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[(Cy)Ru(LL*)Cl] and related half-sandwich compounds—two diastereomers in the same single crystal

Henri Brunner *, Matthias Weber, Manfred Zabel

Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany

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Contents

Abstract

The ruthenium compound [(Cy)Ru(LL*)Cl] (**1**) crystallizes as a 1:1 mixture of the two diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** in the same single crystal, whereas the corresponding osmium compound [(Cy)Os(LL*)Cl] (**2**), almost identical to **1** in the molecular parameters, crystallizes as the pure diastereomer (R_{Os},S_C)-**2**. 1:1 diastereomer co-crystallization is traced back to a molecular recognition motif, the pair formation of fragments (Ar)MXY, in which X and Y are electronegative substituents. Thus, compounds of the type [(Ar)MXYZ], in particular (Cy)Ru derivatives, tend to form inversion pairs of enantiomers and also of diastereomers. Fifteen cases of 1:1 diastereomer co-crystallization in half-sandwich complexes are presented. The discussion is extended to [(Cy)RuLCl$_2$] and related complexes. It is shown that there is a delicate balance between 1:1 diastereomer co-crystallization and crystallization as a pure diastereomer.

Keywords: Enantiomers; Diastereomers; Half-sandwich complexes; 1:1 Diastereomer co-crystallization; Molecular recognition

1. Enantiomers and enantiomer crystallization

Enantiomers are related as image and mirror image. They have the same properties as far as scalars are concerned including solubility. With regard to vector properties they act sign-inverted. Crystallization of a solution containing enantiomers may lead to one of the following cases: conglomerate crystallization, racemate crystallization and crystallization of a solid solution [1,2].

1.1. Conglomerate crystallization

There is the well known story of Pasteur [3]. He crystallized an aqueous solution of sodium ammonium tartrate and he obtained mirror image single crystals

* Corresponding author. Tel.: +49-941-943-4441; fax: +49-941-943-4439.
E-mail address: henri.brunner@chemie.uni-regensburg.de (H. Brunner).

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which he could separate with a looking glass and a pair of tweezers. In his famous experiment he was lucky, because the temperature was below 27 °C. This was also true, when he had to repeat his experiment in the laboratory of Biot, before he was allowed to give his invited talk to the French Academy of Sciences. Today many conglomerate crystals are known. Sixty-five space groups including some of the more frequent ones involve the crystallization of one enantiomer in a single crystal for symmetry reasons, which leads to the conglomerate situation. It is assumed that about 10%, maybe a little less, of all the crystallizations of enantiomers give conglomerates, although the crystals usually are too small for manual separation.

1.2. Racemate crystallization

The vast majority of crystallizations of solutions containing enantiomers are racemate crystallizations (about 90%). In the crystal lattice there are pairs of enantiomers, interrelated by symmetry planes, inversion centers etc. Sodium ammonium tartrate crystallizes from an aqueous solution as a racemate at temperatures above 27 °C. It then forms a monohydrate, whereas the conglomerate is the tetrahydrate.

1.3. Solid solutions

This is a very rare type of crystallization restricted to a couple of cases only. The lattice contains the enantiomers randomly distributed.

2. Diastereomers and diastereomer crystallization

Diastereomers are not related as image and mirror image. They differ in all properties including solubility. The term diastereomers is mainly used in the resolution of enantiomers with the help of enantiomerically pure resolving agents. In this context diastereomers agree in the configuration of the resolving agent and differ in the configuration of the enantiomeric parts to be resolved. Although the over-all molecular shapes of diastereomers are as different as those of different molecules, there will be parts which are similar (the resolving agent) and parts which are image-mirror image related (the racemate).

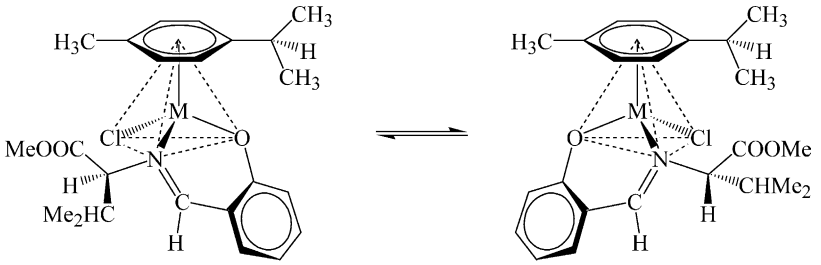
In the crystallization of a solution containing two diastereomers normally they crystallize in separate lattices as two different compounds do, when they crystallize from the same solution. This, of course, is the basis for the resolution of racemic mixtures via conversion of the enantiomers to diastereomers. Occasionally, diastereomers are separated by chromatography, but predominantly it is fractional crystallization which is successfully used for the separation of diastereomers. Even today in the realm of enantioselective catalysis including the 2001 Nobel prizes to Knowles, Noyori and Sharpless, the vast majority of optical resolutions is done by fractional crystallization of diastereomers. After separation, the diastereomers are re-converted to the enantiomers.

Assume that the two diastereomers in an optical resolution crystallize in a 1:1 ratio in the same lattice. Then, repeated fractional crystallization does not lead to a separation. On the contrary, an enrichment of one enantiomer with respect to the other, e.g. by virtue of an asymmetric synthesis, does not show up in the crystalline phase, which as a rule is isolated and processed, but in the supernatant solution, which contains all the impurities and normally is discarded. This may be the reason why optical resolutions based on fractional crystallizations of diastereomers occasionally have been unsuccessful. Thus, crystallization of pure diastereomers or co-crystallization of two diastereomers in one lattice is an important phenomenon for optical resolutions.

3. The startling differences of the diastereomers of [(Cy)Ru(LL*)Cl] (1) and [(Cy)Os(LL*)Cl] (2) on crystallization

The compound [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(LL*)Cl] (**1**), abbreviated as [(Cy)Ru(LL*)Cl], is synthesized by reaction of [(Cy)RuCl$_2$]$_2$ with the ligand LL*H in the presence of base [4]. The ligand LL*H is derived from salicylaldehyde and the methyl ester of (*S*)-valine in a Schiff base condensation. In the reaction a new chiral center at the Ru atom is formed and two diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** arise, which only differ in the metal configuration (Fig. 1). After the reaction there is a diastereomer ratio of 70:30 in $CDCl_3$ solution, which can easily be determined by ^{1}H-NMR spectroscopy, because the diastereomers exhibit different NMR spectra. The 70:30 ratio is the thermodynamic equilibrium between the two diastereomers indicating the chiral induction from the stable valine configuration to the labile Ru configuration. Kinetic measurements established that at room temperature equilibration between the diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** is rapid [4–7].

