# Formation of Peptides at Half-Sandwich Complexes Using β- and γ-Amino Acid Esters and a Facile Dipeptide Synthesis from an *N,O*-Glycinato Half Sandwich Complex $[RuCl(NH_2CH_2CO_2)(\eta^6\text{-}C_6Me_6)]$[‡]

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*Dedicated to Professor Kurt Dehnicke on the occasion of his 70th birthday*

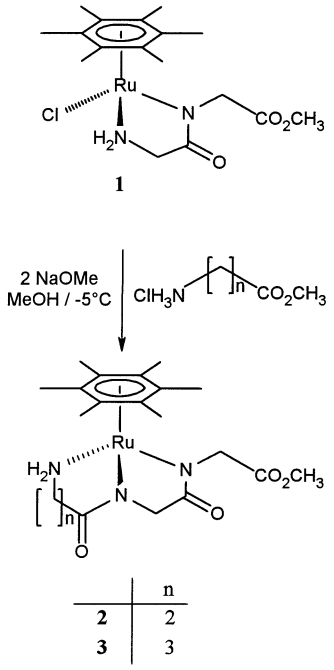
**Keywords:** Peptides / Amino Acids / Ruthenium / Sandwich complexes

The tripeptide ester complexes **2** and **3** are obtained from the diglycine ester complex [RuCl(*N,N′*-glyglyOMe-H$^+$)($\eta^6$-$C_6Me_6$)] and the amino acid esters $H_2N(CH_2)_nCO_2Me$ ($n$ = 2, 3). The reaction of the *N,O*-glycinato complex $[RuCl(NH_2CH_2CO_2)(\eta^6\text{-}C_6Me_6)]$ with the β-, γ- and δ-amino acid methyl esters $H_2N(CH_2)_nCO_2Me$ ($n$ = 2,3,4) in $CH_3OH$ and in the presence of NaOMe affords the $\eta^3$-*N,N′O*-dipeptide complexes $[Ru\{H_2N(CH_2)_nCONCH_2CO_2\}(\eta^6\text{-}C_6Me_6)]$ **5**–**7** in good yields. These complexes are also obtained in a one pot reaction from $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6Me_6)]_2$, glycine and the amino acid ester. The formation of small peptides at the metal represents a facile procedure which does not require either a protecting/activating group or a coupling agent.

The formation of peptides from nonactivated α-amino acid esters,[2] α-amino acids[3] or from cyclopentadienyltitanium, -zirconium and -tantalum α-aminocarboxylates[4] at the metal centres has been reported by several groups. We have shown that half-sandwich complexes of Ru, Rh and Ir promote the formation of linear oligopeptides from amino acid esters[5a] and that the continuous addition of glycine or alanine esters to [RuCl(glyglyglyOMe-H$^+$)(*p*-cymene)] leads to complexes of higher peptides.[5b] Previously we have used di- or tripeptide ester complexes and α-amino acid esters for the elongation of the peptide chain with a defined amino acid sequence. In view of the recent high interest in β-amino acids,[6] which stems from the significant developments in β-peptide chemistry by Seebach[7] and Gellman[8] and their co-workers, we wanted to see whether β- or γ-amino acid esters could be used for peptide synthesis at half-sandwich complexes. We have also found that the condensation of amino acid esters even occurs with an *N,O*-chelate glycinate complex to give dipeptide complexes.

### Formation of $\eta^3$-*N,N′,N′′*-Tripeptide Ester Ruthenium Complexes with N-terminal β-Alanine and γ-Amino Valeric Acid

The $\eta^2$-*N,N′*-diglycine ester complex **1**[9] was found to insert the amino acid esters $H_2N(CH_2)_nCO_2Me$ ($n$ = 2,3) in the presence of NaOMe giving the tripeptide complexes **2** and **3** in high yields (ca. 90%; Scheme 1). The reactions were carried out at low temperatures in order to avoid side reactions, especially cyclisation[10] of the tripeptide ester at the ruthenium centre.




| | n |
|---|---|
| **2** | 2 |
| **3** | 3 |

Scheme 1

Compounds **2** and **3** showed the molecular ions in the FAB-MS spectra. The new complexes contain a six- or seven-membered chelate ring as well as a five-membered ring. Other examples of bis(chelate) complexes with a five- and a seven-membered ring are half-sandwich complexes of Ru, Rh and Ir with L-methionylglycinate;[11] those containing a five- and a six-membered ring are, for example,

