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Stereochemistry of SO_2 Insertion at a Chiral Metal Center: Synthesis and Crystal Structures of $Ru[C_5H_4(neomenthyl)](CO)(PPh_3)R$ (R = Me, SO_2Me)

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Reaction of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Cl (**2**; nmcp = neomenthylcyclopentadienyl) with MeMgBr proceeds stereospecifically to yield $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me (**3**), which reacts in liquid SO_2, undergoing SO_2 insertion to yield $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)SO_2Me (**4**). The corresponding $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Cl undergoes a similar sequence of reactions, also with retention of configuration at ruthenium. The X-ray structures of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me (**3**) and $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)SO_2Me (**4**) have been determined at room temperature with use of Mo Kα radiation (λ = 0.71069 Å). Compound **3** crystallizes in the monoclinic space group $P2_1$ (C_2^2, No. 4) with a = 8.005 (19) Å, b = 15.44 (5) Å, c = 12.974 (33) Å, β = 102.01 (19)°, V = 1568 (7) Å^3, Z = 2, and D_c = 1.291 g cm^{-3}. On the basis of 2344 independent reflections the structure was refined to R = 0.0600. The crystals of **4** are triclinic, space group $P1$ (C_1^1, No. 1), with a = 11.143 (42) Å, b = 12.108 (19) Å, c = 13.440 (27) Å, α = 77.04 (14)°, β = 78.79 (23)°, γ = 67.58 (23)°, V = 1621 (8) Å^3, Z = 2, and D_c = 1.381 g cm^{-3}. The structure was refined to R = 0.0575 on the basis of 4655 independent reflections. NMR (^{1}H, ^{13}C, and ^{31}P) data for the individual epimers are reported, and the extent to which the CD spectrum correlates with the absolute configuration of the metal is discussed.

Introduction

Insertion into a metal–alkyl bond is a fundamental step in many catalytic and stoichiometric reactions of organometallic compounds; consequently, such reactions have been studied in considerable detail.[3] One such reaction, the insertion of sulfur dioxide, has been the subject of numerous synthetic and kinetic studies.[4] Insight into the mechanisms of SO_2 insertions has also been obtained from studying the stereochemistry of such reactions; however, these have focused primarily on the stereochemistry of the alkyl group,[5] and studies on the stereochemistry at the metal have been limited to those of chiral iron[6] and titanium[7] complexes.

We report herein the stereospecific synthesis of the chiral metal alkyl complex Ru(nmcp)(CO)(PPh_3)Me (where nmcp = neomenthylcyclopentadienyl) and the stereochemistry of SO_2 insertion at the chiral ruthenium center. This investigation complements previous studies, by us and by others, in illustrating the value of the neomenthylcyclopentadienyl ligand in providing easy access to optically pure chiral metal centers.[8,9] It also demonstrates once again how useful the neomenthylcyclopentadienyl ligand is as an NMR probe for determining the stereoselectivity of reactions at chiral metal centers.[10]

Experimental Section

General Information. All reactions were performed under nitrogen, although subsequently none of the products were found to be air-sensitive. All elemental analyses were performed by the microanalytical services of the Department of Chemistry at Sheffield University.

Infrared spectra were recorded with a Perkin-Elmer 1600 or Perkin-Elmer 1710 FT infrared spectrophotometer at a resolution of 4 cm^{-1}. Samples were prepared as Nujol mulls, KBr disks, or solutions as indicated. NMR spectra were recorded either with a Bruker AM250 spectrometer operating at 250.13 MHz (^{1}H) or at 62.90 MHz (^{13}C) or with a Bruker WH400 spectrometer operating at 400.13 MHz (^{1}H) or at 100.61 MHz (^{13}C), the ^{2}D-lock signal being used as an internal reference in either case. ^{31}P NMR spectra were recorded at 32.44 MHz on a Bruker WP80SY spectrometer with the ^{2}D-lock signal as an internal reference. All ^{31}P NMR and ^{13}C NMR spectra were run ^{1}H noise-decoupled. Mass spectra were run on a Kratos MS80 spectrometer using the positive ion fast atom bombardment (+ve FAB) or on a Kratos MS25 spectrometer using the electron impact (EI) technique. Circular dichroism spectra were recorded on a Jobin-Yvon Dichrographe III using chloroform as solvent and generally with concentrations of 0.5 mg cm^{-3}.

