Reaction of $[RuCl_2(PPh_3)_3]$ with α-amino acids. Synthesis and X-ray structural characterization of the Schiff base complexes $\{Ru[(CH_3)_2C{:}NCH(R)COO]_2(PPh_3)_2\}$ (R = H, CH_3)

W. S. Sheldrick* and **R. Exner**

Lehrstuhl für Analytische Chemie der Ruhr-Universität Bochum, Universitätsstrasse 150, D-4630 Bochum 1 (F.R.G.)

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Abstract

Complexes of the type $[Ru(aa)_2(PPh_3)_2]$, (aaH = gly (**1**), L-ala (**2**), L-val (**3**)) may be prepared by the reaction of $[RuCl_2(PPh_3)_3]$ with aaH in methanol at reflux. **2** crystallizes as the Δ diastereomer. A crystal structure analysis established that a carboxyl oxygen of the first and an ammine nitrogen of the second L-alaninate ligand are sited *trans* to *cis*-positioned triphenylphosphine ligands. Whereas the $^{31}P\{^1H\}$ NMR spectrum of **3** indicated a similar ligand arrangement for this complex, magnetic equivalence of the phosphorus atoms was established for **1**. The presence of two AB quartets in the $^{31}P\{^1H\}$ NMR spectra of **2** and **3** suggests that both the Λ and Δ diastereomers are present in methanol solution. Reaction of $[RuCl_2(PPh_3)_3]$ with glycine or L-alanine in acetone leads to the formation of the Schiff base complexes $\{Ru[(CH_3)_2C{:}NCH(R)COO]_2(PPh_3)_2\}$, (R = H(**4**), R = CH_3(**5**)). In contrast, **3** is obtained once again with L-valine. Crystal structures were performed for **4** and **5**. The PPh_3 ligands are sited *trans* to one another in **4** and to ammine nitrogens in **5**, which crystallizes as the Λ diastereomer.

Introduction

The reaction of $[RuCl_2(PPh_3)_3]$ with α-amino acids in acetone solution has been studied by Saito *et al.* [1]. They reported the preparation of complexes of the type $[RuCl(aa)(PPh_3)_2]$, (aaH = glycine (glyH), L-serine (L-serH), L-hydroxyproline, L-allohydroxyproline), for which they presented $^{31}P\{^1H\}$ NMR spectral parameters. Elementary analytical data were, however, only provided for the L-serinate complex. Observation of AB spin systems in the respective $^{31}P\{^1H\}$ NMR spectra established magnetic inequivalence of the PPh_3 ligands in each of the four products. The authors assumed that the central ruthenium atoms in these complexes display a square pyramidal coordination geometry, in which one of the phosphine ligands adopts an axial position. In the case of aaH = L-serine, two AB quartets of almost equal intensity were observed in the $^{31}P\{^1H\}$ NMR spectrum, indicating the presence of two isomers. As their $^2J(PP)$ values of 38 and 39 Hz were very similar, it was suggested that these isomers might contain respectively L-or D-serinate chelating ligands. Such amino acidate complexes of ruthenium(II) are of potential utility as homogeneous catalysts [2–4].

We felt that a partial reinvestigation and an extension of the work of Saito *et al.* were appropriate, in order to clarify the following aspects.

(1) Condensation of ketones and primary amines is known to lead to the formation of Schiff bases in a facile reaction via an intermediate hemiaminal [5]. Use of acetone as a solvent for the reaction between $[RuCl_2(PPh_3)_3]$ and amino acids $NH_2C(R)HCOOH$ could, therefore, lead to the formation of ruthenium(II) complexes of Schiff base anions $[(CH_3)_2C{:}NC(R)HCOO^-]$.

(2) It appeared to us to be somewhat remarkable that complexes of the type $[RuCl(aa)(PPh_3)_2]$ could be isolated, in which only one chloride and one phosphine ligand of the educt $[RuCl_2(PPh_3)_3]$ are displaced, although a fourfold molar excess of the amino acid was employed. Under such conditions, with a potentially bidentate ligand, formation of octahedral 18E-complexes of the type $[Ru(ligand)_2(PPh_3)_2]$ would be predicted [6, 7].

(3) It seemed most unlikely, under the reported reaction conditions, that inversion of configuration could occur for the α-carbon atom in aaH = L-ser, leading to the formation of an isomer [RuCl(D-ser)$(PPh_3)_2$], as proposed by Saito *et al.*

*Author to whom correspondence should be addressed.

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We have now studied the reaction of $[RuCl_2(PPh_3)_3]$ with the amino acids glycine, L-alanine (L-alaH) and L-valine (L-valH), employing either methanol or acetone as solvent. In methanol octahedral complexes of the type $[Ru(aa)_2(PPh_3)_2]$ **1–3** could be prepared (aa = gly, L-ala, L-val). When acetone is utilized as solvent for L-valine complex **3** may once again be synthesized. For glycine or L-alanine, however, Schiff base complexes $\{Ru[(CH_3)_2C{:}NCH(R)COO](PPh_3)_2\}$, R = H (**4**), R = CH_3 (**5**) were isolated. Complexes **2**, **4** and **5** were characterized by X-ray structural analyses.

