Metal Complexes of Biologically Important Ligands, CII[◇]

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, CH_2Ph, CHMeEt) with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ afforded the cyclometallated complexes $(\eta^5\text{-}C_5Me_5)(Cl)Ir(L)$ (**1**−**3**) [L = 2-phenyl-4-R-5(4*H*)-oxazolone(*C-o,N*)]. 2-Phenyl-5(4*H*)-oxazolone reacts with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ and palladium(II) acetate to give complexes with a *C-o,N*-bridging oxazolone $[(\eta^5\text{-}C_5Me_5)(Cl)Ir]_2(\mu\text{-}Cl)(\mu\text{-L-H}^+)$ (**4**) and $Pd_3(\mu\text{-ac})_5(\mu\text{-L-H}^+)$ (**5**). 2-Phenyloxazolone anions were added to the π ligands of $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ and $[(\eta^7\text{-}C_7H_7)Cr(CO)_3]^+$ to give the adducts **6**−**11**. Dipeptide derivatives **12**−**18** were obtained by reaction of **1**, **2** and by reaction of the adduct **6** from $[(\eta^5\text{-}C_6H_7)Fe(CO)_3]^+$ 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 $(Ph_3P)_2PtCl_2$ 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].

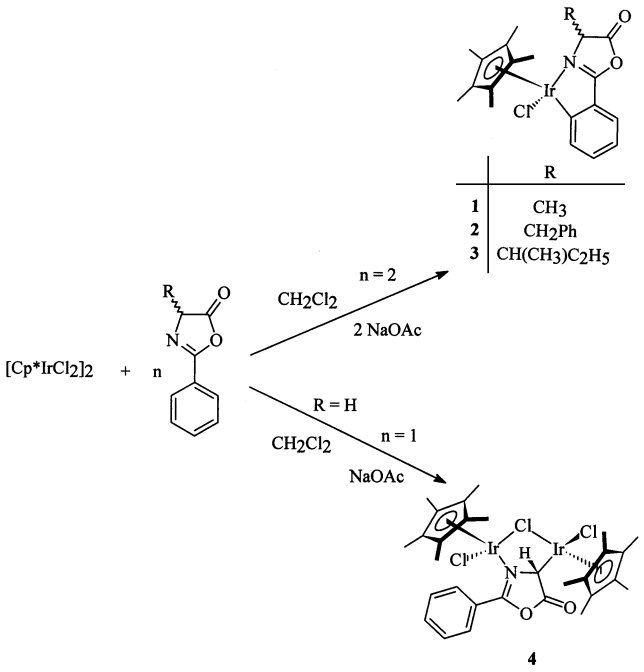
Results and Discussion

1. Cyclometallated Complexes

The reaction of the chloro-bridged iridium(III) complex $[Cp^*IrCl_2]_2$ 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 ^{1}H-NMR signals of the C_5Me_5 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 arrangment of the other four atoms. The ^{1}H-NMR spectrum of **4** exhibits only

[◇] Part CI: Ref.[1].

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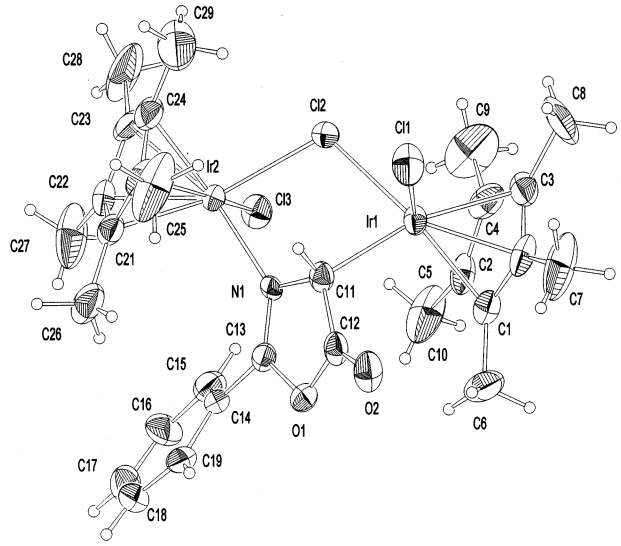
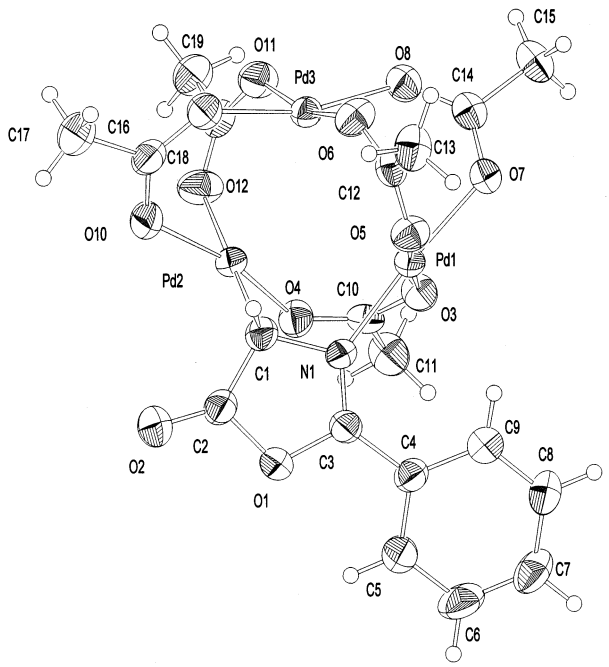
Figure 1. Molecular structure of **4**[a] in the crystal



