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Transmetallation reactions of planar chiral cyclopalladated ferrocenylimines with metallic mercury

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Abstract

A series of optically active 2-chloromercurio-1-[1-(arylimino)ethyl] ferrocenes was synthesized by transmetallation of optically active cyclopalladated ferrocene derivatives with metallic mercury. The structure and absolute configuration of complexes Rp-**4b** were determined by X-ray diffraction, on the basis of which and the CD spectra the absolute configuration of other optically active compounds was ascertained.

1. Introduction

The chemistry of cyclometallated complexes is undoubtedly the most advanced area in modern organometallic chemistry.[1] Over the last few years, interest in cyclometallated complexes has increased exponentially due to their novel application. These compounds are successfully used in organic synthesis, catalysis and photochemistry.[2] Currently, attention is being focused on the transition metals (e.g. Pd, Pt, etc), although there are a few examples of reactions with non-transition metals, such as mercury. Organomercurials have been used extensively in organic synthesis and synthesis of other organometallics due to their ability to accommodate practically all important organic functional groups and their ease in undergoing transmetallation for forming transition metal organometallics which are useful in organic synthesis.

On the other hand, it is well known that ferrocene derivatives are useful substrates in asymmetric synthesis[3] because of their planar chirality which is not prone to racemization. Moreover, cyclomercurated ferrocene derivatives have been used as potential synthetic intermediates. Although studies have been made of the synthesis, structure and properties of mercurated ferrocene derivatives,[4] no findings have been reported so far of the synthesis of optically active cyclomercurated ferrocenylimines. In this paper a convenient method is reported for synthesizing optically active 1,2-disubstituted cyclomercurated

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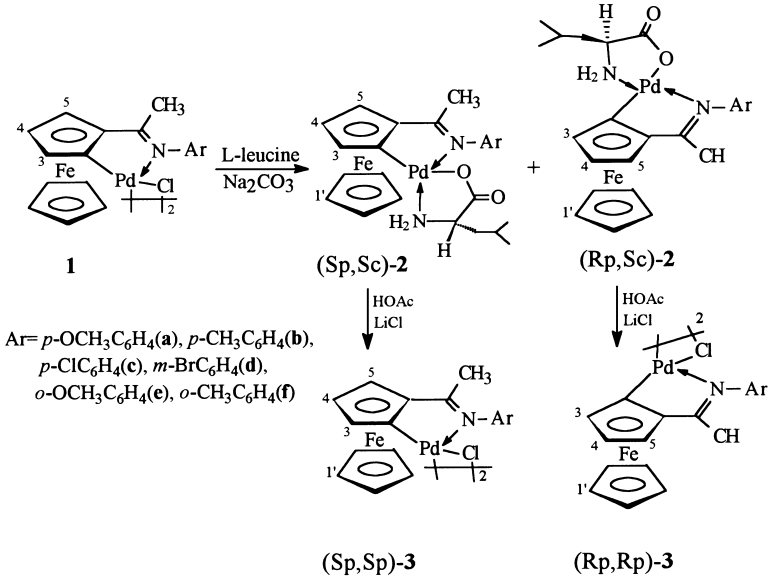
ferrocenylimines by a transmetallation reaction of planar chiral cyclopalladated ferrocenylketimines with metallic mercury.

2. Results and discussion

2.1. Resolution of cyclopalladated ferrocenylimines

Being similar to (Rp,Rp)-**3b**,[5] all other optically active cyclopalladated ferrocenylketimines were obtained in two steps as illustrated in Scheme 1: (i) synthesis of diastereomeric complexes (Sp,Sc)-**2** and (Rp,Sc)-**2**; (ii) reaction of diastereomers with LiCl in acetic acid. Both diastereomeric complexes of compound **2** were clearly discriminated by ^{1}H NMR spectroscopy. In all cases, ^{1}H NMR spectra of the crude products were recorded prior to recrystallization to avoid separation of diastereomers. The ^{1}H NMR spectra of compound **2** showed that the ratio of its diastereomers was nearly 1:1 when the substituents were in the *para*-, *meta*-position of *N*-phenyl ring; and the ratio was about 36:64 when the substituents were in the *ortho*-position of *N*-phenyl ring. This result indicated that the large bulk in *ortho*-substituted ligands resulted in a higher *de*% value. Selected ^{1}H NMR data and specific rotation values of complexes **2** and **3** are given in Tables 1 and 2, respectively.



