH_2), 118.47 (N*C*HCHN), 128.16 (NCH*C*HN), 136.85 (N*C*HN), 170.56 (*C*O) ppm. $C_{10}H_{16}N_2O_2$ (196.25): Calc.: C, 61.20; H, 8.22; N, 14.27. Found: C, 61.17; H, 8.35; N, 14.29%. MS (ESI): *m*/*z* = 197 [M$^+$]. IR 2960, 1737, 1188, 1088, 662 cm^{-1}.

4.2.4. (S)-2-(1-Imidazolyl)-3-methylbutyricacidmethylester **1d**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.034 mol L-valine (3.98 g). The product was obtained as a yellow oil. Yield: 3.83 g (62%). $[\alpha]_D^{25}$ = +9.2 (*c* = 0.06 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.71 (d, *J* = 6.7 Hz, 3H, CH_3), 0.91 (d, *J* = 6.7 Hz, 3H, CH_3,), 2.30–2.42 (m, 1H, $(CH_3)_2CH$), 3.7 (s, 3H, OCH_3), 4.8 (d, *J* = 9.1 Hz, 1H, $(CH_3)_2CHCH$), 6.92 (s, 1H, NC*H*CHN), 7.24 (s, 1H, NCHC*H*N), 7.71 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 18.11 (CH_3), 18.89 (CH_3), 31.16 (*C*H), 52.36 (OCH_3), 64.52 (*C*H), 118.84 (N*C*HCHN), 128.34 (NCH*C*HN), 137.42 (N*C*HN), 170.14 (*C*O) ppm. $C_9H_{14}N_2O_2$ (182.22): Calc.: C, 59.32; H, 7.74; N, 15.37. Found: C, 59.54; H, 7.84; N, 15.40%. MS (ESI): *m*/*z* = 183 [M$^+$]. IR 2967, 1741, 1199, 746, 662 cm^{-1}.

4.2.5. (S)-2-(1-Imidazolyl)-3-methylbutyricacidethylester **1e**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.034 mol L-valine (3.98 g) as well as ethanol in the esterification step. The product was obtained as an orange oil. Yield: 1.65 g (25%). $[\alpha]_D^{25}$ = +13.6 (*c* = 0.18 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.78 (d, *J* = 6.7 Hz, 3H, CH_3), 0.98 (d, *J* = 6.7 Hz, 3H, CH_3), 1.28 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3), 2.39–2.46 (m, 1H, $(CH_3)_2CH$), 4.18–4.30 (m, 2H, OCH_2CH_3), 4.83 (d, *J* = 9.1 Hz, 1H, $(CH_3)_2CHCH$), 6.99 (s, 1H, NC*H*CHN), 7.30 (s, 1H, NCHC*H*N), 7.78 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.90 (OCH_2CH_3), 18.12 (CH_3), 18.87 (CH_3), 31.22 ($(CH_3)_2CH$), 61.22 (CH_2), 64.63 ($(CH_3)_2CHCH$), 118.84 (N*C*HCHN), 128.31 (NCH*C*HN), 137.41 (N*C*HN), 169.61 (*C*O) ppm. $C_{10}H_{16}N_2O_2$ (196.25): Calc.: C, 61.20; H, 8.22; N, 14.27. Found: C, 61.26; H, 8.26; N, 14.22%. MS (ESI): *m*/*z* = 196 [M$^+$]. IR 2968, 1737, 1187, 1020, 737, 662 cm^{-1}.

4.2.6. (S)-2-(1-Imidazolyl)-4-methylpentanoicacidmethylester **1f**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.03 mol L-leucine (4.00 g). The product was obtained as an orange oil. Yield: 4.15 g (71%). $[\alpha]_D^{25}$ = +1.7 (*c* = 0.06 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.90 (d, *J* = 6.6 Hz, 3H, CH_3), 0.94 (d, *J* = 6.5 Hz, 3H, CH_3), 1.11–1.30 (m, 1H, $(CH_3)_2CH$), 1.90–2.15 (m, 2H, CH_2), 3.74 (s, 3H, OCH_3), 5.20–5.25 (m, *J* = 4.9 Hz, 1H, $(CH_3)_2CHCH_2CH$), 6.97 (s, 1H, NC*H*CHN), 7.32 (s, 1H, NCHC*H*N), 7.81 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 20.96 (CH_3), 22.52 (CH_3), 24.22 ($(CH_3)_2CHCH_2$), 40.33 (CH_2), 52.46 (OCH_3), 56.79 (CH_2CHCO), 118.63 (N*C*HCHN), 128.28 (NCH*C*HN), 137.34 (N*C*HN), 170.87 (*C*O) ppm. $C_{10}H_{16}N_2O_2$ (196.25): Calc.: C, 61.20; H, 8.22; N, 14.17. Found: C, 61.23; H, 8.33; N, 14.06%. MS (ESI): *m*/*z* = 196 [M$^+$]. IR 2957, 1742, 1199, 662 cm^{-1}.

