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Optically active transition metal complexes. Part 108. [1] Synthesis, crystal structure and properties of a novel "quasi-meso" dinuclear η^6-benzene–ruthenium(II) complex with chiral salicylaldiminato ligands [2]

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Abstract

The chloride ligand in the diastereomer mixture (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^6\text{-}C_6H_6)Ru(LL^*)Cl]$, **1a** and **1b** (ratio 86:14), was abstracted in acetone at −30 to −40°C by $AgPF_6$ [$HLL^* = (S)$-(1-phenylethyl)salicylaldimine]. X-ray analysis of crystals of the product $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2 \cdot 2CO(CH_3)_2$ **3** shows a dimeric structure with opposite ruthenium configurations. Therefore, the dimer containing two salicylaldiminato ligands with the same chirality can be described as a "quasi-meso" stereoisomer. The complex is supposed to be formed from the solvate complexes with coordinated acetone during crystallisation. This assumption is in accord with the reactivity of **3** towards water in acetone. A conformational analysis based on the NMR spectroscopic results shows that the arrangement of the 1-phenylethyl groups relative to the $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]$ fragments is determined by the face-on orientation of the phenyl substituent with respect to the π-bonded benzene ligands.

Keywords: Arene; Chirality; Ruthenium; Bridging ligand; Crystal structure; Schiff base

1. Introduction

To understand the factors influencing the stereocontrol in enantioselective catalysis is one of the main goals of the research area of optically active transition metal complexes [1]. In this context, the elucidation of the stereochemistry of substitution reactions at cyclopentadienyl–ruthenium(II) complexes with stereogenic metal centers and various mono- and bidentate ligands, especially phosphanes, established a trend towards retention of the metal configuration [2,3]. Retention stereochemistry is also found in the substitution of the chloride ligand in the η^6-benzene complex $[(\eta^6\text{-}C_6H_6)Ru(PPh_3)(CH_3)Cl]$ for the $SnCl_3$ group [4]. In contrast, the metal configuration in η^6-arene–ruthenium complexes with the anions of amino acids as chelating ligands (N,O set of donor atoms) is unstable in solution [5]. Correcting published results [6], we have shown that the metal configuration of η^6-arene–ruthenium(II) complexes with the anion of the chiral Schiff base ligand $HLL^* = (S)$-(1-phenylethyl)salicylaldimine and unidentate ligands, such as chloride, 4- or 2-methylpyridine and triphenylphosphane, is also labile in solution [7]. In the synthesis of the triphenylphosphane complexes we could demonstrate that the chloride abstraction with $AgPF_6$ in the presence of PPh_3 proceeded without retaining the metal configuration [7a,d]. In this paper we present the results of our investigations on the chloride substitution in $[(\eta^6\text{-}C_6H_6)Ru(LL^*)Cl]$ in the absence of other ligands [7a].

2. Results and discussion

Recently, we published our results on the optically active complexes (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^6\text{-}C_6H_6)$-

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[1] For part 107 see Ref. [7c].

[2] Herrn Prof. Dr. M. Herberhold, einem Freund und Kollegen, zum 60. Geburtstag gewidmet.

