Chiral Chloro-Bridged η^6-Phenylglycine Ruthenium(II) Complexes Formed by Dehydrogenation of (*R*)-2,5-Dihydrophenylglycine[‡]

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Dedicated to Professor Kurt Dialer on the occasion of his 80th birthday

Keywords: Ruthenium / Iridium / Palladium / Amino acids

The reaction of N- or C-terminal protected (*R*)-2,5-dihydrophenylglycines with ruthenium(III) chloride gives the chloro-bridged η^6-phenylglycine complexes **1**–**3** without racemization. Dehydrogenation also occurs with (*R*)-2,5-dihydrophenylglycine and $[(n\mathrm{Bu}_3\mathrm{P})\mathrm{PdCl}_2]_2$ on exposure to air to yield the phenylglycinate chelate complex **6**. The structures of a pyridine complex from **2** $[\mathrm{Cl}_2(\mathrm{pyridine})\mathrm{Ru}\{\eta^6\text{-}\mathrm{C}_6\mathrm{H}_5\mathrm{CH}(\mathrm{CO}_2\mathrm{Et})\mathrm{NHCOCF}_3\}]$ **(4)** and of $[\mathrm{Cp}^*(\mathrm{Cl})\mathrm{Ir}(N,O\text{-dihydrophenylglycinate})]$ (**5**) were determined by X-ray diffraction.

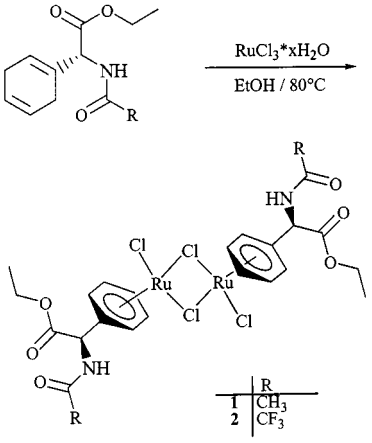
Introduction

The broad scope of the chemistry and application of organometallic complexes of transition metals with α-amino acids and peptides was recently reviewed.[2] Various η^6-arene complexes of aromatic amino acids formed with CpRu and (*p*-cymene)Ru fragments may be useful for the labelling of peptides and proteins.[3−11] Recently, much attention has focused on the development of chiral (arene)ruthenium complexes for the catalytic transfer hydrogenation of ketones[12−19] and for asymmetric Diels−Alder reactions.[20] In addition, there is great interest in the coordination behaviour of ruthenium(II) complexes with ligands tethered to the η^6-arene donor.[21,22] (Arene)ruthenium complexes with functional substituents at the η^6-arene moiety could give rise to homogeneous catalysts which display special solubility properties or can be immobilized on resins.

Our synthetic approach is based on the dehydrogenation of functional cyclohexadienes with ruthenium(III) trichloride in ethanol, a method established by Bennett et al.[23,24] Here we report the synthesis of novel chloro-bridged η^6-phenylglycine ruthenium(II) complexes starting from the synthetic amino acid (*R*)-2,5-dihydrophenylglycine,[25] which is easily accessible by Birch reduction from D-phenylglycine[26] and which is applied as a β-lactam antibiotic side chain.

Results and Discussion

In order to avoid side reactions N- and C-terminal protection of the substrate (*R*)-2,5-dihydrophenylglycine is necessary. Due to the strongly acidic conditions during the dehydrogenation reaction, acid-stable protecting groups (acetyl and trifluoroacetyl) are favourable for the amino terminus. Subsequent reaction of these protected cyclohexadienyl amino acids with ruthenium(III) chloride hydrate in refluxing ethanol produces the novel chloro-bridged η^6-phenylglycine ruthenium(II) complexes **1** and **2** which can be isolated in good yields as orange powders (Scheme 1).



Scheme 1

Protection of the cyclohexadienyl amino acid can also be achieved by protonation with HCl/ethyl acetate to yield the amino acid hydrochloride as an intermediate. During the dehydrogenation reaction, esterification of the carboxylate moiety is observed giving rise to the chloro-bridged η^6-phenylglycine ruthenium(II) complex **3** (Scheme 2).

