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Tetrahedron: *Asymmetry* 19 (2008) 756–760

Novel type of trifunctional chiral N-heterocyclic carbene (NHC) precursors

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Received 6 February 2008; accepted 3 March 2008

Abstract—The synthesis of (*S*)-2-amino-3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate as the parent homologue of a novel generation of chiral NHC precursors is described. Crystallographic data for the novel chiral Ni^{II} complex, and Boc-protected amino acid containing imidazolium moiety are also given. The silver(I) carbene complex of the Boc-protected amino acid has been obtained.

1. Introduction

For a long time, carbenes were assumed to be an extremely reactive species and could not be isolated in a free form. Interest in this class of substances dramatically increased after the work of Arduengo et al.,[1] where the authors reported the isolation of an N-heterocyclic carbene (NHC) in a pure form. The similarity of this type of carbene to phosphine ligands,[2] which are widely used in modern metallocomplex catalysis, their lower toxicity, greater air and moisture stability, and the synthetic availability of a broad range of such compounds resulted in their high popularity in catalysis. In the last ten years, a lot of work devoted to the application of this type of carbene both as ligands in metallocomplex catalysis[2b,3] and as organocatalysts[4] in different reactions has been reported.

Some examples of chiral NHC derivatives and their applications in asymmetric catalysis have recently appeared in the literature.[3b,f,g,4a] However, among the studies devoted to the synthesis and application of chiral NHC's in asymmetric catalysis,[3a,b,g,4a] there is no mention of NHC's containing amino acid moieties, attached to the nitrogen atom of the imidazolium ring.

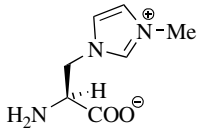

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Figure 1. Chiral zwitterionic carbene precursor.

Herein, we report the asymmetric synthesis of compound **1**: a precursor of the new class of N-heterocyclic carbenes, containing an amino acid moiety as a substituent at the nitrogen atom of the imidazolium ring (Fig. 1). This amino acid or its analogues may in future be used as a tridentate CNO ligand in asymmetric metallocomplex catalysis or may be applied as an organocatalyst in different reactions.

2. Results and discussion

To obtain (*S*)-2-amino-3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate **1**, we applied a well-known approach via the use of chiral Ni(II) complexes previously reported by some of us,[5,6] as outlined in Scheme 1.

Dehydroalanine complex **3** was synthesized from glycine complex **2** in a two-step procedure (Scheme 1), as described

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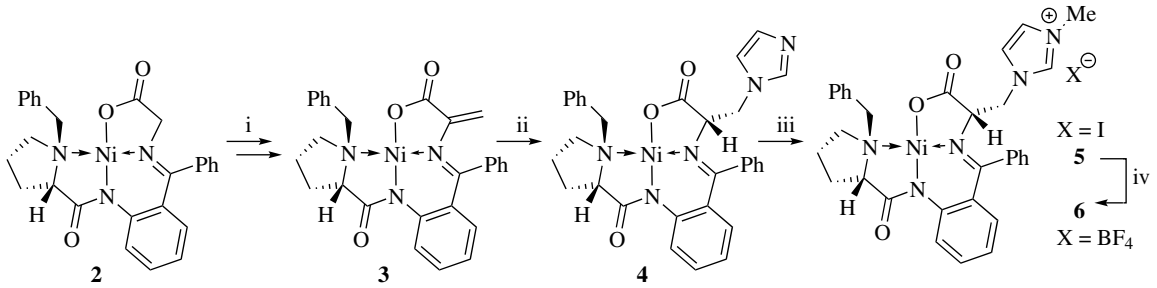
doi:10.1016/j.tetasy.2008.03.002



Scheme 1. Reagents and conditions: (i) (1) CH_2O (5 equiv), KOH (1.25 equiv), MeOH, rt, 2 h then AcOH (1.1 equiv), 84.5%; (2) Ac_2O (3 equiv), Na_2CO_3 (2 equiv), CH_3CN, reflux, 2 h, 93%; (ii) imidazole (1.5 equiv), CH_3CN, 50 °C, 6 h, 71%; (iii) MeI (10 equiv), CH_2Cl_2, rt, 24 h; (iv) ion exchange chromatography (Dowex 1 × 8, $MeOH/H_2O$ (2:1)), 69%.

earlier.[7] The addition of imidazole to the carbon–carbon double bond of **3** led to **4**. The earlier suggested procedure[7] was modified by the additional washing of the chloroform solution of the reaction mixture with 10% aqueous acetic acid solution to remove residual imidazole. Treatment of complex **4** with iodomethane gave the methylated ionic complex **5** with an iodide ion as a counteranion. To characterize the cationic complex, it was converted into a more stable complex **6** with a tetrafluoroborate counteranion via ion exchange on an anion exchange resin. X-ray quality red colored single crystals of **6** were obtained from a $CHCl_3$/MeOH (1:1) solution (Fig. 2).