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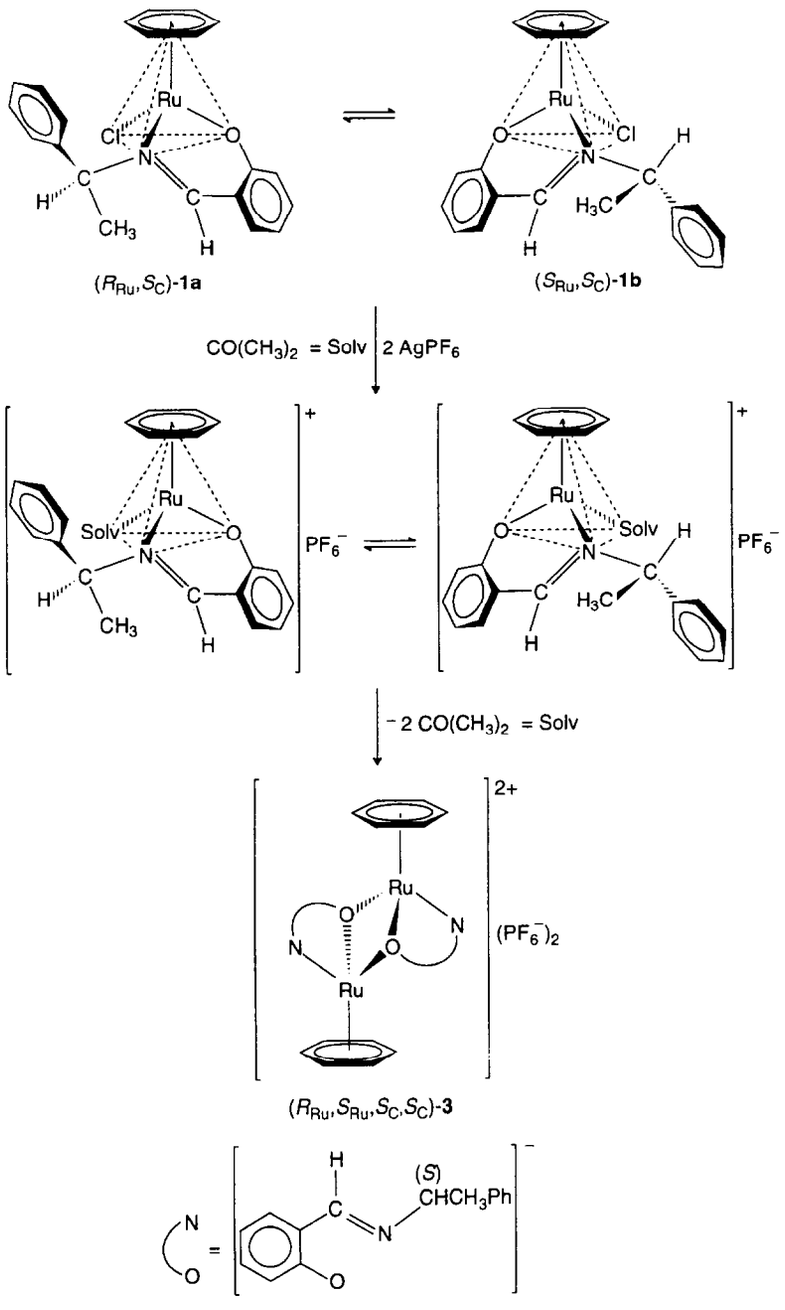
Ru(LL*)Cl], **1a** and **1b**, the metal configuration of which is highly labile in solution [7a,d]. In the substitution products (R_{Ru},S_C)-[$(\eta^6$-$C_6H_6)$Ru(LL*)(L)]PF_6. L = 4- or 2-methylpyridine, the metal configuration is also labile at the temperature of synthesis. Substituting the chloride ligand in **1a/1b** for triphenylphosphane, we were able to separate the two diastereomers (R_{Ru},S_C)- and (S_{Ru},S_C)-[$(\eta^6$-$C_6H_6)$Ru(LL*)-(PPh_3)]PF_6, **2a** and **2b**, although their interconversion occurs even below room temperature. We could show that the diastereomers **2a** and **2b** were formed in a ratio of 1 : 1, whereas the equilibrium ratio at $-(1.0 \pm 0.3)$°C in acetone-d_6 is 94.0 : 6.0 [7a,d]. These ratios are independent of adding triphenylphosphane before or after chloride abstraction by $AgPF_6$ in the solvent acetone. Therefore, we assume that the substitution reaction proceeds via the formation of configurationally labile solvent intermediates, formulated as (R_{Ru},S_C)- and (S_{Ru},S_C)-[$(\eta^6$-$C_6H_6)$Ru(LL*)(solvent)]PF_6, containing coordinated acetone molecules. Arene–ruthenium cations [$(\eta^6$-arene)Ru(solvent)$_{3-x}L_x$]$^{n+}$ with solvent of water, acetone or acetonitrile are well-known and have been investigated with regard to their reactivity [5c,8].

For an perimental proof of the formation of solvent



Scheme 1.

intermediates we tried to isolate and characterise them. Therefore, the chloride ligand in **1** (diastereomer mixture **1a**:**1b** 86:14, $CDCl_3$) was abstracted in acetone with $AgPF_6$ in the temperature range −30 to −40°C without adding other ligands (Scheme 1). After stirring the mixture for 30 to 45 min the resulting red–orange solution was filtered and petroleum ether was added. Crystallisation at 5°C gave red crystals of the compound $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2 \cdot 2CO(CH_3)_2$, **3**, suitable for X-ray analysis in nearly quantitative yield. The crystals are air-stable for months and decompose at about 210°C.

