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Synthesis and Stereochemistry of Diene–Ruthenium(II) Complexes of α-Amino Acids. Crystal Structures of [(cod)Ru(D,L-phe)Cl]$_4$ and Δ-[(nbd)Ru(L-phe)$_2$]

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Abstract

Complexes of the type [(diene)RuCl(aa)]$_n$ (diene = norbornadiene nbd, 1,5-cyclooctadiene cod, Haa = α-amino acid) may be prepared by the reaction of [(diene)RuCl$_2$]$_n$ with Haa in methanol at reflux. The crystal structure of tetrameric [(cod)Ru(D,L-phe)Cl]$_4$ demonstrates that the amino acidate ligands are tridentate with symmetrical carboxyl bridges between individual Ru atoms. Reaction of [(diene)RuCl(aa)]$_n$ with nitrogen bases B leads to the formation of monomeric species [(diene)RuCl(aa)B], in which the amino acidate ligands are bidentate with N,O-coordination. Complexes of the type [(diene)Ru(L-aa)$_2$] may be synthesized from [(diene)RuCl$_2$]$_n$ and the amino acid in H_2O at reflux; the crystal structure of Δ-[(nbd)Ru(L-phe)$_2$] is reported.

Introduction

Only two examples of organometallic ruthenium(II) complexes of α-amino acids have previously been reported. Reaction of [(η^6-C_6H_6)RuCl$_2$]$_2$ with glycine (glyH) in methanol leads to the complex [(η^6-C_6H_6)RuCl(gly)], in which the amino acidate ligand is bidentate with chelating N,O-coordination [1]. An analogous complex was isolated for alanine (D,L-alaH). Treatment of polymeric [(diene)RuCl$_2$]$_n$ (diene = norbornadiene nbd, 1,5-cyclooctadiene cod) with aqueous glycine at reflux yields compounds of the type [(diene)Ru(gly)$_2$]·H_2O [2], which contain two bidentate glycinate ligands, so that in principle three enantiomeric pairs are feasible with respectively N, O or N/O atoms in *trans* position to one another. In the case of diene = cod, it was concluded on the basis of IR spectroscopic data, that two diastereomers could be separated by fractional crystallization. Although crystallographic data were reported by the authors [2], no X-ray structural elucidation was performed.

We have now investigated the reaction of [(diene)RuCl$_2$]$_n$ with amino acids in methanol at reflux, which leads to the isolation of insoluble novel complexes [(diene)RuCl(aa)]$_n$ (aa = gly, D,L-ala, D,L-val), in which the amino acidate ligand must be tridentate. An X-ray structural analysis was performed on the tetrameric species [(cod)RuCl(D,L-phe)] which could be crystallized from a methanol/acetone solution. These complexes [(diene)RuCl(aa)]$_n$ react with nitrogen bases B to yield monomeric species [(diene)RuCl(aa)B]. We have also prepared further complexes of the type [(diene)Ru(aa)$_2$] from aqueous solution for aa = L-val, L-phe and report the crystal structure Δ-[(nbd)Ru(L-phe)$_2$]. We used L-amino acids in order to establish whether a particular chirality at the metal centre is favoured.

Experimental

All reactions were carried out under an argon atmosphere. Solvents were dried and distilled before use. IR spectra (Table 1) were recorded as 1% KBr discs on a Perkin-Elmer 297 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WP 200 spectrometer at 20 °C. Elemental analyses (Table 2) were performed with a Perkin-Elmer 240. The α-amino acids were purchased from Sigma Chemie GmbH

TABLE 1. Selected IR spectroscopic data (KBr, cm^{-1}) for ruthenium(II) complexes

Compound	$\nu(NH_2)$	$\nu(C=O)^a$	$\delta(NH)^a$
1	3290, 3240	1540	1578
2	3320, 3220	1545	1590
3	3310, 3235	1560	1580
4	3250, 3120	1565	1570
5	3220, 3100	1570	1600
6	3310, 3240	1570	1572
7	3290, 3230	1573	1575
8	3220, 3190, 3145	1610	1610
9	3260, 3180, 3140	1635	1600
10	3300, 3210	1590	1575
11	3295, 3230	1620	1580

^{a}Proposed assignments.