To isolate target amino acid **1**, cationic complex **5** or **6** was decomposed with 6 M hydrochloric acid via a standard procedure (Scheme 2).[8] The nature of the complex counteranion did not influence the course of this reaction. Even the less stable iodide complex could be hydrolyzed to the free amino acid without any significant amount of by-product formation. Even unpurified complex **5** (obtained simply by evaporating the reaction mixture without any ion exchange or other purification) could be used to provide amino acid **1.**

Amino acid **1** obtained according to the standard technique[8] was additionally purified on silica. The pure isolated amino acid is an extremely hygroscopic yellowish oil, which

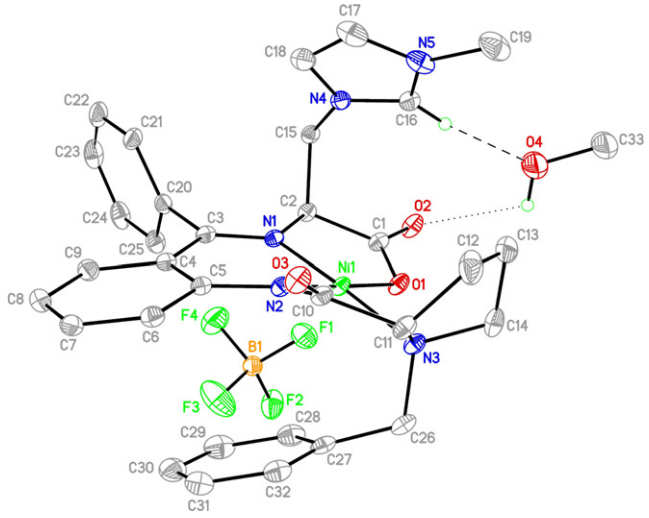
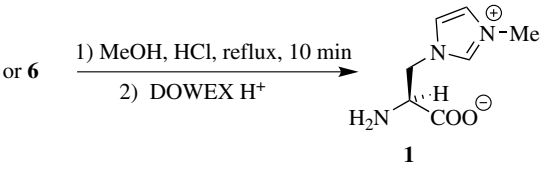


Figure 2. X-ray structure of **6**.



Scheme 2.

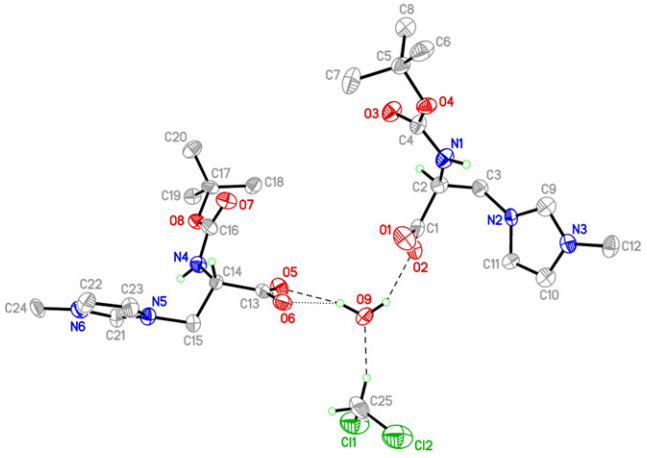
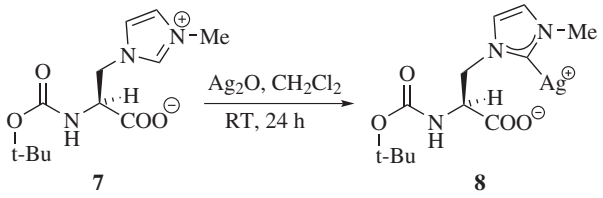


Figure 3. X-ray structure of **7**.

