

Organometallic Complexes of Iridium, Palladium, Chromium and Iron from 2-Phenyl-5(4*H*)-oxazolones – Organometallic Labelled Dipeptides

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Reactions of 2-phenyl-4-R-5(4*H*)-oxazolones (R = Me, CH₂Ph, CHMeEt) with [(η⁵-C₅Me₅)IrCl₂]₂ afforded the cyclometallated complexes (η⁵-C₅Me₅)(Cl)Ir(L) (**1**–**3**) [L = 2-phenyl-4-R-5(4*H*)-oxazolone(*C*-*o*,*N*)]. 2-Phenyl-5(4*H*)-oxazolone reacts with [(η⁵-C₅Me₅)IrCl₂]₂ and palladium(II) acetate to give complexes with a *C*-*o*,*N*-bridging oxazolone [(η⁵-C₅Me₅)(Cl)Ir]₂(μ-Cl)(μ-L-H⁺) (**4**) and Pd₃(μ-ac)₅(μ-L-H⁺) (**5**). 2-Phenyloxazolone anions were added to the π ligands of [(η⁵-C₆H₇)Fe(CO)₃]⁺ and [(η⁷-C₇H₇)Cr(CO)₃]⁺ to give the adducts **6**–**11**. Dipeptide derivatives **12**–**18** were obtained by reac-

tion of **1**, **2** and by reaction of the adduct **6** from [(η⁵-C₆H₇)Fe(CO)₃]⁺ and the anion of 2-phenyloxazolone with α-amino acid esters. These reactions may be used for the labelling of peptides. Saponification of **15**–**18** yields the organometallic substituted peptide acids **19**–**22**. Their dianions (deprotonation of COOH and peptide amide) were used as ligands towards (Ph₃P)₂PtCl₂ to yield the bimetallic complexes **23**–**25**. The structures of **4**, **5**, **9** and **10** were determined by X-ray diffraction.

5(4*H*)-Oxazolones which can be considered as activated α-amino acid derivatives are important intermediates and starting materials in organic synthesis.^[3] Recently, we reported on some metal complexes with neutral 2-phenyl-5(4*H*)-oxazolones.^[4] In the following some cyclometallated complexes from these oxazolones and the use of the delocalized oxazolone anion^[5] as nucleophile for the addition to π-coordinated ligands are described. Some of the compounds obtained may be of use for the labelling of peptides^[6].

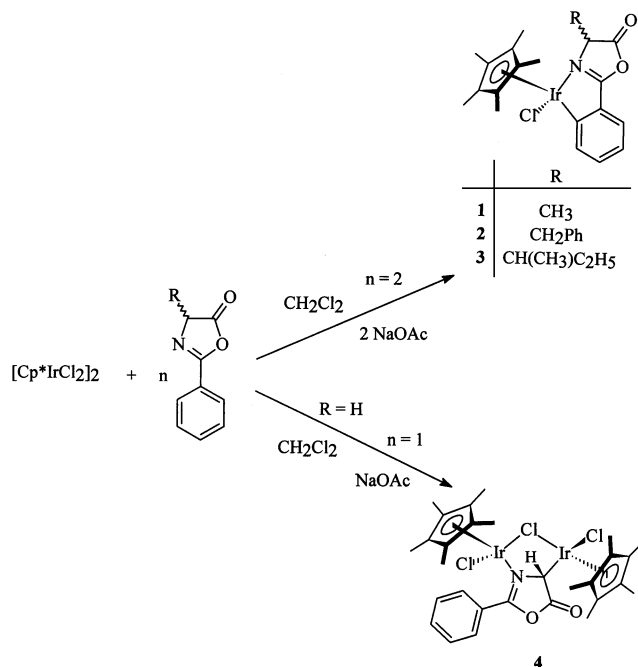
Results and Discussion

1. Cyclometallated Complexes

The reaction of the chloro-bridged iridium(III) complex [Cp*IrCl₂]₂ with the substituted 2-phenyl-4-R-5(4*H*)-oxazolones gave the complexes **1**–**3**. Cyclometallation with phenyl-containing donors has been observed for several iridium complexes^[7].

The complexes **1**–**3** contain an “asymmetric” metal center which causes doubling of the ¹H-NMR signals of the C₅Me₅ ligands (**1**: 5:1; **2**: 20:1; **3**: 1:1), due to diastereoisomer formation.

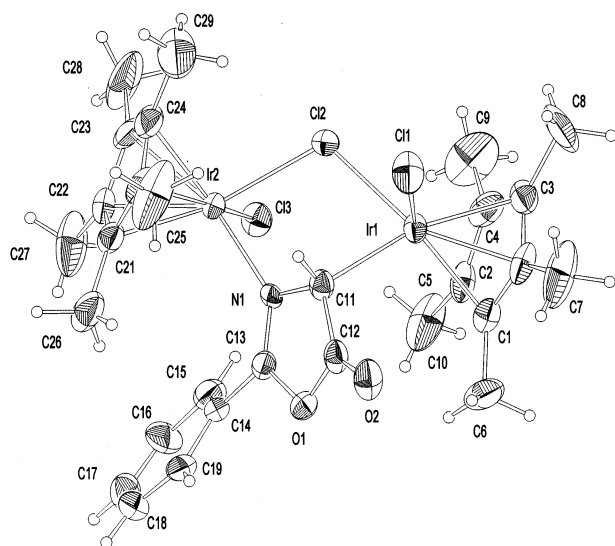
An unexpected complex **4** was obtained from the unsubstituted 2-phenyl-5(4*H*)-oxazolone and its structure was established by X-ray diffraction. In the complex **4** the two



iridium atoms are bridged by a chlorine atom and a *C*-*o*,*N*-bound 2-phenyloxazolone ligand.

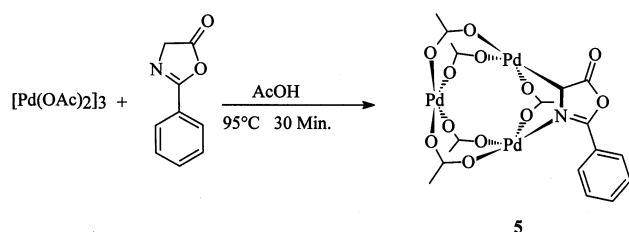
In the five-membered ring Cl–Ir–C–N–Ir the C atom is situated outside the almost planar arrangement of the other four atoms. The ¹H-NMR spectrum of **4** exhibits only

[◇] Part CI: Ref. [1].

Figure 1. Molecular structure of **4**^[a] in the crystal

^[a] Selected bond lengths [Å] and angles [°]: Ir2–N1 2.117(9), Ir1–C11 2.152(12), N1–C13 1.29(2), N1–C11 1.461(14), C11–C12 1.44(2), Ir2–Cl2 2.446(3), Ir1–Cl2 2.436(3); N1–Ir2–Cl2 82.7(2), C11–Ir1–Cl2 80.4(3), C13–N1–C11 106.4(10), N1–Ir2–Cl2–Ir1 3.53(0.27), Cl2–Ir2–N1–C11 37.00(0.72), C11–Ir1–Cl2–Ir2 110.45(0.17), N1–C13–C14–C15 46.68(2.04).

two C₅Me₅ signals which implicates that only one diastereoisomer is formed. The same bridging occurs in the trinuclear palladium complex **5** which was obtained from Pd^{II} acetate and 2-phenyl-5(4*H*)-oxazolone. In **5** one acetate bridge of Pd₃ac₆^[8] is substituted by a *C*-*o*,*N*-bridging 2-phenyloxazolone.

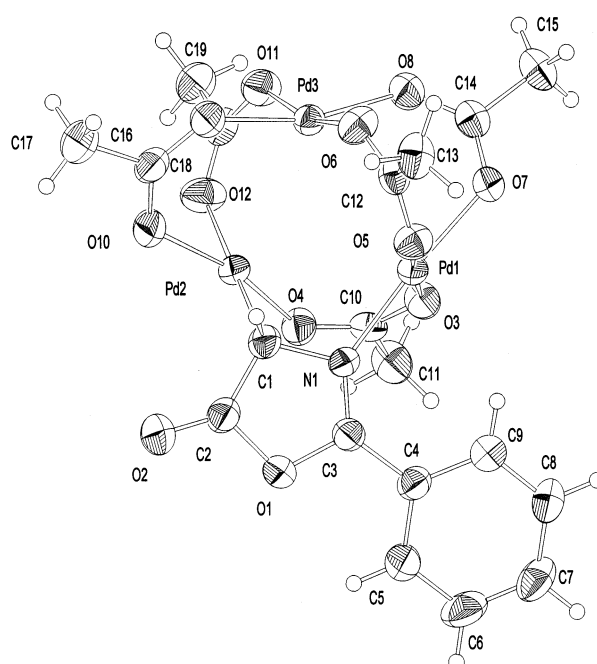


The molecular structure of **5** is very similar to that of Pd₃ac₆^[8] with the exception that the Pd2–O12 distance [2.087(3) Å] is longer than the other Pd–O bonds (ca. 2.01 Å). This can be attributed to the *trans* influence of the strong C donor.