Diastereomeric excesses (de) and reaction stereoselectivities were determined by use of ^{1}H NMR (250.13 MHz) unless otherwise stated and are quoted to an error of ±2%.

Materials. Solvents were dried as follows: tetrahydrofuran was distilled over sodium/benzophenone, diethyl ether was distilled over sodium, dichloromethane was distilled over calcium hydride, and acetone was dried over anhydrous magnesium sulfate.

The complexes (R)- and (S)-[Ru(nmcp)(CO)(PPh_3)(NCMe)]BF_4[9,11] (**1**) and methylmagnesium bromide[12] (1.8 M ether solution) were prepared as described previously. The epimers of Ru(nmcp)(CO)(PPh_3)Cl (**2**) had previously been separated with difficulty by HPLC from a mixture of the $(R)_{Ru}$ and $(S)_{Ru}$ epim-

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Table I. Experimental Data for the X-ray Diffraction Study of (*S*)-Ru(nmcp)(CO)(PPh$_3$)Me (3) and (*R*)-Ru(nmcp)(CO)(PPh$_3$)SO$_2$Me (4)

	3	4
	(A) Crystal Parameters	
cryst syst	monoclinic	triclinic
space group	$P2_1$ (C_2^2, No. 4)	$P1$ (C_1^1, No. 1)
a, Å	8.005 (19)	11.143 (42)
b, Å	15.44 (5)	12.108 (19)
c, Å	12.974 (33)	13.440 (27)
α, deg		77.04 (14)
β, deg	102.01 (19)	78.79 (23)
γ, deg		67.58 (23)
V, Å^3	1568 (7)	1621 (8)
no. of reflns for cell	15	10
Z	2	2
mol wt	609.75	673.81
F(000)	635.93	699.92
D_c, g cm^{-3}	1.291	1.381
solvent	acetone/methanol	dichloromethane/ diethyl ether
color	yellow	pale yellow
habit	elongated blocks	flattened needles
dimens, mm	0.35 × 0.20 × 0.15	0.75 × 0.23 × 0.06
	(B) Intensity Data	
diffractometer	Nicolet R3 4-circle	Nicolet R3 4-circle
radiation	Mo Kα	Mo Kα
wavelength, Å	0.71069	0.71069
monochromator	graphite	graphite
rflns measd	$+h,+k,\pm l$	$+h,\pm k,\pm l$
2θ range, deg	3.5–50	3.5–50
temp, °C	20	20
scan type	ω	ω
scan speed, deg min^{-1}	3.0–29.3	2.0–29.3
scan range, deg	2.0	2.0
bkgd measurement	50% scan time	50% scan time
std rflns	1 (100)	1 (−1,0,3)
no. of rflns collected	2874	5705
no. of rflns used	2344	4655
acceptance criterion	$\|F\|/\sigma(\|F\|) > 3.0$	$\|F\|/\sigma(\|F\|) > 3.0$
R_{merge}	0.0354	0.0154
abs coeff, cm^{-1}	5.63	6.15
min transmissn coeff	0.740	0.672
max transmissn coeff	0.797	0.758
abs method	8 azimuthal scans	7 azimuthal scans
	(C) Structure Solution	
method	Patterson/Fourier	Patterson/Fourier
programs	SHELXTL[a]	SHELXTL[a]
computer	Data General Nova 3	Data General Nova 3
scattering factors	reference[a]	reference[a]
R	0.0600	0.0575
enantiomer	via chiral neomenthyl	via chiral neomenthyl
H refinement	riding mode	riding mode

[a] Sheldrick, G. M. SHELXTL, an Integrated System for Solving, Refining, and Displaying Crystal Structures and Diffraction Data; University of Göttingen: Göttingen, FRG, 1978; revision 4.1, Aug 1983.

ers.[10] A stereospecific synthesis of each epimer is reported below.