Crystallization at +4 °C by diffusion of petroleum ether into a toluene solution of the two diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** afforded dark red single crystals which contained two independent molecules in the ratio 1:1 in the unit cell. In both molecules the chiral carbon atoms of the valine ester groups had the expected (*S*) configuration. Surprisingly, the ruthenium atom Ru1 had (*R*) configuration and the ruthenium atom Ru2 had (*S*) configuration using the priority sequence Cy > Cl > O > N [8,9]. Thus, from a 70:30 mixture in



M = Ru: (R_{Ru},S_C)-**1** (S_{Ru},S_C)-**1**

M = Os: (R_{Os},S_C)-**2** (S_{Os},S_C)-**2**

Fig. 1. Compounds **1** and **2**. **1** crystallizes as a 1:1 pair of diastereomers (R_{Ru},S_C)-**1**/(S_{Ru},S_C)-**1**, **2** crystallizes as the pure diastereomer (R_{Os},S_C)-**2**.

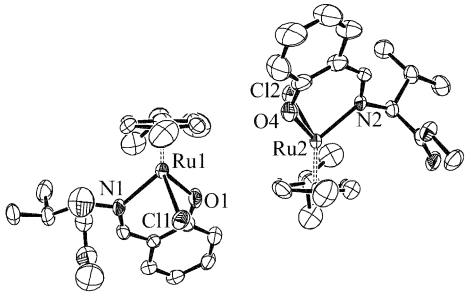


Fig. 2. Molecular structure of the (R_{Ru},S_C)-**1**/(S_{Ru},S_C)-**1** inversion pair with Ru–Ru distance 5.64 Å (50% probability, hydrogen atoms omitted for clarity). (R_{Ru},S_C) diastereomer = Ru2 (right side), (S_{Ru},S_C) diastereomer = Ru1 (left side).

solution the two diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** crystallize in a 1:1 ratio in the same lattice (Fig. 2).

As expected, the bond lengths and bond angles of the two diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** are extremely similar (Table 1). In the complex with (S_{Ru},S_C) configuration the Ru–N and the Ru–Cy(centroid) distances are a little longer, whereas the Ru–O and the Ru–Cl bonds are a little shorter than in the isomer with (R_{Ru},S_C) configuration. Furthermore, two bond angles are smaller and one is almost identical emphasizing the similarity between the two diastereomers.

Fig. 2 shows that the two diastereomers form an 'almost-racemate', connected by an 'almost inversion center'. In our analysis we place this inversion center exactly halfway between Ru1 and Ru2. The deviations of the four different substituents around the Ru atoms Cy(centroid), Cl, O, N from inversion symmetry are marginal, ranging between 0.13 and 0.23 Å. Similarly, the atoms in the ligand backbone and in the cymene rings closely follow this inversion symmetry with deviations below 0.2 Å. Naturally, inconsistencies arise for the chiral nitrogen substituents which for both diastereomers have the same (*S*) configuration, excluding centrosymmetry.

With 5.64 Å the Ru–Ru distance in the 'inversion pair' is extremely short. All the other Ru–Ru distances are longer than 8.6 Å. Thus, in these 'inversion pairs' two diastereomers assemble in the same way as two enantiomers do in a racemate related by an inversion center, forming a kind of supramolecular aggregate on the basis of molecular recognition as discussed below. In the center the pairs of diastereomers (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** are image/mirror image related, towards the outside, however, centrosymmetry is lost. The lattice is formed by translation of these inversion pairs.

If crystals of the 'almost-racemate' of (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** are dissolved in CD_2Cl_2 at −80 °C, the ^{1}H-NMR spectrum shows a ratio of the two diastereomers

Table 1
Bond lengths (Å), bond angles (°) and dihedral angles (°) in the 1:1 lattice of (R_{Ru},S_C)-**1** and (S_{Ru},S_C)-**1** as well as in the monoclinic and orthorhombic modifications of (R_{Os},S_C)-**2**

Complex	(R_{Ru},S_C)-**1** monoclinic	(S_{Ru},S_C)-**1** monoclinic	(R_{Os},S_C)-**2** monoclinic	(R_{Os},S_C)-**2** orthorhombic
Bond lengths (Å)				
M–$C_{centroid}$	1.670	1.689	1.655	1.662
M–Cl	2.446(2)	2.423(2)	2.433(17)	2.4326(11)
M–O	2.062(6)	2.053(6)	2.077(5)	2.060(3)
M–N	2.092(6)	2.120(6)	2.101(5)	2.111(3)
Bond angles (°)				
O–M–Cl	85.15(19)	84.43(18)	84.02(14)	83.47(10)
N–M–Cl	82.94(18)	85.17(17)	83.98(15)	84.13(10)
O–M–N	88.6(2)	88.8(2)	87.3(3)	87.03(13)

of exactly 50:50, the composition of the crystal. At room temperature the ratio changes to 70:30, the equilibrium composition of the two diastereomers.

The osmium complex [(Cy)Os(LL*)Cl] (**2**) (Fig. 1), the analogue of the ruthenium complex [(Cy)Ru-(LL*)Cl] (**1**), has been prepared, analyzed and crystallized [4]. The compound is also configurationally labile in solution. The diastereomer ratio in $CDCl_3$ at room temperature is 64:36, similar to the corresponding ruthenium complex.