[‡] Metal Complexes of Biologically Important Ligands, CXXXVI. – Part CXXXV: see ref.[1]

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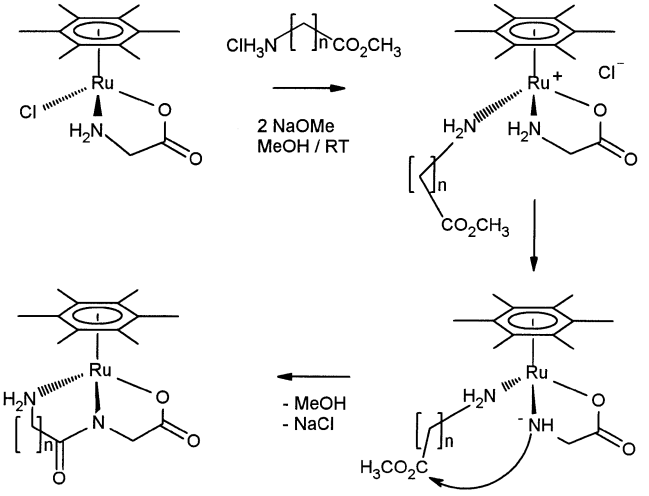
half-sandwich complexes of methioninate.[12] Side reactions (possibly cyclisation of the tripeptides) were observed when amino acid esters $H_2N(CH_2)_nCO_2R$ with longer carbon chains ($n > 3$) were used and the products proved not to be analytically pure.

The IR, $^1H$ and $^{13}C$ NMR spectra of **2** and **3** exhibit the expected signals (see Exp. Sect.)., and successful formation of the tripeptide at the metal is demonstrated by the appearance of only one $^{13}C$ NMR signal for the ester carbonyl group at $\delta = 175$.

### Dipeptide Formation from [RuCl(glycinate)($\eta^6$-$C_6Me_6$)] and Amino Acid Esters

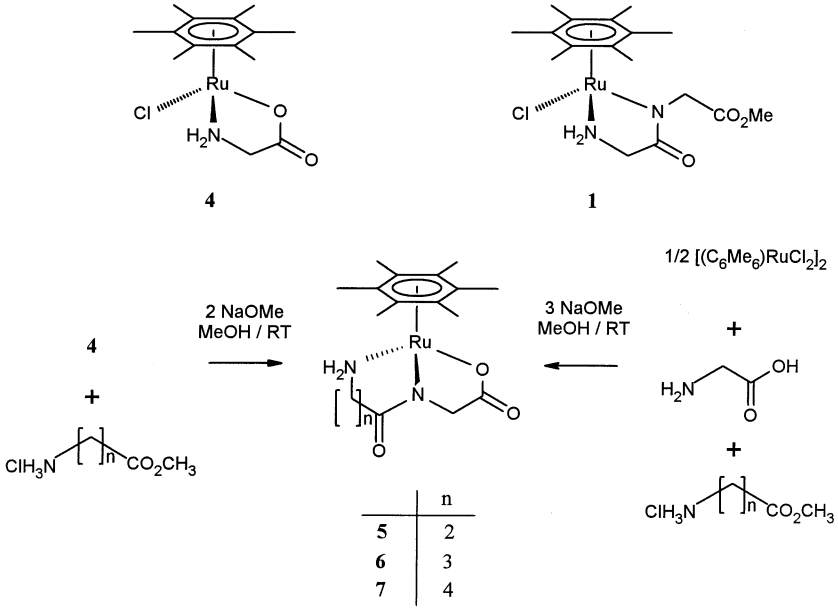
The *N,O*-glycinate ruthenium complex **4**[13] is isoelectronic with the dipeptide ester complex **1** which was successfully used for the peptide synthesis at a metal centre.[5] Complexes **1** and **4** contain three facial coordination sites and a leaving group. Indeed the reaction of **4** with the hydrochlorides of the β-, γ- and δ-amino acid methyl esters $H_2N(CH_2)_nCO_2Me$ ($n = 2-4$) in MeOH at room temperature and in the presence of NaOMe affords the stable, light yellow dipeptide complexes **5**−**7** with yields of up to 97%. The yield decreases with the C-chain length of the amino acid ester (**7**: 67%). No reaction was observed with the ε-amino acid ester $H_2N(CH_2)_5CO_2Me$ and **4**.