Preparation of Epimerically Pure Ru(nmcp)(CO)(PPh$_3$)Cl (2). A solution of $(S)_{Ru}$-[Ru(nmcp)(CO)(PPh$_3$)(NCMe)]BF$_4$ (1; 238 mg, 0.33 mmol) and Bu$_4$NCl (204 mg, 0.73 mmol) in dry acetone (40 cm^3) was refluxed for 2 days. Removal of the solvent in vacuo and chromatography on basic alumina with diethyl ether yielded a yellow band, from which the solvent was removed in vacuo to yield $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Cl (125 mg, 60%) as an orange powder. The stereoselectivity of the reaction was 93%.

Similar treatment of $(R)_{Ru}$-[Ru(nmcp)(CO)(PPh$_3$)(NCMe)]BF$_4$ with Bu$_4$NCl yielded $(S)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Cl (59% yield, 94% stereoselectivity).

The identity and optical purity of each epimer were confirmed by comparison with the reported ^{1}H, ^{13}C, and ^{31}P NMR and infrared spectra.[10]

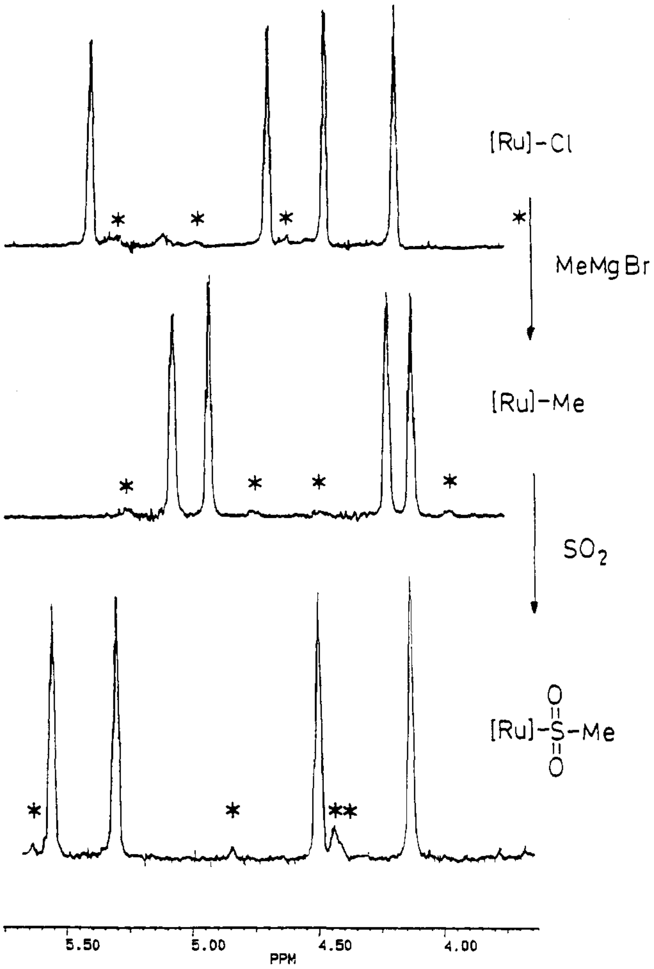

Figure 1. ^{1}H NMR spectra of $(S)_{Ru}$ products formed from $(S)_{Ru}$-[Ru]Cl ([Ru] = Ru(nmcp)(CO)(PPh$_3$)). Asterisks indicate the corresponding $(R)_{Ru}$ epimers.

Preparation of Epimerically Pure Ru(nmcp)(CO)(PPh$_3$)Me (3). Typically, methylmagnesium bromide (2.6 cm^3 of a 1.8 M solution, 7.2 mmol) was added to an orange solution of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Cl (600 mg, 0.95 mmol) in ether (100 cm^3) and the reaction mixture stirred for 2 h to yield a pale yellow solution. After the solution was quenched with acetone and the solvent was removed in vacuo, the product mixture was dissolved in diethyl ether and the solution passed down a small alumina column under reduced pressure to remove magnesium salts. The solvent was removed in vacuo and the residue chromatographed on alumina; a 1:1 mixture of diethyl ether/petroleum ether (40–60 °C) eluted a pale yellow band, which on removal of the solvent in vacuo yielded $(S)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Me (280 mg, 48%; 98% stereoselectivity). Anal. Calcd for C$_{35}$H$_{41}$OPRu: C, 68.95; H, 6.8. Found: C, 69.3; H, 7.0.

