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Copper(II) complexes containing chiral substituted 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridine ligands: Synthesis, X-ray structural studies and asymmetric catalysis

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Abstract

New chiral *N*,*N*-bidentate ligands derived from substituted 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines have been prepared and characterised by means of ^{1}H, ^{13}C NMR spectroscopy and optical rotation. Their Cu(II) complexes were characterized by means of elemental analysis, ^{1}H NMR spectroscopy and MS. By means of X-ray diffraction, molecular geometry of the complex of 2-(1-methyl-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridine with copper(II) chloride was determined. The complex exhibits heterochiral dimeric arrangement of two square pyramids with one terminal and one bridge-forming chlorine atoms and two nitrogen atoms in the bases of the pyramids. The tops of these pyramids are formed by the remaining chlorine atoms. The complexes prepared catalyse the Henry reaction with the overall yields of 41–97% and with the maximum enantioselective excess of 19%.

Keywords: 4,5-Dihydro-1*H*-imidazol-5-one ligands; Copper complexes; Asymmetric catalysis; Henry reaction

1. Introduction

The complex heterocyclic compounds containing a stereogenous centre are particularly used as homogeneous catalysts in a number of asymmetric syntheses [1]. In our previous work [2], we placed two 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridine cycles at 2,6-positions of pyridine and thus prepared chiral ligands formally similar to the well-known *N*,*N*,*N*-tridentate ligands of oxazoline (''Pybox'') [3], terpyridine (''Terpy'') [4] or 2,6-bis(imidazol-2-yl)pyridine [5] and 2,6-bis(1-methylbenzimidazol-2-yl)pyridine [6]. The ligands and complexes prepared by us have the advantage in their asymmetrical carbon atom being quaternary, which prevents racemization by splitting off of α-hydrogen, which happens, e.g., in the oxazolines derived from natural amino acids [7]. On the other hand, the substituted 4,4-dialkyl-4,5-dihydro-2-phenyl-1*H*-imidazol-5-ones derived from pyridine-2,3-dicarboxylic acid are commercially available herbicides [8]. In the case of herbicide *Imazapyr*, its copper(II) complexes were described [9].

This paper deals with synthesis and characterisation of new chiral substituted 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines. In contrast to the previous paper [2], the present paper concerns the derivatives only substituted at 2-position of pyridine ring; this results in obtaining chiral *N*,*N*-bidentate ligands allowing the metal ion to be coordinated with two nitrogen atoms.

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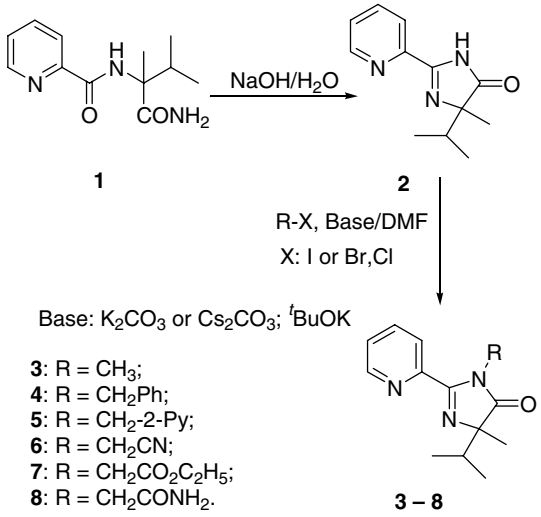
N,*N*-Bidentate ligands [10], such as, e.g., 2,2′-bipyridine and 1,10-phenanthroline play chief roles in key areas such as photovoltaics [11], molecular sensors [12], DNA intercalation [13], molecular wires [14] and supramolecular structures (network, helical, box, etc.) [15]. The diverse applications stem from the fact that the ligands are capable of chelating various metal ions and the resultant complexes possess a wide range of catalytic, magnetic, photophysical and electrochemical properties. Besides the preparation and structural study of the Cu(II) complexes with the newly suggested and prepared *N*,*N*-bidentate ligands, further aim of this work is to verify their catalytic properties using the Henry reaction as the particular model [16].

2. Results and discussion

2.1. Syntheses of ligands

The systems suggested by us are relatively easy to synthesize and further modify, as the case may be. The source of stereogenous centre is the easily accessible and optically pure (*R*)-2-amino-2,3-dimethylbutanamide, $[\alpha]_D^{25} = +59.4°$ ($c = 0.0162$, THF) and (*S*)-2-amino-2,3-dimethylbutanamide, $[\alpha]_D^{25} = -57.1°$ ($c = 0.0654$, THF) [8b]. In analogy with the previous work [2], we used the reaction of the pyridine-2-carbocylic acid activated with methyl chloroformate, with racemic 2-amino-2,3-dimethylbutanamide, with (*R*)-2-amino-2,3-dimethylbutanamide, and with (*S*)-2-amino-2,3-dimethylbutanamide to prepare the corresponding acylated butanamides (pyridine-2-carboxylic acid (1-carbamoyl-1,2-dimethyl-propyl)-amides): **1** racemic (78%), **1**(*R*) (87%), **1**(*S*) (85%). Base catalysed ring closure of **1** gave **2** racemic (76%) and the optically pure 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-on-2-yl)pyridines **2**(*R*) (80%) and **2**(*S*) (82%). The subsequent alkylation of 1-nitrogen atom in 1*H*-imidazol-5-one ring with various groups gave a series of *N*1-substituted 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines **3**–**8** (Scheme 1). In the cases of 2-(4-isopropyl-1,4-dimethyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines **3** and 2-(1-benzyl-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines **4**, we prepared the racemates **3** (69%) and **4** (65%) as well as the optically pure ligands **3**(*R*) (65%), **3**(*S*) (66%), **4**(*R*) (73%) and **4**(*S*) (84%). In the other cases, only the racemates were prepared (**5**–**7**) in the yields of 79–92%. The alkylation, i.e., nucleophilic substitution of dimethyl sulphate (methyl iodide), benzyl bromide, 2-picolyl chloride, chloracetonitrile and ethyl bromoacetate with anion of 4,5-dihydro-1*H*-imidazol-5-one was carried out in anhydrous dimethylformamide (Method A: K_2CO_3 or Cs_2CO_3; Method B: ^{t}BuOK) (Scheme 1). 2-(1-Carbamoyl-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridine **8** (65%) was prepared by partial hydrolysis of nitrile **6**. The ligands prepared in the described way were characterised by means of ^{1}H, ^{13}C NMR spectroscopy, elemental analysis and melting points.

