Journal of Organometallic Chemistry, 470 (1994) 183–187

η^5-Pentamethylcyclopentadienylruthenium(II) complexes containing η^6-coordinated α-amino acids

W.S. Sheldrick and A. Gleichmann

Lehrstuhl für Analytische Chemie, Ruhr-Universität Bochum, D-44780 Bochum (Germany)

(Received August 12, 1993)

Abstract

Reaction of $[Cp^*RuCl_2]_2$ with L-alanine (L-alaH) in methanol at room temperature in the presence of NaOMe yields the complex Na[Cp*RuCl(L-ala)] (**1**), which contains a five-membered N,O-coordinated chelate ring. The analogous complex Na[Cp*RuCl(L-phe)] (**2**) is obtained under similar conditions but at 0°C in 90% yield. At temperatures above 20°C both **2** and the η^6-coordinated complex [Cp*Ru(L-pheH)]Cl (**4**) are obtained, with the proportion of the latter increasing with temperature. Compound **4** is obtained in 88% yield by refluxing $[Cp^*RuCl_2]_2$ and L-phenylalanine (L-pheH) in CH_3OH/CH_3ONa followed by separation from **2**. The analogous ruthenium(II) sandwich complexes **5–10** were obtained from L-tyrosine and L-tryptophane and various derivatives. [Cp*Ru(L-met)] (**3**), prepared by the reaction of $[Cp^*RuCl_2]_2$ with L-methionine (L-metH) in CH_3OH/CH_3ONa, displays N,O,S-coordination.

Key words: Ruthenium; Cyclopentadienyl; Amino acid; π-Bonding

1. Introduction

Ruthenocene and its derivatives are of considerable interest as potential radiopharmaceuticals [1]. For instance, radiolabelled ruthenocenylalanine has been tested as a pancreating imaging agent [2]. Since the complexation of arenes by the $(\eta^5\text{-Cp})Ru^{II}$ and $(\eta^5\text{-Cp}^*)Ru^{II}$ fragments ($Cp^* = C_5Me_5$) is well documented [3,4], it is not surprising that such units have recently been incorporated into biologically active compounds containing aromatic ring systems. Thus $(\eta^5\text{-Cp}^*)Ru^{II}$ complexes of the hormone estradiol have been reported [5,6], as have the complexes formed from the $(\eta^5\text{-Cp})Ru^{II}$ fragment and the ethyl esters of *N*-acetyl-L-phenylalanine, *N*-acetyl-L-tyrosine and *N*-acetyl-L-tryptophane [7]. The latter complexes were prepared by the reaction of the protected α-amino acids with $[CpRu(MeCN)_3]PF_6$ in 1,2-dichloroethane at 40–50°C [7]. The coordinatively unsaturated derivatives $[Cp^*RuCl]_4$ and $[Cp^*RuOMe]_2$ have also been shown to be convenient precursors for the preparation of complexes of the type $[Cp^*Ru(\eta^6\text{-arene})]^+X^-$ [8].

In recent years, a number of publications have described the preparation and structural characterization of half-sandwich complexes of α-amino acids. These include $(\eta^6\text{-arene})Ru^{II}$ (arene = C_6H_6, *p*-cymene), $(\eta^6\text{-}C_6H_6)Os^{II}$, $(\eta^5\text{-Cp}^*)Rh^{III}$ and $(\eta^5\text{-Cp}^*)Ir^{III}$ derivatives in which the amino acidate ligands are bi- or tridentate [9–15]. Such organometallic compounds have chiral centres both at the α-carbon atom in the ligand and at the metal, and possess considerable potential for enantioselective synthesis.

We now report a study of the reaction in methanol of $[Cp^*RuCl_2]_2$ [16,17] with α-amino acids. For ligands such as L-alanine (L-alaH) or L-methionine (L-metH), the formation of $(\eta^5\text{-Cp}^*)Ru^{II}$ complexes with κ^2N,O- (for L-ala) or κ^3N,O,S-coordination (for L-met), respectively, is to be expected [10,18]. In contrast, α-amino acids such as L-phenylalanine (L-pheH), L-tyrosine (L-tyrH) or L-tryptophane (L-trpH), which contain aromatic ring systems in their side chains, are potentially

Correspondence to: Prof. W.S. Sheldrick.

