(η^6-Arene)ruthenium(II) Labeling of Amino Acids and Peptides with Aromatic Side-Chains☆

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Bis(arene)ruthenium(II) complexes of the type [(η^6-cymene)Ru(η^6-aa)]$(CF_3SO_3)_n$ (**2**–**9**) containing L-tyrosine and L-tryptophan derivatives may be prepared by treatment of [(η^6-cymene)Ru{$(CH_3)_2CO$}$_3$]$(CF_3SO_3)_2$ with the appropriate bioligand in CH_2Cl_2 for fully protected compounds and CF_3COOH for α-amino acids (aa) with unprotected amine or carboxylic acid groups. Whereas the tyrosine and tryptophan methyl ester complexes [(η^6-cymene)Ru(η^6-H_2tyrOMe)]$(CF_3SO_3)_3$ (**4**) and [(η^6-cymene)Ru(η^6-H_2trpOMe)]$(CF_3SO_3)_3$ (**8**) contain trications with protonated amino functions, the remaining compounds all exhibit dications. The crystal structure analysis of [(η^6-cymene)Ru(η^6-HtyrOH)]$(CF_3SO_3)_2$ (**5**) confirms a marked distortion towards an η^5-oxohexadienyl coordination with deprotonation of the aromatic side chain. Although facial isomers are formed in an effectively 1:1 ratio for all tryptophan derivatives fractional crystallization allowed an X-ray structural characterization of the β isomer of [(η^6-cymene)Ru(η^6-ActrpOMe)]$(CF_3SO_3)_2$ (**6**). Chemospecific labeling of the tryptophan side chain was established for the mixed dipeptide phenylalanyltryptophan.

η^6-Coordination of organometallic fragments to bioligands offers a wide range of analytical and synthetic perspectives, some of which have been highlighted in recent articles by Jaouen et al.[1] and Krämer[2]. For instance Jaouen and co-workers have successfully developed immunoassay procedures[3,4] based on the incorporation of $Cr(CO)_3$ into steroid hormones. The same research group has also studied the application of Cp^*Ru^{II}-labeled molecules ($Cp^* = C_5Me_5$) in the analysis and molecular recognition of enzyme active sites[5,6].

Although $Cr(CO)_3$ labeling of the aromatic side chains of protected derivatives of the amino acids phenylalanine (L-HpheOH), tyrosine (L-HtyrOH), and tryptophan (L-HtrpOH) was studied by Sergheraert et al. in 1982[7], suprisingly few further examples of η^6-coordination by these bioligands have followed this initial report. With the exception of a very recent study by Steglich, Beck et al. of the introduction of transition metal carbonyl fragments into the side chains of synthetic α-amino acids[8], these appear to be restricted to $CpRu^{II}$ and Cp^*Ru^{II} sandwich complexes. For instance, the preparation of η^6-coordinated $CpRu^{II}$ complexes of the ethyl esters of *N*-acetyl-L-phenylalanine (AcpheOH), *N*-acetyl-L-tyrosine (ActyrOH) and *N*-acetyl-L-tryptophan (ActrpOH) was reported by Moriarty and co-workers in 1987[9]. This organometallic fragment has also been employed by the groups of Pearson[10] and Rich[11] to enable protected *p*-Cl-phenylalanine to participate in diaryl coupling, as required for the total synthesis of cyclic diphenyl ether peptides such as the protease inhibitor K-13. In contrast to its cyclopentadienyl analogue, the Cp^*Ru^{II} half-sandwich offers considerable potential for the labeling of unprotected amino acids and peptides with aromatic side chains. We have employed both $[(Cp^*RuCl)_2(\mu\text{-}Cl)_2]$ and $[Cp^*Ru(MeCN)_3]^+$ for the direct preparation of η^6-coordinated complexes of the free amino acids L-HpheOH, L-HtyrOH and L-HtrpOH[12,13]. Reaction of $[Cp^*Ru(MeCN)_3]^-$ with dipeptides such as HphepheOH or HtrptrpOH also leads to the formation of entropically favored sandwich complexes rather than the alternative κ^1N- or κ^2N,O-coordinated derivatives[13]. Such η^6-coordinated bioligands may be photochemically cleaved at a subsequent stage.

The relative instability of Cp^*Ru^{II} sandwich complexes on contact with water or oxygen restricts the application of this fragment in the field of bioorganometallic chemistry. Although a chemoselective preference for the electron-richer tryptophan aromatic ring system was established for the reaction of Cp^*Ru^{II} with the mixed dipeptides HphetrpOH and HtrppheOH at a 1:1 molar ratio, it proved necessary to separate the indole-coordinated 1:1 product from the 2:1 η^6-trp:η^6-phe coordinated complex by size-exclusion chromatography[13]. These findings prompted us to study the labeling of aromatic amino acids and peptides with the η^6-$CyRu^{II}$ fragment (Cy = *p*-cymene) in the expectation that bis(η^6-arene)Ru^{II} complexes would offer both long-term stability over a wide pH range in aqueous solution and a higher degree of chemospecificity. We have presented examples of the organometallic labeling of phenylalanine derivatives in a recent preliminary article[14]. We now report our investigation of the reaction of [(η^6-cymene)Ru(acetone)$_3$]$^{2+}$ (**1**)[15,16] with both protected and unprotected tyrosine and tryptophan derivatives.

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Results

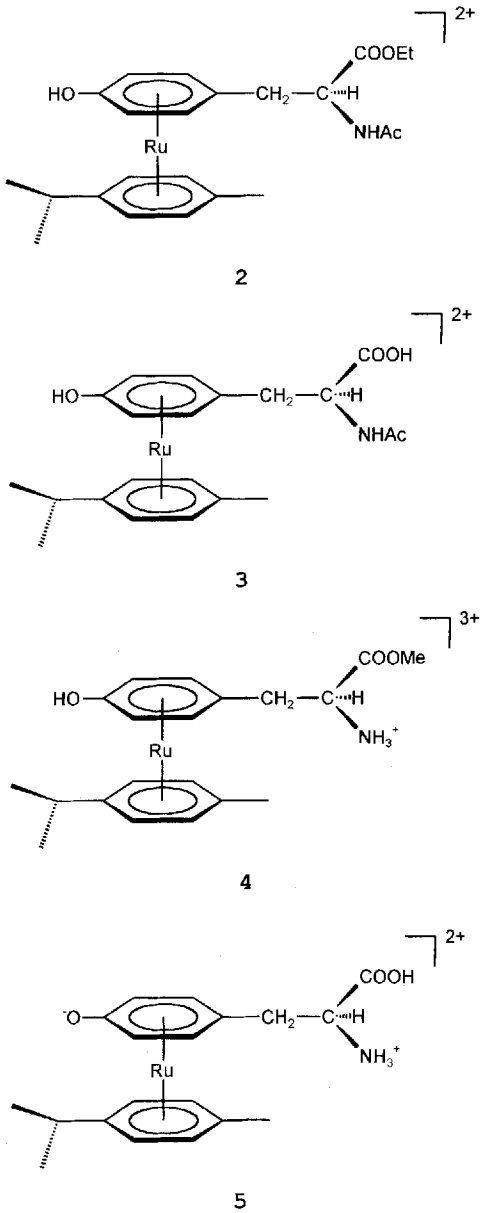
Reaction of chloro bridged ruthenium(II) dimers $[\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}Cl)_2]$ with unprotected amino acids (aa, e.g.s L-alanine, L-valine, L-phenylalanine) in water or methanol at room temperature affords monomeric κ^2N,O-coordinated complexes of the type $[(\eta^6\text{-arene})RuCl(aaH_{-1}\text{-}\kappa^2N,O)]$[17–20]. When the carboxylic acid function is protected as an alkyl ester[18] κN-coordinated compounds such as $[(\eta^6\text{-}C_6H_6)RuCl_2(HalaOMe\text{-}\kappa N)]$ (HalaOMe = L-alanine methyl ester) are obtained. In contrast to the tris(acetonitrile) complex cation $[Cp^*Ru(MeCN)_3]^+$, which delivers the entropically favored sandwich complex as an insoluble product on treatment with the free aromatic acids in thf, the analogous reaction of $[(\eta^6\text{-cymene})Ru(acetone)_3]^{2+}$ (**1**) leads to the formation of κ^2-N,O-chelated compounds in CH_2Cl_2. As we have already reported for phenylalanine derivatives[14], bis(η^6-arene)Ru^{II} sandwich complexes can only be prepared under such conditions for fully protected amino acids such as *N*-acetyltyrosine ethyl ester (ActyrOEt) or *N*-acetyltryptophan methyl ester (ActrpOMe). η^6-Coordination of half-protected or free aromatic amino acids can, however, be achieved for the (η^6-cymene)Ru^{II} fragment by employing CF_3COOH as the reaction medium. The protonation of the amino and carboxylato groups under such strongly acid conditions prevents their incorporation into the Ru^{II} coordination sphere.