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TABLE 2. Analytical data for ruthenium(II) complexes[a]

Compound	C (%)	H (%)	N (%)
$[(nbd)RuCl(gly)]_n$ (1)	35.6(35.71)	4.05(3.99)	4.4(4.62)
$[(nbd)RuCl(D,L\text{-}ala)]_n$ (2)	38.0(37.92)	4.46(4.45)	4.3(4.42)
$[(nbd)RuCl(D,L\text{-}val)]_n$ (3)	41.9(41.80)	5.29(5.26)	4.3(4.06)
$[(cod)RuCl(gly)]_n$ (4)	36.8(37.68)	4.88(5.06)	3.9(4.39)
$[(cod)RuCl(D,L\text{-}ala)]_n$ (5)	38.9(39.70)	5.42(5.45)	3.8(4.21)
$[(cod)RuCl(D,L\text{-}val)]_n$ (6)	42.0(43.27)	6.21(6.14)	3.7(3.88)
$[(cod)RuCl(D,L\text{-}phe)]_4$ (7)	49.8(49.94)	5.58(5.42)	3.7(3.43)
$[(nbd)RuCl(gly)(pip)]$ (8)	43.8(43.35)	6.04(5.98)	7.1(7.22)
$[(nbd)RuCl(D,L\text{-}ala)(nBuNH_2)]$ (9)	43.3(43.13)	6.35(6.46)	7.1(7.18)
$[(nbd)Ru(L\text{-}val)_2]$ (10)	47.9(47.98)	6.59(6.63)	6.5(6.58)
$[(nbd)Ru(L\text{-}phe)_2]\cdot CH_3OH$ (11)	56.5(56.40)	5.47(5.80)	5.1(5.06)

[a]Microanalyses were performed with a Perkin-Elmer 240; calculated values are given in parentheses.

and used as received; $RuCl_3 \cdot 3H_2O$ was a gift from Degussa AG. $[Ru(cod)Cl_2]_n$ and $[Ru(nbd)Cl_2]_n$ were prepared as described in the literature [3–5].

Preparation of Complexes 1–11

[(diene)RuCl(aa)]$_n$ (1–6) (diene = nbd, cod; aaH = amino acid)

In a typical preparation 208 mg (0.79 mmol) of $[Ru(nbd)Cl_2]_n$ and 142 mg (1.59 mmol) of D,L-alanine were heated with stirring for 3 days in 10 ml absolute methanol at reflux (for the other complexes reflux times between 4 and 12 days were necessary to complete reaction). The insoluble yellow product 2 was filtered off and washed with 3 X 5 ml methanol and dried in high vacuum. Yield 160 mg (64%).

[(cod)RuCl(D,L-phe)]$_4$ (7)

A total of 215 mg (0.77 mmol) of $[Ru(cod)Cl_2]_n$ and 125 mg (0.75 mmol) of D,L-phenylalanine was heated with stirring for 4 days in 13 ml absolute methanol at reflux. The remaining insoluble educt $[Ru(cod)Cl_2]_n$ (130 mg, 60%) was filtered off and the orange–yellow solution cooled to –30 °C to yield yellow crystals of 7 which were recrystallized from a methanol/acetone solution. Yield 30 mg (10%).

^{1}H NMR (d_6-DMSO), 1.80–2.40 (8H, cod CH_2), 3.04–4.20 (7H, cod CH, phe CH_2, phe β-CH), 7.30 (5H, phe C_6H_5).

[(nbd)RuCl(gly)(pip)] (8)

A total of 80 mg (0.26 mmol) of **1** and 5 ml of piperidine was heated with stirring for $2\frac{1}{2}$ h in 5 ml absolute methanol at reflux. The solvent was removed at vacuum and the solid dissolved in 3 ml methanol. After filtration the solution was cooled to –30 °C to yield 8 as a deep red solid. Yield 20 mg (20%). ^{1}H NMR (CD_3OD, TMS) 1.4–1.7 (8H, nbd CH_2, pip CH_2), 2.5–2.8 (2H, nbd aliph. CH), 3.3–3.4 (4H, pip CH_2), 3.73, 3.85 (2H, nbd olef. CH), 4.15, 4.33 (2H, nbd olef. CH), 4.65 (s, 2H, gly CH_2).

[(nbd)RuCl(D,L-ala)(nBuNH$_2$)] (9)

A total of 160 mg (0.51 mmol) of **2** and 5 ml of n-$BuNH_2$ was heated with stirring for 15 h at reflux. The solution was cooled to –30 °C yield deep red needles of **9**, which were recrystallized from 1 ml methanol. Yield 25 mg (13%).