1 (Sp,Sc)-**2** (Rp,Sc)-**2**

(Sp,Sp)-**3** (Rp,Rp)-**3**

Scheme 1.

2.2. Transmetallation reaction

(Rp,Rp)-**3** and (Sp,Sp)-**3** reacted with metallic mercury in CH_2Cl_2 for 15 min at room temperature to produce Rp-**4** and Sp-**4**, respectively (Scheme 2). Isolation of the pure compounds **4** was achieved by rapid chromatography on a short silica gel column. After evaporation of the solvent the resulting red solid was recrystallized from dichloromethane–hexane to give red crystals **4**, which were air stable and characterized by elemental analysis, IR and ^{1}H NMR spectra. The IR spectral features of complexes **4** were similar to their racemates;[4b] in this paper are listed only the yields, $[\alpha]_D^{22}$, elemental analysis data, and selected ^{1}H NMR spectra as shown in Table 3. The experimental results indicated that the yields of

Table 1
Yields, m.p.s, $[\alpha]_D^{22}$ values, EA data and selected ^{1}H NMR spectra of complexes **2**

Compd.	Yields (%)[a]	M.P. (°C)[b]	$[\alpha]_D^{22}$	Elemental Analysis[c] C(%)	H(%)	N(%)	^{1}H NMR data H-3	H-4	H-5	H-1′
(Rp,Sc)-**2a**		235	+2438.8	52.53	5.31	4.81	4.66d	4.37t	4.60d	4.33s
	89.5			(52.79)	(5.32)	(4.93)	(2.4)	(2.2)	(2.4)	
(Sp,Sc)-**2a**		236	-2315.2	52.64	5.35	4.83	4.72d	4.38t	4.61d	4.32s
				(52.79)	(5.32)	(4.93)	(2.0)	(2.2)	(2.4)	
(Rp,Sc)-**2b**		>250	+2209.3	54.32	5.48	5.15	4.66d	4.37t	4.60d	4.32s
	94.4			(54.32)	(5.47)	(5.07)	(2.0)	(2.2)	(2.4)	
(Sp,Sc)-**2b**		>250	-2344.8	54.32	5.42	5.12	4.72d	4.38t	4.61d	4.32s
				(54.32)	(5.47)	(5.07)	(2.0)	(2.2)	(2.4)	
(Rp,Sc)-**2c**		230	+2760.9	49.92	4.83	4.72	4.70d	4.42t	4.64d	4.34s
	88.9			(50.29)	(4.75)	(4.89)	(1.2)	(2.4)	(2.0)	
(Sp,Sc)-**2c**		225	-2434.8	50.33	4.77	4.82	4.75d	4.43t	4.64d	4.33s
				(50.29)	(4.75)	(4.89)	(1.6)	(2.4)	(2.0)	
(Rp,Sc)-**2d**		216	+2293.5	46.59	4.59	4.30	4.71d	4.42t	4.64d	4.35s
	90.3			(46.67)	(4.41)	(4.54)	(1.6)	(2.0)	(2.0)	
(Sp,Sc)-**2d**		214	-2555.6	46.58	4.25	4.36	4.76d	4.43t	4.64d	4.33s
				(46.67)	(4.41)	(4.54)	(2.0)	(2.0)	(2.0)	
(Rp,Sc)-**2e**		230	+2202.1	52.65	5.32	4.89	4.64d	4.44bs	4.58d	4.34s
	90.6			(52.79)	(5.32)	(4.93)	(1.6)		(1.6)	
(Sp,Sc)-**2e**		234	-2322.2	52.68	5.45	4.82	4.70d	4.38bs	4.58d	4.35s
				(52.79)	(5.32)	(4.93)	(1.6)		(1.6)	
(Rp,Sc)-**2f**		240	+2475.0	54.20	5.44	4.80	4.66d	4.42bs	4.61d	4.36s
	82.8			(54.32)	(5.47)	(5.07)	(4.8)		(2.4)	
(Sp,Sc)-**2f**		238	-2680.4	54.16	5.45	4.82	4.72d	4.43bs	4.62d	4.35s
				(54.32)	(5.47)	(5.07)	(2.4)		(2.4)	

[a]: A total yield of diastereomers; [b]: Melts with decomposition; [c]: Calculated values in parentheses

the cyclomercurated compounds **4** by transmetallation were much higher than those obtained by direct cyclomercuration.[4b] The yields were not significantly influenced by substituent effect because there was no competitive protonation reaction[4b] in the transmetallation.

