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2-Cyclopentadienylglycine, a new α-amino acid and its use for η^5-complex formation

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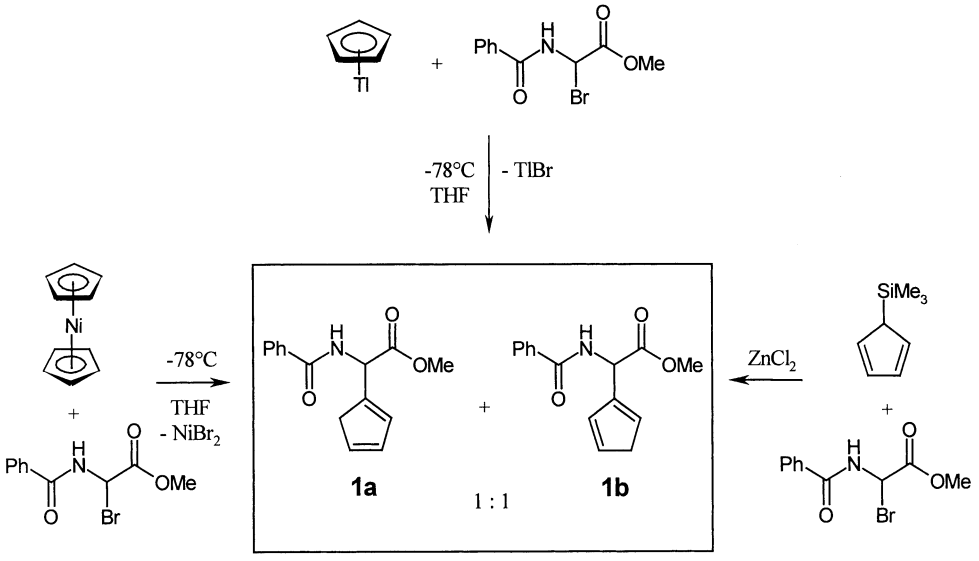
Abstract—The reaction of α-bromohippuric acid methyl ester with nickelocene, cyclopentadienylthallium or cyclopentadienyltrimethylsilane afforded *N*-benzoyl-2-cyclopentadienylglycine methyl ester (**1**) as two double bond isomers **1a** and **1b**. Similarly, the cyclopentadienyl(Cp)-containing dipeptide Z-L-Phe-DL-(Cp)Gly-OMe (**3**) was obtained from Z-L-Phe-DL-Gly(Cl)-OMe and trimethylsilylcyclopentadiene. The amino acids **1a**, **1b** were susceptible to Diels–Alder cycloaddition and yielded dimer **2** as a mixture of regioisomers. Compound **1** and $FeCl_2$ gave 1,1′-ferrocenylene-bis(glycine) (**5**), whereas with $[(COD)RhCl]_2$ rhodium η^5-cyclopentadienylglycine (**6**) and η^5-cyclopentadienyldipeptide complexes like **7** were obtained from **1** or **3**, respectively. Unexpectedly, the η^5-cyclopentadienylglycine complexes proved to be very sensitive to light.

1. Introduction

In the course of our studies on organometallic complexes of α-amino acids and peptides,[1,2] we became interested in new α-amino acids with coordinating side chains. Besides the large variety of complexes of natural α-amino acids with donor groups (e.g. cysteine, histidine),[3] synthetic α-amino acids and peptides with pyridyl and bipyridyl,[4] phosphino[5] or alkinyl[6] substituents have been used in coordination chemistry. The incorporation of metal binding sites into peptides and metal complexes thereof are of interest for the structural modification of peptides, for applications in



Formula 1.

Keywords: amino acids and derivatives; cyclopentadienylglycine; complexes; cyclopentadienes; ferrocenes.

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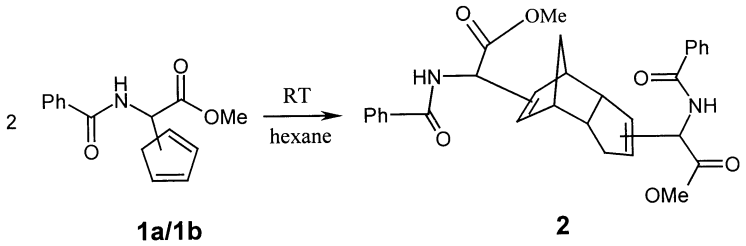


1a/1b **2**

Formula 2.

asymmetric catalysis or as peptide mimetics. A series of metal π-coordinated aromatic amino acids has been reported,[2,7] e.g. for the labeling of peptides.