Experimental

Solvents were dried and distilled before use. IR spectra were recorded as 1% KBr discs on a Perkin-Elmer 297 spectrometer. NMR spectra were recorded on a Bruker AM 400 spectrometer at 20 °C. Elemental analyses were performed with a Perkin-Elmer 240. The amino acids were purchased from Sigma Chemie GmbH; $RuCl_3 \cdot 3H_2O$ was a gift from Degussa AG. $[RuCl_2(PPh_3)_3]$ was prepared as described in the literature [8]. All reactions were carried out under an argon atmosphere.

Preparation of complexes 1–5

$[Ru(aa)_2(PPh_3)_2]$ (aa = gly (1), L-ala (2), L-val (3))

In a typical preparation 224 mg (0.23 mmol) of $[RuCl_2(PPh_3)_3]$, 64 mg (0.72 mmol) of L-alanine and 61 mg (0.73 mmol) of $NaHCO_3$ were heated with stirring for 4 h in 30 ml absolute methanol at reflux. The solvent volume was reduced to 5 ml and the solution left to crystallise at r.t. to yield orange–yellow needle-formed crystals of **2**, which were recrystallised from methanol. Yield 115 mg (61%).

$[Ru(gly)_2(PPh_3)_2] \cdot \frac{3}{2}CH_3OH$ (**1**): *Anal.* Found: C, 60.6; H, 5.16; N, 3.5 calc.: C, 60.65; H, 5.39; N, 3.41%. IR: 3315, 3240m, $\nu(NH_2)$; 3045m, ν(CH); 1620s, ν(CO); 1580s, $\delta(NH_2)$ cm^{-1}. $^{31}P\{^1H\}$ NMR (d_4-methanol, external 85% H_3PO_4 standard): 48.21 (s, 2P) ppm. ^1H NMR (d_4-methanol, TMS): 2.78 (d, 1H, gly-H, $^2J(HH) = 17$ Hz), 3.41 (d, 1H, gly-H), 7.2–7.5 (30 H, Ph-H) ppm.

$[Ru(L\text{-}ala)_2(PPh_3)_2] \cdot CH_3OH$ (**2**): *Anal.* Found: C, 61.4; H, 5.48; N, 3.6. Calc.; C, 61.94; H, 5.56; N, 3.43%. IR: 3305, 3230m, $\nu(NH_2)$; 3050 m, ν(CH); 1610vs, broad, ν(CO) cm^{-1}. $^{31}P\{^1H\}$ NMR (d_4-methanol, external 85% H_3PO_4 standard): species A 55.22 (d, 1P, $^2J(PP) = 32.5$ Hz), 47.50 (d, 1P); species B 53.12 (d, 1P, ^2J)PP) = 32,5 Hz), 44.32 (d, 1P) ppm. ^1H NMR (d_4-methanol, TMS): species A, 0.74 (d, 3H, L-ala-CH_3, $^3J(HH) = 7$ Hz), 1.44 (d, 3H, L-ala-CH_3), 3.25(q, 1H, L-ala-H), 3.85(q, 1H, L-ala-H); species B, 1.18(d, 3H, L-ala-CH_3, $^3J(HH) = 7$ Hz), 1.28 (d, 3H, L-ala-CH_3), 1.67 (q, 1H, L-ala-H), 2.57 (q, 1H, L-ala-H); both species, 7.20–7.75 (30 H, Ph-H) ppm.

$[Ru(L\text{-}val)_2(PPh_3)_2] \cdot 3CH_3OH$ (**3**): *Anal.* Found: C, 61.8; H, 5.81; N, 3.1. Calc.: C, 61.68; H, 6.55; N, 2.94%. IR: 3320, 3250m, $\nu(NH_2)$; 3060, 2960m, ν(CH). $^{31}P\{^1H\}$ NMR (d_4-methanol, external 85% H_3PO_4 standard): species A 54.98 (d, 1P, $^2J(PP) = 31$ Hz), 44.33 (d, 1P); species B 53.34 (d, 1P, $^2J(PP) = 31$ Hz), 44.33 (d, 1P) ppm. ^1H NMR (d_4-methanol, TMS): species A, 0.14, 0.57, 0.81, 0.83 (4d, 12H, L-val-CH_3, $^3J(HH) = 7$ Hz), 1.60, 2.16 (2m, 2H, L-val-βCH), 2.03, 3.18 (2m, 2H, L-val-αCH); species B, 0.25, 0.58, 0.69, 0.77 (4d, 12H, L-val-CH_3, $^3J(HH) = 7$ Hz), 1.82, 2.31 (2m, 2H, L-val-βCH), 1.21, 3.64 (2m, 2H, L-val-αCH).

$\{Ru[(CH_3)_2C{:}NCH(R)COO]_2(PPh_3)_2\}$ (R = H (4), CH_3(5))

In a typical preparation 211 mg (0.22 mmol) of $[RuCl_2(PPh_3)_3]$, 98 mg (1.10 mmol) of L-alanine and 85 mg (1.01 mmol) of $NaHCO_3$ were heated with stirring for 4 h in 50 ml acetone at reflux. The solvent volume was reduced to 5 ml and the solution left to crystallize at −30 °C to yield yellow prismatic crystals of **5**, which were recrystallized from methanol. Yield 150 mg (77%). Under similar conditions the reaction of $[RuCl_2(PPh_3)_3]$ with L-valine in acetone yields **3**. Yield 130 mg (69%).