4.2.7. (2S,3S)-2-(1-Imidazolyl)-3-methylpentanoicacidmethylester **1g**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.03 mol L-isoleucine (4.00 g). The product was obtained as an orange oil. Yield: 3.56 g (60%). $[\alpha]_D^{25}$ = +13.2 (*c* = 0.08 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.88 (t, *J* = 7.2 Hz, 3H, CH_3CH_2), 0.98 (d, *J* = 6.8 Hz, 3H, CH_3CH), 1.01–1.19 (m, 2H, CH_3CH_2), 2.23–2.27 (m, 1H, CH_3CH), 3.80 (s, 3H, CH_3O), 4.93 (d, *J* = 9.4 Hz, 1H, $CH_3CH_2CH(CH_3)CH$), 7.01 (s, 1H, NC*H*CHN), 7.34 (s, 1H, NCHC*H*N), 7.82 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 10.47 (CH_3CH_2), 15.29 (CH_3CH), 24.33 (CH_2), 37.14 (CH_3CH), 52.41 (OCH_3), 63.52 ($CH_2CH(CH_3)CH$), 118.91 (N*C*HCHN), 128.42 (NCH*C*HN), 137.48 (N*C*HN), 170.29 (*C*O) ppm. $C_{10}H_{16}N_2O_2$ (196.25): Calc.: C, 61.20; H, 8.22; N, 14.17. Found: C, 61.00; H, 8.35; N, 13.94%. MS (ESI): *m*/*z* = 196 [M$^+$]. IR 2965, 1742, 1198, 741, 662 cm^{-1}.

4.2.8. (S)-2-(1-Imidazolyl)-3-phenylpropionicacidmethylester **1h**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.03 mol L-phenylalanine (5.00 g). The product was obtained as a brown oil. Yield: 2.52 g (36%). $[\alpha]_D^{25}$ = −59.5 (*c* = 0.08 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 3.27–3.46 (m, 2H, CH_2), 3.68 (s, 3H, OCH_3), 5.39–5.44 (m, 1H, arom. C*H*), 6.83 (s, 1H, NC*H*CHN), 7.09–7.25 (m, 6H, NCHC*H*N, arom. C*H*), 7.57 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 37.48 (CH_2), 52.56 (OCH_3), 59.59 (*C*H), 118.67 (N*C*HCHN), 126.7 (*C*H), 128.09 (NCH*C*H), 128.24 (arom. *C*H), 128.75 (arom. *C*H), 136.25 (arom. *C*), 137.29 (N*C*HN), 170.06 (*C*O) ppm. $C_{13}H_{14}N_2O_2$ (230.27): Calc.: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.19; H, 6.20; N, 11.79%. MS (ESI): *m*/*z* = 230 [M$^+$]. IR 2954, 1740, 1172, 745, 699, 660 cm^{-1}.

4.2.9. (S)-2-(1-Imidazolyl)-4-methylsulfanylbutyricacidmethylester **1i**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.026 mol L-methionine (4.00 g). The product was obtained as a red-brown oil. Yield: 3.11 g (54%). $[\alpha]_D^{25}$ = −31.3 (*c* = 0.09 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 2.02 (s, 3H, SCH_3), 2.24–2.35 (m, 4H, CH_2CH_2), 3.68 (s, 3H, OCH_3), 5.23 (t, *J* = 6.3 Hz, 1H, C*H*), 6.92 (s, 1H, NC*H*CHN), 7.25 (s, 1H, NCHC*H*N), 7.71 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 14.5 (SCH_3), 29.26 (CH_2), 31.1 (CH_2), 52.65 (OCH_3), 57.28 (*C*H), 118.67 (N*C*HCHN), 128.61 (NCH*C*HN), 137.52 (N*C*HN), 170.29 (*C*O) ppm. $C_9H_{14}N_2O_2S$ (214.28): Calc.: C, 50.45; H, 6.59; N, 13.07; S, 14.96. Found: C, 50.64; H, 6.76; N, 12.85; S, 14.33%. MS (ESI): *m*/*z* = 214 [M$^+$]. IR 2918, 1740, 1229, 733, 661 cm^{-1}.