The elemental analysis, a strong absorption band of a carbonyl group at 1720 cm^{-1} in the infrared spectrum of the crystals in KBr matrix and the peak at m/e = 404.1 (Ru isotope pattern) for the $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]^+$ moiety in the FD mass spectrum suggested the formulation of **3** as $[(\eta^6\text{-}C_6H_6)Ru(LL^*)(acetone)]PF_6$ with a coordinated acetone molecule that was lost under the conditions of measuring the mass spectrum. Astonishingly, the crystals were poorly soluble even in polar solvents like DMSO, water, methanol and acetone. Therefore, to obtain the ^1H NMR spectrum a sample of 0.9 mg of **3** had to be stirred vigorously in 1 ml of acetone-d_6 at −40°C for 2 h. The spectrum was measured at temperatures of −40, 0 and 21°C. There were two singlets for the η^6-benzene protons at 5.67 and 4.36 ppm, as well as two doublets for the methyl protons of the 1-phenylethyl group at 2.38 and 2.53 ppm, both in an intensity ratio of 1:1. This was surprising, because we assumed with respect to our previous results that the two diastereomers of $[(\eta^6\text{-}C_6H_6)Ru(LL^*)(acetone)]PF_6$ should be formed in a ratio different from 1:1 [7a,d].

The X-ray analysis of the crystal structure of **3** provides an explanation. In Fig. 1 an ORTEP view of the molecular structure of the cation of **3** is shown. Details of the data collection and structure refinement are given in Table 1. Atomic coordinates and selected bond distances and angles are given in Tables 2 and 3 respectively. Two molecules of acetone and two hexafluorophosphate anions are contained in the unit cell. The cation of **3** is a dimer, bridged by the phenolate oxygen atoms O1 and O2 of the two chelating salicylaldiminato ligands. More interestingly from a stereochemical point of view, the two stereogenic ruthenium centers have different configurations, which can be described as (S_{Ru}) for the right half of the molecule in Fig. 1 with carbon atoms C1–C21 and as (R_{Ru}) for the left half of the molecule with carbon atoms C31–C51 [9]. For this description the phenolate oxygen atom of a salicylaldiminato ligand chelating to the ruthenium atom under consideration gets a higher priority than the bridging-only oxygen atom. Therefore, the dimeric cation of complex **3** can be called a "quasi-meso" stereoisomer, quasi because both 1-phenylethyl carbon atoms C20 and C50 have (*S*) chirality. In accord with the structure of **3**, the $\Delta\varepsilon$ value of the maximum at 377 nm in the CD spectrum is only one third of that of (R_{Ru},S_C)- and (S_{Ru},S_C)-$[(\eta^6\text{-}C_6H_6)Ru(LL^*)Cl]$, **1a** and **1b** (ratio 86:14), which has the lowest $\Delta\varepsilon$ value in the series of chiral η^6-benzene–ruthenium complexes with the (*S*)-(1-phenylethyl)salicylaldiminato ligand (Fig. 2) [7a,d].

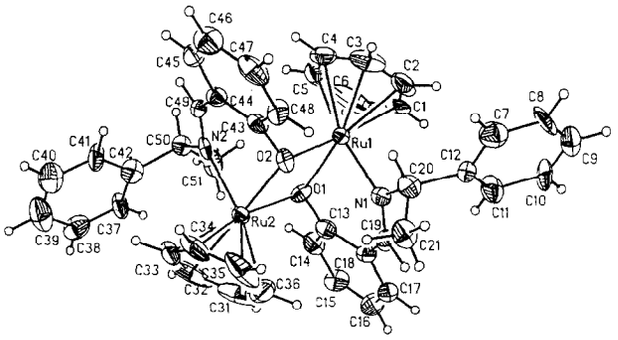


Fig. 1. ORTEP view of the molecular structure of the cation of complex **3** with atom numbering. The PF_6 anions and the acetone molecules have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

Table 1
Summary of crystal data, data collection and structure refinement for complex **3**