Eluting the chromatography column with diethyl ether gave an orange band, which on removal of the solvent left orange crystals of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Br (190 mg, 30%; 99% stereoselectivity). Anal. Calcd for C$_{34}$H$_{38}$BrOPRu: C, 60.50; H, 5.65; Br, 11.85. Found: C, 60.55; H, 5.65; Br, 11.75.

Repetition of this reaction under the same conditions gave yields of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Me between 39% and 72% with corresponding fluctuations in the yields and *stereoselectivity* (50–99%) of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Br. *The stereoselectivity of the methylation reaction remained consistent.*

Treatment of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Cl with MeMgBr in the manner described above typically yielded (*R*)-Ru(nmcp)(CO)(PPh$_3$)Me in yields between 52% and 71% and a stereoselectivity of 98% and corresponding fluctuating yields of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Br with 67–99% stereoselectivity.

Preparation of (*RS*)-Ru(nmcp)(CO)(PPh$_3$)Me. To an orange solution of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)I (60 mg, 0.083 mmol) in THF (25 cm^3) at −78 °C was added a green solution of sodium naphthalenide (4 cm^3 of a 0.2 M solution, 0.8 mmol) to

Table II. ^{1}H NMR[a] (δ/ppm, *J*/Hz) and Infrared[b] (cm^{-1}) Data

	C_5H_4	(+)-neomenthyl	other	IR
(*S*)-Ru(nmcp)(CO)(PPh_3)Me	5.09, 4.94, 4.23, 4.12	2.83 [H(6) br s] 2.07 [H(7) br d; *J* = 12] 1.86–1.13 (8 H; m), 0.89 (Me; d, *J* = 6), 0.85 (Me; d, *J* = 6), 0.62 (Me; d, *J* = 6)	7.44–7.30 (PPh_3) 0.08 (Ru-*Me* d; *J* = 6)	1906[c]
(*R*)-Ru(nmcp)(CO)(PPh_3)Me	5.26, 4.76, 4.49, 3.98	2.83 [H(6) br s] 2.05 [H(7) br d; *J* = 13] 1.87–0.78 (14 H; m) 0.75 (Me; d, *J* = 6)	7.46–7.31 (PPh_3) 0.06 (Ru-*Me* d; *J* = 5)	
(*R*)-Ru(nmcp)(CO)(PPh_3)Br	5.49, 4.65, 4.50, 4.21	2.82 [H(6) br s] 2.23 [H(7) d; *J* = 13] 1.86–1.07 (8 H; m) 0.90 (Me; d, *J* = 6) 0.87 (Me; d, *J* = 6) 0.75 (Me; d, *J* = 6)	7.62–7.28 (PPh_3)	1950[c]
(*S*)-Ru(nmcp)(CO)(PPh_3)Br	5.38, 5.02, 4.54, 3.67	3.08 [H(6) br s] 2.30 [H(7) br d; J = 13] 1.87–1.05 (8 H; m) 0.92 (Me; d, *J* = 6) 0.89 (Me; d, *J* = 6) 0.77 (Me; d, *J* = 6)	7.61–7.33 (PPh_3)	
(*S*)-Ru(nmcp)(CO)(PPh_3)SO_2Me	5.54, 5.29, 4.48, 4.12	2.76 [H(6) br s] 2.18 [H(7) br d; *J* = 14] 1.90–1.08 (8 H; m) 0.90 (Me; d, *J* = 6) 0.78 (Me; d, *J* = 6) 0.68 (Me; d, *J* = 6)	7.68–7.30 (PPh_3) 2.78 (SO_2Me, s)	1957[c] 1176[d] 1043[d]
(*R*)-Ru(nmcp)(CO)(PPh_3)SO_2Me	5.63, 4.83, 4.42, 4.38	3.10 [H(6) m] 2.10 [H(7) d; *J* = 14] 1.95–1.70 (17 H; m)	7.72–7.35 (PPh_3) 2.67 (SO_2Me, s)	

