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Metal complexes of biologically important ligands, CXIV ferrocenyl–oxazolones as N and C donors in Pd(II), Pt(II) and Ir(III) complexes and ferrocenoyl–dipeptides☆

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Abstract

2-Ferrocenyl-4R-5(4H)-oxazolones **1**–**5** were obtained from *N*-ferrocenoyl-α-amino acids and function as N donors in dichloro–phosphine–palladium(II) and platinum(II) complexes **6**–**18**. The reaction of ferrocenyl–oxazolone and ferrocenyl–bis(oxazolone) with $[Cp^*IrCl_2]_2$ afforded trimetallic and pentametallic complexes **19** and **20** with a C,N bridging oxazolone. Ring opening of the ferrocenyl–oxazolones **1**, **2** and **4** with α-amino acid esters gave *N*-ferrocenoyl–dipeptide esters **21**–**26**. In the ferrocene bis(dipeptides) the two peptide esters are aligned parallel by hydrogen bonding. The structures of **6** and **19** were determined by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 2-Ferrocenyl-5(4H)-oxazolones; Ferrocenoyl marked dipeptides; C,N bridging oxazolone; Cyclic voltammetry

1. Introduction

Metal complexes of oxazolines have found great interest as catalysts in asymmetric synthesis [2]. 5(4H)-Oxazolones [3] are important starting materials; the ease of racemisation [3,4] prevents their use in asymmetric catalysis. However metal complexes of oxazolones can provide information on the coordination chemistry of *N*-heterocycles. Moreover ring opening [5a] of organometallic oxazolones gives rise to peptides attached to a metal. In continuation of our studies [5] on oxazolone metal complexes we now report on the synthesis and reaction of 2-ferrocenyl substituted 5(4H)-oxazolones [6]. 4-Ferrocenylmethylene-2-R-5(4H) oxazolones are starting materials for the synthesis of racemic [7] or optically active [8] ferrocenyl alanine which was incorporated into peptides to follow their redox properties [9]. The 1,1′-ferrocenyl bis(alanine) is available from 1,1′-diiodo–ferrocene [10].

2. Synthesis of ferrocenyloxazolones

Ferrocenoyl-α-amino acid esters **1a**–**3a** were synthesized from ferrocene carboxylic acid and α-amino acid esters, according to published procedures (Scheme 1, [11a,12]). The first compounds of this type were reported by Schlögl [7a]. Erker's [13] isocyanate route is another access to cyclopentadienyl-α-amino acid ester substituted metallocenes. Compounds **1a**–**3a** were saponified and from the free acids **1b**–**3b** the oxazolone derivatives **1**–**3** could be obtained. Similary, the ferrocenyl–bis(oxazolones) **4** and **5** were prepared from the ferrocene dicarboxylic acid.

For compounds **1**–**5** the absorptions at 1820 cm^{-1} (CO) are characteristic in their IR-spectra [3]. Only for complexes **3** and **5** the signals of the diastereotopic ring protons (due to stereogenic C-4 oxazolone atoms) were observed in the ^{1}H-NMR spectra. For **5** the two stereo-

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[1] X-ray structure analyses.

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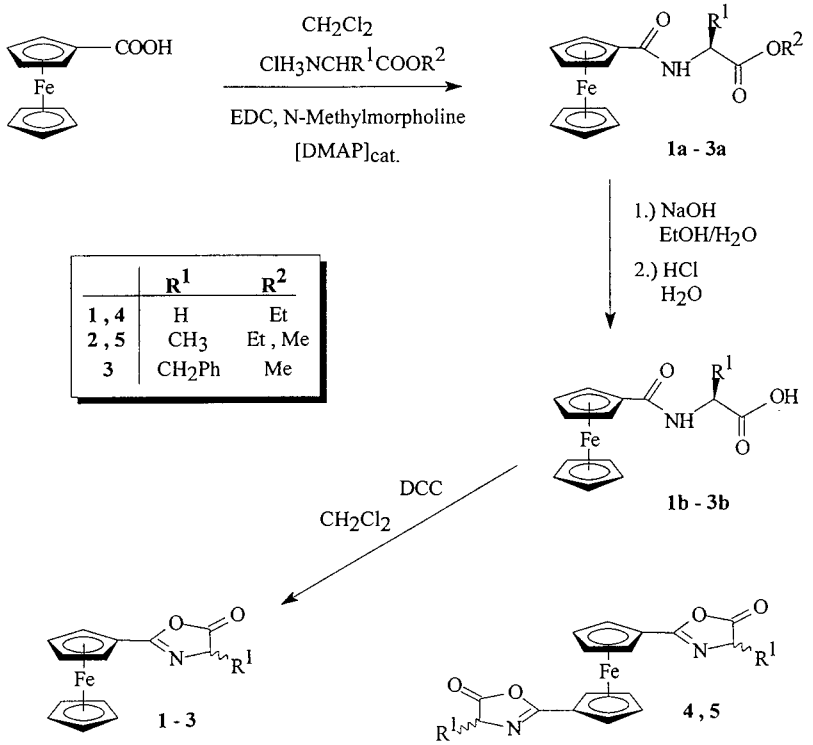


	R^1	R^2
1 , 4	H	Et
2 , 5	CH_3	Et , Me
3	CH_2Ph	Me

Scheme 1.

genic centers give rise to two diastereoisomers (3:2) which can be detected in the ^{1}H- and ^{13}C-NMR spectra.

3. Reactions of ferrocenyloxazolones with chlorobridged metal complexes

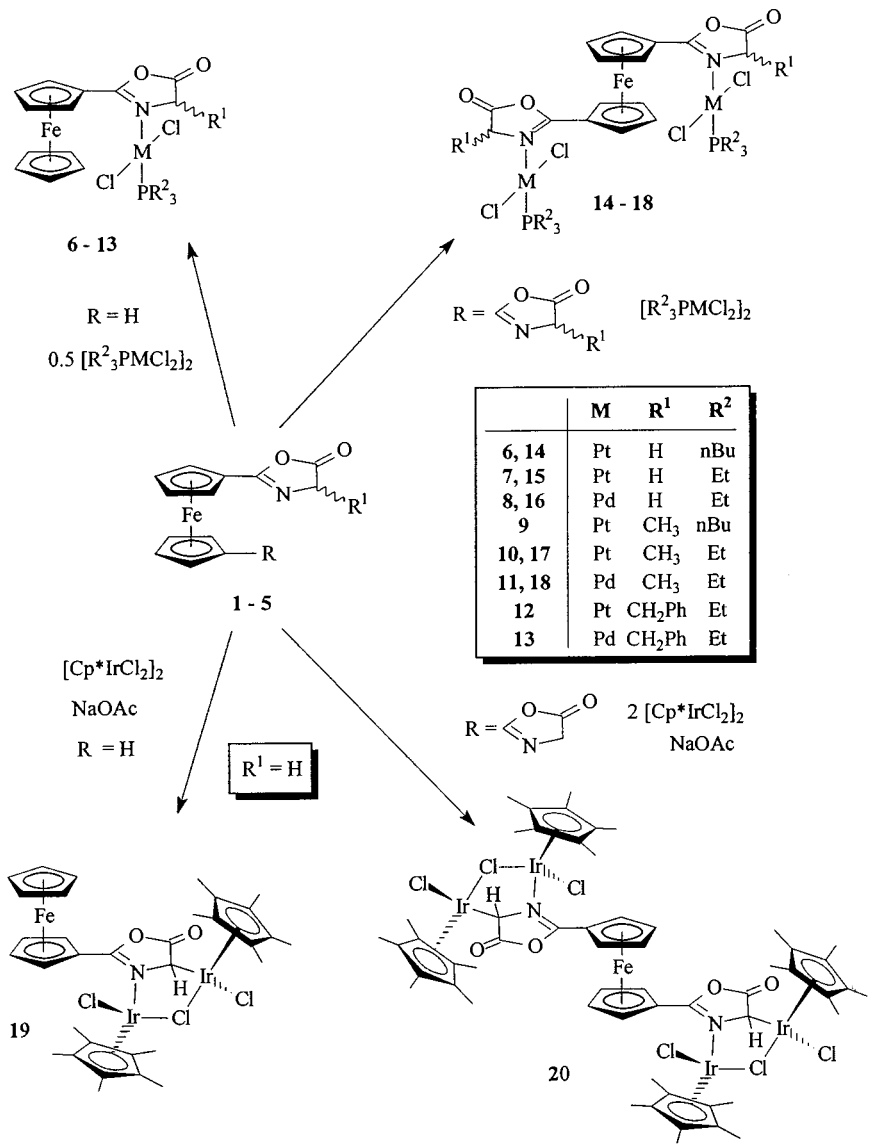
From **1**–**5** and chloro bridged palladium(II) and platinum(II) complexes $[R_3PMCl_2]_2$ the synthesis of a series of *N*-coordinated oxazolone complexes **6**–**18** was achieved (Scheme 2).

As was observed for complexes of 2-phenyl-5(4H)-oxazolones the νC=O (νC=N) IR-absorptions are shifted to higher (lower) wave numbers upon coordination. The ^{1}H-NMR resonances of the ortho C_5H_4 protons show a downfield shift [5b,c] due to the paramagnetic anisotropy of the neighbouring metal atoms [14] by about 0.9 ppm in average. As expected, two sets of ^{1}H- and ^{13}C-NMR signals could be observed for the compounds **17** and **18** which are formed as diastereoisomers (oxazolone C-4: RS and RR/SS). The structure of **6** was ascertained by X-ray structure analysis (see Fig. 1) which shows the close proximity of one ortho proton to the platinum atom. The Pt…H distance was calculated as 2.865 Å and is of the same magnitude as found for a dimetallic oxazolone platinum complex [5c]. Obviously, in palladium(II) and platinum(II) complexes with N and P donors the *trans*-*N*–metal–*P* configuration is preferred as it was observed for other complexes with P and N donors [1,5b,c,15].