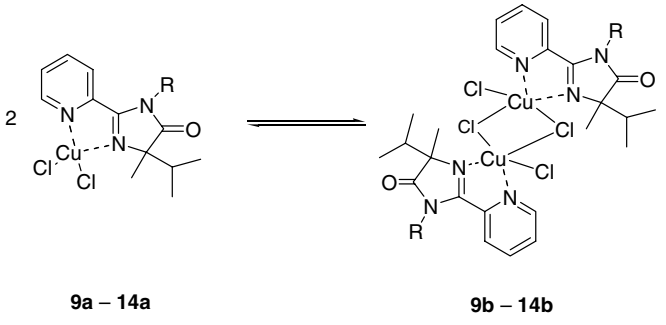


Scheme 1.

2.2. Synthesis and characterisation of complexes

Complexes **9**–**14** were prepared by reactions of cupric chloride with the individual ligands **3**–**8** in ethanol, in the yields of 60–96%. The complexes prepared (**9**–**14**) were characterised by means of elemental analysis, mass spectrometry and ^{1}H NMR. The mass spectrometry results of complexes **9**–**14** show that each of the complexes is present in two forms, i.e., as the monomer **a** and the dimer **b**, which can exist in various proportions in gas phase as well as in solution or solid phase (Scheme 2).

The monomeric form **a** is characterised by the presence of molecular peak $[M-Cl]^+$ in the mass spectrum, while the dimeric form **b** is indicated by characteristic molecular peaks $[2M-Cl]^+$ and $[2M-CuCl_2-2Cl]^+$. With complexes **9**–**14** also measurement of ^{1}H NMR spectra in DMSO-d_6 was carried out, but the spectra obtained only exhibit very broad signals in the region 0.8–11.5 ppm with almost no informative value. The said broadening is most probably due to dynamic processes produced by a coordination of the solvent (Scheme 2) to give mononuclear paramagnetic species (**a**). Compound **10**, as the single one, dissolved sufficiently in chloroform. Its



9: R = CH_3; **10**: R = CH_2Ph; **11**: R = CH_2-2-Py; **12**: R = CH_2CN;
13: R = $CH_2CO_2C_2H_5$; **14**: R = CH_2CONH_2;

Scheme 2.

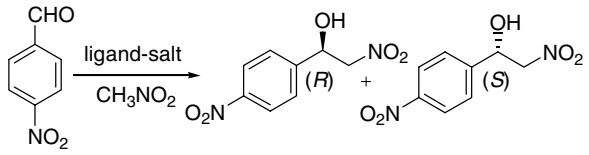
spectrum shows one set of relatively narrow signals, which were ascribed to the respective hydrogen atoms (^{1}H NMR, $CDCl_3$, δ ppm: 0.005 (4H, Py); 1.00 (2H, CH_2); 1.30 (1H,CH); 1.60 (9H, $3\times CH_3$); 3.55 (5H, Ph)), this is most probably caused by antiferromagnetic coupling of two copper nuclei and thus the formation of a dimer (**10b**) in this solvent. In order to verify the structure of complex **9** (made from racemic **3**) in solid phase, we managed to prepare the respective single crystal, which was submitted to X-ray analysis.

Generally, complexes of cupric chloride with neutral ligands containing two or more nitrogen atoms can crystallize either as monomers [17] or as dimers with trigonal bipyramidal geometry of copper(II) central atoms [18a–d].