*2.3. Molecular and crystal structure of Rp-**4b***

The absolute configuration of complex (+)-**4b** was determined by X-ray diffraction. The structure of Rp-**4b** illustrated in Fig. 1 shows clearly that (+)-**4b** has absolute *R*-configuration in the ferrocene moiety which is the same as that of the compound (Rp,Rp)-**3b**.[5] This result indicated that the palladium complexes were converted into mercury complexes without a change of configuration in the ferrocene moiety. The mercury atom in the metallacycle was in a slightly distorted square-planar coordination environment. The Cp rings were almost parallel (dihedral angle 2.44°). The dihedral angle between the substituted Cp ring and the chelate cycle was 6.35°. The distance between N and Hg was 2.68 Å, which indicated a notable strong coordination between them, because the distance was significantly shorter than the sum of the van der Waals radii of N and Hg (3.05–3.15 Å).[6]

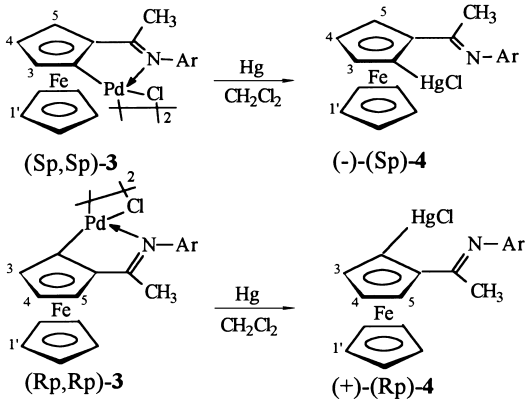
Table 2
Yields, m.p.s, $[\alpha]_D^{22}$ values, EA data and selected ^{1}H NMR spectra of complexes **3**

Compd.	Yields	M.P.	$[\alpha]_D^{22}$	Elemental Analysis[b]			^{1}H NMR data			
	(%)	(°C)[a]		C(%)	H(%)	N(%)	H-3	H-4	H-5	H-1′
Rp,Rp-**3a**	89.9	222	+3172.7	48.35	4.01	2.84	5.13bs	4.48bs	4.73s	4.38s
				(48.14)	(3.83)	(2.96)				
Sp,Sp-**3a**	84.8	220	-3422.2	48.24	3.96	2.90	5.13bs	4.47bs	4.73s	4.38s
				(48.14)	(3.83)	(2.96)				
Rp,Rp-**3b**	92.4	210	+3212.5	49.92	3.91	2.93	5.14bs	4.48bs	4.73s	4.38s
				(49.82)	(3.96)	(3.06)				
Sp,Sp-**3b**	85.1	213	-3688.9	50.22	4.01	2.98	5.14bs	4.48bs	4.73s	4.38s
				(49.82)	(3.96)	(3.06)				
Rp,Rp-**3c**	83.4	220	+3744.4	45.37	3.22	2.86	5.16bs	4.52bs	4.77s	4.39s
				(45.18)	(3.16)	(2.93)				
Sp,Sp-**3c**	94.7	218	-3949.0	45.32	3.26	2.80	5.16bs	4.52bs	4.77s	4.40s
				(45.18)	(3.16)	(2.93)				
Rp,Rp-**3d**	82.7	227	+3131.6	41.99	3.08	2.66	5.16bs	4.53bs	4.77s	4.41s
				(42.48)	(2.97)	(2.75)				
Sp,Sp-**3d**	87.2	230	-3040.0	42.12	3.10	2.59	5.16bs	4.53bs	4.77s	4.41s
				(42.48)	(2.97)	(2.75)				
Rp,Rp-**3e**	89.3	201	+2809.4	48.40	4.01	2.94	5.12bs	4.40bs	4.74s	4.25s
				(48.14)	(3.83)	(2.96)				
Sp,Sp-**3e**	83.6	202	-2750.0	48.37	4.08	2.98	5.12bs	4.40bs	4.74s	4.25s
				(48.14)	(3.83)	(2.96)				
Rp,Rp-**3f**	85.3	198	+3510.0	50.14	4.03	2.90	5.12bs	4.49bs	4.75s	4.40s
				(49.82)	(3.96)	(3.06)				
Sp,Sp-**3f**	88.9	199	-3479.3	50.01	4.01	2.99	5.12bs	4.49bs	4.75s	4.40s
				(49.82)	(3.96)	(3.06)				