Remarkably, the reaction of **1** and **4** with the chloro bridged halfsandwich iridium complex $[Cp^*IrCl_2]_2$ leads to α-metallation of the oxazolone ring to give the C, N and chloro bridged trinuclear and pentanuclear complexes **19** and **20**. Recently, we reported an analogous α-metallation with 2-phenyl–oxazolone [5a]. Complex **19** contains three stereogenic centers; however only one diastereoisomer (as enantiomeric pair $R_{Ir}S_CR_{Ir'}$ and $S_{Ir}R_CS_{Ir'}$) is formed from steric reasons. For compounds **2**, **3** and **5** which contain bulky substituents at the oxazolone ring no reaction with $[Cp^*IrCl_2]_2$ was observed.

The ^{1}H- and ^{13}C-NMR spectra of **20** exhibit two sets of signals which we attribute to the two diastereoisomers $R_{Ir1}S_{C1}R_{Ir1'}R_{Ir2}S_{C2}R_{Ir2'}$ | $S_{Ir1}R_{C1}S_{Ir1'}S_{Ir2}R_{C2}S_{Ir2'}$ and $R_{Ir1}S_{C1}R_{Ir1'}S_{Ir2}R_{C2}S_{Ir2'}$ (*meso* form). In the ^{1}H-NMR spectra of **19** and **20** the signals of the α-CH protons are shifted downfield by 1.7 ppm upon metallation.

The crystal of **19** contained both enantiomers $R_{Ir}S_CR_{Ir'}$ and $S_{Ir}R_CS_{Ir'}$ (Fig. 2). The molecular structure is very similar to that of the diiridium complex with 2-phenyloxazolone [5a].



	M	R^1	R^2
6, 14	Pt	H	nBu
7, 15	Pt	H	Et
8, 16	Pd	H	Et
9	Pt	CH_3	nBu
10, 17	Pt	CH_3	Et
11, 18	Pd	CH_3	Et
12	Pt	CH_2Ph	Et
13	Pd	CH_2Ph	Et

Scheme 2.

4. Formation of dipeptides from ferrocenyloxazolones

The covalently bound ferrocene moiety can act as electron transfer relay between enzymes and metal electrodes [16]. Different methods for the introduction of the ferrocene unit into bio molecules were recently examined [17]. The ferrocenyloxazolones **1**, **2** and **4** provide another route to ferrocenoyl marked dipeptides and the compounds **21**–**26** were obtained by nucleophilic ring opening with α-amino acids[2] (Scheme 3, [3,18]).

Complex **23** is formed as mixture of two diastereoisomers $R_{\alpha\text{-}C}S_{\alpha\text{-}C}$ and $S_{\alpha\text{-}C}S_{\alpha\text{-}C}$ (1:1) which are detected in the ^{1}H-NMR spectrum. In ferrocenyl bisdipeptide derivatives the two dipeptide chains can align parallel by hydrogen bonds [19]. The ^{1}H-NMR signals of the two ferrocenoyl amide groups in **24**–**26** appear at δ 8.5 while for **21**–**23** these resonances are found at δ 6.4, indicating hydrogen bonds (Fig. 3) between the two peptide chains in **24**–**26** as was established by X-ray structure determination for $Fc(COalaproOEt)_2$ [19a].

In addition the ν(N–H) IR absorptions in CH_2Cl_2 of **25** and **26** appear at 3410 cm^{-1} for the free N–H group and at 3315 cm^{-1} for the N–H group involved in H bridging [19,20] while **22** exhibits only one absorption at 3420 cm^{-1}.

[2] Compound **3** did not react with α-amino acid ester; **5** afforded a mixture which was not separated.

5. Electrochemistry

For some compounds, cyclic voltammograms were recorded and the electrochemical data are collected in Table 1. We assume chemically reversible one-electron transfer to occur, although the peak-to-peak separations sometimes showed distinct deviations from the ideal value of 0.059 V. Since under the same conditions for the ferrocene–ferrocinium couple a separation of 0.206 V was observed (entry 9), we suppose that this is due to the effects of uncompensated solution resistance [21a]. In CH_2Cl_2 solutions such deviations were observed earlier [21b]. Each oxazolone substituent increases the formal electrode potential by about 0.3 V (entries 1–3), while their coordination to platinum or palladium had almost no influence (entries 4,5). Two observations are difficult to explain: For compound **4** after three cycles an irreversible peak at 0.7 V occurred and compound **6** showed after two cycles a new reversible couple at 0.430 V (separation 0.042 V) and simultaneously an irreversible peak at 1.74 V. The bridging oxazolone in **19** leads to an only 0.2 V higher potential perhaps due to the greater deviation from coplanarity of the oxazolone and cyclopentadienyl rings disturbing their conjugation (entry 6). For the dipeptide derivatives **23** and **25** potentials in the same range were observed as were found for Fc(COalaproOEt) and Fc-(COalaproOEt)$_2$ [19a]. Each electron-withdrawing amide function raised the value of the reversible oxidation/reduction wave by about 0.2 V (entries 7,8).

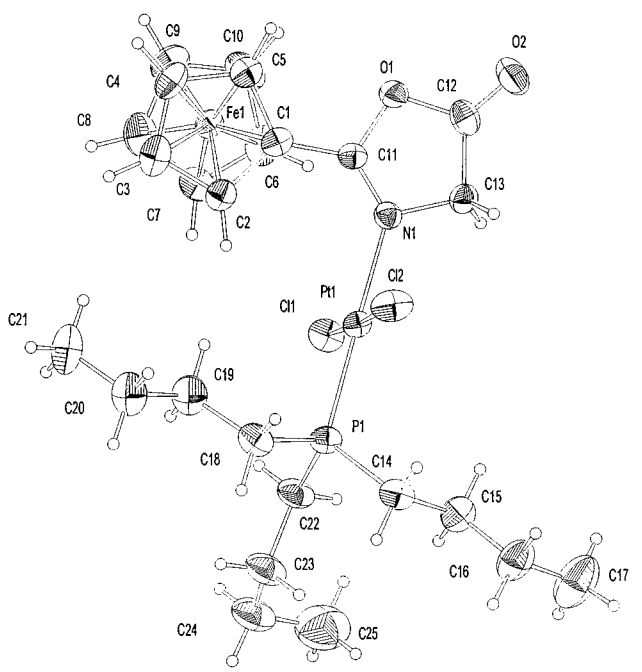


Fig. 1. Molecular structure of **6** in the crystal. Selected bond lengths (Å) and angles (°): Pt(1)–N(1) 2.102(4), Pt(1)–P(1) 2.232(2), Fe(1)–C(1) 2.021(5), N(1)–C(11) 1.275(6), C(1)–C(11) 1.442(7), N(1)–Pt(1)–P(1) 177.08(11), N(1)–Pt(1)–Cl(2) 87.88(11), P(1)–Pt(1)–Cl(1) 94.61(5), N(1)–C(11)–C(1) 130.6(5), O(1)–C(11)–C(1) 114.6(4), C(5)–C(1)–C(11)–N(1) 170.09(0.49), C(2)–C(1)–C(11)–N(1) –14.51(0.81).

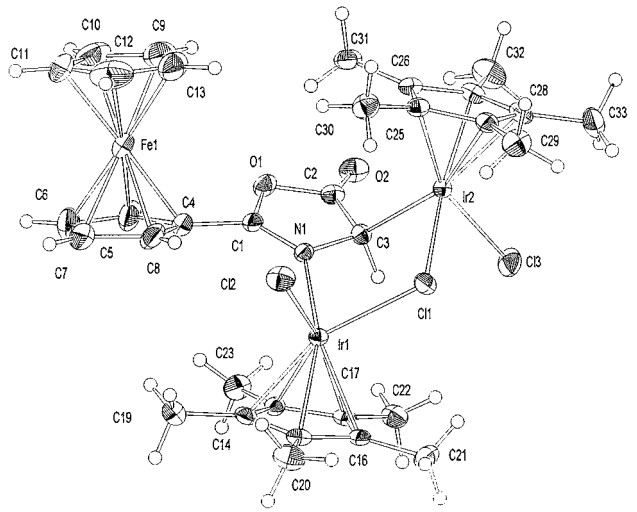
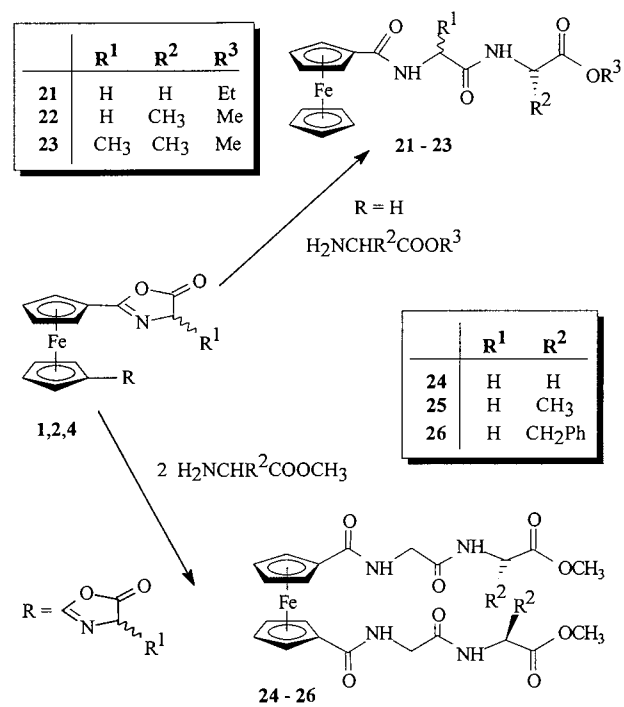