Diffusion of petroleum ether into a toluene solution of [(Cy)Os(LL*)Cl] (**2**) affords two different types of red crystals, both suitable for X-ray analysis. Both contain only the (R_{Os},S_C) diastereomer in the monoclinic and orthorhombic system, respectively. Thus, surprisingly, the osmium compound [(Cy)Os(LL*)Cl] (**2**) crystallizes as a pure diastereomer (R_{Os},S_C)-**2** and not as a 1:1 mixture of two diastereomers. The relevant bond lengths and angles for both modifications are given in Table 1 (last two columns). They are extremely similar to those of the two ruthenium diastereomers. This is a consequence of the well known lanthanide contraction which makes the radii of Ru and Os almost the same. Thus, some of the Os–ligand bonds and ligand–Os–ligand angles are a little shorter, some are a little longer than in the two ruthenium diastereomers. Some are even intermediate between those of the two ruthenium diastereomers.

Given the extreme similarities between the diastereomers (R_{Ru},S_C)-**1**/(S_{Ru},S_C)-**1** and (R_{Os},S_C)-**2**/(S_{Os},S_C)-**2** it is the more surprising that the ruthenium complexes crystallize as two diastereomers in a 1:1 ratio, whilst in the osmium case a single diastereomer crystallizes even in two different modifications. This shows that there is a delicate balance between the two situations crystallization as a pure diastereomer or crystallization as two diastereomers in a 1:1 ratio.

The diastereomers (R_{Os},S_C)-**2** form the lattice with the shortest Os–Os distance being 8.18 Å (monoclinic modification). There are no distances around 5.6 Å as in the 1:1 ruthenium inversion pairs. All the Os–Os distances are in the range of the Ru–Ru distances outside the inversion pairs.

4. The molecular recognition motif for the 1:1 co-crystallization of the diastereomers (R_{Ru},S_C)- and (S_{Ru},S_C)-[(Cy)Ru(LL*)Cl] and related pairs of diastereomers

In the inversion pair (R_{Ru},S_C)-**1**/(S_{Ru},S_C)-**1** the two Ru atoms and the two Cy(centroids) define a 'central plane' (Fig. 3) the dihedral angle Cy1–Ru1–Ru2–Cy2 being 175.7°. The angles Cy1–Ru1–Ru2 = 77.9 and Cy2–Ru2–Ru1 = 78.1° show that the Ru–Cy centroids are slightly inclined towards Ru1–Ru2 forming a lying

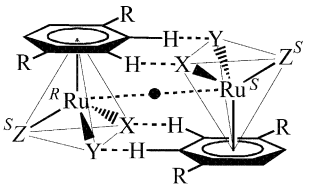


Fig. 3. Inversion pair: molecular recognition motif of the tight inverted pianostools. The two diastereomers have opposite metal configurations (R_M) and (S_M) and the same ligand configuration (S_C).

Z. This leaves the two cymene planes almost parallel to each other (angle 1.7°). Concerning the legs of the half-sandwich pianostools it is the O_{sal} and Cl substituents which point to the inside of the inversion pairs. This turns the N ligands, the chiral substituents of which disturb centrosymmetry, to the outside, the N atoms being close to the central plane (Cy1–Ru1–Ru2–N2 = −2.7° and Cy2–Ru2–Ru1–N1 = −12.1°).

Molecular recognition occurs between two (Cy)Ru(O_{sal})Cl fragments with opposite metal configuration, which approach each other by inversion symmetry (Fig. 3). With almost parallel Ru–Cy centroids in the central plane the fragments orient their O_{sal}–Cl edges towards one another resulting in O1–Cl2 and O2–Cl1 distances of 5.17 and 5.35 Å. There are 2 × 2 hydrogen bonds between the C–H groups of the cymene rings and the O_{sal} and Cl substituents of opposite molecules [distances (angles) C3–H···O2 3.47 Å (163.4°), C29–H···O1 3.31 Å (170.9°), C2–H···Cl2 3.66 Å (143.9°) and C28–H···Cl1 3.74 Å (141.2°)], which arrange the isopropyl and methyl groups of the cymene rings such that together with the O_{sal} and Cl substituents they form a kind of a closed shell around the inner core of the inversion pair. Let us call this motif the tight inverted pianostools.

The same molecular recognition motif is found in other half-sandwich complexes, for which 1:1 co-crystallization of two diastereomers in the same single crystal has been described in the literature (Table 2). In these literature reports the phenomenon of 1:1 diastereomer co-crystallization has been stated, but not analyzed and understood. The inversion pairs of the compounds [(Cy)Ru(O–N)Cl], O–N = salicylaldimine anion derived from (*S*)-1-phenylethylamine (complex **3**) [10], (*R*)-1-hydroxybut-2-ylamine (complex **4**) [11], and (*S*)-2-(2′-methoxy)-1,1′-binaphthylamine (complex **5**) [12], have distances and angles extremely close to (R_{Ru},S_C)-**1**/(S_{Ru},S_C)-**1**, the salicylaldimine anion of which is derived from (*S*)-methyl valinate [4]. Thus, the (*S*)-2-(2′-methoxy)-1,1′-binaphthyl derivative **5** has a Ru–Ru distance of 5.51 Å within the pair, whereas the shortest Ru–Ru distance outside the pairs is 10.52 Å due to the large binaphthyl substituents [12]. The iodo analogue **6** of **1** forms single crystals with two diastereomers in a 1:1 ratio, the recognition pattern being only changed as expected for the substitution of Cl by I [4], although the

Table 2
Half-sandwich complexes which crystallize as 1:1 pairs of diastereomers in the same single crystal

