Inorg. Chem. **1995,** *34,* 3349−3351

Notes

Stereochemistry at the Chiral Ruthenium Atom in Half-Sandwich Compounds of the Type $[(\eta^6\text{-Ar})\text{Ru}(\text{LL}^*)\text{L}']\text{X}$ and $[(\eta^6\text{-Ar})\text{Ru}(\text{LL}^*)\text{Hal}]$. X-ray Structure Analysis of $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{4-Mepy}]\text{PF}_6$ and Appeal for the Proper Use of Stereochemical Terminology

Henri Brunner* and Ralf Oeschey

Institut für Anorganische Chemie der
Universität Regensburg, Universitätsstrasse 31,
D-93053 Regensburg, Germany

Bernd Nuber

Anorganisch-Chemisches Institut der Universität Heidelberg,
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Received December 6, 1994

Introduction

In 1991, Mandal and Chakravarty started to synthesize and resolve half-sandwich ruthenium compounds of the type $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{L}']\text{ClO}_4$, with cymene = 1-isopropyl-4-methylbenzene, LL* = anion of (*S*)-(1-phenylethyl)salicylaldimine and L′ = triphenylphosphane or 4-methylpyridine and $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{Hal}]$, with Hal = a halide ion.[1] In 1992, a detailed study was published,[2] containing valuable preparative information, but also stereochemical misassignments and oversimplifications. In a subsequent paper these misassignments and oversimplifications were repeated and extended.[3] In this Note we address to these mistakes and we correct one of the misassignments on the basis of a new X-ray structure analysis of $(+)_\text{D}$-(R_Ru,S_C)-$[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{4-Mepy}]\text{PF}_6$, **1**.

Experimental Section

Physical Measurements. Elemental analyses were performed by the microanalytical laboratory of the University of Regensburg. Proton NMR spectra with tetramethylsilane as internal standard were measured on a Bruker ARX 400 spectrometer. Circular dichroism (CD) spectra were recorded on a Jasco J-40 A spectrophotometer, and polarimetric measurements were done using a Perkin Elmer 241 instrument.

Table 1. Crystallographic Data for (R_Ru,S_C)-$[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{4-Mepy}]\text{PF}_6$, **1**

chem formula	$C_{31}H_{35}F_6N_2OPRu$
fw	697.66
space group	$P2_12_12_1$ (No. 19)
a, Å	10.815(6)
b, Å	16.200(9)
c, Å	17.477(7)
V, Å^3	3062.0(2)
Z	2
ϱ_calc, g cm^{-3}	1.51
T, K	295
λ(Mo Kα), Å	0.7107
μ, mm^{-1}	0.61
transm coeff	0.93−1.00
R^a	0.044
$R_w{}^b$	0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_c|$. [b] $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$, $w = 1/\sigma^2(F_o)$.

