Metal Complexes of Biologically Important Ligands, XCI[◇]

Introduction of Organometallic Fragments into α-Amino Acids by Reactions of α-Bromoglycine Derivatives with Anionic Organotransition-Metal Compounds☆

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The reactions of protected α-bromoglycine esters $R^1(O)CNHCH(Br)CO_2R^2$ (R^1 = Ph, $OCMe_3$; R^2 = Me, *t*Bu) with organometallic anions of acetylferrocene, $CpFe(CO)(PPh_3)C(O)CH_3$, $(OC)_5M{=}C(OMe)CH_3$ (M = Cr, W), $(OC)_3Cr(\eta^6$-diphenylmethane), $(OC)_3Cr(\eta^6$-fluorene), $(OC)_3Cr(\eta^6$-dihydroanthracene) and of $(OC)_3Cr(\eta^6$-aniline) and $(OC)_3Cr(\eta^6$-*o*-toluidine) provide a method for the introduction of organometallic fragments into the side chains of α-amino acids. The complexes may be useful as markers for α-amino acids in peptides. The compound $(OC)_3Cr(\eta^6$-*o*-$C_6H_4(CH_3)NHC(H)(CO_2Me)NHC(O)Ph$ was characterized by X-ray diffraction.

Recently, the introduction of organotransition-metal fragments into α-amino acids and peptides or precursors thereof has found much interest. Organometallic complexes can be used as markers for α-amino acids in peptides[3] and for the synthesis of (also unnatural) amino acids and peptides[4]. Methods for the addition of organometallic fragments to α-amino acids include e.g. π coordination of $Cr(CO)_3$ or $C_5Me_5Ru^+$ to aromatic substituents of α-amino acids[5] or the nucleophilic addition of anionic Schiff bases from glycine esters to cationic complexes of unsaturated hydrocarbons[6]. In the course of our studies on the directed synthesis of hydrocarbon-bridged complexes by reaction of anionic with cationic complexes[7] we became interested in the use of electrophilic glycine derivatives as synthons. Steglich and coworkers[8] have employed protected α-haloglycine esters for the derivatization of α-amino acids.

Results and Discussion

The following organometallic anions, which have been successfully used for C–C coupling[7], were treated with protected α-bromoglycine esters:

- Enolates of acetylferrocene[9] and the anion from the Davies compound $CpFe(CO)(PPh_3)C(O)CH_3$[10],
- anions from Fischer carbene complexes $(OC)_5M{=}C(OMe)CH_3$[11] (M = Cr, W),
- deprotonated tricarbonylchromium complexes of diphenylmethane, fluorene and dihydroanthracene[12].

These reactions yielded the compounds **1**–**16**.

The compounds **3**–**5** and **13**–**16** contain two stereogenic atoms; the two diastereomers of these complexes (as enantiomeric pairs) are observed in the ^{1}H- and ^{13}C-NMR spectra. A diastereomeric selectivity, which might have been expected from the steric influence of the π-coordinated $Cr(CO)_3$ group[13] or by the chiral induction of the Davies complex $CpFe(CO)(PPh_3)_3C(O)CH_3$[14], could not be detected. For the compounds **1**–**10** the diastereotopic CH_2 groups give rise to two ^{1}H-NMR signals (double doublets) which are typical of methylene groups adjacent to stereogenic centers. The ^{1}H-NMR data of the compounds **11**–**16** were assigned according to those of comparable compounds[12].

In the IR spectra of the carbonyl complexes of **3**–**16** the (ν)CO absorption bands are characteristic: In the case of the enolate complexes **3**–**6** a strong, single absorption at $\tilde{\nu}$ = 1917 cm^{-1} is observed. The carbene compounds **6**–**10** exhibit a sharp (A_1)CO absorption at $\tilde{\nu}$ = 2064/2071 cm^{-1} (Cr, W) and a broad, strong band at $\tilde{\nu}$ = 1930 cm^{-1}. Two CO absorption bands are also typical of the $Cr(CO)_3$ compounds **11**–**16**. All these CO absorptions are much more intense than those of the *N*-acyl groups, indicating the good labeling properties of the synthesized derivatives. **1** and **2** exhibit the oxo band at $\tilde{\nu}$ = 1660 cm^{-1}, clearly separated from the amide absorptions.

The compounds **3**–**6** represent versatile marker molecules which can be detected by ^{1}H-NMR (Cp), ^{31}P-NMR (PPh_3) and IR (CO) spectroscopy.

Steglich and coworkers[15] showed that acylimines from α-haloglycine derivatives can also be added to amines. This reaction path was followed for the reaction of $(OC)_3Cr(\eta^6$-aniline) and $(OC)_3Cr(\eta^6$-*o*-toluidine) with methyl α-bromohippurate and α-ethylthio-substituted dipeptide ester and gave the complexes **17**–**20**.

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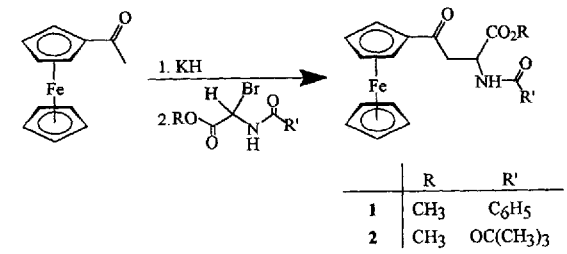
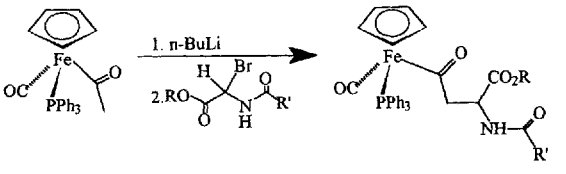
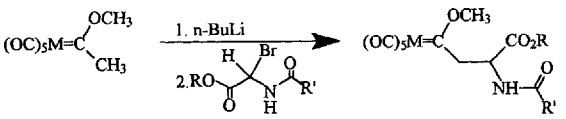


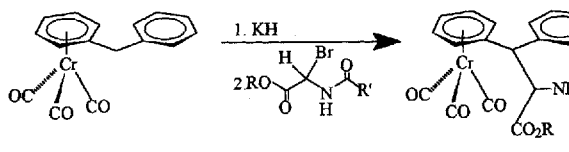
	R	R'
1	CH_3	C_6H_5
2	CH_3	$OC(CH_3)_3$



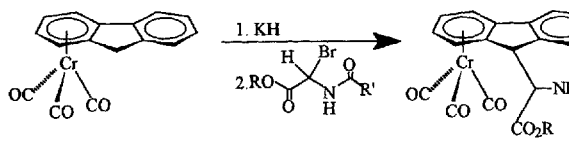
	R	R'
3	CH_3	C_6H_5
4	CH_3	$OC(CH_3)_3$
5	$C(CH_3)_3$	$OC(CH_3)_3$



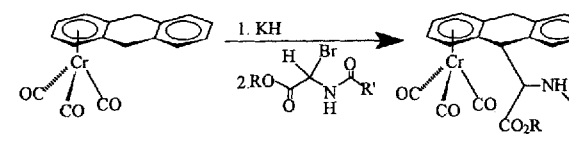
	M	R	R'
6	Cr	CH_3	C_6H_5
7	Cr	CH_3	$OC(CH_3)_3$
8	W	CH_3	C_6H_5
9	W	CH_3	$OC(CH_3)_3$
10	W	$C(CH_3)_3$	$OC(CH_3)_3$



	R	R'
11	CH_3	C_6H_5
12	CH_3	$OC(CH_3)_3$

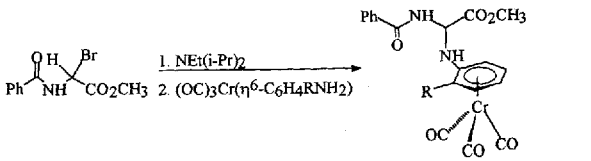


	R	R'
13	CH_3	C_6H_5
14	CH_3	$OC(CH_3)_3$

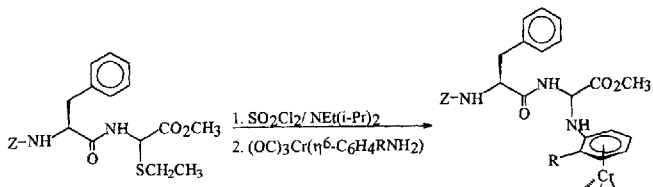


	R	R'
15	CH_3	C_6H_5
16	CH_3	$OC(CH_3)_3$

Compounds **17**–**20** exhibit the typical IR absorptions for π-coordinated $Cr(CO)_3$ fragments. The ^{1}H-NMR spectrum



	R
17	H
18	CH_3



	R
19	H
20	CH_3

of complex **18** shows a double set of signals due to the planar chirality of the $(OC)_3Cr(\eta^6$-*o*-toluidine) fragment (d.e. 45:55). When product **18** was stirred in a small volume of Et_2O, a yellow solid precipitated from the clear solution. Examination of the solution and of the solid by ^{1}H-NMR spectroscopy revealed that the diastereomeric pairs can be separated by this procedure (d.e. 93:7).