[(nbd)Ru(aa)$_2$] (10, 11) (aa = L-val, L-phe)

In a typical preparation 181 mg (0.68 mmol) of $[(nbd)RuCl_2]_n$ and 161 mg (1.37 mmol) of L-valine were heated for 8 h with stirring in 20 ml H_2O at reflux. The solution was filtered and allowed to evaporate to dryness. The solid was dissolved in 3 ml methanol and the solution cooled to –30 °C to yield orange–yellow crystals of **10**. Yields **10** 95 mg (33%), **11** (27%). **10** ^{1}H NMR (D_2O, DSS) 1.0–1.2 (H, val CH_3), 1.47–1.61 (2H, nbd CH_2), 2.37 (2H, val β-CH), 3.8–4.0 (4H, nbd aliph. CH, val α-CH), 4.35–4.65 (4H, nbd olef. CH).

X-ray Structural Analysis for 7 and 11

Crystal and refinement data for 7 and **11** are summarized in Table 3. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections recorded on an Enraf-Nonius CAD4 diffractometer. Intensities were collected on the diffractometer at varied scan rates in the ω or ω–2θ mode with graphite-monochromated Cu Kα radiation. Empirical absorption corrections were applied to the reflection intensities for both data sets. The structures were solved by direct methods (7) or Patterson syntheses (**11**) and refined by full-matrix least-squares. The phenyl rings were refined rigid groups with d(C–C) = 1.395 Å in 7. Anisotropic temperature factors were introduced for the Ru and Cl atoms in 7 and for all non-hydrogen atoms in **11**. Difference syntheses revealed the positions of all

TABLE 3. Crystal and refinement data for [(cod)Ru(D,L-phe)]$_4$ (7) and [(nbd)Ru(L-phe)$_2$]·CH$_3$OH (11)

Compound	7	11
Space group	$P2_1/n$	$P2_12_12_1$
a (Å)	17.403(8)	11.329(1)
b (Å)	25.140(4)	34.186(3)
c (Å)	16.561(6)	6.193(1)
β (°)	93.04(5)	90
V (Å^3)	7235(7)	2399(1)
Z	4	4
D_c (g cm^{-3})	1.50	1.53
Radiation	Cu Kα	Cu Kα
μ (cm^{-1})	86.2	57.3
Scan method	ω	$\omega-2\theta$
$2\theta_{max}$ (°)	105	145
Reflections measured	8216	2800
Reflections observed	5609	2697
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 2\sigma(F_o^2)$
R	0.071	0.024
R_w	0.064	0.025
p	0.014	0.045

hydrogen atoms in **11** and these were included in the final refinement cycles. Hydrogen atoms were not considered for 7. The terminal reliability indices are listed in Table 3, where $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$; weights were applied using the expression $w = (\sigma^2(F_o) + p^2F_o^2)^{-1}$, with values of p as given in Table 3. Calculations were performed with MULTAN-82 [6], SHELX-76 [7] with the SDP suite (Enraf-Nonius) and with local programs. Diagrams were drawn with RSPLOT [8]. Atom positional parameters with isotropic temperature factors are listed in Table 4, bond distances to the Ru atoms in Table 5.

Discussion

As depicted in Fig. 1 the X-ray structural analysis of 7 [(cod)RuCl(D,L-phe)]$_4$, demonstrates that the complex is tetrameric in the solid state with tridentate [N(ammine), O(carboxyl), O(carboxyl′)]-phenylalaninate ligands. The carboxyl groups participate in a five-membered chelate ring via one oxygen atom (On2, n = 1–4) and bridge to a further Ru atom via the second oxygen atom (On1, n = 1,4). This tridentate mode of coordination has, to our knowledge [9, 10], not previously been observed in the solid state for a metal complex of an amino acid. Inspection of the C–O distances in the individual amino acidate ligands of 7 indicates that the carboxyl bridges may be regarded as effectively symmetrical. Differences of respectively 0.024, –0.013, 0.006 and 0.018 Å are observed between Ru–On1-(bridge) and Ru–On2–(chelate) bonds (n = 1–4).

TABLE 4. Atom positional parameters with equivalent isotropic temperature factors (Å^2 × 10^3)

