Bis(2-diphenylphosphinoethyl)phenylphosphineruthenium(II) complexes of amino acids and dipeptides

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Abstract

The monomeric complexes [RuCl(aa)(triphos)] (aaH = L-alaH (**2**), L-valH (**3**)), in which the bioligands display a κ^2N,O coordination, may be prepared by the reaction of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) (triphos = bis(2-diphenylphosphinoethyl)phenylphosphine) with the appropriate amino acid in methanol. An X-ray analysis on **3** established an *OC*-6-35 geometry with the triphosphine ligand in a facial position. This is also the case for triphos in [Ru(glyglyH$_{-1}$)(triphos)] (**4**) and [Ru(metglyH$_{-1}$)(triphos)] (**5**) prepared by cleavage of chloro bridges in **1** by the appropriate dipeptides, which, therefore, require pyramidal metallated peptide nitrogen atoms. The dipeptides display a κ^3N,N',O coordination in both complexes with an angle sum of 344° at the peptide nitrogen in **5** as determined by X-ray analysis.

Key words: Crystal structures; Ruthenium complexes; Amino acid complexes; Peptide complexes

Introduction

A number of publications have appeared in recent years which describe the synthesis and structural characterisation of organometallic complexes of α-amino acids and peptides [1–9]. These have included (η^6-arene)Ru(II) (arene = C_6H_6, *p*-cymene), (η^6-C_6H_6)-Os(II) and (η^5-Cp*)M(III) derivatives (Cp* = C_5Me_5, M = Co, Rh, Ir) in which the amino acidate ligands are bi- or tridentate [1–9]. Such half-sandwich complexes display chirality both at the asymmetrically substituted transition metal atom and at the α-carbon of the bioligand and offer considerable potential for enantioselective synthesis.

A potential alternative to the facially coordinating organometallic ligands should be provided by triphosphines such as ($CH_3C(CH_2PPh_2)_3$) (tripod) or ($PhP(CH_2CH_2PPh_2)_2$) (triphos). Treatment of [$RuCl_2$-$(DMSO)_4$] with tripod in toluene yields the dinuclear complex $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]Cl$ [10]. The structure of the cation was determined by X-ray structural analysis for $[Ru_2(\mu\text{-}Cl)_3(tripod)_2][BPh_4]$, obtained by anion exchange with $Na[BPh_4]$ in CH_3OH [10]. In the same work, the reactivity of complexes of the type $[Ru(solvent)_3(tripod)]^{2+}$ (solvent = DMSO, CH_3CN) towards carbon monoxide was investigated as a preliminary to catalytic studies. King reported the preparation of [$RuCl_2$(triphos)] in 1971 by the reaction of commercial hydrated $RuCl_3$ with triphos in refluxing ethanol in the presence of concentrated HCl and formulated his product as a dimer with two chloro bridges [11]. An alternative synthesis was provided by Suarez and Fontal, who employed [$RuCl_2(DMSO)_4$] and triphos in refluxing toluene [12]. [$RuCl_2$(triphos)] was found to catalyse the homogeneous hydrogenation and isomerisation of olefins under moderate conditions [12]. [$RuCl_2$-$(triphos)_2$] has been prepared by the reaction of [$RuCl_2(PPh_3)_3$] and triphos in a 1:2 molecular ratio in hexane. An X-ray structural analysis established the presence of both a monodentate and a tridentate triphosphine ligand in this monomeric octahedral complex [13]. The κ^3P,P',P'' ligand adopts a meridional arrangement less typical for triphos, which usually displays a facial configuration as in $[Fe_2(\mu\text{-}SH)_3(triphos)_2]ClO_4$ [14].

We have now performed a study of the reactivity of **1** towards amino acids and dipeptides and report the structural characterisation of complexes of the type [RuCl(aa)(triphos)] (aaH = L-alaH (**2**), L-valH (**3**)) and [Ru(dipepH$_{-1}$)(triphos)] (dipepH = glyglyH (**4**), L-metglyH (**5**)).

Experimental

All solvents were dried and distilled before use. IR spectra were recorded as 1% KBr discs on a Perkin-

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Elmer 1760, FAB-MS on a Fisons VG Autospec and NMR spectra on a Bruker AM 400 (400 MHz). Reg-istered δ values are in ppm relative to the signal of the deuterated solvent for ^{1}H NMR spectra and external 85% H_3PO_4 for the $^{31}P\{^1H\}$ NMR spectra. Elemental analyses were performed on a Carlo Erba 1106. $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**) was prepared by the literature procedure from $[RuCl_2(DMSO)_4]$ and triphos in toluene [12]. Amino acids and dipeptides were purchased from Sigma or Bachema.

Preparation of complexes 1–5

$[Ru_2(\mu\text{-}Cl)_3(triphos)_2][BPh_4]$ (1a)

1a was obtained by anion exchange from **1**. 9.6 mg (0.028 mmol) of $NaBPh_4$ were added to a solution of 40 mg (0.028 mmol) of **1** in 10 ml CH_3OH leading to the precipitation of **1a** (yield 85%). Crystals suitable for an X-ray structural analysis were obtained by slow evaporation of a CH_2Cl_2/CH_3OH solution. *Anal.* Found: C, 65.0; H, 5.3. Calc. for $C_{92}H_{86}BP_6Cl_3Ru_2$ (M = 1696.8): C, 65.1; H, 5.1%. FAB-MS: *m/z* (%) 1379(61) [M^+(cation) + 2H], 671(47) [(RuCl(triphos))$^+$], 635(42) [(Ru(triphos))$^+$]. IR: 1485m, 1435s, 1102s ν(P–C) cm^{-1}. ^{1}H NMR (CD_2Cl_2) 1.4–2.7 (m, 16H, CH_2), 6.8–8.1 (m, 70H, C_6H_5) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) 98.5 (t, 1P, PPh), 68.7 (d, 2P, PPh_2) ppm.

[RuCl(L-ala)(triphos)] (2)

A solution of 18 mg (0.20 mmol) L-alaH in 3 ml CH_3OH in the presence of 0.2 ml 1 M methanolic KOH was added to a suspension of 141 mg (0.10 mmol) of **1** in 7 ml CH_3OH. After heating for 12 h at 50 °C the solvent was removed from the yellow solution and the resulting solid dissolved in 4 ml CH_2Cl_2. After filtration of KCl the solution was covered with 10 ml hexane to yield yellow crystals of **2** over 2–3 days (yield 71%). *Anal.* Found: C, 55.8; H, 5.2; N, 1.2. Calc. for $C_{37}H_{39}NO_2P_3ClRu \cdot 1/2CH_2Cl_2$ (M = 801.6): C, 56.2; H, 5.0; N, 1.7%. FAB-MS: *m/z* (%) 759(14) [M^+], 724(25) ($M^+ - {}^{35}Cl$], 671(100) [M$^+$-L-ala]. IR: 3336, 3277, 3226 $\nu(NH_2)$ 1610vs $\nu(CO_2)$ cm^{-1}. ^{1}H NMR (CD_3OD) 0.85, 1.03 (2d, 3H, CH_3), 1.7–3.5 (m, 9H, α-CH, CH_2), 6.8–8.1 (m, 25H, Ph) ppm. $^{31}P\{^1H\}$ NMR (CD_3OD) 103.7, 101.7 (2t, 1P, PPh), 69.7, 67.2 (dd, 1P, PPh_2), 66.4, 65.7 (dd, 1P, PPh_2) ppm.