The (η^6-cymene)Ru^{II} labeled tyrosine-containing complexes $[\eta^6\text{-CyRu}(\eta^6\text{-ActyrOEt})](CF_3SO_3)_2$ (**2**), $[\eta^6\text{-CyRu}(\eta^6\text{-ActyrOH})](CF_3SO_3)_2$ (**3**), $[\eta^6\text{-CyRu}(\eta^6\text{-}H_2tyrOMe)](CF_3SO_3)_3$ (**4**), and $[\eta^6\text{-CyRu}(\eta^6\text{-HtyrOH})](CF_3SO_3)_2$ (**5**) were prepared accordingly in CH_2Cl_2 (**2**) or CF_3COOH (**3**–**5**).

The latter products are obtained in good yield (67–79%) under relatively mild reaction conditions (3 h, 50°C, **3**; 8 h, 40°C, **4**; 6 h, room temperature **5**). Although these sandwich complexes are stable over a wide pH range in aqueous solution, yields deteriorate at higher reaction temperatures owing to their rapid decomposition. As reported for other bis(arene)Ru^{II} compounds containing the ligand, the *p*-cymene ^{1}H-NMR signals are shifted downfield by ca. 1 ppm in comparison to the half-sandwich starting material[16,21,22]. ^{13}C-NMR data reveal a consistent pattern of upfield chemical shifts of ca. 30–40 ppm for the signals of all but one of the carbon atoms directly coordinated to the metal atom in comparison to those registered for the free aromatic ligands. The exception to this rule is provided by the *p*-hydroxy-substituted tyrosine-C atoms which exhibit upfield shifts of only ca. 10 ppm.

It has recently been reported[23,24] that the Cp^*Ru^{II} fragment forms stable sandwich complexes with phenol. Coordination to this and the Cp^*M^{III} (M = Rh, Ir) fragments[25,26] stabilizes the ketonic form of the bonded arene leading, thereby, to a marked enhancement in the acidity of the hydroxo function. In the phenoxo Cp^*Rh^{III} complex $[Cp^*Rh(PhO)]BF_4 \cdot H_2O$[26] distortion towards an η^5-oxohexadienyl coordination mode may be gauged from the short C–O distance of 1.25 Å and the pronounced dihedral angle θ of 14° between the plane of the *m*- and *p*-C atoms and the rest of the ring. This structure differs markedly from that of $[Cp^*Ru(PhO)] \cdot 2\ PhOH$[24] in which the PhO arene systems is almost flat [θ = 4°, *d*(C–O) = 1.28 Å].

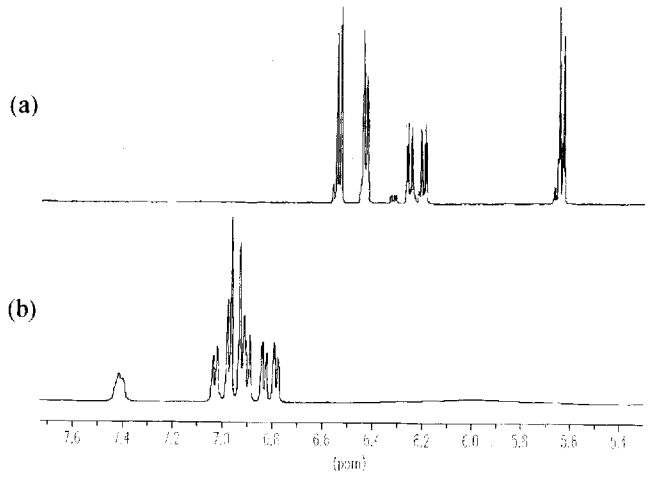
Scheme 1. Cations of **2**–**5**



The (η^6-cymene)Ru^{II} coordination of the aromatic side chain in the tyrosine derivatives **2**–**5** is associated with an analogous marked enhancement in the acidity of the *p*-hydroxy function. This now exhibits the properties of a strong acid and is effectively fully deprotonated in aqueous solution. The associated increase in shielding for the aromatic ring protons causes their resonances to move to values between 5.6 and 6.6 ppm for **2** in D_2O solution. Figure 1 depicts the aromatic regions of the ^{1}H-NMR spectra of this sandwich complex in D_2O and CD_3NO_2.

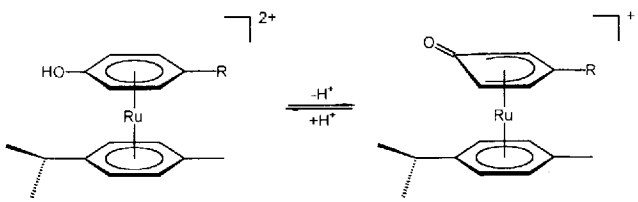
Rapid H/D exchange prevents the observation of the amide proton in D_2O and the *p*-cymene ring protons are

Figure 1. Aromatic regions of the ^{1}H-NMR spectra of [η^6-CyRu(η^6-ActyrOEt)]$(CF_3SO_3)_2$ (**2**) in (a) D_2O and (b) CD_3NO_2