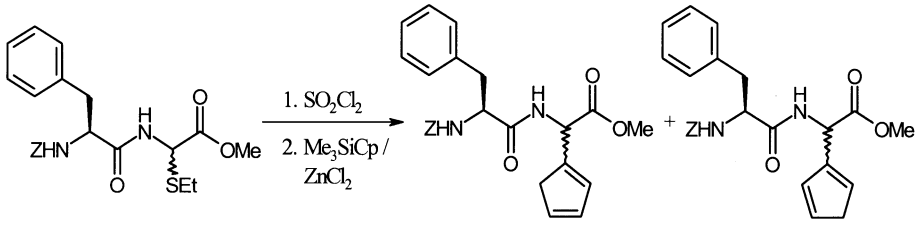
As early as 1957, several metallocenyl alanines (M=Fe, Ru, Mn) were obtained[8] from metallocenes. Recently, cyclopentadienides with amino acid derived substituents could be prepared from *N*-protected alanine and LiCp.[9] The synthesis of a series of optically pure metallocene bis(valines) will be reported elsewhere.[10]

2-Cyclopentadienylglycine (**1**), which to our knowledge has not been reported so far, appears to be an interesting novel ligand with a potentially rich organometallic chemistry. In addition, **1** could exhibit biological activity as was found for 2-cyclopentenyl- and 2-cyclopentylglycine that are growth inhibitors in bacteria.[11] We have applied α-bromohippuric acid methyl ester for the synthesis of this ligand. The chemistry of electrophilic glycine equivalents has been developed by one of us[12,13] and was also used for the incorporation of α-transition metals fragments into amino acids.[14]

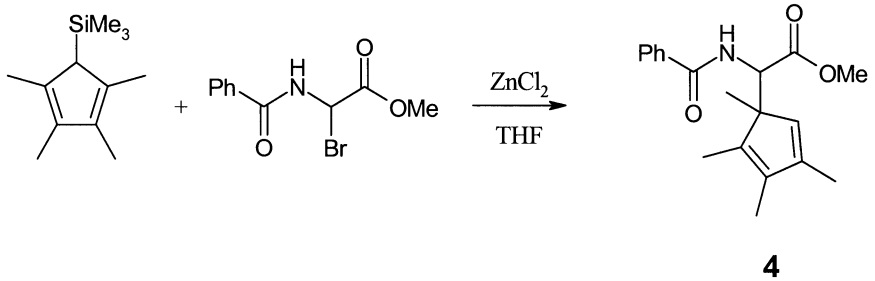
2. Results and discussion

2.1. 2-Cyclopentadienylglycine (1)

The reactions of α-bromohippuric acid esters with alkali cyclopentadienides proceed under dehydrohalogenation of the amino acid derivative with the cyclopentadienyl anion functioning as base.[12] Using the 'soft', non basic cyclopentadienyl transfer agents nickelocene,[15] cyclopentadienylthallium[16] or cyclopentadienyltrimethylsilane in the presence of $ZnCl_2$ we succeeded in the synthesis of *N*-benzoyl-2-cyclopentadienylglycine (**1**). Cyclopentadienyltrimethylsilane has been used before in the synthesis of cyclopentadienyl compounds of main group elements[17] (Formula 1).



3a **3b**



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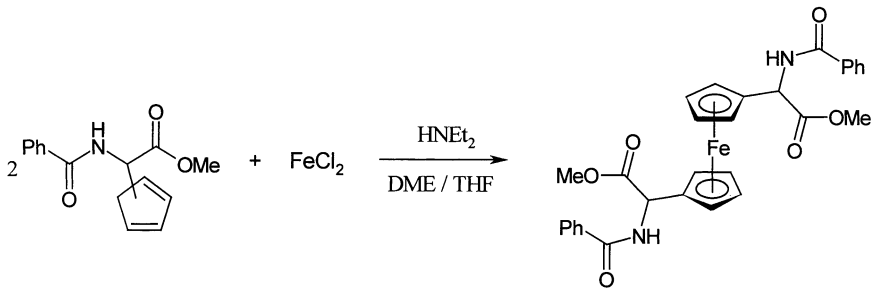
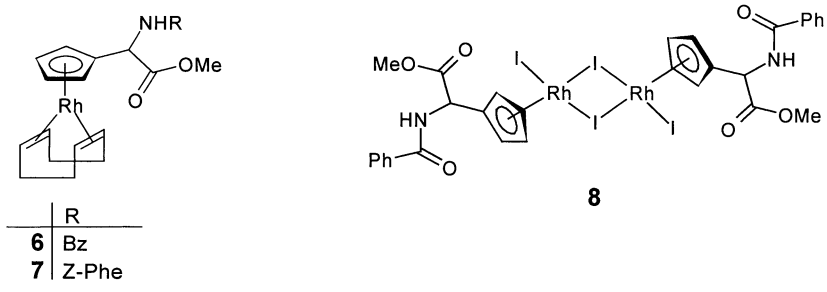
Formula 3.



1a/1b 5



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Formula 4.

The oily product can be purified by column chromatography and consists of a 1:1 mixture of the double bond isomers **1a** and **1b**. The third possible isomer with an unsubstituted C═C bond in the cyclopentadiene ring is not formed.[18] Addition of triethylamine as base to generate the acylimine[12] reduces the yield. This indicates that the reaction proceeds by nucleophilic substitution rather than by the normal elimination/addition mechanism.

The ^{1}H and ^{13}C NMR spectra of **1** exhibit two sets of signals. In the ^{1}H NMR spectrum the different cyclopentadiene rings can be unambiguously identified by the signals of the geminal and the olefinic protons.

In contrast to 2-vinylglycine derivatives, which are easily converted to the corresponding alkylidene isomers,[19] compounds **1a** and **1b** do not show this behavior. Instead the double bond isomers of **1** are subject to Diels–Alder [4π+2π]cycloaddition even at room temperature and yield dimer **2** as a mixture of regioisomers (Formula 2).