The compounds **5**−**7** are also available in a one pot reaction from the chloro-bridged complex [RuCl(μ-Cl)($\eta^6$-$C_6Me_6$)]$_2$,[14] glycine and the hydrochloride of the amino acid methyl ester in the presence of NaOMe (Scheme 2).




Scheme 3

Side products could not be detected. We assume a mechanism similar to that proposed by Yamada et al.[2] and Rode[3] for the $Cu^{II}$-catalyzed formation of peptides from α-amino acids (Scheme 3). The sterically favoured annellation of a five- and a six- or seven-membered ring may promote the formation of the bis(chelate) complexes. This reaction represents a facile peptide formation from an unprotected α-amino carboxylate which doesn't require either an activating group for the free amino acid or a coupling agent. It differs from the formation of the dipeptide esters by the reaction of cyclopentadienyltantalum(V) amino acid carboxylates with free amino acid esters, where the metal carboxylates function as "activated amino acid esters".[4] The




Scheme 2

possibility that in the reaction of **4** with β-, γ- and δ-amino acid esters the latter are added to the metal-activated[4] carboxylate group can be excluded, since then a dipeptide ester complex should be formed that would show IR and NMR spectroscopic data different from those of **5**−**7**; for example, a carbonyl ester absorption at 1730 $cm^{-1}$ would be present instead of a carboxylate band at 1620 $cm^{-1}$.

The peptide formation can be followed from the IR spectra. Compounds **5**−**7** exhibit a strong absorption at 1541−1571 $cm^{-1}$ for the amide group. Further characteristic bands are observed at 3200 (NH) and 1620 $cm^{-1}$ ($CO_2$). In the $^1H$ NMR spectra sharp signals are found which point to a slow epimerization[15] at the chiral metal centre. The $^{13}C$ NMR spectra show the expected signals.

## Experimental Section

**Preparation of 2 and 3:** A solution of the hydrochloride of the amino acid methyl ester (0.2 mmol) and NaOMe (0.2 mmol) in methanol (5 mL) was stirred for 10 min. at room temperature. A solution of **1**[9] (0.2 mmol) in methanol (3 mL) was then added to this mixture, followed by the dropwise addition of a solution of NaOMe (0.2 mmol) in methanol (15 mL) at −15 °C during 2−3 h. The colour of the solution changed from orange to yellow. The solvent was then removed in vacuo and the yellow, oily residue was dissolved in dichloromethane. Sodium chloride was then centrifuged off and the solution was concentrated to 2 mL. The yellow product was precipitated by addition of 50 mL of pentane, washed with more pentane and dried in vacuo.

**[Ru{η³-*N*,*N*′,*N*′′-(β-ala-gly-gly-OMe)}(η⁶-$C_6Me_6$)] (2):** Light yellow powder, yield 91%. − IR (KBr): $\tilde{\nu}$ = 3266 $cm^{-1}$ (m), 3157 (w) [$NH_2$], 1732 (s) [$CO_2CH_3$], 1566 (vs) [Amide-I]. − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 4.72 (d, $^2J$ = 16.8 Hz, 1 H, *H*CH), 4.58 (d, $^2J$ = 16.8 Hz, 1 H, HC*H*), 3.66 (s, 3 H, $CO_2CH_3$), 3.46 (2 d, $^2J$ = 16.8 Hz, 2 H, $CH_2$), 2.97 (m, 1 H, $NH_2$-C$H_2$−$CH_2$−CO), 2.78 (m, 1 H, $NH_2$−C$H_2$−$CH_2$−CO), 2.1−2.3 (m, 2 H, $NH_2$−$CH_2$−C$H_2$−CO), 2.13 [s, 18 H, $C_6(CH_3)_6$]. − $^{13}C$ NMR (100.5 MHz, $CD_3OD$): δ = 182.6, 176.1, 175.6 (*C*ONR and $CO_2CH_3$), 94.8 [$C_6(CH_3)_6$], 55.0, 52.9 ($CH_2$), 50.2 ($CO_2CH_3$), 39.8, 39.4 ($CH_2$−$CH_2$), 16.5 [$C_6(CH_3)_6$]. − MS (FAB+, *m*NBA): *m*/*z* (%) = 480 (5) [M + $H^+$], 502 (4) [M + $Na^+$], 538 (1) [M + $H^+$ + NaCl].