$\{Ru[(CH_3)_2C{:}NCH_2COO]_2(PPh_3)_2\} \cdot 4CH_3OH$ (**4**): *Anal.* Found: C, 60.3; H, 5.32; N, 2.7. Calc.: C, 61.15; H, 6.36; N 2.85%. IR: 3050, ν(CH); 1640s, ν(CO); 1620s, ν(CN) cm^{-1}. $^{31}P\{^1H\}$ NMR (d_4-methanol, external 85% H_3PO_4 standard): 40.40 (s, 2P) ppm. ^1H NMR (d_4-methanol, TMS): 1.99 (s, 6H, CH_3), 2.43 (s, 6H, CH_3), 2.60 (d, 2H gly-H, $^2J(HH) = 19.5$ Hz), 3.55 (d, 2H, gly-H), 7.2–7.7 (30 H, Ph-H) ppm.

$\{Ru[(CH_3)_2C{:}NCH(CH_3)COO]_2(PPh_3)_2\} \cdot 3CH_3OH$ (**5**): *Anal.* Found: C, 62.7; H, 6.28; N, 3.2. Calc.: C, 62.62; H, 6.38; N 2.87%. IR: 3020m, ν(CH); 1615s, ν(CO); 1590s, ν(CN) cm^{-1}. $^{31}P\{^1H\}$ NMR (d_4-methanol, external 85% H_3PO_4 standard): 38.59 (s, 2P) ppm. ^1H NMR (d_4-methanol, TMS): 1.23 (d, 6H, L-ala-CH_3, $^3J(HH) = 7.5$ Hz), 2.02 (s, 6H, CH_3), 2.45 (s, 6H CH_3), 2.72 (q, 2H, L-ala-H), 7.0–7.6 (30 H, Ph-H) ppm.

X-ray structural analyses of 2, 4 and 5

Suitable single crystals were grown from methanol solutions. Crystal and refinement data are summarized in Table 1. 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 either the ω– or θ–2θ mode with

TABLE 1. Crystal and refinement data

Compound	2	4	5
Space group	$P2_12_12_1$	*Pbca*	$P3_221$
a (Å)	13.719(2)	13.890(3)	12.668(1)
b (Å)	25.206(3)	19.099(3)	12.668(1)
c (Å)	11.546(1)	18.157(4)	26.463(2)
V (Å^3)	3993(2)	4817(3)	3678(1)
Z	4	4	3
D_c (g cm^{-3})	1.25	1.35	1.32
Radiation	Mo Kα	Cu Kα	Cu Kα
μ (cm^{-1})	5.1	37.6	36.7
Scan method	ω	ω	θ–2θ
$2\theta_{max}$ (°)	45	130	140
Reflections measured	2972	4087	2716
Reflections observed	2288	2834	2596
Rejection criterion	$F_0^2 < 3\sigma(F_0^2)$	$F_0^2 < 2\sigma(F_0^2)$	$F_0^2 < 2\sigma(F_0^2)$
R	0.059	0.049	0.041
R_w	0.057	0.051	0.039
p	0.014	0.014	0.002

graphite-monochromated radiation. Empirical absorption corrections were applied to the reflection intensities. The structures were solved by Patterson syntheses and refined by full-matrix least-squares. A difference synthesis revealed the position of one disordered methanol oxygen atom O100 in the asymmetric unit of **2**. This atom participates in an O100–H...O12 hydrogen bond of length 2.83 Å to a carbonyl oxygen of a coordinated L-alaninate ligand and was assigned a site occupation factor of 0.5 in the subsequent refinement. The associated methyl carbon atom and a further disordered methanol solvate molecule indicated by the elemental analytical data (1.0 CH_3OH for each molecule of **2**) could not be identified in final difference syntheses and are presumably multiply disordered. The highest rest electron density peak in the final difference synthesis is 0.68 e A^{-3}, [Ru(L-ala)$_2$(Ph$_3$P)$_2$] (**2**) crystallizes in the Δ-configuration as depicted in Fig. 1; an inversion of configuration led to a deterioration of the R factor, which was significant at the 99.5% level for a Hamilton R-test.

{Ru[(CH$_3$)$_2$C:NCH$_2$COO]$_2$(Ph$_3$P)$_2$} (**4**) displays a crystallographic centre of symmetry (Fig. 2); the asymmetric unit contains two methanol solvate molecules with oxygen atoms O100 and O200 and respective carbon atoms C100 and C200.