Following our approach for the derivatisation of peptides[13] the cyclopentadienyl dipeptide **3** was obtained from Z-L-Phe-DL-Gly(SEt)-OMe by treatment with SO_2Cl_2 and subsequent addition of cyclopentadienyltrimethylsilane and $ZnCl_2$ to the intermediary chloride. Use of TlCp improved the yields of **1** and **3**. However, special precautions are necessary because of the toxicity of this compound. As in the case of **1**, only two Cp ring isomers **3a** and **3b** were detected. Due to the directing influence of the phenylalanine residue a low diastereoselectivity (62:38) was observed (Formula 3).

From (tetramethylcyclopentadienyl)trimethylsilane[20] and α-bromohippuric acid methyl ester/$ZnCl_2$ compound **4** was formed in good yield, unexpectedly as one isomer; **4** shows no tendency to undergo Diels–Alder addition and is blocked for η^5-coordination to a metal ion.

2.2. η^5-Complexes

2-Cyclopentadienylglycine (**1**) could be deprotonated in situ with diethylamine and gave with $FeCl_2$ 1.1′-ferrocenylene bis(glycine) (**5**) as a 1:1 mixture of the two expected diastereoisomers. More basic alkali hydrides are not suitable for the deprotonation of **1**. Here, decomposition was observed presumably due to further deprotonation of the amide group (Formula 4).

Surprisingly, complex **5** is very air and light sensitive and can only be purified by column chromatography under argon and exclusion of light. The instability of **5** is in accordance with observations by Schlögl[8a] and Graham[21] who were able to synthesize the light sensitive 1-ferrocenyl hydantoin, which decomposed during the attempted hydrolysis to ferrocenyl glycine. Presumably the instability of **5** is caused by photoinduced coordination of the ester groups and subsequent $\eta^5 \rightarrow \eta^4$ rearrangement. In contrast, the ferrocenyl alanines[8] and valines[10] which possess a CR_2 spacer unit between the cyclopentadienyl group and the α-carbon of the amino acid are much more stable.

From **1**, **3** and $[(COD)RhCl]_2$ the η^5-cyclopentadienylglycine ester complex **6** and the dipeptide derivative **7**

were accessible in the presence of triethylamine. Addition of iodine to **6** yielded the iodo bridged dimer **8**. Again the complexes **6**–**8** were very sensitive to light. In the ^{1}H NMR spectrum of **8** two sets of signals indicate the presence of two diastereoisomers (*RR*/*SS* and *RS*). In the ^{13}C NMR spectra of **6**–**8** characteristic $^{103}Rh-^{13}C$ couplings are observed for the π-coordinated carbon atoms. The FAB mass spectra of **6** and **7** reveal the same fragments (*m*/*z*=391 and 347), which are formed via fragmentation at the *N*-terminus.

3. Conclusion

The novel α-amino acid 2-cyclopentadienylglycine (**1**) provides a vehicle for the introduction of organometallic fragments into amino acids and peptides.

4. Experimental

4.1. General

Nickelocene, cyclopentadienylthallium and cyclopentadienyltrimethylsilane are commercially available. The reactions were carried out in Schlenk tubes under an atmosphere of argon. For centrifugation a Kryofuge 6000i, Heraeus, and for chromatography silica gel Merck (0.063–0.200 mm) were used. IR: Nicolet 520 FT and Perkin–Elmer Model 841. NMR: Jeol GSX270 and Jeol EX400. MS: Finnigan MAT 90.

4.2. DL-*N*-Benzoyl-2-cyclopentadienylglycine methyl ester (1a/1b)

4.2.1. From cyclopentadienylthallium (TlCp). To α-bromohippuric acid methyl ester[12] (692 mg, 2.54 mmol) in THF (40 mL) TlCp (685 mg, 2.54 mol) was added at −78°C. The suspension was stirred for 2 h at −78°C and allowed to warm to room temperature. The precipitate of TlBr was centrifuged off and the solution concentrated in vacuo. The residue was purified by column chromatography (silica gel, $CHCl_3$) to yield 529 mg of **1** (81%) as a colorless oil (1:1 mixture of isomers **1a** and **1b**). IR (KBr): ν (cm^{-1})= 3376br (NH), 3063w, 2952m, 1759vs (C=O), 1660vs, 1527vs (NCO), 1440s, 1333m, 1223m, 1072m, 783w, 715m, 694m (Ph). ^{1}H NMR (270 MHz, $CDCl_3$): δ=3.01 (**1a**), 3.06 (**1b**) (each m, 2H, CH_2), 3.77, 3.78 (each s, 3H, OCH_3), 5.67 (Ψdd, 2H, α-H, **1a/1b**), 6.36–6.57 (m, 6H, H_{olef}, **1a/1b**), 6.88 (Ψt, ^{3}J=8.1 Hz, 2H, NH, **1a/1b**), 7.41–7.52 (m, 6H, *m*- and *p*-C_6H_5, **1a/1b**), 7.79–7.83 (m, 4H, *o*-C_6H_5, **1a/1b**). ^{13}C NMR (100.5 MHz, $CDCl_3$): δ=41.68, 42.05 (each CH_2), 52.80, 52.81 (each OCH_3), 52.55, 53.00 (each α-C), 127.15, 127.27, 128.57, 128.72, 130.11, 130.72, 130.78, 131.76, 131.81, 131.88, 131.98, 133.59, 133.80, 135.32, 141.52, 142.09 (16C, **1a** and **1b**, Cp and Ph), 166.70, 166.83 (each CON), 171.31, 171.39 (each CO_2). MS (FAB): 257 $[M]^+$. Anal. found: C, 65.11; H, 5.50; N, 5.17%. Calcd for $C_{15}H_{15}NO_3 \cdot 1/5\ CHCl_3$ (281.57): C, 64.84; H, 5.44; N, 4.97%.