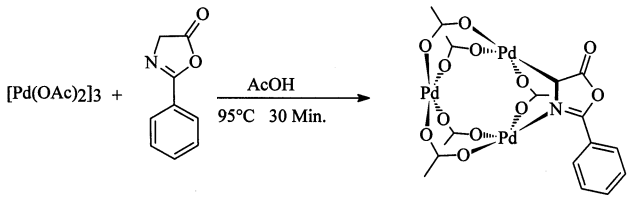
[a] Selected bond lengths [Å] and angles [°]: Ir2−N1 2.117(9), Ir1−C11 2.152(12), N1−C13 1.29(2), N1−C11 1.461(14), C11−C12 1.44(2), Ir2−Cl2 2.446(3), Ir1−Cl2 2.436(3); N1−Ir2−Cl2 82.7(2), C11−Ir1−Cl2 80.4(3), C13−N1−C11 106.4(10), N1−Ir2−Cl2−Ir1 3.53(0.27), Cl2−Ir2−N1−C11 37.00(0.72), C11−Ir1−Cl2−Ir2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

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



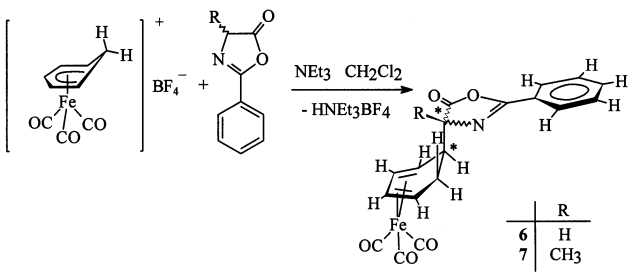
[a] Selected bond lengths [Å] and angles [°]: Pd3−O8 1.995(3), Pd3−O11 2.002(3), Pd2−O12 2.087(3), Pd2−O10 2.019(3), Pd2−C1 2.025(4), Pd1−N1 2.003(3), Pd1−O7 2.015(3), Pd1−O5 2.005(3); O11−Pd3−O6 166.40(13), O12−Pd2−C1 179.57(15), O7−Pd1−N1 175.47(13), O10−Pd2−O4 166.48(12).

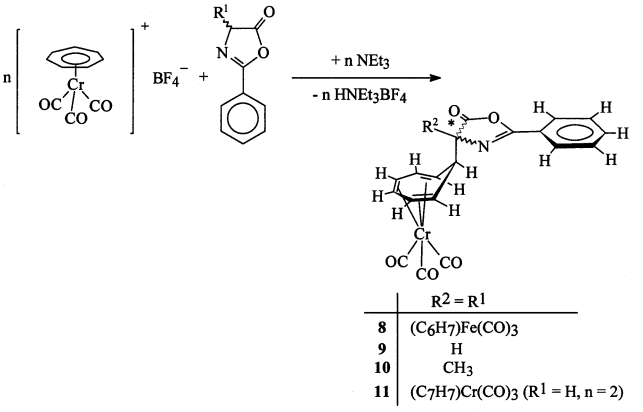
two C_5Me_5 signals which implicates that only one diastereoisomer is formed. The same bridging occurs in the trinuclear palladium complex **5** which was obtained from Pd^{II} acetate and 2-phenyl-5(4*H*)-oxazolone. In **5** one acetate bridge of Pd_3ac_6[8] is substituted by a *C-o,N*-bridging 2-phenyloxazolone.



5

The molecular structure of **5** is very similar to that of Pd_3ac_6[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.





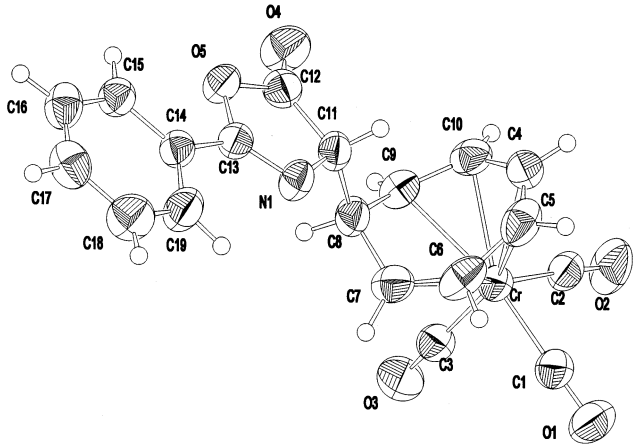
2. Addition of the 2-Phenyloxazolone Anion to Unsaturated Hydrocarbons of Cationic Complexes

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 ^{1}H- and ^{13}C-NMR spectra. For almost all atoms two sets of signals are observed. Interestingly, for **8** one diastereoisomer is formed in high excess. In the ^{1}H-NMR spectrum only some weak signals can be assigned to the second isomer; *exo* addition is proven for **6** and **7** by the signals of

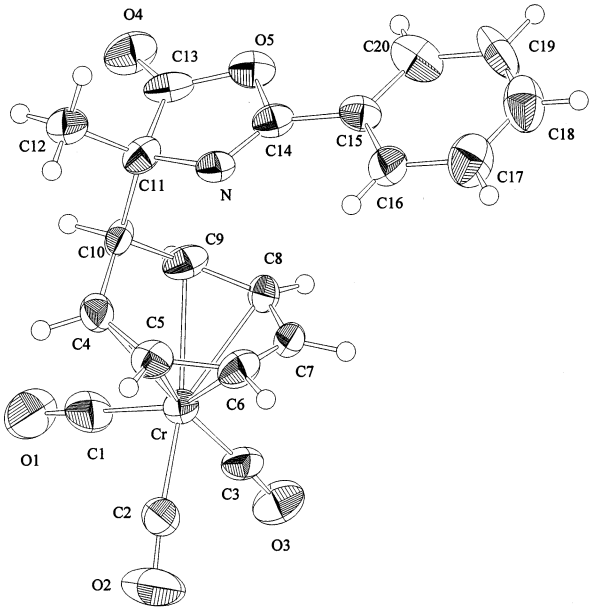
the $CH-CH_2$ group and for **9** and **10** by X-ray structure determination.