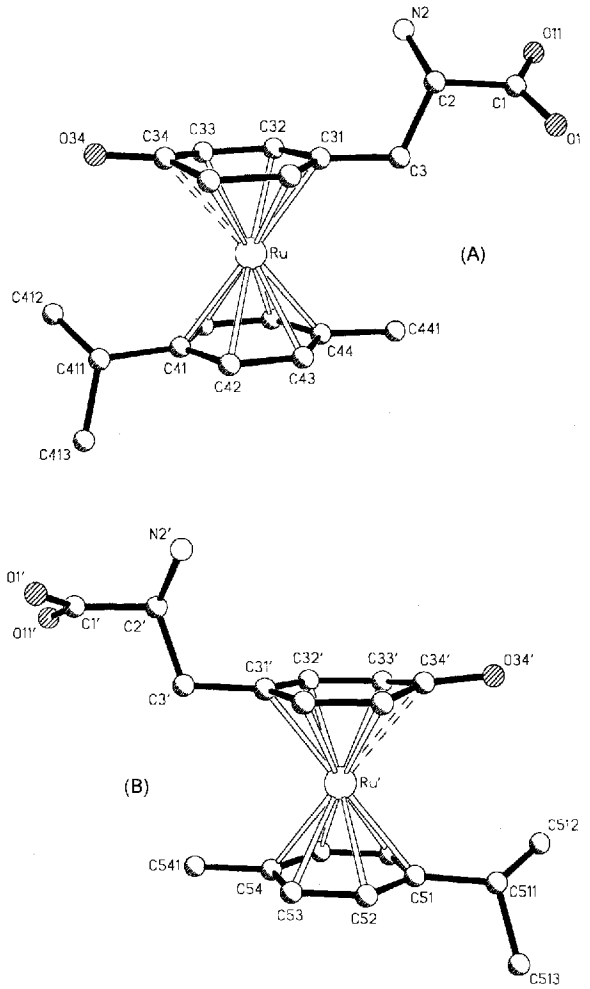
shifted by about 0.5 ppm to afford the typical AB spin system centered at $\delta = 6.48$. The increase in shielding is more pronounced for the tyrosine aromatic protons, in particular for those adjacent to the deprotonated hydroxy function which experience an upfield shift of no less than ca. 1.4 ppm. Further evidence for a dramatic reduction in aromaticity on deprotonation is provided by the striking change in the signal pattern for these *meta* protons from two doublets of doublets at $\delta = 6.89$ and 7.02 in CD_3NO_2 to a doublet of triplets at $\delta = 5.63$ ($^3J = 5.5$ Hz) in D_2O with a long-range coupling constant of 2.0 Hz. On shifting from $\delta = 6.78/6.83$ to $\delta = 6.17/6.22$ on change of solvent, the *ortho* protons retain their doublet of doublets. These ^{1}H-NMR observations suggest that deprotonation of the aromatic side chain in the (η^6-cymene)Ru^{II}-coordinated tyrosine derivatives **2**–**5** may lead to stabilization of an η^5-oxohexadienyl sandwich cation (Scheme 2).

Scheme 2. Stabilization of the ketonic form of the aromatic side chain of tyrosine sandwich complexes **2**–**5** on deprotonation



Confirmation of this proposed coordination mode is provided by the X-ray structural analysis of [η^6-CyRu(η^6-HtyrOH)]$(CF_3SO_3)_2$ (**5**), which crystallizes from methanol/diethylether with two independent cations in the chiral monoclinic space group $P2_1$ (Figure 2). The original product also contains a solvent molecule of CF_3COOH.

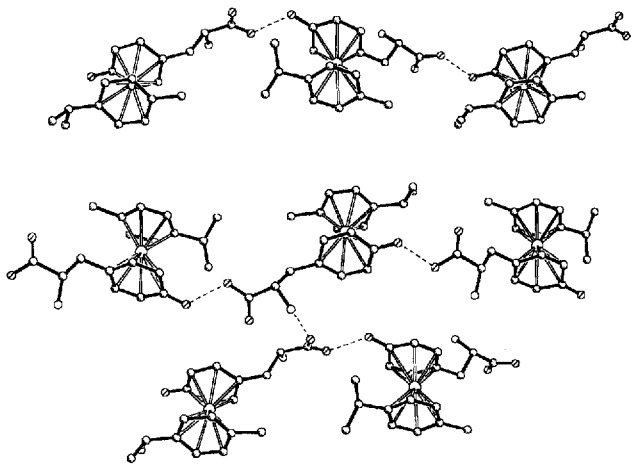
Figure 2. Independent cations of [η^6-CyRu(η^6-HtyrOH)]$(CF_3SO_3)_2$ (**5**)



The ketonic character of the amino acid arene functions may be gauged from their C34–O34 (C34′–034′) distances of 1.268(16) and 1.280(16) Å and the dihedral angles θ of 13.5 and 12.9° between the planes of C33/C34/C35 (C33′/C34′/C35′) and the η^5-coordinated ring atoms C31–C33, C35, and C36 (C31′–C33′, C35′, and C36′). These θ values are similar to that of 14° reported by Jaouen et al. for [Cp*Rh(PhO)]$BF_4 \cdot H_2O$[26] and strikingly larger than that of 4° in [Cp*Ru(PhO)]·2 PhOH[24]. On assuming that full η^5-coordination would lead to an interplanar angle of 40–45°[27], the observed values in **5** can be interpreted as indicating a ca. 30% contribution from such a mode in this tyrosine complex. In accordance with this interpretation, the Ru–C34 distances [2.436(15), 2.404(14) Å] are much longer than those to the remaining ring atoms (2.198–2.241, 2.183–2.257 Å). The observed deprotonation of the *p*-hydroxy substituent in **5** necessitates the protonation of the more basic amino and carboxylato functions and further solution/solid-state evidence for this formulation is provided by the typical lowfield NH_3^+ ^{1}H-NMR

resonance at $\delta = 7.90$ and the ν(CO) IR band at 1735 cm^{-1}. C–N [1.460(15), 1.465(14) Å] and carboxylic acid C–O distances C1–O1/C1′–O1′ 1.206(15), 1.220(15); C1–O11/C1′–O11′ 1.261(14), 1.270(14) Å] in this tyrosine derivative are also in full accordance with such a formulation. These protonated functional groups participate in the O11–H···O34′ (2.48 Å), O11′–H···O34 (2.50 Å) and N2–H···O1 (2.71 Å) hydrogen bonds depicted in Figure 3.

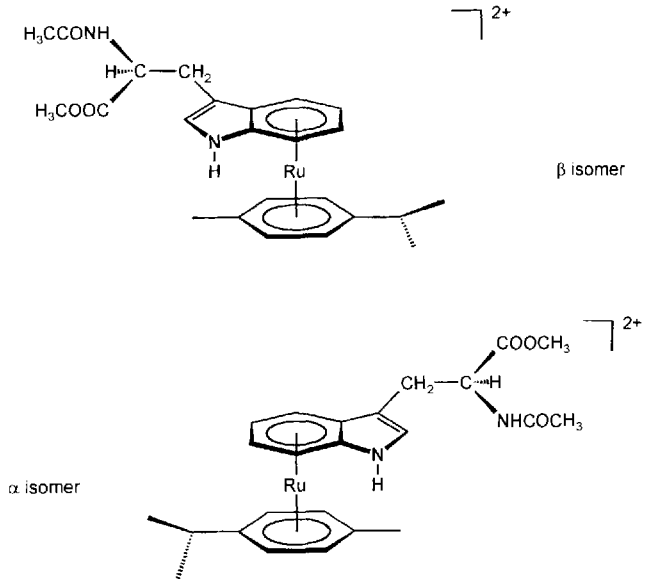
Figure 3. O–H···O and N–H···O hydrogen bonding in the unit cell of **5**



Facial Chirality in Tryptophan Complexes

In contrast to tyrosine, η^6-coordination of the indole system in tryptophan can allow the formation of diastereomers owing to the possibility of facial chirality as depicted for [η^6-CyRu(η^6-AcTrpOMe)]$(CF_3SO_3)_2$ (**6**) in Scheme 3. After