[a]: Decomposes without melting; [b]: Calculated values in parentheses

2.4. *Electronic and circular dichroism spectra*

The IR and ^{1}H NMR spectral features of complexes **4** were similar to their racemates; a general discussion of them can be found in our previous paper.[4b] In this paper our focus is on the CD spectra of the optically active compounds **4** (Fig. 2). The electronic spectra of the ferrocene moiety in complexes Rp-**4** and Sp-**4** showed definite regions of absorption. The bands near 456 nm and 329 nm were assigned to the *d–d* transition of the iron atom and ferrocenyl ring π–π* transition, respectively.[7] The CD spectra of the complexes Rp-**4** and Sp-**4** recorded in dichloromethane exhibited two resolved bands attributable to a *d–d* and π–π* transition. The band above 450 nm is labeled as band I; that between 450 and 360 nm as band II; that between 360 and 350 nm as band III; and that below 350 nm as band IV. The sign pattern of the bands I–IV was positive (band I), negative (II), positive (III) and negative (IV) for the complexes Rp-



Scheme 2.

Table 3
Yields, $[\alpha]_D^{22}$ values, EA data and selected ^{1}H NMR spectra of complexes **4**

Compd.	Yields (%)[a]	$[\alpha]_D^{22}$	Elemental Analysis[a] C(%)	H(%)	N(%)	^{1}H NMR data H-3	H-4	H-5	H-1′
Rp-**4a**	95.6	+694.7	40.49 (40.16)	3.38 (3.19)	2.15 (2.46)	4.46bs	4.66bs	4.84bs	4.26s
Sp-**4a**	93.4	-678.5	40.39 (40.16)	3.06 (3.19)	2.32 (2.46)	4.46bs	4.66bs	4.84bs	4.26s
Rp-**4b**	94.5	+658.3	41.18 (41.32)	3.21 (3.28)	3.60 (3.54)	4.45bs	4.64bs	4.83bs	4.24s
Sp-**4b**	92.5	-677.5	41.04 (41.32)	3.33 (3.28)	3.36 (3.54)	4.45bs	4.64bs	4.83bs	4.24s
Rp-**4c**	93.4	+673.7	39.95[b] (39.94)	3.25 (3.29)	2.20 (2.33)	4.49bs	4.69bs	4.85bs	4.25s
Sp-**4c**	94.7	-653.3	39.89[b] (39.94)	3.20 (3.29)	2.29 (2.33)	4.49bs	4.69bs	4.85bs	4.25s
Rp-**4d**	91.8	+509.9	35.40 (35.03)	3.40 (3.45)	2.20 (2.27)	4.47bs	4.67bs	4.84bs	4.25s
Sp-**4d**	96.3	-556.7	35.36 (35.03)	3.42 (3.45)	2.24 (2.27)	4.47bs	4.67bs	4.84bs	4.25s
Rp-**4f**	96.2	+512.7	40.44 (40.16)	3.42 (3.19)	2.65 (2.46)	4.47bs	4.66bs	4.83bs	4.27s
Sp-**4f**	97.9	-535.6	40.47 (40.16)	3.37 (3.19)	2.68 (2.46)	4.47bs	4.66bs	4.83bs	4.27s
Rp-**4g**	92.8	+713.0	41.54 (41.32)	3.31 (3.28)	3.40 (3.54)	4.47bs	4.67bs	4.85bs	4.26s
Sp-**4g**	96.4	-712.7	41.16 41.32)	3.36 (3.28)	3.35 (3.54)	4.47bs	4.67bs	4.85bs	4.26s