Interestingly, one diastereomer of the dipeptide derivative **19** is formed in high excess. In the ^{13}C-NMR spectrum of **19** just one set of signals is observed, although the ^{1}H-NMR spectrum shows some weak signals which could be assigned to the second isomer. Due to the facial chirality of the $Cr(CO)_3$ fragment four diastereomers of **20** could be formed. In the ^{13}C-NMR spectrum just a double set of signals could be detected. Again the ^{1}H-NMR spectrum shows weak signals of the other isomers. Similar stereoselectivities have been observed in the reactions of α-chloroglycyl peptides with α-amino acid esters and enamines[8d].

Suitable crystals of **18** for X-ray diffraction were grown in a mixture of CH_2Cl_2/pentane (Figure 1).

The crystal of **18** contains one diastereomer (as pairs of enantiomers). Weak hydrogen bonds (2.09 Å) exist between the O atom of the *N*-benzoyl and the amide NH group of the independent molecules.

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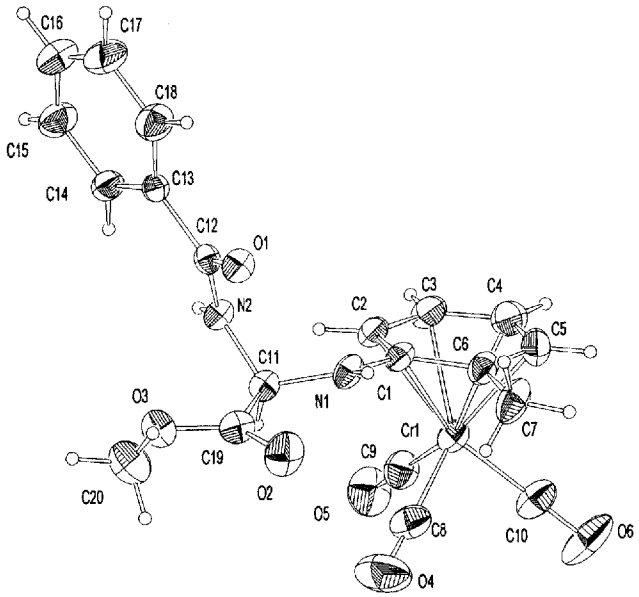
Experimental Section

All reactions were carried out in dry solvents under argon. – NMR: Jeol GSX 270 or Jeol EX 400, tetramethylsilane as internal standard. – IR: 5ZDX FT-IR. – Acetylferrocene (Fluka), $CpFe(CO)(PPh_3)C(O)CH_3$[16], $(OC)_5M{=}C(OMe)CH_3$[17] (M = Cr, W), $(OC)_3Cr(\eta^6$-diphenylmethane), $(OC)_3Cr(\eta^6$-fluorene), $(OC)_3Cr(\eta^6$-dihydroanthracene)[18], $(OC)_3Cr(\eta^6$-aniline) (Aldrich), $(OC)_3Cr(\eta^6$-*o*-toluidine) (Aldrich), methyl α-bromohippurate[8a], α-bromo-Boc-glycine methyl ester[8c], α-bromo-Boc-glycine *tert*-butyl ester[8c] and Z–Phe–Gly(SEt)–OMe[8d] were prepared according to literature procedures or were commercially available

Figure 1. Molecular Structure of **18**[a]



[a] Selected bond lengths [Å] and angles [°]: Cr1–C1 2.317(4), Cr1–C6 2.256(4), Cr1–C9 1.822(5), C9–O5 1.159(6), N1–C1 1.378(5), N1–C11 1.437(5), N2–C11 1.445(5), C1–N1–C11 124.3(3), N1–C11–N2 114.4(3), N1–C11–C19 105.7(3).

compounds. The amine–$Cr(CO)_3$ complexes were recrystallized from Et_2O/pentane before use.

Preparation of the Anionic Organotransition-Metal Compounds:

- To a solution of 114 mg (0.50 mmol) of acetylferrocene in 10 ml of THF was added 20 mg (0.50 mmol) of potassium hydride at ambient temperature. The mixture was stirred for 2 h to give an orange suspension of the enolate.
- To a solution of 227 mg (0.50 mmol) of $CpFe(CO)(PPh_3)C(O)CH_3$ in 10 ml of THF was added 0.32 ml (0.50 mmol) of *n*BuLi (1.6 M in hexane) at −78 °C. Stirring for 1/2 h gave a deep red solution.
- To a solution of 125 mg (0.50 mmol) of $(OC)_5Cr{=}C(OCH_3)CH_3$ or 191 mg (0.50 mmol) of $(OC)_5W{=}C(OCH_3)CH_3$ in 10 ml of THF was added 0.32 ml (0.50 mmol) of *n*BuLi (1.6 M in hexane) at −78 °C. The mixtures were stirred for 1/2 h.
- To solutions of 152 mg (0.50 mmol) of $(OC)_3Cr(\eta^6$-diphenylmethane), 151 mg (0.50 mmol) of $(OC)_3Cr(\eta^6$-fluorene) or 158 mg (0.50 mmol) of $(OC)_3Cr(\eta^6$-dihydroanthracene) in 10 ml of THF were added 107 mg (2.67 mmol) of KH at room temperature [$(OC)_3Cr(\eta^6$-diphenylmethane)] or at −25 °C [$(OC)_3Cr(\eta^6$-fluorene), $(OC)_3Cr(\eta^6$-dihydroanthracene)]. In the case of $(OC)_3Cr(\eta^6$-dihydroanthracene), 142 mg (0.54 mmol) of 18-crown-6 was also added to the reaction mixture. The mixtures were stirred for 2 h at the same temperature. The excess KH was then separated by centrifugation and the deep red solutions of the anions were used directly for the following reactions.

General Procedure for the Reaction of the Anions **1**–**16** *with Electrophilic Glycine Equivalents:* The solution of the anion was cooled to −78 °C and then added to a solution of 122 mg (0.45 mmol) of methyl α-bromohippurate, 121 mg (0.45 mmol) of α-bromo-Boc-glycine methyl ester or 140 mg (0.45 mmol) of α-bromo-Boc-glycine *tert*-butyl ester in 10 ml of THF at −78 °C. The mixtures were stirred at this temperature for 1 h and subsequently allowed to warm to room temperature. The solvents were evaporated. Purification of the crude products is described separately for each compound:

$(\eta^5$-$C_5H_5)Fe[\eta^5$-$C_5H_4COCH_2CH(CO_2CH_3)NHC(O)C_6H_5]$ (**1**): The residue was dissolved in CH_2Cl_2 and the solution was filtered through silica gel with Et_2O. The solvent was evaporated and the residue was washed several times with pentane and dried in vacuo. Yield 157 mg (83%), orange powder, m.p. 76–78 °C. – IR (KBr): $\tilde{\nu}$ = 3329 cm^{-1} br. (NH), 1735 s, 1659 s, 1647 s, 1530 s (CO_2, NCO, C=O). – ^1H NMR ($CDCl_3$, 270 MHz): δ = 3.46 (dd, ^2J = 18.2 Hz, ^3J = 4.0 Hz, 1H, C*H*H′), 3.67 (dd, ^2J = 18.2 Hz, ^3J = 3.7 Hz, 1H, CH*H*′), 3.82 (s, 3H, CH_3), 4.20 (s, 5H, Cp), 4.53–4.57 (m, 2H, Cp), 4.76–4.81 (m, 2H, Cp), 5.07–5.12 (m, 1H, CH), 7.37–7.51 (m, 4H, *m*- and *p*-Ph, NH), 7.81–7.84 (m, 2H, *o*-Ph). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 41.20 (CH_2), 48.70 (CH), 52.80 (CH_3), 69.20, 69.40, 70.0, 72.70, 72.80 (Cp), 127.20, 128.70, 129.60, 131.90 (C_6H_5), 167.10 (CON), 171.90 (CO_2), 201.70 (CpC=O). – $C_{22}H_{21}FeNO_4$ (419.3): calcd. C 63.02, H 5.05, N 3.34; found C 62.33, H 5.02, N 3.47.