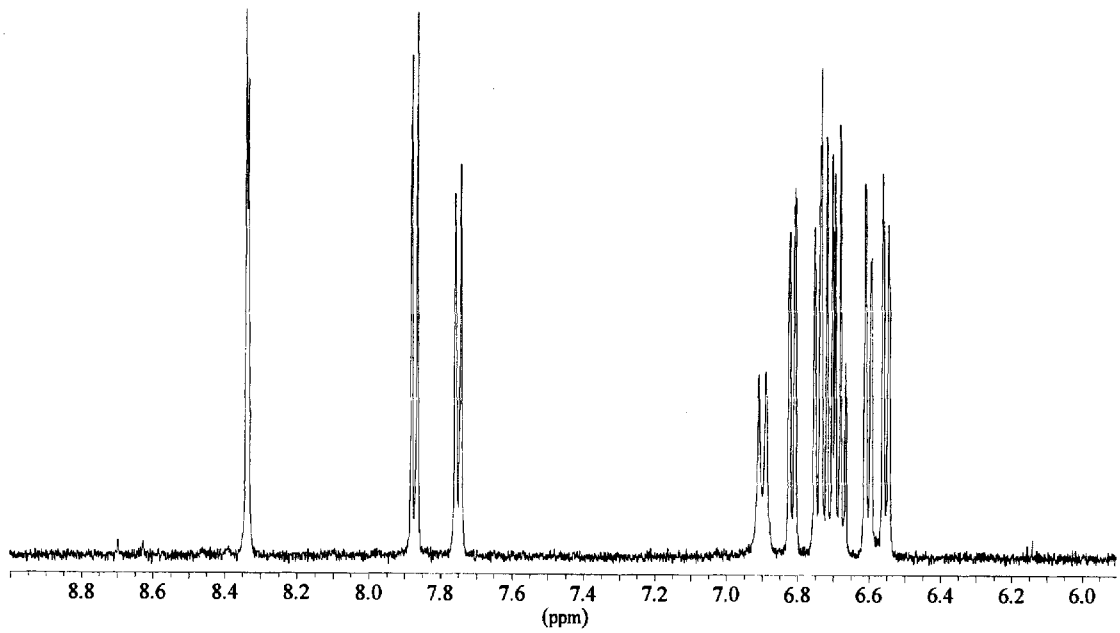
Scheme 3. α and β facial isomers for [η^6-CyRu(η^6-ActrpOMe)]$(CF_3SO_3)_2$ (**6**)



the initial preparation of **6** in CH_2Cl_2 affords such 1 : 1 diastereomeric mixture of **6α** and **6β**, covering of a solution of the product in nitromethane with diethyl ether leads to preferred crystallization of the second diastereomer, whose purity can be confirmed by the absence of a second set of aromatic proton resonances in the ^{1}H-NMR spectrum in CD_3NO_2 (Figure 4).

Characteristic for η^6-coordination of the indole ring system are the opposite shifts experienced by the protons of the bonded arene ring system. Whereas the inner protons H35 and H36 appear at higher field (dd, $\delta = 6.68, 6.72$), a

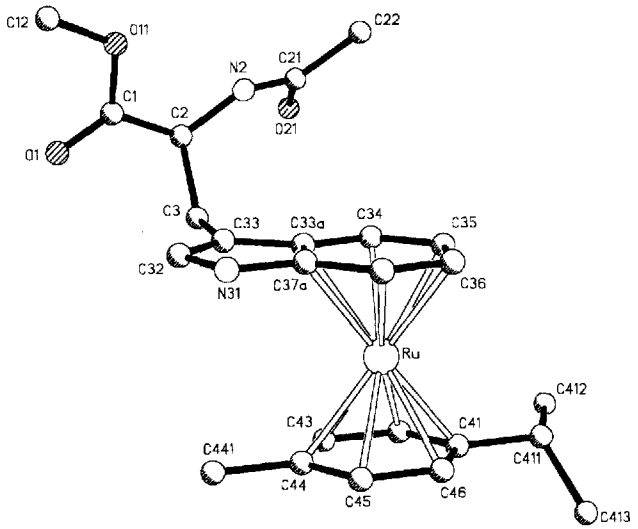
Figure 4. Aromatic region of the ^{1}H-NMR spectrum of **6β** in CD_3NO_2



pronounced lowfield shift to δ = 7.75 (d) and 7.87 (d) is observed for the outer protons H34 and H37. Assignment was achieved by use of an HMQC-TOCSY spectrum.

Metal coordination of the indole six-membered ring also leads to a dramatic change in the electron density distribution in the condensed pyrrole ring. Both H32 (^{1}H NMR: δ = 8.33) and C32 (^{13}C NMR: δ = 143.91) exhibit pronounced lowfield shifts and preliminary ^{1}H-NMR titration data for **6β** and the other tryptophan complexes **7**–**9** indicate that the pK_a value for the indole nitrogen N31 is shifted by more than eight orders of magnitude from 16.8 in the free amino acid[28] to ca. 8 in the CyRu^{II} labeled derivatives. A similar shift has recently been reported for η^6-coordinated indole derivatives[29]. These findings suggest that metalation of N31 should be possible in neutral or weakly alkaline solution and work is in progress to achieve this goal.

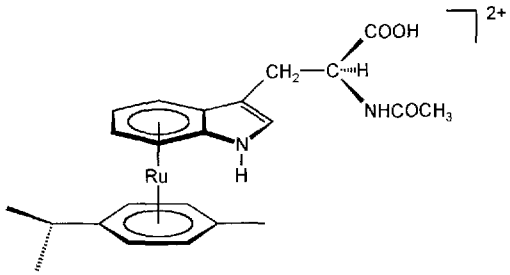
Figure 5. X-ray structure of the cation of **6β**



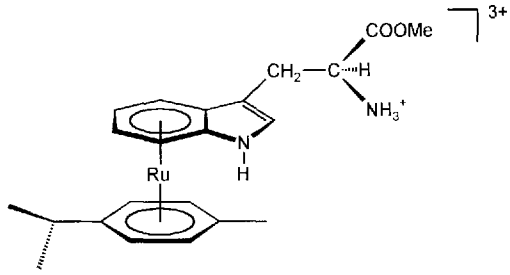
The η^6-coordinated *p*-cymene and indole six-membered ring systems in **6β** are effectively coplanar and display an interplanar distance of 3.45(1) Å that is identical to that of the tyrosine complex **5**. However a degree of ring slippage is apparent from a comparison of the Ru–C33a and Ru–C37a distances of 2.311(7) and 2.296(7) with the opposite Ru–C35 and Ru–36 distances of 2.196(8) and 2.179(8) Å. This is associated with a markedly shorter metal-aromatic plane distance of 1.686(6) Å for *p*-cymene as opposed to 1.761(5) Å for the tryptophan indole system. As may be gauged from the torsion angle of 17.6(5)° for C33a–C36–C46–C43, the conformation of the aromatic rings of the bis(η^6-arene)Ru^{II} sandwich is closer to being staggered.

In both **6β** and the further tryptophan complexes **7**–**9**, the lowfield shift of the *p*-cymene aromatic protons is ca. 0.1–0.15 ppm less than in the analogous tyrosine derivatives **2**–**5**. In contrast to **6**, separation of the facial α- and β-isomers could not be achieved by fractional crystallization for **7**–**9**. A preference for one of the diastereomers is not apparent and their presence in solution leads to doubling of some of the ^{1}H-NMR signals in particular

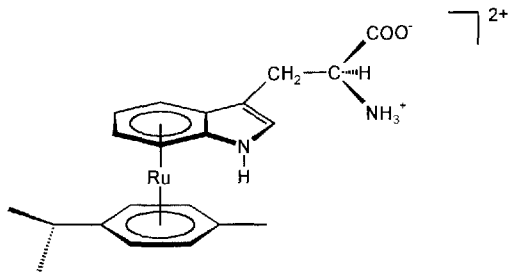
Scheme 4. Cation (α isomers) **7**–**9**



7α



8α



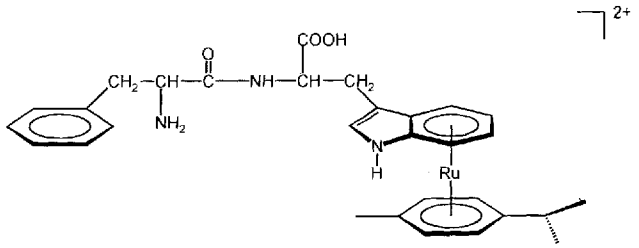
9α

those for the aromatic proton H32 in the range δ = 8.40–8.62. As for the analogous tyrosine complex, [η^6-CyRu(η^6-HtyrOH)](CF$_3$SO$_3$)$_2$ (**5**), the CyRu^{II} derivative of unprotected tryptophan [η^6-CyRu(η^6-HtrpOH)](CF$_3$SO$_3$)$_2$ (**9**) precipitates with a molecule of the solvent CF$_3$COOH. The presence of strong ν(CO) IR absorption bands at both 1737 and 1677 cm^{-1} suggests that both the protonated and deprotonated (zwitterionic) forms of the carboxylato group must be present in the solid state. Attempts to grow crystals suitable for an X-ray structural analysis remained without success.