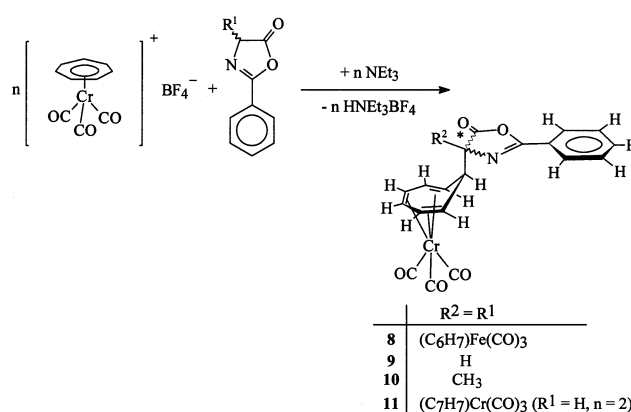
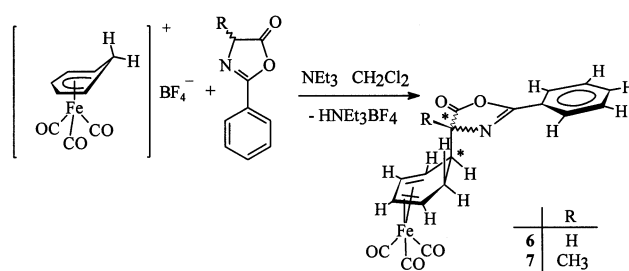
2. Addition of the 2-Phenyloxazolone Anion to Unsaturated Hydrocarbons of Cationic Complexes

The addition of organic and organometallic nucleophiles to π -coordinated hydrocarbons is a very well studied and important reaction^[9]. The addition of the 2-phenyl-5(4*H*)-oxazolone anion to the cyclopentadienyl and the cycloheptatrienyl ligand afforded the complexes **6**–**11**.

In **6** and **7** two stereogenic centers are formed and the two diastereoisomers (**6**: 1:1.2; **7**: 1:1.8) can be detected in their ¹H- and ¹³C-NMR spectra. For almost all atoms two sets of signals are observed. Interestingly, for **8** one diastereoisomer is formed in high excess. In the ¹H-NMR spec-

Figure 2. Molecular structure of **5**^[a] in the crystal

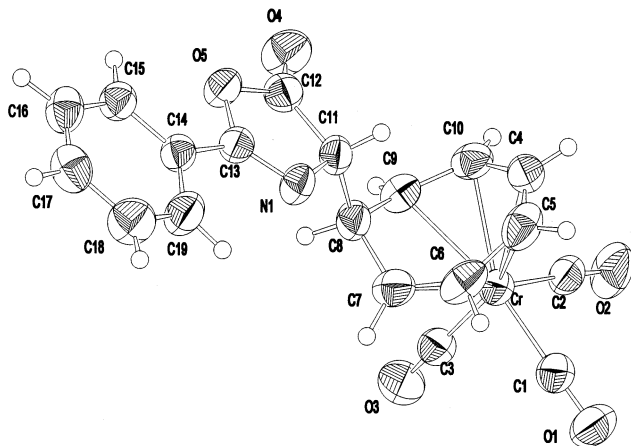
^[a] Selected bond lengths [Å] and angles [°]: Pd3–O8 1.995(3), Pd3–O11 2.002(3), Pd2–O12 2.087(3), Pd2–O10 2.019(3), Pd2–C1 2.025(4), Pd1–N1 2.003(3), Pd1–O7 2.015(3), Pd1–O5 2.005(3); O11–Pd3–O6 166.40(13), O12–Pd2–C1 179.57(15), O7–Pd1–N1 175.47(13), O10–Pd2–O4 166.48(12).



trum only some weak signals can be assigned to the second isomer; *exo* addition is proven for **6** and **7** by the signals of

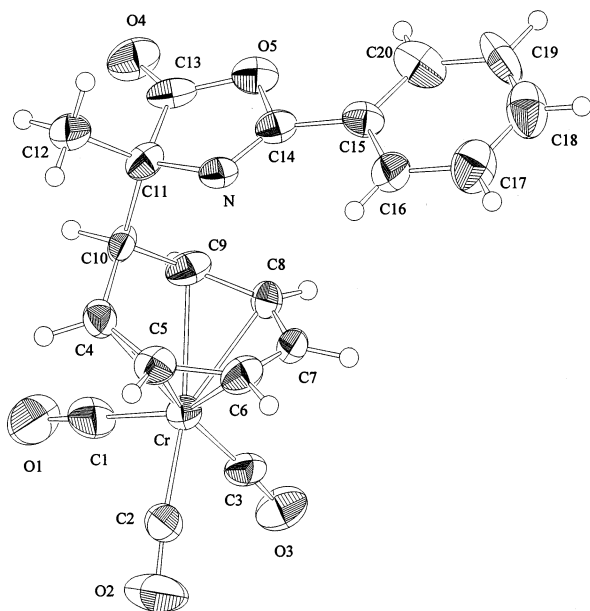
the CH–CH₂ group and for **9** and **10** by X-ray structure determination.

Figure 3. Molecular structure of **9**^[a] in the crystal



^[a] Selected bond lengths [Å] and angles [°]: Cr–C1 1.853(4), Cr–C2 1.849(4), Cr–C3 1.858(4), C1–O1 1.151(4), Cr–C5 2.196(4), Cr–C6 2.201(4), Cr–C7 2.340(4), C8–C11 1.549(5), C13–N1 1.266(4), C13–C14 1.472(4); O5–C13–N1 117.5(3), C14–C13–N1 126.3(3), O4–C12–O5 122.0(3).

Figure 4. Molecular structure of **10**^[a] in the crystal

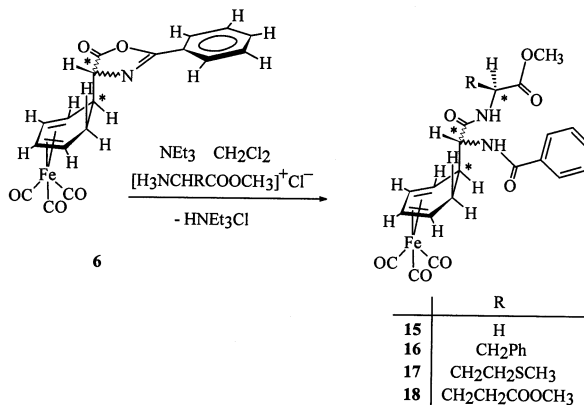
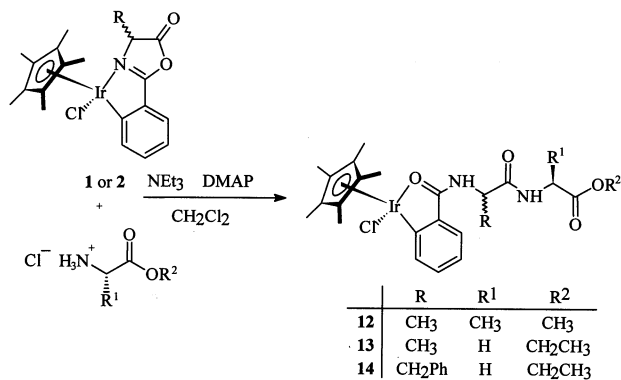


^[a] Selected bond lengths [Å] and angles [°]: Cr–C1 1.840(9), Cr–C2 1.867(8), Cr–C3 1.840(8), C1–O1 1.164(8), Cr–C6 2.175(7), Cr–C5 2.228(7), Cr–C4 2.352(7), C10–C11 1.560(9), C14–N 1.255(8), C15–C14 1.459(10); O5–C14–N 116.3(7), C15–C14–N 129.8(7), O4–C13–O5 121.6(7).

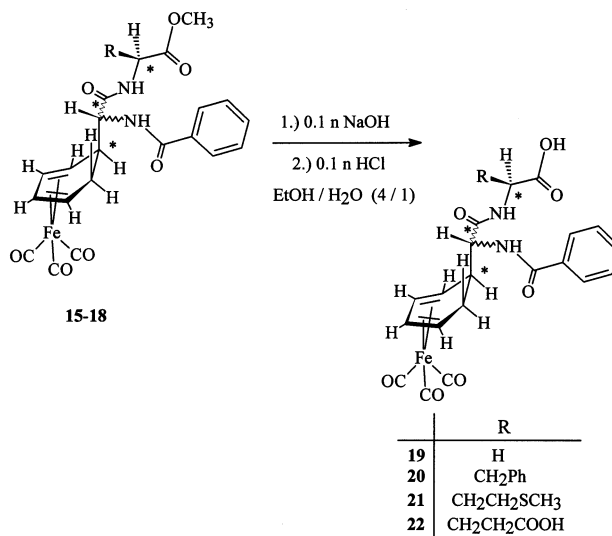
3. Formation of Dipeptide Derivatives from **1**, **2** and **6**

The nucleophilic addition of α -amino acid esters^[10] to **1**, **2** and **6** gave the dipeptide derivatives **12–18**.