{Ru[(CH$_3$)$_2$C:NCH(CH$_3$)COO]$_2$(Ph$_3$P)$_2$} (**5**) lies on a crystallographic twofold axis in the trigonal space group $P3_221$; the Λ-configuration depicted in Fig. 3 was confirmed at the 99.5% significance level by a Hamilton R-test. A difference synthesis revealed the presence of two methanol molecules in the asymmetric unit, one of which (O200, C200) is disordered

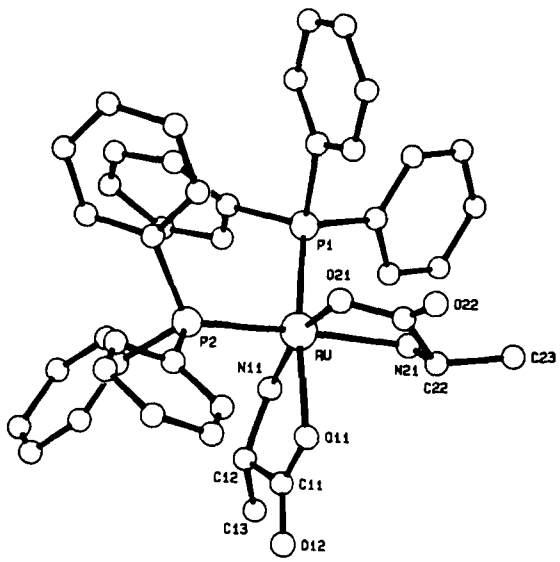

Fig. 1. Molecular structure of [Ru(L-ala)$_2$(PPh$_3$)$_2$] (**2**).

with a site occupation factor of 0.5, which means that there are three methanol solvate molecules associated with each molecule of **5**, as indicated by the elemental analysis. The phenyl rings were refined as rigid groups with d(C–C) = 1.395 Å in **2**, **4** and **5**. Hydrogen atoms were included at geometrically calculated positions with group isotropic temperature factors. Anisotropic temperature factors were introduced for the ruthenium, phosphorus and L-alaninate non-hydrogen atoms in **2** and for all non-hydrogen atoms in **4** (excluding the methanol solvate atoms) and **5**. The terminal reliability indices are listed in Table 1, where $R_w = [\Sigma w(F_0 - F_c)^2/\Sigma wF_0^2]^{1/2}$; weights were applied using the expression $w =$

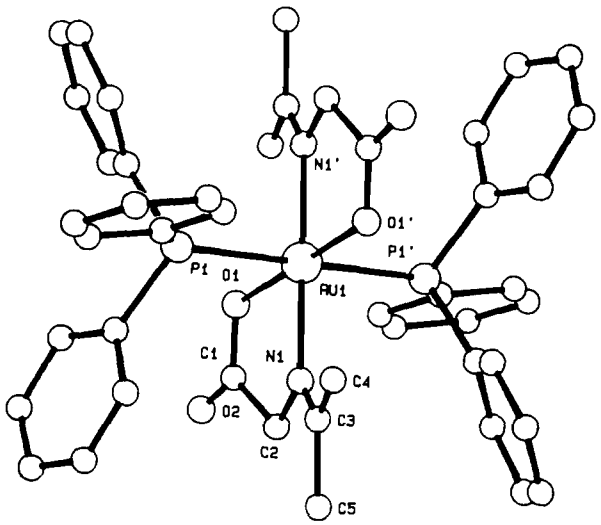

Fig. 2. Molecular structure of $\{Ru[(CH_3)_2C{:}NCH_2COO]_2(PPh_3)_2\}$ (**4**).

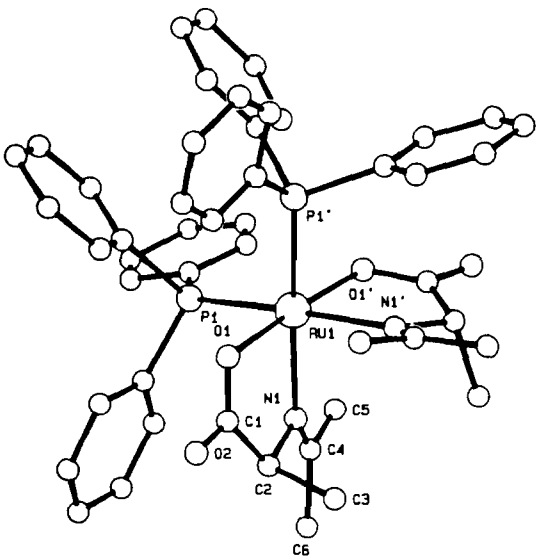

Fig. 3. Molecular structure of $\{Ru[(CH_3)_2C{:}NCH(CH_3)COO]_2(PPh_3)_2\}$ (**5**).

$(\sigma^2(F_0)+p^2F_0^2)^{-1}$, with values of p as given in Table 1. Calculations were performed with SHELX [9], with the SDP suite (Enraf-Nonius) and with local programs. Diagrams were drawn with RSPLOT [10]. Atom positional parameters with equivalent isotropic temperature factors are listed in Table 2, bond distances and angles to the ruthenium atoms in Table 3.