becomes glassy during prolonged drying in vacuo over paraffin and P_2O_5 at 64 °C and slowly decomposes at room temperature in air.[†] The 2-H proton of the imidazolium moiety undergoes H–D exchange in a D_2O solution, which can be monitored by ^{13}C NMR spectroscopy following the appearance of a triplet at 136.28 ppm with $^1J_{DC} = 25$ Hz. The *N*-Boc derivative of compound **1**was obtained by reaction with Boc_2O in THF. Compound **7** is more stable than the free amino acid **1**. The ^1H NMR spectrum ($CDCl_3$) of compound **7** exhibited a strong downfield resonance ($\delta = 9.93$ ppm) for 2-H of the imidazolium ring and an NH signal at $\delta = 6.01$ ppm.

X-ray quality white single crystals of **7** were grown from a CH_2Cl_2/MeOH (1:1) solution (Fig. 3). As can be seen from

[†] The decomposition can be detected by the appearance of a sharp smell and a bright yellow coloring.



Scheme 3.

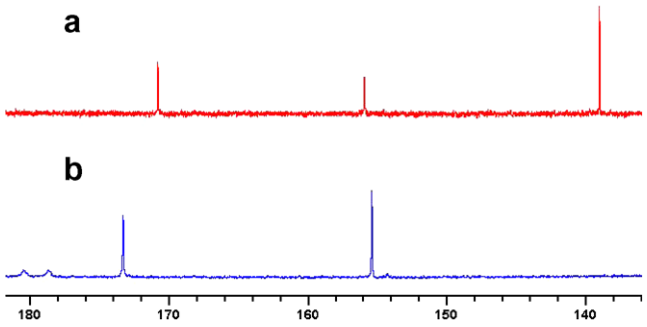


Figure 4. Fragments of ^{13}C NMR spectra of **7** (a) and **8** (b).

Fig. 3, the zwitterionic structure of **7** is clearly established. The charge on the carboxyl group is stabilized by the water molecule of solvation.

The usual precursors of NHC-metal complexes are the corresponding silver complexes, which are routinely applied as ligand transfer reagents.[9,3g] To synthesize the silver-NHC complex **8** from **7**, a very simple procedure (Scheme 3), as suggested by Lin et al., was used.[10]

The elemental analysis of complex **8** proved that it did contain the Ag derivative of **7**. The evidence in favor of the formation of the desired NHC–Ag complex **8** was the disappearance of the NC*H*N resonance in the ^1H NMR at 9.93 ppm and a strong downfield shift of the signal attributed to the NCN fragment in the ^{13}C NMR spectrum of **8**. The latter signal changes from a sharp singlet at 139.04 ppm to a broad doublet at 179 ppm with $^1J_{AgC} = 270$ Hz (Fig. 4), which is in agreement with the reported silver(I)-imidazole-2-ylidenes.[11]

3. Conclusion

In conclusion, we have reported the synthesis of a new type of enantiomerically pure amino acid, bearing an imidazolium moiety. The *N*-Boc derivative of the amino acid can be easily transformed into a chiral silver carbene complex, which potentially can be used in the future as a ligand transfer reagent in reactions involving asymmetric metallocomplex catalysis.

4. Experimental

^1H and proton decoupled ^{13}C NMR spectra were recorded with Bruker AVANCE 300, AVANCE 400, or AVANCE 600 spectrometers at ambient temperature. Chemical shifts are given in ppm relative to tetramethylsilane (δ 0) and were referenced to the indicated residual protons in the solvent, and J values are quoted in Hertz. The resonances of compounds **1**, **6**, **7** were assigned by Hetcor and NOESY experiments. The 2D heteronuclear one-bond proton–carbon correlation experiment was performed in ^1H-detection mode via single-quantum coherence (HSQC). Microanalyses were carried out by the staff of the Nesmeyanov's Institute of Organoelement Compounds, Russian Academy of Sciences Microanalytical department. Optical rotations were measured with a Perkin–Elmer 241 polarimeter, using a cell of 0.5 dm path length at 25 °C. The concentration c is expressed in g/100 ml.

