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# Optically active transition metal complexes. Part 131.<sup>1</sup> Synthesis and epimerization of chiral-at-metal ( $\eta^6$ -arene)ruthenium(II) and ( $\eta^6$ -arene)osmium(II) half-sandwich complexes

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## Abstract

*Ortho*-metalated derivatives of the optically active ligand (*S*)-(–)-*N,N*-dimethyl(1-phenylethyl)amine (**LL\*–H**) react with  $[(\eta^6\text{-}p\text{-cymene})\text{MCl}_2]_2$  (M = Ru, Os) to give the half-sandwich complexes  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]$  (**1a,b**) and  $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2a,b**). In both cases two diastereomers ( $R_M, S_C$ ) and ( $S_M, S_C$ ) arise differing only in the metal configuration. On crystallization the ( $R_M, S_C$ )-isomers of both complexes **1** and **2** were obtained diastereomerically pure. The absolute configurations were established by X-ray structure analyses. Epimerization studies clearly showed that the metal configuration in both complexes is labile in solution. © 2003 Elsevier Science Ltd. All rights reserved.

**Keywords:** Chiral-at-metal complexes; Configurational stability; Epimerization; Diastereomer equilibria; X-ray structure analyses

## 1. Introduction

As a consequence of the ‘lanthanide contraction’ the radii of corresponding 4d and 5d metals are almost identical. This results in very similar bond distances and angles within analogous 4d and 5d compounds including chiral-at-metal complexes [2]. Nevertheless there are examples of significantly different stereochemical behaviour of corresponding 4d and 5d complexes. Recently we described the synthesis and crystal structure of ( $\eta^6\text{-}p\text{-cymene}$ )ruthenium(II) and ( $\eta^6\text{-}p\text{-cymene}$ )osmium(II) half-sandwich complexes with the salicylaldiminato

ligand derived from methyl (*S*)-valinate and chloro ligands [1]. Surprisingly, the Ru compound crystallized with both diastereomers in 1:1 ratio in the same single crystal, whereas its osmium congener, having identical metric molecular parameters, crystallized as a pure diastereomer in two different modifications indicating that subtle differences may result in unexpected alternatives. Recently, we synthesized  $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]$ , **LL\*** = anion of (*S*)-(–)-*N,N*-dimethyl(1-phenylethyl)amine, to correct the misinterpretation of the configurational stability at the metal atom [3,4]. Nelson and co-workers had prepared the mirror image compound using the (*R*)-configured ligand [5]. Here, we describe the corresponding osmium compound  $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  and the investigation of its configurational stability, as such comparisons between second and third row transition metal compounds are rare [2].

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<sup>1</sup> For Part 130, see Ref. [1].

<sup>2</sup> X-ray structure analyses.

## 2. Experimental

### 2.1. Physical measurements

Melting points: Büchi SMP 20, not corrected. IR spectra: Beckman spectrometer IR 4240 (KBr pellets). Mass spectra: Finnigan MAT 95 (field desorption method). Optical rotations: Perkin–Elmer 241 polarimeter at room temperature (r.t.).  $^1\text{H}$  NMR spectra: Bruker ARX 400 (400 MHz) and AC 250 (250 MHz) spectrometer. Elemental analyses: Elementar Vario EL III.

### 2.2. Materials and methods

Reactions were carried out in dry solvents in  $\text{N}_2$  atmosphere using Schlenk techniques. Chemicals were obtained from commercial sources. The precursor (*S*)-(+)-2-[1-dimethylamino]ethyl]phenyllithium (**LiLL\***) was prepared as described in Ref. [6].  $[(\eta^6\text{-}p\text{-Cymene})\text{-RuCl}_2]_2$ ,  $[(\eta^6\text{-}p\text{-Cymene})\text{OsCl}_2]_2$  and  $[(\eta^6\text{-}p\text{-Cymene})\text{-Ru}(\text{LL}^*)\text{Cl}]$  (**1**) were synthesized as published in Refs. [7–11].