Fig. 2. Molecular structure of **19** ($S_{Ir}R_CS_{Ir}$) in the crystal. Selected bond lengths (Å) and angles (°): Ir(1)–N(1) 2.108(4), Ir(1)–Cl(1) 2.4320(14), Ir(2)–C(3) 2.131(5), Ir(2)–Cl(1) 2.4289(14), N(1)–C(1) 1.283(7), N(1)–C(3) 1.470(6), C(1)–C(4) 1.459(8), N(1)–Ir(1)–Cl(1) 83.84(12), Cl(2)–Ir(1)–Cl(1) 85.95(6), C(3)–Ir(2)–Cl(1) 82.32(14), Cl(3)–Ir(2)–Cl(1) 87.91(6), Ir(2)–Cl(1)–Ir(1) 110.19(5), C(1)–N(1)–C(3) 107.8(4), C(1)–N(1)–Ir(1) 134.5(4), N(1)–C(1)–C(4) 131.9(5), C(2)–C(3)–Ir(2) 115.8(4), N(1)–C(3)–Ir(2) 115.6(3), N(1)–Ir(1)–C(l1)–Ir(2) –8.44(0.12), C(3)–N(1)–C(1)–O(1) 2.07(0.59), N(1)–C(1)–C(4)–C(8) 29.93(1.04), Ir(1)–N(1)–C(3)–Ir(2) –72.29(0.38).



Scheme 3.

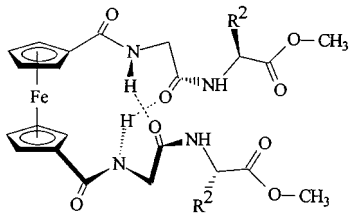


Fig. 3. Intramolecular hydrogen bonds in **24**–**26**. For an X-ray structure analysis of a similar compound see Ref. [19a].

6. Experimental

Most reactions were carried out in dry solvents under nitrogen atmosphere using Schlenk-type glassware. Melting points: Elektrothermal Digital Melting Point Apparatus IA 8103. Melting points are not corrected. IR: Nicolet 520 FT-IR or Perkin–Elmer 841. PE = Polyethylene. NMR: Jeol GSX 270 or Jeol EX 400, using the solvent as internal standard. Cyclic voltammograms: EG&G Potentiostat/Galvanostat Model 263 A. The starting materials were prepared according to literature procedures ($[n\mathrm{Bu_3PPtCl_2}]_2$ [22], $[\mathrm{Et_3PPtCl_2}]_2$ [22], $[\mathrm{Et_3PPdCl_2}]_2$ [23] $[\mathrm{Cp^*IrCl_2}]_2$ [24]). The α-amino acid ester hydrochlorides were purchased from Merck or Fluka, the ferrocenecarboxylic acids from Aldrich.

6.1. Ferrocenoyl amino acid esters *1a*–*5a*

Two different methods could be employed for the preparation:

6.1.1. Method *A* (according to [11a])

A solution of the appropriate ferrocenecarboxylic acid (2 mmol) in 10 ml of CH_2Cl_2 was treated with solid dicyclohexylcarbodiimide (2.2 mmol per carboxylic acid group) and HOBt (equimolar to DCC). The α-amino acid ester hydrochloric acid salt (2.3 mmol per carboxylic acid group) was treated with an equimolar amount of triethylamine in 10 ml of CH_2Cl_2 and the mixture was added to the stirring slurry. Dicyclohexylurea precipitated almost immediately. Stirring was continued at r.t. for 14–20 h and then the urea was filtered off. The filtrate was washed with water (3 × 100 ml) and subsequently dried over $MgSO_4$. After removing the solvent in vacuo the crude product was recrystallized from EtOAc to give the ferrocenoyl amino acid esters in 58–72% yield.

Table 1
Electrochemical data[a]

Entry	Compound	EP_c	E_{Pa}	ΔE_p	E_0
1	**2**	0.546	0.738	0.192	0.642
2	**3**	0.568	0.678	0.110	0.623
3	**4**	0.833	0.940	0.057	0.912[b]
4	**6**	0.598	0.698	0.100	0.648[c]
5	**11**	0.546	0.662	0.116	0.604
6	**19**	0.423	0.630	0.207	0.527
7	**23**	0.470	0.650	0.180	0.560
8	**25**	0.660	0.774	0.114	0.717
9	Ferrocene	0.230	0.436	0.206	0.333

[a] Potentials are given in V versus Ag | AgCl; in CH_2Cl_2; 0.1 M $[n\mathrm{Bu_4N}][PF_6]$; 20°C; Au electrode; Sweep rate 0.100 V s^{-1}.

[b] After three cycles an irreversible peak at 0.7 V occurred.

[c] After two cycles a new reversible couple appeared at 0.430 V with a peak separation of 0.042 V. Simultaneously an irreversible peak at 1.74 V was observed.

6.1.2. Method *B* (according to [12])

To a mixture of the appropriate ferrocenecarboxylic acid (2 mmol), 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide (EDC) (2 mmol per carboxylic acid group), the α-amino acid ester hydrochloric acid salt (2.3 mmol per carboxylic acid group) and a catalytic amount of dimethylaminopyridin (DMAP) (15 mg) in 25 ml of CH_2Cl_2 4-methyl–morpholine (2.8 mmol per carboxylic acid group) in 10 ml of CH_2Cl_2 was added dropwise under N_2 at r.t. The mixture was stirred for 1–3 days. To the clear, red solution, 10 ml of saturated aqueous ammonium chloride solution were added. The organic layer was washed two times with 10 ml of water, dried over $MgSO_4$ and evaporated in vacuo to give the ferrocenoyl amino acid esters reasonably pure in 73–78% yield.

6.2. Ferrocenoyl amino acids *1b*–*5b*

The ferrocenoyl amino acid esters were dissolved in ethanol (or in a mixture of ethanol and THF) and a slight excess of 0.1 n NaOH was added slowly at 0°C [7a]. The deep red solution was stirred for about 2–4 h and then the organic solvents were distilled off. The aqueous solution was cooled to 0°C and an equimolar amount of 0.1 n HCl (to the amount of NaOH) was added dropwise to precipitate the ferrocenoyl amino acids which were collected, washed with water and dried in vacuo at 50°C for several hours.

6.3. 2-Ferrocenyl-5(4H)-oxazolones *1*–*5*

The ferrocenoyl amino acids were suspended in CH_2Cl_2 (about 5 ml per 1 mmol amino acid group). At 0°C a solution of an equimolar amount DCC (to the amino acid groups) in CH_2Cl_2 (about 2 ml per 1 mmol amino acid group) was added dropwise. After 6–14 h stirring at r.t. the precipitated urea was filtered off and washed twice with an small amount of CH_2Cl_2. The combined solutions were concentrated in vacuo and added to an excess of pentane whereby the products precipitated. The products were centrifuged off, washed twice with pentane and dried in vacuo at 50°C (except for **1** which is slightly unstable) for about 8 h to afford the corresponding 2-ferrocenyl-5(4H)-oxazolones **1**–**5**.

1: 1.00 g (4.35 mmol) of ferrocenecarboxylic acid and 0.70 g (5.02 mmol) of glycine ethyl ester hydrochloride were used according to method **A**. Brown powder, yield: 374 mg (32%). IR (KBr): $\tilde{\nu} = 1831$ cm^{-1} vs (C=O), 1652 vs (C=N), 1629 s (C=C), 506 m, 496 m, 484 m (Fe–C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 4.21 (s, 2H, NC$\underline{H}_2$CO), 4.22 (s, 5H, Cp), 4.47 (ψt, $^3J = {}^4J = 2.0$ Hz, 2H, Cp-3,3′), 4.82 (ψt, $^3J = {}^4J = 2.0$ Hz, 2H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 54.91 (N$\underline{C}$H$_2$CO), 68.03 (Cp-1), 68.80/71.52 (Cp-2,3), 70.06 (Cp), 166.83 (OC=N), 176.37 (C=O). $C_{13}H_{11}NFeO_2$ (269.1): Anal.Calc. C 58.03, H 4.12, N 5.21; Found C 57.70, H 4.51, N 5.35.

2: 1.00 g (4.35 mmol) of ferrocenecarboxylic acid and 0.764 g (4.97 mmol) of alanine ethyl ester hydrochloride were used according to method **B**. Orange powder, yield: 583 mg (47%). m.p.: 194–196°C (black). IR (KBr): $\tilde{\nu} = 1817$ cm^{-1} vs (C=O), 1656 vs (C=N), 1628 m (C=C), 503 s, 487 m (Fe–C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.51 (d, $^3J = 7.4$ Hz, 3H, C$\underline{H}_3$), 4.19 (s, 5H, Cp), 4.23 (q, $^3J = 7.4$ Hz, 1H, NC$\underline{H}$(R)CO), 4.45 (m, 2H, Cp-3,3′), 4.81 (m, 2H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 17.24 (C$\underline{H}_3$), 66.79 (N$\underline{C}$H(R)CO), 67.91 (Cp-1), 68.85/68.82 (Cp-2,2′), 70.09 (Cp), 71.53 (Cp-3,3′), 164.86 (O$\underline{C}$=N), 179.31 ($\underline{C}$=O). $C_{14}H_{13}NFeO_2$ (283.1): Anal.Calc. C 59.40, H 4.63, N 4.95; Found C 59.61, H 4.94, N 5.35.