[a]: Calculated values in parentheses; [b]: Contained 1/3 C_6H_{14} per molecule

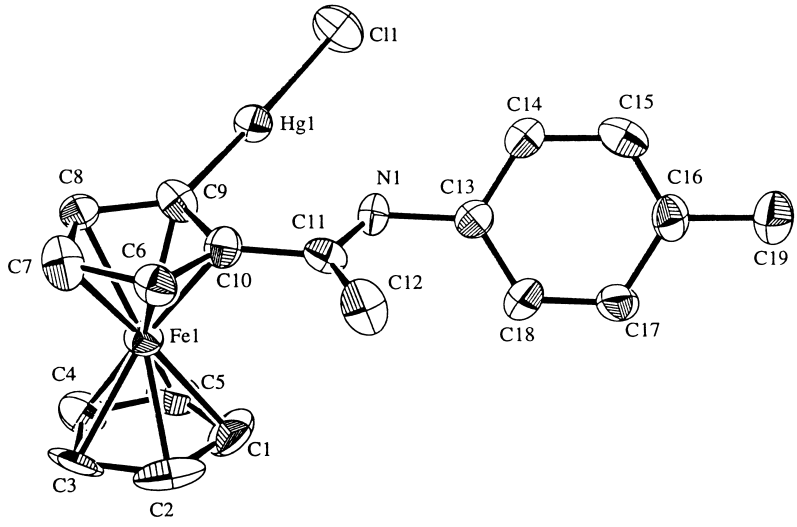


Figure 1. Molecular structure and absolute configuration of (+)-(Rp)-**4b** with atom-numbering scheme. Selected bond lengths (Å) and angles (°): Hg(1)–Cl(1) 2.308(5), Hg(1)–N(1) 2.68(1), Hg(1)–C(9) 2.04(2), N(1)–C(11) 1.28(2), C(9)–C(10) 1.43(2), C(10)–C(11) 1.47(2); Cl(1)–Hg(1)–C(9) 176.4(4), Cl(1)–Hg(1)–N(1) 108.0(3), N(1)–Hg(1)–C(9) 72.3, C(9)–C(10)–C(11) 122(1), C(10)–C(11)–N(1) 117(1), Hg(1)–N(1)–C(11) 106.9(10), Hg(1)–C(9)–C(8) 132(1), C(6)–C(10)–C(11) 128(1)

4. As expected, the sign pattern exhibited by the complexes Sp-**4** was negative (I), positive (II), negative (III) and positive (IV) for the CD bands I–IV. The sign of the Cotton effect of the complexes Rp-**4** was similar to that of (Rp,Rp)-**3**; however the sign of the Cotton effect of the complexes Sp-**4** was opposite to that of (Rp,Rp)-**3**.[5] This result indicated that if the sign of the Cotton effect in the cyclomercurated ferrocenylimines was similar to that of the cyclopalladated ferrocenylimines, they should have the same absolute configuration in the ferrocene moiety.

3. Experimental

3.1. Materials and instruments

Melting points were measured on a WC-1 apparatus and are uncorrected. Elemental analyses were determined with a Carlo Erba 1160 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer by using DMSO as the solvent for the palladium complexes and $CDCl_3$ for mercury complexes, and TMS as an internal standard; all J values were measured in hertz. IR spectra were recorded on a Perkin–Elmer FTIR 1750 spectrophotometer. Preparative TLC was performed on dry silica gel plates developed with dichloromethane:acetone (1:1). Chromatographic work was carried out on a short column packed with dry silica gel under reduced pressure. Optical rotations at 5890 Å were determined by a Perkin–Elmer 341 polarimeter at 22°C. CD spectra were recorded on a GJASCO J-20C automatic recording spectropolarimeter at 20°C.

*3.2. General procedure for the synthesis of complexes Rp,Sc-**2** and Sp,Sc-**2***

To the methanol suspension (10 ml) of the racemic complexes **1** (1 mmol) were added a slight excess of (*S*)-leucine (1.1 mmol) and Na_2CO_3 (1.1 mmol); the mixture was stirred at room temperature until the solution became clear. After evaporation of the solvent in vacuo the crude residue was treated with