Elemental formula	$C_{42}H_{40}F_{12}N_2O_2P_2Ru \cdot 2CO(CH_3)_2$
M	1213.22
Crystal system	Monoclinic
Space group	$C2$ (No. 5)
Crystal colour, shape	Red, parallelepipedic
Crystal size (mm^3)	0.30×0.30×0.40
a (Å)	23.88(2)
b (Å)	14.152(5)
c (Å)	14.687(7)
α (°)	90.00
β (°)	100.35(5)
γ (°)	90.00
V (Å^3)	4883.0
Z	4
D_c (g cm^{-3})	1.65
$F(000)$	2448
μ (mm^{-1})	0.76
hkl ranges	0 to 32, 0 to 19, −20 to 20
2θ range (°)	3.0–55.0
Total no. of unique reflections	7983
No. of observed reflections ($I > 2.5\sigma_I$)	5844
Min, max transmission factors	0.76, 1.00
No. of reflections, 2θ range (°) for empirical absorption correction	8, $6.0 < 2\theta < 41.0$
No. of least-squares parameters	631
Largest shift/e.s.d. in final cycle	0.26
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−1.30, 0.97
$R[R = \Sigma \|\|F_o\| - \|F_c\|\| / \Sigma \|F_c\|]$	0.060
$R_w[R_w = \Sigma \|\|F_o\| - \|F_c\|\| w^{1/2} / \Sigma \|F_o\| w^{1/2}, w = 1/\sigma^2(F_o)]$	0.048

Table 2
Positional parameters ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2 \cdot 2CO(CH_3)_2$ **3**

Atom	x	y	z	U_{eq}
Ru(1)	2578(1)	1413(1)	6528(1)	34(1)
Ru(2)	2323(1)	0	8253(1)	35(1)
O(1)	2650(3)	10(8)	6984(4)	39(2)
O(2)	2319(3)	1428(8)	7839(4)	43(3)
N(1)	3374(4)	1589(9)	7367(6)	44(4)
N(2)	1492(3)	3(9)	7413(5)	38(3)
C(1)	2827(8)	1625(22)	5205(11)	93(10)
C(2)	2729(9)	2519(17)	5589(13)	101(10)
C(3)	2268(11)	2731(14)	5878(10)	90(8)
C(4)	1830(7)	2091(15)	5761(9)	68(7)
C(5)	1866(7)	1270(16)	5402(11)	75(7)
C(6)	2352(14)	989(14)	5117(9)	124(12)
C(7)	3837(6)	4023(12)	6981(10)	71(6)
C(8)	4149(8)	4489(12)	6439(11)	88(7)
C(9)	4522(7)	4057(14)	5994(10)	70(7)
C(10)	4570(6)	3145(13)	6087(9)	64(6)
C(11)	4238(6)	2615(10)	6621(9)	65(6)
C(12)	3891(5)	3057(10)	7098(8)	43(5)
C(13)	3127(5)	−456(10)	6948(7)	46(5)
C(14)	3123(6)	−1382(11)	6623(8)	62(6)
C(15)	3626(6)	−1901(10)	6611(8)	57(5)
C(16)	4141(7)	−1483(12)	6958(10)	69(6)
C(17)	4164(6)	−571(10)	7264(8)	51(5)
C(18)	3675(5)	−54(11)	7250(6)	41(4)
C(19)	3735(5)	922(10)	7574(7)	46(5)
C(20)	3530(5)	2568(8)	7711(8)	51(5)
C(21)	3816(5)	2586(9)	8734(7)	66(5)
C(31)	2894(15)	−1057(23)	8929(14)	141(16)
C(32)	2300(15)	−1286(14)	9019(13)	130(13)
C(33)	2019(7)	−653(19)	9392(12)	87(8)
C(34)	2228(10)	177(16)	9644(9)	79(9)
C(35)	2765(14)	369(15)	9593(11)	115(11)
C(36)	3071(9)	−217(32)	9249(16)	136(17)
C(37)	1082(6)	−2397(11)	7765(9)	61(6)
C(38)	863(6)	−2924(12)	8388(10)	74(7)
C(39)	515(8)	−2495(17)	8930(10)	96(9)
C(40)	380(7)	−1558(13)	8793(10)	79(7)
C(41)	607(5)	−1049(10)	8196(9)	59(5)
C(42)	967(6)	−1447(10)	7659(8)	55(5)
C(43)	1867(5)	1977(9)	8000(7)	39(4)
C(44)	1321(5)	1674(9)	7740(7)	42(5)
C(45)	887(6)	2302(11)	7840(9)	57(5)
C(46)	989(8)	3176(12)	8217(10)	72(7)
C(47)	1556(8)	3449(10)	8447(9)	74(6)
C(48)	1997(6)	2887(10)	8368(8)	52(5)
C(49)	1182(5)	748(9)	7359(7)	38(4)
C(50)	1202(5)	−837(8)	6951(7)	41(4)
C(51)	1567(5)	−1360(9)	6403(8)	64(5)
P(1)	5000	−174(5)	0	60(2)
F(11)	5275(7)	−98(15)	−841(9)	218(9)
F(12)	5391(6)	602(9)	465(8)	157(6)
F(13)	5347(7)	−925(10)	530(9)	212(8)
P(2)	0	1755(4)	5000	62(2)
F(14)	433(4)	962(7)	5414(6)	109(5)
F(15)	225(5)	1745(10)	4105(7)	152(7)
F(16)	445(5)	2503(8)	5392(10)	161(6)
P(3)	2490(2)	762(4)	12411(3)	58(1)
F(21)	3057(5)	562(9)	12078(8)	156(6)
F(22)	1927(5)	1005(8)	12700(9)	151(6)
F(23)	2390(6)	1492(13)	11642(6)	172(7)
F(24)	2789(5)	1473(11)	13095(5)	156(6)
F(25)	2583(4)	−44(10)	13168(6)	130(5)
F(26)	2188(4)	−37(9)	11743(5)	118(4)
O(3)	4128(6)	1146(11)	4686(9)	127(7)
C(25)	4185(7)	472(16)	4311(12)	79(8)
C(26)	3904(7)	−374(16)	4477(13)	137(12)
C(27)	4569(7)	425(13)	3628(10)	116(9)
O(4)	867(8)	455(14)	132(12)	214(11)
C(55)	806(8)	1104(16)	606(14)	95(9)
C(56)	516(7)	976(19)	1335(12)	178(16)
C(57)	1007(10)	1997(16)	494(13)	153(13)