3: 1.00 g (4.35 mmol) of ferrocenecarboxylic acid and 1.072 g (4.97 mmol) of phenylalanine methyl ester hydrochloride were used according to method **A**. Orange powder, yield: 575 mg (37%). m.p.: 103–105°C (red). IR (KBr): $\tilde{\nu} = 1811$ cm^{-1} vs (C=O), 1658 vs (C=N), 1628 w (C=C), 504 s, 487 s (Fe-C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.26 (dd, $^3J = 4.7$ Hz, $^2J = 14.1$ Hz, 1H, C$\underline{H}$H′Ph), 3.35 (dd, $^3J = 4.7$ Hz, $^2J = 14.1$ Hz, 1H, CH$\underline{H}$′Ph), 3.93 (s, 5H, Cp), 4.39/4.41 (each m, each 1H, Cp-3,3′), 4.52 (t br, $^3J = 4.7$ Hz, 1H, NC$\underline{H}$(R)CO), 4.68/4.76 (each s br, each 1H, Cp-2,2′), 7.28 (m, 5H, Ph). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 36.78 (C$\underline{H}_2$Ph), 66.31 (N$\underline{C}$H(R)CO), 68.06/69.23 (Cp-2,2′), 69.95 (Cp), 71.16/71.43 (Cp-3,3′), 127.50 (Ph-4), 128.53/129.98 (Ph-2,2′,3,3′), 135.58 (Ph-1), 164.96 (O$\underline{C}$=N), 177.99 ($\underline{C}$=O). $C_{20}H_{17}NFeO_2$ (359.2): Anal.Calc. C 66.88, H 4.77, N 3.90; Found C 66.14, H 4.86, N 4.20.

4: 1.00 g (3.65 mmol) of ferrocenedicarboxylic acid and 1.061 g (7.60 mmol) of glycine ethyl ester hydrochloride were used according to method **A**. Brown powder, yield: 419 mg (33%). m.p.: 135–138°C (red). IR (KBr): $\tilde{\nu} = 1820$ cm^{-1} vs (C=O), 1666 vs, 1658 sh (C=N), 1627 s (C=C), 511 m, 496 m, 483 m (Fe–C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 4.23 (s, 4H, NC$\underline{H}_2$CO), 4.52 (ψt, $^3J = {}^4J = 2.0$ Hz, 4H, Cp-3,3′), 4.87 (ψt, $^3J = {}^4J = 2.0$ Hz, 4H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 54.82 (N$\underline{C}$H$_2$CO), 70.10 (Cp-1), 70.84/72.93 (Cp-2,2′,3,3′), 164.95 (O$\underline{C}$=N), 175.93 ($\underline{C}$=O). $C_{16}H_{12}N_2FeO_4$ (352.1): Anal.Calc. C 54.58, H 3.44, N 7.96; Found C 55.50, H 3.81, N 8.26.

5: 1.00 g (3.65 mmol) of ferrocenedicarboxylic acid and 1.291 g (8.40 mmol) of alanine methyl ester hydrochloride were used according to method **B**. Orange powder, yield: 517 mg (37%). Diastereoisomeric ratio 3:2 (pair of enantiomers (*S*,*S*) (*R*,*R*) and *meso* product (*R*,*S*)). m.p.: 107–108°C (red). IR (KBr): $\tilde{\nu} = 1820$ cm^{-1} vs (C=O), 1661 vs (C=N), 1628 m (C=C), 515 m, 505 m, 494 m (Fe–C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ *1.55*/1.56 (each d, $^3J = 7.2$ Hz, 3H, C$\underline{H}_3$), 4.28/4.30 (each q, $^3J = 7.5$ Hz, 1H, NC$\underline{H}$(R)CO), 4.54 (m, 4H, Cp-3,3′), 4.84/4.89 (each m, each 2H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ *16.85*/16.94 (C$\underline{H}_3$), 60.70/*60.74* (N$\underline{C}$H(R)CO), 69.90 (Cp-1), 70.65 (intensity of two signals)/*70.86*/70.92 (Cp-2,2′), 72.56/*72.80*/*72.96*/73.16 (Cp-3,3′), 163.03/*163.10* (O$\underline{C}$=N), *178.71*/178.77 ($\underline{C}$=O). $C_{18}H_{16}N_2FeO_4$ (380.2): Anal.Calc. C 56.87, H 4.24, N 7.37; Found C 57.29, H 4.63, N 7.52.

*6.4. General procedure for the preparation of **6–18***

A solution of the appropriate chlorobridged trialkylphosphine complex in CH_2Cl_2 was treated with a slight excess of the corresponding 2-ferrocenyl-5(4H)-oxazolone **1**–**5**. After 3–4 h stirring at r.t., the solution was concentrated in vacuo and an excess of diethylether was added. The precipitate was centrifuged off and the solution was evaporated. The residue was taken up in CH_2Cl_2 and added dropwise to an excess of pentane. The product precipitated either immediately (**a**) or on concentrating the mixture (after adding hexane) in vacuo (**b**). The precipitate was centrifuged off, washed twice with pentane and dried in vacuo at 50°C for several hours.

6: 36 mg (0.134 mmol) of **1** and 62 mg (0.066 mmol) of [*n*Bu$_3$PPtCl$_2$]$_2$ were used. According to **B,** orange powder, yield: 85 mg (87%). For X-ray structure analysis suitable crystals were grown in a CH_2Cl_2/hexane mixture. m.p.: 122°C (red). IR (KBr): $\tilde{\nu} = 1861$ cm^{-1} s, 1841 vs (C=O), 1654 sh, 1640 vs (C=N), 506 s, 497 s, 486 s (Fe–C), (in PE): 345 w (Pt–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 0.98 (t, 9H, $^3J = 7.2$ Hz, *n*Bu–C$\underline{H}_3$), 1.50/1.67/1.89 (each m, each 6H, 3 × *n*Bu–C$\underline{H}_2$), 4.35 (s, 5H, Cp), 4.49 (s, 2H, NC$\underline{H}_2$CO), 4.63 (m, 2H, Cp-3,3′), 5.71 (m, 2H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 13.89 (*n*Bu–$\underline{C}$H$_3$), 21.44 (d, $^1J_{CP} = 39.4$ Hz, *n*Bu–$\underline{C}$H$_2$), 24.17 (d, $^2J_{CP} = 14.1$ Hz, *n*Bu–$\underline{C}$H$_2$), 25.94 (d, $^3J_{CP} = 2.9$ Hz, *n*Bu–$\underline{C}$H$_2$), 53.92 (N$\underline{C}$H$_2$CO), 63.69 (Cp-1), 70.86 (Cp), 71.32/73.07 (Cp-2,2′,3,3′), 170.64 (O$\underline{C}$=N), 170.82 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ −6.10 (s, $^1J_{PPt} = 3499$ Hz). $C_{25}H_{38}NCl_2FeO_2PPt$ (737.4): Anal.Calc. C 40.72, H 5.19, N 1.90; Found C 40.30, H 4.94, N 1.78.

7: 43 mg (0.160 mmol) of **1** and 57 mg (0.074 mmol) of [Et$_3$PPtCl$_2$]$_2$ were used. According to **B,** orange powder, yield: 73 mg (76%). m.p.: 139°C (black). IR

(KBr): $\tilde{\nu}$ = 1863 cm^{-1} s, 1839 vs (C=O), 1639 vs (C=N), 504 w, 497 w, 483 w (Fe–C), (in PE): 345 w (Pt–Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.26 (dt, 9H, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 17.2 Hz, PEt–C$\underline{H}_3$), 1.95 (dq, 6H, $^3J_{HH}$ = 7.7 Hz, $^2J_{HP}$ = 11.1 Hz, PEt–C$\underline{H}_2$), 4.36 (s, 5H, Cp), 4.50 (s, 2H, NC$\underline{H}_2$CO), 4.65 (m, 2H, Cp-3,3′), 5.70 (m, 2H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 7.78 (d, $^2J_{CP}$ = 2.9 Hz, $^3J_{CPt}$ = 17.8 Hz, PEt–$\underline{C}H_3$), 14.12 (d, $^1J_{CP}$ = 40.2 Hz, $^2J_{CPt}$ = 33.8 Hz, PEt–$\underline{C}H_2$), 53.85 (N$\underline{C}H_2$CO), 63.67 (Cp-1), 70.88 (Cp), 71.29/73.16 (Cp-2,2′,3,3′), 170.56 (O$\underline{C}$=N), 170.94 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 1.49 (s, $^1J_{PPt}$/3515 Hz). $C_{19}H_{26}NCl_2FeO_2PPt$ (653.2): Anal.Calc. C 34.94, H 4.01, N 2.14; Found C 35.15, H 3.75, N 2.19.

8: 53 mg (0.197 mmol) of **1** and 53 mg (0.090 mmol) of $[Et_3PPdCl_2]_2$ were used. According to **A,** orange powder, yield: 77 mg (76%). m.p.: 137°C (dark red). IR (KBr): $\tilde{\nu}$ = 1855 cm^{-1} s, 1834 vs (C=O), 1643 vs (C=N), 504 w, 497 w, 484 w (Fe–C), (in PE): 356 w (Pd-Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.32 (dt, 9H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 17.8 Hz, PEt–C$\underline{H}_3$), 2.00 (dq, 6H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HP}$ = 11.3 Hz, PEt–C$\underline{H}_2$), 4.35 (s, 5H, Cp), 4.46 (s, 2H, NC$\underline{H}_2$CO), 4.63 (m, 2H, Cp-3,3′), 5.60 (m, 2H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 8.18 (d, $^2J_{CP}$ = 2.8 Hz, PEt–$\underline{C}H_3$), 16.11 (d, $^1J_{CP}$ = 33.3 Hz, PEt–$\underline{C}H_2$), 53.74 (N$\underline{C}H_2$CO), 64.55 (Cp-1), 70.78 (Cp), 70.91/72.85 (Cp-2,2′,3,3′), 170.43 (O$\underline{C}$=N), 171.57 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 37.35 (s). $C_{19}H_{26}NCl_2FeO_2PPd$ (564.6): Anal. Calc. C 40.42, H 4.64, N 2.48; Found C 39.93, H 4.59, N 2.38.