0022-328X/94/$7.00
SSDI 0022-328X(93)24191-7

capable of yielding complexes of two different types $[Cp^*RuCl(\kappa^2N,O\text{-aa})]^-$ or $[Cp^*Ru(\eta^6\text{-aaH})]^+$ (aaH = α-amino acid).

2. Experimental details

IR spectra were recorded on a Perkin-Elmer 983 or 1760 spectrometer as KBr discs, ^{1}H NMR spectra on a Bruker WP80 or AM400 with registered δ values in ppm. Elemental analyses were performed with a Perkin Elmer 240 or a Carlo Erba 1106. Solvents were purified and dried before use by conventional distillation procedures under argon. All reactions were carried out under argon by use of standard Schlenk techniques. $[Cp^*RuCl_2]_2$ was prepared by published procedures [16,17] from $RuCl_3 \cdot 3H_2O$, which was a gift from Degussa. The α-amino acids were purchased from Sigma and Janssen.

2.1. Preparation of complexes 1–3

Na[(η^5-Cp)RuCl(L-ala)] (1).* L-alaH (29 mg, 0.33 mmol) was added to a solution of 100 mg (0.16 mmol) of $[Cp^*RuCl_2]_2$ in 20 ml of methanol and 0.33 ml of 1 M NaOMe. The solution was stirred for 5 min at room temperature and the solvent then removed. The resulting red solid was washed once with 10 ml of diethyl ether and twice with 10 ml of methanol to give **1** (yield 58%). Anal. Found: C, 41.0; H, 5.3; N, 3.8; M = 382.9. $C_{13}H_{21}NO_2NaClRu$ calcd.: C, 40.8; H, 5.5; N, 3.7%. ^{1}H NMR (400 MHz) (CD_3OD): δ 1.35 (m, 3H, β-CH_3); 1.66 (s, 15H, Cp*); 4.15 (m, 1H, α-CH). IR: $\nu(NH_2)$ 3430m, 3393m; $\nu_{as}(CO_2)$ 1660s cm^{-1}.

Na[(η^5-Cp)RuCl(L-phe)] (2).* A mixture of 55 mg (0.33 mmol) of L-pheH and 100 mg (0.16 mmol) of $[Cp^*RuCl_2]_2$ in 20 ml of methanol and 0.33 ml of 1 M NaOMe was stirred for 5 min at 0°C. After removal of the solvent the orange solid was washed with 10 ml of diethyl ether and 10 ml of methanol to give **2** (yield 90%). Anal. Found: C, 49.8; H, 5.1; N, 3.3; M = 459.0. $C_{19}H_{25}NO_2NaClRu$ calcd.: C, 49.7; H, 5.5; N, 3.1%. ^{1}H NMR (80 MHz) (CD_3OD): δ 1.3–2.0 (m, 15H, Cp*); 2.4–2.7 (m, 2H, β-CH_2); 3.8–3.9 (m, 1H, α-CH); 7.1–7.3 (m, 5H, C_6H_5). IR: $\nu(NH_2)$ 3438m, 3061m; $\nu_{as}(CO_2)$ 1616s cm^{-1}.

[(η^5-Cp)Ru(L-met)] (3).* A mixture of 49 mg (0.33 mmol) of L-metH and 100 mg (0.16 mmol) of $[Cp^*RuCl_2]_2$ in 20 ml methanol containing 0.33 ml of 1 M NaOMe was stirred for 3 h at room temperature. The solvent was removed and the orange solid washed with 10 ml of diethyl ether and 10 ml of methanol to give **3** (yield 78%). Anal. Found: C, 47.0; H, 6.4; N, 3.5; M = 384.5. $C_{15}H_{25}NO_2SRu$ calcd.: C, 46.9; H, 6.6; N, 3.6%. ^{1}H NMR (400 MHz) (CD_3OD): δ 1.6–1.9 (m, 15H, Cp*); 2.10 (m, 2H, β-CH_2); 2.42 (s, 3H, S–CH_3); 2.72 (m, 2H, γ-CH_2); 3.57 (s, 1H, α-CH). IR: $\nu(NH_2)$ 3230m, 3180m; $\nu_{as}(CO_2)$ 1598s cm^{-1}.