### 2.3. $[(\eta^6\text{-}p\text{-Cymene})\text{Os}(\text{LL}^*)\text{Cl}]$ (**2**)

**LiLL\*** (170 mg, 1.10 mmol) was suspended in toluene (50 ml) and cooled to  $-78^\circ\text{C}$ .  $[(\eta^6\text{-}p\text{-Cymene})\text{OsCl}_2]_2$  (395 mg, 0.50 mmol) was added at this temperature. The suspension was stirred for 16 h, the temperature being allowed to come to r.t. Then the solvent was removed. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and filtered through Celite® and  $\text{SiO}_2$ . Yellow orange crystals were obtained by crystallization from  $\text{CH}_2\text{Cl}_2$ /toluene/petroleum ether.

Yield: 205 mg (80%), m.p.  $228^\circ\text{C}$  (dec.). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3060\text{ m}$ ,  $3000\text{ m}$ ,  $2980\text{ s}$ ,  $2860\text{ m}$  (C–H),  $1390\text{ s}$  (C–N).  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ , TMS, signals of the minor diastereomer in parentheses when different to the major diastereomer):  $\delta = 1.12$  (d,  $^3J = 6.9$  Hz, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 1.22 (d,  $^3J = 6.9$  Hz, 3H,  $\text{CHCH}_3$ ), 1.24 (1.32) (d,  $^3J = 6.9$  Hz, 3H,  $\text{CH}(\text{CH}_3)_2$ ), 2.13 (1.78) (s, 3H,  $\text{CH}_3$ -cymene), 2.68 (2.09) (s, 3H,  $\text{NCH}_3$ ), 2.81 (sept,  $^3J = 6.9$  Hz, 1H,  $\text{CH}(\text{CH}_3)_2$ ), 3.36 (3.56) (s, 3H,  $\text{NCH}_3$ ), 4.68 (qd,  $^3J = 6.9$  Hz,  $^4J = 1.6$  Hz, 1H,  $\text{CHCH}_3$ ), 5.00–4.89 (m, 2H, *H*-cymene), 5.53 (d,  $^3J = 5.5$  Hz, 1H, *H*-cymene), 5.62 (d,  $^3J = 5.5$  Hz, 1H, *H*-cymene), 6.80 (ddd,  $^3J = 7.3$  Hz,  $^4J = 1.6$  Hz,  $^4J = 1.4$  Hz, 1H, Ph-*H*), 6.93 (ddd,  $^3J = 7.4$  Hz,  $^3J = 7.3$  Hz,  $^4J = 1.4$  Hz, 1H, Ph-*H*), 7.03 (dddd,  $^3J = 7.4$  Hz,  $^3J = 7.3$  Hz,  $^4J = 1.4$  Hz,  $^4J = 0.9$  Hz, 1H, Ph-*H*), 7.96 (7.50) (dd,  $^3J = 7.4$  Hz,  $^4J = 1.4$  Hz, 1H, Ph-*H*). MS (FD,  $\text{CH}_2\text{Cl}_2$ ):  $m/z$  (rel. int.) = 509 (100) [*M*] rel. to  $^{192}\text{Os}$ .  $[\alpha]_{\text{D}}^{20}$  ( $c = 0.20$ ,  $\text{CH}_2\text{Cl}_2$ ) =  $-57^\circ$ . Anal. Calc. for  $\text{C}_{20}\text{H}_{28}\text{ClNOs}$  (508.1): C 47.28, H 5.55, N 2.76; Found: C 46.99, H 5.54, N 2.74%.

### 2.4. X-ray

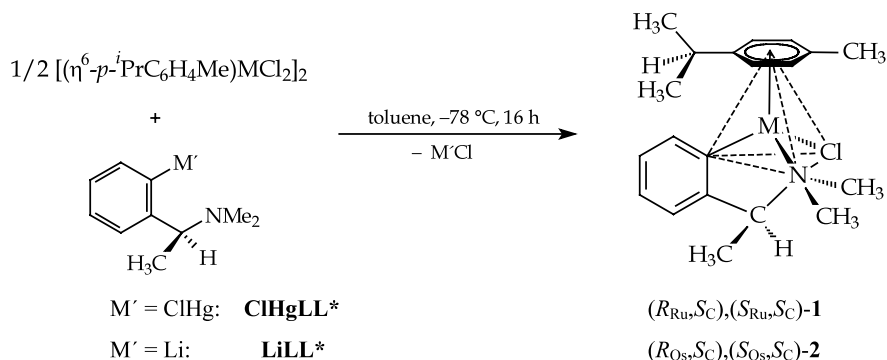
X-ray structural analyses: STOE-IPDS diffractometer (Mo  $\text{K}\alpha$  radiation, 173 K (Oxford Cryosystems Cooler) [12], graphite monochromator), SIR-97 [13] and SHELXL-97 [14]. Crystal data and details of the structure determination are shown in Table 2.