The shift of the carbonyl IR absorption to lower wave-numbers (ca. 1590 cm^{−1}) in **12–14** is characteristic for coordination of the CO function^[11]. The two stereogenic centers of **15** give rise to two diastereoisomers (1:1.2), whereas four diastereoisomers of **16–18** (1:1:1.2:1.2) (from three

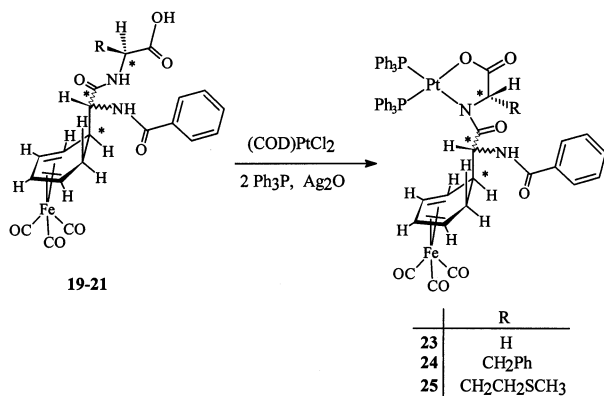


stereogenic centers) were observed in their ¹H-NMR spectra (from the methoxy signals). Saponification of **15–18** could be accomplished to give the free acids **19–22**.



Compounds **19–22** were used as dianionic chelate ligands (deprotonation of the amide and carboxylic group) towards (Ph₃P)₂PtCl₂ to afford the heterobimetallic complexes **23–25**. Recently, several examples for complexes with dianionic *N*-acyl- α -amino carboxylates have been reported^[12] which can be considered as simple models for *O,N* coordination of peptides.

Two diastereoisomers of **23** (as for **15**) and four isomers of **24** and **25** (as for **16** and **17**) were observed in the ^{31}P -NMR spectra.



Conclusions

The reaction of oxazolones with organometallic complexes leads to a versatile chemistry and the reaction of **1**, **2** and **6** with α -amino acid esters (or peptide esters) provides a method for the labelling of peptides at the amino terminus.

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Experimental Section

All reactions were carried out in dry solvents under nitrogen. – NMR: Jeol GSX 270 or Jeol EX 400, using the solvent as internal standard. – IR: Nicolet 520 FT-IR. – The starting materials were prepared according to literature procedures ([Cp*IrCl₂]^[13], [(C₆H₇)Fe(CO)₃]BF₄^[14], [(C₇H₇)Cr(CO)₃]BF₄^[15], (COD)PtCl₂^[16], 2-phenyl-5(4*H*)-oxazolones^[17]). Pd^{II} acetate was purchased from Aldrich and purified by dissolving it in hot benzene, filtering and evaporating off the solvent. Glacial acetic acid was refluxed over KMnO₄ for several hours and distilled prior to use. The α -amino acid ester hydrochlorides were purchased from Merck or Fluka. – PE = polyethylene.

General Procedure for the Preparation of 1–3: To a mixture of the oxazolone and 66 mg (0.81 mmol) of NaOAc in 5 ml of CH₂Cl₂ a deep red solution of 319 mg (0.4 mmol) of [Cp*IrCl₂]₂ in 5 ml of the same solvent was added. After stirring overnight, the light-red mixture was filtered to remove NaCl, and the solvent was removed in vacuo. The yellow product was washed twice with 3 ml of Et₂O and dried in vacuo at 60°C for 5 h.

1: 142 mg (0.81 mmol) of 4-methyl-2-phenyl-5(4*H*)-oxazolone was used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1844 cm⁻¹ s (C=O), 1627 s (C=N); (PE): $\tilde{\nu}$ = 288 cm⁻¹ s (M–Cl). – ¹H NMR (400 MHz, CDCl₃): δ = 1.66 (d, ³J = 7.5 Hz, 3 H, CH₃), 1.76/1.82 [each s, 15H 5:1, C₅(CH₃)₅], 4.43 (q, ³J = 7.5 Hz, 1 H, CHCH₃), 7.04 (m, 1 H, C₆H₄), 7.27 (m, 1 H, C₆H₄), 7.53 (m, 1 H, C₆H₄), 7.82 (m, 1 H, C₆H₄). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 9.44/9.94 [C₅(CH₃)₅], 15.97 (CH₃), 58.86 (CHCH₃), 88.53/89.27 [C₅(CH₃)₅], 122.53, 127.63, 128.84, 134.05, 135.85 (C₆H₄), 166.37 (OC=N), 174.91 (Ir–C), 177.94 (C=O). – C₂₀H₂₃ClIrNO₂ (536.7): calcd. C 44.71, H 4.28, N 2.60; found C 44.46, H 4.75, N 2.41.

2: 204 mg (0.81 mmol) of 4-benzyl-2-phenyl-5(4*H*)-oxazolone was used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1845 cm⁻¹ s (C=O), 1623 s (C=N); (PE): $\tilde{\nu}$ = 292 cm⁻¹ s (M–Cl). – ¹H NMR (270 MHz, CDCl₃): δ = 1.79/1.83 [each s, 15H 20:1, C₅(CH₃)₅], 3.06 (dd, ²J = 15.0 Hz, ³J = 10.7 Hz, 1 H, CHH'), 3.64 (dd, ²J = 15.0 Hz, ³J = 4.6 Hz, 1 H, CHH'), 4.60 (dd, ³J = 4.6 Hz, ³J = 10.6 Hz, 1 H, CHCH₂Ph), 7.07 (m, 1 H, C₆H₄), 7.32 (m, 6 H, C₆H₄ and C₆H₅), 7.55 (m, 1 H, C₆H₄), 7.84 (m, 1 H, C₆H₄). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 9.30/9.40 [C₅(CH₃)₅], 36.80 (CH₂Ph), 62.20 (CHCH₂Ph), 88.40/86.20 [C₅(CH₃)₅], 122.30, 127.40, 127.50, 128.50, 128.70, 129.40, 133.90, 134.70, 135.60 (C₆H₄ and C₆H₅), 166.50 (OC=N), 172.40 (Ir–C), 177.90 (C=O). – C₂₆H₂₇ClIrNO₂ × 0.5 CH₂Cl₂ (655.6): calcd. C 48.53, H 4.27, N 2.13; found C 48.06, H 4.30, N 2.07.

3: 176 mg (0.81 mmol) of 4-(2'-butyl)-2-phenyl-5(4*H*)-oxazolone was used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1844 cm⁻¹ s (C=O), 1626 s (C=N); (PE): $\tilde{\nu}$ = 283 cm⁻¹ s (M–Cl). – ¹H NMR (270 MHz, CDCl₃): δ = 1.28 (m, 2 H, CH₂), 0.83–1.09 (m, 6 H, 2 × CH₃), 1.74/1.75 [each s, 15H 1.2:1, C₅(CH₃)₅], 4.29 [m, 1 H, CH(C₄H₉)], 7.07 (m, 1 H, C₆H₄), 7.28 (m, 1 H, C₆H₄), 7.52 (m, 1 H, C₆H₄), 7.81 (m, 1 H, C₆H₄). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 9.40/9.80 [C₅(CH₃)₅], 11.80 (CH₂CH₃), 14.80 (CHCH₃), 25.80 (CH₂CH₃), 36.60 (CHCH₃), 67.80 (CHC₄H₉), 88.40 [C₅(CH₃)₅], 122.40, 127.30, 131.50, 133.90, 135.90 (C₆H₄), 166.90 (OC=N), 173.20 (Ir–C), 178.30 (C=O). – C₂₃H₂₉ClIrNO₂ (655.6): calcd. C 47.70, H 5.05, N 2.42; found C 48.56, H 5.53, N 2.89.

4: To a mixture of 51 mg (0.32 mmol) of 2-phenyl-5(4*H*)-oxazolone and 26 mg (0.32 mmol) of NaOAc in 5 ml of CH₂Cl₂ a deep red solution of 247 mg (0.31 mmol) of [Cp*IrCl₂]₂ in 5 ml of the same solvent was added. After stirring for 5 h the light red mixture was filtered to remove NaCl, and concentrated in vacuo to about 2 ml. The yellow product was precipitated with 15 ml of Et₂O, washed twice with 3 ml Et₂O and dried in vacuo at 60°C for 5 h. Crystals were obtained from a CH₂Cl₂/pentane mixture. – IR (KBr): $\tilde{\nu}$ = 1792 cm⁻¹ s (C=O), 1608 w (C=N); (PE): $\tilde{\nu}$ = 262 cm⁻¹ s, 288 s, 299 m (M–Cl). – ¹H NMR (270 MHz, CDCl₃): δ = 1.39 [s, 15 H, C₅(CH₃)₅], 1.58 [s, 15 H, C₅(CH₃)₅], 6.12 (s, 1 H, CHIr), 7.27–7.56 (m, 3 H, 3,4,5-C₆H₅), 8.61 (d, ³J = 7.9 Hz, 2 H, 2,6-C₆H₅). – ¹³C NMR (100.5 MHz, CD₂Cl₂): δ = 8.57 [C₅(CH₃)₅], 8.63 [C₅(CH₃)₅], 67.79 (CHIr), 86.86 [C₅(CH₃)₅], 87.12 [C₅(CH₃)₅], 125.91, 128.56, 129.83, 132.49 (C₆H₅), 161.15 (OC=N), 179.00 (C=O). – C₂₉H₃₆Cl₃Ir₂NO₂ (921.4): calcd. C 37.76, H 3.90, N 1.51; found C 37.41, H 3.89, N 1.55.