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

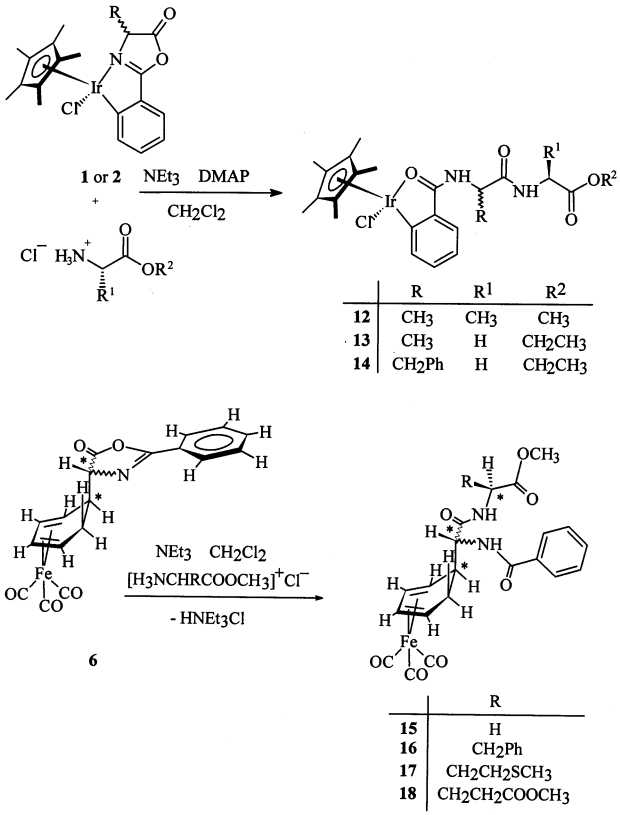


[a] Selected bond lengths [Å] and angles [°]:Cr−C1 1.840(9), Cr−C2 1.867(8), Cr−C3 1.840(8), C1−O1 1.164(8), Cr−C6 2.175(7), Cr−C5 2.228(7), Cr−C4 2.352(7), C10−C11 1.560(9), C14−N 1.255(8), C15−C14 1.459(10); O5−C14−N 116.3(7), C15−C14−N 129.8(7), O4−C13−O5 121.6(7).

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**.

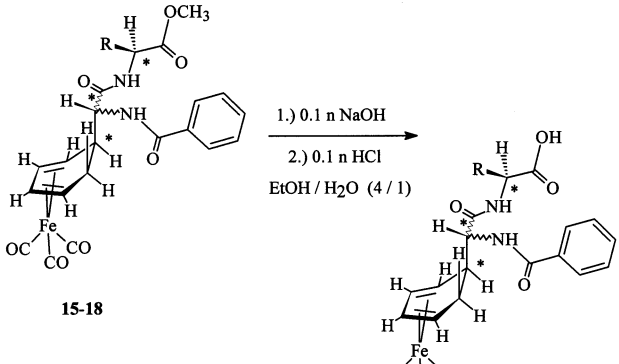
The shift of the carbonyl IR absorption to lower wavenumbers (ca. 1590 cm^{-1}) in **12**−**14** is characteristic for coordination of the CO function[11]. The two stereogenic centers of **15** give rise to two diastereoisomers (1:1.2), whereas four diastereoisomers of **16**−**18** (1:1:1.2:1.2) (from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



	R	R^1	R^2
12	CH_3	CH_3	CH_3
13	CH_3	H	CH_2CH_3
14	CH_2Ph	H	CH_2CH_3

	R
15	H
16	CH_2Ph
17	$CH_2CH_2SCH_3$
18	$CH_2CH_2COOCH_3$

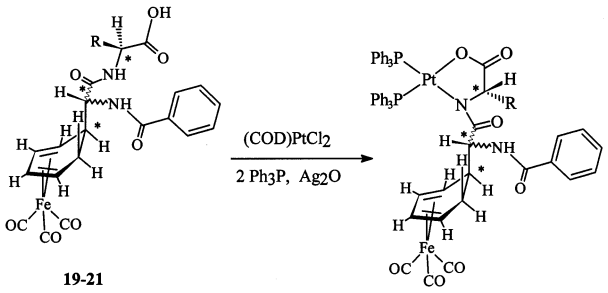
stereogenic centers) were observed in their ^{1}H-NMR spectra (from the methoxy signals). Saponification of **15**−**18** could be accomplished to give the free acids **19**−**22**.



	R
19	H
20	CH_2Ph
21	$CH_2CH_2SCH_3$
22	CH_2CH_2COOH

Compounds **19**−**22** were used as dianionic chelate ligands (deprotonation of the amide and carboxylic group) towards $(Ph_3P)_2PtCl_2$ 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.