Discussion

Octahedral complexes of the type $[Ru(aa)_2(PPh_3)_2]$ containing two bidentate amino acidate ligands may be prepared by the reaction of $[RuCl_2(PPh_3)_3]$ with the respective amino acid in methanol at reflux in the presence of $NaHCO_3$. The configurational chirality of **2** was established to be Δ in the solid state, as depicted in Fig. 1. O11 of the first and N21 of the second L-alaninate ligand are sited *trans* to the triphenylphosphine atoms P1 and P2, so that the coordination may be described as *OC*-6-32 [11]. Alternative ligand arrangements would be *OC*-6-33 (O atoms *trans* to one another) or *OC*-6-22 (N atoms *trans* to one another). Both chelate rings in **2** display an envelope conformation with the amino nitrogen atoms N11 and N21 as respective flaps. Distances from the best least-squares planes through the remaining four ring atoms are as follows: ring 1, Ru −0.006, O11 0.016, C11 −0.019, C12 0.009, N11 −0.477 Å; ring 2, Ru −0.008, O21 0.019, C21 −0.023, C22 0.011, N21 −0.663 Å. The solvate methanol molecule in the unit cell participates in O100–H...O12 hydrogen bonds of length 2.83 Å. It is possible that these or other lattice interactions lead to the observed Δ diastereomer; we observed an analogous preferred crystallization of one diastereomer (also Δ) for $[(nbd)Ru(L\text{-phe})_2]$ (nbd = norbornadiene) [12]. In methanol solution, however, two species are present, as indicated by the $^{31}P\{^1H\}$ and ^1H NMR spectra. The former consists of two AB quartets in an intensity ratio of approximately 5:4. Identical $^2J(PP)$ values are observed for both AB spin systems, so that it seems reasonable to assume that the methanol solution contains both the Δ and Λ diastereomers of $[Ru(L\text{-ala})_2(PPh_3)_2]$ (**2**). Inspection of the Ru–P distances in **2** (Table 3) indicates that the Ru–P1 bond *trans* to O11 (2.298(4) Å) is significantly shorter than the Ru–P2 bond *trans* to N21 (2.318(4) Å). This implies that the degree of d_π–p_π backbonding to P1 must be greater than that to P2, so that a relative deshielding of the latter phosphorus should be expected. A *trans* influence on the Ru–O and Ru–N distances is also apparent. It is, therefore, possible to perform a tentative assignment of the lower field signals in the $^{31}P\{^1H\}$ NMR spectra (55.22 and 53.12 ppm) to those phosphorus atoms in the diastereomers *trans* to L-alaninate nitrogen atoms.

A similar phenomenon is also observed for the methanol solution of **3**, which contains two bidentate L-valinate anions. The $^{31}P\{^1H\}$ NMR spectrum consists of two AB quartets with spectral parameters very similar to those of **2**. Once again the presence of two diastereomers with OC-6-32 coordination may be assumed, with an approximate concentration ratio, in this case, of 1:5.

In contrast to **2** and **3**, the $^{31}P\{^1H\}$ NMR spectrum of a methanol solution of **1** displays a single line at 48.21 ppm, indicating that both phosphorus atoms