[a] Recorded at 250.13 MHz in $CDCl_3$. [b] Recorded in CH_2Cl_2; pairs of epimers gave identical infrared spectra. [c] ν(CO) vs. [d] ν(SO) s.

yield a dark green solution of the anion $[Ru(nmcp)(CO)(PPh_3)]^-$ (ν(CO) 1888 s, 1848 s cm^{-1}) together with a small amount of Ru(nmcp)(CO)(PPh_3)H (ν(CO) 1921 vs cm^{-1}). Addition of MeI (1 cm^3, ca. 200-fold excess) immediately yielded a pale yellow solution, which was warmed to room temperature. An infrared spectrum indicated formation of Ru(nmcp)(CO)(PPh_3)Me (ν(CO) 1912 cm^{-1}) together with a small amount of Ru(nmcp)(CO)(PPh_3)I (ν(CO) 1950 cm^{-1}). The solvent was removed in vacuo and the residue passed down a small alumina column in diethyl ether under reduced pressure. A $^{31}P\{^1H\}$ NMR spectrum after removal of the solvent in vacuo showed the product mixture to consist of 75% (*RS*)-Ru(nmcp)(CO)(PPh_3)Me and 25% (*RS*)-Ru(nmcp)(CO)(PPh_3)I.

Preparation of Epimerically Pure Ru(nmcp)(CO)(PPh_3)SO_2Me (4). Sulfur dioxide was condensed (with use of a methanol/dry ice cold finger) onto $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me (61 mg, 0.1 mmol) at −10 °C. The resultant solution was stirred at −10 °C for a further 1 h and the sulfur dioxide allowed to boil off, yielding $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)SO_2Me (65 mg, 96%) as a lemon solid. The stereoselectivity of the reaction was 99%.

Similar treatment of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me gave $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)SO_2Me (99% stereoselectivity) in 100% yield. Anal. Calcd for $C_{35}H_{41}O_3PRuS$: C, 62.4; H, 6.65. Found: C, 63.4; H, 6.15. MS: *m/e* 675 (8%, M + H$^+$), 595 (100%, M − SO_2Me), 565 (88%).

Crystal Structure Determinations. Crystals of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me (3) suitable for X-ray crystallographic analysis were grown by slow evaporation of solvent from a concentrated acetone solution of the complex. Crystals of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh_3)SO_2Me (4) suitable for X-ray analysis were obtained by allowing hexane to slowly diffuse into a dichloromethane solution of the complex. Experimental details of X-ray data collection and solution and refinement of the structures are presented in Table I.

Results and Discussion

We have reported previously the facile synthesis and separation of the *R* and *S* epimers of Ru(nmcp)(CO)(PPh_3)I.[8] Naturally, therefore, our initial synthetic routes to the desired Ru(nmcp)(CO)(PPh_3)Me were based on the corresponding iodide complex. This complex did not react at all with MeMgBr, and reaction with LiMe yielded only a small amount (10%) of the desired methyl complex; however, reaction of racemic Ru(nmcp)(CO)(PPh_3)I with sodium naphthalenide generated the anionic species $[Ru(nmcp)(CO)(PPh_3)]^-$, which reacts with methyl iodide to give Ru(nmcp)(CO)(PPh_3)Me in >75% yield. Repeating the reaction with either the optically pure *R* or the *S* epimer of Ru(nmcp)(CO)(PPh_3)I at −78 °C gave in each case the *RS* form of Ru(nmcp)(CO)(PPh_3)Me. Whereas 16-electron intermediates of the type $[Ru(nmcp)(CO)(PPh_3)]^+$ are pyramidal,[10,13] the 18-electron anion $[Ru(nmcp)(CO)(PPh_3)]^-$, which is isoelectronic with compounds of the type $CpRhL_2$, would be expected to be "flat" (considering the three ligands as points); the observed lack of stereoselectivity in the reactions of $[Ru(nmcp)(CO)(PPh_3)]^-$ is in keeping with this.