## 3. Results and discussion

### 3.1. Synthesis, $^1\text{H}$ NMR spectra and X-ray structure analyses

The complex ( $R_{\text{Ru}}, S_{\text{C}}$ )- and ( $S_{\text{Ru}}, S_{\text{C}}$ )- $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]$  (**1**), containing the (*S*)-enantiomer of the ligand **LL\***, had been prepared using  $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$  and (*S*)-(+)-2-[1-dimethylamino]ethyl]phenylmercurychloride, **ClHgLL\*** (Scheme 1) according to Refs. [5,3]. X-ray structural analysis of the crystals, obtained from  $\text{CH}_2\text{Cl}_2$  and ether/hexane, confirmed the ( $S_{\text{C}}$ )-configuration at the chiral carbon atom of the ligand. The absolute configuration at the metal atom was ( $R_{\text{Ru}}$ ) using the ligand priority sequence  $\eta^6\text{-}p\text{-cymene} > \text{Cl} > \text{N} > \text{C}$  [15,16]. In fact, complex **1** is the mirror image of the compound ent-**1** described by Nelson and co-workers, who had used the ( $R_{\text{C}}$ )-configured ligand [5]. Solutions of crystals of **1** in  $\text{CDCl}_3$  showed at r.t. in the  $^1\text{H}$  NMR spectrum the signals of both diastereomers ( $R_{\text{Ru}}, S_{\text{C}}$ )-**1** and ( $S_{\text{Ru}}, S_{\text{C}}$ )-**1** in a ratio of 83:17 in accord with Ref. [5]. However, the  $^1\text{H}$  NMR spectrum of a solution of crystals, dissolved and measured at  $-80^\circ\text{C}$ , exhibited only the signals of the major diastereomer ( $R_{\text{Ru}}, S_{\text{C}}$ )-**1**. Measurements at  $-50$ ,  $-20$ ,  $0$  and  $+21^\circ\text{C}$  demonstrated that the second diastereomer was formed only at higher temperatures, indicating the configurational lability of the metal center, which had been overlooked in the Refs. [5,6].

As the synthesis of the osmium complex **2** according to the methodology used in the preparation of the ruthenium compound **1** did not work, we prepared the lithiated ligand **LiLL\*** [6]. Its reaction with  $[(\eta^6\text{-}p\text{-cymene})\text{OsCl}_2]_2$  gave ( $R_{\text{Os}}, S_{\text{C}}$ )- and ( $S_{\text{Os}}, S_{\text{C}}$ )- $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2**) (Scheme 1). Again, the two diastereomers ( $R_{\text{Os}}, S_{\text{C}}$ )-**2** and ( $S_{\text{Os}}, S_{\text{C}}$ )-**2** differ in their  $^1\text{H}$  NMR spectra. The ( $R_{\text{Os}}, S_{\text{C}}$ )-**2**/ $(S_{\text{Os}}, S_{\text{C}})$ -**2** ratio was 93:7 in  $\text{CDCl}_3$  solution at r.t. This ratio is higher than the ratio of the ruthenium analogue **1**. Single crystals of  $[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2**) were grown by diffusion of a 1:1 mixture of toluene and petroleum ether into a  $\text{CH}_2\text{Cl}_2$  solution at  $+4^\circ\text{C}$ . X-ray analysis showed that the crystals of **2** only contained the ( $R_{\text{Os}}, S_{\text{C}}$ )-diastereomer (Fig. 1). The absolute configuration at the osmium atom was ( $R_{\text{Os}}$ ) using the ligand priority sequence  $\eta^6\text{-}p\text{-cymene} > \text{Cl} > \text{N} > \text{C}$  [15,16].