5: A brown suspension of 123 mg (0.55 mmol) of palladium(II) acetate and 88 mg (0.55 mmol) of 2-phenyl-5(4*H*)-oxazolone in 2 ml of glacial acetic acid was heated to 95°C for 30 min whereby the product began to precipitate. After cooling, the mixture was centrifuged. The dark brown residue was washed with 1 ml of glacial acetic acid and twice with 2 ml of water. After drying in vacuo at 50°C for 3 h, the dark brown product was dissolved in 5 ml of trichloromethane, filtered and added to 30 ml of *n*-hexane. The orange precipitate was centrifuged off, washed with pentane and *n*-hexane and dried in vacuo at 50°C for 8 h. Slow concentration of a solution in CH₂Cl₂/hexane (1:10) gave orange prisms, suitable for X-ray analysis. – IR (KBr): $\tilde{\nu}$ = 1807 cm⁻¹ s (C=O), 1608 s, 1592 s, 1569 s (antisym. COO), 1421 s (sym. COO). – ¹H NMR (400 MHz, CDCl₃): δ = 1.48 (s, 3 H, CH₃COO), 1.94 (s, 3 H, CH₃COO), 1.97 (s, 3 H, CH₃COO), 2.00 (s, 3 H, CH₃COO), 2.05 (s, 3 H, CH₃COO), 5.41 (s, 1 H, CHPd), 7.70 (BB', 2 H, 3,5-C₆H₅), 7.79 (A, 1 H, 4-C₆H₅), 9.15 (CC', 2 H, 2,6-C₆H₅). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 22.19 (CH₃COO), 22.76 (CH₃COO), 23.00 (CH₃COO), 23.33 (CH₃COO), 23.39 (CH₃COO), 38.99

(CHPd), 123.78, 129.15, 129.96, 135.00 (C₆H₅), 165.50 (OC=N), 172.93 (C=O), 185.41 (CH₃COO), 185.47 (CH₃COO), 186.86 (CH₃COO), 188.13 (CH₃COO), 188.59 (CH₃COO). – C₁₉H₂₁NO₁₂Pd₃ (774.6): calcd. C 29.46, H 2.73, N 1.81; found C 29.38, H 3.18, N 1.75.

General Procedure for the Preparation of 6 and 7: A stirred mixture of 150 mg (0.49 mmol) of [(C₆H₇)Fe(CO)₃]BF₄ and the appropriate oxazolone in 15 ml of CH₂Cl₂ was cooled (see below). A solution of 64.8 µl (0.47 mmol) of triethylamine in 5 ml of CH₂Cl₂ was slowly added. After 30 min of stirring at low temp., the yellow solution was allowed to warm up to room temp. and stirred for another 2 h. After concentrating to about 4 ml, triethylammonium chloride was precipitated with 40 ml of pentane and filtered off. The filtrate was concentrated and the residue was dissolved in 30 ml of pentane. This yellow solution was filtered through Celite and concentrated in vacuo to about 4 ml. Cooling to –78°C for 3 min gave a colourless precipitate which was filtered off. Removal of the solvent from the filtrate in vacuo gave the yellow, oily product which was dried in vacuo at room temp. for a few days.

6: 75 mg (0.47 mmol) of 2-phenyl-5(4*H*)-oxazolone was used. The addition of NEt₃ was carried out at –15°C. – IR (film NaCl): $\tilde{\nu}$ = 2045 cm^{–1} s (Fe–CO), 1964 s br. (Fe–CO), 1824 s (C=O), 1653 s (C=N). – ¹H NMR (400 MHz, CDCl₃): δ = 1.77 (dm, 1 *H*, ²*J*_{endo} = 15.3 Hz, 6*exo*-C₆H₇)/1.61 (ddd, 1 *H*, ²*J*_{endo} = 15.0 Hz, ³*J*₁ = 3.7 Hz, ³*J*₅ = 2.6 Hz, 6*exo*-C₆H₇), 2.14/2.06 (each ddd, 1 *H*/1 *H*, ²*J*_{exo} = 15.1 Hz, ³*J*₁ = 11.1 Hz, ³*J*₅ = 4.0 Hz, 6*endo*-C₆H₇), 2.74 (m, 1 *H* + 1 *H*, 1-C₆H₇), 2.92 (ddd, 1 *H*, ³*J*₃ = 6.3 Hz, ³*J*₁ = 3.3 Hz, ⁴*J*₄ = 1.4 Hz, 2-C₆H₇)/3.06, 3.06 [m, 1 *H* + 1 *H* (+ 1 *H*, 2-C₆H₇), 5-C₆H₇], 4.20/4.24 [each d, 1 *H*/1 *H*, ³*J*₁ = 6.0 Hz, NCH(C₆H₇)COO], 5.32 (ddd, 1 *H*, ³*J*₂ = 6.1 Hz, ³*J*₄ = 4.4 Hz, ⁴*J*₅ = 1.6 Hz, 3-C₆H₇)/5.39, 5.39 [m, 1 *H* + 1 *H* (+ 1 *H*, 3-C₆H₇), 4-C₆H₇], 7.43–7.60 (ABB', 3 *H* + 3 *H*, 3,4,5-C₆H₅), 7.96–8.00 (CC', 2 *H* + 2 *H*, 2,6-C₆H₅). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 27.77/26.50 (6-C₆H₇), 40.25/40.98 (1-C₆H₇), 59.38/59.39, 59.26/58.83 (2,5-C₆H₇), 70.03/69.99 [CNCH(C₆H₇)COO], 86.06/86.51, 85.83/85.48 (3,4-C₆H₇), 125.95, 128.20, 129.14, 133.16, 126.11, 128.22, 129.12, 133.14 (C₆H₅), 162.07/161.95 [CNCH(C₆H₇)COO], 176.90/177.29 [CNCH(C₆H₇)COO], 211.69 (Fe–CO). Diastereomeric ratio 1.0:1.15. – C₁₈H₁₃FeNO₅ (379.2): calcd. C 57.02, H 3.46, N 3.69; found C 57.38, H 4.14, N 3.48.

7: 86 mg (0.49 mmol) of 4-methyl-2-phenyl-5(4*H*)-oxazolone was used. The addition of NEt₃ was carried out at 0°C. – IR (film NaCl): $\tilde{\nu}$ = 2048 cm^{–1} s (Fe–CO), 1969 s br. (Fe–CO), 1816 s (C=O), 1658 s (C=N). – ¹H NMR (400 MHz, CDCl₃): δ = 1.41/1.43 [each s, 3*H*/3 *H*, NCCH₃(C₆H₇)COO], 1.78 (dm, 1 *H*, ²*J*_{endo} = 15.3 Hz, 6*exo*-C₆H₇)/1.70 (dm, 1 *H*, ²*J*_{endo} = 15.1 Hz, 6*exo*-C₆H₇), 2.04/1.99 (each ddd, 1 *H*/1 *H*, ²*J*_{exo} = 15.2 Hz, ³*J*₁ = 11.0 Hz, ³*J*₅ = 4.3 Hz, 6*endo*-C₆H₇), 2.58 (m, 1 *H*/1 *H*, 1-C₆H₇), 2.72/2.99 (each ddd, 1 *H*/1 *H*, ³*J*₃ = 6.2 Hz, ³*J*₁ = 3.2 Hz, ⁴*J*₄ = 1.3 Hz, 2-C₆H₇), 3.04 (m, 1 *H*/1 *H*, 5-C₆H₇), 5.21/5.31 (each ddd, 1 *H*/1 *H*, ³*J*₂ = 5.6 Hz, ³*J*₄ = 4.3 Hz, ⁴*J*₅ = 1.4 Hz, 3-C₆H₇), 5.30 (m, 1 *H*, 4-C₆H₇)/5.35 (dd, 1 *H*, ³*J*₃ = 5.0 Hz, ³*J*₅ = 6.0 Hz, 4-C₆H₇), 7.42–7.60 (ABB', 3 *H* + 3 *H*, 3,4,5-C₆H₅), 7.98–7.99 (CC', 2 *H* + 2 *H*, 2,6-C₆H₅). – ¹³C NMR (100.5 MHz, CDCl₃): δ = 22.44/22.56 (CH₃), 26.29/25.43 (6-C₆H₇), 46.33/45.45 (1-C₆H₇), 59.16/59.25, 57.63/58.13 (2,5-C₆H₇), 72.85/72.80 [CNCCH₃(C₆H₇)COO], 86.01/86.32, 85.59/85.38 (3,4-C₆H₇), 126.21, 133.06, 126.01, 128.21, 129.12, 133.02 (C₆H₅), 160.27/159.94 [CNCCH₃(C₆H₇)COO], 180.48/179.87 [CNCCH₃(C₆H₇)COO], 211.72 (Fe–CO). Diastereomeric ratio 1.0:1.8. – C₁₉H₁₅FeNO₅ (393.2): calcd. C 58.04, H 3.85, N 3.56; found C 57.50, H 3.79, N 2.84.