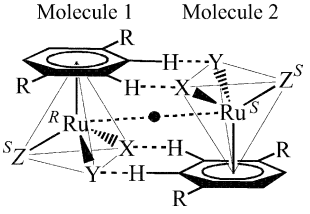
1	[(η^6-*p*-cymene)Ru((*S*)-methyl valinate-salicylaldiminate)Cl]	[4]
3	[(η^6-*p*-cymene)Ru((*S*)-1-phenylethyl-salicylaldiminate)Cl]	[10]
4	[(η^6-*p*-cymene)Ru((*R*)-1-hydroxybut-2-yl-salicylaldiminate)Cl]	[11]
5	[(η^6-*p*-cymene)Ru(2-(*S*)-2′-methoxy-1,1′-binaphthyl-salicylaldiminate)Cl]	[12]
6	[(η^6-*p*-cymene)Ru((*S*)-methyl valinate-salicylaldiminate)I]	[4]
7	[(η^6-*p*-cymene)Os((*S*)-1-phenylethyl-salicylaldiminate)Cl]	[4]
8	[(η^6-*p*-cymene)Ru((*R*)-1-hydroxybut-2-yl-pyrrolylaldiminate)Cl]	[11]
9	[(η^5-C_5H_5)Rh((*S*)-1-phenylethyl-salicylaldiminate)Cl]	[13]
10	[(η^6-C_6Me_6)Ru((*S*)-alaninate)9-ethylguaninate]	[14]
11	[(η^6-*p*-cymene)Ru(*N*-(*S*)-1-phenylethyl-4,6-di-*tert*-butyl-salicylaldiminate)Cl]	[15]
12	[(η^6-*p*-cymene)Ru((*S*)-1-phenylethyl-salicylaldiminate)(H_2O)]ClO_4	[16]
13	[(η^6-*p*-mesitylene)[Ru((*S*)-alaninate)]Cl	[17]
14	[(η^6-*p*-cymene)Ru(chiraphosO)Cl]	[18]
15	[(η^5-C_5Me_5)Ir((*S*)-prolinate)Cl]	[19,20]
16	{(η^6-*p*-cymene)[Ru((*S*)-2-(1-dimethylamino)ethylphenyl-2-ene]Cl}PF_6	[21]
17	[(η^6-C_6Me_6)Ru(κ^2-L-AlaGlyGlyOMe)Cl]	[22]
18	[(η^6-C_6Me_6)Ru((*S*)-alaninate)Cl]	[14]

C–H···I distances are relatively large compared to compounds **1**, **3**–**5** and **7**–**10** (Table 4). In accord with the motif of the inverted pianostools, the Ru–Ru distance of 5.82 Å within the pairs is much smaller than the outside-pair Ru–Ru distances which only start at 7.42 Å.

The crystallization behavior of the (*S*)-1-phenylethyl-salicylaldiminate complexes of Ru **3** [10] and Os **7** [4] is of particular interest, as the (*S*)-methyl valinate Ru and Os complexes **1** and **2** behave differently, the Ru compound **1** crystallizing as a 1:1 diastereomer mixture and the Os compound **2** crystallizing as a pure diastereomer. Surprisingly, the Os compound **7** undergoes 1:1 diastereomer co-crystallization like its Ru congener **3** strictly adhering to the molecular recognition pattern of Fig. 3. Thus, the discrepancy in the behavior of **1** and **2** cannot be a Ru/Os effect.

Interestingly, the pair-formation motif of half-sandwich complexes having a (Cy)M unit and two electronegative substituents X and Y explains the 1:1 diastereomer co-crystallization of three-legged pianostool compounds with ligands other than salicylaldiminates. In complex **8** [11] (Table 2) the unsymmetrical chelate ligand is the anion of the 2-pyrrolaldimine derived from (*R*)-1-hydroxybut-2-ylamine, the pyrrolate nitrogen taking the part of the salicylate oxygen in compounds **1**–**7**. However, the C–H···N(pyrrolate) distances are much larger than the C–H···O(salicylato) distances (Table 4). Surprisingly, the (η^5-C_5H_5)Rh complex **9** joins the club of half-sandwich complexes which show 1:1 diastereomer co-crystallization [13]. A short Rh···Rh distance of 5.49 Å (Table 3) within the pair and strong hydrogen bonds C–H···O (Table 4) originating from the cyclopentadienyl ring establish a molecular recognition motif very similar to Fig. 3. In the first paper in which 1:1 diastereomer co-crystallization of three-legged pianostool complexes was reported, Sheldrick and Heeb described the benzene–ruthenium complex **10** [14]. The diastereomers of **10** do not seem appropriate to form inversion pairs, because the nitrogen atom of the NH_2 group is as little suited as acceptor of a hydrogen bond as the nitrogen atom of the 9-ethylguaninate ligand. Nevertheless, 1:1 co-crystallization of the diastereomers in the form of inverted pianostools occurs. The alaninate oxygen atoms form strong hydrogen bonds to the benzene ligand of the

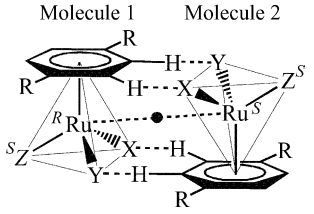
Table 3
Important distances within the inversion pairs in (Å)



	M1···M2	X1···Y2	Y1···X2	Z1···Z2
1 [4]	5.642	5.352	5.174	9.531
3 [10]	5.575	4.943	4.904	9.390
4 [11] 1st pair	5.669	5.069	4.969	9.506
4 [11] 2nd pair	5.614	5.033	4.830	9.400
5 [12]	5.514	4.941	4.979	9.355
6 [4]	5.819	5.295	5.710	9.566
7 [4]	5.583	4.932	4.872	9.316
8 [11]	5.824	4.343	4.667	9.122
9 [13]	5.487	4.908	5.084	9.350
10 [14]	6.015	6.147	6.238	9.517
11 [15]	6.890	6.267	6.246	9.982
12 [16]	5.131	2.652	2.567	7.579
13 [17]	5.932	3.339	3.338	8.178

X = Cl or I (OH_2 in the cation of **12** and N in **13**), Y = O_{sal} or N, Z = N (O in **13**).