Atom	x/a	y/b	z/c	U_{eq}
7				
Ru1	0.0512(1)	0.1504(1)	0.0168(1)	41(1)
Ru2	0.2784(1)	0.1738(1)	0.2647(1)	49(1)
Ru3	0.4899(1)	0.1438(1)	0.0328(1)	41(1)
Ru4	0.2669(1)	0.2239(1)	–0.1852(1)	41(1)
Cl1	–0.0016(2)	0.1285(2)	0.1428(2)	55(3)
Cl2	0.4051(2)	0.1732(2)	0.3287(3)	74(3)
Cl3	0.5317(2)	0.1504(2)	–0.1019(2)	61(3)
Cl4	0.1399(2)	0.2368(2)	–0.2422(2)	62(3)
O11	0.2182(5)	0.2456(4)	–0.0750(6)	50(3)
O12	0.1312(5)	0.1811(4)	–0.0603(5)	44(3)
O21	0.1551(5)	0.1134(4)	0.0668(6)	49(3)
O22	0.1922(5)	0.1626(4)	0.1724(6)	51(3)
O31	0.3297(6)	0.2157(4)	0.1702(6)	56(3)
O32	0.4172(5)	0.1581(4)	0.1267(5)	49(3)
O41	0.3811(5)	0.1233(4)	–0.0238(6)	49(3)
O42	0.3501(5)	0.1939(4)	–0.1017(5)	45(3)
N12	0.0786(6)	0.2235(4)	0.0769(7)	46(3)
N22	0.3111(6)	0.0975(5)	0.2203(7)	50(3)
N32	0.4707(6)	0.2269(4)	0.0173(7)	45(3)
N42	0.2290(6)	0.1431(4)	–0.1783(7)	43(3)
C11	0.1628(8)	0.2254(6)	–0.0406(9)	46(4)
C12	0.1364(9)	0.2564(6)	0.0335(10)	68(5)
C13	0.1030(10)	0.3091(6)	–0.0002(9)	89(6)
C14	0.0663(8)	0.3406(4)	0.0656(7)	82(6)
C15	–0.0104(8)	0.3564(4)	0.0539(7)	105(7)
C16	–0.0450(8)	0.3860(4)	0.1133(7)	128(8)
C17	–0.0030(8)	0.3998(4)	0.1843(7)	110(7)
C18	0.0736(8)	0.3840(4)	0.1959(7)	108(7)
C19	0.1083(8)	0.3544(4)	0.1366(7)	93(6)
C21	0.1987(8)	0.1236(6)	0.1273(9)	43(4)
C22	0.2687(9)	0.0864(5)	0.1406(9)	55(5)
C23	0.2488(8)	0.0266(5)	0.1286(8)	52(4)
C24	0.2007(7)	0.0043(5)	0.1943(7)	72(5)
C25	0.1258(7)	0.0218(5)	0.2046(7)	73(5)
C26	0.0845(7)	0.0017(5)	0.2679(7)	108(7)
C27	0.1182(7)	–0.0358(5)	0.3208(7)	160(10)
C28	0.1931(7)	–0.0533(5)	0.3104(7)	183(12)
C29	0.2344(7)	–0.0332(5)	0.2472(7)	150(10)
C31	0.3866(9)	0.2042(6)	0.1285(9)	52(4)
C32	0.4125(9)	0.2482(6)	0.0728(9)	62(5)
C33	0.4434(9)	0.2943(5)	0.1257(9)	74(5)
C34	0.4725(9)	0.3396(4)	0.0750(8)	72(5)
C35	0.5502(9)	0.3513(4)	0.0906(8)	110(7)
C36	0.5844(9)	0.3925(4)	0.0489(8)	147(10)
C37	0.5408(9)	0.4220(4)	–0.0084(8)	117(8)
C38	0.4631(9)	0.4102(4)	–0.0239(8)	118(8)
C39	0.4290(9)	0.3690(4)	0.0177(8)	130(9)
C41	0.3422(8)	0.1456(6)	–0.0802(9)	48(4)
C42	0.2778(8)	0.1110(6)	–0.1205(9)	57(5)
C43	0.3173(7)	0.0649(5)	–0.1626(9)	69(5)
C44	0.2584(6)	0.0274(4)	–0.2003(9)	65(5)
C45	0.2075(6)	–0.0015(4)	–0.1549(9)	77(6)
C46	0.1553(6)	–0.0366(4)	–0.1933(9)	107(7)
C47	0.1540(6)	–0.0428(4)	–0.2771(9)	151(10)
C48	0.2048(6)	–0.0139(4)	–0.3225(9)	230(16)
C49	0.2571(6)	0.0211(4)	–0.2841(9)	164(11)

(continued)