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

	x/a	*y/b*	*z/c*	U_{eq}
2				
Ru	0.1398(1)	−0.0775(1)	0.2101(1)	24(1)
P(1)	−0.0159(3)	−0.0443(1)	0.1990(4)	33(2)
P(2)	0.1083(3)	−0.1491(2)	0.3304(3)	31(2)
O(11)	0.2870(7)	−0.1023(4)	0.1867(8)	33(6)
O(12)	0.3848(9)	−0.1545(5)	0.0887(12)	77(10)
O(21)	0.1866(7)	−0.0321(4)	0.3530(8)	31(6)
O(22)	0.2749(9)	0.0377(4)	0.3999(9)	48(7)
N(11)	0.1332(9)	−0.1218(4)	0.0527(9)	27(6)
N(21)	0.1933(8)	−0.0072(4)	0.1240(10)	28(7)
C(11)	0.3042(13)	−0.1373(6)	0.1082(14)	42(11)
C(12)	0.2168(12)	−0.1593(6)	0.0461(13)	41(10)
C(13)	0.2405(13)	−0.1730(6)	−0.0829(14)	53(12)
C(21)	0.2428(11)	0.0068(6)	0.3285(12)	30(9)
C(22)	0.2728(11)	0.0122(5)	0.2021(14)	36(9)
C(23)	0.3001(12)	0.0684(5)	0.1710(13)	50(11)
C(112)	−0.0932(8)	0.0477(4)	0.0906(8)	57(5)
C(113)	−0.1110(8)	0.0813(4)	−0.0031(8)	73(6)
C(114)	−0.0695(8)	0.0704(4)	−0.1108(8)	69(6)
C(115)	−0.0102(8)	0.0259(4)	−0.1248(8)	65(6)
C(116)	0.0076(8)	−0.0077(4)	−0.0311(8)	51(5)
C(111)	−0.0339(8)	0.0032(4)	0.0766(8)	35(4)
C(122)	−0.0086(5)	0.0211(4)	0.3900(10)	43(5)
C(123)	−0.0451(5)	0.0517(4)	0.4810(10)	69(6)
C(124)	−0.1454(5)	0.0547(4)	0.4995(10)	65(5)
C(125)	−0.2092(5)	0.0271(4)	0.4271(10)	68(6)
C(126)	−0.1726(5)	−0.0034(4)	0.3361(10)	49(5)
C(121)	−0.0723(5)	−0.0064(4)	0.3176(10)	32(4)
C(132)	−0.1678(8)	−0.1174(4)	0.2511(7)	51(5)
C(133)	−0.2322(8)	−0.1583(4)	0.2236(7)	58(5)
C(134)	−0.2386(8)	−0.1768(4)	0.1100(7)	71(6)
C(135)	−0.1805(8)	−0.1543(4)	0.0238(7)	74(6)
C(136)	−0.1160(8)	−0.1134(4)	0.0512(7)	60(5)
C(131)	−0.1097(8)	−0.0949(4)	0.1649(7)	36(4)
C(212)	−0.0592(8)	−0.1858(3)	0.4519(9)	58(5)
C(213)	−0.1329(8)	−0.1797(3)	0.5341(9)	68(5)
C(214)	−0.1410(8)	−0.1323(3)	0.5957(9)	66(5)
C(215)	−0.0754(8)	−0.0910(3)	0.5752(9)	54(5)
C(216)	−0.0018(8)	−0.0972(3)	0.4930(9)	44(4)
C(211)	0.0064(8)	−0.1446(3)	0.4314(9)	32(4)
C(222)	0.1564(6)	−0.2560(4)	0.2773(8)	47(4)
C(223)	0.1432(6)	−0.3030(4)	0.2155(8)	70(5)
C(224)	0.0654(6)	−0.3079(4)	0.1384(8)	58(5)
C(225)	0.0009(6)	−0.2657(4)	0.1230(8)	52(5)
C(226)	0.0141(6)	−0.2187(4)	0.1849(8)	39(4)
C(221)	0.0919(6)	−0.2138(4)	0.2620(8)	31(4)
C(232)	0.2980(7)	−0.1431(4)	0.4284(8)	43(5)
C(233)	0.3677(7)	−0.1538(4)	0.5131(8)	65(5)
C(234)	0.3442(7)	−0.1861(4)	0.6072(8)	51(5)
C(235)	0.2508(7)	−0.2076(4)	0.6165(8)	58(5)
C(236)	0.1810(7)	−0.1969(4)	0.5318(8)	42(4)
C(231)	0.2046(7)	−0.1646(4)	0.4378(8)	28(4)
O(100)	0.4871(20)	0.2911(10)	0.2605(24)	92(9)
4				
Ru(1)	0.5000	0.0000	0.0000	28(1)
P(1)	0.3523(3)	0.0536(1)	0.0362(1)	32(1)
O(1)	0.5108(3)	0.0891(2)	−0.0666(2)	34(2)

(continued)

TABLE 2. (*continued*)

	x/a	*y/b*	*z/c*	U_{eq}
O(2)	0.4990(3)	0.1282(2)	−0.1808(2)	52(2)
N(1)	0.4361(3)	−0.0358(2)	−0.0979(2)	34(2)
C(1)	0.4908(4)	0.0815(3)	−0.1347(3)	36(3)
C(2)	0.4591(5)	0.0103(3)	−0.1609(3)	44(3)
C(3)	0.3832(4)	−0.0905(3)	−0.1121(3)	44(3)
C(4)	0.3451(4)	−0.1368(3)	−0.0525(4)	53(4)
C(5)	0.3514(6)	−0.1091(4)	−0.1902(4)	73(5)
C(11)	0.2557(4)	0.0077(3)	0.0853(3)	37(3)
C(12)	0.1651(4)	0.0387(3)	0.0917(3)	49(4)
C(13)	0.0913(4)	0.0060(4)	0.1293(4)	59(4)
C(14)	0.1066(4)	−0.0592(4)	0.1610(3)	53(4)
C(15)	0.1951(5)	−0.0903(4)	0.1555(3)	52(4)
C(16)	0.2702(4)	−0.0577(3)	0.1181(3)	46(3)
C(21)	0.3748(4)	0.1280(3)	0.0975(3)	38(3)
C(22)	0.3474(5)	0.1271(3)	0.1708(3)	49(4)
C(23)	0.3735(5)	0.1803(4)	0.2189(4)	62(5)
C(24)	0.4260(5)	0.2360(4)	0.1939(4)	66(5)
C(25)	0.4545(5)	0.2387(3)	0.1211(4)	66(5)
C(26)	0.4299(5)	0.1845(3)	0.0734(4)	49(4)
C(31)	0.2837(4)	0.0871(3)	−0.0425(3)	39(3)
C(32)	0.2278(4)	0.0395(4)	−0.0817(3)	51(4)
C(33)	0.1768(5)	0.0589(4)	−0.1444(4)	63(5)
C(34)	0.1804(5)	0.1261(5)	−0.1691(4)	74(6)
C(35)	0.2349(6)	0.1748(4)	−0.1315(4)	71(5)
C(36)	0.2870(5)	0.1559(3)	−0.0675(4)	53(4)
O(100)	0.5863(5)	0.6358(3)	0.0972(4)	106(2)
O(200)	0.5357(5)	0.2461(3)	0.3783(3)	106(2)
C(100)	0.5699(7)	0.6227(5)	0.0221(5)	95(3)
C(200)	0.6352(8)	0.2391(5)	0.3750(6)	115(3)
5				
Ru1	0.8197(1)	0.8197(1)	1.0000	44(1)
P1	0.6187(1)	0.7764(1)	1.0130(1)	45(1)
O1	0.7928(3)	0.8588(3)	0.9262(1)	54(1)
O2	0.8338(4)	1.0029(4)	0.8701(1)	82(1)
N1	0.8757(3)	1.0128(4)	1.0048(2)	57(2)
C1	0.8353(5)	0.9691(5)	0.9139(2)	62(2)
C2	0.8963(5)	1.0714(5)	0.9537(2)	72(2)
C3	1.0393(6)	1.1431(5)	0.9424(2)	84(2)
C4	0.8851(5)	1.0838(4)	1.0422(2)	66(2)
C5	0.8604(6)	1.0373(5)	1.0964(2)	75(3)
C6	0.9216(6)	1.2168(5)	1.0377(3)	86(3)
C11	0.4988(4)	0.6460(4)	0.9784(2)	47(1)
C12	0.5091(4)	0.6389(4)	0.9265(2)	58(2)
C13	0.4188(5)	0.5426(5)	0.8992(2)	75(2)
C14	0.3158(5)	0.4522(5)	0.9227(2)	78(2)
C15	0.3069(5)	0.4579(5)	0.9742(3)	82(3)
C16	0.3960(5)	0.5539(5)	1.0018(2)	68(2)
C21	0.5953(4)	0.9009(4)	0.9915(2)	53(2)
C22	0.5721(5)	0.9143(5)	0.9421(2)	72(2)
C23	0.5617(6)	1.0168(6)	0.9276(2)	93(3)
C24	0.5734(7)	1.1035(5)	0.9599(3)	113(3)
C25	0.5948(7)	1.0894(6)	1.0091(3)	110(3)
C26	0.6072(5)	0.9906(5)	1.0248(2)	78(2)
C31	0.5510(5)	0.7531(4)	1.0763(2)	52(2)
C32	0.6030(5)	0.7333(5)	1.1170(2)	62(2)
C33	0.5493(5)	0.7123(5)	1.1647(2)	75(2)
C34	0.4448(5)	0.7096(6)	1.1717(2)	90(3)