In the IR spectra of the η^6-phenylglycine ruthenium(II) complexes **1**−**3** the absorptions of the ester function can be observed at about 1740 cm^{-1}. For the amide-protected derivatives **1** and **2** the amide absorptions appear in the typical range. There is no evidence for racemization under the

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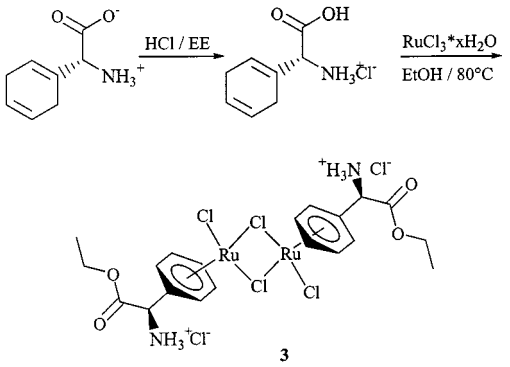


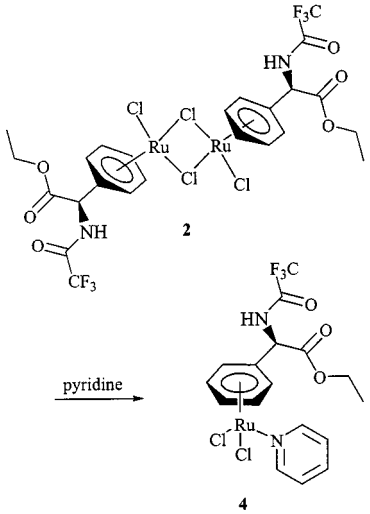
Scheme 2

acidic reaction conditions; this is confirmed by NMR spectroscopy. The ^{1}H NMR spectra of the complexes **1**−**3** display only a single set of signals appearing in the region δ = 5.5−6.1 for the aromatic protons. In the ^{13}C NMR spectra of the compounds **1**−**3** the signals of the aromatic carbon atoms can be observed in the area δ = 80−90 thus confirming an η^6-coordination of phenylglycine to the ruthenium centre.

Compared to the known chloro-bridged arene ruthenium complexes (e.g. arene = benzene, cymene)[23,24] the complexes **1**−**3** exhibit strongly enhanced solubility in polar solvents and even in water, which could make them useful for the labelling of peptides or proteins. Unfortunately, all η^6-phenylglycine ruthenium(II) complexes are sensitive to light in the solid state and in solution leading to greenish decomposition products. This could be due to coordination of the side chain and to a change of the arene coordination mode.

Saponification of the ester group in **3** should lead to deprotection which could allow coordination of the amino acid side chain.

Cleavage of the chloro bridges in complex **2** with pyridine produces the monomeric pyridine adduct **4** (Scheme 3) which was characterized by X-ray diffraction.



Scheme 3

The structure of complex **4** is shown in Figure 1. Relevant bond lengths and angles for complex **4** are collected in Table 1 and the crystallographic data in Table 2.

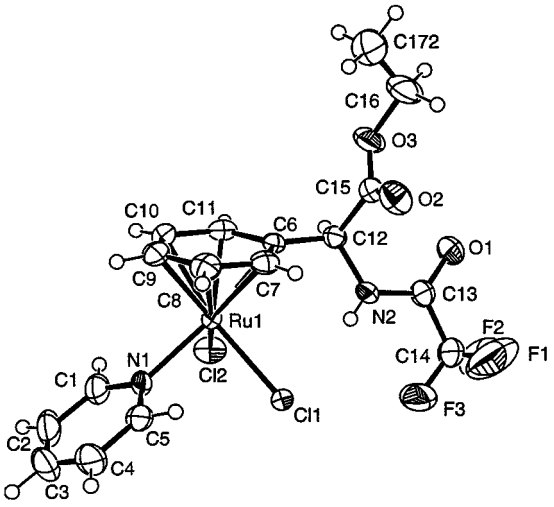


Figure 1. ORTEP projection of the ruthenium complex **4** with the atom numbering scheme