[RuCl(L-val)(triphos)] (3)

A suspension of 101 mg (0.07 mmol) of **1** in 8 ml CH_3OH in the presence of 0.14 ml 1 M methanolic CH_3ONa was stirred for 3 h. After addition of 17 mg (0.14 mmol) L-valH the reaction mixture was refluxed for 4 h leading to a colour change from green to orange. The solution was reduced in volume to 3 ml. Addition of diethyl ether led to precipitation of **3**, which was recrystallised from methanol (yield 63%). *Anal.* Found: C, 59.5; H, 5.8; N, 1.6. Calc. for $C_{39}H_{43}NO_2P_3ClRu$ (M = 787.2): C, 59.5; H, 5.5; N, 1.8%. FAB-MS: *m/z* (%) 787(18) [M^+], 752(23) [$M^+ - {}^{35}Cl$], 671(77) [M^+ – L-val]. IR: 3339, 3240 $\nu(NH_2)$ 1605s $\nu(CO_2)$ cm^{-1}. ^{1}H NMR (CD_3OD) 0.23, 0.72 (2d, 6H, CH_3), 1.5–3.8 (m, 10H, α-CH, β-CH, CH_2), 6.7–8.2 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR (CD_3OD) 102.2 (t, 1P, PPh), 70.0, 66.4 (2dd, 2P, PPh_2).

[Ru(glyglyH$_{-1}$)(triphos)] (4)

A solution of 22.5 mg (0.17 mmol) of glyglyH in 3 ml CH_3OH in the presence of 0.34 ml 1 M methanolic KOH was added to a suspension of 120 mg (0.085 mmol) of **1** in 5 ml CH_3OH. After refluxing for 6 h the solvent was removed and the resulting solid dissolved in 4 ml CH_2Cl_2. After filtration of KCl the solution was covered with 10 ml hexane to yield yellow crystals of **4** over 3–4 days (yield 79%). *Anal.* Found: C, 55.9; H, 5.5; N, 3.0. Calc. for $C_{38}H_{39}N_2O_3P_3Ru \cdot \frac{1}{2}CH_2Cl_2 \cdot H_2O$ (M = 826.2): C, 56.0; H, 5.1; N, 3.4%. FAB-MS: *m/z* (%) 767(35) [M^+], 635(36) [M^+ – glyglyH$_{-1}$]. IR: 3291, 3213, 3135 $\nu(NH_2)$, 1597s $\nu(CO_2)$ cm^{-1}. ^{1}H NMR ($CDCl_3$) 1.35–3.35 (m, 10H, $-CH_2NH_2$, CH_2 (triphos)), 3.5, 4.9 (2d, 2H, $-CH_2COO$), 6.7–7.9 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 90.7 (t, 1P, PPh), 66.0, 61.2 (2t, 2P, PPh_2).

[Ru(L-metglyH$_{-1}$)(triphos)] (5)

A solution of 41 mg (0.20 mmol) of L-metglyH in 4 ml CH_3OH in the presence of 0.40 ml 1 M methanolic KOH was added to a suspension of 141 mg (0.10 mmol) of **1** in 5 ml CH_3OH and the reaction mixture refluxed for 12 h. After removal of the solvent, addition of 3 ml CH_2Cl_2 and subsequent filtration of KCl, the resulting solution was covered with 10 ml hexane to yield yellow crystals of **5** in 2–3 days (yield 80%). *Anal.* Found: C, 55.9; H, 5.4; N, 2.8. Calc. for $C_{41}H_{45}N_2O_3P_3SRu \cdot \frac{1}{2}CH_2Cl_2$ (M = 882.3): C, 56.5; H, 5.3; N, 3.2%. FAB-MS: *m/z* (%) 841(54) [M^+ + H], 796(26) [M^+ + 2H – CH_2S], 635(56) [M^+ – L-metglyH$_{-1}$]. IR: 3275, 3223, 3136 $\nu(NH_2)$, 1605s $\nu(CO_2)$ cm^{-1}. ^{1}H NMR ($CDCl_3$) 1.05–3.40 (m, 13H, α-CH, β-CH_2, γ-CH_2, CH_2 (triphos)), 2.0 (s, 3H, $-SCH_3$), 3.55, 4.98 (2d, 2H, $-CH_2COO$), 6.7–8.1 (m, 25H, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 89.8 (t, 1P, PPh), 65.4, 60.8 (2t, 2P, PPh_2).

X-ray structural analyses of 1a, 3 and 5

Crystal and refinement data are summarised in Table 1. Unit cell constants were obtained for the crystals from least-squares fits to the settings of 25 reflections centred on a Siemens P4 diffractometer. Intensities were collected at 22 °C on the diffractometer at varied scan rates in the ω mode for Mo Kα radiation. Semi-empirical absorption corrections (ψ-scan) were applied to the reflection intensities. The structures were solved

TABLE 1. Crystal and refinement data

Compound	**1a**·2.5CH_2Cl_2·0.5H_2O	**3**·4CH_3OH	**5**·CH_2Cl_2
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$
a (Å)	12.120(2)	9.538(2)	10.422(2)
b (Å)	19.473(4)	19.537(4)	16.542(3)
c (Å)	19.403(4)	12.902(2)	24.788(3)
α (°)	81.26(3)	90	90
β (°)	88.18(3)	108.80(2)	90
γ (°)	85.99(3)	90	90
V (Å^3)	4514(1)	2275.9(8)	4273(1)
Z	2	2	4
F (000)	1964	956	1904
M (g cm^{-1})	1918.1	915.3	924.8
D_c (g cm^{-3})	1.41	1.34	1.44
Radiation	Mo Kα	Mo Kα	Mo Kα
μ (cm^{-1})	7.2	5.4	6.8
Crystal size (mm)	0.21×0.32×0.38	0.36×0.40×0.62	0.24×0.28×0.58
Scan method	ω	ω	ω
2θ Range	$2\theta \leqslant 45°$	$2\theta \leqslant 50°$	$2\theta \leqslant 50°$
Reflections measured	11583	4109	4222
Reflections observed	7485	3448	2391
Rejection criterion	$F_o^2 \leqslant 2\sigma(F_o^2)$	$F_o^2 \leqslant 2\sigma(F_o^2)$	$F_o^2 \leqslant 2\sigma(F_o^2)$
R	0.072	0.051	0.069
R_w	0.067	0.050	0.067
g	0.0001	0.00002	0.0001