9: 17 mg (0.060 mmol) of **2** and 27 mg (0.029 mmol) of $[n\text{Bu}_3PPtCl_2]_2$ were used. According to **B,** orange powder, yield: 28 mg (64%). IR (KBr): $\tilde{\nu}$ = 1860 cm^{-1} sh, 1835 vs (C=O), 1632 vs (C=N), 509 m, 504 m, 486 m (Fe–C), (in PE): 340 w (Pt–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 0.98 (t, 9H, ^3J = 7.0 Hz, nBu–C$\underline{H}_3$), 1.45/1.64/1.90 (each m, each 6H, 3 × nBu–C$\underline{H}_2$), 1.83 (d, 3H, ^3J = 7.3 Hz, CHC$\underline{H}_3$), 4.33 (s, 5H, Cp), 4.63 (m, 3H, Cp-3,3′ and NC$\underline{H}$(R)CO), 5.38/6.07 (each m, each 1H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 13.92 (nBu–$\underline{C}H_3$), 17.16 (CH$\underline{C}H_3$), 21.35 (d, $^1J_{CP}$ = 39.2 Hz, nBu–$\underline{C}H_2$), 24.18 (d, $^2J_{CP}$ = 14.4 Hz, nBu–$\underline{C}H_2$), 26.02 (d, $^3J_{CP}$ = 2.9 Hz, nBu–$\underline{C}H_2$), 60.66 (N$\underline{C}$H(R)CO), 63.80 (Cp-1), 70.88 (Cp), 71.36/71.53 (Cp-2,2′), 72.91/73.20 (Cp-3,3′), 169.19 (O$\underline{C}$=N), 174.34 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ −6.08 (s, $^1J_{PPt}$ = 3501 Hz). $C_{26}H_{40}NCl_2FeO_2PPt$ (751.4): Anal.Calc. C 41.56, H 5.37, N 1.86; Found C 41.40, H 5.52, N 1.75.

10: 46 mg (0.163 mmol) of **2** and 57 mg (0.074 mmol) of $[Et_3PPtCl_2]_2$ were used. According to **A,** orange powder, yield: 89 mg (90%). m.p.: 117–119°C (red). IR (KBr): $\tilde{\nu}$ = 1834 vs (C=O), 1638 vs (C=N), 505 m, 490 w (Fe–C), (in PE): 341 w (Pt–Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.27 (dt, 9H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 17.2 Hz, PEt–C$\underline{H}_3$), 1.85 (d, 3H, ^3J = 7.7 Hz, CHC$\underline{H}_3$), 1.94 (dquint, 3H, $^3J_{HH}$ = $^2J_{HP}$ = 7.6 Hz, $^2J_{HH'}$ = 3.1 Hz, PEt–C$\underline{H}$H′), 1.96 (dquint, 3H, $^3J_{HH}$ = $^2J_{HP}$ = 7.6 Hz, $^2J_{HH'}$ = 3.1 Hz, PEt–CH$\underline{H}$′), 4.35 (s, 5H, Cp), 4.66 (q, 1H, ^3J = 7.5 Hz, NC$\underline{H}$CH$_3$), 4.63/4.66 (each m, each 1H, Cp-3,3′), 5.41/6.03 (each m, each 1H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 7.81 (d, $^2J_{CP}$ = 3.2 Hz, PEt–$\underline{C}H_3$), 14.04 (d, $^1J_{CP}$ = 39.5 Hz, PEt–$\underline{C}H_2$), 17.24 (CH$\underline{C}$H$_3$), 60.66 (N$\underline{C}$H(R)CO), 63.77 (Cp-1), 70.90 (Cp), 71.29/71.53 (Cp-2,2′), 73.02/73.26 (Cp-3,3′). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 1.63 (s, $^1J_{PPt}$ = 3512 Hz). $C_{20}H_{28}NCl_2FeO_2PPt$ (667.3): Anal.Calc. C 36.00, H 4.23, N 2.10; Found C 36.90, H 4.30, N 2.36.

11: 46 mg (0.163 mmol) of **2** and 44 mg (0.074 mmol) of $[Et_3PPdCl_2]_2$ were used. According to **A**, orange powder, yield: 63 mg (78%). m.p.: 128–131°C (red). IR (KBr): $\tilde{\nu}$ = 1830 vs (C=O), 1642 vs (C=N), 505 s, 489 m (Fe–C), (in PE): 354 w (Pd–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.31 (dt, 9H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HP}$ = 17.7 Hz, PEt–C$\underline{H}_3$), 1.99 (dq, 6H, $^3J_{HH}$ = 7.4 Hz, $^2J_{HP}$ = 11.7 Hz, PEt–C$\underline{H}_2$), 1.84 (d, 3H, ^3J = 7.2 Hz, CHC$\underline{H}_3$), 4.33 (s, 5H, Cp), 4.61 (m, 3H, NC$\underline{H}$CH$_3$ and Cp-3,3′), 5.38/5.81 (each m, each 1H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 8.21 (d, $^2J_{CP}$ = 3.2 Hz, PEt–$\underline{C}H_3$), 15.99 (d, $^1J_{CP}$ = 34.2 Hz, PEt–$\underline{C}H_2$), 17.46 (CH$\underline{C}$H$_3$), 60.32 (N$\underline{C}$H(R)CO), 64.54 (Cp-1), 70.82 (Cp), 70.95/71.08 (Cp-2,2′), 72.81/72.90 (Cp-3,3′), 168.48 (O$\underline{C}$=N), 174.95 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 36.79. $C_{20}H_{28}NCl_2FeO_2PPd$ (546.6): Anal. Calc. C 41.52, H 4.88, N 2.42; Found C 41.99, H 4.94, N 2.58.

12: 47 mg (0.131 mmol) of **3** and 49 mg (0.064 mmol) of $[Et_3PPtCl_2]_2$ were used. According to **B**, orange powder, yield: 72 mg (76%). m.p.: 130°C (red). IR (KBr): $\tilde{\nu}$ = 1856 cm^{-1} m, 1834 vs (C=O), 1628 vs (C=N), 504 w, 491 w, 482 w (Fe–C), (in PE): 341 w (Pt–Cl). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 1.25 (dt, 9H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 17.3 Hz, PEt–C$\underline{H}_3$), 1.94 (dq, 6H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HP}$ = 11.1 Hz, PEt–C$\underline{H}_2$), 3.52 (dd, 1H, ^3J = 6.1 Hz, ^2J = 14.5 Hz, C$\underline{H}$H′Ph), 3.74 (dd, 1H, ^3J = 4.9 Hz, ^2J = 14.5 Hz, CH$\underline{H}$′Ph), 4.27 (s, 5H, Cp), 4.66 (m, 2H, Cp-3,3′), 5.04 (ψt, 1H, $^3J \approx$ 5.9 Hz, C$\underline{H}$CH$_2$Ph), 5.47/5.94 (each m, each 1H, Cp-2,2′), 7.25 (ABB′CC′, 1H, Ph-4), 7.32 (BB′ 2H, Ph-3,3′), 7.52 (CC′, 2H, Ph-2,2′). ^{13}C-NMR (100.5 MHz, CD_2Cl_2): δ 7.62 (d, $^2J_{CP}$ = 3.1 Hz, PEt–$\underline{C}H_3$), 14.06 (d, $^1J_{CP}$ = 41.3 Hz, PEt–$\underline{C}H_2$), 36.33 ($\underline{C}H_2$Ph), 63.77 (Cp-1), 65.97 (N$\underline{C}$H(R)CO), 70.86 (Cp), 71.47/71.51 (Cp-2,2′), 73.21/73.29 (Cp-3,3′), 127.36 (Ph-4), 128.45/130.21 (Ph-2,2′,3,3′), 135.09 (Ph-1), 169.99 (O$\underline{C}$=N), 172.60 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 1.88 (s, $^1J_{PPt}$ = 3520 Hz). $C_{26}H_{32}NCl_2FeO_2PPt$ (743.4): Anal.Calc. C 42.01, H 4.34, N 1.88; Found C 42.01, H 4.41, N 2.04.

