Identification of the Absolute Configuration of 1-[4-(Nitrophenylthio)ethyl]ferrocene, -ruthenocene, and -osmocene

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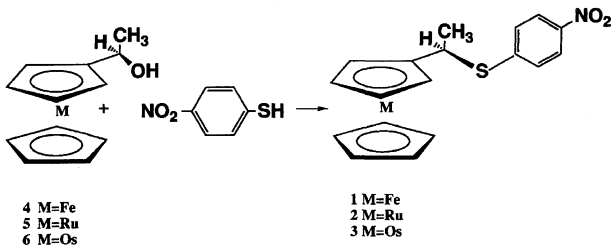
(−)-1-[4-(Nitrophenylthio)ethyl]ferrocene, (+)-1-[4-(nitrophenyl)thioethyl]ruthenocene, and (+)-1-[4-(nitrophenylthio)ethyl]osmocene all have the absolute configuration of *R*. These compounds were prepared by substitution of (*R*)-(−)-1-(hydroxyethyl)ferrocene, -ruthenocene, and -osmocene with 4-nitrobenzenethiol, showing that the substitution proceeded with retention of configuration.

Crystals of optically active 1-[4-(nitrophenylthio)-ethyl] derivatives of ferrocene, ruthenocene, and osmocene are promising materials for second harmonic generation (SHG).[1] The optical activity, that is, chiral structure, is essential for this SHG activity. The levorotatory derivative of ferrocene ((−)-1) and dextrorotatory derivatives of ruthenocene ((+)-2) and osmocene ((+)-3) are prepared by acid-catalyzed substitution (*R*)-(−)-1-(hydroxyethyl)ferrocene ((*R*)-(−)-4), (*R*)-(−)-1-(hydroxyethyl)ruthenocene ((*R*)-(−)-5), (*R*)-(−)-1-(hydroxyethyl)osmocene ((*R*)-(−)-6) with 4-nitrobenzenethiol, respectively.[1] Nucleophilic substitution of 1-(hydroxyethyl)ferrocene was studied with various nucleophiles and it has been generally accepted that the reaction should proceed with retention of configuration at the asymmetric carbon atom, via a S_N1 mechanism, based on chemical correlation[2] and theoretical considerations about the stability of the intermediary carbonium ion.[3] The retentive nature of the nucleophilic substitution would be extended to 1-(hydroxyethyl)ruthenocene and -osmocene because the occurrence of a stable carbonium ion, which is the key intermediate in thre S_N1 substitution with retention of configuration, was found not only for 1-(hydroxyethyl)-ferrocene[3,4] but also for 1-(hydroxyethyl)ruthenocene and -osmocene.[3] Although no direct evidence has been reported for this configurational retention in the substitution reactions, we tentatively assigned the *R*-configuration to the products obtained by the nucleophilic substitution with 4-nitrobenzenethiol from the above knowledge. These assignments have been justified as described below (Scheme 1).



Scheme 1.

Experimental and Discussion

The compounds ((−)-1, (+)-2, (+)-3) were synthesized by the trifluoroacetic acid-catalyzed substitution in the way described previously.[1] Single crystals were obtained from acetone.

The experimental conditions and the summary of structure analysis are shown in Table 1. For the ferrocene and ruthenocene, X-ray diffraction data were collected on an Enraf–Nonius four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation (λ= 1.5418 Å). The iron and ruthenium anomalous dispersion terms for Cu $K\alpha$ ($\Delta f''$=3.204 for Fe, and 3.296 for Ru)[5] are much larger than that for Mo $K\alpha$ ($\Delta f''$=0.845 for Fe, 0.836 for Ru) and this effect has an advantage even considering the problem due to the higher crystal absorption when using Cu $K\alpha$ radiation. Empirical absorption corrections using psi scans were made. The Bijvoet pairs were treated as independent reflections. In the course of the refinement with all observed reflection $|F_o| \geq 3\sigma|F_o|$, two refinements were used. The refinement with the configuration shown in this article with anisotropic thermal parameters for non-H atoms and without H atoms, gave the R factor 0.068 for ferrocene and 0.047 for ruthenocene. On the other hand in the model with the opposite enanthiomorph it was 0.130 for ferrocene and 0.068 for ruthenocene, even though the calculation was repeated from the isotropic