2.2. Preparation of complexes 4–10

In a typical preparation (in this case of **4**), 55 mg (0.33 mmol) of L-pheH were added to 100 mg (0.16 mmol) of $[Cp^*RuCl_2]_2$ in 50 ml of methanol and 0.33 ml of 1 M NaOMe. The solution was stirred for 3 h under reflux. After removal of the solvent the yellow solid was dissolved in 2 ml of ethanol. Addition of 5 ml of CH_2Cl_2 led to the precipitation of **4**, which was filtered off and dried in vacuum (yield 88%). Compound **4** may be recrystallized from a methanol solution. Any variations in the reaction conditions are noted below for the individual complexes **5–10**.

[(η^5-Cp)Ru(η^6-L-pheH)]Cl (4).* Anal. Found: C, 52.2; H, 6.1; N, 3.0; Cl, 12.6; M = 459.9. $C_{19}H_{26}NO_2ClRu \cdot 1/2C_2H_5OH$ calcd.: C, 52.2; H, 6.0; N, 3.2; Cl, 13.3%. ^{1}H NMR (400 MHz) (CD_3OD): δ 2.04, 2.06 (2s, 15H, Cp*); 3.0 (m, 2H, β-CH_2); 4.25 (m, 1H, α-CH); 5.95–6.05 (m, 5H, η^6-C_6H_5). ^{1}H NMR (D_2O): δ 1.81, 1.86 (2s, 15H, Cp*); 2.82 (2d, 2H, β-CH_2); 4.1 (2t, 1H, α-CH); 5.65–5.85 (m, 5H, η^6-C_6H_5). IR: $\nu(NH_2)$ 3030 m; $\nu_{as}(CO_2)$ 1750s cm^{-1}.

[(η^5-Cp)Ru(η^6-L-ClpheH)]Cl (5).* (L-ClpheH = L-*p*-chlorophenylalanine); yield 38%. Anal. Found: C, 48.5; H, 5.4; N, 3.4; M = 471.4. $C_{19}H_{25}NO_2Cl_2Ru$ calcd.: C, 48.4; H, 5.3; N, 3.0%. ^{1}H NMR (80 MHz) (CD_3OD): δ 2.02, 2.04 (2s, 15H, Cp*); 2.96–3.10 (m, 2H, β-CH_2); 4.28–4.39 (m, 1H, α-CH); 5.92–6.07 (2s, 4H, *p*-Cl–C_6H_4). IR: $\nu(NH_2)$ 3120m; $\nu_{as}(CO_2)$ 1730s cm^{-1}.

[(η^5-Cp)Ru(η^6-L-tyrH)]Cl (6).* Reaction time 1 h with 0.40 mmol of L-tyrosine; excess L-tyrosine was filtered off before solvent removal; yield 90%. Anal. Found: C, 50.4; H, 6.0; N, 3.4; M = 479.9. $C_{19}H_{26}NO_3ClRu \cdot 1/2C_2H_5OH$ calcd.: C, 50.4; H, 5.8; N, 3.1%. ^{1}H NMR (400 MHz) (CD_3OD): δ 2.0 (2s, 15H, Cp*); 2.90 (m, 2H, β-CH_2); 4.15 (m, 1H, α-CH); 5.65–5.90 (m, 4H, *p*-HO–C_6H_4). IR: $\nu(NH_2)$ 3110m; $\nu_{as}(CO_2)$ 1720s cm^{-1}.

[(η^5-Cp)Ru(η^6-L-dopa)]Cl (7).* (L-dopa = L-3,4-Dihydroxyphenylalanine); yield 90%. Anal. Found: C, 42.9; H, 5.4; N, 2.5; M = 468.9. $C_{19}H_{26}NO_4ClRu$ calcd.: C, 42.4; H, 5.3; N, 2.4%. ^{1}H NMR (80 MHz) (CD_3OD): δ 1.92 (s, 15H, Cp*); 2.81 (m, 2H, β-CH_2); 4.26 (m, 1H, α-CH); 5.46 (m, 1H, η^6-L-dopa); 5.72 (m, 2H, η^6-L-dopa). IR: $\nu(NH_2)$ 3100m; $\nu_{as}(CO_2)$ 1740s cm^{-1}.