TABLE 4. *(continued)*

Atom	x/a	y/b	z/c	U_{eq}
C111	0.0046(8)	0.0705(6)	−0.0125(8)	55(5)
C112	0.0502(8)	0.0878(6)	−0.0755(8)	60(5)
C113	0.0192(9)	0.1090(6)	−0.1583(8)	68(5)
C114	−0.0280(10)	0.1604(6)	−0.1547(9)	86(6)
C115	−0.0243(8)	0.1908(6)	−0.0741(8)	51(4)
C116	−0.0665(8)	0.1740(5)	−0.0088(8)	50(4)
C117	−0.1213(8)	0.1258(5)	−0.0109(10)	71(5)
C118	−0.0842(8)	0.0712(6)	−0.0217(11)	86(6)
C119	0.2753(9)	0.2514(7)	0.3291(9)	73(5)
C212	0.2095(8)	0.2459(6)	0.2777(9)	61(5)
C213	0.1307(9)	0.2316(6)	0.3106(11)	83(6)
C214	0.1171(9)	0.1737(6)	0.3336(11)	83(6)
C215	0.1882(8)	0.1372(6)	0.3320(10)	68(5)
C216	0.2548(9)	0.1428(6)	0.3833(9)	71(5)
C217	0.2599(10)	0.1860(6)	0.4504(10)	90(6)
C218	0.2739(10)	0.2427(7)	0.4214(9)	89(6)
C311	0.5746(8)	0.1587(6)	0.1287(8)	56(5)
C312	0.6124(8)	0.1531(5)	0.0567(8)	53(4)
C313	0.6570(9)	0.1020(5)	0.0357(10)	74(5)
C314	0.6081(7)	0.0561(6)	0.0013(10)	74(5)
C315	0.5212(7)	0.0622(6)	0.0123(8)	51(4)
C316	0.4886(8)	0.0647(6)	0.0877(7)	50(4)
C317	0.5346(8)	0.0636(6)	0.1703(8)	67(5)
C318	0.5722(10)	0.1166(6)	0.1959(9)	80(6)
C411	0.3362(7)	0.2941(5)	−0.1631(8)	46(4)
C412	0.2753(8)	0.3097(6)	−0.2167(7)	61(5)
C413	0.2851(9)	0.3173(7)	−0.3080(8)	67(5)
C414	0.2744(9)	0.2649(6)	−0.3583(10)	72(5)
C415	0.2881(8)	0.2126(5)	−0.3108(8)	56(5)
C416	0.3566(7)	0.2035(5)	−0.2641(9)	53(4)
C417	0.4241(8)	0.2439(6)	−0.2589(9)	69(5)
C418	0.4187(7)	0.2854(6)	−0.1913(9)	63(5)
11				
Ru1	−0.0847(1)	0.6463(1)	0.4025(1)	24(1)
O11	−0.1107(2)	0.6114(1)	0.1291(4)	35(1)
O12	−0.0162(3)	0.5722(1)	−0.0933(5)	54(2)
O21	0.0497(2)	0.6708(1)	0.2126(5)	33(1)
O22	0.1940(3)	0.7146(1)	0.2040(6)	45(2)
N11	0.0264(3)	0.5969(1)	0.4683(6)	30(2)
N21	0.0101(3)	0.6781(1)	0.6416(5)	29(2)
C11	−0.0268(4)	0.5880(1)	0.0832(7)	34(2)
C12	0.0654(3)	0.5805(1)	0.2598(7)	33(2)
C13	0.1038(4)	0.5374(1)	0.2739(8)	41(2)
C14	0.0104(4)	0.5099(1)	0.3595(7)	35(2)
C15	−0.0855(4)	0.4992(1)	0.2326(8)	47(2)
C16	−0.1689(5)	0.4726(1)	0.3095(12)	62(3)
C17	−0.1566(5)	0.4564(1)	0.5083(11)	61(3)
C18	−0.0650(5)	0.4670(1)	0.6380(9)	60(3)
C19	0.0200(4)	0.4940(1)	0.5658(9)	49(3)
C21	0.1184(3)	0.6956(1)	0.3025(7)	30(2)
C23	0.2240(4)	0.6968(1)	0.6606(8)	37(2)
C24	0.2707(3)	0.6556(1)	0.6491(6)	33(2)
C25	0.2629(4)	0.6312(1)	0.8276(9)	52(3)
C26	0.3061(5)	0.5930(2)	0.8164(11)	64(3)
C27	0.3571(4)	0.5794(1)	0.6289(11)	62(3)
C28	0.3654(4)	0.6034(2)	0.4504(9)	51(3)
C29	0.3230(3)	0.6413(1)	0.4597(7)	41(2)
C11	−0.2357(4)	0.6752(1)	0.2576(8)	38(2)
C112	−0.1989(3)	0.6973(1)	0.4321(8)	35(2)
C113	−0.2700(4)	0.6828(1)	0.6291(8)	38(2)
C114	−0.2140(3)	0.6420(1)	0.6571(6)	33(2)
C115	−0.2510(4)	0.6199(1)	0.4827(7)	37(2)
C116	−0.3290(4)	0.6467(1)	0.3456(7)	41(2)
C117	−0.3875(4)	0.6719(2)	0.5207(10)	51(3)
O1	0.4142(4)	0.7468(1)	0.1826(8)	74(2)
C1	0.4753(5)	0.7273(2)	0.0189(11)	57(3)