Table 4
The C–H···X/Y hydrogen bonds within the inversion pairs (distances in (Å) and angles in (°))



	C–H···X2	C–H···Y2	C–H···X1	C–H···Y1	∢CHX2	∢CHY2	∢CHX1	∢CHY1
1 [4]	3.66	3.47	3.74	3.31	143.9	163.4	141.2	170.9
3 [10]	3.52	3.43	3.52	3.34	143.7	170.2	138.8	170.9 [a]
4 [11] 1st pair	3.52	3.61	3.68	3.41	149.0	168.1	144.1	171.5
4 [11] 2nd pair	3.69	3.22	3.74	3.30	143.4	165.9	143.6	170.1
5 [12]	3.43	3.18	3.52	3.46	143.7	141.5	149.1	140.3
6 [4]	4.41	3.47	3.91	3.40	161.6	134.1	154.2	129.3
7 [4]	3.58	3.48	3.50	3.36	144.9	171.2	139.3	177.6
8 [11]	3.51	3.96	3.86	4.44	127.6	164.3	131.0	164.0
9 [13]	3.65	3.27	3.90	3.51	153.1	145.5	136.9	151.6
10 [14]	3.31	4.92	3.32	5.02	137.5	148.2	144.0	164.3
11 [15]	4.74	6.05	4.88	6.15	81.5	134.8	82.3	134.0
12 [16]	3.85	3.81	3.92	3.80	111.7	107.6	98.0	112.3 [a]
13 [17]	4.66	4.93	4.65	4.64	–	–	–	–

X = Cl or I (OH_2 in the cation of **12** and N in **13**), Y = O_{sal} or N, Z = N (O in **13**).
[a] Hydrogen atoms added by calculation (not included in the original file).

neighboring molecule (Table 4). Although the Ru–Ru distance is a little longer than in compounds **1** and **3**–**9** (Table 3), all the characteristics of inversion pairs, such as the lying Z of the centroid–Ru–Ru–centroid arrangement, are present. In the inverted pianostools of the complexes **1** and **3**–**9** the diastereomers approach each other with their 'racemic' sides. In compound **10** this is different. Here, the alaninate ligands, which disturb centrosymmetry, are in the middle of the pairs. However, the differences between the hydrogen and the methyl substituents at the chiral center of alanine are not very large. The [(Cy)Ru(O–N)Cl] complex **11** of (*S*)-1-phenylethyl-salicylaldiminate with *t*-Bu substituents in 4- and 6-position of the salicyl ring also shows 1:1 diastereomer co-crystallization [15]. However, the molecular recognition motif of the inverted pianostools is somewhat distorted as discussed in the following analysis chapter.

Unlike **1**–**11**, compound **12** is a salt. Inspite of the positive charges, the cations (R_{Ru},S_C)- and (S_{Ru}, S_C)-[(Cy)Ru(O–N)$(OH_2)]_2^{2+}$, O–N = (*S*)-1-phenylethyl-salicylaldiminate, arrange in a 1:1 manner [16]. Compound [(mesitylene)Ru(O–N)Cl] (**13**) [17], in which O–N is the (*S*)-alaninate ligand, in the crystal also forms 1:1 (R_{Ru},S_C)-**13**/(S_{Ru},S_C)-**13** pairs. In both compounds **12** and **13** there are short intermolecular Ru–Ru distances (Table 3). However, the hydrogen bonds C–H···X/Y in both cases are lost and most important, the angles cymene1–Ru1–Ru2 120.5° and cymene2–Ru2–Ru1 118.0° for **12** and mesitylene1–Ru1–Ru2 125.4° and mesitylene2–Ru2–Ru1 122.1° for **13** are much larger than 90°, whereas for **1**–**11** they are smaller than 90° (lying Z arrangement).

In Faller's compound [(Cy)Ru(chiraphosO)Cl]SbF_6 **14** [18], which also shows 1:1 diastereomer co-crystallization, the unsymmetrical chelate ligand is the monoxide of chiraphos. The (Cy)Ru fragment and the two electronegative substituents O_{PP} and Cl could build up the molecular recognition motif of the inverted pianostools. However, they do not do it. Instead, a structure is formed, in which the diastereomeric cations are separated by the large SbF_6 anions. Beck's and Carmona's compound [(C_5Me_5)Ir(O–N)Cl] (**15**) [19,20], in which O–N is the (*S*)-prolinate ligand, and Nelson's salt [(C_6H_6)Ru(C–N)(dbp)]PF_6 **16** [21], in which C–N is the *ortho*-metallated ligand C_6H_5–CH(Me)–NMe_2 and dbp is 1-phenylbenzodiphosphole, also show 1:1 diastereomer co-crystallization. In both cases, however, the structural prerequisites are so different that the molecular recognition motif of Fig. 3 cannot be set up. This also holds for the (C_6Me_6)Ru complex **17** [22]. The shortest Ru···Ru distances in its crystal is 7.17 Å. With the alaninate oxygen and the chloro ligand the benzene–ruthenium complex **18** has all the prerequisites to form hydrogen bonds to the benzene ring of a neighboring molecule and thus to establish the molecular recognition motif of Fig. 3. However, this was not observed. Due to the small size of the alaninate ligand two short inter-

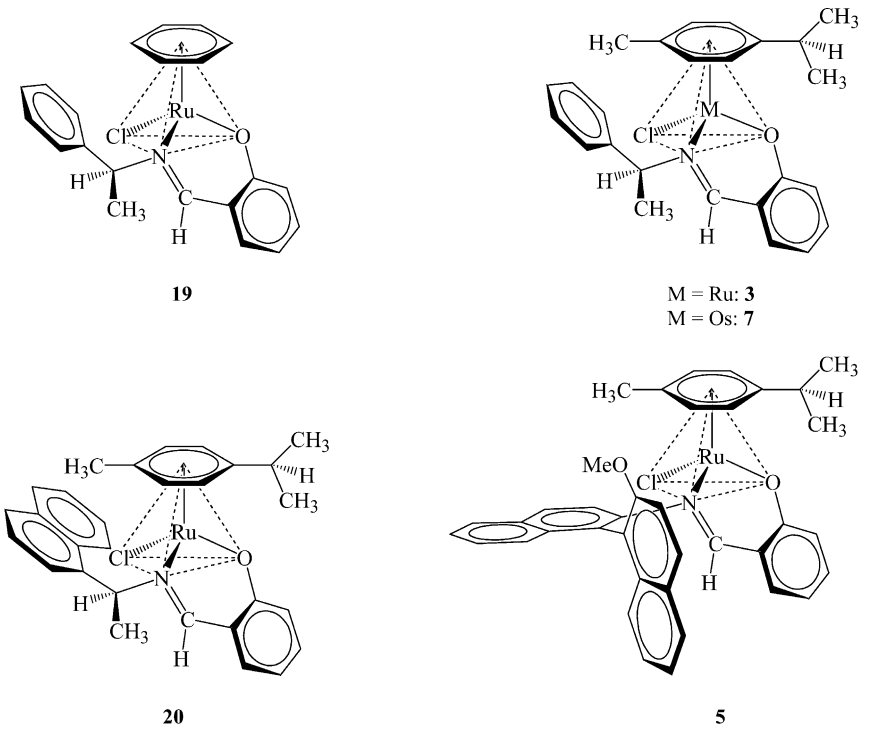


Fig. 4. Compounds **3**, **5**, **7**, **19** and **20**. **3**, **5** and **7** crystallize as 1:1 pairs of diastereomers (R_M,S_C)/(S_M,S_C) (only (R_M,S_C) isomers shown), **19** and **20** crystallize as pure diastereomers (R_M,S_C).

molecular Ru–Ru distances of 5.85 and 5.98 Å were found, but not the shape of the inverted pianostools.