$(\eta^5$-$C_5H_5)Fe[\eta^5$-$C_5H_4COCH_2CH(CO_2CH_3)NHC(O)OC(CH_3)_3]$ (**2**): The residue was taken up in a mixture of Et_2O/pentane (1:3) and chromatographed [Et_2O/pentane (1:3), silica gel]. The second orange elution afforded **2**. Yield 149 mg (80%), orange powder, m.p. 53–54 °C. – IR (KBr): $\tilde{\nu}$ = 3375 cm^{-1} br. (NH), 1752 s, 1664 s, 1684 s, 1504 s (CO_2, NCO, C=O). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.37 [s, 9H, $C(CH_3)_3$], 3.25 (dd, ^2J = 17.9 Hz, ^3J = 3.9 Hz, 1H, C*H*H′), 3.44 (dd, ^2J = 17.9 Hz, ^3J = 3.6 Hz, 1H, CH*H*′), 3.71 (s, 3H, OCH_3), 4.17 (s, 5H, Cp), 4.46–4.48 (m, 2H, Cp), 4.52–4.58 (m, 1H, CH), 4.73–4.68 (m, 2H, Cp), 5.61 (d, ^3J = 8.1 Hz, 1H, NH). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 28.31 [$C(CH_3)$], 41.64 (CH_2), 49.44 (CH), 52.53 (OCH_3), 69.13, 69.19, 69.93, 72.60, 77.78 (Cp), 79.89 [$C(CH_3)_3$], 155.48 (CON), 172.05 (CO_2), 201.76 (CpC=O). – $C_{20}H_{25}NO_5Fe$ (415.2): calcd. C 57.85, H 6.07, N 3.37; found C 57.74, H 6.02, N 3.37.

$(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)COCH_2CH(CO_2CH_3)NHC(O)C_6H_5$ (**3**): The residue was taken up in a mixture of Et_2O/pentane (2:1) and chromatographed [Et_2O/pentane (2:1), silica gel]. The second orange elution afforded **3**. Yield 157 mg (54%), yellow powder, m.p. 54 °C. – IR (KBr): $\tilde{\nu}$ = 3432 cm^{-1} br. (NH), 1917 s (CO), 1751 s, 1596 s, 1664 s, 1509 m (CO_2, NCO, C=O). – ^1H NMR (270 MHz, $CDCl_3$): δ = 2.98 (dd, ^2J = 18.4 Hz, ^3J = 3.3 Hz, 1H, C*H*H′), 3.30 (dd, ^2J = 17.6 Hz, ^3J = 4.6 Hz, 1H, CH*H*′), 3.46 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 3.91 (m, 1H, C*H*H′), 3.99 (dd, ^2J = 18.4 Hz, ^3J = 3.7 Hz, 1H, CH*H*′), 4.20–4.23 (m, 1H, CH), 4.35 (d, ^2J = 1.1 Hz, 5H, Cp), 4.43 (d, ^2J = 1.2 Hz, 5H, Cp), 4.52–4.55 (m, 1H, CH), 6.57 (d, ^3J = 9.5 Hz, 1H, NH), 6.87 (d, ^3J = 7.1 Hz, 1H, NH), 7.76–7.17 (m, 40H, C_6H_5, PPh_3). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 49.76 (CH), 49.85 (CH), 52.19 (CH_3), 52.97 (CH_3), 64.70 (CH_2), 65.10 (CH_2), 85.32 (Cp), 85.42 (Cp), 127.30, 127.40, 128.22, 128.34, 128.44, 128.51, 129.94, 130.01, 131.50, 131.60, 133.43, 133.51, 134.61, 134.65, 136.40, 136.52 (C_6H_5, PPh_3), 166.20 (CON), 166.54 (CON), 172.55 (CO_2), 172.77 (CO_2), 275.22 (CpC=O), 278.31 (CpC=O). – ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 75.98, 76.05. – $C_{20}H_{32}FeNO_5P$ (645.5): calcd. C 66.98, H 4.99, N 2.17; found C 66.86, H 5.22, N 2.20.

$(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)COCH_2CH(CO_2CH_3)NHC(O)OC(CH_3)_3$ (**4**): The residue was taken up in a mixture of petroleum ether/ethyl acetate (4:1) and chromatographed [petroleum ether/ethyl acetate (4:1), silica gel]. The second orange elution afforded **4**. Yield 40 mg (14%), yellow powder, m.p. 109 °C. – IR (KBr): $\tilde{\nu}$ = 3442 cm^{-1} br. (NH), 1919 s (CO), 1743 s, 1712 s, 1603 s, 1495 m (CO_2, NCO, C=O). – ^1H NMR (400 MHz, $CDCl_3$): δ = 1.41 [s, 9H, $C(CH_3)_3$], 1.42 [s, 9H, $C(CH_3)_3$], 2.83 (dd, ^2J = 19.9 Hz,

^3J = 2.7 Hz, 1H, CHH'), 3.06 (dd, ^2J = 17.3 Hz, ^3J = 5.4 Hz, 1H, CHH'), 3.39 (s, 3H, CH_3), 3.57 (dd, ^2J = 17.3 Hz, ^3J = 3.7 Hz, 1H, CHH'), 3.65 (s, 3H, CH_3), 3.78 (dd, ^2J = 19.9 Hz, ^3J = 4.7 Hz, 1H, CHH'), 3.82–3.86 (m, 1H, CH), 3.92–3.96 (m, 1H, CH), 4.36 (m, 5H, Cp), 4.37 (d, ^2J = 1.1 Hz, 5H, Cp), 4.53 (d, ^3J = 9.5 Hz, 1H, NH), 4.95 (d, ^3J = 7.9 Hz, 1H, NH), 7.30–7.47 (m, 30H, PPh_3). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 28.26 [$C(CH_3)_3$], 28.36 [$C(CH_3)_3$], 50.46 (CH), 50.59 (CH), 52.02 (CH_3), 52.07 (CH_3), 65.01 (CH_2), 65.46 (CH_2), 78.91 [$C(CH_3)_3$], 79.35 [$C(CH_3)_3$], 85.20 (Cp), 85.33 (Cp), 128.15, 128.29, 129.90, 129.98, 133.25, 133.50, 135.90, 136.54 (PPh_3), 155.50 (CON), 155.75 (CON), 172.96 (CO_2), 173.30 (CO_2), (CpC=O not observed). – ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 75.70, 76.13. – $C_{34}H_{36}FeNO_6P$ (641.5): calcd. C 63.66, H 5.66, N 2.18; found C 63.14, H 6.39, N 2.20.