Chemospecificity

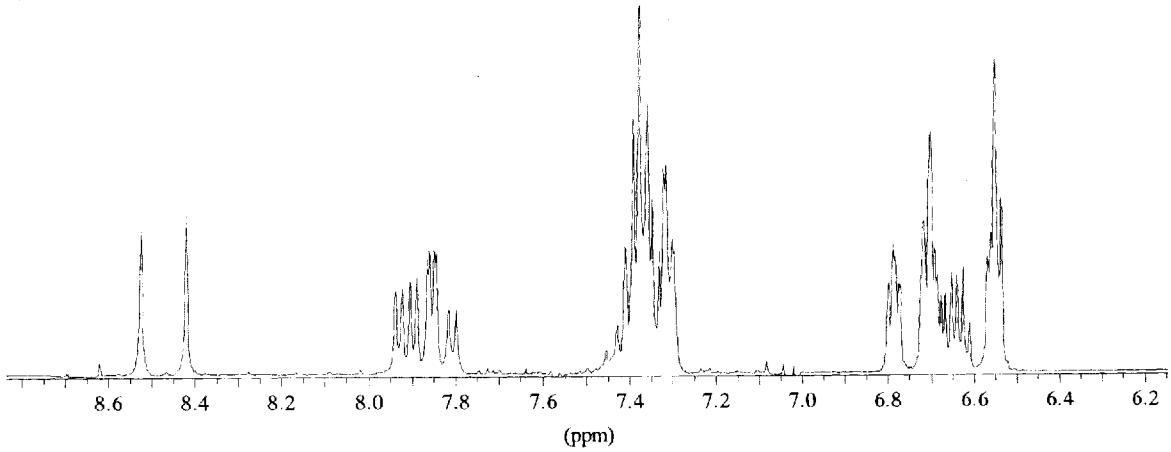
Koefod and Mann[30] have demonstrated that kinetically controlled η^6-coordination of the Cp*Ru^{II} moiety leads to a preference for partially localized arene π systems (e.g. indole) over highly delocalized arenes (e.g. phenyl). This kinetically derived chemospecificity was also confirmed by Trudell et al.[31] for the same organometallic fragment with tryptamine derivatives. In contrast the reaction of Cp*Ru^{II} complexes with HphetrpOH or HtrppheOH at a 1:1 molar ratio provides a mixture of the η^6-indole coordinated 1:1 product and the 2:1 η^6-trp:η^6-phe complex[13]. These find-

Scheme 5. Cation (β isomer) of **10**



10β

Figure 6. Aromatic region of the ^{1}H-NMR spectrum of [η^6-CyRu(η$^6_{ind}$-HphetrpOH)](CF$_3$SO$_3$)$_2$ (**10**) in CD$_3$NO$_2$



ings led us to study the analogous reaction of [(η^6-cymene)Ru(acetone)$_3$]$^{2+}$ (**1**) with these mixed dipeptides for a 1:1 stoichiometry. FAB mass spectra for the products of both reactions exhibit molecular ions at *m/z* 736 corresponding to [M − CF$_3$SO$_3$]$^+$ for the 1:1 product. η^6-Indole coordination is confirmed in both cases by the characteristic shifts of the tryptophan aromatic protons depicted in Fig. 6 for the α- and β-isomers of [η^6-CyRu(η$^6_{ind}$-HphetrpOH)](CF$_3$SO$_3$)$_2$ (**10**) in CD$_3$NO$_2$. In contrast, the aromatic protons of the phenylalanine side chains retain their typical ^{1}H-NMR resonance region at ca. δ = 7.4. Exemplary full analytical data are reported for **10** in the Experimental Section.

Our findings indicate the potential of (η^6-arene)Ru^{II} labeling of amino acids and peptides with aromatic side chains. The long-term stability of such sandwich complexes in aqueous solution for a wide pH range (2−12) could open a copious range of analytical and synthetic perspectives, for example the chemospecific labeling and metalation of tryptophan side chains or the nucleophilic substitution of η^6-coordinated tyrosine aromatic ring systems.

Experimental Section

All manipulations and reactions were carried out under Ar in carefully dried solvents using standard Schlenk techniques. − FT-IR[32]: KBr, Perkin-Elmer 1760. − FAB MS: Fisons VG Autospec with 3-nitrobenzyl alcohol as the matrix. − ^{1}H- and ^{13}C-NMR: Bruker DRX 400: chemical shifts are given in δ values relative to the signal of the deuterated solvent CD$_3$NO$_2$ [δ(^{1}H) = 4.43, δ(^{13}C) = 62.8]. − Elemental analyses: Mikroanalytisches Laboratorium Beller, Göttingen. − The starting compound [(η^6-cymene)Ru(acetone)$_3$](CF$_3$SO$_3$)$_2$ (**1**) was prepared from RuCl$_3$ · *x*H$_2$O (Heräus, Karlsruhe) by abstracting the chloride ions of the intermediate product [{(η^6-cymene)RuCl}$_2$(μ-Cl)$_2$][33] with Ag(CF$_3$SO$_3$) in acetone[14]. The amino acids and peptides were purchased from Bachem (Heidelberg) and Calbiochem-Novabiochem (Bad Soden) and used as received.

[η^6-CyRu(η^6-ActyrOEt)](CF$_3$SO$_3$)$_2$ (**2**): *N*-acetyltyrosine ethyl ester (ActyrOEt, 88.5 mg, 0.4 mmol) was added to a solution of **1** (245 mg, 0.4 mmol) in 10 ml of CH$_2$Cl$_2$ and the suspension refluxed for 3 h. After removal of the solvent the resulting precipitate was washed with CH$_2$Cl$_2$ and diethyl ether and dried in vacuum to afford **2**. Yield 204 mg (65%). − C$_{25}$H$_{29}$NO$_{10}$F$_6$S$_2$Ru (782.7): calcd. C 38.4, H 3.7, N 1.8; found C 38.6, H 4.1, N 1.9. − FAB MS; *m/z* (%): 636 (2) [M$^+$ − CF$_3$SO$_3$]$^+$, 486 (100) [M − 2 CF$_3$SO$_3$]$^+$, 412 (3) [M − 2 CF$_3$SO$_3$ − COOEt]$^+$, 353 (6) [M − 2 CF$_3$SO$_3$ − Cy]$^+$. − ^{1}H NMR (CD$_3$NO$_2$): δ = 1.38 (t, 3H, OEt), 1.46 (dd, 6H, Cy), 2.10 (s, 3H, Ac), 2.57 (s, 3H, Cy), 3.07 (sp, 1H, Cy), 3.08 (dd, 1H, β-H), 3.30 (dd, 1H, β-H), 4.33 (q, 2H, OEt), 4.98 (dd, 1H, α-H), 6.78 (dd, 1H, Ph), 6.83 (dd, 1H, Ph), 6.89 (dd, 1H, Ph), 6.92 (dd, 2H, Cy), 6.97 (dd, 2H, Cy), 7.02 (dd, 1H, Ph), 7.40 (d, 1H, NH). − ^{13}C NMR (CD$_3$NO$_2$): δ = 14.43 (OCH$_2$*C*H$_3$), 19.04 (Cy), 22.53 (Cy + Ac), 32.76 (Cy), 36.09 (β-C), 54.19 (α-C), 63.81 (O*C*H$_2$CH$_3$), 82.42, 82.46 (Ph), 93.17, 93.24, 95.25, 95.40 (Cy), 95.98, 96.02, 107.29 (Ph), 113.07 (Cy), 122.05 (q, CF$_3$SO$_3$), 122.51 (Cy), 143.54 (Ph), 170.75 (COO), 173.66 (NHCO). − IR: ṽ = 3275 (NH), 1741 (CO), 1563 m cm^{-1} (NH).