Preparative Work. The diastereomeric mixture of $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{4-Mepy}]\text{PF}_6$, **1** was synthesized in a slightly different manner as the published[2] procedure for preparing the corresponding perchlorate. A 150 mg (0.30 mmol) sample of the diastereomeric mixture of $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{Cl}]^2$ was suspended in 30 mL of cooled acetone at a temperature of −30 °C. To this suspension was added AgPF_6 (76 mg, 0.30 mmol), and the mixture was stirred for 1 h resulting in a red solution containing precipitated AgCl. Addition of 0.044 mL (42 mg, 0.45 mmol) of 4-methylpyridine induced a color change of the solution to yellow. After 30 min of stirring at −30 °C the solution was filtered through Celite while cold and the solvent was evaporated. The residue was washed several times with petroleum ether and crystallized from tetrahydrofuran/diethyl ether (5:3) at −25 °C, yielding 180 mg (0.26 mmol, 86%) of prismatic crystals suitable for X-ray structure determination. Further crystallization of the mother liquor increased the yield to 90%. Both fractions contained only one pure diastereomer, as determined by proton NMR spectroscopic analysis of solutions prepared and measured at −80 °C. Anal. Calcd for $[(\eta^6\text{-cymene})\text{Ru}(\text{LL}^*)\text{4-Mepy}]\text{PF}_6$, $C_{31}H_{35}F_6N_2OPRu$: C, 53.37; H, 5.06; N, 4.02. Found: C, 53.31; H, 5.05; N, 4.02. $[\alpha]^{22}_\text{D} = +167°$ ($c = 0.4$, acetone). CD (22 °C, $c = 4.81 \times 10^{-4}$ mol L^{-1}, CH_2Cl_2, recorded on Jasco J-40 A with $d = 0.2$ cm, diastereomeric mixture) λ_max ($\Delta\epsilon$ [L mol^{-1} cm^{-3}]); λ_0: 286 (2.7), 322 (−8.2), 351 (−5.2), 402 (−15.5), 461 (8.4); 297, 434. ^{1}H-NMR (400 MHz, acetone-d_6, TMS; thermodynamically more stable (R_Ru,S_C)-diastereomer measured at −80 °C, thermodynamically less stable (S_Ru,S_C)-diastereomer measured at 21 °C in parentheses; Sal = aromatic part of the salicylaldimine chelate ring): $\delta = 0.80$ (d, ^3J(H,H) = 6.9 Hz, 3 H, CH_3-^{i}Pr), 1.14 (1.19) (d, ^3J(H,H) = 6.9 (6.7) Hz, 3 H, CH_3-^{i}Pr), 1.87 (s, 3 H, CH_3-cymene), 1.94 (d, ^3J(H,H) = 6.9 Hz, 3 H, CHCH_3), 2.45 (2.25) (s, 3 H, CH_3-4-Mepy), 2.37 (2.77) (sept, ^3J(H,H) = 6.9 (6.7) Hz, 1 H, CH-^{i}Pr), 4.73, 5.65 (AB, ^3J(H,H) = 5.7 Hz, 2 H, cymene), 5.71, 6.00 (AB, ^3J(H,H) = 6.5 Hz, 2 H, cymene), 6.5 (q, ^3J(H,H) = 6.9 Hz, 1 H, CH_3CH), 6.52 (ddd, $^3J(\text{H}_3,\text{H}_4)$ = 7.9 Hz, $^3J(\text{H}_4,\text{H}_5)$ = 7.0 Hz, $^4J(\text{H}_4,\text{H}_6)$ = 1.0 Hz, 1 H, H_4-Sal), 6.98 (dd, $^3J(\text{H}_5,\text{H}_6)$ = 8.2 Hz, $^4J(\text{H}_4,\text{H}_6)$ = 1.0 Hz, 1 H, H_6-Sal), 7.32 (m, 2 H, H_3/H_5-Sal), 7.52 (d, ^3J(H,H) = 6.2 Hz, 2 H, H_3/H_5-4-Mepy), 7.55−7.66 (m, 5 H, Ph), 8.66 (8.26) (dd, ^3J(H,H) = 6.3, ^5J(H,H) = 1.2 Hz, 2 H, H_2/H_6-4-Mepy), 8.70 (8.47) (s, 1 H, N═CH).

X-ray Crystallography. Diffraction data were collected with a SYNTEX-NICOLET R3 diffractometer from a red prismatic crystal of dimensions 0.40 × 0.45 × 0.90 mm in the ω-scan mode (2θ range from 3.0 to 60.0°). There were 6466 unique reflections of which 5059 with $I > 2.5\sigma(I)$ were used for the structure solution and refinement by Patterson-Fourier methods with SHELXTL PLUS programs[4] on a MICROVAX II computer. The positions of the H atoms were calculated with the option HFIX. An empirical absorption correction was done with seven reflections in the 2θ range from 7.0 to 45.0°. The absolute Ru configuration was determined by measuring part of the Friedel pairs in the 2θ range from 3.0 to 42.5° (Tables 1−3). Further details of the crystal structure determination can be requested from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, under the deposit number CSD-58737.

Results and Discussion

The argumentation in refs 1−3 is based on the assumption that two compounds have the same (or opposite) configurations if their CD spectra are similar (or opposite) to each other. It is well-known that application of this assumption is restricted to special cases, and uncritical use may lead to wrong assignments.