(η^5-C_5H_5)Fe(CO)(PPh_3)COCH$_2$CH($CO_2C(CH_3)_3$)NHC(O)-OC(CH_3)$_3$ (**5**): The residue was taken up in a mixture of petroleum ether/ethyl acetate (3:2) and chromatographed [petroleum ether/ethyl acetate (3:2), silica gel]. The first orange elution yielded **5**. Yield 74 mg (24%), yellow powder, m.p. 158°C. – IR (KBr): $\tilde{\nu}$ = 3433 cm^{-1} br. (NH), 1919 s (CO), 1709 s, 1612 s, 1484 m (CO_2, NCO, C=O). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.26 [s, 9H, $C(CH_3)_3$], 1.40 [s, 9H, $C(CH_3)_3$], 1.42 [s, 18H, $C(CH_3)_3$], 2.84–2.88 (m, 2H, CHH'), 3.47–3.49 (m, 2H, CHH'), 3.71 ("q", ^3J = 5.0 Hz, 1H, CH), 3.98 ("q", ^3J = 5.4 Hz, 1H, CH), 4.38 (br., 10H, Cp), 4.58 (d, ^3J = 9.6 Hz, 1H, NH), 4.90 (d, ^3J = 7.6 Hz, 1H, NH), 7.31–7.46 (m, 30H, PPh_3). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 27.66 [$C(CH_3)_3$], 27.91 [$C(CH_3)_3$], 28.28 [$C(CH_3)_3$], 28.37 [$C(CH_3)_3$], 51.22 (CH), 51.28 (CH), 64.93 (CH_2), 65.59 (CH_2), 78.57 [$C(CH_3)_3$], 79.02 [$C(CH_3)_3$], 80.57 [$C(CH_3)_3$], 80.83 [$C(CH_3)_3$], 85.17 (Cp), 85.39 (Cp), 128.18, 128.21, 129.89, 133.31, 133.79, 135.94, 136.57 (PPh_3), 155.45 (CON), 155.84 (CON), 171.58 (CO_2), 171.72 (CO_2), (CpC=O not observed). – 31P NMR (109.3 MHz, $CDCl_3$): δ = 75.83, 76.29. – $C_{37}H_{42}FeNO_6P$ (683.5): calcd. C 65.01, H 6.19, N 2.05; found C 64.58, H 6.26, N 2.05.

(OC)$_5$Cr=C(OCH$_3$)CH$_2$CH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$ (**6**): The purification was carried out as described for **1**. Yield 107 mg (54%), yellow powder, m.p. 89°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} br. (NH), 2064 s, 1924 br. (CO), 1745 s, 1642 m, 1530 s (CO_2, NCO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 3.79 (s, 3H, CH_3), 3.85 (dd, ^2J = 15.6 Hz, ^3J = 5.4 Hz, 1H, CHH'), 3.99 (dd, ^2J = 15.6 Hz, ^3J = 4.7 Hz, 1H, CHH'), 4.84 (s, 3H, CH_3), 5.08–5.11 (m, 1H, CH), 6.86 (d, ^3J = 5.9 Hz, 1H, NH), 7.43–7.51 (m, 3H, *m*- and *p*-Ph), 7.73–7.81 (m, 2H, *o*-Ph). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 50.40 (CH), 52.90 (CH_3), 63.30 (CH_2), 67.90 (CH_3), 127.00, 128.70, 131.90, 133.50 (C_6H_5), 166.70 (CON), 171.60 (CO_2), 215.90 (CO), 222.80 (CO), 356.60 (Cr=C). – $C_{18}H_{15}CrNO_9$ (441.3): calcd. C 48.99, H 3.39, N 3.17; found C 49.01, H 3.84, N 3.35.

(OC)$_5$Cr=C(OCH$_3$)CH$_2$CH(CO$_2$CH$_3$)NHC(O)OC(CH$_3$)$_3$ (**7**): The residue was dissolved in CH_2Cl_2 and filtered through silica gel with Et_2O. The solvent was evaporated, the residue was dissolved in petroleum ether and filtered again through silica gel. The starting material was eluted with petroleum ether and the product with diethyl ether. The solvent was removed by evaporation and the residue was stirred at −78°C in 5 ml of pentane to yield **7**, after centrifugation, as a yellow solid. Yield 116 mg (59%), yellow powder, m.p. 84°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3443 cm^{-1} br. (NH), 2065 s, 1935 br. (CO), 1743 s, 1712 m, 1508 s (CO_2, NCO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.41 [s, 9H, $C(CH_3)_3$], 3.71 (s, 3H, CH_3), 3.81 (dd, ^2J = 18.7 Hz, ^3J = 6.1 Hz, 1H, CHH'), 3.90 (dd, ^2J = 18.7 Hz, ^3J = 5.6 Hz, 1H, CHH'), 4.60 ("q", 1H, CH), 4.80 (s, 3H, CH_3), 5.12 (d, ^3J = 8.3 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 28.20 [$C(CH_3)_3$], 51.10 (CH), 52.70 (CH_3), 63.80 (CH_2), 67.80 (CH_3), 80.30 [$C(CH_3)_3$], 154.90 (CON), 171.60 (CO_2), 215.90 (CO), 222.90 (CO), 357.20 (Cr=C). – $C_{16}H_{19}CrNO_{10}$ (437.3): calcd. C 43.94, H 4.38, N 3.20; found C 44.42, H 4.28, N 3.69.

(OC)$_5$W=C(OCH$_3$)CH$_2$CH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$ (**8**): The purification was carried out as described for compound **5**. Yield 134 mg (52%), yellow powder, m.p. 106°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3235 cm^{-1} br. (NH), 2071 s, 1943 br. (CO), 1749 s, 1639 m, 1571 s (CO_2, NCO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 3.73 (dd, ^2J = 16.5 Hz, ^3J = 5.7 Hz, 1H, CHH'), 3.80 (s, 3H, CH_3), 3.82 (dd, ^2J = 16.5 Hz, ^3J = 5.9 Hz, 1H, CHH'), 4.66 (s, 3H, CH_3), 5.10–5.12 (m, 1H, CH), 6.80 (d, ^3J = 7.3 Hz, 1H, NH), 7.42–7.52 (m, 3H, *m*- and *p*-Ph), 7.76–7.99 (m, 2H, *o*-Ph). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 50.80 (CH), 53.30 (CH_3), 66.10 (CH_2), 70.90 (CH_3), 127.90, 129.60, 132.90, 133.50 (C_6H_5), 167.90 (CON), 172.70 (CO_2), 198.20 (CO), 212.30 (CO), 330.20 (W=C). – $C_{18}H_{15}NO_9W$ (573.1): calcd. C 37.69, H 2.64, N 2.44; found C 37.43, H 2.83, N 2.39.

(OC)$_5$W=C(OCH$_3$)CH$_2$CH(CO$_2$CH$_3$)NHC(O)OC(CH$_3$)$_3$ (**9**): The purification was carried out as described for compound **7**. Yield 177 mg (69%), yellow powder, m.p. 112°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3377 cm^{-1} br. (NH), 2072 s, 1956 br. (CO), 1741 s, 1708 m, 1516 s (CO_2, NCO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.37 [s, 9H, $C(CH_3)_3$], 3.49 (dd, ^2J = 17.1 Hz, ^3J = 6.7 Hz, 1H, CHH'), 3.66 (dd, ^2J = 17.1 Hz, ^3J = 5.4 Hz, 1H, CHH'), 3.68 (s, 3H, CH_3), 4.56 (s, 3H, CH_3), 4.55–4.59 (m, 1H, CH), 5.10 (d, ^3J = 7.8 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 28.21 [$C(CH_3)_3$], 51.18 (CH), 52.65 (CH_3), 66.04 (CH_2), 70.33 (CH_3), 80.25 [$C(CH_3)_3$], 154.84 (CON), 171.54 (CO_2), 196.77 (CO), 203.12 (CO), 330.07 (W=C). – $C_{16}H_{19}NO_{10}W$ (569.2): calcd. C 33.76, H 3.36, N 2.46; found C 33.86, H 3.52, N 2.57.

(OC)$_5$W=C(OCH$_3$)CH$_2$CH(CO$_2$C(CH$_3$)$_3$)NHC(O)OC-(CH$_3$)$_3$ (**10**): The purification was carried out as described for compound **7**. Yield 179 mg (65%), yellow powder, m.p. 113°C (dec.). – IR (neat): $\tilde{\nu}$ = 3424 cm^{-1} br. (NH), 2068 s, 1951 br. (CO), 1729 s, 1705 m, 1497 s (CO_2, NCO). – ^1H NMR (270 MHz, $CDCl_3$): δ = 1.41, 1.43 [s, 18H, $C(CH_3)_3$], 3.58 (dd, ^2J = 17.0 Hz, ^3J = 6.2 Hz, 1H, CHH'), 3.69 (dd, ^2J = 17.0 Hz, ^3J = 4.7 Hz, 1H, CHH'), 4.43 ("q", 1H, CH), 4.60 (s, 3H, CH_3), 5.13 (d, ^3J = 8.1 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 27.88 [$C(CH_3)$], 28.26 [$C(CH_3)$], 51.76 (CH), 66.50 (CH_2), 70.22 (CH_3), 80.04 [$C(CH_3)$], 82.51 [$C(CH_3)$], 154.99 (CON), 170.11 (CO_2), 196.85 (CO), 202.99 (CO), 330.62 (W=C). – $C_{19}H_{25}NO_{10}W$ (611.3): calcd. C 37.33, H 4.12, N 2.29; found C 37.51, H 4.15, N 2.32.