[η^6-CyRu(η^6-ActyrOH)](CF$_3$SO$_3$)$_2$ (**3**): *N*-acetyltyrosine (ActyrOH, 89.3 mg, 0.4 mmol) was added to a solution of **1** (245 mg, 0.4 mmol) in 5 ml of CF$_3$COOH. After stirring for 3 h at 50°C the product was precipitated with 15 ml diethyl ether and the solvent removed. The resulting solid was washed with diethyl ether and dried in vacuum to provide **3**. Yield 239 mg (79%). − C$_{23}$H$_{27}$NO$_{10}$F$_6$S$_2$Ru (756.7): calcd. C 36.5, H 3.6, N 1.9; found C 36.0, H 3.6, N 1.9. − FAB MS; *m/z* (%): 622 (2) [M − CF$_3$SO$_3$]$^+$, 472 (100) [M − 2 CF$_3$SO$_3$]$^+$, 339 (7) [M − 2 CF$_3$SO$_3$ − Cy]$^+$. − ^{1}H NMR (CD$_3$NO$_2$): δ = 1.47 (dd, 6H, Cy), 2.21 (s, 3H, Ac), 2.58 (s, 3H, Cy), 3.10 (sp, 1H, Cy), 3.11 (dd, 1H, β-H), 3.35 (dd, 1H, β-H), 5.00 (dd, 1H, α-H), 6.81 (dd, 1H, Ph), 6.82 (dd, 1H, Ph), 6.84 (dd, 1H, Ph), 6.92 (dd, 2H, Cy), 6.98 (dd, 2H, Cy), 7.03 (dd,

1H, Ph), 7.74 (d, 1H, NH), 9.00 (br s, 1H, OH). – ^{13}C NMR (CD_3NO_2): δ = 19.03 (Cy), 22.36 (Ac), 22.55, 32.78 (Cy), 35.79 (β-C), 54.34 (α-C), 82.63 (Ph), 93.26, 93.37, 95.36, 95.51 (Cy), 95.91, 96.11, 107.00 (Ph), 113.27, 122.66 (Cy), 122.83 (q, $CF_3SO_3^-$), 143.54 (Ph), 171.03 (COO), 175.61 (NHCO). – IR: $\tilde{\nu}$ = 1738 s, 1662 s (CO), 1563 m cm^{-1} (NH).

[η^6-CyRu(η^6-H$_2$tyrOMe)](CF$_3$SO$_3$)$_3$ (**4**): A solution of tyrosine methyl ester hydrochloride HtyrOMe·HCl (92.7 mg, 0.4 mmol) in 5 ml of CH_3OH was stirred with $Ag(CF_3SO_3)$ (104 mg, 0.4 mmol) for 10 min and the precipitated AgCl filtered off. After washing with CH_3OH the solvent was removed and a solution of **1** (245 mg, 0.4 mmol) in 5 ml of CF_3COOH added to the resulting solid. After heating at 40°C for 8 h diethyl ether (15 ml) was added to the solution to precipitate **4** which was washed with diethyl ether and dried in vacuum. Yield 239 mg (68%). – $C_{23}H_{28}NO_{12}F_9S_3Ru$ (878.7): calcd. C 31.4, H 3.2, N 1.6; found C 31.8, H 3.5, N 1.9. – FAB MS; *m/z* (%): 730 (1) $[M - CF_3SO_3]^+$, 580 (100) $[M - 2\ CF_3SO_3]^+$, 430 (100) $[M - 3\ CF_3SO_3]^+$, 237 (7) $[CyRu]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.48 (d, 6H, Cy), 2.61 (s, 3H, Cy), 3.13 (sp, 1H, Cy), 3.52 (m, 2H, β-H), 3.95 (s, 3H, OMe), 4.68 (br, 1H, α-H), 6.90 (d, 2H, Ph), 6.95–7.03 (2 dd, 5H, Ph + Cy), 7.16 (d, 1H, Ph), 7.93 (br s, 3H, NH_3^+). – ^{13}C NMR (CD_3NO_2): δ = 19.17, 22.40, 22.75, 32.76 (Cy), 33.53 (β-C), 54.83 (α-C), 55.01 (OMe), 82.44, 82.95 (Ph), 93.35, 93.68, 95.47, 95.78 (Cy), 96.13, 97.06, 104.55 (Ph), 113.61, 122.91 (Cy), 121.80 (q, $CF_3SO_3^-$), 143.45 (Ph), 168.89 (COO). – IR: $\tilde{\nu}$ = 1756 s (CO), 1626 m, 1563 m (NH cm^{-1}.

[η^6-CyRu(η^6-H$_2$tyrOH)](CF$_3$SO$_3$)$_2$ (**5**): A solution of **1** (245 mg, 0.4 mmol) and tyrosine (72.5 mg, 0.4 mmol) in 5 ml of CF_3COOH was stirred at room temperature for 6 h. Diethyl ether (15 ml) was added to provide a colorless precipitate of **5** which was washed with diethyl ether and dried in vacuum. Crystals of **5** for X-ray analysis were grown in CH_3OH solution covered with diethyl ether. Yield 222 mg (67%). – $C_{21}H_{25}NO_9F_6S_2Ru \cdot CF_3COOH$ (828.7): calcd. C 33.3, H 3.2, N 1.7; found C 33.7, H 3.5, N 2.1. – FAB MS, *m/z* (%): 566 (2) $[M - CF_3SO_3]^+$, 416 (100) $[M - 2\ CF_3SO_3]^+$, 369 (8) $[M - 2\ CF_3SO_3 - Cy]^+$, 237 (4) $[CyRu]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.46 (d, 6H, Cy), 2.57 (s, 3H, Cy), 3.09 (sp, 1H, Cy), 3.39–3.51 (m, β-H), 4.62–4.67 (m, α-H), 6.60 (dd, 1H, Ph), 6.85–6.99 (m, 6H, Cy + Ph), 7.90 (br, NH_3^+). – ^{13}C NMR (CD_3NO_2): δ = 19.07, 22.53, 22.73, 32.83 (Cy), 33.78, 35.92 (β-C), 54.83–56.44 (α-C), 82.06–82.39 (Ph), 92.80, 93.00, 94.83, 95.03 (Cy), 96.20, 97.24, 102.82 (Ph), 112.56 (Cy), 121.83 (q, $CF_3SO_3^-$), 142.28 (Ph), 169.31, 170.92 (COO). – IR: $\tilde{\nu}$ = 1735 s (CO), 1558 m, 1538 m (NH) cm^{-1}.