Isotropic U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

The reason is that the contributions of the two metal chromophors to the CD spectrum nearly compensate each other.

In the solid state structure of **3** two different conformations of the 1-phenylethyl groups are observed. According to our conformational analysis [7] the 1-phenylethyl group bonded to N1 adopts the favored conformation. The C20–H bond is directed towards the bridging phenolate O2 to minimize steric hindrance and the phenyl substituent C7–C12 is in a position for the stabilizing interaction with the η^6-benzene ligand C1–C6, called "β-phenyl effect" [10] and $\pi-\pi$ edge-to-face or T-shaped interaction [11,12]. The same β-phenyl effect is found for the phenyl substituent C37–C42 and

Table 3
Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2 \cdot 2CO(CH_3)_2$ **3**

Bond distances (Å)		Bond angles (°)	
Ru(1)–O(1)	2.093(11)	O(1)–Ru(1)–O(2)	74.9(4)
Ru(1)–O(2)	2.125(7)	O(1)–Ru(2)–O(2)	74.1(4)
Ru(1)–N(1)	2.086(8)	O(1)–Ru(1)–N(1)	84.9(4)
Ru(1)–C(1)	2.153(18)	O(2)–Ru(1)–N(1)	81.2(3)
Ru(1)–C(2)	2.160(22)	O(1)–Ru(2)–N(2)	86.8(3)
Ru(1)–C(3)	2.164(19)	O(2)–Ru(2)–N(2)	82.9(4)
Ru(1)–C(4)	2.157(17)	Ru(1)–O(1)–Ru(2)	105.2(4)
Ru(1)–C(5)	2.157(15)	Ru(1)–O(2)–Ru(2)	105.4(4)
Ru(1)–C(6)	2.132(13)	Ru(1)–O(1)–C(13)	118.8(8)
Ru(2)–O(1)	2.146(7)	Ru(1)–N(1)–C(19)	123.8(9)
Ru(2)–O(2)	2.110(11)	Ru(1)–O(2)–C(43)	121.5(6)
Ru(2)–N(2)	2.141(8)	Ru(2)–N(2)–C(49)	120.2(8)
Ru(2)–C(31)	2.145(30)	O(2)–C(43)–C(44)	120.8(11)
Ru(2)–C(32)	2.145(20)	O(1)–C(13)–C(18)	122.4(12)
Ru(2)–C(33)	2.148(21)	N(2)–C(49)–C(44)	129.3(10)
Ru(2)–C(34)	2.111(16)	N(1)–C(19)–C(18)	126.7(10)
Ru(2)–C(35)	2.124(18)	C(13)–C(18)–C(19)	120.8(11)
Ru(2)–C(36)	2.118(21)	C(43)–C(44)–C(49)	122.6(12)
O(1)–C(13)	1.326(16)		
O(2)–C(43)	1.385(16)		
N(1)–C(19)	1.279(17)		
N(1)–C(20)	1.498(16)		
N(2)–C(49)	1.282(17)		
N(2)–C(50)	1.478(16)		