4.2.2. From dicyclopentadienylnickel. To α-bromohippuric acid methyl ester (409 mg, 1.50 mmol) in THF (30 mL) $NiCp_2$ (142 mg, 0.75 mmol) was added at −78°C. After 10 min, a light violet precipitate of $NiBr_2$ was formed. The suspension was stirred for 15 h and allowed to warm to room temperature. The solid was centrifuged off and the solvent removed in vacuo. The residue was dissolved in dichloromethane (5 mL) and after centrifugation, the solution was again concentrated in vacuo. The residue was purified by column chromatography (silica gel, $CHCl_3$) to yield 330 mg of **1** (78%) (1:1 mixture of isomers **1a** and **1b**).

4.2.3. From trimethylsilylcyclopentadiene. To α-bromohippuric acid methyl ester (578 mg, 2.12 mmol) in THF (15 mL) trimethylsilylcyclopentadiene (700 μl, 4.24 mmol) and a solution of $ZnCl_2$ (579 mg, 4.24 mmol) in THF (5 mL) were added. The mixture was stirred for 16 h at room temperature. After addition of water (20 mL), the mixture was extracted with $CHCl_3$ (3×15 mL). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, $CHCl_3$) to yield 381 mg **1** (64%) as a colorless oil (1:1 mixture of isomers **1a** and **1b**).

4.3. Dimerization of 1

The addition of *n*-hexane (30 mL) to a solution of **1** (123 mg, 0.48 mmol) in $CHCl_3$ (10 mL) led to the precipitation of an oil. After stirring the mixture for 24 h at room temperature, the oil was transformed to a colorless powder that was centrifuged off and dried in vacuo to yield 121 mg of dimers **2** (91%). The NMR spectra indicated a mixture of regioisomers. IR (KBr): ν (cm^{-1})=3063w, 2953m, 1750vs (C=O), 1659vs, 1525vs (NCO), 1487s, 1438s, 1332m, 1225m, 1074m, 782w, 714m, 693m (Ph). MS (FAB): 515(3) $[M]^+$. Anal. found: C, 65.08; H, 5.56; N, 5.54%. Calcd for $C_{30}H_{30}N_2O_6 \cdot 1/3\ CHCl_3$ (555.04): C, 65.64; H, 5.51; N, 5.05%.

4.4. *N*-Benzyloxycarbonyl-L-phenylalanyl-DL-2-[cyclopentadien-1(or 3)-yl]glycine methyl ester (3a/3b)

To Z-L-Phe-DL-Gly(SEt)-OMe[13] (547 mg, 1.27 mmol) in CH_2Cl_2 (15 mL) was added dropwise a solution of SO_2Cl_2 in CH_2Cl_2 (1.39 mL, 1.0 M) at 0°C. After stirring for 30 min, the volatile components were removed in vacuo, and the residue was dried in vacuo for 2 h. The resulting α-chloroglycyl peptide was dissolved in THF (15 mL), and trimethylsilylcyclopentadiene (630 μl, 3.81 mmol) was added. After addition of $ZnCl_2$ (346 mg, 2.54 mmol), the mixture was stirred for 7 h. Then, the mixture was quenched with water (20 mL) and extracted with $CHCl_3$ (3×15 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, $CHCl_3$) to yield 287 mg of **3** (52%) as a colorless oil. The NMR spectra indicated a 62:38 mixture of diastereomers, each consisting of the two Cp-isomers **3a** and **3b** (1:1). IR (KBr): ν (cm^{-1})=3374w (NH), 3067m, 3011w, 2971m, 1749br, vs (C=O), 1658br, vs, 1524vs (NCO), 1487s, 1385w, 1331m, 1221m, 1157m, 783w, 770w, 713s, 693m (Ph). ^{1}H NMR (270 MHz, $CDCl_3$): δ=2.83, 2.87 (each m, 2H, CH_2, Cp-isomers), 2.96–3.02 (m, 2H, CH_2Phe), 3.61, 3.62, 3.63, 3.64 (each s, 3H, OCH_3), 4.50 (pt, br, ^{3}J=6.9 Hz, 1H, N*H*(Phe)), 4.98, 4.99

(2s, 2H, OCH_2), 5.33–5.38 (m, 1H, α-H), 5.44–5.48 (m, 1H, α-H), 6.18–6.37 (m, 3H, H_{olef}), 6.88 (s, br, 1H, NH), 7.03–7.31 (m, 10H, Ph). MS (FAB): 435(7) $[M]^+$, $C_{25}H_{26}N_2O_5$ (434.49).