[η^6-CyRu(η^6-ActrpOMe)](CF$_3$SO$_3$)$_2$ (**6β**): ActrpOMe (104.1 mg, 0.4 mmol) and **1** (245 mg, 0.4 mmol) were stirred in 10 ml of CH_2Cl_2 for 6 h at room temperature. The resulting yellow precipitate was washed with CH_2Cl_2 and diethyl ether and dried in vacuum to afford **6** in 89% yield (283 mg). The β isomer **6β** was obtained as needle shaped crystals from a CH_3NO_2 solution covered with diethyl ether. – $C_{26}H_{30}N_2O_9F_6S_2Ru$ (793.7): calcd. C 39.4, H 3.8, N 3.5; found C 39.2, H 3.2, N 3.1. – FAB MS; *m/z* (%): 645 (1) $[M - CF_3SO_3]^+$, 495 (100) $[M - 2\ CF_3SO_3]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.40 (2 d, 6H, Cy), 2.01 (s, 3H, Ac), 2.11 (s, 3H, Cy), 2.87 (sp, 1H, Cy), 3.33 (dd, 1H, β-H), 3.50 (dd, 1H, β-H), 4.91 (dd, 1H, α-H), 6.55 (d, 1H, Cy), 6.60 (d, 1H, Cy), 6.68 (dd, 1H, ind), 6.72 (dd, 1H, ind), 6.74 (d, 1H, Cy), 6.81 (d, 1H, Cy), 6.91 (d, 1H, NH), 7.75 (d, 1H, ind), 7.87 (d, 1H, ind), 8.33 (d, 1H, ind), 11.26 (br s, 1H, ind-NH). – ^{13}C NMR (CD_3NO_2): δ = 17.29, 22.70 (Cy), 22.84 (Ac), 27.83 (β-C), 32.74 (Cy), 53.48 (Ome), 53.58 (α-C), 81.67, 86.81, 88.92, 89.11 (ind), 90.84, 91.04, 93.60 (Cy), 93.74 (br, ind + Cy), 104.17 (ind), 110.09 (Cy), 114.32/114.47 (ind), 119.28 (Cy), 122.29 (q, CF_3SO_3), 143.91 (ind), 171.95 (NHCO), 172.92 (COO). – IR: $\tilde{\nu}$ = 3324 m (NH), 1743 s, 1651 s (CO), 1554 s (NH) cm^{-1}.

[η^6-CyRu(η^6-ActrpOH)](CF$_3$SO$_3$)$_2$ (**7**): *N*-acetyltryptophan (ActrpOH, 98.5 mg, 0.4 mmol) and **1** (245 mg, 0.4 mmol) were stirred for 4 h at room temperature in 5 ml of CF_3COOH. After precipitation with diethyl ether, solvent removal and washing the resulting product was dried in vacuum to afford **7**. Yield 250 mg (80%). – $C_{25}H_{29}N_2O_9F_6S_2Ru$ (779.7): calcd. C 38.5, H 3.6, N 3.6; found C 38.2, H 3.7, N 3.5. – FAB MS; *m/z* (%): 631 (10) $[M - CF_3SO_3]^+$, 481 (100) $[M - 2\ CF_3SO_3]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.39/1.41 (2 d, 6H, Cy), 2.10/2.13 (2 s, 3H, Cy), 2.13 (s, 3H, Ac), 2.88 (2 sp, 1H, Cy), 3.43 (2 dd, 1H, β-H), 3.51 (2 dd, 1H, β-H), 3.88 (s, 3H, OMe), 4.95 (m, 1H, α-H), 6.56 (d, 1H, Cy), 6.61 (d, 1H, Cy), 6.66–6.74 (mm, 3H, ind + Cy), 6.82 (2 d, 1H, Cy), 7.02 (d, 1H, ind), 7.87 (d, 1H, ind), 8.40/8.43 (2 s, 1H, ind), 11.27 (br s, 1H, ind-NH). – ^{13}C NMR (CD_3NO_2): δ = 17.36/17.41, 22.73 (Cy), 22.77 (Ac), 27.26/27.53 (β-C), 32.72 (Cy), 53.83 (α-C), 81.62/81.68, 86.97, 87.05, 89.02 (ind), 89.09, 90.87, 91.09 (Cy), 93.57, 93.81 (ind + Cy), 104.22 (ind), 110.12 (Cy), 114.14/114.31 (ind), 119.35 (Cy), 122.43 (q, $CF_3SO_3^-$), 144.09/144.37 (ind), 173.07 (NHCO), 173.22 (COO). – IR: $\tilde{\nu}$ = 3333 w (NH), 1736 s, 1661 s (CO), 1542 s (NH) cm^{-1}. – The pure diastereomer 7**β** can be prepared in quantitative yield by a base-catalysed ester cleavage from **6β** (pH = 4.8).

[η^6-CyRu(η^6-H$_2$trpOMe)](CF$_3$SO$_3$)$_3$ (**8**): A solution of tryptophan methyl ester hydrochloride HtrpOMe·HCl (101.9 mg, 0.4 mmol) was stirred in methanol with $Ag(CF_3SO_3)$ (104 mg, 0.4 mmol) for 10 min and the precipitated AgCl filtered off. After washing with CH_3OH the solvent was removed and a solution of **1** (245 mg, 0.4 mmol) in 5 ml of CF_3COOH added followed by heating to 50°C for 8 h. Addition of diethyl ether led to precipitation of **8** which was washed and dried in vacuum. Yield 234 mg (65%). – $C_{25}H_{29}N_2O_{11}F_9S_3Ru$ (901.8): calcd. C 33.2, H 3.2, N 3.1; found C 33.3, H 3.2, N 3.1. – FAB MS; *m/z* (%): 753 (5) $[M - CF_3SO_3]^+$, 603 (17) $[M - 2\ CF_3SO_3]^+$, 453 (100) $[M - 3\ CF_3SO_3]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.39/1.41 (2 d, 6H, Cy), 2.13/2.16 (2 s, 3H, Cy), 2.89 (2 sp, 1H, Cy), 3.70–3.86 (mm, 2H, β-H), 3.92/3.98 (2 s, 3H, OMe), 4.68 (m, 1H, α-H), 6.57–6.78 (mm, 5H, ind + Cy), 6.84 (d, 1H, Cy), 7.91 (mm, 2H, ind), 8.54/8.57 (2 s, 1H, ind), 11.40 (br s, 1H, ind-NH). – ^{13}C NMR (CD_3NO_2): δ = 17.32/17.45, 22.64/22.67/22.80 (Cy), 25.63/25.85 (β-C), 32.72 (Cy), 54.69/54.80/54.85/55.00 (α-C + OMe), 81.89, 86.74, 89.09/89.19, 89.44 (ind), 91.01, 91.07, 91.19 (Cy), 93.73, 93.83 (ind + Cy), 103.82/104.06 (ind), 110.38/111.26/111.33 (Cy), 114.18/114.27 (ind), 119.55 (Cy), 122.11 (q, $CF_3SO_3^-$), 145.54 (ind), 169.53 (COO). – IR: $\tilde{\nu}$ = 1752 s (CO), 1603 sh, 1524 m (NH) cm^{-1}.