The chemistry of (η^6-arene)Ru half-sandwich compounds is dominated by (Cy)Ru derivatives due to preparative reasons. α-Phellandrene, leading to the 1,4-isopropyl-methyl substitution pattern, is a convenient commercially available starting material. Therefore, much less benzene and other arene derivatives than *p*-cymene complexes have been prepared. Surprisingly, examples for the phenomenon of 1:1 diastereomer co-crystallization pile up for (Cy)Ru half-sandwich complexes. Obviously, the 1,4-substitution pattern in *p*-cymene favors the phenomenon, as [(η^6-C_6H_6)Ru(O–N)Cl] (**19**) (Fig. 4), the benzene analogue of **3**, crystallizes as the pure (R_{Ru},S_C) diastereomer [6]. Probably, two methyl groups in 1,4-position would also do the job. On the other hand, it should be kept in mind that it is not a 'must' for (Cy)Ru half-sandwich compounds to show 1:1 diastereomer co-crystallization. There are (Cy)Ru–salicylaldiminate complexes which crystallize as pure diastereomers including the PPh_3 derivatives [5]. Thus, there is a delicate balance between the two situations 1:1 diastereomer co-crystallization and crystallization as a pure diastereomer. In this respect, the intimately related Ru and Os compounds **1** and **2** behave disparately showing 1:1 diastereomer co-crystallization and crystallization as a pure diastereomer, respectively, whereas Ru and Os compounds **3** and **7**, related in the same way, behave similarly both crystallizing as 1:1 diastereomer mixtures. In addition, the compound [(Cy)Ru(O–N)Cl] (**20**) (Fig. 4), the O–N ligand of which is the salicylaldiminate derived from (*S*)-1-naphthylethylamine, would have all the requirements for the formation of inversion pairs, but it crystallizes as a pure diastereomer [4]. In fact, the (*S*)-1-naphthylamine derivative **20** is structurally closer to the (*S*)-1-phenylethylamine derivative **3** than the (*S*)-2-(2′-methoxy)-1,1′-binaphthylamine derivative **5** which follows **3** in 1:1 diastereomer co-crystallization [12]. In solution the diastereomer ratios of complexes **1**–**20** vary depending on compound type and substitution pattern. In both crystallization alternatives (diastereomer ratio 50:50 or 100:0) asymmetric transformations with respect to the metal configuration are involved [7], although they probably are not the reason for realizing one or the other.

5. Analysis of the molecular recognition motif in compounds of the type [(Ar)MXYZ], X and Y being electronegative substituents

The molecular recognition motif of the inverted pianostools (Fig. 3) is strictly obeyed in compounds **1** and **3**–**9** (two pairs for compound **4**) including the lying Z for the arrangement Ar(centroid)–M–M–Ar(centroid). These pairs are shown in Fig. 5 in a slight top view with respect to the π-bonded ligand. The M1···M2 distances given in Table 3 are in the narrow range between 5.58 and 5.82 Å. Similarly the X1···Y2 and