by Patterson and difference syntheses and refined by full-matrix least-squares. The positions of three CH_2Cl_2 molecules and one disordered H_2O (site occupation factor 0.5) in the asymmetric unit of **1** were revealed by difference syntheses. One of the CH_2Cl_2 molecules (C(3'), Cl(31)) is disordered about a crystallographic centre of symmetry. Four CH_3OH molecules are contained in the asymmetric unit of **3**, one CH_2Cl_2 molecule in the asymmetric unit of **5**. Anisotropic temperature factors were introduced for the Ru, Cl, P, B and methylene C atoms in **1**, for all but the methanol solvate non-hydrogen atoms in **3** and for the Ru, P, S, O and N atoms in **5**. Hydrogen atoms were included where possible at geometrically calculated positions with group isotropic temperature factors. The absolute configurations of **3** and **5** were determined by use of Roger's η factor. Terminal reliability indices are listed in Table 1 where $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$; weights were applied using the expression $w = (\sigma^2(F_o) + gF_o^2)^{-1}$, with values of g as given in Table 1. Calculations were performed with the SHELXTL program system (Siemens). Atom coordinates and equivalent isotropic temperature factors are listed in Table 2.

Discussion

Reaction of $[RuCl_2(DMSO)_4]$ with triphos in refluxing toluene leads to the formation of $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]Cl$ (**1**), which contain a triply chloro bridged dinuclear cation and not a neutral dimer $[\{RuCl(\mu\text{-}Cl)(triphos)\}_2]$ [11] or a square pyramidal monomer [15] as previously formulated.

The structure of the cation as depicted in Fig. 1 was established by X-ray structural analysis for $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]BPh_4$ (**1a**) obtained by anion exchange

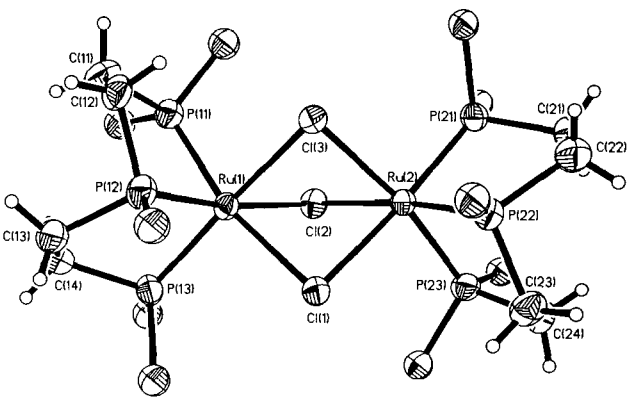


Fig. 1. Structure of the cation $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$ in **1a** (the ellipsoids represent 50% probability) with phenyl rings omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Cl(1) 2.504(3), Ru(1)–Cl(2) 2.515(3), Ru(1)–Cl(3) 2.492(3), Ru(2)–Cl(1) 2.506(3), Ru(2)–Cl(2) 2.537(3), Ru(2)–Cl(3) 2.492(3), Ru(1)–P(11) 2.314(3), Ru(1)–P(12) 2.247(3), Ru(1)–P(13) 2.306(3), Ru(2)–P(21) 2.280(3), Ru(2)–P(22) 2.257(3), Ru(2)–P(23) 2.301(3); P(11)–Ru(1)–P(12) 83.1(1), P(11)–Ru(1)–P(13) 97.4(1), P(12)–Ru(1)–P(13) 82.7(1), P(21)–Ru(2)–P(22) 83.9(1), P(21)–Ru(2)–P(23) 94.1(1), P(22)–Ru(2)–P(23) 83.6(1).