X-ray crystallography confirms the η^6-coordination of phenylglycine, but reveals racemisation at the α-carbon leading to a 1:1 mixture of enantiomers in the crystal. This racemisation occurs due to the basicity of pyridine which is also a typical feature of free phenylglycine.[27]

(*R*)-2,5-dihydrophenylglycine reacts with base and the chloro-bridged complex [Cp*IrCl$_2$]$_2$ to give the *N*,*O*-chelate **5** (Scheme 4).

As confirmed by NMR spectroscopy, complex **5** is produced as a 1:1 mixture of the diastereomers R_CR_{Ir} and R_CS_{Ir}. Two sets of signals in the ^{1}H NMR spectrum of **5** reveal the typical pattern of a monosubstituted cyclohexadiene moiety with a multiplet in the area δ = 2.61−2.79 for the aliphatic protons and a multiplet in the range δ = 5.62−5.84 for the olefinic protons.

Only one diastereomer crystallises from dichloromethane (confirmed by NMR spectroscopy) which was assigned to the R_CS_{Ir} configuration by X-ray diffraction. The structure of complex **5** (shown in Figure 2) is analogous to that of half-sandwich complexes (arene)(Cl)M(α-aminocarboxylate) with other α-amino acids.[2,28,29] Due to the rather high standard deviations a closer discussion of the bonding parameters is not appropriate.[40]

The cyclohexadiene moiety in 2,5-dihydrophenylglycine shows a strong tendency towards rearomatisation to a phenyl group when exposed to air. This was demonstrated by the synthesis of complex **6** from (*R*)-2,5-dihydrophenylglycine and [(*n*Bu$_3$P)PdCl$_2$]$_2$ in nondegassed methanol (Scheme 5).

The ^{1}H NMR spectrum of complex **6** does not show any signals of a cyclohexadiene moiety. In contrast the typical pattern of a monosubstituted benzene is observed in the area δ = 7.33−7.69. As confirmed by an ^{31}P NMR experi-

Table 1. Selected bond lengths [Å], angles [°] and torsion angles [°] of complex **4**

Ru1−N1	2.130(3)	N1−Ru1−Cl2	86.76(10)	C7−C6−C12−N2	32.9(5)
Ru1−C11	2.156(4)	C7−C6−C12	122.6(4)	C11−C6−C12−C15	119.0(4)
Ru1−C6	2.182(3)	N2−Cl2−C6	111.7(3)	C11−C6−C12−N2	121.1(4)
C6−C12	1.507(5)	C6−C12−C15	108.4(3)	C6−C7−C8−C9	2.39(4)
Ru1−Cl2	2.3908(11)	C1−N1−Ru1	122.1(3)	C8−C9−C10−C11	0.19(4)
Ru1−Cl1	2.4167(10)	N1−Ru1−C7	130.67(14)		
C6−C7	1.418(5)	C6−C7−C8	122.2(4)		

Table 2. Selected crystallographic data of complex **4**[40]

Empirical formula	$C_{17}H_{17}N_2O_3F_3Cl_2Ru$
Formula mass	565.85
Temperature	200(3) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 23.6573(15) Å, α = 90° b = 11.5507(5) Å, β = 102.930(8)° c = 14.9545(10) Å, γ = 90°
Volume	3982.8(4) Å^3
Z	4
Absorption coefficient	1.103 mm^{-1}
F(000)	1336
Crystal size	0.30 × 0.18 × 0.12 mm
Theta range for data collection	1.77 to 25.85°
Index ranges	$-29 \le h \le 28$, $-11 \le k \le 14$, $-1 \le l \le 14$
Reflections collected	7380
Independent reflections	5102 [R(int) = 0.0308]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.8900 and 0.8179
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7380/0/578
Goodness-of-fit on F^2	0.953
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0359, $wR2$ = 0.0867
R indices (all data)	$R1$ = 0.0586, $wR2$ = 0.0927
Largest diff. peak and hole	1.107 and −0.626 e Å^{-3}

ment, complex **6** is produced as a mixture of the *cis* and *trans* isomers **6a** and **6b** in the ratio 2:3. For several other Pd and Pt complexes with P and N donors[30−36] the *trans* P−M−N configuration is favoured.