Table 1. Summary of Crystal Data

Formula	$FeSO_2NC_{18}H_{17}$	$RuSO_2NC_{18}H_{17}$	$OsSO_2NC_{18}H_{17}$
Molecular weight	367.253	412.48	501.61
Crystal data			
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$
a/Å	6.089(1)	5.966(1)	5.968(1)
b/Å	12.291(1)	12.600(1)	12.612(1)
c/Å	11.329(2)	11.314(2)	11.318(2)
β/°	101.19(1)	101.03(1)	100.94(1)
V/Å^3	831.8(2)	834.7(2)	836.4(2)
Z	2	2	2
D_{calc}/g cm^{-3}	1.466	1.641	1.991
Measurement			
Crystal size/mm	0.6×0.1×0.3	0.7×0.1×0.2	0.6×0.1×0.6
Radiation/Å	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
The number of reflections			
independent	2751	2477	3704
used $\|F_o\| \geq 3\sigma\|F_o\|$	2488	2343	3422
$2\theta_{max}$/°	130	120	55
hkl range	$7 \geq h \geq 0$	$6 \geq h \geq 0$	$7 \geq h \geq 0$
	$14 \geq k \geq -14$	$14 \geq k \geq -14$	$16 \geq k \geq -16$
	$12 \geq l \geq -12$	$12 \geq l \geq -12$	$14 \geq l \geq -14$
Absorption			
μ/cm^{-1}	85.9	95.2	82.0
correction Ψscan			
correction factor	max 0.998	0.995	1.000
	min 0.683	0.774	0.810
Decay/I	No	No	No
Refinement			
R	0.050	0.041	0.032
wR	0.061	0.049	0.051
Residual peaks/e Å^{-3}	0.52—0.7	1.03—0.89	0.99—1.02

$w(\mathrm{Fe}) = 1/(0.0117|F_o|^2 - 0.3167|F_o| + 2.607)$. $w(\mathrm{Ru}) = 1/(0.0083|F_o|^2 - 0.2610|F_o| + 3.693)$.
$w(\mathrm{Os}) = 1/(187.9|\sin\theta/\lambda|^2 - 186.7|\sin\theta/\lambda| + 46.50)$.

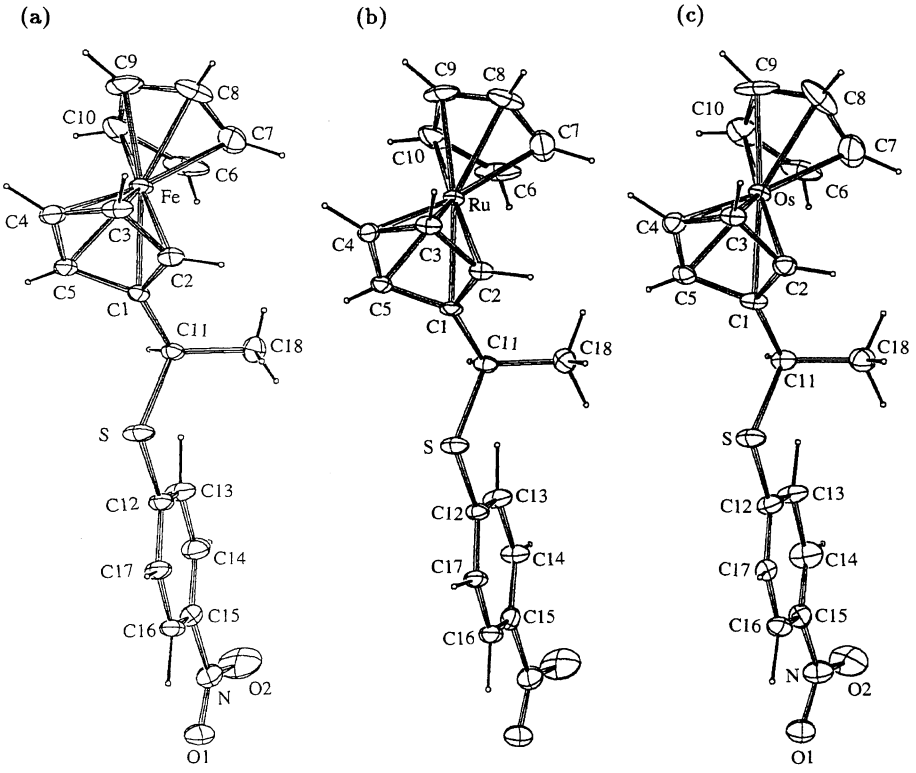


Fig. 1. (a) Molecular structure 1 along with the labeling scheme. (b) Molecular structure 2. (c) Molecular structure 3.