Scheme 1. Synthesis of  $[(\eta^6\text{-}p\text{-cymene})\text{M}(\text{LL}^*)\text{Cl}]$  (**1**) and (**2**); only the diastereomer with  $(R_{\text{M}},S_{\text{C}})$ -configuration shown.

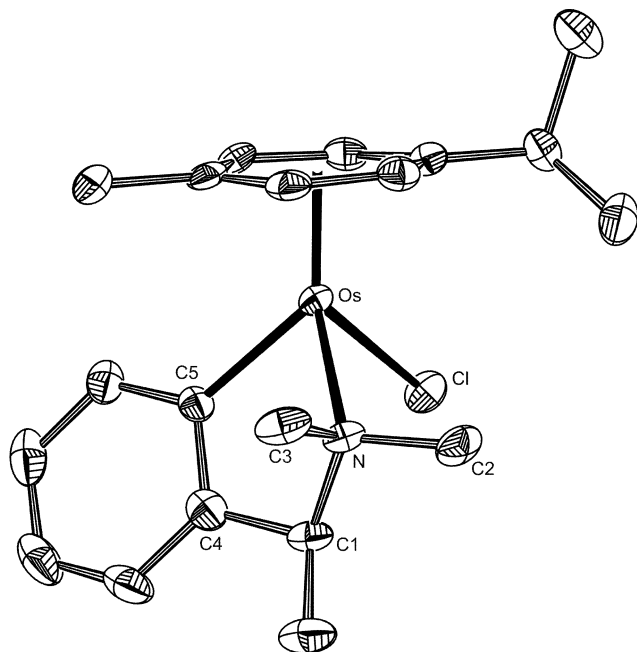


Fig. 1. Structure of  $(R_{\text{Os},S_{\text{C}}})\text{-}[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2**).

The crystallographic parameters of  $(R_{\text{Ru},S_{\text{C}}})\text{-}[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]$  (**1**) and  $(R_{\text{Os},S_{\text{C}}})\text{-}[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2**) are given in Table 1. Relevant bond lengths, bond angles and torsional angles are listed in Table 2. As expected, they are extremely similar to each other for the two congeners **1** and **2**.

### 3.2. Epimerization studies

The ruthenium and osmium half-sandwich complexes **1** and **2** were compared with respect to the configurational stability at the metal atom in a detailed kinetic study. During the epimerization studies the samples stayed within the Bruker ARX 400 spectrometer (for the temperature constancy see Ref. [2]). Evaluation was done by integration of the  $\text{NCH}_3$   $^1\text{H}$  NMR signals.

Powdered crystals of **2** were dissolved at  $-80$   $^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  showing only the signals of the major diastereomer  $(R_{\text{Os},S_{\text{C}}})\text{-2}$ . Similar to ruthenium complex **1**, on

Table 1

Crystallographic data for compounds  $(R_{\text{Ru},S_{\text{C}}})\text{-}[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]$  (**1**) and  $(R_{\text{Os},S_{\text{C}}})\text{-}[(\eta^6\text{-}p\text{-cymene})\text{Os}(\text{LL}^*)\text{Cl}]$  (**2**)