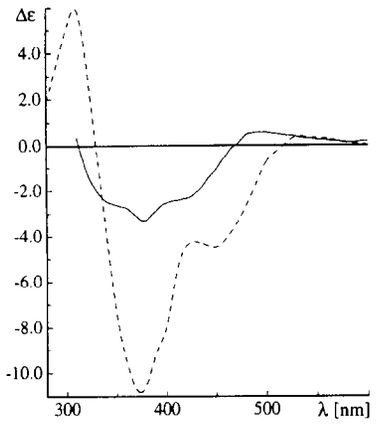


Fig. 2. CD spectra of complex **3**, ——— ($c = 4.78 \times 10^{-4}$ mol l^{-1}, acetone, $\Delta\epsilon$ [dm^3 mol^{-1} cm^{-1}], 22°C) and of the mixture of the chloro complexes **1a** and **1b** (**1a**:**1b** 86:14, $CDCl_3$), ----- ($c = 9.57 \times 10^{-4}$ mol l^{-1}, CH_2Cl_2, $\Delta\epsilon$ [dm^3 mol^{-1} cm^{-1}], 22°C).

the η^6-benzene ligand C31–C36. However, the methyl group C51 is oriented towards the phenolate O1, implying severe steric hindrance. For the overall system this arrangement allows a symmetric and compact structure in the solid state.

From the ^{1}H NMR spectra of compounds of the type **3** it was concluded [7] that the conformation found in the solid state is retained in solution. For compound **3** this is obviously true for the favored conformation of the 1-phenylethyl group bonded to N1, but not for the 1-phenylethyl group bonded to N2 suffering severe steric hindrance. This 1-phenylethyl group in solution orients the hydrogen C50–H towards the phenolate O1. As a consequence the phenyl substituent C37–C42 loses its π–π interaction with the η^6-benzene ligand C31–C36. That means there is no highfield shift of the signal of the η^6-benzene ligand C31–C36, whereas the η^6-benzene ligand C1–C6 remains in the anisotropy beam of the phenyl substituent C7–C12. Not only that, by the rotation of the N2–C50 bond of about 120°, the η^6-benzene ligand C1–C6 gains an additional anisotropy contribution from the phenyl ring C37–C42. Therefore, its η^6-C_6H_6 signal is shifted upfield by 1.31 ppm with respect to its C31–C36 counterpart.

Warming up the acetone solutions of **3** from −40°C to room temperature, the ^{1}H NMR signals of a further species arose to the extent of nearly 30% at room temperature. The protons of its η^6-benzene ligand gave a broad singlet at 6.00 ppm, assigned to the aqua complex $[(\eta^6\text{-}C_6H_6)Ru(LL^*)(H_2O)]PF_6$ **4** [5c]. **4** was synthesised independently as a mixture with **3** in the ratio **4**:**3** 72:28 by abstracting the chloride ligand in **1** in acetone with $AgPF_6$ at −30 to −35°C and adding water until the ratio water:acetone (solvent) was 5:1. By this water addition, complexes **4** and **3** precipitate as a 72:28 mixture. Obviously, at room temperature the dimer **3** is in equilibrium with the aqua complex **4**, the proportions depending on the amount of water present in the solvent acetone. The broad signal for the η^6-benzene ligand of **4** is indicative of dynamic processes supported by the coalescence not only of the signal of the η^6-benzene ligand at −75°C, but also of the water signal (3.55 ppm) at −55°C [7a].

When the chloride ligand in complex **1** was abstracted with $AgPF_6$ at −30°C in acetone-d_6 containing the "normal" water content, and the ^{1}H NMR spectrum was measured within a few minutes at −40°C, only the aqua complex **4** was seen. During warm up of the sample, complex **3** is formed (usually more than 70%) in quantities dependent on the quantity of water present in acetone-d_6.