Table 2. Fractional Atomic Coordinates and Thermal Parameters for Non-Hydrogen Atoms

Atom	x	y	z	B_{eq}[a)]/Å^2
a) $FeSO_2NC_{18}H_{17}$				
Fe1	0.7669(1)	0.5000	0.8699(1)	3.21(2)
S1	0.6732(2)	0.1258(1)	0.8215(1)	4.55(3)
O1	0.0268(11)	−0.2710(4)	0.5606(5)	7.50(17)
O2	−0.1548(10)	−0.1361(6)	0.4671(7)	9.41(21)
N1	−0.0056(11)	−0.1748(5)	0.5444(5)	6.00(18)
C1	0.7567(7)	0.3342(3)	0.8570(4)	2.94(12)
C2	0.9776(7)	0.3736(4)	0.8512(5)	3.58(11)
C3	1.0569(8)	0.4319(4)	0.9600(5)	4.28(13)
C4	0.8925(9)	0.4288(4)	1.0325(4)	4.10(13)
C5	0.7067(8)	0.3683(4)	0.9695(4)	3.56(11)
C6	0.5128(15)	0.5663(5)	0.7507(10)	8.08(28)
C7	0.7199(16)	0.5933(6)	0.7177(7)	6.79(24)
C8	0.8418(12)	0.6503(5)	0.8118(9)	6.69(26)
C9	0.7186(17)	0.6612(5)	0.9026(8)	6.94(26)
C10	0.5183(13)	0.6116(5)	0.8659(8)	6.43(23)
C11	0.6110(7)	0.2645(4)	0.7652(4)	3.21(11)
C12	0.4665(9)	0.0426(4)	0.7368(4)	3.68(12)
C13	0.2671(10)	0.0813(5)	0.6682(5)	4.60(14)
C14	0.1108(9)	0.0100(5)	0.6058(5)	4.74(14)
C15	0.1571(10)	−0.0989(4)	0.6139(4)	4.34(14)
C16	0.3503(11)	−0.1405(4)	0.6809(5)	4.66(15)
C17	0.5079(10)	−0.0679(4)	0.7413(5)	4.31(14)
C18	0.6562(10)	0.2753(5)	0.6391(4)	4.86(15)
b) $RuSO_2NC_{18}H_{17}$				
Ru1	0.75951(6)	0.5000	0.86672(4)	2.59(1)
S1	0.6807(3)	0.1230(2)	0.8219(2)	3.82(5)
O1	0.0037(13)	−0.2574(5)	0.5559(6)	6.03(22)
O2	−0.1669(14)	−0.1242(8)	0.4610(8)	8.22(27)
N1	−0.0199(13)	−0.1628(7)	0.5387(7)	4.86(23)
C1	0.7649(13)	0.3275(9)	0.8587(7)	2.97(24)
C2	0.9900(11)	0.3686(5)	0.8529(6)	3.02(16)
C3	1.0668(12)	0.4250(6)	0.9616(7)	3.60(19)
C4	0.9042(13)	0.4200(6)	1.0346(6)	3.42(18)
C5	0.7157(12)	0.3595(5)	0.9729(7)	2.98(17)
C6	0.4829(23)	0.5748(7)	0.7444(13)	8.03(41)
C7	0.6938(22)	0.6016(9)	0.7098(10)	6.41(35)
C8	0.8181(21)	0.6560(9)	0.8008(16)	6.40(42)
C9	0.7058(27)	0.6668(10)	0.8900(15)	6.05(39)
C10	0.4919(17)	0.6187(7)	0.8606(10)	5.70(29)
C11	0.6196(11)	0.2599(5)	0.7675(6)	2.83(17)
C12	0.4672(16)	0.0435(7)	0.7362(8)	3.20(20)
C13	0.2661(16)	0.0854(8)	0.6673(9)	4.28(24)
C14	0.1059(13)	0.0163(7)	0.6015(8)	3.99(22)
C15	0.1452(15)	−0.0887(7)	0.6096(7)	3.78(22)
C16	0.3423(16)	−0.1341(7)	0.6770(8)	3.83(22)
C17	0.5056(18)	−0.0650(7)	0.7386(9)	3.62(24)
C18	0.6641(13)	0.2723(7)	0.6409(7)	3.94(20)
c) $OsSO_2NC_{18}H_{17}$				
OS1	0.75996(4)	0.5000	0.86731(2)	3.00(1)
S1	0.6816(5)	0.1227(2)	0.8214(2)	4.38(5)
O1	0.0013(31)	−0.2583(10)	0.5556(13)	7.61(37)
O2	−0.1644(22)	−0.1219(11)	0.4571(14)	7.97(35)
N1	−0.0233(25)	−0.1599(10)	0.5326(13)	5.96(34)
C1	0.7740(19)	0.3283(10)	0.8590(14)	2.98(27)
C2	0.9905(17)	0.3674(7)	0.8516(9)	3.76(21)
C3	1.0714(16)	0.4254(6)	0.9641(9)	3.69(20)
C4	0.9075(20)	0.4191(8)	1.0348(9)	4.06(22)
C5	0.7174(16)	0.3602(7)	0.9738(9)	3.37(20)
C6	0.4743(31)	0.5747(9)	0.7482(19)	7.26(46)
C7	0.6808(63)	0.5946(17)	0.7032(19)	9.29(89)
C8	0.8189(36)	0.6564(19)	0.7937(35)	8.60(88)
C9	0.7045(47)	0.6700(12)	0.8827(28)	7.55(74)
C10	0.4896(29)	0.6208(11)	0.8595(17)	6.50(42)
C11	0.6168(15)	0.2582(7)	0.7678(8)	3.48(19)
C12	0.4648(38)	0.0446(12)	0.7363(16)	4.37(33)
C13	0.2648(26)	0.0856(11)	0.6637(14)	4.55(30)
C14	0.1129(20)	0.0079(22)	0.6010(12)	5.70(33)
C15	0.1504(24)	−0.0929(11)	0.6064(9)	4.44(31)
C16	0.3487(32)	−0.1334(9)	0.6763(11)	5.15(35)
C17	0.5023(34)	−0.0628(12)	0.7373(15)	3.97(31)
C18	0.6615(20)	0.2711(9)	0.6411(11)	4.86(26)