---

(1) Mandal, S. K.; Chakravarty, A. R. *J. Organomet. Chem.* **1991**, *417*, C59.

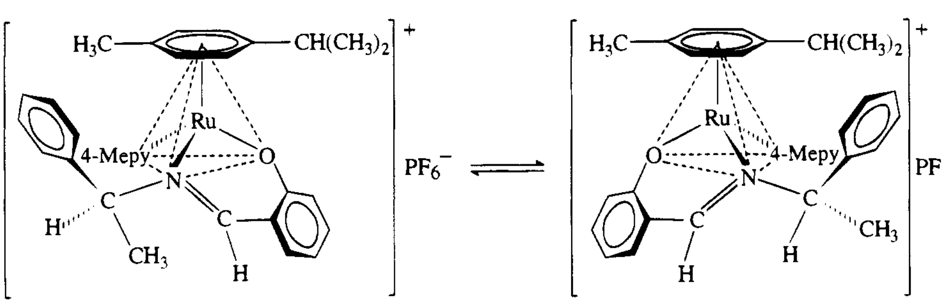
(2) Mandal, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1627.

(3) Mandal, S. K., Chakravarty, A. R., *Inorg. Chem.* **1993**, *32*, 3851.

(4) Sheldrick, G. M. *SHELXTL PLUS, A Program for Crystal Structure Determination*; Release 4.11/V; Siemens Analytical X-ray Instruments: Madison, WI, 1990.

0020-1669/95/1334-3349$09.00/0

Scheme 1



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

Without supporting evidence it should not be applied to compounds of the type [(η^6-Ar)Ru(LL*)Hal] with Hal = halide (giving neutral complexes) and [(η^6-Ar)Ru(LL*)L′]ClO$_4$ with ligands L′ being as different as water, 4-methylpyridine, trimethyl phosphite, and triphenylphosphane (giving cationic complexes). In the series of the optically active Re compounds (η^5-C$_5$H$_5$)Re(NO)(PPh$_3$)L, there is a surprising correlation of the optical rotation at the Na$_D$ line and the configuration at the Re atom. Usually, a compound that is dextrorotatory at 589 nm has the R_{Re}-configuration. Out of over one hundred compounds of that type there are only three R_{Re}-configurated products having (−)-rotation at the Na$_D$ line.[5] One of these is the derivative with L = quinoline, whereas the derivative with L = isoquinoline is dextrorotatory.[5] In the series [(η^6-Ar)Ru(LL*)L′]X the situation is not so clear-cut. For example, the two diastereomers (R_{Ru},S_C)- and (S_{Ru},S_C)-[(η^6-C$_6$H$_6$)Ru(LL*)PPh$_3$]PF$_6$, differing in the Ru-configuration,[6] both have negative optical rotations at the Na$_D$ line ($[\alpha]_D^{-18} = -1076°$ and $[\alpha]_D^{-35} = -92°$; c = 0.08, CH$_2$Cl$_2$).[7] Moreover, the CD curves shown in refs 1−3, which are called similar, are relatively different from each other, especially in the lower wavelength region, and no safe conclusions can be drawn from a comparison. In the following, one of the misassignments based on a comparison of the CD spectra in refs 1−3 is specifically addressed.

For the compound [(η^6-cymene)Ru(LL*)PPh$_3$]ClO$_4$ an X-ray crystallographic determination had revealed R_{Ru},S_C-configuration.[2] The corresponding 4-methylpyridine derivative [(η^6-cymene)Ru(LL*)4-Mepy]ClO$_4$ was obtained as a 76:24 mixture of diastereomers.[1−3] From the CD spectra depicted in refs 1−3 it was concluded that the major diastereomer of [(η^6-cymene)-Ru(LL*)4-Mepy]ClO$_4$ had S_{Ru},S_C-configuration. This assignment is wrong. We prepared the corresponding PF$_6$ compound [(η^6-cymene)Ru(LL*)4-Mepy]PF$_6$ by treating [(η^6-cymene)Ru(LL*)Cl] with an equimolar amount of AgPF$_6$ and an 1.5-fold excess of 4-methylpyridine in acetone at −30 °C for 1 h. After filtration of the precipitated AgCl the solution was evaporated and the residue was washed with petroleum ether to remove excess 4-methylpyridine. Crystallization from THF/ether 5:3 gave red prisms of **1** in 90% yield. According to an X-ray crystallographic analysis, **1** has R_{Ru},S_C-configuration (Figure 1). Dissolution of **1** at −80 °C in acetone-d_6 showed that it was diastereomerically pure. The corresponding benzene compound [(η^6-C$_6$H$_6$)Ru(LL*)4-Mepy]PF$_6$ equilibrates with respect to the Ru configuration at −35 °C in acetone with a half life of $\tau_{1/2}$ = 80 min.[8] A similar equilibration is observed for [(η^6-cymene)-Ru(LL*)4-Mepy]PF$_6$, the equilibrium R_{Ru},S_C:S_{Ru},S_C at room temperature in acetone-d_6 being 76:24 and in CDCl$_3$ being 82:18 (Scheme 1).[8]