19-21

	R
23	H
24	CH_2Ph
25	$CH_2CH_2SCH_3$

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 ($[Cp^*IrCl_2]_2$[13], $[(C_6H_7)Fe(CO)_3]BF_4$[14], $[(C_7H_7)Cr(CO)_3]BF_4$[15], $(COD)PtCl_2$[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 $KMnO_4$ 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 CH_2Cl_2 a deep red solution of 319 mg (0.4 mmol) of $[Cp^*IrCl_2]_2$ 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 Et_2O 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, $CDCL_3$): δ = 1.66 (d, ^3J = 7.5 Hz, 3 H, CH_3), 1.76/*1.82* [each s, 15H 5:*1*, $C_5(CH_3)_5$], 4.43 (q, ^3J = 7.5 Hz, 1 H, C*H*CH_3), 7.04 (m, 1 H, C_6H_4), 7.27 (m, 1 H, C_6H_4), 7.53 (m, 1 H, C_6H_4), 7.82 (m, 1 H, C_6H_4). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 9.44/9.94 [$C_5(CH_3)_5$], 15.97 (CH_3), 58.86 (*C*HCH_3), 88.53/89.27 [$C_5(CH_3)_5$], 122.53, 127.63, 128.84, 134.05, 135.85 (C_6H_4), 166.37 (OC=N), 174.91 (Ir−C), 177.94 (C=O). − $C_{20}H_{23}ClIrNO_2$ (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, $CDCl_3$): δ = 1.79/*1.83* [each s, 15H 20:*1*, $C_5(CH_3)_5$], 3.06 (dd, ^2J = 15.0 Hz, ^3J = 10.7 Hz, 1 H, C*H*H′), 3.64 (dd, ^2J = 15.0 Hz, ^3J = 4.6 Hz, 1 H, CH*H*′), 4.60 (dd, ^3J = 4.6 Hz, ^3J = 10.6 Hz, 1 H, C*H*CH_2Ph), 7.07 (m, 1 H, C_6H_4), 7.32 (m, 6 H, C_6H_4 and C_6H_5), 7.55 (m, 1 H, C_6H_4), 7.84 (m, 1 H, C_6H_4). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 9.30/9.40 [$C_5(CH_3)_5$], 36.80 (*C*H_2Ph), 62.20 (*C*HCH_2Ph), 88.40/86.20 [$C_5(CH_3)_5$], 122.30, 127.40, 127.50, 128.50, 128.70, 129.40, 133.90, 134.70, 135.60 (C_6H_4 and C_6H_5), 166.50 (OC=N), 172.40 (Ir−C), 177.90 (C=O). − $C_{26}H_{27}ClIrNO_2$ × 0.5 CH_2Cl_2 (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, $CDCl_3$): δ = 1.28 (m, 2 H, CH_2), 0.83−1.09 (m, 6 H, 2 × CH_3), 1.74/*1.75* [each s, 15H 1.2:*1*, $C_5(CH_3)_5$], 4.29 [m, 1 H, C*H*(C_4H_9)], 7.07 (m, 1 H, C_6H_4), 7.28 (m, 1 H, C_6H_4), 7.52 (m, 1 H, C_6H_4), 7.81 (m, 1 H, C_6H_4). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 9.40/9.80 [$C_5(CH_3)_5$], 11.80 (CH_2CH_3), 14.80 ($CHCH_3$), 25.80 (CH_2CH_3), 36.60 (*C*HCH_3), 67.80 (*C*HC_4H_9), 88.40 [$C_5(CH_3)_5$], 122.40, 127.30, 131.50, 133.90, 135.90 (C_6H_4), 166.90 (OC=N), 173.20 (Ir−C), 178.30 (C=O). − $C_{23}H_{29}ClIrNO_2$ (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 CH_2Cl_2 a deep red solution of 247 mg (0.31 mmol) of $[Cp^*IrCl_2]_2$ 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 Et_2O, washed twice with 3 ml Et_2O and dried in vacuo at 60°C for 5 h. Crystals were obtained from a CH_2Cl_2/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, $CDCl_3$): δ = 1.39 [s, 15 H, $C_5(CH_3)_5$], 1.58 [s, 15 H, $C_5(CH_3)_5$], 6.12 (s, 1 H, C*H*Ir), 7.27−7.56 (m, 3 H, 3,4,5-C_6H_5), 8.61 (d, ^3J = 7.9 Hz, 2 H, 2,6-C_6H_5). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 8.57 [$C_5(CH_3)_5$], 8.63 [$C_5(CH_3)_5$], 67.79 (*C*HIr), 86.86 [$C_5(CH_3)_5$], 87.12 [$C_5(CH_3)_5$] 125.91, 128.56, 129.83, 132.49 (C_6H_5), 161.15 (OC=N), 179.00 (C=O). − $C_{29}H_{36}Cl_3Ir_2NO_2$ (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 1ml 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 CH_2Cl_2/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, $CDCl_3$): δ = 1.48 (s, 3 H, CH_3COO), 1.94 (s, 3 H, CH_3COO), 1.97 (s, 3 H, CH_3COO), 2.00 (s, 3 H, CH_3COO), 2.05 (s, 3 H, CH_3COO), 5.41 (s, 1 H, CHPd), 7.70 (BB′, 2 H, 3,5-C_6H_5), 7.79 (A, 1 H, 4-C_6H_5), 9.15 (CC′, 2 H, 2,6-C_6H_5). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 22.19 (*C*H_3COO), 22.76 (*C*H_3COO), 23.00 (*C*H_3COO), 23.33 (*C*H_3COO), 23.39 (*C*H_3COO), 38.99