All reagents and starting materials were purchased from Aldrich or Acros, and used without purification unless otherwise stated. Silica Gel 60 (0.040–0.063 mm) (Merck) was used for column chromatography. Dowex 50W × 8 and Dowex 1 × 8 from Aldrich were used for ion exchange chromatography. All solvents were purified in the usual way.[12]

4.1. X-ray structure determination

Data were collected on Bruker SMART APEX II CCD (for **6**) and Bruker SMART 1000 CCD (for **7**) diffractometers (λ(MoK$_\alpha$)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program (versions 2.03[13] for **6** and 2.01[14] for **7**). For

Table 1. Crystallographic data for **6** and **7**

Compound	**6**·CH_3OH	**7**·1/2CH_2Cl_2·1/2H_2O
Empirical formula	$C_{33}H_{36}N_5O_4NiBF_4$	$C_{12.5}H_{21}N_3O_{4.5}Cl$
Fw	712.19	320.77
T (K)	100(2)	120(2)
Crystal size (mm)	0.20 × 0.20 × 0.15	0.30 × 0.08 × 0.06
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.1950(3)	8.8820(19)
b (Å)	12.1158(3)	14.613(3)
c (Å)	23.0563(6)	24.314(5)
V (Å^3)	3127.27(14)	3155.7(12)
Z	4	8
d_c (g cm^{-3})	1.513	1.350
F(000)	1480	1360
μ (mm^{-1})	0.692	0.264
$2\theta_{max}$ (°)	61	52
Index range	$-15 \leqslant h \leqslant 15$, $-17 \leqslant k \leqslant 17$, $-32 \leqslant l \leqslant 32$	$-10 \leqslant h \leqslant 10$, $-17 \leqslant k \leqslant 17$, $-29 \leqslant l \leqslant 30$
No. of reflections collected	42,470	21,489
No. of unique reflections	9449	6087
No. of reflections with $I > 2\sigma(I)$	8386	2864
Data/restraints/parameters	9449/1/429	6087/0/369
R_1; wR_2 ($I > 2\sigma(I)$)	0.0340; 0.0793	0.0742; 0.1717
R_1; wR_2 (all data)	0.0413; 0.0825	0.2023; 0.2137
GOF on F^2	1.024	1.030
Absolute structure parameter	0.010(7)	0.02(16)
T_{min}; T_{max}	0.874; 0.903	0.926; 0.986

details see Table 1. The structures were solved by direct methods and refined by a full-matrix least squares technique on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The independent part of the unit cell of **6** contains one methanol solvate molecule, and the independent part of the unit cell of **7** contains one methylene chloride and one water solvate molecule. The absolute structures of **6** and **7** were objectively determined by the refinement of Flack parameters to 0.010(7) and 0.02(16), respectively. The hydrogen atoms of the NH-groups in **7** as well as the solvate methanol molecule in **6** and the solvate water molecule in **7** were localized in the difference-Fourier map and included in the refinement with fixed positional and thermal parameters. The other hydrogen atoms in both compounds were placed in calculated positions and refined within the riding model with fixed thermal parameters ($U_{iso}(H) = 1.5U_{eq}(C)$ for the CH_3-groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for the other groups). All calculations were carried out using the SHELXTL PLUS program (versions 6.12[15] for **6** and 5.10[16] for **7**). Crystallographic data for **6** and **7** have been deposited with the Cambridge Crystallographic Data Center. CCDC 674217 and 674218 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

4.2. [(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2- carboxamido]phenyl}(phenyl)methyleneamino)-3-(1*H*-imidazol-1-yl)propanoato-*N*, *N*′,*N*″,*O*] nickel(II) 4