13: 48 mg (0.134 mmol) of **3** and 38 mg (0.064 mmol) of $[Et_3PPdCl_2]_2$ were used. According to **B**, orange powder, yield: 68 mg (81%). m.p.: 121–122°C (red). IR (KBr): $\tilde{\nu}$ = 1850 cm^{-1} s, 1831 vs (C=O), 1632 vs (C=N), 503 m, 490 m, 480 w (Fe–C), (in PE): 353 w (Pd–Cl). ^{1}H-NMR (400 MHz, CD_2Cl_2): δ 1.29 (dt, 9H, $^3J_{HH}$ =

7.6 Hz, $^3J_{HP}$ = 17.9 Hz, PEt–C$\underline{H}_3$), 1.98 (dq br, 6H, $^3J_{HH}$ = 7.3 Hz, $^2J_{HP}$ = 11 Hz, PEt–C$\underline{H}_2$), 3.57 (m br, 2H, C$\underline{H}_2$Ph), 4.22 (s, 5H, Cp), 4.63 (s br, 2H, Cp-3,3′), 5.02 (s br, 1H, C$\underline{H}$CH$_2$Ph), 5.51/5.67 (each s br, each 1H, Cp-2,2′), 7.23 (*A*BB′CC′, 1H, Ph-4), 7.31 (BB′, 2H, Ph-3,3′), 7.54 (CC′, 2H, Ph-2,2′). ^{13}C-NMR (100.5 MHz, CD_2Cl_2): δ 8.01 (d, $^2J_{CP}$ = 3.9 Hz, PEt–$\underline{C}$H$_3$), 16.16 (d, $^1J_{CP}$ = 33.7 Hz, PEt–$\underline{C}$H$_2$), 36.44 ($\underline{C}$H$_2$Ph), 64.64 (Cp-1), 65.84 (N$\underline{C}$H(R)CO), 70.71 (Cp), 70.71/70.93 (Cp-2,2′), 72.84/72.94 (Cp-3,3′), 127.36 (Ph-4), 128.43/130.36 (Ph-2,2′,3,3′), 135.08 (Ph-1), 169.38 (O$\underline{C}$=N), 173.33 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 37.77 (s). $C_{26}H_{32}NCl_2FeO_2PPd$ (654.7): Anal. Calc. C 47.70, H 4.93, N 2.14; Found C 47.14, H 4.87, N 2.33.

14: 30 mg (0.085 mmol) of **4** and 77 mg (0.082 mmol) of [*n*Bu$_3$PPtCl$_2$]$_2$ were used. According to **B**, 71 mg of **14** were obtained after washing with diethylether/CH_2Cl_2 (10:1) as an orange powder (yield: 65%). m.p.: 166°C (dark red). IR (KBr): $\tilde{\nu}$ = 1864 cm^{-1} s, 1837 vs (C=O), 1640 vs (C=N), 505 w, 495 m (Fe–C), (in PE): 347 w (Pt–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 0.97 (t, 18H, ^3J = 7.3 Hz, *n*Bu–C$\underline{H}_3$), 1.49/1.64/1.86 (each m, each 12H, 3 × *n*Bu–C$\underline{H}_2$), 4.54 (s, 4H, NC$\underline{H}_2$CO), 4.81 (ψt, *J* = 2.0 Hz, 4H, Cp-3,3′), 5.85 (ψt, *J* = 2.2 Hz, 4H, Cp-2,2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 13.72 (*n*Bu–$\underline{C}$H$_3$), 21.82 (d, $^1J_{CP}$ = 39.8 Hz, *n*Bu–$\underline{C}$H$_2$), 24.01 (d, $^2J_{CP}$ = 15.1 Hz, *n*Bu–$\underline{C}$H$_2$), 25.58 (s, *n*Bu–$\underline{C}$H$_2$), 54.14 (N$\underline{C}$H$_2$CO), 66.43 (Cp-1), 73.59/75.22 (Cp-2,2′,3,3′), 169.41 (O$\underline{C}$=N), 169.92 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ −5.81 (s, $^1J_{PPt}$ = 3518 Hz). $C_{40}H_{66}N_2Cl_4FeO_4P_2Pt_2$ (1288.7): Anal. Calc. C 37.28, H 5.16, N 2.17; Found C 36.74, H 5.15, N 2.02.

15: 49 mg (0.139 mmol) of **4** and 107 mg (0.139 mmol) of [Et$_3$PPtCl$_2$]$_2$ were used. According to **A**, 137 mg of **15** were obtained after washing with diethylether/CH_2Cl_2 (10:1) as an orange powder (yield: 82%). m.p.: 180°C (black). IR (KBr): $\tilde{\nu}$ = 1863 cm^{-1} s, 1841 vs (C=O), 1640 vs (C=N), 507 w, 497 w (Fe–C), (in PE): 345 w (Pt–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.24 (dt, 18H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 17.2 Hz, PEt–C$\underline{H}_3$), 1.92 (dq, 12H, $^3J_{HH}$ = 7.6 Hz, $^2J_{HP}$ = 11.0 Hz, PEt–C$\underline{H}_2$), 4.54 (s, 4H, NC$\underline{H}_2$CO), 4.82 (ψt, 4H, Cp-3,3′), 5.86 (ψt, 4H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 7.78 (d, $^2J_{CP}$ = 2.9 Hz, PEt–$\underline{C}$H$_3$), 14.10 (d, $^1J_{CP}$ = 40.7 Hz, PEt–$\underline{C}$H$_2$), 54.11 (N$\underline{C}$H$_2$CO), 66.38 (Cp-1), 73.47/75.40 (Cp-2,2′,3,3′), 167.30 (O$\underline{C}$=N), 169.98 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 1.88 (s, $^1J_{PPt}$ = 3527 Hz). $C_{28}H_{42}N_2Cl_4FeO_4P_2Pt_2 \cdot CH_2Cl_2$ (1205.3): Anal. Calc. C 28.90, H 3.68, N 2.32; Found C 29.02, H 3.62, N 2.28.

16: 35 mg (0.099 mmol) of **4** and 59 mg (0.099 mmol) of [Et$_3$PPdCl$_2$]$_2$ were used. According to **A**, 57 mg of **16** were obtained after recrystallisation from CH_2Cl_2/pentane as an orange powder (yield: 56%). m.p.: 205°C (black). IR (KBr): $\tilde{\nu}$ = 1856 cm^{-1} s, 1838 vs (C=O), 1643 vs (C=N), 514 w, 493 w (Fe–C), (in PE): 358 w (Pd–Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.29 (dt, 18H, $^3J_{HH}$ = 7.4 Hz, $^3J_{HP}$ = 18.0 Hz, PEt–C$\underline{H}_3$), 1.96 (s br, 12H, PEt–C$\underline{H}_2$), 4.51 (s, 4H, NC$\underline{H}_2$CO), 4.80 (s br, 4H, Cp-3,3′), 5.74 (s br, 4H, Cp-2,2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 8.15 (d, $^2J_{CP}$ = 3.5 Hz, PEt–$\underline{C}$H$_3$), 16.28 (d, $^1J_{CP}$ = 30.3 Hz, PEt–$\underline{C}$H$_2$), 54.02 (N$\underline{C}$H$_2$CO), 67.34 (Cp-1), 73.04/74.97 (Cp-2,2′,3,3′), 168.87 (O$\underline{C}$=N), 171.10 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 38.21 (s). $C_{28}H_{42}N_2Cl_4FeO_4P_2Pd_2 \cdot CH_2Cl_2$ (1028.0): Anal. Calc. C 33.88, H 4.31, N 2.72; Found C 33.97, H 4.49, N 2.62.

17: 23 mg (0.061 mmol) of **5** and 45 mg (0.059 mmol) of [Et$_3$PPtCl$_2$]$_2$ were used. On adding diethylether the product precipitated. The mixture was evaporated and the residue dissolved in CH_2Cl_2. According to **A**, 58 mg of **17** were obtained after washing with diethylether/CH_2Cl_2 (10:1) as a red powder (yield: 86%). Diastereomeric ratio 3:*2*. m.p.: 199–202°C (black). IR (KBr): $\tilde{\nu}$ = 1865 cm^{-1} m, 1835 s (C=O), 1639 vs (C=N), 511 w, 490 w (Fe–C), (in PE): 344 w (Pt–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.27 (m, 18H, PEt–C$\underline{H}_3$), 1.87 (d, 6H, ^3J = 7.2 Hz, CHC$\underline{H}_3$), 1.96 (m, 12H, PEt–C$\underline{H}_2$), 4.75 (q, 2H, ^3J = 7.4 Hz, NC$\underline{H}$CH$_3$), *4.82*/4.85 (each m, 4H, Cp-3,3′), *5.55*/5.69 (each m, 2H, Cp-2), 6.13/*6.32* (each m, 2H, Cp-2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 7.82 (d, $^2J_{CP}$ = 3.4 Hz, PEt–$\underline{C}$H$_3$), 14.06 (d, $^1J_{CP}$ = 39.9 Hz, PEt–$\underline{C}$H$_2$), *17.10*/17.13 (CH$\underline{C}$H$_3$), *60.84*/60.66 (N$\underline{C}$H(R)CO), *66.04*/66.15 (Cp-1), *73.30*, 73.37/*73.79*, 73.89 (Cp-2,2′), 75.64, *75.68*/75.73, *75.89* (Cp-3,3′), 167.99 (O$\underline{C}$=N), 173.50/*173.55* ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 2.08/*2.11* (each s, $^1J_{PPt}$ = 3521 Hz). $C_{30}H_{46}N_2Cl_4FeO_4P_2Pt_2$ (1148.5): Anal. Calc. C 31.38, H 4.04, N 2.44; Found C 31.41, H 4.10, N 2.38.

18: 36 mg (0.095 mmol) of **5** and 50 mg (0.095 mmol) of [Et$_3$PPdCl$_2$]$_2$ were used. As for **17** according to **A**, 79 mg of **18** were obtained after washing with diethylether/CH_2Cl_2 (10:1) as an orange powder (yield: 92%). Diastereomeric ratio 3:*2*. m.p.: 188–192°C (black). IR (KBr): $\tilde{\nu}$ = 1855 cm^{-1} s, 1831 s (C=O), 1644 vs (C=N), 512 m, 490 w (Fe–C), (in PE): 356 m (Pd–Cl). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.32 (dt, 18H, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 17.6 Hz, PEt–C$\underline{H}_3$), 1.87 (d, 6H, ^3J = 7.7 Hz, CHC$\underline{H}_3$), 2.00 (m, 12H, PEt–C$\underline{H}_2$), 4.67 (q, 2H, ^3J = 7.6 Hz, NC$\underline{H}$CH$_3$), *4.78*/4.83 (each s br, 4H, Cp-3,3′), *5.50*/5.64 (each s br, 2H, Cp-2), 5.94/*6.13* (each s br, 2H, Cp-2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 8.22 (d, $^2J_{CP}$ = 3.2 Hz, PEt–$\underline{C}$H$_3$), 16.05 (d, $^1J_{CP}$ = 34.2 Hz, PEt–$\underline{C}$H$_2$), 17.35 (CH$\underline{C}$H$_3$), *60.50*/60.57 (N$\underline{C}$H(R)CO), *66.80*/66.92 (Cp-1), *73.04*/73.30 (Cp-2,2′), 75.41 (Cp-3,3′), 167.18 (O$\underline{C}$=N), 174.24 ($\underline{C}$=O). ^{31}P-NMR (109.4 MHz, $CDCl_3$): δ 37.73 (s). $C_{30}H_{46}N_2Cl_4FeO_4P_2Pd_2$ (971.2): Anal. Calc. C 31.38, H 4.04, N 2.44; Found C 31.41, H 4.10, N 2.38.