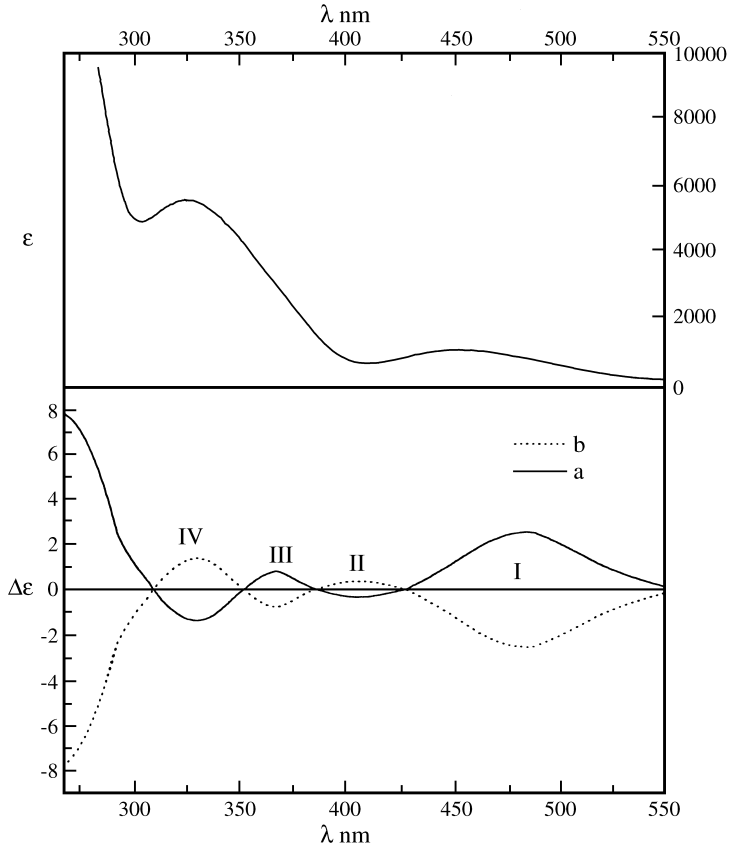


Figure 2. Electronic and CD spectra in dichloromethane of compounds Rp-**4b** (a) and Sp-**4b** (b)

CH_2Cl_2 in order to remove the unreacted amino acid. Further evaporation of the CH_2Cl_2 and treatment of the residue with CH_2Cl_2–petroleum ether (b.p. 60–90°C) (1:3) afforded a mixture of diastereomers **2**. Separation of diastereomers **2** was easily achieved by chromatography of a mixture of diastereomers on a silica gel plate developed with dichloromethane:acetone (1:1). The first TLC band was (Rp,Sc)-**2** and the second band was (Sp,Sc)-**2**.

*3.3. Reaction of Rp,Sc-**2** and Sp,Sc-**2** with lithium chloride*

A methanol solution (1 ml) of 0.05 mmol complexes (Rp,Sc)-**2**, (Sp,Sc)-**2** and 0.1 mmol of LiCl was mixed with acetic acid (6 ml). The mixture was stirred at room temperature for about 10 min, then filtered, and washed with petroleum ether three times. The solid obtained was recrystallized from CH_2Cl_2–petroleum ether (60–90°C) to produce compound (Rp,Rp)-**3** and (Sp,Sp)-**3**, respectively.

*3.4. General procedure for the synthesis of compounds Rp-**4** and Sp-**4***

Metallic mercury was stirred vigorously in a dichloromethane solution of (Rp,Rp)-**3** (0.03 mmol) and also in that of (Sp,Sp)-**3** (0.03 mmol), each for 15 min at room temperature. After removing the palladium black and unreacted metallic mercury by rapid chromatography on a short silica gel column and evaporating the solvent, the resulting red solid was recrystallized from dichloromethane–hexane to give red crystalline Rp-**4** and Sp-**4**, respectively.

3.5. X-Ray crystal structure determination of Rp-**4b**

Crystal data: $C_{19}H_{18}NClFeHg$; M=552.25; red prisms; crystal size: 0.70×0.60×0.25 mm; orthorhombic; space group: $P2_12_12_1$ (#19); a=9.250(9) Å, b=27.676(9) Å, c=6.964(2) Å, Z=4, V=1782.7600 Å^3, Dc=2.06 g cm^{-3}, F(000)=1048.00, μ(MoKα)=95.85 cm^{-1}.

Data collection: all measurements were made on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated MoKα radiation (λ=0.71070 Å); The data were collected at 18±1°C to a maximum 2θ value of 55.0°. A total of 60 images of 3.00° oscillation was collected, each being exposed for 14.0 min. The crystal-to-detector distance was 120.00 mm with the detector at the zero swing position. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[8] and expanded by using Fourier techniques. Some non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full matrix least-squares refinement was based on 1756 observed reflection (I>3.00σ(I)) and 204 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 2.27 and −1.52e$^-$/Å^3, respectively. The absolute configuration of Rp-**4b** was confirmed by the significance of the difference between the two sigma weighted R-factors, which was judged by the Hamilton test.[9] The final R-factors were 0.043 (Rw=0.059) and 0.058 (0.081) for R- and S-configuration in the ferrocene moiety, respectively. All calculations were performed using the teXsan[10] crystallographic software package of the Molecular Structure Corporation.

Acknowledgements

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