4.5. DL-*N*-Benzoyl-2-(2,3,4,5-tetramethylcyclopentadien-5-yl)glycine methyl ester (4)

To α-bromohippuric acid methyl ester (431 mg, 1.58 mmol) in THF (10 mL) were added 1-trimethylsilyl-2,3,4,5-tetramethylcyclopentadiene[20] (1.24 g, 6.34 mmol) and a solution of $ZnCl_2$ (432 mg, 3.17 mmol) in THF (10 mL). After stirring for 14 h, the mixture was quenched with water (5 mL) and extracted with $CHCl_3$ (3×15 mL). The combined organic phases were dried over Na_2SO_4, concentrated in vacuo and purified by column chromatography (silica gel, $CHCl_3$) to afford 351 mg of **4** (71%) as a light yellow resin. IR (KBr): ν (cm^{-1})=3069w, 2967m, 1744vs (C=O), 1665vs, 1518vs (NCO), 1486s, 1446m, 1353m, 1206s, 1156m, 1026m, 760w, 713s, 693s (Ph). ^1H NMR (270 MHz, $CDCl_3$): δ=1.08 (s, 3H, CH_3), 1.67 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.92 (d, ^3J=1.8 Hz, 3H, CH_3), 3.75 (s, 3H, OCH_3), 4.57 (d, ^3J=7.6 Hz, 1H, α-H), 5.84 (s, br, 1H, H_{olef}), 5.92 (d, ^3J=7.3 Hz, 1H, NH), 7.31–7.41 (m, 3H, *m*- and *p*-C_6H_5), 7.47–7.52 (m, 2H, *o*-C_6H_5). MS (FAB): 313(12) $[M]^+$, 314(61) $[M+H]^+$. $C_{19}H_{23}NO_3$ (313.39).

4.6. Bis[η^5-DL-*N*-benzoyl-2-cyclopentadienylglycine methyl ester]iron(II) (5)

To α-bromohippuric acid methyl ester (271 mg, 0.99 mmol) in THF (20 mL) was added at −78°C cyclopentadienylthallium (268 mg, 0.99 mmol). The suspension was stirred for 2 h at −78°C and then allowed to warm to room temperature. After removal of TlBr by centrifugation, the solution was concentrated in vacuo and the residue taken up in DME (5 mL). To this solution diethylamine (206 μL, 1.99 mmol) and then $FeCl_2$ (63 mg, 0.49 mmol) in THF (5 mL) were added dropwise. The mixture was stirred for 4 h, concentrated under reduced pressure, and the residue extracted with diethyl ether (10 mL). After concentration in vacuo, the product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate 3/1) to yield 86 mg of **5** (31%) as an orange resin. IR (CD_2Cl_2): ν (cm^{-1})=3342s (NH), 3010m, 2956m, 1747vs (C=O), 1668vs, 1509s (NCO), 1482s, 1389s, 1218m. ^1H NMR (400 MHz, CD_2Cl_2): δ=3.81 (s, 6H, OCH_3), 4.24–4.34 (m, 8H, Cp), 5.52 (d, ^3J=7.9 Hz, 2H, α-H), 7.03 (d, ^3J=8.1 Hz, 2H, NH), 7.42–7.54 (m, 6H, *m*- and *p*-C_6H_5), 7.81–7.87 (m, 4H, *o*-C_6H_5). ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ=51.76 (OCH_3), 52.38 (α-C), 66.67, 68.34, 68.94, 69.32 (Cp), 84.80 (*ipso*-C, Cp), 127.01, 128.46, 131.64, 133.62 (Ph), 166.39 (CON), 170.86 (CO_2). MS (FAB): 568(14) $[M]^+$, 448(4), 328(5), 312(23), 281(11). HR FAB MS: found 568.1301, calcd 568.1297. $C_{30}H_{28}FeN_2O_6$ (568.40).

4.7. η^4-Cycloocta-1,5-diene-[η^5-DL-*N*-benzoyl-2-cyclopentadienylglycine methyl ester]rhodium(I) (6)

To a solution of **1** (250 mg, 0.87 mmol) in MeOH (7 mL) were added $[(COD)RhCl]_2$ (210 mg, 0.44 mmol) and triethylamine (113 μL, 0.87 mmol). The mixture was stirred for 3 h and the solvent removed in vacuo. The residue was purified by chromatography (silica gel, THF) to yield 288 mg of **6** (71%) as a yellow resin. IR (KBr): ν (cm^{-1})=3355w, 2916vs, 2828vs (COD), 1746vs (C=O), 1662br, vs, 1515s (NCO), 1473s, 1324m, 1261s, 1214s, 1164m, 1090m, 874m, 798m, 743m, 711s, 692m (Ph), 386m (Rh-COD). ^1H NMR (270 MHz, $CDCl_3$): δ=1.85 (m, 4H, H_{aliph}-COD), 2.14 (m, 4H, H_{aliph}-COD), 3.78 (s, 3H, OCH_3), 3.95 (m, 4H, H_{olef}-COD) 5.01 (m, 2H, Cp), 5.17 (m, 1H, Cp), 523 (m, 1H, Cp), 5.49 (d, ^3J=7.3 Hz, 1H, α-H), 7.01 (d, ^3J=7.0 Hz, 1H, NH), 7.41–7.53 (m, 3H, *m*- and *p*-C_6H_5), 7.82–7.88 (m, 2H, *o*-C_6H_5). ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ=32.25 (C_{aliph}-COD), 32.27 (C_{aliph}-COD), 51.25 (OCH_3), 52.38 (α-C), 64.09 (d, J_{RhC}=2.8 Hz, C_{olef}-COD), 64.23 (d, J_{RhC}=2.7 Hz, C_{olef}-COD), 85.29 (d, J_{RhC}=3.2 Hz, Cp), 86.03 (d, J_{RhC}=4.4 Hz, Cp), 87.22 (d, J_{RhC}=4.6 Hz, Cp), 87.26 (d, J_{RhC}=3.4 Hz, Cp), 102.88 (d, J_{RhC}=3.0 Hz, *ipso*-C, Cp), 127.01, 128.65, 131.84, 133.99 (Ph), 166.43 (CON), 170.87 (CO_2). MS (FAB): 467(82) $[M]^+$, 359(75) $[M-COD]^+$, 347(32). HRMS (FAB): found 467.1007; calcd 467.0961. $C_{23}H_{26}NO_3Rh$ (467.37).