Conclusion

The chiral chloro-bridged η^6-phenylglycine ruthenium complexes **1**−**3** can be synthesized by a dehydrogenation reaction of derivatives of (*R*)-2,5-dihydrophenylglycine without racemization. The reaction provides an easy access to organometallic complexes with π-coordinated optically active amino acids, and further ligands can be introduced into the chloro-bridged compounds. Cleavage of the chloro bridges in **2** with pyridine to form the monomeric complex **4** leads to a 1:1 mixture of enantiomers. In the reaction of (*R*)-2,5-dihydrophenylglycine with the complex $[Cp^*IrCl_2]_2$ the *N,O*-chelate **5** is produced. The strong tendency of 2,5-dihydrophenylglycine towards rearomatisation in air was demonstrated with the synthesis of complex **6** from (*R*)-2,5-dihydrophenylglycine and $[(nBu_3P)PdCl_2]_2$ in nondegassed methanol.

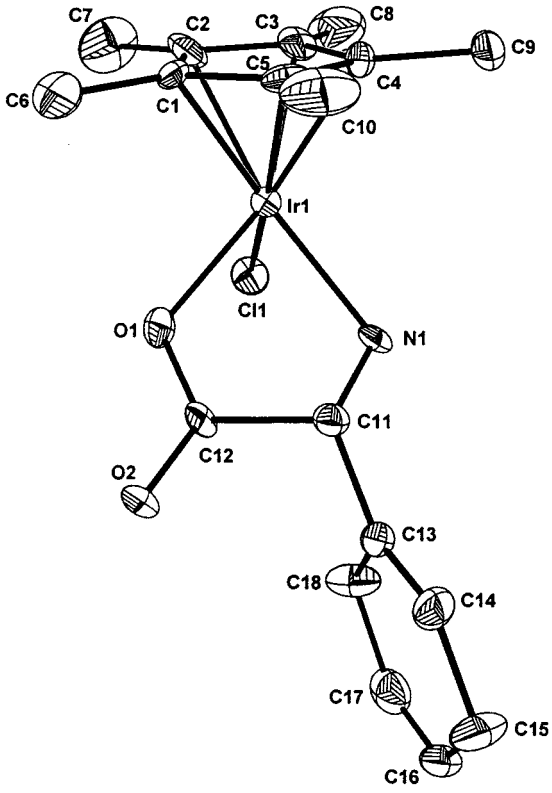
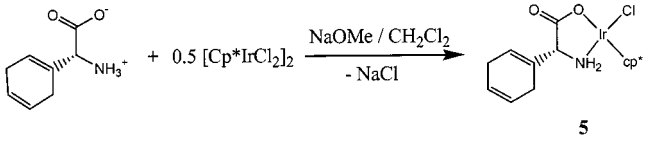
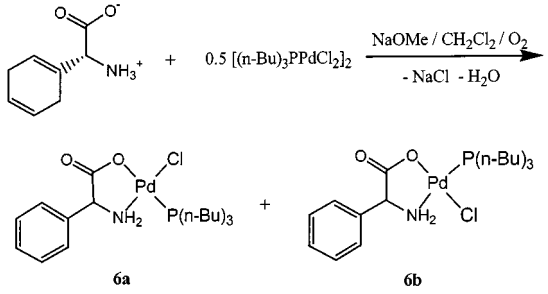


Figure 2. ORTEP projection of the iridium complex **5** with the atom numbering scheme