6.5. General procedure for the preparation of **19** and **20**

A solution of the chlorobridged complex $[Cp^*IrCl_2]_2$ in CH_2Cl_2 was treated with a slight excess of the appropriate 2-ferrocenyl-5(4H)-oxazolone **1** or **4** and solid NaOAc. After stirring for 14 h (**19**) or 30 h (**20**) the mixture was evaporated and dried in vacuo for 3 h. The residue was taken up in CH_2Cl_2 and filtered through Celite to remove NaCl. The solution was evaporated and dried again. A concentrated solution of the residue in CH_2Cl_2 was added dropwise to an excess of pentane whereby the product precipitated (**20**). For **19** the mixture has to be concentrated in vacuo to complete the precipitation. The product was centrifuged off, washed twice with pentane and dried in vacuo at 50°C for several hours.

19: 50 mg (0.186 mmol) of **1**, 130 mg (0.163 mmol) of $[Cp^*IrCl_2]_2$ and 15 mg of NaOAc (0.183 mmol) were used. Orange powder, yield: 138 mg (82%). For X-ray structure analysis suitable crystals were grown in a CH_2Cl_2/pentane mixture. m.p.: 252°C (dec.). IR (KBr): $\tilde{\nu} = 1794\ cm^{-1}$ vs (C=O), 1606 vs (C=N), 510 w, 490 w (Fe–C), (in PE): 302 w, 265 w (Ir–Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.39 (s, 15H, Cp*–C$\underline{H}_3$), 1.69 (s, 15H, Cp*–C$\underline{H}_3$), 4.30 (s, 5H, Cp), 4.42 (m, 1H, Cp-3), 4.47 (m, 1H, Cp-3′), 4.86 (m, 1H, Cp-2), 5.95 (s, 1H, NC$\underline{H}$IrCO), 6.09 (m, 1H, Cp-2′). ^{13}C-NMR (100.5 MHz, $CDCl_3$): δ 8.96/9.13 (Cp*–$\underline{C}H_3$), 66.78 (N$\underline{C}$HIrCO), 70.09 (Cp), 70.60 (Cp-1), 70.28/70.90/71.08/72.22 (Cp-2,2′,3,3′), 86.83/86.99 (Cp*–$\underline{C}$), 164.41 (O$\underline{C}$=N), 180.80 ($\underline{C}$=O). $C_{33}H_{40}NCl_3FeIr_2O_2$ (1029.33): Anal. Calc. C 38.51, H 3.92, N 1.36; Found C 38.30, H 3.94, N 1.28.

20: 42 mg (0.119 mmol) of **4**, 180 mg (0.226 mmol) of $[Cp^*IrCl_2]_2$ and 19 mg of NaOAc (0.232 mmol) were used. 106 mg of **20** were obtained after recrystallisation from a CH_2Cl_2/pentane mixture as an orange powder (yield: 46%). Two diastereoisomers. Diastereoisomeric ratio 1.1:*1*. m.p.: 240°C (dec.). IR (KBr): $\tilde{\nu} = 1794\ cm^{-1}$ vs (C=O), 1606 vs (C=N), 512 w (Fe–C), (in PE): 296 w, 266 w (Ir–Cl). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.38/*1.40* (each s, 30H, Cp*–C$\underline{H}_3$), *1.69*/1.70 (each s, 30H, Cp*–C$\underline{H}_3$), 4.61 (m, 2H, Cp-3), 4.68 (m, 2H, Cp-3′), *4.93*/4.98 (each m, 2H, Cp-2), *5.97*/5.98 (each s, 2H, NC$\underline{H}$IrCO), *6.17*/6.22 (each m, 2H, Cp-2′). ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ *9.16*/*9.42*/9.09 (Cp*–$\underline{C}H_3$), 66.75/*66.87* (N$\underline{C}$HIrCO), 71.58/72.07/72.30/72.38/73.03/73.09/73.27/73.46/73.55 (Cp-2,2′,3,3′), 86.95/87.02/87.06 (Cp*–$\underline{C}$), *162.70*/162.80 (O$\underline{C}$=N), *180.16*/180.34 ($\underline{C}$=O). $C_{56}H_{70}N_2Cl_6FeIr_4O_4 \times 1.75\ CH_2Cl_2$ (2021.3): Anal. Calc. C 34.32, H 3.67, N 1.39; Found C 34.18, H 3.69, N 1.24.

6.6. General procedure for the preparation of **21**–**26**

The appropriate α-amino acid ester hydrochloric acid salt was suspended in CH_2Cl_2. An equimolar amount of NaOMe (methanolic solution) was added. The clear solution (for glycine ester hydrochloride 5 ml of MeOH had to be added) was stirred for 10 min. Then the 2-ferrocenyl-5(4H)-oxazolone was added and the mixture was stirred until the characteristic IR-absorption of the oxazolone carboxyl group (at about 1820 cm^{-1}) disappeared. The solution was then evaporated and the residue was dried in vacuo for 2 h. It was dissolved in CH_2Cl_2 and the solution was filtered through Celite to remove NaCl. For complete removal of NaCl the solution was centrifuged for several min. If NaCl still remained, it was pelleted on the bottom of the Schlenk tube and the solution could be transferred into another tube. It was concentrated in vacuo to about 1 ml and added dropwise at 0°C to an excess of pentane whereby the product precipitated. The precipitate was centrifuged off, washed twice with cold pentane and dried in vacuo at r.t. for several days.

21: 33 mg (0.122 mmol) of **1** and 17 mg (0.122 mmol) of glycine ethyl ester hydrochloric acid salt were used. After stirring for 3 d **21** was obtained as a yellow oil. IR (CH_2Cl_2): $\tilde{\nu} = 1746\ cm^{-1}$ vs (COOR), 1661 vs (amide I), 1515 vs (amide II). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.27 (t, $^3J = 7.1$ Hz, 3H, OCH$_2$C$\underline{H}_3$), 4.07 (d, $^3J = 7.8$ Hz, 2H, NHC$\underline{H}_2$), 4.09 (d, $^3J = 7.8$ Hz, 2H, NHC$\underline{H}_2$), 4.18 (q, $^3J = 7.1$ Hz, 2H, OC$\underline{H}_2$CH$_3$), 4.22 (s, 5H, Cp), 4.36 (m, 2H, Cp-3,3′), 4.69 (m, 2H, Cp-2,2′), 6.34 (br, 1H, N$\underline{H}$CH$_2$), 6.59 (br, 1H, N$\underline{H}$CH$_2$). $C_{17}H_{20}N_2FeO_4 \cdot 0.85\ CH_2Cl_2$ (444.4): Anal. Calc. C 48.24, H 4.92, N 6.30; Found C 48.23, H 5.06, N 6.41.

22: 28 mg (0.104 mmol) of **1** and 15 mg (0.108 mmol) of alanine methyl ester hydrochloric acid salt were used. The reaction mixture was stirred for 6 h. For further purification a hot solution in EtOAc was filtered and evaporated. The residue was taken up in CH_2Cl_2 and precipitated and washed as above. Yellow powder. IR (CH_2Cl_2): $\tilde{\nu} = 3421\ cm^{-1}$ m (NH); (KBr): 3402 s br, 3298 s br (NH), 1745 vs (COOR), 1656 sh, 1638 vs (amide I), 1539 vs (amide II), 500 m, 486 m (Fe–C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 1.44 (d, $^3J = 7.0$ Hz, 3H, C$\underline{H}_3$), 3.74 (s, 3H, OC$\underline{H}_3$), 4.08 (m, 2H, NHC$\underline{H}_2$), 4.22 (s, 5H, Cp), 4.36 (m, 2H, Cp-3,3′), 4.59 (dq, $^3J_{H(CH)} = {}^3J_{H(NH)} = 7.2$ Hz, 1H, NHC$\underline{H}$CH$_3$), 4.71 (m, 2H, Cp-2,2′), 6.50 (br, 1H, N$\underline{H}$CH$_2$), 6.90 (d br, $^3J = 7.4$ Hz, 1H, N$\underline{H}$CHCH$_3$). $C_{17}H_{20}N_2FeO_4 \times 0.2\ CH_2Cl_2$ (389.2): Anal. Calc. C 53.08, H 5.28, N 7.20; Found C 53.16, H 5.83, N 7.17.