General Procedure for the Preparation of 8–11: A stirred mixture of [(C₇H₇)Cr(CO)₃]BF₄ and the appropriate oxazolone in 15 ml of

THF was cooled to 0°C. A solution of triethylamine in 5 ml of THF was slowly added. After stirring overnight, the red solution was concentrated to about 4 ml, triethylammonium chloride was precipitated with 40 ml of Et₂O and filtered off. The filtrate was taken to dryness and the residue was dissolved in 30 ml of Et₂O. This solution was filtered through Celite and the solvent was removed in vacuo. The residue was dissolved in 1 ml of CH₂Cl₂ and added to excess pentane to give the product as orange solid which was washed twice with pentane and dried in vacuo at 50°C for several hours.

8: 98 mg (0.31 mmol) of [(C₇H₇)Cr(CO)₃]BF₄, 117 mg (0.31 mmol) of **6** and 43.5 µl (0.31 mmol) of NEt₃ were used. The reaction was carried out in CH₂Cl₂ instead of THF. The CH₂Cl₂/pentane mixture had to be slowly concentrated to give the product. – IR (KBr): $\tilde{\nu}$ = 2045 cm^{–1} s (Fe–CO), 1979 s br. (Fe–CO, Cr–CO), 1924 s, 1884 s, 1878s, 1870 s (Cr–CO), 1807 s (C=O), 1653 s (C=N). – ¹H NMR (270 MHz, CDCl₃): δ = 1.42 (ddd, 1 *H*, ²*J*_{endo} = 14.9 Hz, ³*J*₁ = 3.6 Hz, ³*J*₅ = 2.5 Hz, 6*exo*-C₆H₇), 1.87 (2.00) (ddd, 1 *H*, ²*J*_{exo} = 14.9 Hz, ³*J*₁ = 10.8 Hz, ³*J*₅ = 4.2 Hz, 6*endo*-C₆H₇), 2.59 (ddd, 1 *H*, ³*J*_{endo} = 10.6 Hz, ³*J*_{exo} = 3.5 Hz, ³*J*₂ = 3.5 Hz, 1-C₆H₇), 2.68 (ddd, 1 *H*, ³*J*₃ = 5.1 Hz, ³*J*₁ = 3.5 Hz, ⁴*J*₄ = 2.2 Hz, 2-C₆H₇), 2.94 (3.06) (ddd, 1 *H*, ³*J*₄ = 7.9 Hz, ³*J*_{endo} = 3.7 Hz, ³*J*_{exo} = 2.2 Hz, 5-C₆H₇), 3.61 (m, 3 *H*, 1,2,7-C₇H₇), 4.82 (5.00) (m, 2 *H*, 3,6-C₇H₇), 5.23 (5.36) (m, 2 *H*, 3,4-C₆H₇), 5.85 (m, 1 *H*, 4-C₇H₇), 5.98 (m, 1 *H*, 5-C₇H₇), 7.50 (BB', 2 *H*, 3,5-C₆H₅), 7.60 (A, 1 *H*, 4-C₆H₅), 7.86 (7.78) (CC', 2 *H*, 2,6-C₆H₅). Diastereoisomeric ratio about 13:1. – ¹³C NMR (100.4 MHz, CDCl₃): δ = 26.70 (6-C₆H₇), 41.12 (1-C₇H₇), 44.44 (1-C₆H₇), 56.51, 58.62 (2,5-C₆H₇), 62.39, 64.27 (2,7-C₇H₇), 83.34 (NCRR'COO), 85.56, 86.18 (3,4-C₆H₇), 97.50, 98.03, (4,5-C₇H₇), 102.04, 102.29 (3,6-C₇H₇), 125.60, 128.25, 129.21, 133.23 (C₆H₅), 160.30 [OC(Ph)N], 176.91 (CRR'COO), 211.52 (Fe–CO). – C₂₈H₁₉CrFeNO₈ (605.3): calcd. C 55.56, H 3.16, N 2.31; found C 55.50, H 3.05, N 2.24.

9: 250 mg (0.80 mmol) of [(C₇H₇)Cr(CO)₃]BF₄, 125 mg (0.78 mmol) of 2-phenyl-5(4*H*)-oxazolone and 108.1 µl (0.78 mmol) of NEt₃ were used. The product could not be obtained analytically pure. For X-ray analysis suitable crystals were grown in an CH₂Cl₂ pentane mixture. – IR (KBr): $\tilde{\nu}$ = 1981 cm^{–1} s, 1915 s, 1883 s (Cr–CO), 1820 s (C=O), 1651 s (C=N). – ¹H NMR (400 MHz, CDCl₃): δ = 3.12 [d, 1 *H*, NCH(C₇H₇)CO], 3.55 (m, 1 *H*, 2-C₇H₇), 3.65 (m, 1 *H*, 7-C₇H₇), 3.75 (m, 1 *H*, 1-C₇H₇), 4.90 (m, 1 *H*, 3-C₇H₇), 5.05 (m, 1 *H*, 6-C₇H₇), 6.00 (m, 1 *H*, 4-C₇H₇), 6.05 (m, 1 *H*, 5-C₇H₇), 7.40–7.65 (ABB', 3 *H*, 3,4,5-C₆H₅), 7.88 (CC', 2 *H*, 2,6-C₆H₅). – ¹³C-NMR (100.4 MHz, CDCl₃): δ = 40.14 (1-C₇H₇), 61.79, 62.15 (2,7-C₇H₇), 70.96 [NCH(C₇H₇)CO], 97.99, 98.25 (4,5-C₇H₇), 100.90, 101.17 (3,6-C₇H₇), 125.67, 128.17, 129.12, 133.29 (C₆H₅), 162.42 [OC(C₆H₅)N], 175.00 [NCH(C₇H₇)COO].

10: 500 mg (1.59 mmol) of [(C₇H₇)Cr(CO)₃]BF₄, 279 mg (1.59 mmol) of 4-methyl-2-phenyl-5(4*H*)-oxazolone and 222 µl (1.59 mmol) of NEt₃ were used. – IR (KBr): $\tilde{\nu}$ = 1980 cm^{–1} s, 1915 s, 1887 s (Cr–CO), 1806 s (C=O), 1651 s (C=N). – ¹H NMR (400 MHz, CDCl₃): δ = 1.24 [s, 3 *H*, NCCH₃(C₇H₇)CO], 3.43 (2-C₇H₇), 3.67 (7-C₇H₇), 3.69 (1-C₇H₇), 4.73 (3-C₇H₇), 5.01 (6-C₇H₇), 5.84 (4-C₇H₇), 6.04 (5-C₇H₇) (each pseudo-t, ³*J* ≈ 8 Hz), 7.47 (BB', 2 *H*, 3,5-C₆H₅), 7.57 (A, 1 *H*, 4-C₆H₅), 7.88 (CC', 2 *H*, 2,6-C₆H₅). – ¹³C-NMR (100.4 MHz, CDCl₃): δ = 18.63 (CH₃), 45.93 (1-C₇H₇), 62.79, 63.62 (2,7-C₇H₇), 76.19 [NC(CH₃)(C₇H₇)CO], 97.34, 98.01 (4,5-C₇H₇), 102.33, 102.47 (3,6-C₇H₇), 125.68, 128.24, 129.15, 133.14 (C₆H₅), 160.00 [OC(C₆H₅)N], 178.69 [NC(CH₃)(C₇H₇)COO]. – C₂₀H₁₅CrNO₅ (401.3): calcd. C 59.86, H 3.77, N 3.49; found C 59.42, H 3.96, N 3.29.

11: 200 mg (0.64 mmol) of $[(C_7H_7)Cr(CO)_3]BF_4$, 50 mg (0.31 mmol) of 2-phenyl-5(4*H*)-oxazolone and 86.5 μ l (0.62 mmol) of NEt_3 were used. – IR (KBr): $\tilde{\nu}$ = 1980 cm^{-1} s, 1915 s, 1887 s (Cr–CO), 1807 s (C=O), 1651 s (C=N). – 1H NMR (400 MHz, $CDCl_3$): δ = 3.32 (2- C_7H_7), 3.49 (7- C_7H_7), 3.69 (1- C_7H_7), 4.77 (3- C_7H_7), 4.85 (6- C_7H_7), 5.85 (4- C_7H_7), 5.96 (5- C_7H_7) (each pseudo-t, $^3J \approx 8$ Hz), 7.49 (BB', 2 H, 3,5- C_6H_5), 7.58 (A, 1 H, 4- C_6H_5), 7.77 (CC', 2 H, 2,6- C_6H_5). – ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 40.32 (1- C_7H_7), 61.46, 63.30 (2,7- C_7H_7), 85.49 $[NC(C_7H_7)_2CO]$, 97.57, 98.05 (4,5- C_7H_7), 101.93, 102.42 (3,6- C_7H_7), 125.22, 128.19, 129.12, 133.34 (C_6H_5), 160.45 $[OC(C_6H_5)N]$, 175.08 $[NC(C_7H_7)_2COO]$. – $C_{29}H_{19}Cr_2NO_8$ (613.5): calcd. C 56.78, H 3.12, N 2.28; found C 56.03, H 3.45, N 2.19.

General Procedure for the Preparation of 12–14: To a mixture of **1** or **2** respectively, α -amino acid ester hydrochloride and about 2 mg of DMAP in 10 ml of CH_2Cl_2 69.6 μ l (0.5 mmol) of NEt_3 was added. After stirring for about 20 h, the solvent was removed in vacuo. The residue was washed twice with 5 ml of water and dried in vacuo at 60°C for 5 h.