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for (R_{Ru},S_C)-[(η^6-cymene)Ru(LL*)4-Mepy]PF$_6$, **1**

atom	x	y	z	U_{eq}[a]
Ru(1)	9007(1)	1266(1)	155(1)	35(1)
N(1)	9225(4)	167(2)	765(2)	38(1)
O(1)	7359(3)	815(2)	−214(2)	45(1)
C(1)	10278(5)	1078(3)	−812(3)	49(2)
C(2)	9312(5)	1604(3)	−1029(3)	53(2)
C(3)	9038(6)	2322(3)	−616(3)	51(2)
C(4)	9706(5)	2544(3)	26(3)	47(2)
C(5)	10675(4)	2032(3)	261(3)	48(2)
C(6)	10936(5)	1307(3)	−145(3)	47(1)
C(7)	7103(4)	37(3)	−326(2)	40(2)
C(8)	6246(5)	−179(3)	−889(3)	49(2)
C(9)	5885(6)	−975(4)	−988(3)	64(2)
C(10)	6337(6)	−1595(4)	−533(3)	66(2)
C(11)	7189(5)	−1409(3)	13(3)	56(2)
C(12)	7618(5)	−603(3)	121(3)	44(2)
C(13)	8563(5)	−479(3)	673(3)	45(2)
C(14)	10194(5)	150(3)	1366(3)	42(2)
C(15)	9789(6)	−286(4)	2092(3)	65(2)
C(16)	12475(6)	171(4)	1323(3)	57(2)
C(17)	13610(6)	−97(5)	1066(4)	77(3)
C(18)	13681(8)	−724(5)	561(4)	85(3)
C(19)	12627(7)	−1082(4)	304(3)	76(3)
C(20)	11483(6)	−816(3)	546(3)	63(2)
C(21)	11397(5)	−175(3)	1065(3)	41(2)
N(2)	8036(4)	1625(2)	1169(2)	37(1)
C(22)	8607(5)	1959(3)	1760(3)	45(2)
C(23)	8026(5)	2237(3)	2394(3)	53(2)
C(24)	6772(5)	2131(4)	2473(3)	50(2)
C(25)	6181(5)	1775(3)	1869(3)	51(2)
C(26)	6806(5)	1529(3)	1241(3)	43(2)
C(27)	6106(7)	2417(4)	3165(3)	86(3)
C(28)	10634(7)	304(4)	−1240(3)	72(3)
C(29)	9391(5)	3320(3)	453(3)	69(2)
C(30)	9687(8)	−9(5)	−1777(5)	128(5)
C(31)	11820(7)	445(5)	−1664(4)	118(4)
P(1)	2906(2)	7655(1)	7800(1)	50(1)
F(11)	3976(4)	7332(2)	8319(2)	100(2)
F(12)	1832(4)	7987(3)	7278(2)	99(2)
F(13)	2190(4)	6836(2)	7915(2)	90(2)
F(14)	3651(3)	8473(2)	7664(2)	87(2)
F(15)	2268(4)	8048(3)	8505(2)	113(2)
F(16)	3544(4)	7268(3)	7083(2)	120(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Another point of criticism of refs 1−3 is the assignment of retention and inversion stereochemistry of the metal atom in substitution reactions. The terms retention and inversion imply

---

(5) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Z. Naturforsch.* **1992**, *47B*, 1175.