Another possible arrangement of these complexes is dimeric with square pyramidal geometry (SPY) of copper atoms which are connected by two chlorine bridges; in their bases there are bidentate nitrogen ligands, one terminal and one bridge-forming chlorine atoms; the remaining bridge chlorine atoms are in alternative arrangement at the tops of the two pyramides [18e]. Only the small variation of this geometry was found in complexes where the distance between the two copper atoms that is shorter than the sum of the respective van der Waals radii [19]. As examples of special oligomeric formations can be given complexes with chelate-forming ligands containing a large spacer [20a], tridentate [20b] or tetradentate ligands [20b], or a complex with only one bridge-forming chlorine atom [20c]. On the basis of X-ray analysis, we found out that complex **9** is preferably separated from the solvent system of ethanol–hexane in the form of dimer **9b** (Fig. 1). The molecular geometry **9b** can best be described as a dimeric arrangement of two square pyramids with one terminal chlorine atom and one bridge-forming chlorine atom (Cl2 for Cu1) and two nitrogen atoms placed in the bases of the pyramids. The tops of these pyramids are occupied by the remaining bridge-forming chlorine atoms (Cl2a for Cu1). This arrangement is very close to the latter structures described in the literature [18e]. Molecule **9b** is composed of two almost planar formations that can be defined by the nitrogen atoms of one of the ligands, the copper atom, one bridge chlorine atom and one terminal chlorine atom (N1, N7, Cu1, Cl1 and Cl2). The ligands are mutually in heterochiral arrangement. The distances between the atoms Cu and Cl in **9b** considerably depend on their position (Cu1 Cl1 2.2413(5) – terminal, Cu1 Cl2 2.2917(5) – bridge-forming atom in the base, Cu1 Cl2a 2.7934(5) – bridge-forming atom at the top), which is typical of this structural motif [18e]. Other structural parameters also agree with the literature data about this type of compounds [21].

2.3. Study of enantioselectivity in the Henry reaction

For a model we chose the nitroaldol (Henry) reaction [16] of 4-nitrobenzaldehyde with nitromethane (Scheme 3). This reaction produces 2-nitro-1-(4-nitrophenyl)ethanol, i.e., a stereogenic centre is formed at carbon-1. Even



Scheme 3.

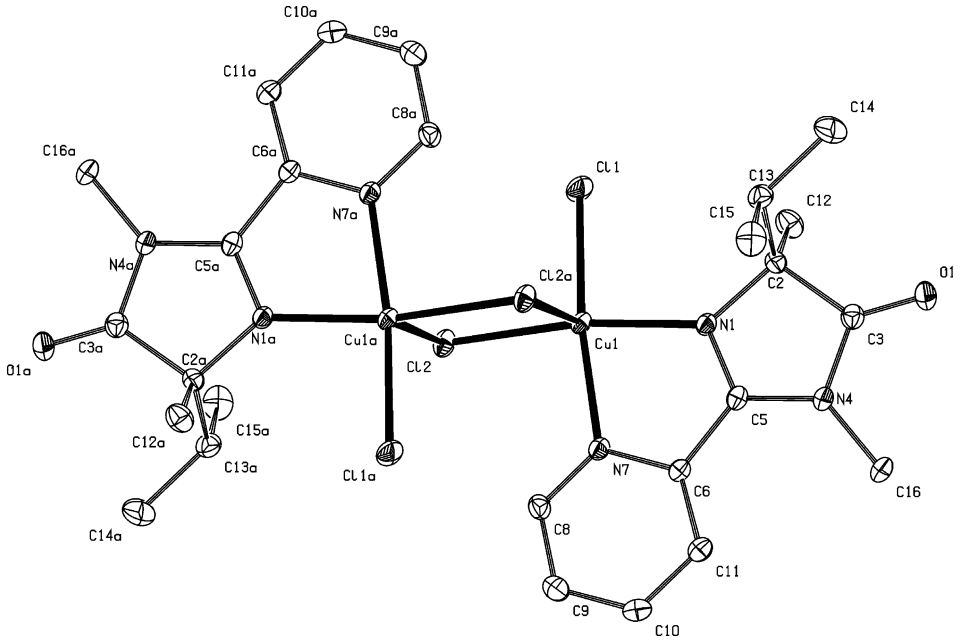


Fig. 1. Molecular structure of **9b**, ORTEP 40% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cu1–N1 2.0183(14), Cu1–N7 2.0588(15), Cu1–Cl1 2.2413(5), Cu1–Cl2 2.2917(5), Cu1–Cl2a 2.7934(5), Cu1–Cu1a 3.6364(3), N1–Cu1–N7 79.38(6), N1–Cu1–Cl1 94.58(4), N7–Cu1–Cl1 170.00(4), N1–Cu1–Cl2 169.10(4), N7–Cu1–Cl2 93.02(4), Cl1–Cu1–Cl2 91.80(1), N1–Cu1–Cl2a 98.41(4), N7–Cu1–Cl2a 89.41(4), Cl1–Cu1–Cl2a 99.41(2), Cl2–Cu1–Cl2a 89.24(2), Cu1–Cl2–Cu1a 90.76(2).

Table 1
Survey of conditions and yields of nitroaldolisation of 4-nitrobenzaldehyde with nitromethane (Method D)

Ligand	Salt	Mol% of catalyst	Time	Temperature (°C)	Overall yield (%)	ee (%)
3(*R*)	Copper(II) chloride/TEA	5	6 d	−20	59	8.9 (*R*)
3(*R*)	Copper(II) acetate	5	27 d	−20	41	18.6 (*R*)
3(*S*)	Copper(II) acetate	5	14 d	0	75	14.4 (*S*)
3(*R*)	Copper(II) acetate	10	14 d	0	97	13.6 (*R*)
3(*S*)	Copper(II) acetate	20	14 d	0	96	14.5 (*S*)
3(*S*)	Copper(II) acetate	5	19 h	25	49	10.5 (*S*)
3(*S*)	Copper(II) benzoate	5	23 h	25	79	11.2 (*S*)
3(*S*)	Copper(II) isophthalate	5	29 h	25	61	9.9 (*S*)
3(*S*)	Copper(II)pivaloate	5	6 d	0	56	4.1 (*S*)
3(*S*)	Copper(II) pivaloate	5	21 h	25	81	3.4 (*S*)
4(*R*)	Copper(II) acetate	5	10 d	0	63	11.2 (*R*)
4(*R*)	Copper(II) acetate	5	26 h	25	54	10.1 (*R*)