(*continued*)

TABLE 2. (*continued*)

	x/a	*y/b*	*z/c*	U_{eq}
C35	0.3904(5)	0.7324(6)	1.1309(2)	92(3)
C36	0.4421(5)	0.7518(5)	1.0835(2)	74(2)
O100	0.8185(4)	0.6959(4)	1.1938(2)	140(2)
C100	0.8325(6)	0.6077(6)	1.2078(3)	117(3)
O200	0.2232(8)	0.8683(8)	0.1514(4)	126(4)
C200	0.3218(11)	−0.0223(12)	0.1695(11)	134(7)

TABLE 3. Bond distances (Å) and angles (°) to the ruthenium atoms

2			
Ru–P1	2.298(4)	Ru–P2	2.318(4)
Ru–O11	2.132(10)	Ru–O21	2.108(10)
Ru–N11	2.135(10)	Ru–N21	2.160(12)
P1–Ru–P2	98.3(2)	P1–Ru–O11	168.7(3)
P2–Ru–O11	91.4(3)	P1–Ru–O21	97.4(3)
P2–Ru–O21	90.6(3)	O11–Ru–O21	88.2(4)
P1–Ru–N11	96.0(4)	P2–Ru–N11	95.5(3)
O11–Ru–N11	77.2(4)	O21–Ru–N11	164.3(5)
P1–Ru–N21	89.5(3)	P2–Ru–N21	167.9(3)
O11–Ru–N21	81.9(4)		
N11–Ru–N21	92.9(5)	O21–Ru–N21	79.1(4)
4			
Ru1–P1	2.385(1)	Ru1–O1	2.093(3)
Ru1–N1	2.101(4)		
P1–Ru1–O1	82.7(1)	P1–Ru1–N1	90.6(1)
O1–Ru1–N1	78.8(1)	P1–Ru1–P1	180.0
P1–Ru1–O1	97.3(2)	P1′–Ru1–N1	89.4(2)
O1′–Ru1–N1	101.2(2)	O1′–Ru1–O1	180.0
N1′–Ru1–N1	180.0		
5			
Ru1–P1	2.346(1)	Ru1–O1	2.085(2)
Ru1–N1	2.183(2)		
P1–Ru1–P1′	97.5(1)	P1–Ru1–O1	84.6(1)
P1–Ru1–O1′	98.2(1)	P1–Ru1–N1	87.7(1)
P1–Ru1–N1′	173.1(1)	O1–Ru1–O1′	175.7(1)
O1–Ru1–N1	77.7(1)	O1–Ru1–N1′	99.1(1)
N1–Ru1–N1′	87.4(1)		

are magnetically equivalent. Possible ligand arrangements are, therefore, OC-6-33 (P atoms *cis*, O atoms *trans* to one another), OC-6-22 (P atoms *cis*, N atoms *trans* to one another) OC-6-13 (P atoms *trans*, O atoms *cis* to one another) or OC-6-12 (P atoms *trans*, N atoms *cis* to one another). As the phosphorus signal is close to the higher field values of one of the diastereomers of **2** and **3** (47.50 and 48.70 ppm, respectively), it may tentatively be concluded that **1** displays an OC-6-22 ligand arrangement. Because both the Λ and Δ diastereomers for an OC-6-22 geometry would be expected to yield the same phosphorus signal, it is not possible to establish whether both are present in a methanol solution of **1**.