(CHPd), 123.78, 129.15, 129.96, 135.00 (C_6H_5), 165.50 (OC=N), 172.93 (C=O), 185.41 (CH_3COO), 185.47 (CH_3COO), 186.86 (CH_3COO), 188.13 (CH_3COO), 188.59 (CH_3COO). − $C_{19}H_{21}NO_{12}Pd_3$ (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 $[(C_6H_7)Fe(CO)_3]BF_4$ and the appropriate oxazolone in 15 ml of CH_2Cl_2 was cooled (see below). A solution of 64.8 µl (0.47 mmol) of triethylamine in 5 ml of CH_2Cl_2 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 NEt_3 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). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = *1.77* (dm, *1 H*, $^2J_{6endo}$ = 15.3 Hz, 6*exo*-C_6H_7)/1.61 (ddd, 1 H, $^2J_{6endo}$ = 15.0 Hz, $^3J_1$ = 3.7 Hz, $^3J_5$ = 2.6 Hz, 6*exo*-C_6H_7), *2.14*/2.06 (each ddd, *1 H*/1 H, $^2J_{6exo}$ = 15.1 Hz, $^3J_1$ = 11.1 Hz, $^3J_5$ = 4.0 Hz, 6*endo*-C_6H_7), 2.74 (m, *1 H* + 1 H, 1-C_6H_7), *2.92* (ddd, *1 H*, $^3J_3$ = 6.3 Hz, $^3J_1$ = 3.3 Hz, $^4J_4$ = 1.4 Hz, 2-C_6H_7)/3.06, 3.06 [m, *1 H* + 1 H (+ 1 H, 2-C_6H_7), 5-C_6H_7], *4.20*/4.24 [each d, *1 H*/1 H, $^3J_1$ = 6.0 Hz, NC*H*(C_6H_7)COO], *5.32* (ddd, *1 H*, $^3J_2$ = 6.1 Hz, $^3J_4$ = 4.4 Hz, $^4J_5$ = 1.6 Hz, 3-C_6H_7)/5.39, 5.39 [m, *1 H* + 1 H (+ 1 H, 3-C_6H_7), 4-C_6H_7], 7.43−7.60 (ABB′, *3 H* + 3 H, 3,4,5-C_6H_5), 7.96−8.00 (CC′, *2 H* + 2 H, 2,6-C_6H_5). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = *27.77*/26.50 (6-C_6H_7), *40.25*/40.98 (1-C_6H_7), *59.38*/59.39, *59.26*/58.83 (2,5-C_6H_7), *70.03*/69.99 [CN*C*H(C_6H_7)COO], *86.06*/86.51, *85.83*/85.48 (3,4-C_6H_7), *125.95, 128.20, 129.14, 133.16,* 126.11, 128.22, 129.12, 133.14 (C_6H_5), *162.07*/161.95 [*C*NCH(C_6H_7)COO], *176.90*/177.29 [CNCH(C_6H_7)*C*OO], 211.69 (Fe−*C*O). Diastereomeric ratio *1.0*:1.15. − $C_{18}H_{13}FeNO_5$ (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 NEt_3 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). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = *1.41*/1.43 [each s, *3H*/3 H, NCC*H*$_3$(C_6H_7)COO], *1.78* (dm, *1 H*, $^2J_{6endo}$ = 15.3 Hz, 6*exo*-C_6H_7)/1.70 (dm, 1 H, $^2J_{6endo}$ = 15.1 Hz, 6*exo*-C_6H_7), *2.04*/1.99 (each ddd, *1 H*/1 H, $^2J_{6exo}$ = 15.2 Hz, $^3J_1$ = 11.0 Hz, $^3J_5$ = 4.3 Hz, 6*endo*-C_6H_7), 2.58 (m, *1 H*/1 H, 1-C_6H_7), *2.72*/2.99 (each ddd, *1 H*/1 H, $^3J_3$ = 6.2 Hz, $^3J_1$ = 3.2 Hz, $^4J_4$ = 1.3 Hz, 2-C_6H_7), 3.04 (m, *1 H*/1 H, 5-C_6H_7), *5.21*/5.31 (each ddd, *1 H*/1 H, $^3J_2$ = 5.6 Hz, $^3J_4$ = 4.3 Hz, $^4J_5$ = 1.4 Hz, 3-C_6H_7), *5.30* (m, *1 H*, 4-C_6H_7)/5.35 (dd, 1 H, $^3J_3$ = 5.0 Hz, $^3J_5$ = 6.0 Hz, 4-C_6H_7), 7.42−7.60 (ABB′, *3 H* + 3 H, 3,4,5-C_6H_5), 7.98−7.99 (CC′, *2 H* + 2 H, 2,6-C_6H_5). − ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = *22.44*/22.56 (CH_3), *26.29*/25.43 (6-C_6H_7), *46.33*/45.45 (1-C_6H_7), *59.16*/59.25, *57.63*/58.13 (2,5-C_6H_7), *72.85*/72.80 [CN*C*CH$_3$(C_6H_7)COO], *86.01*/86.32, *85.59*/85.38 (3,4-C_6H_7), *126.21, 133.06,* 126.01, 128.21, 129.12, 133.02 (C_6H_5), *160.27*/159.94 [*C*NCCH$_3$(C_6H_7)COO], *180.48*/179.87 [CNCCH$_3$(C_6H_7)*C*OO], 211.72 (Fe−*C*O). Diastereomeric ratio *1.0*:1.8. − $C_{19}H_{15}FeNO_5$ (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 $[(C_7H_7)Cr(CO)_3]BF_4$ 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 Et_2O and filtered off. The filtrate was taken to dryness and the residue was dissolved in 30 ml of Et_2O. This solution was filtered through Celite and the solvent was removed in vacuo. The residue was dissolved in 1 ml of CH_2Cl_2 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 $[(C_7H_7)Cr(CO)_3]BF_4$, 117 mg (0.31 mmol) of **6** and 43.5 µl (0.31 mmol) of NEt_3 were used. The reaction was carried out in CH_2Cl_2 instead of THF. The CH_2Cl_2/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). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.42 (ddd, 1 H, $^2J_{6endo}$ = 14.9 Hz, $^3J_1$ = 3.6 Hz, $^3J_5$ = 2.5 Hz, 6*exo*-C_6H_7), 1.87 (*2.00*) (ddd, 1 H, $^2J_{6exo}$ = 14.9 Hz, $^3J_1$ = 10.8 Hz, $^3J_5$ = 4.2 Hz, 6*endo*-C_6H_7), 2.59 (ddd, 1 H, $^3J_{6endo}$ = 10.6 Hz, $^3J_{6exo}$ = 3.5 Hz, $^3J_2$ = 3.5 Hz, 1-C_6H_7), 2.68 (ddd, 1 H, $^3J_3$ = 5.1 Hz, $^3J_1$ = 3.5 Hz, $^4J_4$ = 2.2 Hz, 2-C_6H_7), 2.94 (*3.06*) (ddd, 1 H, $^3J_4$ = 7.9 Hz, $^3J_{6endo}$ = 3.7 Hz, $^3J_{6exo}$ = 2.2 Hz, 5-C_6H_7), 3.61 (m, 3 H, 1,2,7-C_7H_7), 4.82 (*5.00*) (m, 2 H, 3,6-C_7H_7), 5.23 (*5.36*) (m, 2 H, 3,4-C_6H_7), 5.85 (m, 1 H, 4-C_7H_7), 5.98 (m, 1 H, 5-C_7H_7), 7.50 (BB′, 2 H, 3,5-C_6H_5), 7.60 (A, 1 H, 4-C_6H_5), 7.86 (*7.78*) (CC′, 2 H, 2,6-C_6H_5). Diastereoisomeric ratio about 13:*1*. − ^{13}C NMR (100.4 MHz, $CDCl_3$): δ = 26.70 (6-C_6H_7), 41.12 (1-C_7H_7), 44.44 (1-C_6H_7), 56.51, 58.62 (2,5-C_6H_7), 62.39, 64.27 (2,7-C_7H_7), 83.34 (N*C*RR′COO), 85.56, 86.18 (3,4-C_6H_7), 97.50, 98.03, (4,5-C_7H_7), 102.04, 102.29 (3,6-C_7H_7), 125.60, 128.25, 129.21, 133.23 (C_6H_5), 160.30 [O*C*(Ph)N], 176.91 (CRR′*C*OO), 211.52 (Fe−CO). − $C_{28}H_{19}CrFeNO_8$ (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 $[(C_7H_7)Cr(CO)_3]BF_4$, 125 mg (0.78 mmol) of 2-phenyl-5(4*H*)-oxazolone and 108.1 µl (0.78 mmol) of NEt_3 were used. The product could not be obtained analytically pure. For X-ray analysis suitable crystals were grown in an CH_2Cl_2 pentane mixture. − IR (KBr): $\tilde{\nu}$ = 1981 cm^{-1} s, 1915 s, 1883 s (Cr−CO), 1820 s (C=O), 1651 s (C=N). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.12 [d, 1 H, NC*H*(C_7H_7)CO], 3.55 (m, 1 H, 2-C_7H_7), 3.65 (m, 1 H, 7-C_7H_7), 3.75 (m, 1 H, 1-C_7H_7), 4.90 (m, 1 H, 3-C_7H_7), 5.05 (m, 1 H, 6-C_7H_7), 6.00 (m, 1 H, 4-C_7H_7), 6.05 (m, 1 H, 5-C_7H_7), 7.40−7.65 (ABB′, 3 H, 3,4,5-C_6H_5), 7.88 (CC′, 2 H, 2,6-C_6H_5). − ^{13}C-NMR (100.4 MHz, $CDCl_3$): δ = 40.14 (1-C_7H_7), 61.79, 62.15 (2,7-C_7H_7), 70.96 [N*C*H(C_7H_7)CO], 97.99, 98.25 (4,5-C_7H_7), 100.90, 101.17 (3,6-C_7H_7), 125.67, 128.17, 129.12, 133.29 (C_6H_5), 162.42 [O*C*(C_6H_5)N], 175.00 [NCH(C_7H_7)*C*OO].