4.2.10. (S)-2-(1-Imidazolyl)-succinicaciddimethylester **1j**

The synthesis was performed following the procedure described above for the preparation of **1a** using 0.034 mol L-aspartate (4.53 g). The product was obtained as a yellow oil. Yield: 2.25 g (31%). $[\alpha]_D^{25}$ = −8.9 (*c* = 0.06 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 3.12–3.33 (m, 2H, CH_2), 3.59 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 5.49–5.54 (m, 1H, C*H*), 6.88 (s, 1H, NC*H*CHN), 7.24 (s, 1H, NCHC*H*N), 7.73 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 36.38 (CH_2), 51.84 (OCH_3), 52.79 (OCH_3), 54.88 (*C*H), 118.68 (N*C*HCHN), 128.43 (NCH*C*HN), 137.54 (N*C*HN), 169.35 (*C*O), 170.01 (*C*O) ppm. $C_9H_{12}N_2O_4S$ (212.27): Calc.: C, 50.94; H, 5.70; N, 13.20. Found: C, 50.93; H, 5.86; N, 13.07%. MS (ESI): *m*/*z* = 212 [M$^+$]. IR 2956, 1730, 1167, 661 cm^{-1}.

4.3. Synthesis of the bisimidazolium salts

4.3.1. 1,1′-Bis-[(S)-1-methoxycarbonylethyl]-3,3′-methylenediimidazolium diiodide **2a**

The imidazole **1a** (3.99 g, 0.026 mol), diiodomethane (1.04 mL, 0.013 mol) and 10 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 3 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 3.15 g (42%). $[\alpha]_D^{25}$ = +2.6 (*c* = 0.02 mol/L, methanol). m.p.: decomposition at 170.8 °C. ^{1}H NMR (DMSO-d_6): δ 1.78 (d, *J* = 7.3 Hz, 6H, C*H*$_3$), 3.75 (s, 6H, OC*H*$_3$), 5.68 (q, *J* = 7.3 Hz, 2H, C*H*), 6.73 (s, 2H, NC*H*$_2$ N), 8.04 (s, 2H, NC*H*CHN), 8.08 (s, 2H, NCHC*H*N), 9.59 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 16.95 (*C*H$_3$), 53.15 (O*C*H$_3$), 57.08 (*C*H), 58.45 (N*C*H$_2$N), 121.94 (N*C*HCHN), 122.53 (NCH*C*HN), 137.89 (N*C*HN), 168.89 (*C*O) ppm. $C_{15}H_{22}I_2N_4O_4$ (576.16): Calc.: C, 31.27; H, 3.85; N, 9.72. Found: C, 31.28; H, 3.71; N, 9.82%. IR 3071, 1746, 1166, 761, 616 cm^{-1}.

4.3.2. 1,1′-Bis-[(S)-1-ethoxycarbonylethyl]-3,3′-methylenediimidazolium diiodide **2b**

The imidazole **1b** (1.12 g, 6.7 mmol), diiodomethane (0.27 mL, 3.3 mmol) and 4 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 4 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 1.01 g (50%). m.p.: decomposition at 107 °C. $[\alpha]_D^{25}$ = +3.7 (*c* = 0.01 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 1.23 (t, *J* = 7.1 Hz, 6H, CH$_2$C*H*$_3$), 1.78 (d, *J* = 7.3 Hz, 6H, CHC*H*$_3$), 4.11 (q, *J* = 6.9 Hz, 4H, C*H*$_2$CH$_3$), 5.67 (q, *J* = 7.3 Hz, 2H, C*H*CH$_3$), 6.75 (s, 2H, NC*H*$_2$ N), 8.05 (s, 2H, NC*H*CHN), 8.08 (s, 2H, NCHC*H*N), 9.61 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.83 (CH$_2$*C*H$_3$), 17.06 (CH*C*H$_3$), 57.32 (*C*HCH$_3$), 58.53 (N*C*H$_2$N), 62.26 (*C*H$_2$CH$_3$), 121.98 (N*C*HCHN), 123.04 (NCH*C*HN), 137.97 (N*C*HN), 168.5 (*C*O) ppm. $C_{17}H_{26}I_2N_4O_4$ (604.22): Calc.: C, 33.79; H, 4.34; N, 9.27. Found: C, 33.75; H, 4.37; N, 9.25%. IR 3072, 1747, 1165, 1014, 751, 615 cm^{-1}.