To a solution of nickel complex **3** (10 g, 0.0196 mol) in CH_3CN (100 ml), imidazole (2.1 g, 0.0309 mol) was added. The reaction mixture was stirred at 50 °C for 6 h, the reaction being monitored by TLC (Silicagel, $CHCl_3$/acetone 5:1). Then, the reaction mixture was cooled to room temperature and filtered through a glass pored filter. The solution was evaporated on a rotary evaporator and the residue dissolved in $CHCl_3$ (100 ml) and washed with aqueous acetic acid (30 ml 10% solution). The organic layer was isolated, washed with water (3 × 30 ml), and evaporated. The residue was recrystallized from benzene/acetone (6:1) to give complex **4** in a pure form. Yield 8 g (71%). De >99% according to ^{1}H NMR data. Mp 204–207 °C, $[\alpha]_D^{25} = +2356$ (*c* 0.05, MeOH). Anal. Calcd for $C_{31}H_{29}N_5NiO_3{\cdot}C_6H_6$: C, 67.70; H, 5.37; N, 10.67. Found: C, 67.91; H, 5.68; N, 10.81. ^{1}H NMR (400 MHz, $CDCl_3$): 1.83 (m, 1H, δ-Pro), 2.03 (m, 1H, γ-Pro), 2.39 (m, 1H, γ-Pro), 2.57 (m, 2H, β-Pro), 3.18 (dd, 1H, δ-Pro, $^3J_1$ 7.3, $^3J_2$ 9.4), 3.48 (d, 1H, C*H*$_2$(Bn), ^3J 12.8), 3.81 (dd, 1H, C*H*$_2$–N_{Imid}, ^2J 16.3, ^3J 4.6), 4.26 (m, 3H, CH_2(Bn), CH_2–N_{Imid}, $NCHCO_2$), 6.67 (d, 2H, Ar, *J* 4.1), 6.95 (d, 1H, Ar, *J* 7.1), 6.67 (s, 1H, Imid), 7.18 (m, 2H, Ar), 7.20–7.35 (m, 5H, Ar), 7.50–7.60 (m, 4H, Ar), 8.01 (d, 2H, Ar, *J* 7.3), 8.28 (d, 1H, Ar, *J* 8.7); ^{13}C NMR (75 MHz, $CDCl_3$): 23.24 (C-13), 30.80 (C-12), 49.03 (C-15), 57.55 (C-14), 63.68 (C-26), 70.36 (C-2), 70.63 (C-11), 120.75 (C-8, C-17 or C18), 123.63 (C-9), 125.55 (C-4), 126.87 (C-30), 127.40 (C-21 or C-25), 128.86 (C-29, C-31), 128.93 (C-22, C-24), 129.45 (C-23), 129.66 (C-7), 130.08 (C-17 or C18), 130.34 (C-6), 131.52 (C-28, C-32), 133.14 (C-22, C-24), 133.29 (C-27), 133.67 (C-21 or C-25), 134.07 (C-20), 138.39 (C-16), 143.50 (C-5), 172.73 (C-10), 176.86 (C-3), 180.61 (C-1).

4.3. ({1-[(*S*)-2-({2-[(2*S*,1R_N)-1-Benzylpyrrolidine-2-carboxamido]phenyl}(phenyl)methyleneamino)-2-carboxylato-*N*,*N*′,*N*″,*O*]-nickel(II)}ethyl)-3-methyl-1*H*-imidazol-3-ium tetrafluoroborate 6

To a solution of complex **4** (8 g, 0.0138 mol) in CH_2Cl_2 (50 ml), iodomethane (19.7 g, 8.65 ml, 0.138 mol) was added. The reaction mixture was stirred at room temperature for 24 h, the reaction being monitored by TLC (Silicagel, MeOH/CH_2Cl_2 (1:1)). Then, the reaction mixture was evaporated on a rotary evaporator, the residue was dissolved in MeOH/H_2O (2:1) (20 ml), and passed through a column containing ion exchange resin Dowex 1 × 8 in BF_4^- form (100 g). The resulting solution was evaporated. The residue was recrystallized from MeOH to give complex **5** in a pure form. Yield 6.5 g (69%). De >99% according to ^{1}H NMR data. Mp 203–204 °C, $[\alpha]_D^{25} = +2386$ (*c* 0.056, MeOH). Anal. Calcd for $C_{32}H_{22}BF_4N_5NiO_3{\cdot}H_2O$: C, 55.05; H, 4.91; N, 10.03. Found: C, 54.91; H, 4.60; N, 9.95. ^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD (1:1)): 2.16 (m, 1H, δ-Pro), 2.21 (m, 1H, γ-Pro), 2.57 (m, 2H, β-Pro), 3.21 (m, 1H, γ-Pro), 3.35 (dd, 1H, δ-Pro, $^3J_1$ 7.0, $^3J_2$ 10.0), 3.48 (d, 1H, C*H*$_2$(Bn), ^3J 12.0), 3.54 (dd, 1H, α-Pro, $^3J_1$ 8.0, $^3J_2$ 10.0), 3.91 (s, 3H, CH_3N_{Imid}), 4.15 (dd, 1H, $NCHCO_2$, $^3J_1$ 4.0, $^3J_2$ 8.0), 4.18 (d, 1H, C*H*$_2$(Bn), ^3J 12.0), 4.27 (dd, 1H, C*H*$_2$–N_{Imid}, ^2J 15.0, ^3J 4.0), 4.68 (dd, 1H, C*H*$_2N_{Imid}$, ^2J 15.0, ^3J 4.0), 6.68 (s. 1H, Imid), 6.69 (d, 1H, Ar, *J* 5.0), 6.72 (dd, 1H, Ar, $^3J_1$ 8.0, $^3J_2$ 15.0), 7.16 (m, 2H, Ar), 7.20 (m, 1H, Ar, *J* 5.0 cannot have m and J), 7.35 (t, 2H, Ar, *J* 8.0), 7.40 (m, 1H, Ar), 7.52 (d, 1H, Imid, *J* 2.0), 7.61–7.70 (m, 3H, Ar), 7.99 (d, 1H, Ar, *J* 9.0), 8.21 (d, 2H, Ar, *J* 8.0), 8.73 (s, 1H, Imid). ^{13}C NMR (150MHz, $CDCl_3$/CD_3OD (1:1)): 24.32 (C-13), 31.21 (C-12), 36.54 (C-19), 51.97 (C-15), 58.65 (C-14), 64.65 (C-26), 68.94 (C-2), 71.55 (C-11), 121.38 (C-8), 122.44 (C-17), 123.75 (C-9), 124.14 (C-18), 125.80 (C-4), 126.90 (C-30), 127.58 (C-21 or C-25), 128.96 (C-29, C-31), 128.98 (C-22, C-24), 129.81 (C-23, C-7), 130.67 (C-6), 131.25 (C-28, C-32), 133.21 (C-22, C-24), 133.25 (C-27), 133.79 (C-21 or C-25), 134.11 (C-20), 138.31 (C-16),143.15 (C-5), 174.97 (C-10), 177.49 (C-3), 181.90 (C-1).