TABLE 5. Bond distances (Å) to the ruthenium atoms in 7 and 11

7			
Ru1–Cl1	2.388(4)	Ru3–Cl3	2.388(4)
Ru1–O21	2.159(9)	Ru3–O41	2.130(9)
Ru1–O12	2.086(9)	Ru3–O32	2.088(9)
Ru1–N12	2.132(11)	Ru3–N32	2.129(11)
Ru1–C111	2.209(15)	Ru3–C311	2.143(15)
Ru1–C112	2.192(15)	Ru3–C312	2.161(14)
Ru1–C115	2.194(14)	Ru3–C315	2.155(15)
Ru1–C116	2.154(14)	Ru3–C316	2.190(14)
Ru2–Cl2	2.396(4)	Ru4–Cl4	2.378(4)
Ru2–O31	2.122(10)	Ru4–O11	2.123(10)
Ru2–O22	2.103(9)	Ru4–O42	2.090(9)
Ru2–N22	2.141(12)	Ru4–N42	2.140(11)
Ru2–C211	2.226(17)	Ru4–C411	2.157(14)
Ru2–C212	2.189(15)	Ru4–C412	2.225(15)
Ru2–C215	2.177(16)	Ru4–C415	2.151(15)
Ru2–C216	2.173(16)	Ru4–C416	2.151(14)
11			
Ru1–O11	2.091(3)	Ru1–O21	2.099(3)
Ru1–N11	2.146(4)	Ru1–N21	2.129(4)
Ru1–C111	2.169(5)	Ru1–C112	2.180(4)
Ru1–C114	2.157(4)	Ru1–C115	2.147(5)

The C–O bond distances all fall within the relatively narrow range 1.239(15)–1.277(15) Å. Carboxyl groups binding two metal atoms more or less equally have previously been observed in complexes such as [Ag(glyH)]NO_3 [11], [Ag(glyglyH)]NO_3 [12] and [Nd$(glyH)_3(OH_2)_2$]$Cl_3 \cdot H_2O$ [13]. The Ru–O bond configuration about the carboxyl groups is *anti–syn* relative to C–O*n*1 and C–O*n*2 for each of the phenylalanate ligands in 7. The coordination spheres of the Ru atoms each display the bridging O atom sited *trans* to a 1,5-cyclooctadiene C–C double bond, the chelate O atom *trans* to a terminal chlorine. A *trans* influence on the Ru–O bond lengths is evidenced by the following values