(OC)$_3$Cr[μ-η^6-C$_{13}$H$_{11}$CH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$] (**11**): The residue was dissolved in CH_2Cl_2 and filtered through silica gel with Et_2O. The solvent was evaporated and the residue was stirred twice with pentane at −20°C and then dried in vacuo. Yield 178 mg (80%), yellow powder, m.p. 82–83°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3295 cm^{-1} br. (NH), 1967 vs, 1887 vs (CO), 1743 s, 1650 m, 1523 m (CO_2, NCO). – ^1H NMR (270 MHz, [D$_6$]acetone): δ = 3.42 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 4.27 (d, ^3J = 10.4 Hz, 1H, CH), 4.42 (d, ^3J = 9.3 Hz, 1H, CH), 5.36–5.73 [m, 10H, CH, C_6H_5-η^6-Cr(CO)$_3$], 5.88 [d, ^3J = 6.3 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 6.18 [d, ^3J = 6.3 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 7.25–7.55 (m, 16H, Ph), 7.64–7.69 (m, 2H, Ph), 7.73 (d, ^3J = 8.3 Hz, 1H, NH), 7.88–7.93 (m, 2H, Ph), 8.09 (d, ^3J = 8.7 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 52.13 (CH), 52.22 (CH), 52.30 (CH_3), 52.55 (CH_3), 57.44 (CH), 57.51 (CH), 91.17, 91.50, 91.99, 92.30, 96.22, 96.38, 96.74, 97.42, 98.90, 99.93, 113.12, 113.18 [12C, C_6H_5-

η^6-Cr(CO)$_3$], 128.01, 128.35, 128.40, 128.45, 129.02, 129.07, 129.17, 129.22, 129.91, 129.96, 132.20, 132.30, 134.70, 134.81, 139.25, 139.74 (16C, Ph), 167.11 (CON), 167.22 (CON), 171.39 (CO_2), 172.08 (CO_2), 233.85 (CO), 233.99 (CO). – $C_{26}H_{21}CrNO_6$ (495.5): calcd. C 63.02, H 4.27, N 2.83; found C 62.67, H 4.31, N 2.97.

(OC)$_3$Cr[μ-η^6-$C_{13}H_{11}$CH(CO$_2$CH$_3$)NHC(O)OC(CH$_3$)$_3$] (**12**): The purification was carried out as described for compound **11**. Yield 117 mg (53%), yellow powder, m.p. 139°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3405 cm^{-1} br. (NH), 1967 vs, 1886 vs (CO), 1745 s, 1713 s, 1498 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 1.29 [s, 9H, C(CH$_3$)$_3$], 1.34 [s, 9H, C(CH$_3$)$_3$], 3.41 (s, 3H, CH$_3$), 3.61 (s, 3H, CH$_3$), 4.03 (d, ^3J = 9.6 Hz, 1H, CH), 4.24 (d, ^3J = 8.2 Hz, 1H, CH), 4.81–4.96 (m, 2H, CH), 5.32–6.04 [m, 11H, NH, C_6H_5-η^6-Cr(CO)$_3$)], 6.48 (m, 1H, NH), 7.29–7.47 (m, 10H, Ph). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 28.17 [C(*C*H$_3$)$_3$], 28.29 [C(*C*H$_3$)$_3$], 52.05 (CH), 52.13 (CH), 52.32 (CH$_3$), 52.81 (CH$_3$), 58.41 (CH), 58.64 (CH), 79.72 [*C*(CH$_3$)$_3$], 79.84 [*C*(CH$_3$)$_3$], 91.49, 91.69, 92.16, 92.50, 94.84, 96.01, 96.33, 96.63, 97.19, 98.68, 112.72, 113.17 [12C, C_6H_5-η^6-Cr(CO)$_3$], 128.49, 128.50, 128.58, 129.21, 129.92, 130.08, 139.05, 139.18 (8C, Ph), 155.77 (CON), 156.06 (CON), 171.61 (CO_2), 172.36 (CO_2), 234.12 (CO), 234.25 (CO). – $C_{24}H_{25}CrNO_7$ (491.5): calcd. C 58.65, H 5.13, N 2.85; found C 58.54, H 5.13, N 3.09.

(OC)$_3$Cr[μ-η^6-$C_{13}H_9$CH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$] (**13**): The purification was carried out as described for compound **11**. Yield 175 mg (79%), yellow powder, m.p. 76–78°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3283 cm^{-1} br. (NH), 1963 vs, 1880 vs (CO), 1744 s, 1646 m, 1516 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 3.73 (s, 3H, CH$_3$), 3.84 (s, 3H, CH$_3$), 4.80 (d, ^3J = 5.3 Hz, 1H, CH), 4.83 (d, ^3J = 4.1 Hz, 1H, CH), 5.54 (dd, ^3J = 5.3 Hz, ^3J = 8.2 Hz, 1H, CH), 5.61–5.75 [m, 4H, C_6H_4-η^6-Cr(CO)$_3$], 5.79 (dd, ^3J = 4.1 Hz, ^3J = 9.3 Hz, 1H, CH), 6.23 [d, ^3J = 6.2 Hz, 1H, C_6H_4-η^6-Cr(CO)$_3$], 6.38–6.47 [m, 2H, C_6H_4-η^6-Cr(CO)$_3$], 6.51 [d, ^3J = 6.2 Hz, 1H, C_6H_4-η^6-Cr(CO)$_3$], 7.29–7.83 (m, 18H, Ph), 8.02 (m, 2H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 50.41 (CH), 50.55 (CH), 51.88 (CH$_3$), 52.49 (CH$_3$), 52.70 (CH), 55.41 (CH), 87.80, 87.85, 93.22, 93.45, 96.03, 96.09, 96.38, 96.74, 104.12, 111.74, 114.61, 114.21 [12C, C_6H_4-η^6-Cr(CO)$_3$], 121.21, 123.46, 126.14, 127.89, 127.90, 128.61, 128.83, 128.95, 129.23, 129.31, 129.51, 132.26, 134.83, 137.68, 138.31, 140.35, 141.92, 144.27 (20C, Ph), 167.90 (CON), 168.72 (CON), 171.44 (CO_2), 172.41 (CO_2), 234.31 (CO), 234.50 (CO). – $C_{26}H_{19}CrNO_6$ (493.4): calcd. C 63.29, H 3.88, N 2.84; found C 63.21, H 3.97, N 3.01.

(OC)$_3$Cr[μ-η^6-$C_{13}H_{11}$CH(CO$_2$CH$_3$)NHC(O)OC(CH$_3$)$_3$] (**14**): The purification was carried out as described for compound **11**. Yield 121 mg (55%), yellow powder, m.p. 122°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3377 cm^{-1} br. (NH), 1963 vs, 1881 vs (CO), 1747 s, 1710 s, 1693 s, 1523 s (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 1.27 [s, 9H, C(CH$_3$)$_3$], 1.29 [s, 9H, C(CH$_3$)$_3$], 3.77 (s, 3H, CH$_3$), 3.86 (s, 3H, CH$_3$), 4.62 (d, ^3J = 5.0 Hz, 1H, CH), 4.74 (d, ^3J = 3.9 Hz, 1H, CH), 5.02 ("q", ^3J = 5.1 Hz, 1H, CH), 5.27 ("q", ^3J = 4.3 Hz, 1H, CH), 5.61–5.85 [m, 4H, C_6H_4-η^6-Cr(CO)$_3$)], 6.13 (d, ^3J = 5.7 Hz, 1H, NH), 6.41–6.55 [m, 3H, NH, C_6H_4-η^6-Cr(CO)$_3$)], 7.31–7.51, 7.62–7.65, 7.77–7.85 (m, 8H, Ph). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 27.76 [6C, C(*C*H$_3$)$_3$], 50.23 (CH), 50.35 (CH), 52.20 (CH$_3$), 52.33 (CH$_3$), 56.18 (CH), 56.76 (CH), 79.26 [2C, *C*(CH$_3$)$_3$], 87.53, 87.81, 92.27, 92.69, 92.86, 92.99, 93.19, 93.36, 111.56, 111.91, 114.13, 114.27 [12C, C_6H_4-η^6-Cr(CO)$_3$], 120.57, 120.97, 125.47, 125.58, 128.64, 128.94, 129.16, 139.99, 141.35, 142.65 (10C, Ph), 155.78 (2C, CON), 171.36 (CO_2), 171.53 (CO_2), 234.26 (CO), 234.33 (CO). – $C_{24}H_{23}CrNO_7$ (489.4): calcd. C 58.89, H 4.74, N 2.86; found C 58.68, H 5.05, N 2.89.