4.4. (*S*)-2-Amino-3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate 1

To a solution of complex **4** (8 g, 0.0138 mol) in CH_2Cl_2 (50 ml), iodomethane (19.7 g, 8.65 ml, 0.138 mol) was added. The reaction mixture was stirred at room temperature for 24 h, the reaction being monitored by TLC [Silicagel, MeOH/CH_2Cl_2 (1:1)]. Then, the reaction mixture was evaporated on a rotary evaporator and the residue was dissolved in MeOH (30 ml). Next 6 M HCl (30 ml) was added to the methanol solution and the reaction mixture was refluxed for 10 min and then cooled to room temperature. The solvent was evaporated and a small volume of water was added to the residue. The resultant precipitate of (*S*)-BBP hydrochloride was filtered and washed with water. The filtrate was neutralized by aqueous ammonia to pH ≈ 6–7 and the remaining (*S*)-BBP was extracted with

$CHCl_3$ (3 × 30 ml). The aqueous layer was filtered through a paper filter and absorbed onto strongly acidic ion exchange resin Dowex 50W × 8 (100 g) and carefully washed with water, until the washings became neutral. The desired amino acid (as was shown before[5,8] no racemization of the amino acid moiety takes place under the reaction conditions, thus the ee of the isolated amino acid **1** can be assumed to be equal to de of the initial complex **4** or **6**) was washed off with 5% aqueous ammonia. The obtained solution was evaporated to give 2.3 g of amino acid containing some impurities as a yellow oil. (*S*)-(1-Methyl)-imidazol-3-ylidene-alaninate was purified using column chromatography (Silicagel, MeOH). Contaminants were washed off with MeOH and the desired amino acid was washed off with MeOH/H_2O (1:1). Yellowish oil. Yield 1.7 g (73%). $[\alpha]_D^{25} = -18.4$ (*c* 1.4, H_2O) (ee >99% according to de >99% of the initial complex **6**). Anal. Calcd for $C_7H_{11}N_3O_2 \cdot 1/4\ H_2CO_3$: C, 47.15; H, 6.28; N, 22.75. Found: C, 47.15; H, 6.32; N, 22.12. ^{1}H NMR (400 MHz, D_2O): 3.57 (t, 1H, $CHCO_2$, *J* 5.8), 3.74 (s, 3H, CH_3), 4.24 (d, 2H, CH_2N_{Imid}, *J* 5.8), 7.28 (d, 1H, =C*H*$N_{Imid}CH_3$, *J* 2.0), 7.29 (d, 1H, =C*H*$N_{Imid}CH_2$, *J* 2.0). ^{13}C NMR (150 MHz, D_2O): 35.7 (CH_3), 53.04 (CH_2), 55.88 (*C*HCO_2), 122.63 (=*C*$HN_{Imid}CH_2$), 123.62 (=*C*$HN_{Imid}CH_3$), 136.28 (t, NCDN, ^1J 25.0), 177.69 (COO^-).