Unfortunately, separation of the *R* and *S* epimers of Ru(nmcp)(CO)(PPh_3)Me proved impossible either by crystallization techniques or by use of HPLC. Therefore, the synthesis of optically pure Ru(nmcp)(CO)(PPh_3)Me from the corresponding chloride was attempted.

$(R)_{Ru}$- and $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Cl[10] was obtained in 93 and 94% de, respectively, from the reaction of tetrabutylammonium chloride with the corresponding optically pure [Ru(nmcp)(CO)(PPh_3)(NCMe)]BF_4 (1). We had previously[10] established the absolute configuration of the chloride complex by a combination of CD spectroscopy and X-ray crystallography, and its optical purity was readily determined by ^{1}H and ^{31}P NMR spectroscopy. It should be emphasized that, in this study and our previous work, the neomenthylcyclopentadienyl ligand has been found to

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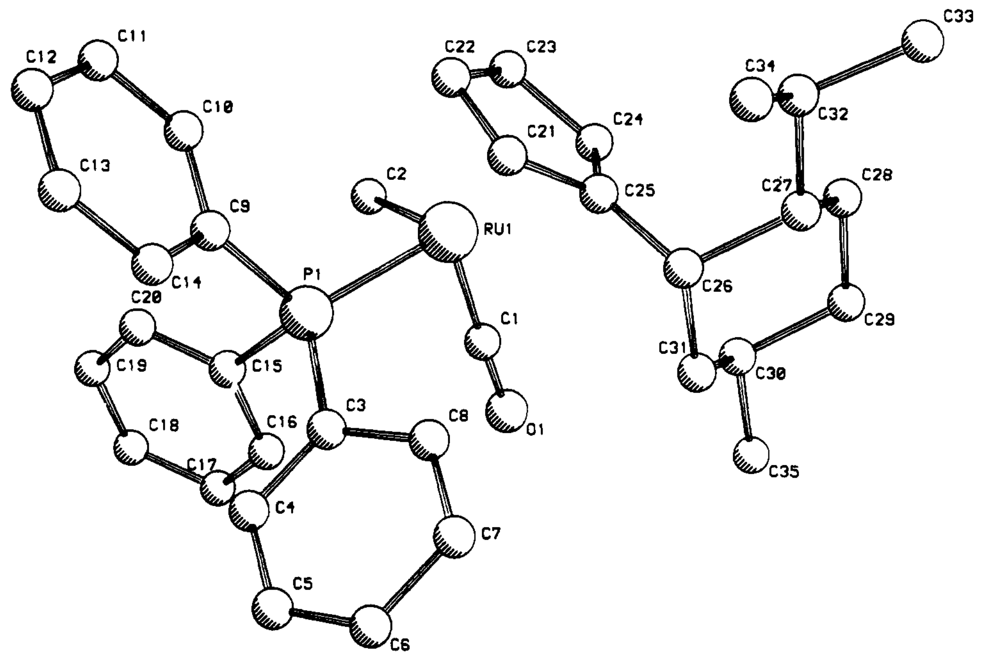

Figure 2. Molecular structure of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)Me (3).

Table III. $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR Data Recorded in $CDCl_3$ (δ/ppm, *J*/Hz)