though the Henry reaction is very similar to aldolization, in the literature there are but few examples in which high enantioselectivity was attained [16]. The nitroaldol reaction is usually catalysed by a combination of a Lewis acid and a Brønsted base, i.e., two chemically incompatible species, for which it is necessary to optimise the reaction conditions. At first, we used the experimental conditions already optimised for the copper(II) complex derived from (4*S*,4*S*′)-2,2′-propan-2,2′-diylbis(4-isopropyl-4,5-dihydro-1,3-oxazole) [16e] (Method C). At these conditions, we applied the method to complex **9**(*R*), which in combination with one equivalent of triethylamine (−20 °C) will very probably exist in the form of monomer **9a** with coordinated triethylamine [16c]. However, using this Method C, we only achieved a yield of ca. 9% enantioselective excess, the total (chemical) yield being 56%. Besides this application of pure complex, we also tried a combination of the respective optically pure ligand **3** or **4** with corresponding copper(II) carboxylates (Method D). The catalytic role should be played by the complexes formed in situ; however, we did not manage to prepare these complexes in crystalline form. The reactions were found to proceed with yields of 41–97% (Table 1).

It is well known that optical yield is significantly affected by temperature, which can also be seen from Table 1. Further decrease in temperature would probably lead to somewhat higher optical yield than 18.6%; however, at the same time the reaction would be unacceptably prolonged to as much as several months. We did not succeed in increasing the optical yield even by using bulky anions (benzoate, pivaloate and isophtalate) either. Also increased concentration of catalyst did not affect enantioselectivity (Table 1).

3. Conclusion

Substituted 2-(4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridines form complexes with copper(II) chloride, and these complexes exist in the monomer and dimer forms that are in equilibrium in solution. On the basis of X-ray analysis, we found out that the complex of 2-(1-methyl-4-isopropyl-4-methyl-4,5-dihydro-1*H*-imidazol-5-one-2-yl)pyridine separated from the solution in the form of a heterochiral dimer of two square pyramids with one terminal chlorine atom and one bridge-forming chlorine atom and two nitrogen atoms in the bases of each pyramid. The tops of the pyramids are occupied by the remaining bridge-forming chlorine atoms. When studying the Henry nitroaldol reaction, we achieved high chemical yields (97%) but only low enantioselectivity (19% at the most).

4. Experimental

4.1. NMR measurements

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance spectrometer at 500.13 (^{1}H) and 125.76 MHz (^{13}C) in DMSO-d_6. The ^{1}H and ^{13}C chemical shifts were referenced to the central peaks of solvent ($\delta = 2.55$ and 39.60, respectively). All 2D experiments (gradient-selected gs-COSY, gs-HSQC, gs-HMBC) were performed using the manufacturer's software (XWINNMR 3.1). The proton-proton connectivities were found using gs-COSY. (The protonated carbons were assigned by gs-HSQC and the quaternary carbons by gs-HMBC spectra.)

4.2. MS measurements

Mass spectra of complexes were measured on a VG Platform II mass spectrometer (Micromass, Manchester, UK) with chemical ionisation at atmospheric pressure (APCI) and quadrupole analyser (0–3000 Da).

4.3. Optical rotatory power determination

Optical rotation was measured on a Perkin–Elmer 341 instrument, concentration c is given in g/100 mL.

4.4. HPLC analyses

The optical purity of 2-nitro-1-(4-nitrophenyl)ethanol was determined by means of HPLC using a Chiralcel OD–H column (85:15 hexane: propane-2-ol, 0.8 mL/min, 220 nm; (*R*)-isomer: $t_R = 20.3$ min, (*S*)-isomer: $t_R = 25.4$ min).

4.5. X-ray crystallography

The single crystals of **9** were grown from ca. 10% solution into which ethanol–hexane was charged via slow vapour diffusion. The relevant crystallographic parameters and procedures are: Data for colourless crystal were collected at 150(2) K on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å), a graphite monochromator, the structure was solved by direct methods (SIR-92 [22a]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares technique (SHELXL-97 [22b]). The hydrogen atoms were mostly localised on a difference Fourier map, however, to ensure uniformity of treatment of all crystals, all hydrogen atoms were recalculated into idealised positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or of $1.5U_{eq}$ for the methyl moiety. The absorption corrections were carried out using either multi-scan procedure (PLATON [22c] or SORTAV [22d]) or Gaussian integration from crystal shape (Coppens [22e]). Empirical formula: $C_{26}H_{34}Cl_4Cu_2N_6O_2$; formula weight: 731.47; crystal system: triclinic; space group: $P\bar{1}$; unit cell dimensions: a, b, c, α, β, γ (Å, °): 6.91100(10), 9.4370(3), 12.2190(4), 102.6140(13), 93.269(2), 104.8110(18); volume (Å^3) 746.44(4); $Z = 1$; D_{calc} (Mg/m^3): 1.627; absorption coefficient (mm^{-1}): 1.819; $F(000)$ 374; crystal size (mm): $0.3 \times 0.2 \times 0.075$; θ range for data collection: 1.0–27.5; h range $-8 \rightarrow 8$; k $-12 \rightarrow 12$; l $-15 \rightarrow 15$; reflections collected: 12 184; T_{min}, T_{max}: 0.672, 0.937; independent/observed reflections: ($I > 2\delta(I)$) 3089/3409; R_{int} ($R_{int} = \sum |F_o^2 - F_{o,mean}^2| \sum F_o^2$) 0.034; absorption corrected multi-scans (SORTAV) number of parameters 186; S all data ($S = [\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{1/2}$): 1.071; R_1, wR_2 [$I > 2\delta(I)$] ($R(F) = \sum\|F_o| - |F_c\|\sum|F_o|$, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)(\sum w(F_o^2)^2)]^{1/2}$) 0.026, 0.061; R_1, wR_2 (all data): 0.031, 0.064; $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3): 0.366, −0.477; CCCD deposition No. 278396.