12: 268 mg (0.5 mmol) of **1** and 70 mg (0.5 mmol) of L-alanine methyl ester hydrochloride were used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1745 cm^{-1} w ($COOCH_3$), 1628 m (free C=O), 1592 m (coord. C=O); (PE): $\tilde{\nu}$ = 286 cm^{-1} w (M–Cl). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.20–1.80 [m, 21 H, $C_5(CH_3)_5$ and 2 $\times$ CH_3], 3.75 (m, 3 H, $COOCH_3$), 4.49 [m, 1 H, $NHCH(CH_3)COOCH_3$], 4.68 [m, 1 H, $NHCH(CH_3)CONH$], 6.95 (m, 1 H, C_6H_4), 7.27 (m, 1 H, C_6H_4), 7.42 (m, 1 H, C_6H_4), 7.75 (m, 1 H, C_6H_4). – $C_{24}H_{32}ClIrN_2O_4$ (639.7): calcd. C 45.02, H 5.00, N 4.37; found C 44.95, H 5.08, N 4.63.

13: 268 mg (0.5 mmol) of **1** and 70 mg (0.5 mmol) of glycine ethyl ester hydrochloride were used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1752 cm^{-1} s ($COOEt$), 1655 m (free C=O), 1593 m (coord. C=O); (PE): $\tilde{\nu}$ = 283 cm^{-1} w (M–Cl). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.24 (m, 3 H, $COOCH_2CH_3$), 1.48 [m, 3 H, $NHCH(CH_3)CONH$], 1.68 [m, 15 H, $C_5(CH_3)_5$], 3.80 (m, 1 H, $NHCHH'COOEt$), 3.95 (m, 1 H, $NHCHH'COOEt$), 4.14 (m, 2 H, $COOCH_2CH_3$), 4.64 [m, 1 H, $NHCH(CH_3)CONH$], 6.92 (m, 1 H, C_6H_4), 7.26 (m, 1 H, C_6H_4), 7.52 (m, 1 H, C_6H_4), 7.75 (m, 1 H, C_6H_4). – $C_{24}H_{32}ClIrN_2O_4$ (639.7): calcd. C 45.02, H 5.00, N 4.37; found C 44.14, H 5.02, N 4.67.

14: 328 mg (0.5 mmol) of **2** and 70 mg (0.5 mmol) of glycine ethyl ester hydrochloride were used. Yellow powder. – IR (KBr): $\tilde{\nu}$ = 1743 cm^{-1} m ($COOEt$), 1670 m (free C=O), 1592 s (coord. C=O); (PE): $\tilde{\nu}$ = 282 cm^{-1} w (M–Cl). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.21 (m, 3 H, $COOCH_2CH_3$), 1.65 [m, 15 H, $C_5(CH_3)_5$], 3.27 (m, 2 H, $NHCH_2COOEt$), 4.14 (m, 2 H, $COOCH_2CH_3$), 4.77 [m, 1 H, $NHCH(CH_2Ph)CONH$], 6.94 (m, 1 H, C_6H_4), 7.31 (m, 1 H, C_6H_4), 7.59 (m, 1 H, C_6H_4), 7.75 (m, 1 H, C_6H_4). – $C_{30}H_{36}ClIrN_2O_4$ (716.3): calcd. C 50.30, H 5.07, N 3.91; found C 51.05, H 5.23, N 4.55.

General Procedure for the Preparation of 15–18: Equimolar amounts of **6**, α -amino acid methyl ester hydrochloride and NEt_3 were stirred in about 20 ml of CH_2Cl_2 at room temp. for a few days (see below). The solvent was removed in vacuo, and the residue was taken up in Et_2O . Insoluble $HNEt_3BF_4$ was centrifuged off. The yellow solution was filtered through Celite, concentrated in vacuo to about 1 ml and added to excess pentane. The colourless precipitate was collected, washed once with pentane and dried in vacuo for a few days.

15: 59 mg (0.155 mmol) of **6**, 20 mg (0.159 mmol) of glycine methyl ester hydrochloride and 22.2 μ l (0.159 mmol) of NEt_3 were

used and stirred for 7 d. – IR (KBr): $\tilde{\nu}$ = 3283 cm^{-1} m br. (N–H), 2047 s (Fe–CO), 1975 s br. (Fe–CO), 1755 s ($COOCH_3$), 1637 s/1661 s (CONH-I), 1531 s/1550 s (CONH-II). – 1H NMR (400 MHz, $CDCl_3$): δ = 1.52/1.48 (each dm, 1 $H/1$ H, $^2J_{endo}$ = 14.5 Hz, 6*exo*- C_6H_7), 1.97/2.04 (each ddd, 1 $H/1$ H, $^2J_{exo}$ = 15.0 Hz, 3J_1 = 11.0 Hz, 3J_5 = 5.0 Hz, 6*endo*- C_6H_7), 2.68/2.73 (each dddd, 1 $H/1$ H, $^3J_{endo}$ = 10.6 Hz, 3J_7 = 6.9 Hz, 3J_2 = $^3J_{exo}$ = 3.5 Hz, 1- C_6H_7), 3.04 (m, 2 $H/2$ H, 2,5- C_6H_7), 3.72 (s, 1 $H/1$ H, OCH_3), 3.92/3.97 (each t, 1 $H/1$ H, $^3J_{CHH'}$ = 5.2, $CONHCH_2COOCH_3$), 4.00, 4.05 (each dd, 1 H, 1 H, 2J = 20.9 Hz, $^3J_{NH}$ = 5.4 Hz, $NHCHH'COOCH_3$), 4.06, 4.16 (each dd, 1 H, 1 H, 2J = 27.0 Hz, $^3J_{NH}$ = 5.4 Hz, $NHCHH'COOCH_3$), 4.45/4.51 [each dd, 1 $H/1$ H, $^3J_{NH}$ = 8.4 Hz, 3J_1 = 6.9 Hz, $CH(C_6H_7)CONH$], 5.32 (m, 2 H, 3,4- C_6H_7), 5.36 (dd, 1 H, 3J_2 = 3J_4 = 4.8 Hz, 3- C_6H_7), 5.41 (dd, 1 H, 3J_3 = 3J_5 = 4.7 Hz, 4- C_6H_7), 6.82/6.90 (each d, 1 $H/1$ H, $^3J_{CH}$ = 5.2 Hz, $CHNHCOPh$), 7.40–7.53 (ABB', 3 $H/3$ H, 3,4,5- C_6H_5), 7.76–7.82 (CC', 2 $H/2$ H, 2,6- C_6H_5). – ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.93/27.98 (6- C_6H_7), 40.47/41.37 (1- C_6H_7), 57.86/58.43, 59.27/61.17 (2,5- C_6H_7), 59.79 ($NHCH_2COOCH_3$), 85.51/85.19, 85.99/86.27 (3,4- C_6H_7), 128.96, 132.27, 134.02, 127.39, 129.02, 132.37, 133.81 (C_6H_5), 167.72, 171.36, 167.74, 170.15, 171.31 ($COOCH_3$, $PhCONH$, $CONH$), 211.69 (Fe–CO). Diastereomeric ratio 1.0:1.15. – $C_{21}H_{20}FeN_2O_7$ (468.2): calcd. C 53.87, H 4.31, N 5.98; found C 54.22, H 4.74, N 5.81.

16: 100 mg (0.264 mmol) of **6**, 58 mg (0.269 mmol) of phenylalanine methyl ester hydrochloride and 37.5 μ l (0.269 mmol) of NEt_3 were used and stirred for 3 d. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3396 cm^{-1} m br., 3286 s br. (N–H), 2045 s (Fe–CO), 1967 s br. (Fe–CO), 1747 s ($COOCH_3$), 1636 s (CONH-I), 1534 s (CONH-II). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.39 (m, 1 H, 6*exo*- C_6H_7), 1.95 (m, 1 H, 6*endo*- C_6H_7), 2.59 (m, 1 H, 1- C_6H_7), 2.85–3.22 (m, 4 H, 2,5- C_6H_7 , $PhCH_2$), 3.69, 3.71, 3.72, 3.73 (4 s, 3 H, OCH_3), 4.29–4.55 (m, 1 H, $PhCONHCH$), 4.85 [m, 1 H, $CONHCH(CH_2Ph)$], 5.32 (m, 2 H, 3,4- C_6H_7), 6.50 (m, 2 H, 2 NH), 7.02–7.19 (m, 5 H, $CH_2C_6H_5$), 7.42–7.55 (m, 3 H, 3,4,5- C_6H_5), 7.72–7.79 (m, 2 H, 2,6- C_6H_5). – $C_{28}H_{26}FeN_2O_7$ (558.4): calcd. C 60.23, H 4.69, N 5.02; found C 60.59, H 5.17, N 5.15.