**[Ru{η³-*N*,*N*′,*N*′′-(γ-abu-gly-gly-OMe)}(η⁶-$C_6Me_6$)] (3):** Light yellow powder, yield 86%. − IR (KBr): $\tilde{\nu}$ = 3225 $cm^{-1}$ (m) [$NH_2$], 1749 (s), 1741 (s), 1732 (s) [$CO_2CH_3$], 1585 (vs), 1569 (vs) [Amide-I]. − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 4.38 (d, $^2J$ = 17.6 Hz, 1 H, *H*CH), 3.79 (d, $^2J$ = 17.6 Hz, 1 H, HC*H*), 3.75 (s, 3 H, $CO_2CH_3$), 3.22 (ddd, $^2J$ = 11.3, $^3J$ = 7.7 Hz, $^3J$ = 3.7 Hz, 1 H, $NH_2$−C$H_2$−$CH_2$−$CH_2$−CO), 3.10 (d, $^2J$ = 16.2 Hz, 1 H, *H*CH), 2.86 (dt, $^2J$ = 11.2, $^3J$ = 7.8 Hz, 1 H, $NH_2$−C$H_2$−$CH_2$−$CH_2$−CO), 2.55 (d, $^2J$ = 16.4 Hz, 1 H, HC*H*), 2.22−2.26 (m, 2 H, $CH_2$), 2.10 [s, 18 H, $C_6(CH_3)_6$], 1.95−2.10 (m, 2 H, $NH_2$−$CH_2$−C$H_2$−$CH_2$−CO). − $^{13}C$ NMR (100.5 MHz, $CD_3OD$): δ = 184.2, 182.2, 174.8 (*C*ONR and $CO_2CH_3$), 94.0 [$C_6(CH_3)_6$], 55.8, 55.2 ($CH_2$), 53.5 ($CO_2CH_3$), 47.1, 34.2, 24.4 ($CH_2$−$CH_2$−$CH_2$), 16.1 [$C_6(CH_3)_6$]. − MS (FAB+, *m*NBA): *m*/*z* (%) = 494 (7) [M + $H^+$], 516 (4) [M + $Na^+$], 552 (1) [M + $H^+$ + NaCl].

**General Procedure for the Synthesis of 5−7 from [RuCl(glycinate)(η⁶-$C_6Me_6$)]:** A solution of 0.3 mmol of NaOMe in methanol was added dropwise to a solution of 0.15 mmol of **4**[13] and 0.15 mmol of the hydrochloride of the amino acid methyl ester in 5 mL of dried methanol. The yellow solution was then stirred for 2 h (**5**, **6**) or 6 h (**7**) at room temperature. The solvent was removed in vacuo and the residue dissolved in 5 mL of dichloromethane containing a very small amount of methanol (ca. 0.1 mL). Sodium chloride was then centrifuged off and the solution concentrated to 2 mL. The product was precipitated with diethyl ether, washed with $Et_2O$ and dried in vacuo.

**General Procedure for the Synthesis of 5−7 from [$RuCl_2$(η⁶-$C_6Me_6$)]₂:** A solution of 0.6 mmol of NaOMe in methanol was added to a mixture of 0.1 mmol of [$RuCl_2$(η⁶-$C_6Me_6$)]₂,[14] 0.2 mmol of glycine and 0.2 mmol of the hydrochloride of the amino acid methyl ester in 5 mL of methanol. Stirring for 2−6 h gave a yellow solution from which the solvent was then removed in vacuo. The residue was dissolved in 5 mL of dichloromethane containing a very small amount of methanol (ca. 0.1 mL). Sodium chloride was centrifuged off and the solution concentrated to 2 mL. The product was precipitated with diethyl ether, washed with $Et_2O$ and dried in vacuo.

**[Ru{η³-*N*,*N*′,*O*-(β-Ala-Gly-$CO_2$)}(η⁶-$C_6Me_6$)] (5):** Light yellow powder, yield 97%. − IR (KBr): $\tilde{\nu}$ = 3246 $cm^{-1}$ (m), 3150 (m) [$NH_2$], 1611 (vs) [$CO_2$Ru], 1571 (vs) [Amide-I]. − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 4.59 (d, $^2J$ = 17.35 Hz, 1 H, *H*CH), 3.53 (d, $^2J$ = 17.35 Hz, 1 H, HC*H*), 2.97−2.93 (m, 2 H, C$H_2$−$CH_2$), 2.75−2.73 8m, 2 H, $CH_2$−C$H_2$), 2.16 (s, 18 H, $C_6Me_6$). − $^{13}C$ NMR (100.5 MHz, $CD_3OD$): δ = 183.4, 174.6 (*C*ONR and R*C*$O_2$Ru), 91.9 [$C_6(CH_3)_6$], 53.6 ($CH_2$), 48.6, 38.1 ($CH_2$−$CH_2$), 14.7 [$C_6(CH_3)_6$]. − $C_{17}H_{26}N_2O_3Ru{\cdot}H_2O$ (425.49): calcd. C 47.98, H 6.63, N 6.58; found C 47.98, H 6.46, N 6.55.