4.8. η^4-Cycloocta-1,5-diene-[*N*-benzyloxycarbonyl-L-phenylalanyl-η^5-DL-2-cyclopentadienylglycine methyl ester]rhodium(I) (7)

To a solution of the cyclopentadienyl dipeptide **3** (131 mg, 0.30 mmol) in MeOH (10 mL) were added $[(COD)RhCl]_2$ (74 mg, 0.15 mmol) and NEt_3 (45 μL, 0.30 mmol). The mixture was stirred for 3 h, the solvent removed in vacuo, and the residue purified by chromatography (silica gel, THF) to yield 108 mg **7** (56%) as a yellow powder. IR (KBr): ν (cm^{-1})=3311w, 2931m, 2872m, 2828m, 1743vs, 1709vs, 1662vs (C=O), 1520s (NCO), 1498s, 1325m, 1260s, 1217s, 1042m, 874m, 741m, 698m (Ph). ^1H NMR (270 MHz, C_6D_6): δ=1.83 (m, 4H, H_{aliph}-COD), 2.18 (m, 4H, H_{aliph}-COD), 3.12 (m, 2H, CH_2(Phe)), 3.31, 3.33 (s, 3H, OCH_3), 3.87 (m, 4H, H_{olef}-COD), 4.81–5.02 (m, 7H, Cp, CH and CH_2), 5.51, 5.57 (d, ^3J=7.2 Hz, 1H, α-H), 5.69 (m, 1H, NH), 6.99–7.22 (m, 11H, Ph and NH). ^{13}C NMR (100.5 MHz, C_6D_6): δ=32.37 (C_{aliph}-COD), 32.51 (C_{aliph}-COD), 38.94 (CH_2), 51.11 (OCH_3), 51.66 (CH), 56.51 (CH), 64.12 (d, J_{RhC}= 5.4 Hz, C_{olef}-COD), 64.27 (d, J_{RhC}=5.3 Hz, C_{olef}-COD), 67.78 (CH_2), 85.43 (d, J_{RhC}=3.2 Hz, Cp), 86.02 (d, J_{RhC}=3.1 Hz, Cp), 86.92 (d, J_{RhC}=3.9 Hz, Cp), 87.16 (d, J_{RhC}=4.1 Hz, Cp), 102.58 (d, J_{RhC}=4.1 Hz, *ipso*-C, Cp), 126.75, 128.08, 128.37, 128.56, 129.72, 130.55, 133.12, 136.85, 137.15 (Ph), 156.12 (CON), 167.32 (CON), 170.52 (CO_2). MS (FAB): 644(16) $[M]^+$, 536(7) $[M-COD]^+$, 460(5), 391(14), 347(8). $C_{33}H_{37}N_2O_5Rh$ (644.57).

4.9. μ-Diiodo-bis[η^5-DL-*N*-benzoyl-2-cyclopentadienylglycine methyl ester iodorhodium(III)] (8)

6 (293 mg, 0.63 mmol) was taken up in diethyl ether (15 mL), and a solution of iodine (158 mg, 0.63 mmol) in diethyl ether (5 mL) was added dropwise at 0°C. Immediately, a violet precipitate was formed which after stirring for 1 h was centrifuged off and washed with diethyl ether. The product was crystallized from dichloromethane/*n*-hexane and dried in vacuo to yield 112 mg of **8** (27%) as a violet

powder. IR (KBr): ν (cm^{-1})=3097m, 2917w, 1743vs (C═O), 1661vs, 1518s (NCO), 1486s, 1313s, 1227m, 1036w, 847w, 745w, 711w, 691w. ^1H NMR (270 MHz, CD_2Cl_2): δ=3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.50 (m, 2H, Cp), 5.69–5.75 (m, 6H, α-H and Cp), 5.93 (m, 2H, Cp), 7.48–7.63 (m, 6H, *m*- and *p*-C_6H_5), 7.87 (d, ^3J=7.8 Hz, 1H, NH), 7.89 (d, ^3J=7.8 Hz, 1H, NH), 8.05–8.09 (m, 4H, *o*-C_6H_5). ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ=50.12 (α-C), 50.19 (OCH_3), 83.19 (d, J_{RhC}=8.3 Hz, Cp) 83.71 (d, J_{RhC}=8.9 Hz, Cp), 86.38 (d, J_{RhC}=5.5 Hz, Cp), 87.69 (d, J_{RhC}=5.1 Hz, Cp), 98.39 (d, J_{RhC}=8.3 Hz, ipso-C, Cp), 127.77, 128.68, 132.39, 132.49 (Ph), 167.02 (CON), 167.49 (CO_2). Anal. found: C, 28.01; H, 2.50; N, 2.09%. Calcd for $C_{30}H_{28}N_2I_4O_6Rh_2{\cdot}CH_2Cl_2$ (1310.92): C, 28.39; H, 2.31; N, 2.13%.