Reaction of $[RuCl_2(PPh_3)_3]$ with glycine or L-alanine in acetone leads to the formation of the Schiff base complexes $\{Ru[(CH_3)_2C{:}NCH(R)COO]_2(PPh_3)_2\}$ (R = H(**4**), R = CH_3 (**5**)). In contrast, when acetone is utilized as solvent for L-valine, the complex **3** may once again be synthesized. The molecular structure of **4** is depicted in Fig. 2. The complex contains a crystallographic centre of symmetry and displays the OC-6-12 ligand *trans* to one another. As a result of the marked reduction is the degree of d_π–p_π backbonding in individual *trans*-positioned Ru–P bonds, the distance Ru1–P1 (2.385(1) Å) is much longer than the Ru–P distances in **2** (2.298(4) and 2.318(4) Å). A δ value of 40.40 is observed for the atoms in the $^{31}P\{^1H\}$ NMR spectrum of **4**.

The crystal structure analysis of **5** established an OC-6-33 geometry for this complex as displayed in Fig. 3. **5** crystallizes as the Λ diastereomer. Only one signal at 38.59 ppm is observed in the $^{31}P\{^1H\}$ NMR spectrum of **5** in methanol. This is at higher field than in **4**, as would be expected, on account of the increased degree of d_π–p_π backbonding in the Ru–P bonds in **5**, which are sited *trans* to nitrogen atoms. The Ru1–N1 distance in **5** falls within a general trend observed for the complexes **2**, **4** and **5**: Ru–N *trans* to N, 2.101(4) Å in **4**; Ru–N *trans* to O, 2.135(10) Å in **2**; Ru–N *trans* to P, 2.160(12) Å in **2**, 2.183(2) Å in **5**.

We were unable to repeat the work of Saito *et al.* with glycine. Even with equimolar quantities of $[RuCl_2(PPh_3)_3]$ and glycine in methanol or acetone only the respective products **1** and **4** could be isolated. Both complexes gave only one signal in their $^{31}P\{^1H\}$ NMR spectra in methanol, with respective values of 48.21 and 40.40 ppm. Saito *et al.* report a minor AB quartet with δ values of 44.2 and 56.0 ppm, in addition to a major peak at *c.* 40.4 ppm, for the $^{31}P\{^1H\}$ NMR spectrum of their glycinato complex in $CDCl_3$, which they formulated as $[Ru(gly)Cl(PPh_3)_2]$. They assigned the major peak at 40.4 ppm to the educt $[RuCl_2(PPh_3)_3]$. In view

of the fact that they used a fourfold excess of amino acid this latter conclusion would appear, in the light of our work, to be unfounded. We propose, therefore, that the peak at 40.4 ppm is due to the Schiff base complex $\{Ru[(CH_3)_2C{:}NCH_2COO]_2(PPh_3)_2\}$ (**4**) and that the AB quartet is due to an asymmetric isomer of $[Ru(gly)_2(PPh_3)_2]$ (**1**) with magnetically inequivalent phosphorus atoms. For instance the δ values of 44.2 and 56.0 ppm are similar to those of 44.3 and 55.0 ppm observed for $[Ru(L\text{-val})_2(PPh_3)_2]$.

We also repeated the work of Saito *et al.* on the reaction of $[RuCl_2(PPh_3)_3]$ with L-serine in acetone. We obtained the complex $[Ru(L\text{-ser})_2(PPh_3)_2]$ (**6**). *Anal.* Found: C, 59.8; H, 4.5; N, 3.4. Calc.: C, 60.50; H, 5.08; N, 3.36%. The $^{31}P\{^1H\}$ NMR spectrum taken in $CDCl_3$, which displays two AB quartets of almost equal intensity, is essentially identical to that of Saito *et al.* for their proposed compound $[Ru(L\text{-ser})Cl(PPh_3)_2]$. We propose, therefore, in analogy to **2** and **3**, that both the Δ and Λ isomers of **6** are present in $CDCl_3$ solution. An assignment of the coordination geometry is not possible.

Our results for L-valine and for L-serine suggest that Schiff base formation in acetone is less favourable for amino acids with longer α-side chains. It seems probable, therefore, that kinetic factors will control which type of complex, $[Ru(aa)_2(PPh_3)_2]$ or $\{Ru[(CH_3)_2C{:}NCH(R)COO]_2(PPh_3)_2\}$, will be formed by the reaction of $[RuCl_2(PPh_3)_3]$ with amino acidate ligands in acetone. No evidence was obtained, in the course of our work, for the existence of square-pyramidal complexes of the type $[Ru(aa)Cl(PPh_3)_2]$ proposed by Saito *et al.*

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