4.3.3. 1,1′-Bis-[(S)-1-butoxycarbonylethyl]-3,3′-methylenediimidazolium diiodide **2c**

The imidazole **1c** (2 g, 0.01 mol), diiodomethane (0.40 mL, 0.005 mol) and 4 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 4 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 1.85 g (56%). m.p.: decomposition at 123.5 °C. $[\alpha]_D^{25}$ = +3.4 (*c* = 0.01 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.88 (t, *J* = 7.4 Hz, 6H, O(CH$_2$)$_3$C*H*$_3$), 1.25–1.38 (m, 4H, OCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.54–1.63 (m, 4H, OCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.78 (d, *J* = 7.3 Hz, 6H, C*H*$_3$), 4.09–5.64 (m, 4H, OC*H*$_2$), 5.68 (q, *J* = 7.3 Hz, 2H, C*H*), 6.73 (s, 2H, NC*H*$_2$N), 8.05 (s, 4H, NC*H*C*H*N), 9.58 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.47 (CH$_2$*C*H$_3$), 17.06 (CH*C*H$_3$), 18.44 (*C*H$_2$), 29.86 (*C*H$_2$), 57.24 (*C*H), 59.11 (N*C*H$_2$N), 65.83 (O*C*H$_2$), 122.00 (N*C*HCHN), 123.10 (NCH*C*HN), 138.00 (N*C*HN), 168.57 (*C*O) ppm. $C_{21}H_{34}I_2N_4O_4$ (660.33): Calc.: C, 38.20; H, 5.19; N, 8.48. Found: C, 38.21; H, 5.22; N, 8.41%. IR 2958, 1748, 1196, 1167, 731, 615 cm^{-1}.

4.3.4. 1,1′-Bis-[(S)-1-methoxycarbonyl-2-methylpropyl]-3,3′-methylenediimidazolium diiodide **2d**

The imidazole **1d** (3.66 g, 0.02 mol), diiodomethane (0.80 mL, 0.01 mol) and 5 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 0.5 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 2.78 g (44%). m.p.: decomposition at 167 °C. $[\alpha]_D^{25}$ = +24.2 (*c* = 0.01 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.85 (d, *J* = 6.7 Hz, 6H, C*H*$_3$), 0.95 (d, *J* = 6.7 Hz, 6H, C*H*$_3$), 2.39–2.51 (m, 2H, (CH$_3$)$_2$C*H*), 3.78 (s, 6H, OC*H*$_3$), 5.39 (d, *J* = 7.7 Hz, 2H, (CH$_3$)$_2$CHC*H*), 6.74 (s, 2H, NC*H*$_2$ N), 8.02 (s, 4H, NC*H*C*H*N), 8.11 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 18.04 (*C*H$_3$), 18.46 (*C*H$_3$), 31.48 ((CH$_3$)$_2$*C*H), 53.25 (O*C*H$_3$), 58.85 (N*C*H$_2$N), 66.66 (*C*H), 121.94 (N*C*HCHN), 123.76 (NCH*C*HN), 138.17 (N*C*HN), 168.18 (*C*O) ppm. $C_{19}H_{30}I_2N_4O_4$ (632.27): Calc.: C, 36.09; H, 4.78; N, 8.86. Found: C, 36.22; H, 4.58; N, 8.84%. IR 3051, 1741, 1158, 769, 633 cm^{-1}.

4.3.5. 1,1′-Di-[(S)-1-ethoxycarbonyl-2-methylpropyl))-3,3′-methylenediimidazolium diiodide **2e**

The imidazole **1e** (0.65 g, 3.3 mmol), diiodomethane (0.13 mL, 1.7 mmol) and 5 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 8 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 0.36 g (32%). m.p.: decomposition at 188 °C. $[\alpha]_D^{25}$ = −16.7 (*c* = 0.02 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.86 (d, *J* = 6.7 Hz, 6H, C*H*$_3$CH), 0.97 (d, *J* = 6.7 Hz, 6H, C*H*$_3$CH), 1.26 (t, *J* = 7.1 Hz, 6H, C*H*$_3$CH$_2$O) 2.43–2.52 (m, 2H, (CH$_3$)$_2$C*H*), 4.19–4.32 (m, 4H, OC*H*$_2$CH$_3$), 5.40 (d, *J* = 7.6 Hz, 2H, (CH$_3$)$_2$CHC*H*), 6.74 (s, 2H, NC*H*$_2$N), 8.01 (s, 2H, NC*H*CHN), 8.12 (s, 2H, NCHC*H*N), 9.70 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 13.86 (*C*H$_3$CH), 17.95 (*C*H$_3$CH), 18.36 (*C*H$_3$CH$_2$O), 31.44 ((CH$_3$)$_2$*C*H), 58.80 (N*C*H$_2$N), 62.31 (CH$_3$*C*H$_2$O), 66.61 ((CH$_3$)$_2$CH*C*H), 121.85 (N*C*HCHN), 123.74 (NCH*C*HN), 138.07 (N*C*HN), 167.59 (*C*O) ppm. $C_{21}H_{34}I_2N_4O_4$ (660.33): Calc.: C, 38.20; H, 5.19; N, 8.48. Found: C, 37.50; H, 4.99; N, 8.46%. IR 3026, 1732, 1199, 1158, 1017, 770 cm^{-1}.