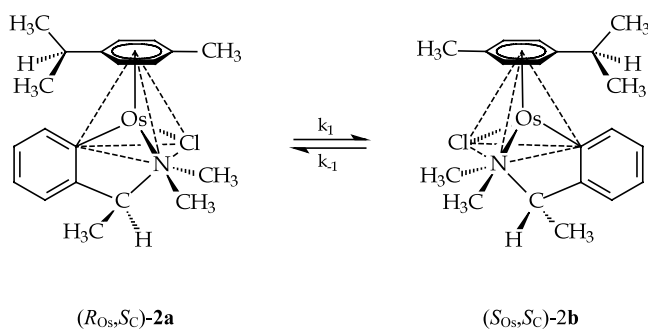
| Compound   | <b>1</b>                                 | <b>2</b>                                 |
|--|--|--|
| Empirical formula  | $\text{C}_{20}\text{H}_{28}\text{ClNRu}$ | $\text{C}_{20}\text{H}_{28}\text{ClNOs}$ |
| Formula weight ( $\text{g mol}^{-1}$ )                   | 418.95                                   | 508.11                                   |
| Crystal system   | monoclinic                               | monoclinic                               |
| Space group  | $\text{P}2_1$                            | $\text{P}2_1$                            |
| Z  | 2  | 2  |
| a ( $\text{\AA}$ )                                       | 10.1038(9)                               | 14.0254(14)                              |
| b ( $\text{\AA}$ )                                       | 6.5964(4)                                | 6.5794(4)                                |
| c ( $\text{\AA}$ )                                       | 14.0109(13)                              | 10.1229(10)                              |
| $\alpha$ ( $^\circ$ )                                    | 90                                       | 90                                       |
| $\beta$ ( $^\circ$ )                                     | 93.882(11)                               | 93.790(12)                               |
| $\gamma$ ( $^\circ$ )                                    | 90                                       | 90                                       |
| V ( $\text{\AA}^3$ )                                     | 931.67(13)                               | 932.09(14)                               |
| $\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )              | 1.493                                    | 1.810                                    |
| Absorption coefficient ( $\text{mm}^{-1}$ )              | 0.984                                    | 6.983                                    |
| Absorption correction                                    | none                                     | numerical                                |
| Max/min transmission                                     | –  | 0.7287/0.4647                            |
| F(0 0 0)   | 432                                      | 496                                      |
| $\theta$ range ( $^\circ$ )                              | 2.4–27.8                                 | 2.56–25.78                               |
| Reflections  | 15 999                                   | 13 002                                   |
| $R_{\text{int}}$   | 0.0346                                   | 0.0490                                   |
| Data/parameters  | 4346/432                                 | 3540/208                                 |
| Goodness-of-fit on $F^2$                                 | 1.081                                    | 1.032                                    |
| $R_1/wR_2$ [ $I > 2\sigma(I)$ ]                          | 0.0168/0.0389                            | 0.0170/0.0402                            |
| $R_1/wR_2$ (all data)                                    | 0.0181/0.0386                            | 0.0176/0.0403                            |
| Largest difference peak and hole ( $\text{e \AA}^{-3}$ ) | 0.471/–0.255                             | 1.410/–0.578                             |
| CCDC No.   | 193 340                                  | 193 341                                  |

raising the temperature the signals of the minor diastereomer  $(S_{\text{Os},S_{\text{C}}})\text{-2}$  grew—a process which continued on warming. Thus, the configuration at the osmium atom is labile in solution and an equilibrium between the two diastereomers  $(R_{\text{Os},S_{\text{C}}})$  and  $(S_{\text{Os},S_{\text{C}}})$  is established (Scheme 2). Measurements at r.t. gave the equilibrium ratio  $(R_{\text{Os},S_{\text{C}}})\text{:}(S_{\text{Os},S_{\text{C}}}) = 93\text{:}7$  in  $\text{CD}_2\text{Cl}_2$ , which for **1** had been  $(R_{\text{Ru},S_{\text{C}}})\text{:}(S_{\text{Ru},S_{\text{C}}}) = 90\text{:}10$ .

After dissolving the powdered crystals of  $(R_{\text{Ru},S_{\text{C}}})\text{-2}$  at  $-80$   $^\circ\text{C}$  and warming up to  $+5$   $^\circ\text{C}$ ,  $^1\text{H}$  NMR spectra were recorded at defined time intervals for more than 1.5 half-lives. The data analyzed perfectly accord-

Table 2  
Selected bond lengths, bond angles and torsional angles of ( $R_{Ru,S_C}$ )-**1** and ( $R_{Os,S_C}$ )-**2**; estimated standard deviations are shown in parentheses

| (a) Bond lengths (Å)         | ( $R_{Ru,S_C}$ )- <b>1</b> | ( $R_{Os,S_C}$ )- <b>2</b> |
|------------------------------|----------------------------|----------------------------|
| M–C <sub>cymene center</sub> | 1.708                      | 1.694                      |
| M–Cl                         | 2.4393(5)                  | 2.4412(10)                 |
| M–C5                         | 2.0640(18)                 | 2.077(4)                   |
| M–N                          | 2.2020(15)                 | 2.221(3)                   |
| (b) Bond angles (°)          |                            |                            |
| Cl–M–C5                      | 86.75(5)                   | 86.38(11)                  |
| N–M–Cl                       | 88.36(5)                   | 86.96(8)                   |
| N–M–C5                       | 77.86(7)                   | 77.50(14)                  |
| (c) Torsional angles (°)     |                            |                            |
| C5–M–N–C1                    | 32.14(12)                  | 31.9(2)                    |
| C5–M–N–C2                    | 152.11(16)                 | 151.0(3)                   |
| C5–M–N–C3                    | –88.20(13)                 | –88.8(3)                   |