4.5. (*S*)-2-(*tert*-Butoxycarbonylamino)-3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate 7

To an emulsion of amino acid **1** (250 mg, 1.48 mmol) in THF (1 ml), Boc_2O (438 mg, 0.46 ml, 2 mmol) was added. The reaction mixture was stirred at room temperature for 48 h. Solvent was evaporated on a rotary evaporator and the residue was purified using column chromatography (Silicagel, MeOH). The desired product was obtained as white crystals. Yield 180 mg (57%). Mp 91–95 °C. $[\alpha]_D^{25} = +118$ (*c* 1.02, $CHCl_3$) (ee >99% according to ee >99% of the initial amino acid **1**). Anal. Calcd for $C_{12}H_{19}N_3O_4 \cdot H_2O$: C, 50.16; H, 7.37; N, 14.63. Found: C, 49.87; H, 6.81; N, 14.54. ^{1}H NMR (300 MHz, $CDCl_3$): 1.41 (s, 9H, ^{t}Bu), 4.01 (s, 3H, CH_3), 4.17 (m, 1H, $CHCO_2$), 4.63–4.85 (m, 2H, CH_2N_{Imid}), 6.01 (d, 1H, NH, *J* 1.2), 7.08 (s, 1H, =C*H*$N_{Imid}CH_3$), 7.18 (s, 1H, =C*H*$N_{Imid}CH_2$), 9.93 (s, 1H, NCHN). ^{13}C NMR (75 MHz, $CDCl_3$): 28.41 ($C(CH_3)_3$), 36.29 (NCH_3), 51.61 (CH_2), 56.15 (*C*HCO_2), 79.39 ($C(CH_3)_3$), 121.74 (=*C*$HN_{Imid}CH_2$), 123.37 (=*C*$HN_{Imid}CH_3$), 139.04 (NCHN), 156.00 (OC(O)NH), 170.62 (COO^-).

4.6. (*S*)-(1-(2-(*tert*-Butoxycarbonylamino)-2-carboxylatoethyl)-3-methyl-1*H*-imidazol-2-ylidene)silver(I) 8

To a solution of Boc-protected amino acid **7** (50 mg, 0.186 mmol) in CH_2Cl_2 (3 ml), Ag_2O (21.6 mg, 0.093 mmol) was added. The resulting suspension was stirred for 24 h in the dark and then filtered. Solvent was removed on a rotary evaporator. The desired product was obtained as a white solid. Yield 55 mg (80%). Mp 195 °C (decomposition). $[\alpha]_D^{25} = +60.0$ (*c* 1.02, $CHCl_3$). Anal. Calcd for $C_{12}H_{18}AgN_3O_4$: C, 38.27; H, 4.82; N, 11.17; Ag, 28.68. Found: C, 38.32; H, 4.82; N, 11.17; Ag, 28.6. ^{1}H NMR (300 MHz, $CDCl_3$): 1.42 (s, 9H, ^{t}Bu), 3.76 (s, 3H, CH_3), 4.33 (m, 1H, $CHCO_2$), 4.52 (dd, 1H, CH_2N_{Imid}, ^2J 13.8, ^{3}J 4.2), 4.79 (d, 1H, CH_2N_{Imid}, ^2J 13.8), 5.55 (d, 1H, NH, *J* 3.3), 6.84 (s, 1H, =C*H*$N_{Imid}CH_3$), 6.85 (s, 1H, =C*H*$N_{Imid}CH_2$). ^{13}C NMR (150 MHz, $CDCl_3$): 28.44 ($C(CH_3)_3$), 38.97 (NCH_3), 52.16 (CH_2), 56.30 (*C*HCO_2), 79.37 ($C(CH_3)_3$), 120.97 (=C*H*$N_{Imid}CH_2$), 123.43 (=C*H*$N_{Imid}CH_3$), 155.37 (OC(O)NH), 173.19 (COO^-), 179.6 (d, NCAgN, $^1J_{AgC}$ 270).

Acknowledgments

The authors thank INTAS (05-1000008-7822), ISTC (G-1361), and RFBR (08-03-00466) for financial support.

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