4.3.6. 1,1′-Bis-[(S)-1-methoxycarbonyl-3-methylbutyl]-3,3′-methylenediimidazolium diiodide **2f**

The imidazole **1f** (5.18 g, 0.026 mol), diiodomethane (1.05 mL, 0.013 mol) and 7 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 48 h at 70 °C and 24 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a colorless powder. Yield: 2.24 g (26%). m.p.: decomposition at 127 °C. $[\alpha]_D^{25}$ = +3.4 (*c* = 0.02 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.88 (d, *J* = 6.6 Hz, 6H, C*H*$_3$), 0.92 (d, *J* = 6.5 Hz, 6H, C*H*$_3$), 1.27–1.40 (m, 2H, (CH$_3$)$_2$C*H*), 1.99–2.13 (m, 4H, C*H*$_2$), 3.76 (s, 6H, OC*H*$_3$), 5.62–5.67 (m, 2H, (CH$_3$)$_2$CHCH$_2$C*H*), 6.74 (s, 2H, NC*H*$_2$ N), 8.10 (s, 4H, NC*H*C*H*N), 9.69 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 21.04 (*C*H$_3$), 22.28 (*C*H$_3$), 24.10 ((CH$_3$)$_2$*C*H), 39.50 (CH*C*H$_2$CH), 53.37 (O*C*H$_3$), 58.92 (N*C*H$_2$N), 60.00 ((CH$_3$)$_2$CHCH$_2$*C*H), 122.32 (N*C*HCHN), 123.21 (NCH*C*HN), 138.25 (N*C*HN), 168.81 (*C*O) ppm. $C_{21}H_{34}I_2N_4O_4$ (660.33): Calc.: C, 38.20; H, 5.19; N, 8.48. Found: C, 38.09; H, 5.22; N, 8.51%. IR 3058, 2961, 1736, 1208, 1168, 764, 631 cm^{-1}.

4.3.7. 1,1′-Bis-[(1S,2S)-1-methoxycarbonyl-2-methylbutyl)]-3,3′-methylenediimidazolium diiodide **2g**

The imidazole **1 g** (1.94 g, 9.9 mmol), diiodomethane (0.39 mL, 4.9 mmol) and 6 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 24 h at 70 °C and 3 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a pale yellow powder. Yield: 1.09 g (34%). m.p.: decomposition at 150 °C. $[\alpha]_D^{25}$ = +25.1 (*c* = 0.02 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 0.85 (t, *J* = 7.5 Hz, 6H, C*H*$_3$CH$_2$), 0.94 (d, *J* = 6.8 Hz, 6H, C*H*$_3$CH), 1.01–1.31 (m, 4H, CH$_3$C*H*$_2$), 2.20–2.28 (m, 2H, CH$_3$C*H*), 3.79 (s, 6H, C*H*$_3$O), 5.43 (d, *J* = 7.7 Hz, 2H, CH$_3$CH$_2$CH(CH$_3$)C*H*), 6.73 (s, 2H, NC*H*$_2$N), 8.04 (s, 2H, NC*H*CHN), 8.12 (s, 2H, NCHC*H*N), 9.71 (s, 2H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 10.73 (*C*H$_3$CH$_2$), 14.79 (*C*H$_3$CH), 24.39 (*C*H$_2$), 37.45 (CH$_3$*C*H), 53.20 (O*C*H$_3$), 58.79 (N*C*H$_2$N), 65.85 (CH$_2$CH(CH$_3$)*C*H), 121.94 (N*C*HCHN), 123.69 (NCH*C*HN), 138.18 (N*C*HN), 168.17 (*C*O) ppm. $C_{21}H_{34}N_4O_4I_2$ (660.33): Calc.:

C, 38.20; H, 5.19; N, 8.48. Found: C, 38.23; H, 5.23; N, 8.43%. IR 3045, 2967, 1740, 1203, 1157, 766, 633 cm^{-1}.