17: 100 mg (0.264 mmol) of **6**, 54 mg (0.270 mmol) of methionine methyl ester hydrochloride and 37.6 μ l (0.270 mmol) of NEt_3 were used and stirred for 7 d. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} s br., 3290 s br. (N–H), 2044 s (Fe–CO), 1970 s br. (Fe–CO), 1745 s ($COOCH_3$), 1636 s (CONH-I), 1535 s (CONH-II). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.46 (m, 1 H, 6*exo*- C_6H_7), 1.88–2.20 (m, ca. 3 H, 6*endo*- C_6H_7 , CH_2), 1.99, 2.01, 2.04, 2.05 (4 s, 3 H, SCH_3), 2.48 (m, 2 H, CH_2), 2.70 (m, 1 H, 1- C_6H_7), 3.03 (m, 2 H, 2,5- C_6H_7), 3.68, 3.69, 3.75, 3.76 (4 s, 3 H, OCH_3), 4.40–4.69 [m, 2 H, $PhCONHCH$, $CONHCH(R)$], 5.36 (m, 2 H, 3,4- C_6H_7), 6.67–7.08 (m, 2 H, 2 NH), 7.39–7.56 (m, 3 H, 3,4,5- C_6H_5), 7.75–7.83 (m, 2 H, 2,6- C_6H_5). – $C_{24}H_{26}FeN_2O_7S$ (542.4): calcd. C 53.15, H 4.83, N 5.16; found C 52.65, H 4.51, N 5.36.

18: 100 mg (0.264 mmol) of **6**, 57 mg (0.269 mmol) of glutamic acid dimethyl ester hydrochloride and 37.5 μ l (0.269 mmol) of NEt_3 were used and stirred for 7 d. The product precipitated from the concentrated ether solution without adding pentane. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} s br., 3287 s br. (N–H), 2045 s (Fe–CO), 1970 s br. (Fe–CO), 1741 s ($COOCH_3$), 1637 s (CONH-I), 1535 s (CONH-II). – 1H NMR (270 MHz, $CDCl_3$): δ = 1.46 (m, 1 H, 6*exo*- C_6H_7), 1.99 (m, 2 H, CH_2), 2.18 (m, 1 H, 6*endo*- C_6H_7), 2.38 (m, 2 H, CH_2), 2.71 (m, 1 H, 1- C_6H_7), 3.00 (m, 2 H, 2,5- C_6H_7), 3.60, 3.61, 3.62, 3.63, 3.67, 3.68, 3.73, 3.74 (8 s, 6 H, 2 OCH_3), 4.50 [m, 2 H, $PhCONHCH$, $CONHCH(R)$], 5.36 (m, 2 H, 3,4- C_6H_7), 6.65–7.17 (m, 2 H, 2 NH), 7.42–7.56 (m, 3 H,

3,4,5-C₆H₅), 7.75–7.84 (m, 2 H, 2,6-C₆H₅). – C₂₅H₂₆FeN₂O₉ (554.3): calcd. C 54.17, H 4.73, N 5.05; found C 53.95, H 4.38, N 5.28.

General Procedure for the Preparation of 19–22: To a solution of **15–18** in 10 ml of ethanol/water (4:1) a slight excess of NaOH (0.1 N) was slowly added. After stirring for a few hours, an equimolar amount of HCl (0.1 N) was added and after 30 min of further stirring the solvents were removed under reduced pressure. The residue was taken up in Et₂O/THF (1:1) (**19**), Et₂O/acetone (10:1) (**22**), or Et₂O (**20**, **21**) and filtered through Celite to remove NaCl. After concentrating in vacuo, the solution was added to excess pentane to precipitate the colourless product which was collected, washed once with pentane and dried in vacuo at 50°C for a few days.

19: 43 mg (0.092 mmol) of **15**, 0.93 ml of 0.1 N NaOH and 0.93 ml of 0.1 N HCl were used. – IR (KBr): $\tilde{\nu}$ = 3407 cm^{−1} m br., 3305 s br. (O–H, N–H), 2046 s (Fe–CO), 1793 s br. (Fe–CO), 1729 s (COOH), 1637 s (CONH-I), 1535 s (CONH-II). – ¹H NMR (400 MHz, [D₆]acetone): δ = 1.60 (m, 1 H, 6*exo*-C₆H₇), ca. 2.00 (m, 6*endo*-C₆H₇), 2.80 (m, 1 H, 1-C₆H₇), 3.27 (m, 2 H, 2,5-C₆H₇), 3.96 (m, 2 H, CH₂), 4.48 (m, 1 H, PhCONHCH), 5.61 (m, 2 H, 3,4-C₆H₇), 7.42–7.58 (m, 3 H, 3,4,5-C₆H₅), 7.88–8.00 (m, 2 H, 2,6-C₆H₅), 9.96 (s, 1 H, COOH). – C₂₀H₁₈FeN₂O₇ (454.2): calcd. C 52.89, H 3.99, N 6.17; found C 52.44, H 3.90, N 6.16.

20: 70 mg (0.125 mmol) of **16**, 1.3 ml of 0.1 N NaOH and 1.3 ml of 0.1 N HCl were used. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3428 cm^{−1} s br. (O–H, N–H), 2045 s (Fe–CO), 1970 s br. (Fe–CO), 1729 s (COOH), 1641 s (CONH-I), 1523 s (CONH-II). – ¹H NMR (270 MHz, CDCl₃): δ = 1.34 (m, 1 H, 6*exo*-C₆H₇), 1.91 (m, 1 H, 6*endo*-C₆H₇), 2.37–3.33 (m, 5 H, CH₂, 1-C₆H₇, 2,5-C₆H₇), 3.63, 4.38 (2 m, 1 H, PhCONHCH), 4.78 [m, 1 H, CONHCH(CH₂Ph)], 5.28 (m, 2 H, 3,4-C₆H₇), 6.72 (m, 1 H, NH), 6.96–7.60 (m, 9 H, NH, CH₂C₆H₅, 3,4,5-C₆H₅), 7.66–7.86 (m, 2 H, 2,6-C₆H₅). – C₂₇H₂₄FeN₂O₇ (544.3): calcd. C 59.58, H 4.44, N 5.15; found C 59.59, H 4.61, N 5.19.

21: 51 mg (0.094 mmol) of **17**, 0.98 ml of 0.1 N NaOH and 0.98 ml of 0.1 N HCl were used. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3403 cm^{−1} m br., 3300 s br. (O–H, N–H), 2047 s (Fe–CO), 1970 s br. (Fe–CO), 1723 s (COOH), 1636 s (CONH-I), 1532 s (CONH-II). – ¹H NMR (400 MHz, [D₆]acetone): δ = 1.60 (m, 1 H, 6*exo*-C₆H₇), ca. 2.00 (m, 6*endo*-C₆H₇, CH₂, SCH₃), 2.56 (m, 2 H, CH₂), 2.78 (m, 1 H, 1-C₆H₇), 3.24 (m, 2 H, 2,5-C₆H₇), 4.38–4.64 [m, 2 H, PhCONHCH, CONHCH(CH₂Ph)], 5.57 (m, 2 H, 3,4-C₆H₇), 7.43–7.57 (m, 3 H, 3,4,5-C₆H₅), 7.88–7.95 (m, 2 H, 2,6-C₆H₅). – C₂₃H₂₄FeN₂O₇S (528.4): calcd. C 52.29, H 4.58, N 5.30; found C 52.73, H 4.70, N 5.27.

22: 95 mg (0.171 mmol) of **18**, 3.5 ml of 0.1 N NaOH and 3.5 ml of 0.1 N HCl were used. Four stereoisomers. – IR (KBr): $\tilde{\nu}$ = 3429 cm^{−1} s br. (O–H, N–H), 2047 s (Fe–CO), 1971 s br. (Fe–CO), 1723 s, 1720 s (2 COOH), 1644 s (CONH-I), 1527 s (CONH-II). – ¹H NMR (270 MHz, [D₆]acetone): δ = 1.59 (m, 1 H, 6*exo*-C₆H₇), ca. 2.00 (m, 6*endo*-C₆H₇, CH₂), 2.42 (m, 2 H, CH₂), 2.84 (m, 1 H, 1-C₆H₇), 3.20 (m, 2 H, 2,5-C₆H₇), 4.50 [m, 2 H, PhCONHCH, CONHCH(CH₂Ph)], 5.54 (m, 2 H, 3,4-C₆H₇), 7.41–7.62 (m, 3 H, 3,4,5-C₆H₅), 7.87–7.95 (m, 2 H, 2,6-C₆H₅). – C₂₃H₂₂FeN₂O₉ (526.3): calcd. C 52.49, H 4.21, N 5.32; found C 52.33, H 3.94, N 5.04.

General Procedure for the Preparation of 23–25: To a solution of (COD)PtCl₂ in 10 ml of CH₂Cl₂ two equiv. of PPh₃, one equivalent of **19–21** and a slight excess of Ag₂O were added. This mixture was refluxed in the dark for 6 h and then, after cooling to room

temp., filtered through Celite. The solvent was evaporated and the residue dried in vacuo for 2 h. After dissolving in 1 ml of CH₂Cl₂, petroleum ether was added to precipitate the colourless product which was washed with petroleum ether and dried in vacuo at room temp. for several days.