23: 56 mg (0.198 mmol) of **2** and 27 mg (0.193 mmol) of alanine methyl ester hydrochloric acid salt were used. After 14 h stirring **23** was obtained as a yellow powder. Two diastereoisomers. Diastereoisomeric ratio 1:1. m.p.: 124–126°C (red). IR (KBr): $\tilde{\nu} = 3281\ cm^{-1}$ vs (NH), 1756 vs (COOR), 1669 vs, 1641 vs, 1629 vs (amide I), 1544 vs, 1538 vs (amide II), 496 s, 484 s (Fe–C). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.44 (d, $^3J =$ 7.0 Hz, 3H, CH(C$\underline{H}_3$)COOCH$_3$), 1.45/1.46 (each d, $^3J = 7.1$ Hz, 3H, CH(C$\underline{H}_3$)CONH), 3.72/3.76 (each s,

Table 2
Crystal data and structure refinement for **6** and **19**

Compound number	**6** (M1763)[a]	**19** (M1839)
Empirical formula	$C_{25}H_{38}Cl_2FeNO_2PPt$	$C_{33}H_{40}Cl_3FeIr_2NO_2$
Formula weight	737.37	1029.26
Temperature (K)	295(2)	294(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (Nr.: 14)	$P\bar{1}$ (Nr.: 2)
Unit cell dimensions		
a (Å)	9.852(3)	10.621(3)
b	13.575(4)	12.1012(13)
c	22.093(6)	14.892(2)
α (°)		70.631(10)
β	101.43(2)	80.64(2)
γ		66.282(14)
Volume (Å^3)	2896.1(15)	1652.2(5)
Z	4	2
Density (calculated) (g cm^{-3})	1.691	2.069
μ (Mo–K$_\alpha$) (mm^{-1})	5.587	8.741
$F(000)$	1456	984
Crystal size (mm)	$0.20\times0.33\times0.53$	$0.20\times0.33\times0.47$
2θ range (°)	4.82–47.94	4.50–47.94
Index ranges	$-h-k\pm l$	$+h\pm k\pm l$
Reflections collected	4820	5480
Independent reflections	4524 [R_{int} 0.0266]	5166 [R_{int} 0.0158]
Absorption correction	Psi-scan	Psi-scan
Max. and min. transmission	0.9990 and 0.5752	1.0000 and 0.5121
Data/parameters	3828/341	4526/389
Goodness-of-fit on F^2	1.097	1.122
Final R indices [$I>2\sigma(I)$]	R_1/0.0261, wR_2/0.0600	R_1/0.0221, wR_2/0.0500
R indices (all data)	R_1/0.0366, wR_2/0.0662	R_1/0.0287, wR_2/0.0535
Largest diff. peak and hole (e Å^{-3})	0.789 and −0.830	0.698 and −0.786

[a] One n-butyl group disordered, split.

3H, OC$\underline{H}_3$), 4.20/4.21 (each s, 5H, Cp), 4.36 (m, 2H, Cp-3,3′), 4.57/4.58 (each dq, $^3J_{CH}=^3J_{NH}=7.2$ Hz, 1H, NHC$\underline{H}$CH$_3$), 4.66 (m, 1H, Cp-2), 4.67 (dq, $^3J_{H(CH)}=^3J_{H(NH)}=7.4$ Hz, 1H, NHC$\underline{H}$CH$_3$), 4.71/4.73 (each m, 1H, Cp-2′), 6.22/6.27 (each d br, $^3J=7.4$ Hz, 1H, N$\underline{H}$CH), 6.72/6.86 (each d br, $^3J=7.2$ Hz, 1H, N$\underline{H}$CH). $C_{18}H_{22}N_2FeO_4$ (386.2): Anal. Calc. C 55.98, H 5.74, N 7.25; Found C 56.26, H 6.01, N 7.34.

24: 39 mg (0.111 mmol) of **4** and 28 mg (0.223 mmol) of glycine methyl ester hydrochloric acid salt were used. Only 5 h stirring were necessary to complete the reaction. After recrystallisation from EtOAc **24** was obtained as a slightly brown powder. m.p.: 173–174°C (black). IR (KBr): $\tilde{\nu}=3407$ cm^{-1} s br, 3297 s br (NH), 1750 vs (COOR), 1667 vs, 1639 vs (amide I), 1546 vs br (amide II), 510 w, 493 m (Fe–C). ^{1}H-NMR (270 MHz, CDCl$_3$): δ 3.76 (s, 6H, OC$\underline{H}_3$), 3.96 (m, 4H, NHC$\underline{H}_2$), 4.11 (m, 4H, NHC$\underline{H}_2$), 4.41 (s br, 4H, Cp-3,3′), 4.82 (s br, 4H, Cp-2,2′), 6.83 (m, 2H, N$\underline{H}$CH$_2$COOCH$_3$), 8.48 (m, 2H, N$\underline{H}$CH$_2$CONH). $C_{22}H_{26}N_4FeO_8\times0.1$ CH_2Cl_2 (538.8): Anal. Calc. C 49.26, H 4.90, N 10.40; Found C 49.23, H 4.71, N 10.35.

25: 50 mg (0.142 mmol) of **4** and 39 mg (0.279 mmol) of alanine methyl ester hydrochloric acid salt were used. After 24 h stirring **25** was obtained as a slightly brown powder. m.p.: 218°C (dec.). IR (CH_2Cl_2): $\tilde{\nu}=3410$ cm^{-1} m, 3310 m (NH); (KBr): 3286 vs br (NH), 1740 vs (COOR), 1668 vs, 1639 vs (amide I), 1548 vs (amide II), 495 m (Fe–C). ^{1}H-NMR (270 MHz, CDCl$_3$): δ 1.47 (d, $^3J=7.2$ Hz, 6H, CHC$\underline{H}_3$), 3.75 (s, 6H, OC$\underline{H}_3$), 3.79 (dd, $^3J=6.2$ Hz, $^2J=16.0$ Hz, 2H, NHC$\underline{H}$H′), 4.04 (dd, $^3J=6.2$ Hz, $^2J=15.7$ Hz, 2H, NHCH$\underline{H}$′), 4.38 (s br, 2H, Cp-3), 4.44 (s br, 2H, Cp-3′), 4.59 (ψquint, $^3J_{H(CH)}=^3J_{H(NH)}=6.7$ Hz, 2H, NHC$\underline{H}$CH$_3$), 4.83 (s br, 4H, Cp-2,2′), 6.59 (d, $^3J=6.4$ Hz, 2H, N$\underline{H}$CHCH$_3$), 8.62 (t, $^3J=6.4$ Hz, 2H, N$\underline{H}$CH$_2$). $C_{24}H_{30}N_4FeO_8\times0.4$ CH_2Cl_2 (592.3): Anal. Calc. C 49.48, H 5.24, N 9.46; Found C 49.46, H 5.41, N 9.34.

26: 40 mg (0.114 mmol) of **4** and 50 mg (0.232 mmol) of phenylalanine methyl ester hydrochloric acid salt were used. After 24 h stirring **26** was obtained as a slightly yellow powder. m.p.: 89–92°C (red). IR (CH_2Cl_2): $\tilde{\nu}=3409$ cm^{-1} m, 3319 m (NH); (KBr): 1745 vs (COOR), 1639 vs (amide I), 1546 vs (amide II), 495 m (Fe–C). ^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.14 (dd, $^3J=6.1$ Hz, $^2J=14.0$ Hz, 2H, C$\underline{H}$H′Ph), 3.18 (dd, $^3J=6.1$ Hz, $^2J=14.0$ Hz, 2H, CH$\underline{H}$′Ph), 3.73 (s, 6H, OC$\underline{H}_3$), 3.78 (dd, $^3J=6.3$ Hz, $^2J=16.3$ Hz, 2H, NHC$\underline{H}$H′), 3.88 (dd, $^3J=6.3$ Hz, $^2J=16.3$ Hz, 2H, NHCH$\underline{H}$′), 4.39 (m, 2H, Cp-3), 4.44 (m, 2H, Cp-3′), 4.80 (m, 2H, Cp-2), 4.82 (m, 2H, Cp-2′), 4.89 (dt, $^3J_{H(CH)}=6.0$ Hz, $^3J_{H(NH)}=7.4$ Hz, 2H, NHC$\underline{H}$CH$_2$Ph), 7.16 (d, $^3J=7.4$ Hz, 2H, N$\underline{H}$CHCH$_2$Ph), 7.18 (ABB′CC', 4H, Ph-2,2′), 7.25 (A, 2H, Ph-4), 7.32 (BB', 4H, Ph-3,3′), 8.54 (t, $^3J=6.3$ Hz, 2H, N$\underline{H}$CH$_2$). ^{13}C-NMR (100.5 MHz, CDCl$_3$): δ 38.05 (C$\underline{H}_2$Ph), 42.86 (NHC$\underline{H}_2$), 52.47 (OC$\underline{H}_3$), 53.81 (NHC$\underline{H}$(R)CO), 70.52/70.76/71.52/71.61 (Cp-2,2′,3,3′), 75.89 (Cp-1), 128.71 (Ph-4), 129.44/135.86 (Ph-2,2′,3,3′), 135.86 (Ph-1), 170.69/171.12/171.81 (COOCH$_3$, 2·CONH). $C_{36}H_{38}N_4FeO_8$ (710.6): Anal. Calc. C 60.85, H 5.39, N 7.89; Found C 60.53, H 5.67, N 7.90.

6.7. X-ray diffraction analyses [25]

Data collection: Enraf–Nonius CAD4 Diffractometer, Mo–K$_\alpha$ radiation, λ 0.71073 Å, graphite monochromator, cell constants from 25 centered reflections, ω-scan (**6**) or ω–2θ-scan (**19**), intensity of three standard reflections checked every two hours. Structure solution by SHELXS-86 and refinement by SHELXL-93 (G.M. Sheldrick, University of Göttingen, Germany) non-hydrogen atoms refined anisotropically, hydrogens with $U_1/1.2\times U_{eq}$ of the adjacent carbon atom. Full-

matrix refinement against F^2. See Table 2 for crystal data and structure refinement.

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