(6) Assignment of the Ru configuration according to the priority sequence C$_6$H$_6$ > PPh$_3$ > O > N.

(7) Brunner, H.; Oeschey, R.; Nuber, B. *Angew. Chem.* **1994**, *106*, 941; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 866.

(8) Brunner, H.; Oeschey, R.; Nuber, B. To be submitted for publication.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in (R_{Ru},S_C)-[(η^6-cymene)Ru(LL*)4-Mepy]PF$_6$, **1**

Ru(1)–N(1)	2.088(4)	O(1)–Ru(1)–N(1)	87.4(1)
Ru(1)–O(1)	2.031(3)	O(1)–Ru(1)–N(2)	82.2(1)
Ru(1)–N(2)	2.142(4)	N(1)–Ru(1)–N(2)	86.0(1)
Ru(1)–C(1)	2.199(5)	C(1)–Ru(1)–C(2)	37.4(2)
Ru(1)–C(2)	2.166(5)	C(1)–Ru(1)–C(6)	37.9(2)
Ru(1)–C(3)	2.179(5)	C(2)–Ru(1)–C(3)	37.6(2)
Ru(1)–C(4)	2.216(5)	C(3)–Ru(1)–C(4)	36.6(2)
Ru(1)–C(5)	2.198(5)	C(4)–Ru(1)–C(5)	37.0(2)
Ru(1)–C(6)	2.152(5)	C(5)–Ru(1)–C(6)	37.5(2)

that the reactions under consideration are kinetically controlled and that there is no subsequent epimerization. This is not the case for compounds of the type [(η^6-Ar)Ru(LL*)Hal] and [(η^6-Ar)Ru(LL*)L′]X. For some of these compounds we could show that they epimerized with respect to the Ru atom at room temperature or even below room temperature[7] and, obviously, Mandal and Chakravarty are well aware of these facts (e.g. ref 3: "an equilibrium S_{Ru}-**1** $\rightleftharpoons$ R_{Ru}-**1** ... operative in solution"). Obviously, all the CD spectra of refs 1–3 were measured at room temperature using solutions equilibrated with respect to the Ru configuration. These diastereomer equilibria are governed by the energy differences of the respective diastereoisomers. They definitely do not reflect the stereochemistry of the formation of individual diastereomers prior to equilibration. At best these relationships can be called formal inversions or formal retentions, but it is completely inappropriate to use the well-defined stereochemical terms inversion and retention in these cases, as done throughout refs 1–3.

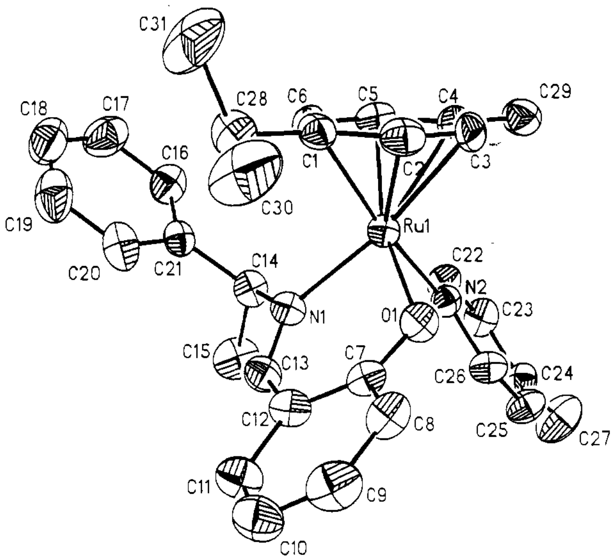


Figure 1. ORTEP plot of the crystal structure of (R_{Ru},S_C)-[(η^6-cymene)-Ru(LL*)4-Mepy]PF$_6$, **1** (thermal ellipsoids at 40% level, hydrogen atoms and PF$_6$ anion omitted for clarity).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this work.

Supplementary Material Available: Further details of the structure determination have been deposited with the number CSD-58737 at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

IC9413732