4.3.8. 1,1′-Bis-[(S)-1-methoxycarbonyl-2-phenylethyl]-3,3′-methylenediimidazolium diiodide ***2h***

The imidazole **1 h** (2 g, 8.7 mmol), diiodomethane (0.35 mL, 4.3 mmol) and 7 mL acetonitrile were added to a ACE pressure tube. The reaction mixture was stirred for 12 h at 70 °C and 3 h at 80 °C. The product was precipitated with diethyl ether and washed with ethyl acetate. The product was obtained as a yellow powder. Yield: 0.83 g (26%). m.p.: decomposition at 81 °C. $[\alpha]_D^{25} = -2.2$ (*c* = 0.01 mol/L, methanol). ^{1}H NMR (DMSO-d_6): δ 3.41–3.72 (m, 4H, C*H*$_2$), 3.80 (s, 6H, OC*H*$_3$), 5.98–6.05 (m, 2H, C*H*), 6.57–6.60 (m, 2H, NC*H*$_2$N), 7.10–7.22 (m, 10H, C*H* arom.), 7.72 (s, 1H, NC*H*CHN), 7.74 (s, 1H, NC*H*CHN), 8.05 (s, 2H, NCHC*H*N), 9.43 (s, 1H, NC*H*N), 9.46 (s, 1H, NC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 36.99 (*C*H$_2$), 53.26 (O*C*H$_3$), 58.29 (N*C*H$_2$N), 62.39 (*C*H), 62.48 (*C*H), 121.60 (N*C*HCHN), 123.30 (NCH*C*HN), 123.40 (NCH*C*HN), 127.25 (*C*H arom.), 128.55 (*C*H arom.), 134.38 (*C* arom.), 137.87 (N*C*HN), 137.91 (N*C*HN), 167.65 (*C*O) ppm. $C_{27}H_{30}I_2N_4O_4$ (728.36): Calc.: C, 44.52; H, 4.15; N, 7.69. Found: C, 44.34; H, 4.04; N, 7.54%. IR 3059, 1742, 1158, 748, 701, 614 cm^{-1}.

4.4. Synthesis of the metal carbene complexes

4.4.1. 1,1′-Bis-(1-methoxycarbonylethyl)-3,3′-methylenediimidazoline-2,2′-diylidenepalladium(II) diiodide ***3a***

Palladium(II) acetate (0.071 g, 0.32 mmol) and **2a** (0.2 g, 0.32 mmol) were dissolved in 5 mL dimethylsulfoxide. The mixture was stirred for 1 h at 40 °C, 3 h at 60 °C, 4 h at 80 °C, 12 h at r.t. and 1 h at 100 °C. After removal of the dimethylsulfoxide in vacuum, the resulting solid was washed with cold tetrahydrofuran and methanol. The product was obtained as a yellow powder. Yield: 0.093 g (39%). m.p.: decomposition at 250 °C. ^{1}H NMR (DMSO-d_6): δ 1.50 (d, *J* = 7.5 Hz, C*H*$_3$), 1.69 (d, *J* = 7.1 Hz, C*H*$_3$), 1.70 (d, *J* = 7.4 Hz, C*H*$_3$), 3.60 (s, OCC*H*$_3$), 3.63 (s, OCC*H*$_3$), 3.69 (s, OCC*H*$_3$), 6.02 (br, CH$_3$C*H*), 6.23 (br, CH$_3$C*H*) 6.24 (br, CH$_3$C*H*), 6.33 (s, NC*H*$_2$N), 7.54–7.58 (m, NC*H*CHN), 7.67–7.68 (m, NCHC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 16.28 (*C*H$_3$), 16.91 (*C*H$_3$), 18.59 (*C*H$_3$), 52.57 (OC*C*H$_3$), 52.60 (OC*C*H$_3$), 52.75 (OC*C*H$_3$), 58.78 (CH$_3$*C*H), 62.86 (N*C*H$_2$N), 119.90 (N*C*HCHN), 120.14 (N*C*HCHN), 120.92 (N*C*HCHN), 122.17 (NCH*C*HN), 122.44 (NCH*C*HN), 169.85 (*C*O), 169.88 (*C*O) 170.11 (*C*O) ppm. $C_{15}H_{20}N_4O_4I_2Pd \cdot 0.5\ C_2H_6SO$: Calc.: C, 26.71; H, 3.22; N, 7.79; S, 2.23. Found: C, 26.94; H, 3.19; N, 7.52; S, 2.11%. IR 3154, 3113, 2943, 1741, 1462, 1414, 1309, 1206, 1176, 1087, 980, 752, 678 cm^{-1}.

4.4.2. 1,1′-Bis-(1-methoxycarbonylethyl)-3,3′-methylenediimidazoline-2,2′-diylideneplatinum(II) diiodide ***3b***