Scheme 4



Scheme 5

Experimental Section

General Remarks: All reactions were performed under an atmosphere of argon in Schlenk tubes. Ethanol was degassed prior to use. NMR measurements were recorded on Jeol GSX 270 and Jeol EX 400 spectrometers. IR analyses were obtained on a Nicolet 520 FT-IR spectrometer. Derivatives of (*R*)-2,5-dihydrophenylglycine were prepared according to literature procedures .[25,37]

1: $RuCl_3 \cdot 3H_2O$ (347 mg, 1.32 mmol) was added to *N*-acetyl-(*R*)-2,5-dihydrophenylglycine ethyl ester[25] (1.221 g, 5.47 mmol) in 100 mL of ethanol and the mixture heated under reflux. The dark solution turned green after approximately 1 h. After an additional 4 h the reaction was complete, resulting in a clear red solution which was reduced in vacuo to half of the volume. Upon cooling to −30 °C for 16 h orange microcrystals of **1** precipitated which were filtered off, washed with cold ethanol and dried in vacuo. Yield: 851 mg (82%). − IR (KBr): $\tilde{\nu}$ = 3304 m, 3077 w, 2960 w, 1740 vs (CO_2), 1664 vs, 1531 s (NCO), 1447 m, 1371 m, 1296 m, 1209 m, 1023 m, 857 m cm^{-1}. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.23 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 2.13 (s, 6 H, CH_3), 4.17 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 4.18 (q, ^3J = 7.1 Hz, 2 H, OCH'_2), 5.14 (d, ^3J = 6.5 Hz, 2 H, α-H), 5.52−5.83 (m, 10 H, H_{arom}), 7.90 (d, *J* = 6.4 Hz, 2 H, NH). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.88 (CH_2CH_3), 22.57 (CH_3), 54.82 (α-C), 62.34 (CH_2CH_3), 80.20, 80.29, 81.58, 83.13, 92.89 (C_{arom}), 167.76 (CO_2), 170.81 (CON). − $C_{24}H_{30}Cl_4N_2O_6Ru_2$ (786.46): calcd. C 36.65, H 3.84, N 3.56; found C 36.22, H 3.93, N 3.42.

2: $RuCl_3 \cdot 3H_2O$ (347 mg, 1.32 mmol) was added to 825 mg (2.98 mmol) of *N*-trifluoroacetyl-(*R*)-2,5-dihydrophenylglycine ethyl ester (prepared according to references [37] and [25]) in 20 mL of ethanol and the mixture heated under reflux. The dark solution turned greenish-brown after approximately 1 h. After an additional 4 hours the reaction was complete, resulting in a clear red solution which was reduced in vacuo to half of the volume. Upon cooling to −30 °C orange microcrystals of **2** precipitated which were filtered off, washed with cold ethanol and dried in vacuo. Yield 351 mg (71%). − IR (KBr): $\tilde{\nu}$ = 3077 m, 2989 m, 2601 w, 1744 vs (CO_2), 1635 w, 1544 m, 1467 w, 1371 w, 1285 m, 1236 s, 1182 m, 1021 m, 860 w cm^{-1}. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.25 (t, ^3J = 7.1 Hz, 6 H, CH_2CH_3), 4.21 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 4.24 (q, ^3J = 7.0 Hz, 2 H, OCH'_2), 5.37 (d, ^3J = 7.0 Hz, 2 H, α-H), 5.53 (q, *J* = 5.4 Hz, 2 H, H_{arom}), 5.60 (q, *J* = 5.9 Hz, 2 H, H_{arom}), 5.69 (d, *J* = 5.8 Hz, 4 H, H_{arom}), 5.98 (t, *J* = 5.4 Hz, 2 H, H_{arom}), 9.03 (s, br, NH). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.54 (CH_2CH_3), 54.87 (α-C), 63.02 (CH_2CH_3), 78.55, 79.03, 82.55, 84.97, 87.51, 89.43 (C_{arom}), n.o. (CF_3), 156.98 (CON), 166.23 (CO_2). − $C_{24}H_{24}Cl_4F_6N_2O_6Ru_2 \cdot 2EtOH$ (986.54): calcd. C 34.09, H 3.67, N 2.84; found C 34.45, H 3.37, N 2.95.