a) $B_{eq}=(4/3)\sum_i\sum_j\beta_{ij}(\boldsymbol{a}_i\cdot\boldsymbol{a}_j)$.

stage. In the case of osmocene, X-ray diffraction data were collected on a Rigaku AFC-5 four circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). The Os anomalous dispersion term for Mo $K\alpha$ is $\Delta f''$=7.605. After calculations in the similar way above described, the R factor was 0.033 for the structure shown in this article and 0.048 for the opposite enantiomorph. From these results, the absolute configuration was identified as those shown by this article.

The structures were refined by the full-matrix least-squares method using UNICSIII[6] with the hydrogen parameters being fixed in the refinement. For ferrocene the positions of 12 hydrogen atoms were located from the difference Fourier maps, while the remainder were added by the calculated positions. The hydrogen atom attached to C11 was shown in the Fourier map. For ruthenocene and osmocene the positions of hydrogen atoms were located on the calculated positions. The final atomic coordinates were shown in Table 2.[7] The temperature factors of the five-membered carbon atoms of the metallocenes that did not have the substituent had a tendency to be larger. However, the disorder could not be found in the difference Fourier maps. As shown in Tables 1 and 2, the three crystals were isostructural. The ORTEP[8] drawing of molecular structures is shown in Fig. 1. The structures were drawn with the correct absolute configuration. The con-

Table 3. Bond Distances and Bond Angles

1) Bond distances (Å)			
	Fe	Ru	Os
Metal–C1	2.044(4)	2.176(11)	2.168(12)
Metal–C2	2.052(5)	2.177(7)	2.193(10)
Metal–C3	2.040(5)	2.157(7)	2.181(9)
Metal–C4	2.049(5)	2.177(7)	2.183(9)
Metal–C5	2.048(5)	2.183(7)	2.176(9)
Metal–C6	2.017(8)	2.157(12)	2.174(17)
Metal–C7	2.044(8)	2.153(11)	2.181(21)
Metal–C8	2.042(7)	2.154(13)	2.194(27)
Metal–C9	2.049(7)	2.150(13)	2.179(16)
Metal–C10	2.037(7)	2.179(10)	2.207(16)
S1–C11	1.834(4)	1.845(7)	1.828(9)
S1–C12	1.756(5)	1.759(9)	1.759(18)
C1–C11	1.500(6)	1.483(11)	1.534(15)
C11–C18	1.517(7)	1.513(11)	1.516(16)