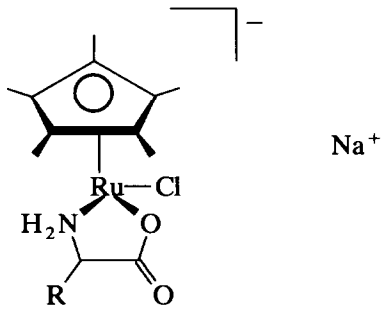
[(η^5-Cp)Ru(η^6-DL-PhserH)]Cl (8).* (DL-Phser = DL-threo-β-phenylserine); yield 38%. Anal. Found: C, 50.7; H, 5.7; N, 3.2; M = 452.9. $C_{19}H_{26}NO_3ClRu$ calcd.: C, 50.4; H, 5.8; N, 3.1%. ^{1}H NMR (80 MHz) (CD_3OD): δ 1.99, 2.02 (2s, 15H, Cp*); 4.25 (m, 1H, β-CH); 5.1 (m, 1H, α-CH); 5.85–6.23 (m, 5H, η^6-C_6H_5). IR: $\nu(NH_2)$ 3056m; $\nu_{as}(CO_2)$ 1742s cm^{-1}.

[(η^5-Cp)Ru(η^6-L-trpH)]Cl (9).* Yield 44%. Anal. Found: C, 53.0; H, 5.8; N, 5.6; $M = 499.0$. $C_{21}H_{27}N_2O_2ClRu \cdot 1/2C_2H_5OH$ calcd.: C, 53.0; H, 5.7; N, 5.9%. ^{1}H NMR (400 MHz) (CD_3OD): δ 1.70–1.85 (m, 15H, Cp*); 3.25 (m, 2H, β-CH_2); 4.14 (m, 1H, α-CH); 5.66, 6.40–6.55 (m, 4H, η^6-L-trpH); 7.7 (s, 1H, C=CH, L-trpH). IR: $\nu(NH_2)$ 3100m; $\nu_{as}(CO_2)$ 1730s cm^{-1}.

[(η^5-Cp)Ru(η^6-L-HOtrpH)]Cl (10).* (L-HOtrpH = 5-Hydroxy-L-tryptophane); yield 45%. Anal. Found: C, 45.4; H, 5.4; N, 4.8; $M = 492.0$. $C_{21}H_{27}N_2O_3ClRu$ calcd.: C, 44.9; H, 5.5; N, 4.6%. ^{1}H NMR (80 MHz) (CD_3OD): δ 1.70 (2s, 15H, Cp*); 3.25 (m, 2H, β-CH_2); 4.28 (m, 1H, α-CH); 5.4–5.6 (m, 4H, η^6-L-HOtrpH); 6.2–6.4 (m, 2H, η^6-L-HOtrpH); 7.67–7.77 (m, 1H, C=CH, L-trpH). IR: $\nu(NH_2)$ 3150 m; $\nu_{as}(CO_2)$ 1740s cm^{-1}.

3. Discussion

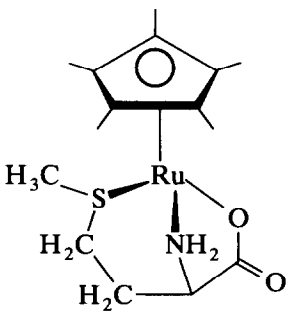
The η^5-pentamethylcyclopentadienylruthenium(II) complex Na[Cp*RuCl(L-ala)] (1) may be prepared at room temperature by the reaction of $[Cp^*RuCl_2]_2$ with L-alaH in methanol in the presence of NaOMe, with the solvent acting as a reducing agent. The IR spectrum of 1 displays $\nu(NH_2)$ bands for a coordinated amino group at 3430 and 3393 cm^{-1}, and a $\nu_{as}(CO_2)$ absorption at 1660 cm^{-1}, close to the typical range 1600–1645 cm^{-1} for monodentate carboxylate coordination. This means that the formation of a five-membered chelate ring, like that in the analogous ruthenium(II) complex [(η^6-C_6H_6)RuCl(L-ala)] [11], may be assumed. Diastereomers of rhodium and iridium complexes of the type [(η^5-Cp*)MCl(ala)] (M = Rh, Ir; aa = L-phe, L-trp) have been shown to display separate



R = Me (1); R = Ph (2)