3: (*R*)-2,5-dihydrophenylglycine (600 mg, 3.92 mmol) was stirred with 10 mL of a solution of HCl in ethyl acetate (approx. 2 M) for 1 h. To this suspension $RuCl_3 \cdot 3H_2O$ (205 mg, 0.78 mmol) and 35 mL of ethanol were added and the resulting mixture heated under reflux for 16 h. The orange precipitate was filtered off, washed with cold ethanol and dried in vacuo. Yield 472 mg (78%). − IR (KBr): $\tilde{\nu}$ = 3063 m, 2990 w, 2601 w, 1746 vs (CO_2), 1637 w, 1472 s, 1374 m, 1294 m, 1240 s, 1185 m, 1098 m, 1008 m, 857 m cm^{-1}. − ^1H NMR (270 MHz, CD_3OD): δ = 1.25 (t, ^3J = 7.2 Hz, 6 H, CH_2CH_3), 4.29 (q, ^3J = 7.2 Hz, 2 H, OCH_2), 4.31 (q, ^3J = 7.2 Hz, 2 H, OCH'_2), 5.17 (s, 2 H, α-H), 5.85−6.14 (m, 10 H, H_{arom}), 7.48 (s, NH_3). − ^{13}C NMR (67.9 MHz, CD_3OD): δ = 13.24 (CH_2CH_3), 55.48 (α-C), 63.96 (CH_2CH_3), 83.12, 83.27, 85.03 (C_{arom}), 165.94 (CO_2). − $C_{20}H_{28}Cl_6N_2O_4Ru_2$ (775.31): calcd. C 30.98, H 3.64, N 3.61; found C 30.09, H 3.77, N 3.27.

4: A solution of the ruthenium complex **2** (99 mg, 0.12 mmol) in 10 mL of pyridine was stirred for 12 h. The solvent was then removed under reduced pressure and the residue dried in vacuo. Recrystallisation from dichloromethane/hexane afforded orange crystals suitable for X-ray diffraction. Yield 128 mg (91%). − IR (KBr): $\tilde{\nu}$ = 3201 m, 3062 m, 2981 w, 1748 vs (C=O), 1725 vs, 1636 m, 1604 m, 1545 s, 1447 s, 1216 s, 1181 s, 1164 s, 1069 m, 1017 m, 860 w, 761 s, 695 s cm^{-1}. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 1.27 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3), 4.28 (pt, ^3J = 7.1 Hz, 2 H, OCH_2), 5.44 (d, ^3J = 6.9 Hz, 1 H, α-H), 5.53−5.72 (m, 3 H, H_{arom}), 5.95 (m, 1 H, H_{arom}), 6.09 (m, 1 H, H_{arom}), 7.48 (m, 3 H, H_{py}), 8.98 (m, 2 H, H_{py}), 9.01(s, br, NH). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.84 (CH_2CH_3), 55.73 (α-C), 63.01 (CH_2CH_3), 81.48, 81.65, 86.47, 87.11, 88.67, 88.93 (C_{arom}), 125.11, 129.16, 138.48 (py), 155.12 (CON), 166.80 (CO_2). − $C_{17}H_{17}Cl_2F_3N_2O_3Ru \cdot 1/2py$ (565.85): calcd. C 41.39, H 3.48, N 6.19; found C 41.43, H 3.66, N 6.34.