4.6. Synthesis of ligands

4.6.1. (±)-2-[N-(2-Aminocarbonyl-2,3-dimethylbutyl)-aminocarbonyl]pyridine (1)

A mixture of picolinic acid (15 mmol) and triethylamine (15 mmol) in 50 mL dry THF was treated with a solution of ethyl chloroformate (15 mmol) in 15 mL dry THF added drop by drop. After 30 min, 2-amino-2,3-dimethylbutanamide (15 mmol) in 20 mL THF was added to the suspension formed, and the mixture was stirred 3 h. The triethylammonium chloride formed was removed by filtration and washed with 10 mL THF. The removal of THF by means of distillation left a yellowish crude product. This was recrystallized from toluene to give white crystalline substance **1** in the yield of 78%, m.p.189–190 °C.

^{1}H NMR (DMSO-d_6, δ ppm): 8.97 (s, 1H, NH), 8.71 (m, 1H, PyH_6), 8.06 (m, 2H, PyH_3, H_5), 7.65 (m, 1H, PyH_4), 7.40 (s, 1H, NH_2), 7.26 (s, 1H, NH_2), 2.35 (m, 1H, i-PrCH), 1.65 (s, 3H, CH_3), 0.98 (d, 3H, i-PrCH_3), 0.95 (d, 3H, i-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 174.7, 162.4, 150.4, 148.4, 138.0, 126.5, 121.4, 62.5, 34.6, 18.2, 17.6, 17.5. Anal. Calc. for $C_{12}H_{17}N_3O_2$: C, 61.26; H, 7.28; N, 17.86. Found: C, 61.10; H, 7.25; N, 17.83%.

4.6.2. (R)-2-[N-(2-Aminocarbonyl-2,3-dimethylbutyl)aminocarbonyl]pyridine (1(R))

In a similar manner, the compound **1**(R) was prepared as white crystals in a yield of 87%, m.p. 135–136 °C, $[\alpha]_D^{25} = -39.1°$ ($c = 1.0$, CH_3OH). The elemental analysis is comparable with that of **1**, and the ^{1}H and ^{13}C NMR spectra are identical with those of **1**.

4.6.3. (S)-2-[N-(2-Aminocarbonyl-2,3-dimethylbutyl)aminocarbonyl]pyridine (1(S))

In a similar manner, the compound **1**(S) was prepared as white crystals in a yield of 85%, m.p. 136–138 °C, $[\alpha]_D^{25} = +38.4°$ ($c = 0.9$, CH_3OH). The elemental analysis is comparable with that of **1**, and the ^{1}H and ^{13}C NMR spectra are identical with those of **1**.

4.6.4. (±)-2-(4-Isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (2)

A mixture of **1** (2.1 mmol) and 20 mL 1 M NaOH (20 mmol) was stirred at room temperature. After 5 h, the mixture was neutralised with concd. HCl to pH ≈ 7 and extracted with 4×25 mL CH_2Cl_2. The solution was evaporated until dry to give the product as white crystals in a yield of 76%, m.p. 88–91 °C; ^{1}H NMR (DMSO-d_6, δ ppm): 11.43 (s, 1H, NH), 8.73 (d, 1H, PyH_6), 8.22 (d, 1H, PyH_5), 8.03 (m, 1H, PyH_3), 7.64 (m, 1H, PyH_4), 1.97 (m, 1H, i-PrCH), 1.29 (s, 3H, CH_3), 1.01 (d, 3H, i-PrCH_3), 0.80 (d, 3H, i-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 187.0, 159.2, 149.3, 147.4, 137.6, 126.4, 121.7, 74.7, 34.2, 21.3, 16.9, 16.8. Anal. Calc. for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.12; H, 6.92; N, 19.10%.

4.6.5. (R)-2-(4-Isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (2(R))

In a similar manner, the compound **2**(R) was prepared as pure colourless oil in a yield of 80%, $[\alpha]_D^{25} = +19.0°$ ($c = 2.4$, CH_3OH). The elemental analysis is comparable with that of **2**, and the ^{1}H and ^{13}C NMR spectra are identical with those of **2**.

4.6.6. (S)-2-(4-Isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (2(S))

In a similar manner, compound **2**(S) was prepared as pure colourless oil in a yield of 82%, $[\alpha]_D^{25} = -18.0°$ ($c = 2.0$, CH_3OH). The elemental analysis is comparable with that of **2**, and the ^{1}H and ^{13}C NMR spectra are identical with those of **2**.