3. Conclusions

The dimeric cation $\{[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2\}^{2+}$ of complex **3**, with LL^* the anion of (*S*)-(1-phenylethyl)salicylaldimine, is formed by condensation of two cations $[(\eta^6\text{-}C_6H_6)Ru(LL^*)(acetone)]^+$ during the attempted isolation of the solvate complex by crystallisation. As the two ruthenium centers have different configurations, complex **3** can be understood as a "quasi-meso" stereoisomer.

4. Experimental section

All preparations and reactions were performed under a nitrogen atmosphere using the Schlenk technique. Acetone was dried over Sikkon (Fluka) and saturated with nitrogen in a circulation apparatus. Preparation of samples for NMR measurements was performed under nitrogen by dissolving the samples in cold acetone-d_6 using thin Schlenk tubes. The acetone-d_6 was saturated with argon, but it was not dried. The cold solutions were filled into cooled NMR tubes which were sealed with rubber septa.

4.1. Physical measurements and materials

IR spectra were measured with a Beckman IR 4240 spectrometer. Mass spectra were obtained by the field desorption method (Finnigan MAT 95). ^{1}H NMR spectra were measured on a Bruker ARX 400 spectrometer. The circular dichroism (CD) spectra were recorded with a Jasco J-40 A spectrophotometer, and the polarimetric measurements were carried out with a Perkin-Elmer 241 instrument. Melting points were determined with a Büchi SMP 20 apparatus.

The diastereomer mixture of complexes (R_{Ru},S_C)– and (S_{Ru},S_C)–$[(\eta^6\text{-}C_6H_6)Ru(LL^*)Cl]$, **1a** and **1b** (ratio 86:14 in $CDCl_3$), was prepared as published [7d].

$RuCl_3 \cdot xH_2O$ was received from Hereaus and from Degussa. $AgPF_6$ was obtained from Johnson-Matthey and stored in polyethylene flasks under argon. $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ [13] and (*S*)-(+)-(1-phenylethyl)salicylaldimine [14] were prepared by the literature methods.

4.2. Preparation of $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2 \cdot 2CO(CH_3)_2$ 3

To the diastereomer mixture (R_{Ru},S_C)- and (S_{Ru},S_C)-[(η^6-C_6H_6)Ru(LL*)Cl], **1a** and **1b** (ratio **1a**:**1b** 86:14, $CDCl_3$) (201 mg, 0.46 mmol) was added 6 ml of acetone. The mixture was cooled to −30 to −40°C and $AgPF_6$ (116 mg, 0.46 mmol) was added. After stirring the mixture for 30–45 min, precipitated AgCl was removed by filtration from the red-orange suspension through Celite at −30 to −40°C. To the cold solution was added cold petroleum ether until the ratio of acetone/petroleum ether was 1:1. Crystallisation at 5°C for two days gave a first fraction of 130–150 mg of parallelepipedic red crystals. A second crop of 50–60 mg of crystals of **3** suitable for X-ray analysis was obtained by adding petroleum ether until the ratio of acetone/petroleum ether was 2:3. Yield 260–270 mg (0.21–0.22 mmol, 93–95%), m.p. >210°C (decomp.). Anal. found: C, 47.26; H, 4.32; N, 2.32. $C_{42}H_{40}F_{12}N_2O_2P_2Ru_2 \cdot 2CO(CH_3)_2$ Calc.: C, 47.53; H, 4.32; N, 2.32%. FD mass spectrum (acetone): *m/z* 404.1 ($[M]^{2+}$, 100), refers to ^{102}Ru. IR (cm^{-1}, KBr): 1720 vs ν(CO), 1620 vs ν (CN). ^1H NMR (400 MHz, acetone-d_6, −40°C, TMS): δ (ppm, *J* (Hz)) 2.38, 2.53 (d, $^3J_{HH}$ 7.0, 3H, CHCH_3); 4.36, 5.67 (s, 6H, η^6-C_6H_6); 6.45, 6.72 (q, $^3J_{HH}$ 7.0, 1H, CH_3CH); 7.35–8.05 (m, 18H, arom. H): 9.52, 9.68 (s, 1H, N=CH). $(\alpha)^{22}$ ($= 100\alpha/lc$, where α (deg) is the observed rotation, *l* (dm) is the path length and *c* (g/100 ml solution) is the concentration) (*c* = 0.08, acetone): (589 nm) − 89, (578 nm) − 93, (546 nm) − 100°. CD data ($c = 4.78 \times 10^{-4}$ mol l^{-1}, 22°C, acetone): λ_{max} ($\Delta\epsilon$ [dm^3 mol^{-1} ml]); λ_0: 377 (−3.3), 493 (0.6); 312,470 nm.