5: A suspension of (*R*)-2,5-dihydrophenylglycine (58 mg, 0.38 mmol) in 10 mL of methanol was stirred with a 1.3 M solution of NaOMe in methanol (290 μL, 0.38 mmol). After 30 min. $[Cp^*IrCl_2]_2$ [38] (150 mg, 0.19 mmol) was added and the mixture stirred for an additional 2 h. The solvent was then removed at reduced pressure and the residue dissolved in 5 mL of dichloromethane. After filtration through Celite the clear yellow solution was set aside. Within 12 h yellow crystals of **5** precipitated. Yield 181 mg (86%). − IR (KBr): $\tilde{\nu}$ = 3223 m, 3223 m (NH), 2917 w, 1637 vs (C=O), 1455 m, 1361 s, 1256 m, 1163 m, 1034 m, 960 m cm^{-1}. − ^1H NMR (270 MHz, CD_3OD): δ = 1.70 (s, 15 H, CH_3), 2.61−2.79 (m, 4 H, CH_2), 3.87 (d, *J* = 14.9 Hz, 1 H, α-H), 5.62−5.84 (m, 3 H, CH). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 8.70 ($C_5(CH_3)_5$), 24.75, 26.63 (CH_2), 59.90 (α-C), 84.24 ($C_5(CH_3)_5$), 123.60, 124.87, 126.22, 126.48 (CH), 177.98 (CO_2). − $C_{18}H_{25}ClIrNO_2 \cdot 1/2CH_2Cl_2$ (557.54): calcd. C 39.86, H 4.88, N 2.51; found C 40.10, H 5.13, N 2.40.

6: A suspension of (*R*)-2,5-dihydrophenylglycine (61 mg, 0.40 mmol) in 7 mL of nondegassed methanol was stirred with a 1.3 M solution of NaOMe in methanol (304 μL, 0.40 mmol). After 30 min. $[(nBu_3P)PdCl_2]_2$ [39] (150 mg, 0.20 mmol) was added and the mixture stirred for an additional 12 h. The yellow precipitate was then removed by centrifugation, dried in vacuo and redissolved in dichloromethane. After filtration through Celite the solvent was removed under reduced pressure. The residue was recrystallized from dichloromethane/*n*-hexane. Yield 169 mg (83%). − IR (KBr): $\tilde{\nu}$ = 3216 s (NH), 3121 m, 2930 vs, 2872 s, 1634 vs (C=O), 1597 m, 1465 m, 1455 m, 1377 s, 1210 m, 1093 m, 907 m, 804 w, 787 w, 762 m, 725 m, 699 s cm^{-1}. − ^1H NMR (270 MHz, CD_2Cl_2): δ = 0.86−0.98 (m, 9 H, CH_3, *n*Bu), 1.39−1.84 (m, 18 H, CH_2, *n*Bu), 3.59 (m, br, NH_2), 4.61 (m, 1 H, α-H), 7.33−7.45 (m, 3 H- and *p*-C_6H_5), 7.61−7.69 (m, 2 H, *o*-C_6H_5). − ^{13}C NMR (100.5 MHz, CD_2Cl_2): δ = 13.54 ($PCH_2CH_2CH_2CH_3$, A+B), 25.92 ($PCH_2CH_2CH_2CH_3$, A), 25.94 ($PCH_2CH_2CH_2CH_3$, B), 24.15 (d, *J* = 14.5 Hz, $PCH_2CH_2CH_2CH_3$, A), 24.24 (d, *J* = 14.0 Hz, $PCH_2CH_2CH_2CH_3$, B), 21.78 (d, *J* = 30.0 Hz, $PCH_2CH_2CH_2CH_3$, A), 22.82 (d, *J* = 31.0 Hz, $PCH_2CH_2CH_2CH_3$, B), 61.41 (α-C, A), 64.12 (α-C, B), 127.20, 128.28, 128.66, 129.09 (Ph, A+B), 181.29 (CO_2, A+B). − 31P NMR (109.4 MHz, CD_2Cl_2): δ = 27.55 (s, A), 28.80 (s, B); (1.5:1). − $C_{20}H_{35}ClNO_2PPd \cdot H_2O$ (512.34): calcd. C 46.88, H 7.28, N 2.73; found C 46.83, H 7.50, N 2.64.

Acknowledgments

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[40] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-151248 (**4**). Copies of this data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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