4.6.7. Procedures of N-alkylation of 2-(4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (2)

Method A: A mixture of compound **2** (10 mmol) and potassium or cesium carbonate (15 mmol) in 10 mL dry DMF kept under argon atmosphere was treated with the

respective alkylation agent (12 mmol) (the alkylation agent in the synthesis of **3**: dimethylsufate; **4**: benzyl bromide; **5**: picolyl chloride; **6**: chloroacetonitrile; **7**: ethyl bromoacetate). The reaction mixture was heated at 160 or 90 °C for a period of 48 or 24 h, respectively. The inorganic salts formed were removed by filtration, DMF was distilled off, and the crude product was dissolved in ethyl acetate and filtered through a 1 cm silica gel layer. After distilling off of ethyl acetate, products **3**–**7** were obtained.

Method B: Compound **2**(*R*) or **2**(*S*) (3.6 mmol) kept under argon atmosphere was treated with potassium *tert*-butoxide (5.4 mmol). The mixture was stirred at room temperature, and after 1 h, *t*-butyl alcohol was distilled off. The evaporation residue was dissolved in 10 mL dry DMF, the solution was cooled to r.t., and methyl iodide (6 mmol) was added thereto under argon atmosphere. The suspension formed was stirred at r.t. for a period of 3 h. After distilling off DMF, the evaporation residue was mixed with water, and the emulsion formed was extracted with 2×30 mL ether. The removal of ether by distillation left product **3**(*R*) or **3**(*S*), respectively.

*4.6.7.1. (±)-2-(1-Methyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**3**). Method A:* Yellowish oil, yield 69%; ^{1}H NMR (DMSO-d_6, δ ppm): 8.70 (d, 1H, PyH_6), 8.04 (d, 1H, PyH_3), 7.99 (m, 1H, PyH_5), 7.60 (m, 1H, PyH_4), 3.27 (s, 3H, NCH_3), 1.94 (m, 1H, *i*-PrCH), 1.24 (s, 3H, CH_3), 0.95 (d, 3H, *i*-PrCH_3), 0.73 (d, 3H, *i*-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 186.0, 159.2, 149.1, 149.0, 137.7, 126.0, 124.0, 73.0, 34.4, 29.0, 21.3, 16.9, 16.7. Anal. Calc. for $C_{13}H_{17}N_3O$: C, 67.51; H, 7.41; N, 18.17. Found: C, 67.44; H, 7.52; N, 18.28%.

*4.6.7.2. (R)-2-(1-Methyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**3**(R)). Method B:* Yellowish oil, yield 65%, $[\alpha]_D^{25} = +28.6°$ ($c = 0.61$, CH_2Cl_2). The elemental analysis is comparable with that of **3**, and the ^{1}H and ^{13}C NMR spectra are identical with those of racemic compound **3**.

*4.6.7.3. (S)-2-(1-Methyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**3**(S)). Method B:* Yellowish oil, yield 66%, $[\alpha]_D^{25} = -27.8°$ ($c = 0.51$, CH_2Cl_2). The elemental analysis is comparable with that of **3**, and the ^{1}H and ^{13}C NMR spectra are identical with those of **3**.

*4.6.7.4. (±)-2-(1-Benzyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**4**). Method A:* White crystals, yield 65%, m.p. 46–49 °C; ^{1}H NMR (DMSO-d_6, δ ppm): 8.71 (d, 1H, PyH_6), 8.00 (d, 1H, PyH_3), 7.96 (m, 1H, PyH_5), 7.59 (m, 1H, PyH_4), 7.08–7.25 (m, 5H, Ph), 5.23 (dd, 2H, CH_2), 2.05 (m, 1H, *i*-PrCH), 1.34 (s, 3H, CH_3), 1.01 (d, 3H, *i*-PrCH_3), 0.80 (d, 3H, *i*-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 186.0, 158.3, 148.9, 148.8, 137.8, 137.7, 128.4, 127.2, 127.1, 126.0, 123.8, 72.9, 44.4, 34.4, 21.3, 16.9, 16.8. Anal. Calc. for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.31; H, 6.78; N, 13.56%.

*4.6.7.5. (R)-2-(1-Benzyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**4**(R)). Method A:* White crystals; yield 73%, m.p. 39–42 °C, $[\alpha]_D^{25} = +19.4°$ ($c = 1.0$, CH_2Cl_2). The elemental analysis is comparable with that of **4**, and the ^{1}H and ^{13}C NMR spectra are identical with those of racemic compound **4**.

*4.6.7.6. (S)-2-(1-Benzyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**4**(S)). Method A:* Yellowish oil; yield 84%, $[\alpha]_D^{25} = -20.1°$ ($c = 1.1$, CH_2Cl_2). The elemental analysis is comparable with that of **4**, and the ^{1}H and ^{13}C NMR spectra are identical with those of racemic compound **4**.