(OC)$_3$Cr[μ-η^6-$C_{14}H_{11}$CH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$] (**15**): The purification was carried out as described for compound **11**. Yield 167 mg (73%), yellow powder, m.p. 87–89°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3318 cm^{-1} br. (NH), 1963 vs, 1882 vs (CO), 1743 s, 1662 m, 1518 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 3.50 (s, 3H, CH$_3$), 3.71 (s, 3H, CH$_3$), 4.18 (d, ^3J = 8.6 Hz, 1H, CH), 4.35 (d, ^3J = 7.2 Hz, 1H, CH), 4.91 (d, ^3J = 9.4 Hz, 1H, CH), 4.95 (d, ^3J = 9.4 Hz, 1H, CH), 5.09 (d, ^3J = 7.1 Hz, 1H, CH), 5.13 (d, ^3J = 7.1 Hz, 1H, CH), 5.44–5.79 [m, 8H, CH, C_6H_4-η^6-Cr(CO)$_3$], 5.82 [d, ^3J = 6.5 Hz, 1H, C_6H_4-η^6-Cr(CO)$_3$], 6.06 [d, ^3J = 6.8 Hz, 1H, C_6H_4-η^6-Cr(CO)$_3$], 7.13–7.60 (m, 16H, NH, Ph), 7.75–7.93 (m, 4H, Ph). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 34.51 (CH$_2$), 34.74 (CH$_2$), 48.41 (CH), 48.85 (CH), 52.36 (CH$_3$), 52.69 (CH$_3$), 57.70 (CH), 58.84 (CH), 92.33, 92.75, 93.52, 94.41, 94.53, 94.84, 95.51, 96.24, 108.92, 108.99, 110.41, 110.72 [12C, C_6H_5-η^6-Cr(CO)$_3$], 127.31, 127.46, 128.11, 128.23, 128.29, 128.63, 128.73, 128.87, 129.13, 129.23, 129.28, 129.36, 132.43, 132.56, 134.54, 134.75, 134.79, 134.87, 135.51, 135.65 (20C, Ph), 167.11 (CON), 167.22 (CON), 171.48 (CO_2), 171.51 (CO_2), 220.59 (2C, CO). – $C_{27}H_{21}CrNO_6$ (507.1): calcd. C 63.90, H 4.17, N 2.76; found C 63.58, H 4.30, N 2.85.

(OC)$_3$Cr[μ-η^6-$C_{13}H_{11}$CH(CO$_2$CH$_3$)NHC(O)OC(CH$_3$)$_3$] (**16**): The purification was carried out as described for compound **11**. Yield 120 mg (53%), yellow powder, m.p. 142°C (dec.). – IR (KBr): $\tilde{\nu}$ = 3386 cm^{-1} br. (NH), 1965 vs, 1887 vs (CO), 1741 m, 1714 m, 1510 w (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 1.29 [s, 9H, C(CH$_3$)$_3$], 1.31 [s, 9H, C(CH$_3$)$_3$], 3.75 (s, 3H, CH$_3$), 3.77 (s, 3H, CH$_3$), 4.05 (d, ^3J = 9.1 Hz, 1H, CH), 4.18–4.29 (m, 5H, CH), 4.44 ("t", ^3J = 9.8 Hz, 1H, CH), 4.75 ("q", ^3J = 5.9 Hz, 1H, CH), 5.56–5.91 [m, 8H, C_6H_4-η^6-Cr(CO)$_3$], 6.02 (d, ^3J = 9.6 Hz, 1H, NH), 6.60 (d, ^3J = 10.6 Hz, 1H, NH), 7.18–7.33 (m, 8H, Ph). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 27.83 [6C, C(*C*H$_3$)$_3$], 33.99 (CH$_2$), 34.21 (CH$_2$), 48.13 (CH), 48.80 (CH), 51.76 (CH$_3$), 52.08 (CH$_3$), 58.67 (CH), 60.39 (CH), 73.50 [*C*(CH$_3$)$_3$], 79.41 [*C*(CH$_3$)$_3$], 92.11, 92.52, 93.94, 93.97, 95.16, 95.69, 108.21, 108.68, 109.97, 110.42 [12C, C_6H_4-η^6-Cr(CO)$_3$], 126.95, 126.99, 127.69, 127.75, 128.16, 128.24, 128.37, 128.64, 133.22, 134.55, 135.06, 135.43 (12C, Ph), 155.20 (CON), 155.27 (CON), 170.77 (CO_2), 170.94 (CO_2), 233.85 (CO), 233.91 (CO). – $C_{25}H_{25}CrNO_7$ (503.5): calcd. C 59.64, H 5.00, N 2.78; found C 59.82, H 5.38, N 3.05.

General Procedure for the Preparation of **17–20**: To a solution of 122 mg (0.45 mmol) of methyl α-bromohippurate or 182 mg of α-chloro dipeptide ester (generated in situ from 194 mg of α-ethylthio dipeptide ester with 1 equiv. of SO_2Cl_2 in CH_2Cl_2 at 0°C) in 10 ml of THF was added 80.9 μl (0.47 mol) of ethyl(diisopropyl)amine at –78°C. The mixtures were stirred for 1/2 h and then 115 mg (0.50 mmol) of (OC)$_3$Cr(η^6-aniline) or 117 mg (0.50 mmol) of (OC)$_3$Cr(η^6-*o*-toluidine) was added. After stirring for 1/2 h at the same temperature the suspension was allowed to warm to room temperature and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 and filtered through silica gel with Et_2O. The solvent was evaporated and the residue was washed several times with pentane at 0°C and dried in vacuo.

(OC)$_3$Cr[μ-η^6-C_6H_5NHCH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$] (**17**): Yield 168 mg (89%), yellow powder, m.p. 76°C. – IR (KBr): $\tilde{\nu}$ = 3376 cm^{-1} br. (NH), 1953 vs, 1867 vs (CO), 1744 s, 1639 s, 1552 s (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 3.77 (s, 3H, CH$_3$), 5.02 [t, ^3J = 6.4 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.39 [d, ^3J = 7.6 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.46 [d, ^3J = 5.8 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.82 [t, ^3J = 6.5 Hz, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.95–6.00 (m, 1H, CH), 6.20 (d, ^3J = 6.2 Hz, 1H, NH), 7.46–7.61

(m, 3H, C_6H_5), 7.96 (d, ^3J = 7.3 Hz, 2H, C_6H_5), 8.57 (d, ^3J = 8.2 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 53.78 (CH_3), 60.48 (CH), 78.01, 78.23, 85.74, 98.64, 98.79 [5C, C_6H_5-η^6-Cr(CO)$_3$], 128.81, 129.72, 132.75, 133.16, 134.94 [7C, C_6H_5, C_6H_5-η^6-Cr(CO)$_3$)], 168.07 (CON), 169.95 (CO_2), 235.17 (CO). – $C_{19}H_{16}CrN_2O_6$ (420.3): calcd. C 54.29, H 3.84, N 6.66; found C 55.01, H 4.59, N 6.42.