[η^6-CyRu(η^6-HtrpOH)](CF$_3$SO$_3$)$_2$ (**9**): A solution of **1** (245 mg, 0.4 mmol) and tryptophan (81.7 mg, 0.4 mmol) in 5 ml of CF_3COOH was stirred at room temperature for 24 h. After precipitation with diethyl ether, **9** was washed and dried in vacuo. Yield 235 mg (69%). – $C_{23}H_{26}N_2O_8F_6S_2Ru \cdot CF_3COOH$ (851.7): calcd. C 35.3, H 3.2, N 3.3; found C 34.9, H 3.3, N 3.3. – FAB MS; *m/z* (%): 589 (10) $[M - CF_3SO_3]^+$, 572 (17) $[M - 2\ CF_3SO_3]^+$, 439 (100) $[M - 3\ CF_3SO_3]^+$. – ^{1}H NMR (CD_3NO_2): δ = 1.38/1.40 (2 d, 6H, Cy), 2.13/2.15 (2 s, 3H, Cy), 2.86 (2 sp, 1H, Cy), 3.74 (mm, 2H, β-H), 4.59 (m, 1H, α-H), 6.56 (d, 1H, Cy), 6.58–6.75 (mm, 4H, ind + Cy), 6.82 (2 d, 1H, Cy), 7.87 (d, 1H, ind), 7.92 (d, 1H, ind), 8.56/8.62 (2 s, 1H, ind), 11.59 (br, 1H, ind-NH). – ^{13}C NMR (CD_3NO_2): δ = 17.43/17.50, 22.67/22.82 (Cy), 25.95 (β-C), 32.72 (Cy), 54.76/54.92 (α-C), 81.77, 86.97/87.08, 89.13/89.24, 89.33 (ind), 90.94, 91.12, 93.64 (Cy), 93.83, 93.91 (ind + Cy), 104.10/104.24

(ind), 110.27/111.37/111.55 (Cy), 114.32/114.60 (ind), 119.46 (Cy), 121.95 (q, $CF_3SO_3^-$), 145.76/145.96 (ind), 171.63 (COO). – IR: $\tilde{\nu}$ = 1737 s, 1677 s (CO), 1600 sh, 1523 m (NH) cm^{-1}.

[η^6-CyRu(η^6_{ind}-HphetrpOH)](CF$_3$SO$_3$)$_2$ (**10**): A solution of phenylalanyltryptophan (HphetrpOH·0.9 H_2O, 147 mg, 0.4 mmol) and **1** (245 mg, 0.4 mmol) in 5 ml of CF_3COOH was stirred for 4 h at room temperature. Addition of diethyl ether led to precipitation of **10** which was washed and dried in vacuum. Yield 324 mg (81%). – $C_{32}H_{35}N_3O_9F_6S_2Ru \cdot CF_3COOH$ (998.9): calcd. C 40.9, H 3.6, N 4.2; found C 40.5, H 3.7, N 4.2. – FAB MS; *m/z* (%): 736 (3) $[M - CF_3SO_3]^+$, 719 (4) $[M - CF_3SO_3 - NH_3]^+$, 586 (100) $[M - 2\ CF_3SO_3]^+$, 540 (5) $[M - CF_3SO_3 - COOH]^+$, 453 (13) $[M - 2\ CF_3SO_3 - Cy]^+$. – ^1H NMR (CD_3NO_2): δ = 1.37–1.41 (4 d, 6H, Cy), 2.11/2.12 (2 s, 3H, Cy), 2.86 (2 sp, 1H, Cy), 3.30–3.60 (mm, 4H, β-H), 4.61 (m, 1H, α_C-H), 4.99 (m, 1H, α_N-H), 6.53–6.72 (mm, 5H, ind + Cy), 6.79/6.81 (2 d, 1H, Cy), 7.44 (m, 5H, Ph), 7.72–7.85 (4 dd, 2H, ind), 8.41/8.48 (2 s, 1H, ind), 11.56 (br s, 1H, ind-NH). – ^{13}C NMR (CD_3NO_2): δ = 17.38/17.47, 22.67/22.73/22.77/22.82 (Cy), 27.21/27.57 (β_C-C), 32.72 (Cy), 38.13/38.19 (β_N-C), 53.87/54.19 (α_C-C), 56.48 (α_N-C), 81.66/81.75, 87.08, 88.93/88.97, 89.00/89.06 (ind), 90.87, 90.98, 91.05, 93.55, 93.77 (ind + Cy), 104.10/104.22 (ind), 110.07/110.14 (Cy), 114.217114.33/115.22 (ind), 119.32 (Cy), 122.06 (q, $CF_3SO_3^-$), 129.42, 129.46, 130.53, 131.01, 134.88, 134.94 (Ph), 144.60/145.01 (ind), 169.34 (COO), 172.71 (CONH). – IR: $\tilde{\nu}$ = 1733 m, 1680 s (CO), 1597 sh, 1541 m (NH) cm^{-1}.

X-ray Structural Analyses: Siemens P4 diffractometer, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Semi-empirical absorption corrections were applied to the intensity data by use of ψ scans. The structure were solved by a combination of Patterson and Fourier difference syntheses and refined by full-matrix least-squares against F^2 (SHELXL-93[34]). Hydrogen atoms were included at calculated positions with isotropic temperature factors[35].

5: $C_{21}H_{25}NO_9F_6S_2Ru$, M = 714.6, monoclinic, space group $P2_1$ (No. 4), a = 12.860(3), b = 10.706(2), c = 20.455(4) Å, β = 106.66(3)°, V = 2698.0(10) Å^3, Z = 4, $D_{calcd.}$ = 1.759 g·cm^{-3}, μ = 0.828 mm^{-1}. Crystal size: 0.54 × 0.30 × 0.29 mm; ω scan, scan range 2θ ≤ 50° ($0 \le h \le 15$, $0 \le k \le 12$, $-24 \le l \le 23$), 5232 reflections collected (R_{int} = 0.043); max./min. transmission 0.562/0.498; 679 parameters refined; $w^{-1} = [\sigma^2(F_o^2) + (0.050 \cdot P)^2 + 9.90 \cdot P]$ where $P = [\mathrm{Max}(F_o^2, 0) + 2 \cdot F_c^2]/3$, R = 0.048 for 4079 reflections with $I > 2\sigma(I)$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ = 0.123 (all data); largest difference peak: 0.80 eÅ^{-3}. Anisotropic temperature factors for all cation non-hydrogen atoms for the first $CF_3SO_3^-$ anion and S atoms of the remaining three anions, all of which exhibit rotational disorder.

6: $C_{26}H_{30}N_2O_9F_6S_2Ru$, M = 793.7, monoclinic, space group $P2_1$ (No. 4), a = 10.019(2), b = 15.116(3), c = 10.986(2) Å, β = 101.70(3)°, V = 1629.0(5) Å^3, Z = 2, $D_{calcd.}$ = 1.618 g·cm^{-3}, μ = 0.695 mm^{-1}. Crystal size: 0.53 × 0.21 × 0.17 mm; ω scan, scan range 2θ ≤ 50° ($0 \le h \le 11$, $0 \le k \le 17$, $-13 \le l \le 12$), 3090 reflections collected, 2936 symmetry-independent reflections (R_{int} = 0.026); max./min. transmission 0.627/0.570; 395 parameters refined; $w^{-1} = [\sigma^2(F_o^2) + (0.078 \cdot P)^2 + 0.83 \cdot P]$ where $P = [\mathrm{Max}(F_o^2, 0) + 2 \cdot F_c^2]/3$, R = 0.059 for 2053 reflections with $I > 2\sigma(I)$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ = 0.162 (all data); largest difference peak: 0.83 eÅ^{-3}. Anisotropic temperature factors for all non-hydrogen atoms.

☆ Dedicated to Professor *W. Beck* on the occasion of his 65th birthday.

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[35] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +44(0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk).

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