Scheme 2. Epimerization of the complexes **2a,b**.

ing to first-order (Fig. 2), the half-life for the approach to equilibrium being 62 min at 5 °C ( $k = 1.87 \times 10^{-4} \text{ s}^{-1}$ ). The half-life in the epimerization of the ruthenium complex **1** in  $\text{CD}_2\text{Cl}_2$  had been 34 min at +6 °C [3].

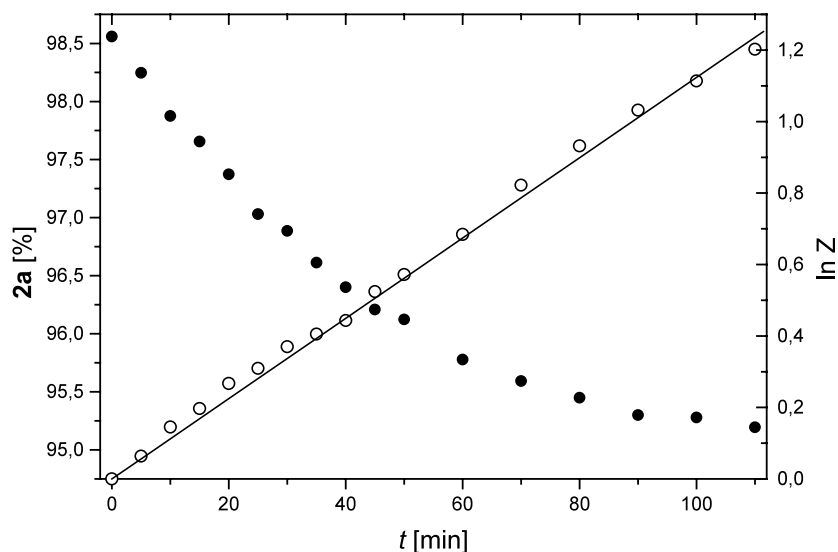


Fig. 2. Epimerization of the complex ( $R_{Os,S_C}$ )-**2** in  $\text{CD}_2\text{Cl}_2$  at 5 °C. Equilibrium ratio ( $R_{Os,S_C}$ )-**2**:( $S_{Os,S_C}$ )-**2** = 93:7 and interpretation according to a first-order rate law.  $Z = ([2a]_0 - [2a]_\infty) / ([2a] - [2a]_\infty)$ .

Thus the configuration at the osmium atom in **2** is more stable than the configuration at the ruthenium atom but only by a factor of about 2. Both half-lives show that solutions of the complexes **1** and **2** cannot be handled at r.t. without fast change of the metal configuration.

#### 4. Conclusions

We synthesized and characterized the complex ( $R_{Os,S_C}$ )- and ( $S_{Os,S_C}$ )-[( $\eta^6$ -*p*-cymene)Os(LL\*)Cl] (**2**). It is analogous to ( $R_{Ru,S_C}$ )/( $S_{Ru,S_C}$ )-[( $\eta^6$ -*p*-cymene)-Ru(LL\*)Cl] (**1**), the configurational lability at the metal atom of which had been overlooked in the literature. Complex (**2**) crystallizes as the ( $R_{Os,S_C}$ )-diastereomer. In solution the configuration at the Os atom is labile and an equilibrium between the two diastereomers ( $R_{Os,S_C}$ )-**2** and ( $S_{Os,S_C}$ )-**2** is established. In  $\text{CD}_2\text{Cl}_2$  the ratio is 93:7, the major diastereomer having ( $R_{Os,S_C}$ )-configuration.

#### 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center. Supplementary data are available from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>) on request, quoting the deposition nos. given in Table 1.

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