*4.6.7.7. (±)-2-(1-(2-Picolyl)-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**5**). Method A:* Yellowish crystals; yield 82%, m.p. 100–102 °C; ^{1}H NMR (DMSO-d_6, δ ppm): 8.55 (d, 1H, PyH_6), 8.34 (d, 1H, Py), 8.05 (d, 1H, PyH_3), 7.92 (m, 1H, PyH_5), 7.66 (m, 1H, Py), 7.50 (m, 1H, PyH_4), 7.17–7.18 (m, 2H, Py), 5.36 (dd, 2H, CH_2), 2.06 (m, 1H, *i*-PrCH), 1.37 (s, 3H, CH_3), 1.05 (d, 3H, *i*-PrCH_3), 0.86 (d, 3H, *i*-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 186.1, 158.8, 155.6, 149.2, 148.9, 148.5, 137.8, 137.5, 136.6, 125.7, 123.6, 122.1, 121.0, 73.1, 46.0, 34.3, 21.3, 17.1, 16.9. Anal. Calc. for $C_{18}H_{20}N_4O$: C, 70.11; H, 6.54; N, 18.17. Found: C, 70.29; H, 6.64; N, 18.26%.

*4.6.7.8. (±)-2-(1-Cyanomethyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl) pyridine (**6**). Method A:* Yellowish oil; yield 92%. ^{1}H NMR (DMSO-d_6, δ ppm): 8.79 (d, 1H, PyH_6), 8.23 (d, 1H, PyH_3), 8.08 (m, 1H, PyH_5), 7.70 (m, 1H, PyH_4), 5.10 (dd, 2H, CH_2), 2.05 (m, 1H, *i*-PrCH), 1.34 (s, 3H, CH_3), 1.00 (d, 3H, *i*-PrCH_3), 0.81 (d, 3H, *i*-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 185.0, 155.9, 149.0, 147.9, 138.2, 126.7, 123.7, 116.5, 73.2, 34.7, 31.2, 20.8, 16.7, 16.7. Anal. Calc. for $C_{14}H_{16}N_4O$: C, 65.61; H, 6.29; N, 21.86. Found: C, 65.85; H, 6.42; N, 21.73%.

*4.6.7.9. (±)-2-(1-Ethoxycarbonylmethyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazol-5-one-2-yl)pyridine (**7**). Method A:* Yellowish oil; yield 79%; ^{1}H NMR (DMSO-d_6, δ ppm): 8.58 (d, 1H, PyH_6), 8.17 (d, 1H, PyH_3), 7.98 (m, 1H, PyH_5), 7.56 (m, 1H, PyH_4), 4.02 (q, 2H, OCH_2CH$_3$), 4.70 (dd, 2H, CH_2), 2.00 (m, 1H, *i*-PrCH), 1.28 (s, 3H, CH_3), 1.07 (t, 3H, OCH$_2$$CH_3$), 0.99 (d, 3H, *i*-Pr$CH_3$), 0.79 (d, 3H, *i*-Pr$CH_3$). ^{13}C NMR (DMSO-$d_6$, δ ppm): 185.3, 168.4, 157.1, 148.4, 148.3, 137.6, 126.0, 123.2, 73.1, 60.7, 34.3, 34.2, 21.0, 16.8, 16.6, 13.9. Anal. Calc. for $C_{16}H_{21}N_3O_3$: C, 63.35; H, 6.98; N, 13.85. Found: C, 63.41; H, 6.91; N, 13.84%.

*4.6.8. (±)-2-(1-Carbamoylmethyl-4-isopropyl-4-methyl-4,5-dihydro-1H-imidazo-5-one-2-yl)pyridine (**8**)*

A mixture of 1 M aqueous NaOH (40 mmol) and solution of compound **7** (3.6 mmol) in 10 mL methanol was stirred at r.t. for a period of 5 h. After adjusting pH $\approx$ 7 (conc. HCl), the mixture was extracted with 3×30 mL $CHCl_3$. The com-

bined extracts were filtered with charcoal, the solvent was evaporated, and product **8** was obtained as white crystalline solid in a yield of 65%, m.p. 136–138 °C; ^{1}H NMR (DMSO-d_6, δ ppm): 8.66 (d, 1H, PyH_6), 8.13 (d, 1H, PyH_3), 8.00 (m, 1H, PyH_5), 7.59 (m, 1H, PyH_4), 7.55 and 6.98 (2 × s, 2H, NH_2), 4.68 (dd, 2H, CH_2), 2.02 (m, 1H, *i*-PrCH), 1.32 (s, 3H, CH_3), 1.04 (d, 3H, *i*-PrCH_3), 0.84 (d, 3H, *i*-PrCH_3). ^{13}C NMR (DMSO-d_6, δ ppm): 186.0, 169.2, 158.6, 149.3, 148.6, 137.6, 125.8, 123.5, 73.1, 43.8, 34.3, 21.2, 17.2, 16.9. Anal. Calc. for $C_{14}H_{18}N_4O_2$: C, 61.30; H, 6.61; N, 20.42. Found: C, 61.18; H, 6.56; N, 20.57%.

4.7. Synthesis of the copper(II) complexes

A solution of racemic ligand **3** or **4**–**8** (0.2 mmol) and $CuCl_2 \cdot 2H_2O$ (0.2 mmol) in 10 mL ethanol was stirred at r.t. for ca. 20 min. The resulting solution was evaporated until dry, and product **9** or **10**–**14**, respectively, was mixed with 10 mL ether, filtered and dried in a dessiccator.

4.7.1. Complex *9*

Complex **9** was prepared from ligand **3** and $CuCl_2 \cdot 2H_2O$ as light green powder in a yield of 73%, m.p. 249–259 °C. Anal. Calc. for $C_{13}H_{17}Cl_2CuN_3O$: C, 42.69; H, 4.68; N, 11.49. Found: C, 42.77; H, 4.79; N, 11.35%. ESI-MS ($M = 364$): $[M-Cl]^+$ m/z 328.9, $[2M-CuCl_2-Cl]^+$ m/z 560.0, $[2M-Cl]^+$ m/z 694.9.