(OC)$_3$Cr[μ-η^6-C$_6$H$_4$(CH$_3$)NHCH(CO$_2$CH$_3$)NHC(O)C$_6$H$_5$] (**18**): Yield 166 mg (85%), yellow powder, m.p. 65°C. – IR (KBr): $\tilde{\nu}$ = 3285 cm^{-1} br. (NH), 1951 vs, 1864 vs (CO), 1750 s, 1646 s, 1520 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 2.20 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 5.03–5.13 [m, 2H, C_6H_4-η^6-Cr(CO)$_3$], 5.39–5.55 [m, 4H, C_6H_4-η^6-Cr(CO)$_3$, NH], 5.62–5.74 [m, 2H, CH, C_6H_4-η^6-Cr(CO)$_3$], 5.79–5.93 [m, 3H, C_6H_4-η^6-Cr(CO)$_3$, NH], 6.14 ("t", ^3J = 8.3 Hz, 1H, CH), 7.44–7.63 (m, 6H, C_6H_5), 7.87–8.01 (m, 4H, C_6H_5), 8.41 (d, ^3J = 8.5 Hz, 1H, NH), 8.71 (d, ^3J = 7.9 Hz, 1H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 16.99 (CH_3), 17.02 (CH_3), 53.19 (CH_3), 53.45 (CH_3), 59.41 (CH), 60.74 (CH), 75.79, 76.78, 86.11, 86.23, 92.63, 94.08, 96.14, 96.38, 99.77, 99.94 [10C, C_6H_4-η^6-Cr(CO)$_3$], 127.94, 128.04, 128.17, 128.96, 129.21, 129.49, 132.40, 134.08 [14C, C_6H_5, C_6H_5-η^6-Cr(CO)$_3$], 167.71 (CON), 167.24 (CON), 169.83 (CO_2), 169.64 (CO_2), 235.80 (CO). – $C_{20}H_{18}CrN_2O_6$ (434.4): calcd. C 55.31, H 4.18, N 6.44; found C 55.55, H 4.37, N 6.50.

(OC)$_3$Cr[μ-η^6-C$_6$H$_5$NHCH(CO$_2$CH$_3$)NHC(O)CH(CH$_2$-C$_6$H$_5$)NHC(O)OCH$_2$C$_6$H$_5$] (**19**): Yield 196 mg (73%), yellow powder, m.p. 101°C. – IR (KBr): $\tilde{\nu}$ = 3395 cm^{-1} br. (NH), 1955 vs, 1869 vs (CO), 1746 m, 1709 m, 1672 m, 1551 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 2.88–2.99 (m, 1H, C*H*H'), 3.17–3.29 (m, 1H, CH*H'*), 3.73 (s, 3H, CH_3), 4.43–4.49 (m, 1H, CH), 4.83–5.05 [m, 3H, CH_2, C_6H_5-η^6-Cr(CO)$_3$], 5.19–5.23 [m, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.38–5.43 [m, 1H, C_6H_5-η^6-Cr(CO)$_3$], 5.73–5.79 [m, 2H, C_6H_5-η^6-Cr(CO)$_3$], 6.09–6.13 (m, 1H, NH), 6.47–6.53 (m, 1H, CH), 6.80 (d, ^3J = 7.2 Hz, 1H, NH), 7.20–7.31 (m, 10H, C_6H_5), 8.19–8.25 (m, 1H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 38.15 (CH_2), 53.18 (CH_3), 56.59 (CH), 59.55 (CH), 66.43 (CH_2), 76.89, 77.00, 78.77, 85.07, 97.99 [5C, C_6H_5-η^6-Cr(CO)$_3$], 127.08, 128.09, 128.28, 128.83, 128.89, 129.91, 129.94, 131.77, 137.99 [11C, C_6H_5, C_6H_5-η^6-Cr(CO)$_3$], 156.54 (CON), 168.94 (CON), 172.19 (CO_2), 235.55 (CO). – $C_{29}H_{27}N_3O_8Cr$ (597.5): calcd. C 58.29, H 4.55, N 7.03; found C 57.54, H 4.69, N 6.22.

(OC)$_3$Cr[μ-η^6-C$_6$H$_4$(CH$_3$)NHCH(CO$_2$CH$_3$)NHC(O)CH-(CH$_2$C$_6$H$_5$)NHC(O)OCH$_2$C$_6$H$_5$] (**20**): Yield 160 mg (58%), yellow powder, m.p. 107°C. – IR (KBr): $\tilde{\nu}$ = 3405 cm^{-1} br. (NH), 1952 vs, 1864 vs (CO), 1747 m, 1707 m, 1673 m, 1523 m (CO_2, NCO). – ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 2.16 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.98 (dd, ^2J = 13.8 Hz, ^3J = 8.9 Hz, 2H, C*H*H'), 3.22 (dd, ^2J = 13.8 Hz, ^3J = 5.5 Hz, 2H, CH*H'*), 3.78 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 4.41–4.51 (m, 2H, CH), 5.02 (s, 4H, CH_2), 5.08 ["t", ^3J = 6.3 Hz, 2H, C_6H_4-η^6-Cr(CO)$_3$], 5.26–5.43 [m, 4H, C_6H_4-η^6-Cr(CO)$_3$], 5.59–5.75 [m, 4H, CH, C_6H_4-η^6-Cr(CO)$_3$], 5.86 ("d", ^3J = 6.2 Hz, 2H, NH), 6.65 (d, 2H, NH), 7.17–7.38 (m, 20H, C_6H_5), 8.29 ("d", ^3J = 7.8 Hz, 2H, NH). – ^{13}C NMR (100.4 MHz, [D$_6$]acetone): δ = 16.96 (CH_3), 17.08 (CH_3), 37.98 (CH_2), 53.16 (CH_3), 53.39 (CH_3), 56.84 (CH), 56.91 (CH), 60.00 (CH), 60.07 (CH), 66.36 (CH_2), 76.75, 76.93, 86.01, 86.17, 93.70, 93.90, 96.24, 96.31, 99.60, 99.77 [10C, C_6H_4-η^6-Cr(CO)$_3$], 127.03, 128.01, 128.11, 128.22, 128.77, 129.06, 129.23, 129.82, 137.65, 137.79 [22C, C_6H_5, C_6H_5-η^6-Cr(CO)$_3$], 156.49 (CON), 169.29, 169.37 (CON), 172.02, 172.20 (CO_2), 235.53 (CO), 235.76 (CO). – $C_{30}H_{29}CrN_3O_8$ (611.6): calcd. C 58.92, H 4.78, N 6.87; found C 58.97, H 4.70, N 6.81.

X-ray Structure Determination of **18**[19]: $C_{20}H_{18}CrN_2O_6$, M = 434.36, T = 293(2) K, wavelength 0.71073 Å, triclinic, $P\bar{1}$ (No. 2), crystal size 0.30 × 0.33 × 0.53 mm, a = 9.295(4), b = 13.006(2), c = 18.449(7) Å, α = 97.88(2), β = 98.27(3), γ = 107.76(3)°, V = 2062.8(13) Å^3, Z = 4, d(calcd.) = 1.399 g/cm^3, μ = 0.592 mm^{-1}, F(000) = 896, Θ range 2.20–21.98°, index ranges $-9 \leq h \leq 9$; $-13 \leq k \leq 13$; $0 \leq l \leq 19$, 5232 collected reflections, 5040 independent reflections (R_{int} = 0.0178), max./min. transmission 0.9982 and 0.7587, data/restraints/parameters: 5040/0/527, GOF = 0.896, $R1$ = 0.0486, $wR2$ = 0.1433, $F > 4\sigma(F)$ = 4068, wheights: $w = 1/[\sigma^2F_o^2 + (0.1055\,P)^2 + 1.3748P]$; $P = (F_o^2 + 2F_c^2)/3$, $R1$ = 0.0615, $wR2$ = 0.1534 (all data), largest diff. peak/hole = 0.459/−0.503 e · Å^{-3}.

☆ Dedicated to Professor *Victor Gutmann* on the occasion of his 75th birthday.

[1] M. Maurus, B. Aechter, W. Hoffmüller, K. Polborn, W. Beck, *Z. Anorg. Allg. Chem.*, in press.

[2] X-ray diffraction.