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References

1. Part 135 of Metal complexes with biologically important ligands; Part 134: Dialer, H.; Schumann, S.; Polborn, K.; Steglich, W.; Beck, W. *Eur. J. Inorg. Chem.*, submitted for publication.
2. Severin, K.; Bergs, R.; Beck, W. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1634.
3. Lanrie, St. H. *Comprehensive Coordination Chemistry*, Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 739.
4. (a) Sugimoto, N.; Watanabe, H.; Ide, A. *Tetrahedron* **1960**, *11*, 231. (b) Imperiali, B.; Fisher, St. L. *J. Am. Chem. Soc.* **1991**, *113*, 8527. Imperiali, B.; Fisher, St. L. *J. Org. Chem.* **1992**, *57*, 757. (c) Bozell, J. J.; Vogt, C. E.; Gozum, J. *J. Org. Chem.* **1991**, *56*, 2584. (d) Bernauer, K.; Stoeckli-Evans, H.; Hugi-Cleary, D.; Hilgers, H. J.; Abd-el-Khalek, H.; Porret, J.; Sauvain, J.-J. *Helv. Chim. Acta* **1992**, *75*, 2327. (e) Imperiali, B.; Prins, Th. J.; Fisher, St. L. *J. Org. Chem.* **1993**, *58*, 1613. (f) Schmidt, B.; Ehlert, D. K. *Tetrahedron Lett.* **1998**, *39*, 3999. (g) Walkup, G. K.; Imperiali, B. *J. Org. Chem.* **1998**, *63*, 6727. (h) Haas, K.; Nöth, H.; Beck, W. *Z. Naturforsch.* **1999**, 989.
5. (a) Gilbertson, S. R.; Starkey, G. W. *J. Org. Chem.* **1996**, *61*, 2922. (b) Gilbertson, S. R.; Wang, X. *J. Org. Chem.* **1996**, *61*, 434. (c) Tepper, M.; Stelzer, O.; Häusler, T.; Sheldrick, W. S. *Tetrahedron Lett.* **1997**, *38*, 2257. (d) Porte, A. M.; van der Donk, W. A.; Burgess, K. *J. Org. Chem.* **1998**, *63*, 5262. (e) Gilbertson, S. R.; Xie, D. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 2750. (f) Gilbertson, S. R.; Pawlick, R. V. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 902. (g) Gilbertson, S. R.; Chen, G.; McLoughlin, M. *J. Am. Chem. Soc.* **1994**, *116*, 4481. (h) Gilbertson, S. R.; Wang, X.; Hoge, G. S.; Klug, C. A.; Schaefer, J. *Organometallics* **1996**, *15*, 4678. (i) Gali, H.; Karra, S. R.; Reddy, V. S.; Volkert, W. A.; Katti, K. V. *Angew. Chem., Int. Ed. Engl.* **2020**, *38*, 1999. (j) Kraatz, H. B.; Pletsch, A. *Tetrahedron: Asymmetry* **2000**, *11*, 1617. (k) Brauer, D. J.; Schenk, S.; Roßenbach, S.; Tepper, M.; Stelzer, O.; Häusler, T.; Sheldrick, W. S. *J. Organomet. Chem.* **2000**, *598*, 116.
6. (a) Kayser, B.; Altman, J.; Beck, W. *Chem. Eur. J.* **1999**, *5*, 754. (b) Kayser, B.; Altman, J.; Nöth, H.; Knizek, J.; Beck, W. *Eur. J. Inorg. Chem.* **1998**, 1791. (c) Rodbotten, S.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1997**, *51*, 873. (d) Brosch, O.; Weyhermüller, T.; Metzler-Nolte, N. *Inorg. Chem.* **1999**, *38*, 5308.
7. (a) Herebian, D. A.; Schmidt, C. S.; Sheldrick, W. S.; van Wüllen, C. *Eur. J. Inorg. Chem.* **1998**, 1991. (b) Grotjahn, D. B. *Coord. Chem. Rev.* **1999**, *190–192*, 1125. (c) Krämer, R. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1197.
8. (a) Schlögl, K. *Monath. Chem.* **1957**, *88*, 601. (b) Hauser, C. R.; Lindsay, J. K. *J. Org. Chem.* **1957**, *22*, 1246. (c) Osgerby, J. M.; Pauson, P. L. *J. Chem. Soc.* **1958**, 656. (d) Pospísek, J.; Toma, S.; Fric, I.; Bláha, K. *Collection Czechoslov. Chem. Commun.* **1980**, *45*, 435. (e) Cuingnet, E.; Sergheraert, C.; Tartar, A.; Dautrevaux, M. *J. Organomet. Chem.* **1980**, *195*, 325. (f) Brunet, J. C.; Cuingnet, E.; Gras, H.; Marcincal, P.; Mocz, A.; Sergheraert, C.; Tartar, A. *J. Organomet. Chem.