TABLE 2. Atom positional parameters with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
Compound **1a**				
Ru(1)	−689(1)	3466(1)	2937(1)	27(1)
P(11)	−2471(3)	3787(1)	2562(2)	36(1)
P(12)	−772(3)	4553(1)	3201(2)	36(1)
P(13)	−1114(3)	3184(1)	4108(1)	33(1)
C(11)	−2754(9)	4733(5)	2576(6)	40(5)
C(12)	−1682(9)	5107(5)	2578(5)	39(4)
C(13)	−1500(10)	4604(5)	4057(5)	45(5)
C(14)	−2024(9)	3916(5)	4345(5)	40(4)
C(111)	−4696(7)	3836(3)	3043(4)	52(3)
C(112)	−5605(7)	3568(3)	3425(4)	71(4)
C(113)	−5536(7)	2884(3)	3770(4)	65(4)
C(114)	−4558(7)	2468(3)	3732(4)	63(4)
C(115)	−3649(7)	2735(3)	3350(4)	52(3)
C(116)	−3718(7)	3419(3)	3006(4)	42(3)
C(121)	−2563(7)	4214(3)	1107(4)	55(3)
C(122)	−2776(7)	4122(3)	425(4)	66(4)
C(123)	−3152(7)	3494(3)	294(4)	68(4)
C(124)	−3316(7)	2958(3)	845(4)	60(4)
C(125)	−3103(7)	3050(3)	1526(4)	50(3)
C(126)	−2727(7)	3678(3)	1657(4)	39(3)
C(131)	1284(7)	4753(3)	3738(4)	54(3)
C(132)	2158(7)	5144(3)	3863(4)	66(4)
C(133)	2206(7)	5829(3)	3529(4)	61(4)
C(134)	1380(7)	6122(3)	3069(4)	67(4)
C(135)	506(7)	5731(3)	2944(4)	54(3)
C(136)	458(7)	5047(3)	3278(4)	37(3)
C(141)	80(5)	3565(3)	5221(4)	53(3)
C(142)	955(5)	3499(3)	5681(4)	64(4)
C(143)	1818(5)	2993(3)	5638(4)	63(4)
C(144)	1806(5)	2554(3)	5133(4)	56(3)
C(145)	931(5)	2621(3)	4672(4)	41(3)
C(146)	68(5)	3127(3)	4716(4)	36(3)
C(151)	−1487(6)	1778(4)	4210(3)	48(3)
C(152)	−1945(6)	1158(4)	4500(3)	68(4)
C(153)	−2694(6)	1151(4)	5061(3)	73(4)
C(154)	−2987(6)	1764(4)	5333(3)	75(4)
C(155)	−2530(6)	2383(4)	5043(3)	54(3)
C(156)	−1780(6)	2391(4)	4482(3)	38(3)
Cl(1)	1329(2)	3106(1)	3042(1)	33(1)
Cl(2)	−655(2)	2330(1)	2466(1)	33(1)
Cl(3)	−13(2)	3854(1)	1724(1)	33(1)
Ru(2)	1135(1)	2731(1)	1874(1)	27(1)
P(21)	922(3)	2531(1)	760(1)	32(1)
P(22)	2803(3)	3078(2)	1467(2)	35(1)
P(23)	2108(3)	1683(1)	2213(1)	35(1)
C(21)	2306(9)	2365(5)	372(5)	39(4)
C(22)	3110(10)	2899(6)	554(5)	46(5)
C(23)	3894(9)	2525(5)	1970(6)	44(5)
C(24)	3567(9)	1754(6)	1989(6)	45(5)
C(211)	785(5)	3917(3)	53(3)	41(3)
C(212)	451(5)	4446(3)	−483(3)	52(3)
C(213)	−303(5)	4319(3)	−970(3)	50(3)
C(214)	−722(5)	3664(3)	−921(3)	53(3)
C(215)	−388(5)	3136(3)	−386(3)	44(3)
C(216)	366(5)	3262(3)	101(3)	33(3)
C(221)	−965(6)	1789(3)	841(3)	42(3)
C(222)	−1642(6)	1297(3)	661(3)	49(3)
C(223)	−1240(6)	838(3)	211(3)	55(3)
C(224)	−160(6)	872(3)	−58(3)	53(3)
C(225)	517(6)	1364(3)	123(3)	44(3)
C(226)	114(6)	1823(3)	573(3)	33(3)
C(231)	2710(5)	4404(4)	1880(3)	47(3)
C(232)	3066(5)	5068(4)	1891(3)	64(4)
C(233)	3965(5)	5297(4)	1473(3)	60(4)
C(234)	4509(5)	4861(4)	1044(3)	61(4)
C(235)	4153(5)	4197(4)	1034(3)	51(3)
C(236)	3253(5)	3969(4)	1452(3)	37(3)
C(241)	3018(5)	1434(3)	3555(4)	49(3)
C(242)	3038(5)	1158(3)	4262(4)	56(3)
C(243)	2134(5)	818(3)	4576(4)	56(4)
C(244)	1211(5)	755(3)	4185(4)	65(4)
C(245)	1191(5)	1032(3)	3478(4)	50(3)
C(246)	2095(5)	1371(3)	3163(4)	34(3)
C(251)	656(5)	712(3)	1916(3)	39(3)
C(252)	386(5)	66(3)	1767(3)	54(3)
C(253)	1220(5)	−417(3)	1602(3)	57(4)
C(254)	2324(5)	−254(3)	1586(3)	62(4)
C(255)	2594(5)	392(3)	1735(3)	50(3)
C(256)	1760(5)	875(3)	1900(3)	36(3)
B	5416(8)	7797(5)	2686(5)	49(6)
C(61)	4251(6)	8967(4)	2977(4)	58(4)
C(62)	4121(6)	9551(4)	3315(4)	65(4)
C(63)	4937(6)	9685(4)	3759(4)	62(4)
C(64)	5884(6)	9235(4)	3864(4)	76(4)
C(65)	6014(6)	8651(4)	3525(4)	65(4)
C(66)	5198(6)	8517(4)	3082(4)	54(3)
C(71)	3364(8)	7681(4)	2276(3)	75(4)
C(72)	2556(8)	7693(4)	1777(3)	92(5)
C(73)	2839(8)	7827(4)	1069(3)	89(5)
C(74)	3928(8)	7950(4)	860(3)	99(5)
C(75)	4735(8)	7939(4)	1359(3)	79(4)
C(76)	4453(8)	7804(4)	2067(3)	52(3)
C(81)	5244(7)	7049(4)	3973(4)	61(4)
C(82)	5161(7)	6424(4)	4424(4)	93(5)
C(83)	5101(7)	5803(4)	4156(4)	95(5)
C(84)	5125(7)	5807(4)	3436(4)	83(5)
C(85)	5208(7)	6432(4)	2985(4)	69(4)
C(86)	5268(7)	7053(4)	3253(4)	49(3)
C(91)	6987(7)	8471(4)	1946(5)	83(5)
C(92)	8032(7)	8527(4)	1627(5)	94(5)
C(93)	8781(7)	7945(4)	1671(5)	103(6)
C(94)	8486(7)	7308(4)	2035(5)	128(7)
C(95)	7441(7)	7253(4)	2354(5)	101(5)
C(96)	6692(7)	7834(4)	2310(5)	58(4)
C(1′)	6778(14)	218(8)	2299(8)	126(7)
Cl(11)	5919(7)	476(4)	1569(4)	205(2)
Cl(12)	7057(6)	1000(4)	2592(4)	205(2)
C(2′)	10439(18)	8881(12)	3839(13)	266(15)
Cl(21)	9213(8)	9360(5)	3560(5)	262(3)
Cl(22)	10671(8)	8236(5)	3293(5)	262(3)
C(3′)	4489(15)	−376(10)	223(22)	176(19)
Cl(31)	4106(8)	527(5)	28(5)	268(4)
Ow	6601(27)	6352(16)	1143(16)	194(13)
Compound **3**				
Ru	6211(1)	0	2811(1)	32(1)
Cl	7459(3)	−1129(1)	2926(3)	50(1)
P(2)	5204(3)	1037(1)	2720(2)	38(1)
P(1)	5265(3)	37(2)	945(2)	35(1)

(continued)

TABLE 2. (*continued*)