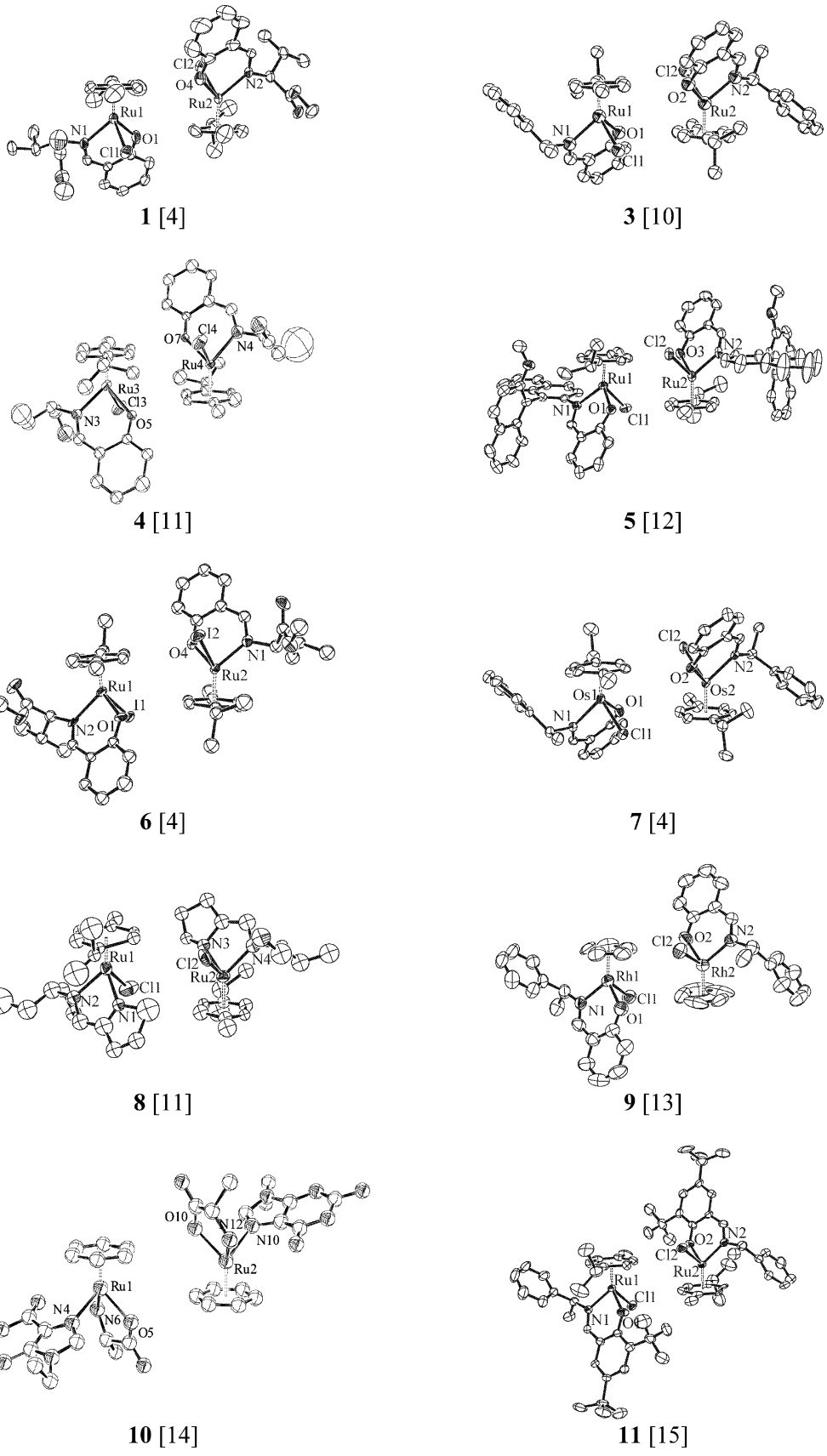


Fig. 5. Compounds **1** and **3**–**11** showing 1:1 diastereomer co-crystallization based on the molecular recognition motif of the inverted pianostools.

Y1···X2 distances are between 4.34 and 5.35(5.71) Å, X being the halogen and Y the oxygen of the salicyl system or the nitrogen of the pyrrolyl system. The distances Z1···Z2 range between 9.12 and 9.56 Å indicating that the nitrogen substituents are far apart from each other pointing away from the center of the pairs. Table 4 gives the details concerning the C–H···X/Y hydrogen bonds within the pairs. They are all in the same range. Remarkably, the set of complexes in Fig. 5 not only comprises Ru compounds but also Os and Rh compounds, not only cymene derivatives but also a cyclopentadienyl derivative, not only chloro ligands but also a iodo ligand and not only salicylaldiminates but also a pyrrolylaldiminate. In addition, most of the compounds differ appreciably in the chiral nitrogen substituent.

Inspection of the formulas in Fig. 5 shows that in all the pairs with *p*-cymene ligands the isopropyl and the methyl substituents of the cymene rings are on opposite sides following inversion symmetry, except compound **1**, in which the two isopropyl and the two methyl groups are on the same sides. Furthermore, the isopropyl substituent usually is on the side of the oxygen substituent in the same molecule (and the halogen substituent in the opposite molecule), except for the iodo derivative **6** and molecule 2 of compound **1**. In complex **8** the isopropyl substituents are on the side of the pyrrolyl system.

Compounds **1** and **3**–**11** (both pairs of **4**) strictly adhere to the molecular recognition pattern of the inverted pianostools as substantiated by Tables 3 and 4 as well Fig. 5. In compound **11** the two *tert*-Bu substituents of the salicyl rings are oriented towards the outside of the pairs. Nevertheless, the expected hydrogen bridges are lost (Table 4). In part, this is due to a rotation of the cymene ring with respect to the O_{sal} and Cl substituents of the other molecule in the pair. Actually, in compound **11** there are C–H···Cl hydrogen bridges of 3.641 and 3.790 Å between the C–H bond next to the methyl substituent and the chloro ligand of the opposite molecule. Thus, compound **11** can be considered another example of the molecular recognition pattern of Fig. 3.

As outlined above compounds **12** and **13**, although arranging in the form of inverting pianostools actually deviate appreciably from the lying Z of the tight inverted pianostools motif. Compounds **14**–**17** have structural prerequisites excluding pair formation or realize structures far away from the molecular recognition pattern of the inverted pianostools.

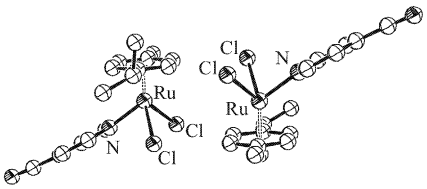
The molecular recognition motif of Fig. 3 explains the increased occurrence of 1:1 diastereomer co-crystallization of compounds [(Ar)MXY(NR*)] on the basis of a centrosymmetric arrangement of two mirror image (Ar)MXY fragments. A consequence should be that other compounds having the structural element (Ar)MXY with X and Y electronegative substituents should establish this molecular recognition motif as well, even if they have nothing to do with chirality, diastereomer co-crystallization etc. As the motif was increasingly found for [(Cy)Ru(O_{sal})Hal] compounds we made a search in the Cambridge File for (*p*-cymene)Ru–halide complexes, expecting pair formation as indicated in Fig. 3 with the orientation of the ligands L to the outside of the pairs. We found 19 entries. Ten of them which nicely fit the molecular recognition pattern are shown in Fig. 6. The ligands L are pyridine, amine and, in particular, phosphine derivatives [23–31]. The compounds strictly comply with the molecular recognition pattern in Fig. 3. All the Ru···Ru distances within the pairs are between 5.59 and 5.90 Å. Nine [(Cy)RuLCl_2] systems do not fit this pattern. In these nine compounds the ligands L are carbene [32] and, again, phosphine derivatives [28,30,33–37] similar to those which fit the pattern. In these compounds there are no inversion pairs with Ru···Ru distances in the range 5.60–5.80 Å. Thus, the situation corresponds to the compounds listed in Table 2: the molecular recognition motif of the tight inverted pianostools is an attractive possibility, but it is not reinforced. There are always examples which could follow it, but fail to do so.

The analysis given for the compounds [(Cy)RuLCl_2] could easily be extended to related systems. A representative example is the compound [(Cy)Ru(O–N)Cl] [38] in which the unsymmetrical chelate ligand O–N is the anion of 8-hydroxyquinoline (Fig. 7). The chiral molecules form a racemate with a perfect inversion center between the two enantiomers of the molecular recognition pairs according to Fig. 3. The Ru···Ru distance is 5.34 Å and the hydrogen bonds C–H···O 3.279 Å (angle 125.8°) and C–H···Cl 3.674 Å (angle 160.0°) are conform with the pattern of Tables 3 and 4.