10: 500 mg (1.59 mmol) of $[(C_7H_7)Cr(CO)_3]BF_4$, 279 mg (1.59 mmol) of 4-methyl-2-phenyl-5(4*H*)-oxazolone and 222 µl (1.59 mmol) of NEt_3 were used. − IR (KBr): $\tilde{\nu}$ = 1980 cm^{-1} s, 1915 s, 1887 s (Cr-CO), 1806 s (C=O), 1651 s (C=N). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 [s, 3 H, NCC*H*$_3$(C_7H_7)CO], 3.43 (2-C_7H_7), 3.67 (7-C_7H_7), 3.69 (1-C_7H_7), 4.73 (3-C_7H_7), 5.01 (6-C_7H_7), 5.84 (4-C_7H_7), 6.04 (5-C_7H_7) (each pseudo-t, $^3J \approx 8$ Hz), 7.47 (BB′, 2 H, 3,5-C_6H_5), 7.57 (A, 1 H, 4-C_6H_5), 7.88 (CC′, 2 H, 2,6-C_6H_5). − ^{13}C-NMR (100.4 MHz, $CDCl_3$): δ = 18.63 (CH_3), 45.93 (1-C_7H_7), 62.79, 63.62 (2,7-C_7H_7), 76.19 [N*C*(CH_3)(C_7H_7)CO], 97.34, 98.01 (4,5-C_7H_7), 102.33, 102.47 (3,6-C_7H_7), 125.68, 128.24, 129.15, 133.14 (C_6H_5), 160.00 [O*C*(C_6H_5)N], 178.69 [NC(CH_3)(C_7H_7)*C*OO]. − $C_{20}H_{15}CrNO_5$ (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 µl (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 [N*C*(C_7H_7)$_2$CO], 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 [O*C*(C_6H_5)N], 175.08 [NC(C_7H_7)$_2$*C*OO]. − $C_{29}H_{19}Cr_2NO_8$ (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** respectivly, α-amino acid ester hydrochloride and about 2 mg of DMAP in 10 ml of CH_2Cl_2 69.6 µl (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 × CH_3], 3.75 (m, 3 H, $COOCH_3$), 4.49 [m, 1 H, NHC*H*(CH_3)$COOCH_3$], 4.68 [m, 1 H, NHC*H*(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(C*H*$_3$)CONH], 1.68 [m, 15 H, $C_5(CH_3)_5$], 3.80 (m, 1 H, NHC*H*H′COOEt), 3.95 (m, 1 H, NHCH*H*′COOEt), 4.14 (m, 2 H, $COOCH_2CH_3$), 4.64 [m, 1 H, NHC*H*(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, CO-OCH_2CH_3), 4.77 [m, 1 H, NHC*H*(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 µl (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, $^2J_{6endo}$ = 14.5 Hz, 6*exo*-C_6H_7), *1.97*/2.04 (each ddd, *1 H*/1 H, $^2J_{6exo}$ = 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, $^3J_{6endo}$ = 10.6 Hz, $^3J_7$ = 6.9 Hz, $^3J_2$ = $^3J_{6exo}$ = 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, CON*H*CH_2COOCH_3), 4.00, 4.05 (each dd, 1 H, 1 H, ^2J = 20.9 Hz, $^3J_{NH}$ = 5.4 Hz, NHC*H*′$COOCH_3$), *4.06*, *4.16* (each dd, *1 H*, *1 H*, ^2J = 27.0 Hz, $^3J_{NH}$ = 5.4 Hz, NHCH*H*′$COOCH_3$) *4.45*/4.51 [each dd, *1 H*/1 H, $^3J_{NH}$ = 8.4 Hz, $^3J_1$ = 6.9 Hz, C*H*(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, CHN*H*COPh), 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 (NH*C*H_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 (*C*$OOCH_3$, Ph*C*ONH, *C*ONH), 211.69 (Fe−*C*O). 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 µl (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, PhCONHC*H*), 4.85 [m, 1 H, CONHC*H*(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 µl (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, PhCONHC*H*, CONHC*H*(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 µl (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, PhCONHC*H*, CONHC*H*(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-C_6H_5), 7.75−7.84 (m, 2 H, 2,6-C_6H_5). − $C_{25}H_{26}FeN_2O_9$ (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 Et_2O/THF (1:1) (**19**), Et_2O/acetone (10:1) (**22**), or Et_2O (**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), 1973 s br. (Fe−CO), 1729 s (COOH), 1637 s (CONH-I), 1535 s (CONH-II). − ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.60 (m, 1 H, 6*exo*-C_6H_7), ca. 2.00 (m, 6*endo*-C_6H_7), 2.80 (m, 1 H, 1-C_6H_7), 3.27 (m, 2 H, 2,5-C_6H_7), 3.96 (m, 2 H, CH_2), 4.48 (m, 1 H, PhCONHC*H*), 5.61 (m, 2 H, 3,4-C_6H_7), 7.42−7.58 (m, 3 H, 3,4,5-C_6H_5), 7.88−8.00 (m, 2 H, 2,6-C_6H_5), 9.96 (s, 1 H, COOH). − $C_{20}H_{18}FeN_2O_7$ (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). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.34 (m, 1 H, 6*exo*-C_6H_7), 1.91 (m, 1 H, 6*endo*-C_6H_7), 2.37−3.33 (m, 5 H, CH_2, 1-C_6H_7, 2,5-C_6H_7), 3.63, 4.38 (2 m, 1 H, PhCONHC*H*), 4.78 [m, 1 H, CONHC*H*(CH_2Ph)], 5.28 (m, 2 H, 3,4-C_6H_7), 6.72 (m, 1 H, NH), 6.96−7.60 (m, 9 H, NH, $CH_2C_6H_5$, 3,4,5-C_6H_5), 7.66−7.86 (m, 2 H, 2,6-C_6H_5). − $C_{27}H_{24}FeN_2O_7$ (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). − ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 1.60 (m, 1 H, 6*exo*-C_6H_7), ca. 2.00 (m, 6*endo*-C_6H_7, CH_2, SCH_3), 2.56 (m, 2 H, CH_2), 2.78 (m, 1 H, 1-C_6H_7), 3.24 (m, 2 H, 2,5-C_6H_7), 4.38−4.64 [m, 2 H, PhCONHC*H*, CONHC*H*(CH_2Ph)], 5.57 (m, 2 H, 3,4-C_6H_7), 7.43−7.57 (m, 3 H, 3,4,5-C_6H_5), 7.88−7.95 (m, 2 H, 2,6-C_6H_5). − $C_{23}H_{24}FeN_2O_7S$ (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). − ^{1}H NMR (270 MHz, [D$_6$]acetone): δ = 1.59 (m, 1 H, 6*exo*-C_6H_7), ca. 2.00 (m, 6*endo*-C_6H_7, CH_2), 2.42 (m, 2 H, CH_2), 2.84 (m, 1 H, 1-C_6H_7), 3.20 (m, 2 H, 2,5-C_6H_7), 4.50 [m, 2 H, PhCONHC*H*, CONHC*H*(CH_2Ph)], 5.54 (m, 2 H, 3,4-C_6H_7), 7.41−7.62 (m, 3 H, 3,4,5-C_6H_5), 7.87−7.95 (m, 2 H, 2,6-C_6H_5). − $C_{23}H_{22}FeN_2O_9$ (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)$PtCl_2$ in 10 ml of CH_2Cl_2 two equiv. of PPh_3, one equivalent of **19**−**21** and a slight excess of Ag_2O 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 CH_2Cl_2, 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)$PtCl_2$, 11 mg (0.024 mmol) of **19**, 13 mg (0.05 mmol) of PPh_3 and 12 mg (0.052 mmol) of Ag_2O 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). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.55 (m, 1 H, 6*exo*-C_6H_7), 1.98 (m, 6*endo*-C_6H_7), 2.60 (m, 1 H, 1-C_6H_7), 3.05 (m, 4 H, 2,5-C_6H_7, NCH_2COO), 4.40 [m, 1 H, NHC*H*(C_6H_7)CON], 5.35 (m, 2 H, 3,4-C_6H_7), 6.99−7.82 (m, 35 H, 7 C_6H_5). − ^{31}P NMR: δ = 2.97 (d, $^2J_{P\text{-}P}$ = 18.6 Hz, $^1J_{P\text{-}Pt}$ = 3665 Hz, P *trans* to O), *4.08* (d, $^2J_{P\text{-}P}$ = 23.1 Hz, $^1J_{P\text{-}Pt}$ could not be determined, P *trans* to O), *10.36* (d, $^2J_{P\text{-}P}$ = 23.1 Hz, $^1J_{P\text{-}Pt}$ could not be determined, P *trans* to N), 18.61 (d, $^2J_{P\text{-}P}$ = 18.6 Hz, $^1J_{P\text{-}Pt}$ = 3921 Hz, P *trans* to N). Diastereomeric ratio 6:*1*. − $C_{56}H_{46}FeN_2O_7P_2Pt \times 0.5\ CH_2Cl_2$ (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)$PtCl_2$, 23 mg (0.042 mmol) of **20**, 22 mg (0.084 mmol) of PPh_3 and 20 mg (0.086 mmol) of Ag_2O 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). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.48 (m, 1 H, 6*exo*-C_6H_7), 1.85 (m, 6*endo*-C_6H_7), 2.24 (m, 1 H, 1-C_6H_7), 2.90 (m, 4 H, 2,5-C_6H_7, CH_2Ph), 3.72 [m, 1 H, NC*H*(CH_2Ph)COO], 4.30 [m, 1 H, NHC*H*(C_6H_7)CON], 5.25 (m, 2 H, 3,4-C_6H_7), 6.78−7.82 (m, 40 H, 8 C_6H_5). − ^{31}P NMR: δ = 2.85, 2.87, 2.92, 2.98 (each d, $^2J_{P\text{-}P}$ = 18.9 Hz, $^1J_{P\text{-}Pt}$ = 3669 Hz, P *trans* to O), 18.33, 18.36, 18.38, 18.41 (each d, $^2J_{P\text{-}P}$ = 18.3 Hz, $^1J_{P\text{-}Pt}$ = 3893 Hz, P *trans* to N). Diastereomeric ratio about 1:1:1.5:1.5. − $C_{63}H_{52}FeN_2O_7P_2Pt \times 0.5\ CH_2Cl_2$ (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)$PtCl_2$, 19 mg (0.036 mmol) of **21**, 18.9 mg (0.072 mmol) of PPh_3 and 18 mg (0.078 mmol) of Ag_2O 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). − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.52 (m, 1 H, 6*exo*-C_6H_7), 1.85 (m, 6*endo*-C_6H_7, CH_2), 1.94, 2.01, 2.03 [each s, together 3 H, SCH_3 (1:1:2)], 2.50 (m, 3 H, 1-C_6H_7, CH_2), 2.98 (m, 2 H, 2,5-C_6H_7), 3.52, 3.74 [each m, together 1 H, NC*H*($CH_2CH_2SCH_3$)COO], 4.40 [m, 1 H, NHC*H*(C_6H_7)CON], 5.31 (m, 2 H, 3,4-C_6H_7), 7.08−7.89 (m, 35 H, 7 C_6H_5). − ^{31}P NMR: δ = 2.79, 2.80, 2.91, 2.97 (each d, $^2J_{P\text{-}P}$ = 19.2 Hz, $^1J_{P\text{-}Pt}$ = 3690 Hz, P *trans* to O), 18.24, 18.25, 18.34, 18.41 (each d, $^2J_{P\text{-}P}$ = 19.2 Hz, $^1J_{P\text{-}Pt}$ = 3881 Hz, P *trans* to N). Diastereomeric ratio about 1:1:1:2. − $C_{59}H_{52}FeN_2O_7P_2PtS \times CH_2Cl_2$ (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-2Θ 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 × 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	$2 \times C_{29}H_{36}Cl_3Ir_2NO_2 \times 1.5\ CH_2Cl_2$	$C_{19}H_{21}NO_{12}Pd_3$	$C_{19}H_{13}CrNO_5$	$C_{20}H_{15}CrNO_5$
Formula weight	1970.06	774.57	387.30	401.33
T [K]	295(2)	294(2)	293(2)	293(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2/c$	$P2_1/n$
Unit-cell dimensions				
a [Å]	18.0641(19)	8.562(3)	31.384(2)	9.0240(10)
b [Å]	17.3233(24)	941.8(3)	6.6040(10)	10.373(3)
c [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
V [Å^3]	6749.5(1.7)	1181.5(6)	3329.1(6)	1776.2(7)
Z	4	2	8	4
Density (calcd.) [g/cm^3]	1.939	2.177	1.546	1.501
μ (Mo-K_a) [mm^{-1}]	8.261	2.323	0.718	0.676
F(000)	3756	752	1584	824
Crystal size [mm]	$0.43 \times 0.37 \times 0.10$	$0.47 \times 0.27 \times 0.07$	$0.55 \times 0.23 \times 0.08$	$0.05 \times 0.10 \times 0.38$
2θ 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 [R(int) = 0.0447]	3693 [R(int) = 0.0171]	2921 [R(int) = 0.0372]	3133 [R(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 F^2	1.076	1.079	1.038	0.990
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0451, $wR2$ = 0.1077	$R1$ = 0.0247, $wR2$ = 0.0640	$R1$ = 0.0434, $wR2$ = 0.0783	$R1$ = 0.0753, $wR2$ = 0.1057
R indices (all data)	$R1$ = 0.0685, $wR2$ = 0.1260	$R1$ = 0.0309, $wR2$ = 0.0686	$R1$ = 0.0847, $wR2$ = 0.0933	$R1$ = 0.1961, $wR2$ = 0.1412
Largest diff. peak and hole [eÅ^{-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 CH_2Cl_2 disordered, split, Cp* disordered, not split.

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