Atom	x	y	z	U_{eq}
P(3)	4117(3)	−371(2)	3088(2)	38(1)
C(11)	4082(12)	804(5)	549(8)	43(4)
C(12)	4818(13)	1384(5)	1334(7)	46(5)
C(13)	3358(11)	1012(6)	2877(10)	53(5)
C(14)	2677(11)	295(4)	2668(9)	46(4)
C(112)	2622(3)	−586(2)	−367(2)	54(5)
C(113)	1806(3)	−1124(2)	−986(2)	77(6)
C(114)	2523(3)	−1717(2)	−1146(2)	72(7)
C(115)	4058(3)	−1773(2)	−686(2)	102(9)
C(116)	4875(3)	−1236(2)	−67(2)	82(7)
C(111)	4157(3)	−642(2)	92(2)	40(5)
C(122)	8005(3)	−217(2)	682(2)	41(4)
C(123)	9082(3)	−171(2)	167(2)	65(6)
C(124)	8838(3)	240(2)	−759(2)	70(6)
C(125)	7516(3)	603(2)	−1171(2)	62(6)
C(126)	6438(3)	557(2)	−656(2)	62(6)
C(121)	6683(3)	147(2)	271(2)	45(4)
C(132)	6135(3)	1782(2)	4685(2)	73(6)
C(133)	7027(3)	2258(2)	5407(2)	81(7)
C(134)	8057(3)	2642(2)	5094(2)	82(7)
C(135)	8193(3)	2551(2)	4059(2)	74(6)
C(136)	7301(3)	2075(2)	3336(2)	58(5)
C(131)	6271(3)	1691(2)	3649(2)	48(5)
C(142)	4129(3)	−18(2)	5224(2)	60(5)
C(143)	4496(3)	−131(2)	6348(2)	77(6)
C(144)	5192(3)	−739(2)	6805(2)	87(8)
C(145)	5520(3)	−1234(2)	6139(2)	91(8)
C(146)	5153(3)	−1121(2)	5015(2)	67(6)
C(141)	4458(3)	−513(2)	4558(2)	39(4)
C(152)	1566(3)	−1195(2)	2434(2)	53(5)
C(153)	761(3)	−1781(2)	1991(2)	65(6)
C(154)	1443(3)	−2316(2)	1620(2)	80(7)
C(155)	2930(3)	−2265(2)	1692(2)	75(7)
C(156)	3736(3)	−1679(2)	2135(2)	49(5)
C(151)	3054(3)	−1144(2)	2506(2)	44(5)
O(1)	8281(8)	453(3)	2843(5)	37(3)
O(2)	10360(8)	943(4)	3842(6)	48(3)
N	7507(8)	12(7)	4561(5)	42(3)
C(1)	9193(12)	625(5)	3738(8)	36(4)
C(2)	8806(12)	450(6)	4785(7)	40(4)
C(3)	10192(13)	165(6)	5703(8)	54(5)
C(4)	10616(16)	−558(7)	5421(12)	76(7)
C(5)	9869(16)	178(9)	6816(9)	95(8)
C(1′)	1796(25)	3080(12)	993(17)	172(9)
O(1′)	2251(23)	2658(10)	1865(15)	237(9)
C(2′)	7474(21)	7287(7)	4825(15)	103(6)
O(2′)	7458(11)	6596(5)	4567(8)	91(3)
C(3′)	9375(16)	1528(7)	1217(11)	87(5)
O(3′)	10015(12)	1858(6)	2150(9)	105(4)
C(4′)	7486(21)	6982(10)	1916(16)	135(7)
O(4′)	6752(15)	6464(7)	2250(11)	141(5)
Compound **5**				
Ru	7398(2)	6048(1)	1563(1)	36(1)
P(1)	7331(6)	5300(3)	2337(2)	47(2)
P(2)	5317(5)	5655(3)	1478(2)	44(2)
P(3)	6481(5)	7160(3)	1951(2)	42(2)
O(1)	9367(10)	6476(6)	1682(5)	40(5)
O(2)	11375(12)	6001(9)	1738(5)	69(6)
O(3)	9483(12)	5221(7)	235(5)	62(6)
N(1)	8250(14)	5275(8)	1081(5)	36(6)
N(2)	7406(17)	6663(7)	778(4)	37(5)
C(11)	5588(13)	5237(11)	2578(7)	47(6)
C(12)	4745(17)	5035(10)	2074(6)	44(6)
C(13)	4257(17)	6592(9)	1488(8)	58(6)
C(14)	4654(12)	7068(11)	1996(7)	47(6)
C(1)	10222(20)	5908(13)	1607(9)	54(6)
C(2)	9778(16)	5089(10)	1344(6)	26(4)
C(3)	8613(20)	5418(11)	570(8)	44(5)
C(4)	7483(20)	5999(10)	364(5)	41(4)
C(5)	7737(17)	6282(8)	−227(6)	35(5)
C(6)	6415(21)	6473(12)	−496(8)	62(6)
C(7)	6448(23)	8133(13)	−350(9)	83(8)
S	5464(6)	7275(4)	−179(2)	76(3)
C(112)	7604(9)	5743(8)	3418(5)	79(6)
C(113)	8309(9)	5943(8)	3878(5)	98(9)
C(114)	9644(9)	5990(8)	3851(5)	115(9)
C(115)	10274(9)	5836(8)	3365(5)	72(7)
C(116)	9569(9)	5636(8)	2906(5)	56(6)
C(111)	8234(9)	5589(8)	2932(5)	58(6)
C(122)	8097(11)	3852(5)	2787(4)	59(6)
C(123)	8285(11)	3018(5)	2799(4)	50(6)
C(124)	8109(11)	2561(5)	2331(4)	72(8)
C(125)	7746(11)	2940(5)	1852(4)	70(6)
C(126)	7558(11)	3775(5)	1841(4)	59(5)
C(121)	7734(11)	4231(5)	2308(4)	56(6)
C(132)	5409(8)	4469(7)	685(4)	47(5)
C(133)	4887(8)	3979(7)	283(4)	49(5)
C(134)	3608(8)	4078(7)	130(4)	45(5)
C(135)	2852(8)	4665(7)	379(4)	53(6)
C(136)	3375(8)	5155(7)	781(4)	57(6)
C(131)	4654(8)	5056(7)	934(4)	37(5)
C(142)	5747(10)	8489(6)	1305(5)	56(6)
C(143)	6012(10)	9185(6)	1007(5)	92(8)
C(144)	7275(10)	9451(6)	951(5)	86(7)
C(145)	8274(10)	9020(6)	1191(5)	94(8)
C(146)	8009(10)	8324(6)	1489(5)	72(7)
C(141)	6746(10)	8059(6)	1546(5)	44(5)
C(152)	6013(10)	7751(8)	3008(4)	51(6)
C(153)	6436(10)	8061(8)	3500(4)	78(7)
C(154)	7747(10)	8124(8)	3605(4)	94(8)
C(155)	8635(10)	7878(8)	3217(4)	86(8)
C(156)	8212(10)	7569(8)	2725(4)	74(8)
C(151)	6901(10)	7505(8)	2620(4)	41(6)
C′	10178(27)	3220(19)	122(10)	160(14)
Cl(1′)	10398(12)	3358(7)	−568(5)	218(5)
Cl(2′)	8578(15)	3073(8)	279(6)	285(7)

Equivalent isotropic temperature factors U_{eq} are defined as one third of the trace of the orthogonalised U_{ij} tensor.

from **1**. Both **1** and **1a** display effectively identical FAB mass spectra (matrix nitrobenzylalcohol) with a molecular ion $[M^+(\text{cation})+2\text{H}]$ at *m/z* 1379. The $^{31}P\{^1H\}$ NMR spectrum of **1a** in CD_2Cl_2 displays a triplet at 98.5 for the central phosphorus atom of the triphos ligand and a doublet at 68.7 ppm for the magnetically equivalent terminal phosphorus atoms. Chemical shifts of 98.5 and 68.5 ppm were reported for **1** by Suarez

and Fontal, who formulated the complex as a monomer [12].