**[Ru{η³-*N*,*N*′,*O*-(γ-Abu-Gly-$CO_2$)}(η⁶-$C_6Me_6$)] (6):** Light yellow powder, yield 92%. − IR (KBr): $\tilde{\nu}$ = 3260 $cm^{-1}$ (m), 3224 (m) [$NH_2$], 1621 (vs, br) [$CO_2$Ru], 1568 (vs) [Amide-I]. − $^1H$ NMR (400 MHz, $CD_3OH$): δ = 5.88 (br. t, 1 H, $NH_2$), 4.81 (br. m, 1 H, $NH_2$), 3.38 (m, 1 H, $NH_2$−$CH_2$−$CH_2$−$CO_2$), 2.99−3.11 (m, 2 H, -$CH_2$- + gly), 2.58−2.52 (m, 1 H, -$CH_2$-), 2.24−2.35 (m, 2 H, -$CH_2$- + gly), 2.14 (s, 18 H, $C_6Me_6$), 2.11−1.85 (m, 2 H, -$CH_2$-). − $^{13}C$ NMR (100.5 MHz, $CD_3OD$): δ = 184.9, 184.1 (*C*ONR and R*C*$O_2$Ru), 92.7 [$C_6(CH_3)_6$], 53.3 ($CH_2$), 45.3 (N−$CH_2$−$CH_2$−$CH_2$−CO), 34.2 (N−$CH_2$−$CH_2$−$CH_2$−CO), 24.5 (N−$CH_2$−$CH_2$−$CH_2$−CO), 16.0 [$C_6(CH_3)_6$]. − $C_{18}H_{28}N_2O_3Ru{\cdot}H_2O$ (439.49): calcd. C 49.19, H 6.88, N 6.37; found C 49.83, H 6.64, N 6.22.

**[Ru{η³-*N*,*N*′,*O*-(δ-APS-Gly−$CO_2$-)}($C_6Me_6$)] (7):** Light yellow powder, yield 67%. − IR (KBr): $\tilde{\nu}$ = 3224 $cm^{-1}$ (m) [$NH_2$], 1626 (vs, br) [$CO_2$Ru], 1541 (vs) [Amide-I]. − $^1H$ NMR (400 MHz, $CD_3OD$): δ = 3.29−3.25 (m, 2 H, $CH_2$), 3.05 (d, $^2J$ = 17.05 Hz, 1 H, *H*CH), 3.03−2.96 (m, 1 H, $CH_2$), 2.56 (d, $^2J$ = 17.35 Hz, 1 H, HC*H*), 2.31−2.25 (m, 2 H, C$H_2$−$CH_2$), 2.12 (s, 18 H, $C_6Me_6$), 1.82−1.80 (m, 1 H, $CH_2$), 1.79−1.61 (m, 1 H, $CH_2$), 1.50−1.41 (m, 1 H, $CH_2$). − $^{13}C$ NMR (100.5 MHz, $CD_3OD$): δ = 185.1, 176.8 (*C*ONR and R*C*$O_2$Ru), 92.3 [$C_6(CH_3)_6$], 51.2 ($CH_2$), 45.0 (N−$CH_2$−$CH_2$−$CH_2$−$CH_2$−CO), 33.8 (N−$CH_2$−$CH_2$−$CH_2$−$CH_2$−CO), 26.4 (N−$CH_2$−$CH_2$−$CH_2$−$CH_2$−CO), 22.8 (N−$CH_2$−$CH_2$−$CH_2$−$CH_2$−CO), 15.9 [$C_6(CH_3)_6$]. − $C_{19}H_{28}N_2O_3Ru{\cdot}H_2O$ (453.46): calcd. C 50.32, H 7.11, N 6.18; found C 50.10, H 6.66, N 5.99.

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