23: 9 mg (0.024 mmol) of (COD)PtCl₂, 11 mg (0.024 mmol) of **19**, 13 mg (0.05 mmol) of PPh₃ and 12 mg (0.052 mmol) of Ag₂O were used. – IR (KBr): $\tilde{\nu}$ = 3410 cm^{−1} s br. (N–H), 2042 s (Fe–CO), 1965 s br. (Fe–CO), 1653 s br. (coord. COO, CONH-I), 1512 s (CONH-II). – ¹H NMR (270 MHz, CDCl₃): δ = 1.55 (m, 1 H, 6*exo*-C₆H₇), 1.98 (m, 6*endo*-C₆H₇), 2.60 (m, 1 H, 1-C₆H₇), 3.05 (m, 4 H, 2,5-C₆H₇, NCH₂COO), 4.40 [m, 1 H, NHCH(C₆H₇)CON], 5.35 (m, 2 H, 3,4-C₆H₇), 6.99–7.82 (m, 35 H, 7 C₆H₅). – ³¹P NMR: δ = 2.97 (d, ²J_{P-P} = 18.6 Hz, ¹J_{P-Pt} = 3665 Hz, P *trans* to O), 4.08 (d, ²J_{P-P} = 23.1 Hz, ¹J_{P-Pt} could not be determined, P *trans* to O), 10.36 (d, ²J_{P-P} = 23.1 Hz, ¹J_{P-Pt} could not be determined, P *trans* to N), 18.61 (d, ²J_{P-P} = 18.6 Hz, ¹J_{P-Pt} = 3921 Hz, P *trans* to N). Diastereomeric ratio 6:1. – C₅₆H₄₆FeN₂O₇P₂Pt × 0.5 CH₂Cl₂ (1214.3): calcd. C 55.89, H 3.90, N 2.31; found C 55.16, H 3.90, N 2.32.

24: 16 mg (0.043 mmol) of (COD)PtCl₂, 23 mg (0.042 mmol) of **20**, 22 mg (0.084 mmol) of PPh₃ and 20 mg (0.086 mmol) of Ag₂O were used. – IR (KBr): $\tilde{\nu}$ = 3430 cm^{−1} m br. (N–H), 2042 s (Fe–CO), 1967 s br. (Fe–CO), 1653 s br. (coord. COO, CONH-I), 1509 s (CONH-II). – ¹H NMR (270 MHz, CDCl₃): δ = 1.48 (m, 1 H, 6*exo*-C₆H₇), 1.85 (m, 6*endo*-C₆H₇), 2.24 (m, 1 H, 1-C₆H₇), 2.90 (m, 4 H, 2,5-C₆H₇, CH₂Ph), 3.72 [m, 1 H, NCH(CH₂Ph)COO], 4.30 [m, 1 H, NHCH(C₆H₇)CON], 5.25 (m, 2 H, 3,4-C₆H₇), 6.78–7.82 (m, 40 H, 8 C₆H₅). – ³¹P NMR: δ = 2.85, 2.87, 2.92, 2.98 (each d, ²J_{P-P} = 18.9 Hz, ¹J_{P-Pt} = 3669 Hz, P *trans* to O), 18.33, 18.36, 18.38, 18.41 (each d, ²J_{P-P} = 18.3 Hz, ¹J_{P-Pt} = 3893 Hz, P *trans* to N). Diastereomeric ratio about 1:1:1.5:1.5. – C₆₃H₅₂FeN₂O₇P₂Pt × 0.5 CH₂Cl₂ (1304.5): calcd. C 58.01, H 4.02, N 2.15; found C 57.78, H 4.33, N 2.04.

25: 13.5 mg (0.036 mmol) of (COD)PtCl₂, 19 mg (0.036 mmol) of **21**, 18.9 mg (0.072 mmol) of PPh₃ and 18 mg (0.078 mmol) of Ag₂O were used. – IR (KBr): $\tilde{\nu}$ = 3415 cm^{−1} s br. (N–H), 2042 s (Fe–CO), 1967 s br. (Fe–CO), 1652 s br. (coord. COO, CONH-I), 1512 s (CONH-II). – ¹H NMR (270 MHz, CDCl₃): δ = 1.52 (m, 1 H, 6*exo*-C₆H₇), 1.85 (m, 6*endo*-C₆H₇, CH₂), 1.94, 2.01, 2.03 [each s, together 3 H, SCH₃ (1:1:2)], 2.50 (m, 3 H, 1-C₆H₇, CH₂), 2.98 (m, 2 H, 2,5-C₆H₇), 3.52, 3.74 [each m, together 1 H, NCH(CH₂CH₂SCH₃)COO], 4.40 [m, 1 H, NHCH(C₆H₇)CON], 5.31 (m, 2 H, 3,4-C₆H₇), 7.08–7.89 (m, 35 H, 7 C₆H₅). – ³¹P NMR: δ = 2.79, 2.80, 2.91, 2.97 (each d, ²J_{P-P} = 19.2 Hz, ¹J_{P-Pt} = 3690 Hz, P *trans* to O), 18.24, 18.25, 18.34, 18.41 (each d, ²J_{P-P} = 19.2 Hz, ¹J_{P-Pt} = 3881 Hz, P *trans* to N). Diastereomeric ratio about 1:1:1:2. – C₅₉H₅₂FeN₂O₇P₂PtS × CH₂Cl₂ (1330.9): calcd. C 54.15, H 4.09, N 2.11; found C 53.53, H 4.23, N 2.31.

X-ray Diffraction Analyses^[18]: Data collection: Enraf Nonius CAD4 Diffractometer (**4**, **5**), Siemens P4 Diffractometer (**9**, **10**), Mo-K α radiation, λ = 0.71073 Å, graphite monochromator, cell constants from 25 centered reflections, ω -2 θ scan, intensity of three standard reflections checked every 2 h. Structure solution by SHELXS-86 and refinement by SHELXL-93 (G. M. Sheldrick, University of Göttingen, Germany), non-hydrogen atoms refined anisotropically, hydrogen atoms with $U_i = 1.2 \times U_{eq}$ of the adjacent carbon atom (**4**, **5**, **10**). For **9** hydrogen atoms found and refined freely. Full-matrix refinement against F^2 . See Table 1 for crystal data and structure refinement.

Table 1. Crystal data and structure refinement for **4**, **5**, **9** and **10**

Compound number	4 (M1403) ^[a]	5 (M1550)	9	10
Empirical formula	2 × C ₂₉ H ₃₆ Cl ₃ Ir ₂ NO ₂ × 1.5 CH ₂ Cl ₂	C ₁₉ H ₂₁ NO ₁₂ Pd ₃	C ₁₉ H ₁₃ CrNO ₅	C ₂₀ H ₁₅ CrNO ₅
Formula weight	1970.06	774.57	387.30	401.33
<i>T</i> [K]	295(2)	294(2)	293(2)	293(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
Unit-cell dimensions				
<i>a</i> [Å]	18.0641(19)	8.562(3)	31.384(2)	9.0240(10)
<i>b</i> [Å]	17.3233(24)	941.8(3)	6.6040(10)	10.373(3)
<i>c</i> [Å]	21.5724(38)	15.907(4)	16.7890(10)	19.333(5)
α [°]	90	101.72(2)	90	90
β [°]	91.048(11)	92.73(2)	106.92(11)	101.040(10)
γ [°]	90	108.61(2)	90	90
<i>V</i> [Å ³]	6749.5(1.7)	1181.5(6)	3329.1(6)	1776.2(7)
<i>Z</i>	4	2	8	4
Density (calcd.) [g/cm ³]	1.939	2.177	1.546	1.501
μ (Mo- <i>K</i> α) [mm ⁻¹]	8.261	2.323	0.718	0.676
<i>F</i> (000)	3756	752	1584	824
Crystal size [mm]	0.43 × 0.37 × 0.10	0.47 × 0.27 × 0.07	0.55 × 0.23 × 0.08	0.05 × 0.10 × 0.38
2 θ range [°]	4.96–48.02	4.68–47.94	5–50	4.3–50
Index ranges	$\pm h + k + l$	$-h \pm k \pm l$	$+h + k \pm l$	$+h + k \pm l$ and $-h - k \pm l$
Reflections collected	10544	3978	3680	6657
Independent reflections	10253 [<i>R</i> (int) = 0.0447]	3693 [<i>R</i> (int) = 0.0171]	2921 [<i>R</i> (int) = 0.0372]	3133 [<i>R</i> (int) = 0.1596]
Absorption correction	ψ scan	ψ scan	ψ scan	N/A
Max. and min. transmission	0.991 and 0.240	0.998 and 0.683	0.238 and 0.209	
Data/parameters	7643/798	3239/321	2921/274	3133/244
Goodness-of-fit on <i>F</i> ²	1.076	1.079	1.038	0.990
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0451, <i>wR</i> 2 = 0.1077	<i>R</i> 1 = 0.0247, <i>wR</i> 2 = 0.0640	<i>R</i> 1 = 0.0434, <i>wR</i> 2 = 0.0783	<i>R</i> 1 = 0.0753, <i>wR</i> 2 = 0.1057
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0685, <i>wR</i> 2 = 0.1260	<i>R</i> 1 = 0.0309, <i>wR</i> 2 = 0.0686	<i>R</i> 1 = 0.0847, <i>wR</i> 2 = 0.0933	<i>R</i> 1 = 0.1961, <i>wR</i> 2 = 0.1412
Largest diff. peak and hole [e Å ⁻³]	1.639 and –1.381	0.557 and –0.539	0.212 and –0.273	0.374 and –0.401

^[a] Two independent molecules, 1.5 CH₂Cl₂ disordered, split, Cp* disordered, not split.

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