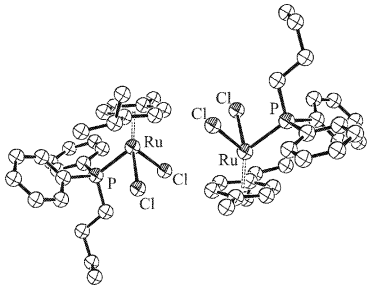
In the literature there are scattered examples of other 1:1 diastereomer co-crystallizations, e.g. Ref. [31]. However, systematic analyses are missing. Argumentation usually is as for the known disorder in racemic crystals containing *sec*-butyl groups [39,40], for which an explanation of 1:1 diastereomer crystallization was offered on the basis of 'a minor difference in steric interactions between the chirality of one center, e.g. (*R*) and (*S*) butyl'. This, however, cannot be the whole story, as the compounds discussed in the present review are very different from each other and their 1:1 diastereomer co-crystallization is based on a common principle, pair formation due to molecular recognition of their 'racemic sides'.

6. Conclusion

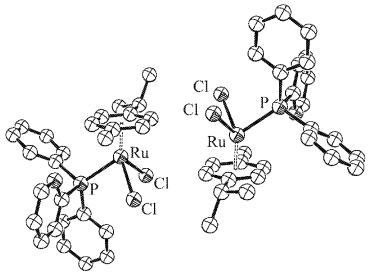
Half-sandwich complexes of the type [(Ar)MXYZ], in which X and Y are electronegative substituents, tend to form inversion pairs in the solid state, characterized by



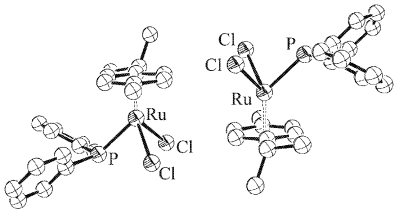
L = 4-cyanopyridine [22]



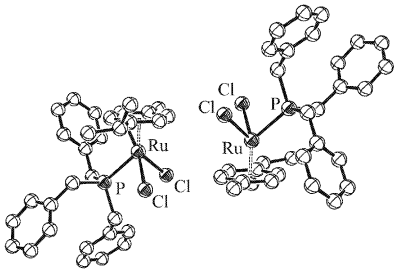
L = *n*-butyl(diphenyl)phosphine [23]



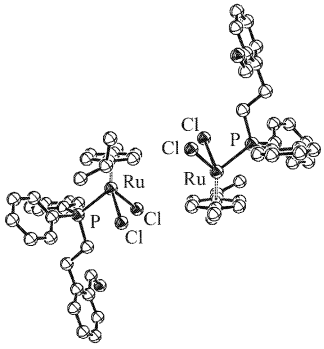
L = diphenyl(2-pyridyl)phosphine [24]



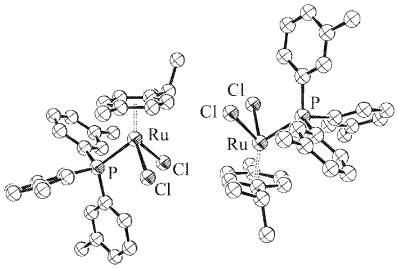
L = diphenylphosphine [24]



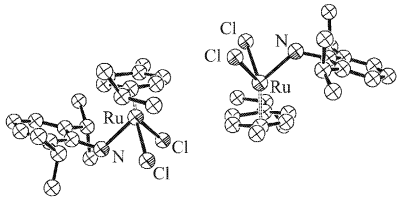
L = tribenzylphosphine [25]



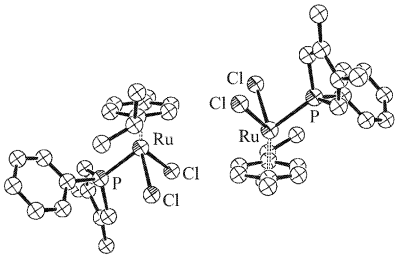
L = (hydroxymethylphenylethyl)diphenylphosphine [26]



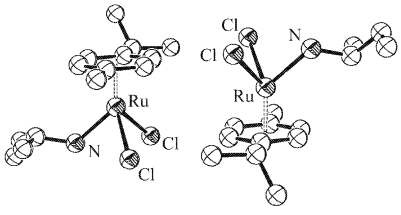
L = tris(3-methylphenyl)phosphine [27]



L = 2,6-diisopropylaniline [28]



L = 1-phenyl-3,4-dimethylphosphole [29]



L = (*R,S*)-*sec*-butylamine [30]

Fig. 6. Compounds of the type [(Cy)RuLCl$_2$] strictly adhering to the molecular recognition motif of the inverted pianostools.

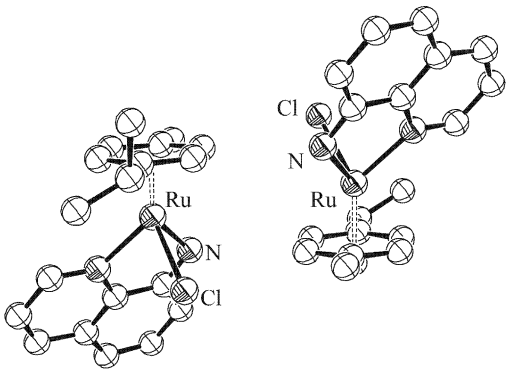


Fig. 7. Complex [(Cy)Ru(O–N)Cl] [37] in which the chelate ligand O–N is the anion of 8-hydroxyquinoline showing the molecular recognition motif of the inverted pianostools.

short M···M distances and hydrogen bonds C–H···X/Y between the two molecules of a pair. In these compounds the metal atom is a chiral center. With a given chirality in the Z substituent, usually a NR* group, two diastereomers are formed which only differ in the metal configuration. As a consequence of the pair formation two diastereomers approach each other with their 'racemic sides' resulting in an unusually preferred 1:1 diastereomer co-crystallization.

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