The cation $[Ru_2(\mu\text{-}Cl)_3(triphos)_2]^+$ in **1a** displays a cofacial dioctahedral structure in which the common face contains the three bridging chlorine atoms. It is instructive to compare the molecular dimensions of **1a** with those of the analogous cation $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]^+$ [10] or with the related species $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]^+$ [16] and $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$ [17]. Average values of 2.49, 2.48 and 2.49 Å, respectively, are observed for the Ru–Cl distances in these complexes, 2.31, 2.32 and 2.29 Å for the Ru–P distances. Whereas the average Ru–P(terminal) bond length of 2.30 Å in **1a** is similar to the above values, the Ru–P(central) bonds display a marked shortening (av. 2.252 Å). A *trans* influence on the opposite Ru–Cl(2) bonds is apparent, as these are significantly longer (av. 2.526 Å) than the Ru–Cl(1) or Ru–Cl(3) bonds (av. 2.499 Å). Ru–Cl–Ru angles in **1a** are on average narrower (84.4°) than in $[Ru_2(\mu\text{-}Cl)_3(tripod)_2]^+$ (87.8°) with the consequence that the Ru...Ru distance is significantly shorter in the former cation (3.369 as opposed to 3.455 Å). The significant differences between the Ru–P(terminal) and the Ru–P(central) bond distances in the facially coordinated triphos ligands of the dinuclear cation **1a** may be assumed to be the result of ring strain in the associated five-membered RuPCCP chelate rings. In the meridionally coordinated and severely strained κ^3P,P',P'' triphos ligand of $[RuCl_2(triphos)_2]$ [13], the central Ru–P distance of 2.296(1) Å is also much shorter than the terminal Ru–P bond lengths of 2.390(2) and 2.358(2) Å. These latter bonds are sited opposite to one another with a P–Ru–P angle of 161.9(1)° so that a mutual *trans* influence will to some extent be responsible for their lengthening (av. 2.374 Å) in comparison to the terminal Ru–P distances in **1a** (av. 2.30 Å). A degree of correlation between the positions of the phosphorus resonances in the $^{31}P\{^1H\}$ NMR spectra of **1a** and $[RuCl_2(triphos)_2]$ in CD_2Cl_2 and the associated Ru–P distances is apparent. The signals for the central phosphorus atoms of the κ^3P,P',P'' ligands of $[RuCl_2(triphos)_2]$ and **1a** are at lower field (106.2 and 98.5 ppm, respectively) than for the terminal phosphorus atoms (51.2 and 68.7 ppm, respectively). In contrast the resonance for the central coordinated phosphorus atom of the monodentate κ^1P triphos ligand in $[RuCl_2(triphos)_2]$ is observed at relatively high field (23.6 ppm). This phosphorus adopts a position in the octahedral coordination sphere opposite to the central phosphorus of the tridentate linear phosphine ligand. The Ru–P distance to the monodentate ligand (2.397(1) Å) is 0.101 Å longer than that for the *trans*-sited bond.

Reaction of **1** with the amino acids (aaH) L-alanine and L-valine in the presence of base (KOH and CH_3ONa, respectively) leads to the formation of complexes of the type [RuCl(L-aa)(triphos)] (**2** and **3**), which are analogous in structure to organometallic half-sandwich Ru(II) complexes such as [RuCl(L-ala)(η^6-arene)] (arene = C_6H_6 [3], *p*-cymene [4]). The amino acidato ligands display a κ^2N,O coordination mode in **2** and **3**. Three geometrical isomers, for each of which the metal atom is a chiral centre, are possible for the L-alaninato and L-valinato complexes of the (triphos)Ru(II) fragment. The possible isomers *OC*-6-24 (a), *OC*-6-25 (b) and *OC*-6-35 (c) [18] are depicted for complex **2** in Fig. 2. In each case only one of the diastereomers is given. Single crystals suitable for an X-ray analysis were obtained for both **2** and **3**. As the molecular dimensions for both complexes are very similar, full structural details have been restricted in this paper to the L-valinato complex **3** for the sake of

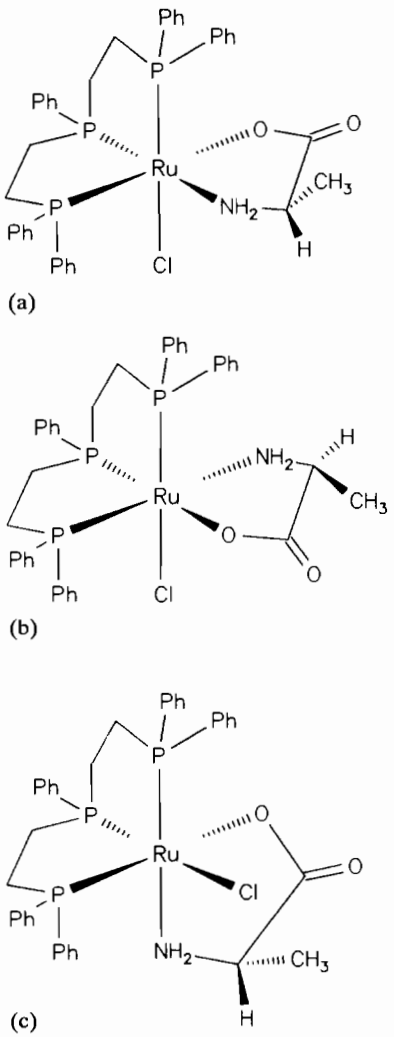


Fig. 2. Geometrical isomers of [RuCl(L-ala)(triphos)] (**2**): *OC*-6-24 (a), *OC*-6-25 (b), *OC*-6-35 (c). In each case only one of the diastereomers is depicted.

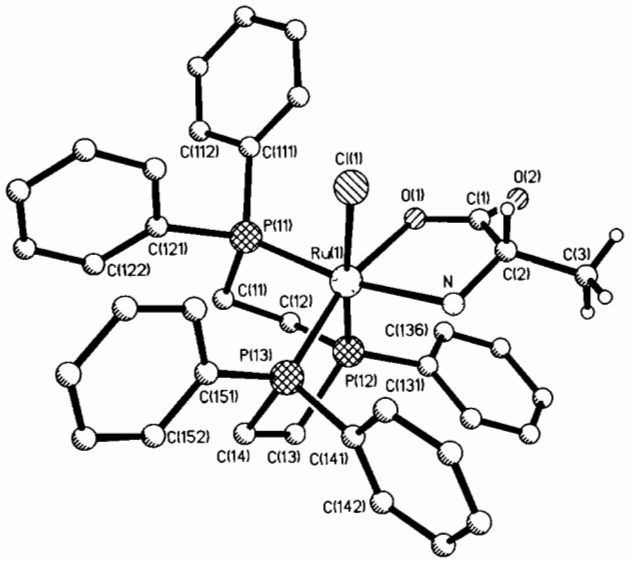


Fig. 3. Molecular structure of the $S_{Ru}S_C$ diastereomer of **2**.