4.7.2. Complex *10*

Complex **10** was prepared from ligand **4** and $CuCl_2 \cdot 2H_2O$ as light green powder in a yield of 78%, m.p. 258–264 °C. Anal. Calc. for $C_{19}H_{21}Cl_2CuN_3O$: C, 51.65; H, 4.79; N, 9.51. Found: C, 51.60; H, 4.86; N, 9.69%. ESI-MS ($M = 440$): $[M-Cl]^+$ m/z 405.0, $[2M-CuCl_2-2Cl]^+$ m/z 677.2, $[2M-Cl]^+$ m/z 846.9.

4.7.3. Complex *11*

Complex **11** was prepared from ligand **5** and $CuCl_2 \cdot 2H_2O$ as light green powder in a yield of 79%, m.p. 170–172 °C. Anal. Calc. for $C_{18}H_{20}Cl_2CuN_4O$: C, 48.82; H, 4.55; N, 12.65. Found: C, 48.76; H, 4.51; N, 12.72%. ESI-MS ($M = 441$): $[M\text{-}Cl]^+$ m/z 406.0, $[2M\text{-}CuCl_2\text{-}Cl]^+$ m/z 714.2, $[2M\text{-}Cl]^+$ m/z 848.9.

4.7.4. Complex *12*

Complex **12** was prepared from ligand **6** and $CuCl_2 \cdot 2H_2O$ as light green powder in yield 85%, m.p. 204–210 °C. Anal. Calc. for $C_{14}H_{16}Cl_2CuN_4O$: C, 43.03; H, 4.13; N, 14.34. Found: C, 43.07; H, 4.15; N, 14.46%. ESI-MS ($M = 389$): $[M-Cl]^+$ m/z 353.9, $[2M-Cl]^+$ m/z 744.9.

4.7.5. Complex *13*

Complex **13** was prepared from ligand **7** and $CuCl_2 \cdot 2H_2O$ as light green powder in a yield of 76%, m.p. 188–194 °C. Anal. Calc. for $C_{16}H_{21}Cl_2CuN_3O_3$: C, 43.90; H, 4.83; N, 9.60. Found: C, 43.94; H, 4.81; N, 9.41%. ESI-MS ($M = 436$): $[M-Cl]^+$ m/z 401.0, $[2M-CuCl_2-Cl]^+$ m/z 704.2, $[2M-Cl]^+$ m/z 839.1.

4.7.6. Complex *14*

Complex **14** was prepared from ligand **8** and $CuCl_2 \cdot 2H_2O$ as light green powder in a yield of 89%, m.p. 224–228 °C. Anal. Calc. for $C_{14}H_{18}Cl_2CuN_4O_2$: C, 41.14; H, 4.44; N, 13.71. Found: C, 41.18; H, 4.53; N, 13.43%. ESI-MS ($M = 407$): $[M-Cl]^+$ m/z 371.9, $[2M-CuCl_2-Cl]^+$ m/z 647.3, $[2M-Cl]^+$ m/z 779.0.

4.8. Nitroaldol (Henry) reaction of 4-nitrobenzaldehyde with nitromethane

Method C: A solution of complex **9**(*R*) (mol% are given in Table 1) in 5 mL CH_2Cl_2 was added at a temperature of −40 °C to a mixture of 4-nitrobenzaldehyde (2 mmol), nitromethane (20 mmol) and triethylamine (0.1 mmol), and the reaction mixture was stirred at the chosen temperature (see Table 1). The reaction course was monitored by means of TLC (Merck silica gel plates (60), ethyl acetate/hexane 1/4). The mixture was evaporated under reduced pressure, and the evaporation residue was mixed with ether and filtered through a 1 cm silica gel layer. The filtrate was extracted with aqueous solution of sodium hydrogensulphite (1 g in 50 mL H_2O). After evaporation of the ether, the product 2-nitro-1-(4-nitrophenyl)ethanol was obtained as a crystalline solid (m.p. 79–82 °C; ^{1}H NMR ($CDCl_3$, δ ppm): 8.21 (d, 2H, $H_{3,5}$), 7.61 (d, 2H, $H_{2,6}$), 5.60 (dd, 1H, CH), 4.59–4.57 (m, 2H, CH_2), 3.58 (s, 1H, OH). Anal. Calc. for $C_8H_8N_2O_5$: C, 45.29; H, 3.80; N, 13.20. Found: C, 45.31; H, 3.96; N, 13.36%). The optical yields given in Table 1 were determined by measuring the optical rotatory power of product [16a]. The results obtained in the described way were subsequently verified by means of HPLC of the crude reaction mixture.

Method D: A mixture of ligand **3**(*S*) or **4**(*R*) (mol% are given in Table 1) and cupric salt (0.01 mmol) (acetate, benzoate, isophthalate or pivaloate) in 3 mL absolute ethanol was stirred for a period of 30 min. The clear solution obtained was treated with nitromethane (20 mmol) and 4-nitrobenzaldehyde (2 mmol), and the reaction mixture was stirred at 25 or 0 °C, respectively. After the reaction, the mixture was processed and analysed in the same way as in the preceding Method C.

5. Supplementary data

A full list of crystallographic data and parameters including fractional coordinates is deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

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