^{1}H NMR resonances for their Cp* methyl protons [14]. The observed differences in the chemical shifts (*e.g.* 0.33 ppm in CD_3OD solution for M = Ir, aa = L-trp) are presumably caused by the anisotropy effect of the aromatic ring of L-phe or L-trp on the Cp* protons. In contrast, the splitting of the Cp* signals is much smaller for the analogous complexes of aliphatic amino acidate ligands (*e.g.* aa = gly, L-val, L-pro) and in many cases is not resolvable [14,15,18]. This is also the case for $[Cp^*RuCl(L\text{-ala})]^-$ (1), for which only one resonance was recorded in CD_3OD solution for the Cp* methyl protons. The analogous complex Na[Cp*RuCl(L-phe)] (2), which may be synthesized by the reaction of $[Cp^*RuCl_2]_2$ with L-phe in CH_3OH/CH_3ONa at 0°C, displays a series of Cp* signals (δ 1.3–2.0 ppm) in its 80 MHz ^{1}H NMR spectrum in CD_3OD. These could be the result of the establishment of dissociation equilibria in solution, as has often been reported for analogous (η^6-arene)Ru^{II} complexes [9,10]. An alternative tentative explanation would be the restricted rotation of the Cp* ligand.

Sulphur-containing amino acids such as methionine (L-metH) are potentially tridentate through an N,O,S-coordination mode, which has been confirmed by X-ray structural analysis for complexes such as [Cp*Co(L-met)]$FeCl_4$ [18] and [(nbd)RuCl(DL-met)] (nbd = norbornadiene) [19]. Reaction of $[Cp^*RuCl_2]_2$ with L-metH at room temperature in methanol in the presence of NaOMe gives the neutral complex [Cp*Ru(L-met)] (3). The $\nu(NH_2)$ bands in the IR spectrum at 3230 and 3180 cm^{-1}, typical for a coordinating amino group, and the $\nu_{as}(CO_2)$ absorption at 1598 cm^{-1} confirm N,O-coordination. Relative to that for the free amino acid, the position of the $-SCH_3$ proton resonance in the ^{1}H NMR spectrum of 3 in CD_3OD solution is shifted by 0.26 ppm to lower field, which is in accordance with the expected N,O,S-coordination mode. Models indicate that on steric grounds only the diastereomer with R_{Co} configuration can be formed by 3. In principle the adoption of either an R_S or an S_S



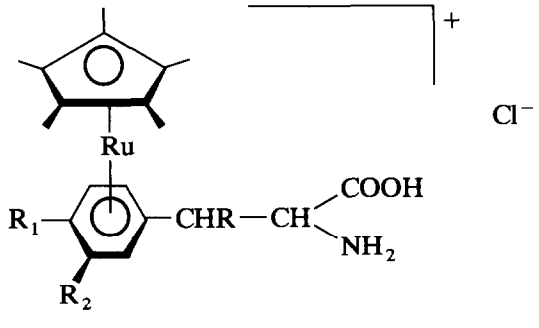
(3)

configuration at the thioether sulphur atom should be possible. The former configuration was established by X-ray structural analysis for $[Cp^*Co(L\text{-met})]^+$ and the latter for [Cp*Co(μ-L-S-Mecys)$CoCl_3$] (L-S-MecysH = L-S-methylcysteine). The observation of only one resonance in each case for the $-SCH_3$ and α-carbon protons in the ^{1}H NMR spectrum of 3 is in accordance

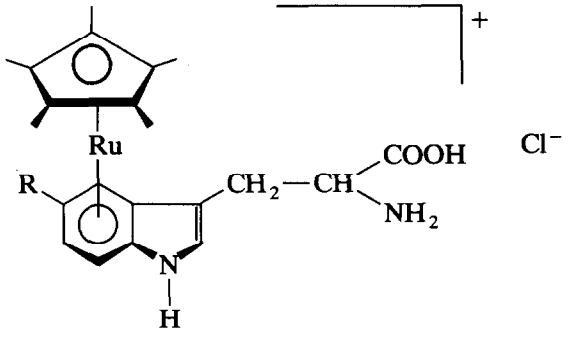
with the presence of only one diastereomer (with either the R_S or S_S configuration) in CD_3OD solution. As for **2**, the 400 MHz ^1H NMR spectrum of **3** displays a series of Cp* proton resonances at δ 1.6–1.9 ppm, close to the value of δ 1.66 ppm observed for the Cp* protons in **1**.