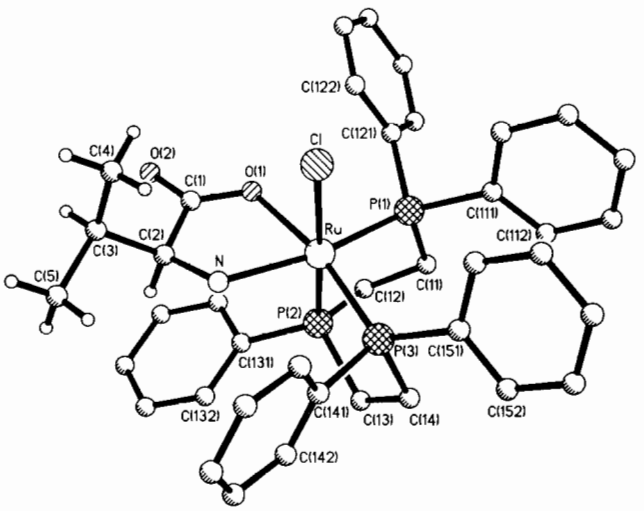
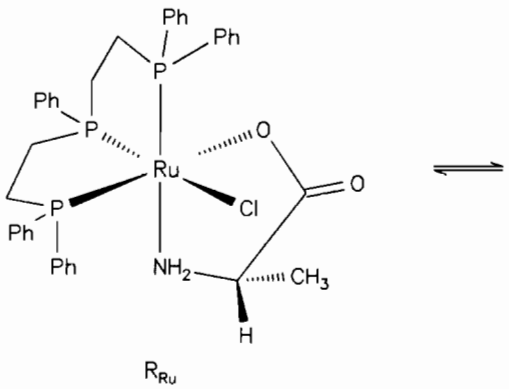


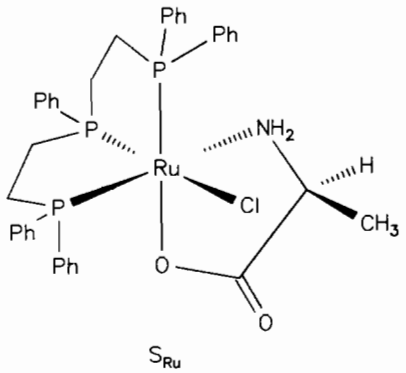
Fig. 4. Molecular structure of **3** with $R_{Ru}S_C$ configuration. Selected bond lengths (Å) and angles (°): Ru–Cl 2.488(3), Ru–P(1) 2.285(2), Ru–P(2) 2.229(3), Ru–P(3) 2.258(4), Ru–O(1) 2.152(8), Ru–N 2.197(6) Å; P(1)–Ru–P(2) 84.2(1), P(1)–Ru–P(3) 96.2(1), P(2)–Ru–P(3) 84 9(1), Cl–Ru–O(1) 86.9(2), Cl–Ru–N 81.3(3), O(1)–Ru–N 76.6(3).

brevity*. Both **2** and **3** adopt *OC*-6-35 geometries with the terminal Cl atom *trans* to the central phosphorus of the linear triphosphine ligand. The asymmetric unit of **2** (space group *P*1) contains a diastereomeric pair of which the complex with the $S_{Ru}S_C$ configuration is displayed in Fig. 3. In contrast, **3** (space group $P2_1$) crystallises as the $R_{Ru}S_C$ diastereomer, the molecular structure of which is depicted in Fig. 4.

NMR solution studies on **2** confirm the presence of diastereomers, whereas only one set of ^1H and ^{31}P NMR resonances is observed for **3**. The $^{31}P\{^1H\}$ NMR spectrum of **2** in CD_3OD displays signals at 103.7



R_{Ru}



S_{Ru}

and 101.7 ppm for the central phosphorus of the triphos ligand in the diastereomeric pair and at 69.7/67.2 and 66.4/65.7 ppm, respectively, for the terminal phosphorus atoms. The apposite resonances for the $R_{Ru}S_C$ diastereomer of **3** are recorded at 102.2, 70.0 and 66.4 ppm. Integral values for the signals of the methyl protons at 0.85 and 1.03 ppm in the ^1H NMR spectrum of **2** yield a ratio 1:14 for the two diastereomers of [RuCl(L-ala)(triphos)] in CD_3OD solution.

As may be seen from Fig. 4, the five-membered amino acidato chelate ring in **3** displays a relatively flat envelope configuration in which N is displaced 0.29 Å from the best least-squares plane through the remaining four atoms. The Ru–P distance *trans* to O(1) (2.258(4) Å) is significantly shorter than that *trans* to N (2.285(2) Å), indicating a greater degree of d_π–p_π backbonding for the former bond. An analogous effect is observed in **2** and in $[Ru(L\text{-ala})_2(PPh_3)_2]$, for which respective Ru–P bond lengths of 2.318(4) and 2.298(4) Å were reported [19].

Metallated peptide nitrogen atoms usually display a trigonal planar geometry [20–22]. In an early review

*$[RuCl(L\text{-ala})(triphos)]\cdot CH_2Cl_2\cdot H_2O$ (**2**), triclinic *P*1, $a = 9.514(4)$, $b = 12.520(5)$, $c = 17.869(5)$ Å, $\alpha = 105.08(4)$, $\beta = 92.65(3)$, $\gamma = 106.49(3)°$, $V = 1958.0(4)$ Å^3, $Z = 2$, $M = 965.1$, $D_c = 1.46$ g cm^{-3}, $R = 0.074$, $R_w = 0.070$, $w = 1/\sigma(F_o)^2$, for 3654 observed reflections ($2\theta_{max} = 45°$, Mo Kα, 5496 measured reflections, $F_o^2 > 2\sigma(F_o^2)$, semi-empirical absorption correction).