* **1981**, *216*, 73. (g) Soine, W. H.; Guyer, C. E.; Knapp, Jr., F. F. *J. Med. Chem.* **1984**, *27*, 803. (h) Carlström, A.-S.; Frejd, T. *J. Org. Chem.* **1990**, *55*, 4175. Carlström, A.-S.; Frejd, T. *J. Org. Chem.* **1991**, *56*, 1289. Carlström, A.-S.; Frejd, T. *Synthesis* **1989**, 414. (i) Brunner, H.; König, W.; Nuber, B. *Tetrahedron: Asym.* **1993**, *4*, 699. (j) Jackson, R. F. W.; Turner, D.; Block, M. H. *Synlett* **1996**, 862. (k) Basu, B.; Chattopadhyay, S. K.; Ritzén, A.; Frejd, T. *Tetrahedron: Asym.* **1997**, *8*, 1841. (l) Kira, M.; Matsubara, T.; Shinohara, H.; Sisido, M. *Chem. Lett.* **1997**, 89. For a stereoselective synthesis of ferrocenyl-β-amino acids see: Adamczyk, M.; Reddy, R. E.; Rege, S. D. *Synth. Commun.* **2000**, *30*, 1389.
9. Kunz, D.; Fröhlich, R.; Erker, G. *Organometallics* **2001**, *20*, 572.
10. Dialer, H.; Polborn, K.; Ponikwar, W.; Sünkel, K.; Beck, W. *Eur. J. Inorg. Chem.* submitted for publication.
11. (a) Cramer, V.; Rehfeldt, A. G.; Speener, F. *Biochemistry* **1980**, *19*, 3074. (b) Santoso, S.; Kemmer, T.; Trowitzsch, W. *Liebigs Ann. Chem.* **1981**, 658. (c) Dennis, R. L.; Plant, W. J.; Skinner, C. G.; Sutherland, G. L.; Shive, W. *J. Am. Chem. Soc.* **1955**, *77*, 2362. (d) Harding, W. M.; Shive, W. *J. Biol. Chem.* **1954**, *206*, 401.
12. (a) Jaroch, S.; Schwarz, T.; Steglich, W.; Zistler, P. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1771. (b) Burgess, V. A.; Easton, C. J.; Hay, M. P.; Steel, P. J. *Aust. J. Chem.* **1988**, *41*, 701. (c) Bretschneider, T.; Miltz, W.; Münster, P.; Steglich, W. *Tetrahedron* **1988**, *44*, 5403. (d) Münster, P.; Steglich, W. *Synthesis* **1987**, 223. (e) Kober, R.; Steglich, W. *Liebigs Ann. Chem.* **1983**, 599. (f) Kober, R.; Papadopoulos, K.; Miltz, W.; Enders, D.; Steglich, W. *Tetrahedron* **1985**, *41*, 1693. (g) Trojandt, G.; Herr, U.; Polborn, K.; Steglich, W. *Chem. Eur. J.* **1997**, *3*, 1254.
13. (a) Apitz, G.; Jäger, M.; Jaroch, S.; Kratzel, M.; Schäffeler, L.; Steglich, W. *Tetrahedron* **1993**, *49*, 8223. (b) Schumann, S.; Zeitler, K.; Jäger, M.; Polborn, K.; Steglich, W. *Tetrahedron* **2000**, *56*, 4187.
14. (a) Kayser, B.; Missling, C.; Knizek, J.; Nöth, H.; Beck, W. *Eur. J. Inorg. Chem.* **1998**, 375. (b) Kayser, B.; Nöth, H.; Schmidt, M.; Steglich, W.; Beck, W. *Chem. Ber.* **1996**, *129*, 1617. (c) Kayser, B.; Polborn, K.; Steglich, W.; Beck, W. *Chem. Ber./Recueil* **1997**, *130*, 171.
15. Rufanov, K. A.; Kazennova, N. B.; Churakov, A. V.; Lemenovskii, D. A.; Kuz'mina, L. G. *J. Organomet. Chem.* **1995**, *485*, 173.

16. (a) Nesmeyanov, A. N.; Materikova, R. B.; Kochetkova, N. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 1334. (b) Blais, M. S.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1998**, *17*, 3775.
17. (a) Ashe, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 1233. (b) Jutzi, P.; Kuhn, M. *Chem. Ber.* **1974**, *107*, 1228. (c) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 583.
18. (a) Ohta, H.; Kobori, T.; Fujisawa, T. *J. Org. Chem.* **1977**, *42*, 1231. (b) Van de Weghe, P.; Bied, C.; Collin, J.; Marcalo, J.; Santos, I. *J. Organomet. Chem.* **1994**, *475*, 121.
19. Afzali-Ardakani, A.; Rapoport, H. *J. Org. Chem.* **1980**, *45*, 4817.
20. Courtot, P.; Pichon, R.; Salaun, J. Y.; Toupet, L. *Can. J. Chem.* **1991**, *69*, 661.
21. Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416.