The effectively quantitative formation of the N,O-coordinated complex Na[Cp*RuCl(L-phe)] (**2**) at 0°C can be monitored by a change in colour of the methanol solution from brown to orange which takes place within 5 min. In contrast, the reaction of $[Cp^*RuCl_2]_2$ and $[L\text{-phe}]^-$ at room temperature yields both **2** and the sandwich complex $[Cp^*Ru(\eta^6\text{-L-pheH})]Cl$ (**4**), which contains an η^6-coordinated L-phenylalanine, as confirmed by the observation of a pronounced upfield shift of the phenyl proton resonances from δ 7.1–7.3 in **2** to δ 5.65–5.85 in **4**. The latter signals lie in the typical region for η^6-coordinated arenes [5–8]. Complex **4** may be prepared in 88% yield by carrying out the reaction between $[Cp^*RuCl_2]_2$ and $[L\text{-phe}]^-$ under reflux in methanol for 3 h. The raw product obtained upon initial removal of the solvent from the reaction mixture contains approximately 10% of the N,O-coordinated complex **2**, which may then be separated from the sandwich complex **4** by redissolving the solid in ethanol and precipitating **4** with CH_2Cl_2, in which **2** is very soluble.

Complex **4** is a yellow air-stable solid. Its IR spectrum contains $\nu(NH_2)$ and $\nu_{as}(CO_2)$ bands at 3030 and 1750 cm^{-1}, respectively, values characteristic of a non-coordinated amino function and a protonated carboxylate group. Two sets of ^1H NMR resonances with integrations in *ca.* 30:70 ratio are observed for the Cp* methyl protons and the α- and β-hydrogen atoms



$R_1 = R_2 = R = H$ (**4**)
$R_1 = Cl;\ R_2 = R = H$ (**5**)
$R_1 = OH;\ R_2 = R = H$ (**6**)
$R_1 = R_2 = OH;\ R = H$ (**7**)
$R_1 = R_2 = H;\ R = OH$ (**8**)



R = H (**9**)
R = OH (**10**)

of L-pheH in **4**. Because of the energetically unfavourable nature of rotation about the C–C bond to the phenyl ring, the ruthenium atom in **4** will be expected to display facial chirality. The presence of this chirality and the chiral centre of the amino acid will lead to the formation of diastereomers, in accordance with the observation of two sets of ^1H NMR resonances for **4**. The ^1H NMR spectra of the analogous complexes **5**, **6** and **8** also indicate the presence of diastereomers in solution, with integration ratios of 35:65 (**6** and **8**) and 38:62 (**5**), for the analogous complexes **5**, **6** and **8**. The Cp* proton resonances in **4–8** lie in the range δ 1.92–2.06 and are shifted generally downfield with respect to those of the N,O-coordinated complex **2**, for which a series of signals between δ 1.3 and 2.0 ppm were recorded. Downfield shifts are also observed for the α- and β-hydrogens of L-pheH in **4** in comparison to **2**.

The relative yields of the sandwich and N,O-coordinated half-sandwich complex for a particular amino acid are influenced by the presence of electron-withdrawing substituents in the aromatic ring system. Using ^1H NMR spectroscopy (*i.e.* integrals of the phenyl protons), we were able to observe the time dependence of the formation of the η^6-coordinated complexes for L-phenylalanine and L-*p*-chlorphenylalanine in CD_3OD at 75°C. Table 1 indicates that equilibrium is reached slowly in both cases (>3 h) but that the maximum yield of **4** (*ca.* 80%) is much greater than for **5** (*ca.* 40%). This finding is in accordance with the reduced proclivity of the phenyl ring in L-ClpheH to form η^6-coordinated complexes, as a result of the electron-withdrawing influence of the chlorine substituent. In contrast to **4** and **5**, complexes **6** and **7** are unstable in aqueous solution and decompose rapidly on exposure to air.