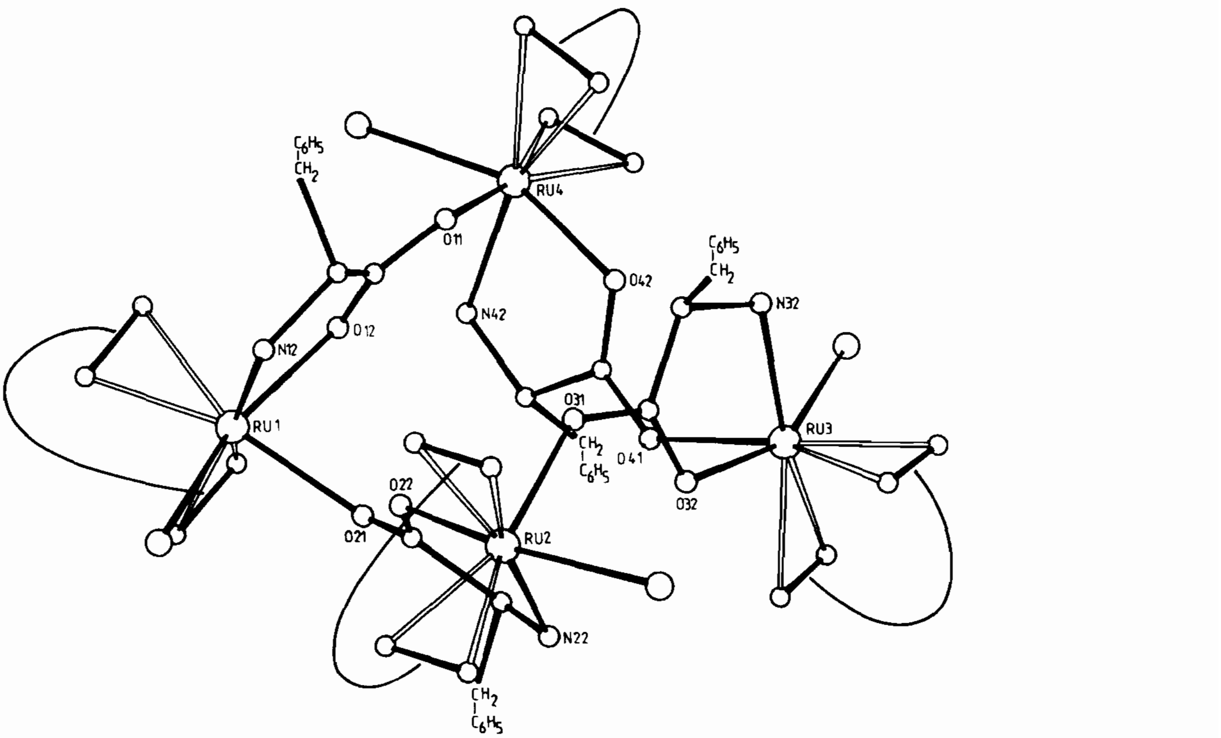

Fig. 1. Structure of [(cod)Ru(D,L-phe)Cl]$_4$ (7). The cod and phenyl rings are omitted for clarity.

Ru1–O21	2.159(9) Å	Ru1–O12	2.086(9) Å
Ru2–O31	2.122(10) Å	Ru2–O22	2.103(9) Å
Ru3–O41	2.130(9) Å	Ru3–O32	2.088(9) Å
Ru4–O11	2.123(10) Å	Ru4–O42	2.090(9) Å

Figure 2 displays the individual coordination spheres of the Ru atoms. The configurational chiralities are respectively Λ,*R*, Δ,*S*, Λ,*R* and Δ,*S*, where the second position refers to the amino acidate ligand. As 7 crystallizes in the centrosymmetric space group $P2_1/n$ enantiomeric pairs are present in the unit cell. Deviations from the best least-squares plane are small for the chelate rings in the coordination spheres of Ru1 and Ru4. The nitrogen atoms in the five-membered rings of Ru2 and Ru3 are displaced by respectively −0.289 and 0.105 Å from the least-squares planes through the remaining four ring atoms, which means that an envelope distortion is observed in both cases.

The IR spectrum of 7 corresponds to the crystal structure. As a result of the symmetrical bridging coordination mode of the carboxyl group the ν(C=O) signal is shifted to a lower wave number (1573 cm^{-1}) than in complexes in which a single carboxyl oxygen is binded to a metal (e.g. 1620 cm^{-1} in **11**). In the presumably polymeric complexes [(diene)RuCl(aa)$_n$] (1–6), which are insoluble in a range of polar and non-polar solvents such as H_2O, CH_3OH, CH_2Cl_2, DMSO, diethyl ether and benzene, ν(C=O) occurs at even lower wave numbers (1540–1570 cm^{-1}), in accordance with participation of carboxyl groups in symmetrical bridges as in 7. The ν(NH$_2$) bonds are observed at wave numbers (3100–3320 cm^{-1}) similar to those in 7 (3230, 3290 cm^{-1}), which suggests that the amino group is also *trans* to a cod double bond in 1–6. Upon reaction of [(diene)RuCl(aa)]$_n$ with nitrogen bases B to yield monomeric complexes [(diene)RuCl(aa)B] (8, 9), it may be assumed that the amino acidate chelate ring remains intact and that the Ru–O bond to the bridging O(carboxyl) is replaced by a Ru–N bond to the base; ν(C=O) shifts to respectively 1610 and 1635 cm^{-1} in 8 and 9.

Both of the phenylalaninate ligands in Δ-[(nbd)-Ru(L-phe)$_2$] (II) participate in five-membered chelate rings with N,O-coordination as depicted in Fig. 3. N11 of the first and O21 of the second amino acidate ligand are sited *trans* to nbd double bonds, so that the coordination may be described as *OC*-6-32 [14]. The configurational chirality of this tris-bidentate complex may be designated as Δ. Alternative ligand arrangements would be *OC*-6-13 (O atoms *trans*) or *OC*-6-33 (N atoms *trans*). The solvate methanol molecule in the unit cell participates in two hydrogen bonds, namely an O1–H...O22 interaction of length 2.73 Å to the first molecule and an O1...H–N21 interaction of length 2.99 Å to a symmetry related molecule (0.5 + *x*, 0.5 − *y*, 1 − *z*). It is possible that these or other lattice interactions lead to the ob-