Platinum(II) acetylacetonate (0.034 g, 0.087 mmol) and **2a** (0.05 g, 0.087 mmol) were dissolved in 3 mL dimethylsulfoxide. The mixture was stirred for 3 h at 40 °C, 3 h at 60 °C, 1.5 h at 80 °C, 1 h at 100 °C, 12 h at rt and 1 h at 130 °C. The dimethylsulfoxide was removed in vacuum and the resulting solid was washed with cold tetrahydrofuran and methanol. The product was obtained as a yellow powder. Yield: 0.032 g (45%). m.p.: decomposition at 295 °C. ^{1}H NMR (DMSO-d_6): δ 1.45 (d, *J* = 7.5 Hz, C*H*$_3$), 1.71 (d, *J* = 7.4, C*H*$_3$), 3.61 (s, OC*H*$_3$), 3.69 (s, OC*H*$_3$), 6.03–6.31 (m, NC*H*$_2$N, C*H*), 7.53–7.54 (m, NC*H*CHN), 7.60–7.62 (m, NCHC*H*N) ppm. ^{13}C NMR (DMSO-d_6): δ 16.15 (*C*H$_3$), 18.31 (*C*H$_3$), 52.56 (O*C*H$_3$), 52.70 (O*C*H$_3$), 57.91 (*C*H), 58.93 (*C*H), 62.30 (N*C*H$_2$N), 119.39 (N*C*HCHN), 120.38 (N*C*HCHN), 121.07 (NCH*C*HN), 121.41 (NCH*C*HN), 150.80 (N*C*N), 152.36 (N*C*N), 169.71 (*C*O), 169.91 (*C*O) ppm. $C_{15}H_{20}N_4O_4I_2Pt \cdot 0.65\ C_2H_6SO$: Calc.: C, 23.87; H, 2.94; N, 6.83; S, 2.54. Found: C, 23.81; H, 2.62; N, 6.64; S, 2.81%. IR 3155, 3114, 1742, 1207, 1088, 750, 683 cm^{-1}.

4.4.3. 1,1′-Bis-(1-methoxycarbonyl-2-methylpropyl)-3,3′-methylenediimidazoline-2,2′-diylidene-palladium(II) diiodide ***3c***

Palladium(II) acetate (0.071 g, 0.32 mmol) and **2d** (0.2 g, 0.32 mmol) were dissolved in 5 mL dimethylsulfoxide. The mixture was stirred for 1 h at 40 °C, 3 h at 60 °C, 4 h at 80 °C, 12 h at r.t. and 1 h at 100 °C. The dimethylsulfoxide was removed in vacuum and the resulting solid was washed with cold tetrahydrofuran and methanol. The product was obtained as a yellow powder. Yield: 0.192 g (82%). m.p.: decomposition at 240 °C. ^{1}H NMR (DMSO-d_6): δ 0.47 (d, *J* = 6.7 Hz, C*H*$_3$), 0.72 (d, *J* = 6.5 Hz, C*H*$_3$), 1.06 (d, *J* = 6.5 Hz, C*H*$_3$), 2.32–2.51 (m overlapped by DMSO-d_6, (CH$_3$)$_2$C*H*)), 3.63 (s, OCC*H*$_3$), 3.72 (s, OCC*H*$_3$), 5.60–5.72 (br, (CH$_3$)$_2$CHC*H*), 5.85–5.98 (br, (CH$_3$)$_2$CHC*H*), 6.36 (s, NC*H*$_2$N), 7.48 (s, NCHC*H*N), 7.64 (s, NC*H*CHN), 7.70–7.72 (m, NC*H*CHN) ppm. ^{13}C NMR (DMSO-d_6): δ 18.41 (*C*H$_3$), 18.79 (*C*H$_3$), 19.05 (*C*H$_3$), 19.10 (*C*H$_3$), 30.20 ((CH$_3$)$_2$*C*H), 31.11 ((CH$_3$)$_2$*C*H), 52.34 (OC*C*H$_3$), 52.40 (OC*C*H$_3$), 59.31 ((CH$_3$)$_2$CH*C*H), 62.82 (N*C*H$_2$N), 120.94 (N*C*HCHN), 121.69 (NCH*C*HN), 121.96 (NCH*C*HN), 122.19 (N*C*HCHN), 169.10 (*C*O), 169.66 (*C*O) ppm. $C_{19}H_{28}N_4O_4I_2Pd$ (736.68): Calc.: C, 30.98; H, 3.83; N, 7.61. Found: C, 30.93; H, 3.48; N, 7.41%. IR 3163, 3127, 2969, 1739, 1458, 1414, 1201, 1168, 993, 799, 744, 727, 671 cm^{-1}.