[20], Freeman concluded that when a metal atom is bonded to three donor groups of a peptide molecule, the central one of which is a peptide nitrogen, then the three donor atoms and the metal must be effectively coplanar. A typical example is provided by [Ru(glyglyH$_{-1}$)(PPh$_3$)$_2$(CH$_3$OH)], in which the anion [glyglyH$_{-1}$]$^{2-}$ displays a κ^3N,N',O coordination mode involving the amino and peptide nitrogens and a carboxylate oxygen atom [23]. An exception to the above rule is given by the half-sandwich complex [RhCp*{L-asp(β-Me)glyglyEtH$_{-2}$}], which contains a bridging metallated peptide nitrogen atom with pyramidal geometry (angle sum = 346.1°) [7]. Reaction of **1** with the dipeptides glyglyH and metglyH in the presence of two equivalents of KOH yields the complexes [Ru(glyglyH$_{-1}$)(triphos)] (**4**) and [Ru(metglyH$_{-1}$)-(triphos)] (**5**). The observation of ν(CO$_2$) at 1597 cm^{-1} in the IR spectrum of **4** is characteristic for a coordinated carboxylate group and is in accordance with a κ^3N,N',O coordination mode for the anion [glyglyH$_{-1}$]$^{2-}$. Four geometrical isomers may be proposed for **4**, the first of which, *mer-OC*-14 (a) contains a triphos ligand in the energetically unfavourable meridional placement (Fig. 5). This *mer*-isomer requires a trigonal planar metallated peptide nitrogen in the dipeptide ligand. The remaining three *fac*-isomers *fac-OC*-54, *fac-OC*-53 and *fac-OC*-43 would allow the adoption of the energetically favourable facial position by the linear triphosphine ligand at the cost of the peptide nitrogen atom displaying a pyramidal geometry. The structure of one of these, the *fac-OC*-54 isomer with the carboxylate oxygen *trans* to the central phosphorus atom, is depicted in Fig. 5. For methionine derivatives, the thioether S atom is a coordination site in triphenylphosphineruthenium(II) complexes such as [RuCl(D,L-met)(PPh$_3$)$_2$] or [RuCl(L-metMe)$_2$(PPh$_3$)]Cl [24]. However, the resonance of the S-methyl protons in the ^{1}H NMR spectrum of **5** (2.0 ppm in CD$_3$OD) remains effectively unshifted in comparison to the parent dipeptide (2.1 ppm in D$_2$O), indicating that the S atom does not participate in the ruthenium coordination sphere. This finding is confirmed by the X-ray structural analysis of **5**, which yields the structure depicted in Fig. 6. The dipeptide anion displays the κ^3N,N',O coordination mode in this *fac-OC*-54 isomer for which the $S_{Ru}S_C$ diastereomer is observed in the crystal lattice.

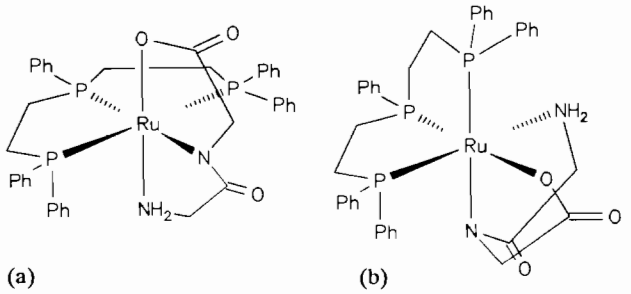


Fig. 5. Geometrical isomers of [Ru(glyglyH$_{-1}$)(triphos)] (**4**): *mer-OC*-14 (a) and *fac-OC*-54 (b).

The ^{31}P{^{1}H} NMR spectrum of **5** in CDCl$_3$ displays three triplets at 89.83 ppm for the central phosphorus atom and 65.38/60.82 ppm for the terminal phosphorus atoms, indicating the presence of only one diastereomer in solution. As the ^{31}P{^{1}H} NMR spectrum of **4** is virtually identical to that of **5**, with triplets at 90.74, 65.98 and 61.22 ppm, it may be assumed that **4** is also present in solution as the *fac-OC*-54 isomer. The sum of the bond angles at the peptide nitrogen N(1) in **5** is 344°, a value intermediate between the idealised pyramidal and trigonal planar geometries. Both of the five-membered chelate rings of the dipeptide ligand display an envelope conformation with N(1) and C(4), respectively, as flap, at distances of 0.69 and 0.68 Å from the best least-squares planes through the remaining ring atoms. Similar ring conformations are observed for the coordinated triphosphine ligand, as is also the case for **3**. The flap atoms are C(11) and C(13) at 0.68 and 0.77 Å, respectively, from the least-squares planes of the other four atoms. A marked *trans* influence on the Ru–P(2) bond length in **5** is apparent. In contrast to **3**, the Ru–P(2) distance of 2.274(5) Å in **5** is similar to the Ru–P distances to the terminal phosphorus atoms (2.285(5), 2.287(5) Å). This indicates a lesser degree of d_π–p_π backbonding for the central Ru–P bond, which is sited *trans* to the relatively short Ru–N(peptide) bond (2.10(1) Å). The degree of strain in the facially coordinated dipeptide in **5** is underlined by a comparison with [Ru(glyglyH$_{-1}$](PPh$_3$)$_2$], in which the κ^3N,N',O coordinated bioligand adopts the energetically favour-

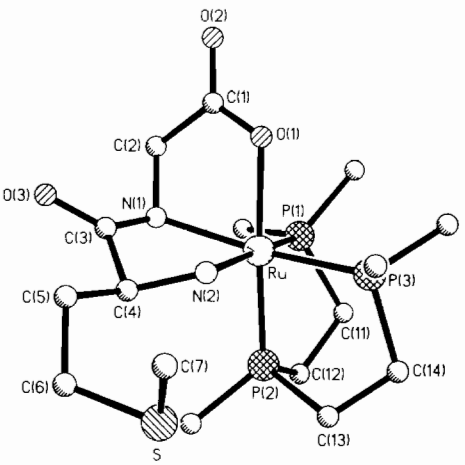


Fig. 6. Molecular structure of **5** with phenyl rings omitted for clarity. Selected bond lengths (Å) and angles (°) Ru–P(1) 2.285(5), Ru–P(2) 2.274(5), Ru–P(3) 2.287(5), Ru–O(1) 2 19(1), Ru–N(1) 2.10(1), Ru–N(2) 2 19(1); P(1)–Ru–P(2) 83.9(2), P(1)–Ru–P(3) 93.9(2), P(2)–Ru–P(3) 82 5(2), O(1)–Ru–N(1) 75 7(5), O(1)–Ru–N(2) 88.0(5), N(1)–Ru–N(2) 77.1(5); Ru–N(1)–C(2) 111 3(9), Ru–N(1)–C(3) 119(1), C(2)–N(1)–C(3) 114(2).

able meridional placement. Respective bond lengths for **5** and [Ru(glyglyH$_{-1}$)(PPh$_3$)$_2$] are as follows: Ru–O 2.19(1)/2.096(7), Ru–N(peptide) 2.10(1)/2.016(8), Ru–N(amino) 2.19(1)/2.131(7) Å.

The present work demonstrates that chiral ruthenium(II) amino acidato complexes of the type [RuCl(aa)(triphos)] and [Ru(dipepH$_{-1}$)(triphos)] may be prepared by reaction of [Ru$_2$(μ-Cl)$_3$(triphos)$_2$]Cl (**1**) with the appropriate bioligand in methanol. Such derivatives are analogous to organometallic half-sandwich complexes and contain facially coordinated triphos ligands even at the cost of forcing a metallated peptide nitrogen to display the energetically unfavourable pyramidal geometry.

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