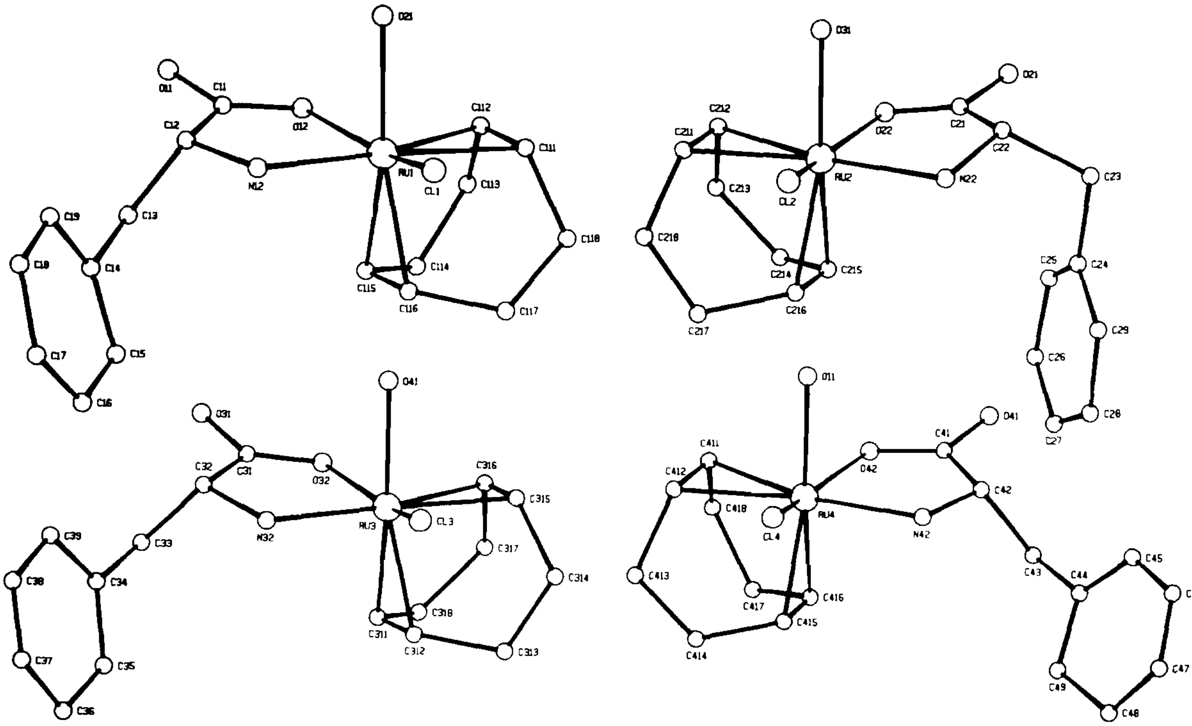

Fig. 2. Coordination spheres of the four Ru atoms of $[(cod)Ru(D,L\text{-}phe)Cl]_4$ with the numbering scheme.

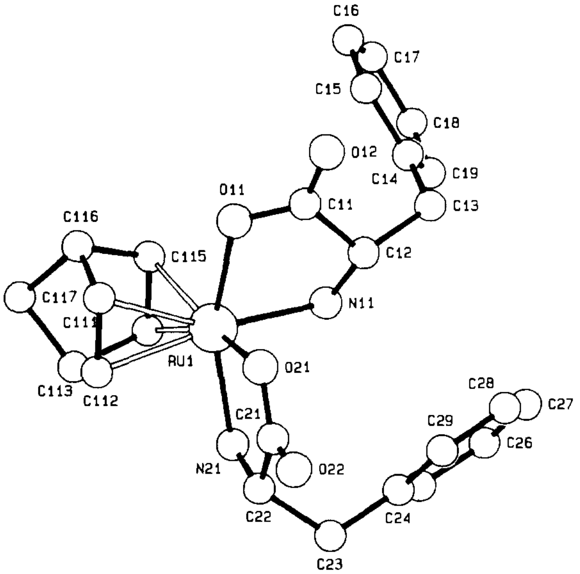

Fig. 3. Structure of Δ-$[(nbd)Ru(L\text{-}phe)_2]$ (11).

served crystallization of the Δ diastereomer; intramolecular steric contacts cannot be responsible for the preference of this chirality at the central ruthenium atom. Comparison of the Ru1–N11 (2.146 Å) and Ru1–N21 (2.129 Å) distances suggests that the Ru–olefin(cod) bond exhibits a small *trans* influence on the former bond. A similar, though not significant difference, is found for Ru1–O21 (2.099 Å) and Ru1–O11 (2.091 Å). Ru–N and Ru–O distances in **11** are similar to those in the amino acidate chelate rings of **7**.

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