4.3. Preparation of the 72:28 mixture of $[(\eta^6\text{-}C_6H_6)Ru(LL^*)(H_2O)]PF_6$ 4 and $[(\eta^6\text{-}C_6H_6)Ru(LL^*)]_2(PF_6)_2$ 3

To **1** (267 mg, 0.61 mmol) was added 50 ml of acetone and the mixture was cooled to −40°C. After adding $AgPF_6$ (154 mg, 0.61 mmol) and another 10 ml of acetone the mixture was stirred for 1 h at −30 to −35°C. The resulting dark-red solution was then filtered through Celite. After concentration of the solution to about 10 ml, 50 ml of water was added slowly with stirring in small portions of about 5 ml. The precipitation was completed by keeping the solution for 3 h at 5°C. The brick-red, microcrystalline precipitate was washed with diethyl ether and dried in vacuum. The following analytical data refer to the 72:28 mixture of the aqua complex **4**; and the dimer **3**. Yield 270 mg, m.p. >250°C (decomp., darkening at 220°C), FD mass spectrum (acetone): *m/z* 404.1. IR (cm^{-1}, KBr): 3540 s ν(OH), 3600–3300, 3100–2600 ν(OH), 1620 vs ν (CN). ^1H NMR (400 MHz, acetone-d_6, −40°C, TMS; the signal pattern indicates a 28:72 mixture of the dimeric complex **3** and the monomeric aqua coomplex **4**; only the signals for the aqua complex **4** are given; Sal = aromatic part of the salicylaldiminato ligand): δ (ppm, *J* (Hz)) 2.03 (d, $^3J_{HH}$ 7.0, 3H, CHCH_3); 6.00 (s, 6H, η^6-C_6H_6); 6.51 (q, $^3J_{HH}$ 7.0, 1H, CH_3CH); 6.53 (ddd, $^3J_{HH}$ 7.9, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.1, 1H. H^4–Sal); 6.91 (dd, $^3J_{HH}$ 8.5, $^4J_{HH}$ 1.1, 1H, H^6–Sal); 7.17 (dd, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.8, 1H, H^3–Sal); 7.28 (ddd, $^3J_{HH}$ 8.5, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.8, 1H, H^5–Sal); 7.32–8.29 (m, 5H, arom. H); 8.30 (s, 1H, N=CH). $(\alpha)^{22}$ (*c* = 0.08, acetone): (589 nm) − 171, (578 nm) − 186, (546 nm) − 230°. CD data ($c = 3.40 \times 10^{-4}$ mol l^{-1}, calculated contains only compound **3**, 22°C, acetone): λ_{max} ($\Delta\epsilon$ [dm^3 mol^{-1} ml]); λ_0: 383 (−4.6), 407 (−4.6), 500 (0.3); 477 nm.

4.4. Crystallography

The details of the crystal structure determination are summarised in Table 1. The structure was solved using a combination of Patterson–Fourier and least-squares methods.

4.5. Data collection

X-ray diffraction data were collected at 20°C with a SYNTEX-NICOLET R3 diffractometer using Mo Kα radiation (λ = 0.71073 Å) with a graphite-crystal monochromator. Cell constants were obtained from least-squares refinement of the setting angles of 26 centered reflections in the range $4.0° < 2\theta < 23.0°$. The data were collected in the ω-scan mode and in all cases three standard reflections were measured every 100 reflections. No profound loss of intensity was observed. The data were corrected for Lorentz and polarisation factors.

4.6. Structure Solution and Refinement

The structure of **3** was solved using Patterson–Fourier methods with SHELXTL PLUS Release 4.11/V programs [15] on a Micro VAX II computer. The hydrogen atoms were added in calculated positions with the option HFIX of the SHELXTL PLUS program package [15]. They were included in the structure factor calculations but were not refined. Neutral atom scattering factors were used [16]. The absolute configuration was determined by refinement of the least-square variable η =

1.1(1) [17] and by measuring the Friedel pairs in the range $3.0° < 2\theta < 40.0°$ [h, k, l min/max: 1/23, −14/−1, −15/15].

Further details of the crystal structure determination can be requested from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, under the deposit number CSD-404318.

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