4.4.4. 1,1′-Bis-(1-methoxycarbonyl-2-methylpropyl)-3,3′-methylenediimidazoline-2,2′-diylidene-platinum(II) diiodide ***3d***

Platinum(II) acetylacetonate (0.062 g, 0.16 mmol) and **2d** (0.1 g, 0.16 mmol) were dissolved in 6 mL dimethylsulfoxid. The mixture was stirred for 2 h at 40 °C, 1.5 h at 60 °C, 1.5 h at 80 °C, 1 h at 100 °C, 12 h at r.t. and 1 h at 130 °C. The dimethylsulfoxide was removed in vacuum and the resulting solid was washed with cold tetrahydrofuran and methanol. The product was obtained as a yellow powder. Yield: 0.033 g (30%). m.p.: decomposition at 244 °C. ^{1}H NMR (DMSO-d_6): δ 0.43 (d, *J* = 6.7 Hz, C*H*$_3$), 0.70 (d, *J* = 6.7 Hz, C*H*$_3$), 1.05–1.10 (m, C*H*$_3$), 2.29–2.31 (m, (CH$_3$)$_2$C*H*), 2.50–2.53 (m, (CH$_3$)$_2$C*H*, overlapped by DMSO-d_6), 3.62 (s, OC*H*$_3$), 3.71 (s, OC*H*$_3$), 5.78 (d, *J* = 8 Hz, C*H*), 6.02–6.07 (m, NC*H*$_2$N and C*H*), 6.17 (d, *J* = 13.2 Hz, NC*H*$_2$N), 7.45–7.46 (m, NC*H*CHN), 7.60–7.63 (m, NC*H*CHN) ppm. ^{13}C NMR (DMSO-d_6): δ 18.36 (*C*H$_3$), 18.64 (*C*H$_3$), 18.85 (*C*H$_3$), 18.97 (*C*H$_3$), 29.87 ((CH$_3$)$_2$*C*H), 31.04 ((CH$_3$)$_2$*C*H), 52.09 (O*C*H$_3$), 52.19 (O*C*H$_3$), 62.13 (N*C*H$_2$N), 65.70 (*C*H), 68.48 (*C*H), 120.26 (N*C*HCHN), 120.77 (N*C*HCHN), 120.90 (NCH*C*HN), 150.80 (N*C*N), 151.62 (N*C*N), 168.87 (*C*O), 169.41 (*C*O) ppm. $C_{19}H_{28}N_4O_4I_2Pt$ (825.35): Calc.: C, 27.65; H, 3.42; N, 6.79. Found: C, 27.44; H, 3.42; N, 6.53%. IR 2971, 1734, 1305, 1206, 729, 680 cm^{-1}.

4.5. Structure determination of compound ***3a***

Single crystals suitable for the X-ray diffraction study were grown by condensing methanol into a solution of **3a** in DMSO. The crystal was stored under perfluorinated ether, transferred on a glass capillary and fixed. Preliminary examination and data collection were carried out on an area detecting system (kappa-CCD; Nonius) at the window of a sealed X-ray tube (Nonius, FR590) and graphite-monochromated Mo–K_α radiation (λ = 0.71073 Å). The unit cell parameters were determined. Data collection was performed at 198 K and all reflexes were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. The absorption correction was applied using SADABS [70]. We used the non-chiral spacegroup $P\bar{1}$ to solve the structure because the twinned crystal could not be solved in the chiral spacegroup *P*1. After merging the independent reflections were used for all calculations. The structure was solved by a combination of direct methods [71] and difference Fourier syntheses [72]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions using the SHELXL riding model. Full-matrix least-

Table 2
Crystallographic data for complex **3a**.

3a	
Measurement	M. Taige
Formula	$C_{15}H_{20}I_2N_4O_4Pd \cdot C_2H_6OS$
Formula weight	680.55
Color/shape	Yellow/plate
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	8.842(5)
b (Å)	9.594(6)
c (Å)	14.449(11)
α (°)	75.077(5)
β (°)	84.914(6)
γ (°)	78.492(5)
V (Å^3)	1159.66(13)
Z	2
ρ_{calc} (g/cm$^{3)}$	1.949
μ (mm^{-1})	3.486
F(000)	644
Diffractometer	Nonius kappa-CCD
Temperature (K)	198 ± 2
$\theta_{min/max}$ (°)	3.21/26.00
Data collected (h, k, l)	±10, ±11, ±17
Reflections integrated	25584
Independent reflections (all data)	4552
Observed reflections [$I > 2\sigma(I)$]	4074
Parameter refined	239
R_1 (observed/all data)	0.0317/0.0382
wR_2 (observed/all data)	0.0741/0.0767
Goodness-of-fit	1.125
Residual electron density (e Å^{-3})	0.862/−1.149

squares refinements with 239 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. Details of the structure determination are given in Table 2. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography* [73]. All calculations were performed with the programs COLLECT [74], DIRAX [75], EVALCCD [76], SIR92 [71], SADABS [70], the SHELXL-97 package [72,77] and ORTEP-III [78]. In addition, one molecule DMSO became apparent in the final difference Fourier maps but the severe disorder could not be modeled properly. This problem was solved by using the PLATON [79] calc squeeze procedure.

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