The sandwich complexes **9** and **10** may be prepared under similar conditions for L-tryptophane and its 5-hydroxy derivative (L-HO-trpH). Whereas the ^1H NMR signals of the protons of the η^6-coordinated six-mem-

TABLE 1. Time dependence of the yields of the sandwich complexes **4** and **5** at 75°C in CD_3OD solution, as revealed by ^1H NMR spectroscopy

Time (min)	Yield (%) of **4** [a]	Yield (%) of **5** [a]
1	10.5	7.5
3	16.0	11.9
5	21.7	13.1
10	33.1	16.4
15	47.5	20.5
20	54.8	21.5
30	59.9	26.3
60	67.2	31.8
90	73.2	35.0
120	76.0	37.7
180	79.5	39.4

[a] Yields are based on the relative integral values of the proton resonances of the η^6-coordinated phenyl rings.

bered ring undergo a pronounced shift to lower field (δ 5.4–6.55 ppm), the resonance of the pyrrole proton remains virtually unaffected (δ *ca.* 7.7 ppm). The values for the $\nu(NH_2)$ and $\nu_{as}(CO_2)$ bands in the IR spectra of **9** and **10** are characteristic for non-coordinated amino functions and protonated carboxylate groups, respectively. The η^6-coordination of the asymmetrically substituted six-membered ring of L-tryptophane derivatives will introduce chirality at the ruthenium atom, so that the formation of diastereomers is to be expected for such complexes. Two sets of ^1H NMR resonances with integrations in the ratio 30:70 were recorded for such diastereomers of **10** in CD_3OD solution.

This study has shown that η^6-coordinated (η^5-Cp*)Ru^{II} complexes of the unprotected aromatic amino acids L-pheH, L-tyrH, L-trpH and their derivatives may be prepared by direct reaction of $[Cp^*RuCl_2]_2$ with these acids. Typical reactions of the amino and carboxylate functions should be possible for the complexes **4–10**. Further NMR spectroscopic studies of the solution behaviour of these complexes are in progress.

Acknowledgement

We are grateful to the Fonds der Chemischen Industrie, Frankfurt, for their continuing financial support.

References

1 M. Wenzel, P. Asindraza and G. Schachschneider, *J. Labelled Compd. Radiopharm.*, *20* (1983) 1061.
2 W.H. Soine, C.E. Guyer and F.F. Knapp, Jr., *J. Med. Chem.*, *27* (1984) 803.
3 E.L. Muetterties, J.R. Bleeke and E. Wacherer, *Chem. Rev.*, *82* (1982) 499.
4 R.M. Moriarty, U.S. Gill and Y.Y. Ku, *J. Organomet. Chem.*, *350* (1988) 157.
5 D. Vichard, M. Gruselle, H.E. Amouri and G. Jaouen, *J. Chem. Soc., Chem. Commun.*, (1991) 46.
6 D. Vichard, M. Gruselle, H.E. Amouri, G. Jaouen and J. Vaissermann, *Organometallics*, *11* (1992) 976.
7 R.M. Moriarty, Y.-Y. Ku and U.S. Gill, *J. Chem. Soc., Chem. Commun.*, (1987) 1837.
8 U. Koelle and J. Kossakowski, *J. Chem. Soc., Chem. Commun.*, (1988) 549.
9 D.F. Dersnah and M.C. Baird, *J. Organomet. Chem.*, *127* (1977) C55.
10 W.S. Sheldrick and S. Heeb, *J. Organomet. Chem.*, *377* (1989) 357.
11 W.S. Sheldrick and S. Heeb, *Inorg. Chim. Acta*, *168* (1990) 93.
12 H. Werner, T. Daniel, O. Nürnberg, W. Knaup and U. Meyer, *J. Organomet. Chem.*, *445* (1993) 229.
13 D. Carmona, A. Mendoza, F.J. Lahoz, L.A. Oro, M.P. Lamata and E. San Jose, *J. Organomet. Chem.*, *396* (1990) C17.
14 R. Krämer, K. Polborn, H. Wanjek, I. Zahn and W. Beck, *Chem. Ber.*, *123* (1990) 767.
15 R. Krämer, K. Polborn and W. Beck, *Chem. Ber.*, *124* (1991) 2429.
16 T.D. Tilley, R.H. Grubbs and J.E. Bercaw, *Organometallics*, *3* (1984) 274.
17 N. Oshima, H. Suzuki and Y. Moro-Oka, *Chem. Lett.*, (1984) 1161.
18 W.S. Sheldrick, E. Hauck and S. Korn, *J. Organomet. Chem.*, in press.
19 W.S. Sheldrick and R. Exner, *J. Organomet. Chem.*, *386* (1990) 375.