[3] [3a] G. Jaouen, A. Vessiéres, I. S. Butler, *Acc. Chem. Res.* **1993**, *26*, 361–369. – [3b] M. Salmain, M. Gunn, A. Gorfti, S. Top, G. Jaouen, *Bioconjugate Chem.* **1993**, *4*, 425–433. – [3c] A. Gorfti, M. Salmain, G. Jaouen, M. J. McGlinchey, A. Bennouna, A. Mousser, *Organometallics* **1996**, *15*, 142–151. – [3d] A. J. Gleichmann, J. M. Wolff, W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.* **1995**, 1549–1554. – [3e] J. M. Wolff, A. J. Gleichmann, W. S. Sheldrick, *J. Inorg. Biochem.* **1995**, *59*, 219. – [3f] R. Krämer, *Angew. Chem.* **1996**, *108*, 1287–1289; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1197–1199. – [3g] M. Schweiger, T. Ederer, K. Sünkel, W. Beck, *J. Organomet. Chem.*, in press.

[4] [4a] G. R. Stephenson, *Studies in Natural Products Chemistry*, Elsevier Science B. V., **1995**, vol. 16, p. 395. – [4b] K. Schlögl, *Monatsh. Chem.* **1957**, *88*, 601–621. – [4c] J.-C. Brunet, E. Cuingnet, H. Gras, P. Marcinical, A. Mocz, C. Sergheraert, A. Tartar, *J. Organomet. Chem.* **1981**, *216*, 73–77. – [4d] A. J. Pearson, P. R. Bruhn, F. Gouzoules, S.-Han Lee, *J. Chem. Soc., Chem. Commun.* **1989**, 659–661. – [4e] A. J. Pearson, P. R. Bruhn, *J. Org. Chem.* **1991**, *56*, 7092–7097. – [4f] W. Beck, R. Krämer, *Angew. Chem.* **1991**, *103*, 1492–1493; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1467–1469. – [4g] M. J. Dunn, R. F. W. Jackson, G. R. Stephenson, *Synlett* **1992**, 905–906. – [4h] J. Barker, S. L. Cook, M. L. Lasterra-Sánchez, S. E. Thomas, *Inorg. Chim. Acta* **1994**, *220*, 137–143.

[5] [5a] C. Sergheraert, A. Tartar, *J. Organomet. Chem.* **1982**, *240*, 163–168. – [5b] C. Sergheraert, J.-C. Brunet, A. Tartar, *J. Chem. Soc., Chem. Commun.* **1982**, 1417–1418. – [5c] W. S. Sheldrick, A. J. Gleichmann, *J. Organomet. Chem.* **1994**, *470*, 183–187. – [5d] R. M. Moriarty, Yi-Yin Ku, U. S. Gill, *J. Chem. Soc., Chem. Commun.* **1987**, 1837–1838.

[6] [6a] F. Rose-Munch, K. Aniss, *Tetrahedron Lett.* **1990**, *31*, 6351–6354. – [6b] F. Rose-Munch, K. Aniss, E. Rose, *J. Organomet. Chem.* **1990**, *385*, C1–C3. – [6c] F. Rose-Munch, K. Aniss, E. Rose, J. Vaisserman, *J. Organomet. Chem.* **1991**, *415*, 223–255. – [6d] M. Chaari, J.-P. Lavergne, Ph. Viallefont, *Synth. Commun.* **1989**, *19*, 1211–1216. – [6e] M. Chaari, A. Jenhi, J.-P. Lavergne, Ph. Viallefont, *J. Organomet. Chem.* **1991**, *401*, C10–C13. – [6f] M. Chaari, A. Jenhi, J.-P. Lavergne, Ph. Viallefont, *Tetrahedron* **1991**, *47*, 4619–4630.

[7] W. Beck, B. Niemer, M. Wieser, *Angew. Chem.* **1993**, *105*, 969–996; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 923, and literature cited therein. – [10d,11d,12e].

[8] [8a] R. Kober, W. Steglich, *Liebigs Ann. Chem.* **1983**, 599–609. – [8b] R. Kober, K. Papadopoulos, W. Miltz, D. Enders, W. Steglich, *Tetrahedron* **1985**, *41*, 1693–1701. – [8c] P. Münster, W. Steglich, *Synthesis* **1987**, 223–225. – [8d] G. Apitz, M. Jäger, S. Jaroch, S. Kratzel, L. Schäffeler, W. Steglich, *Tetrahedron* **1993**, *49*, 8223–8232. – T. Bretschneider, W. Miltz, P. Münster, W. Steglich, *Tetrahedron* **1988**, *44*, 5403–5414. – [8e] V. A. Burgess, C. J. Easton, M. P. Hay, P. J. Steel, *Aust. J. Chem.* **1988**, *41*, 701–710. – [8f] S. Jaroch, T. Schwarz, W. Steglich, P. Zistler, *Angew. Chem.* **1993**, *105*, 1803–1805; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1771.

[9] [9a] C. R. Hauser, T. A. Mashburn, *J. Org. Chem.* **1961**, *26*, 1795–1800. – [9b] P. Braunstein, T. M. Gomes Carneiro, D. Matt, *J. Organomet. Chem.* **1989**, *367*, 117–132.
[10] [10a] L. S. Liebeskind, M. E. Welker, R. W. Fengl, *J. Am. Chem. Soc.* **1986**, *108*, 6328–6343. – [10b] S. G. Davies, *Aldrichim. Acta* **1990**, *23*, 31 and literature cited therein. – [10c] S. G. Davies, A. E. Derome, J. P. McNally, *J. Am. Chem. Soc.* **1991**, *113*, 2854–2861. – [10d] J. Breimair, M. Wieser, B. Wagner, K. Polborn, W. Beck, *J. Organomet. Chem.* **1991**, *421*, 55–64.
[11] [11a] C. G. Kreiter, *Angew. Chem.* **1968**, *80*, 402; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 390. – [11b] C. P. Casey, W. R. Brunsvold, *J. Organomet. Chem.* **1976**, *118*, 309–323. – [11c] C. P. Casey, R. L. Anderson, *J. Am. Chem. Soc.* **1974**, *96*, 1230–1231. – [11d] J. Breimair, T. Weidmann, B. Wagner, W. Beck, *Chem. Ber.* **1991**, *124*, 2431–2434.
[12] [12a] A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, S. Andre, *J. Organomet. Chem.* **1978**, *154*, 45–63. – [12b] A. N. Nesmeyanov, N. A. Ustynyuk, L. N. Novikova, T. N. Rybina, *J. Organomet. Chem.* **1980**, *184*, 63–75. – [12c] A. Ceccon, A. Gambaro, G. Agostini, A. Venzo, *J. Organomet. Chem.* **1981**, *217*, 79–89. – [12d] A. Ceccon, A. Gambaro, A. Venzo, *J. Organomet. Chem.* **1984**, *275*, 209–222. – [12e] J. Breimair, M. Wieser, W. Beck, *J. Organomet. Chem.* **1992**, *441*, 429–439.
[13] A. Jenhi, J. P. Lavergne, Ph. Viallefont, *J. Organomet. Chem.* **1991**, *401*, C14–C16.
[14] [14a] G. Bashiardes, S. G. Davies, *Tetrahedron Lett.* **1988**, *29*, 6509–6512. – [14b] G. Bashiardes, S. P. Collingwood, S. G. Davies, S. C. Preston, *J. Organomet. Chem.* **1989**, *364*, C29–C32. – [14c] S. P. Collingwood, S. G. Davies, S. C. Preston, *Tetrahedron Lett.* **1990**, *31*, 4067–4068.
[15] W. Steglich, M. Jäger, S. Jaroch, P. Zistler, *Pure Appl. Chem.* **1994**, *66*, 2167–2170.
[16] J. P. Bibler, A. Wojicki, *Inorg. Chem.* **1966**, *5*, 889–892.
[17] [17a] E. O. Fischer, A. Maasböl, *Chem. Ber.* **1967**, *100*, 2445–2456. – [17b] E. O. Fischer, U. Schubert, W. Kleine, H. Fischer, *Inorg. Synth.* **1979**, *19*, 164–172.
[18] [18a] T. E. Bitterwolf, R. Herzog, P. D. Rockswold, *J. Organomet. Chem.* **1987**, *320*, 197–209. – [18b] S. Top, G. Jaouen, *J. Organomet. Chem.* **1979**, *182*, 381–392.
[19] Further details of the crystal structure determination are available from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-405792.

[96194]