2) Bond angles (°)			
	Fe	Ru	Os
C1–Metal–C2	41.2(2)	39.0(3)	37.4(4)
C2–Metal–C3	40.8(2)	38.2(3)	37.4(4)
C3–Metal–C4	40.4(2)	37.0(3)	36.8(4)
C4–Metal–C5	40.7(2)	38.2(3)	38.0(4)
C5–Metal–C1	40.9(2)	38.5(3)	39.3(5)
C1–C11–C18	114.4(4)	114.5(6)	112.3(10)
C1–C11–S1	103.7(3)	104.6(5)	104.6(8)
C11–S1–C12	105.9(2)	105.8(4)	104.8(8)
S1–C12–C13	124.1(4)	123.0(7)	124.4(16)
S1–C12–C17	116.5(4)	116.9(7)	116.5(17)
C1–C2–C3	107.0(5)	106.4(6)	106.1(9)
C2–C3–C4	109.2(4)	110.5(6)	108.8(8)
C3–C4–C5	107.8(4)	107.9(6)	109.7(9)
C4–C5–C1	108.3(5)	108.1(7)	106.1(9)
C5–C1–C2	107.7(4)	107.2(6)	109.2(10)
C10–C6–C7	106.7(7)	106.7(10)	109.8(15)
C6–C7–C8	106.8(8)	106.8(13)	104.9(22)
C7–C8–C9	109.7(8)	110.6(13)	107.8(23)
C8–C9–C10	108.1(8)	110.8(13)	112.6(22)
C9–C10–C6	108.7(8)	105.1(12)	104.9(20)

3) Tortion angles (°)				
	Fe	Ru	Os	Fe-B[9]
M–C1–C11–C18	66.1(5)	65.8(9)	69(1)	77.5
C2–C1–C11–C18	−26.1(7)	−26(1)	−26(2)	−19.4
C5–C1–C11–C18	157.9(5)	158.1(8)	158(1)	166.7
M–C1–C11–S	−173.7(3)	−172.9(5)	−171.3(7)	−159.6
C2–C1–C11–S	94.1(5)	95.3(9)	94(1)	103.6
C5–C1–C11–S	−81.9(5)	−80.6(9)	−83(1)	−70.3

figuration of the C11 atoms was *R*-, the same as that of (−)-2,2,2-trifluorohydroxyethyl)ferrocene.[9] As a whole, the molecular configuration resembled the B-conformer of (−)-(2,2,2-trifluorohydroxyethyl)ferrocene.[9] The angles between the five-membered ring C1, C2, C3, C4, C5, and the phenyl ring were 78.2°, 79.9°, and 79.9° for ferrocene, ruthenocene, and osmocene, respectively.

The selected bond lengths, angles, and torsion angles for non-hydrogen atoms are listed in Table 3. The metallocene moiety were eclipsed, almost like those reported for other metalocene derivatives.[10—12] The average metal–carbon distances were 2.04(1), 2.17(1), and 2.18(1) for Fe–C, Ru–C, and Os–C, respectively; these values were compatible with the previously reported structures.[10—12]

Thus the absolute configuration of these crystals has been identified as *R*.

References

1) Y. Yamazaki, K. Hosono, H. Matsuda, N. Minami, M. Asai, and H. Nakanishi, *Biotechnol. Bioeng.*, **38**, 1218 (1991).

2) G. W. Gokel, D. Marquarding, and I. K. Ugi, *J. Org. Chem.*, **37**, 3052 (1972); A. Ratajczak and B. Misterkiewics, *J. Organomet. Chem.*, **91**, 73 (1975).

3) E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961).

4) T. D. Turbitt and W. E. Watts, *J. Chem. Soc., Perkin Trans 2*, **1974**, 177.

5) "International Tables for X-Ray Crystallography," Kynoch Press, Birminham (1974), Vol. 4, p. 149.

6) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res. (Jpn.)*, **55**, 69 (1978).

7) C. K. Johnson, "ORTEP II, Report ORNL-5138," Oak Ridge National Labolatory, Tennessee, U. S. A. (1976).

8) The lists of structure factors, the atomic parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms and the comparison of the observed and calculated structure factor table for selected Bijvoet pairs are deposited as Document No. 68020 at the Office of the Editor of Bull. Chem. Soc. Jpn.

9) M. Goto, Y. Yamazaki, and M. Uebayasi, *Bull. Chem. Soc. Jpn.*, **66**, 666 (1993).

10) M. O. Albers, D. C. Liles, D. J. Robinson, A. Shaver, E. Singleton, M. B. Wiege, J. C. A. Boeyens, and D. C. Levendis, *Organometallics*, **5**, 2321 (1986).

11) P. Seiler and J. D. Dunitz, *Acta Crystallogr., Sect. B*, **B36**, 2946 (1980).

12) S. Ohba, Y. Saito, S. Kamiyama, and A. Kasahara, *Acta Crystallogr., Sect. C*, **C40**, 53 (1984).