	$^{13}C\{^1H\}^a$			$^{31}P\{^1H\}^b$
	C_5H_4	(+)-neomenthyl	other	PPh_3
(*S*)-Ru(nmcp)(CO)(PPh_3)Me	110.4 [C(1) d; *J* = 4.8] 92.7 (d; *J* = 4.4), 87.9, 87.5 (*J* = 5.2), 84.7	48.3 (C(12)), 45.2 (C(7)), 36.3 (C(6)), 35.7 (C(10)), 29.8 (C8), 27.8 (C(13)), 24.5 (C(11)), 22.7 (Me), 22.0 (Me), 20.6 (Me)	207.9 (CO; d, *J* = 20.2), 137.5–127.7 (PPh_3), –27.2 (Me; d, *J* = 10.4)	64.0
(*R*)-Ru(nmcp)(CO)PPh_3)Me	107.5 [C(1) d; *J* = 8.0] 95.7, 87.9, 86.0 (d; *J* = 2.0), 84.2	48.1 (C(12), d; *J* = 2.0), 44.4 (C(7)), 35.7 (C(10)), 35.4 (C(6)), 29.6 (C(8)), 28.0 (C(13)), 24.7 (C(11)), 22.0 (Me), 22.0 (Me), 20.6 (Me)	207.9 (CO; d, *J* = 20.4), 137.5–127.7 (PPh_3), –26.8 (Me; d, *J* = 10.3)	62.9
(*R*)-Ru(nmcp)(CO)(PPh_3)Br	106.9 [C(1) d; *J* = 8.7] 95.8, 86.6, 82.3, 80.6	48.5 (C(12)), 43.5 (C(7)), 35.5 (C(10)), 34.9 (C(6)), 29.6 (C(8)), 27.8 (C(13)), 24.5 (C(11)), 22.6 (Me), 22.0 (Me), 20.6 (Me)	203.7 (CO; d, *J* = 20.4), 136.5–127.0 (PPh_3)	48.9
(*S*)-Ru(nmcp)(CO)(PPh_3)Br	108.4 [C(1) d; *J* = 9.0] 99.4, 87.3, 83.0, 76.8	47.9 (C(12)), 43.5 (C(7)), 35.5 (C(10)), 34.9 (C(6)), 29.6 (C(8)), 28.2 (C(13)), 24.7 (C(11)), 22.6 (Me), 22.0 (Me), 20.6 (Me)	203.9 (CO; d, *J* = 20.9), 136.5–127.0 (PPh_3)	47.9
(*S*)-Ru(nmcp)(CO)(PPh_3)SO_2Me	116.3 [C(1) d; *J* = 3.0] 93.3, 91.4, 90.1 (d; *J* = 7.5), 85.7	47.6 (C(12)), 43.7 (C(7)), 35.8 (C(6)), 35.2 (C(10)), 29.3 (C(8)), 27.9 (C(13)), 24.4 (C(11)), 22.5 (Me), 21.9 (Me), 20.3 (Me)	203.6 (CO; d, *J* = 18.6), 60.7 (SO_2Me, s)	47.3
(*R*)-Ru(nmcp)(CO)(PPh_3)SO_2Me	112.6 [C(1) d; *J* = 6.8] 102.7, 89.6, 88.1, 83.9	47.8 (C(12)), 45.0 (C(7)), 35.5 (C(6)), 35.4 (C(10)), 29.7 (C(8)), 28.1 (C(13)), 24.1 (C(11)), 22.5 (Me), 21.8 (Me), 20.5 (Me)	203.5 (CO; d, *J* = 18.6), 60.1 (SO_2Me)	47.7

[a] Recorded at 62.90 MHz; numbering system shown in Figures 2 and 3. [b] Recorded at 32.44 MHz.

exert no significant directing effect on the stereochemical course of the reaction, as evidenced by the virtually identical diastereomeric excesses obtained for both epimers in this and other reactions reported herein.

Reaction of Ru(nmcp)(CO)(PPh_3)Cl (**2**) with MeMgBr yielded the corresponding methyl complex **3** in a highly stereospecific reaction; thus, $(R)_{Ru}$-**2** gave $(R)_{Ru}$-**3** with 98% stereoselectivity and $(S)_{Ru}$-**2** gave $(S)_{Ru}$-**3** with 99% stereoselectivity as indicated by ^1H NMR spectroscopy (Figure 1). These results are in keeping with the stereoselectivity reported for the methylation of Ru(Cp){$Ph_2PCH(Me)CH_2PPh_2$}Cl.[14] It is interesting to note, however, that although the corresponding methylation of either (*R*)- or (*S*)-Ru(nmcp)(CO)(PPh_3)Cl with MeMgCl proceeded with overall retention of configuration at the ruthenium we found that the stereoselectivity of the reaction was totally irreproducible, yielding between 19 and 95% de of product.

The absolute configuration of the methyl complex was established by determining the X-ray crystal structure of the $(S)_{Ru}$ epimer (Figure 2).

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[14] Consiglio, G.; Morandini, F.; Ciani, G.; Sironi, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 333.

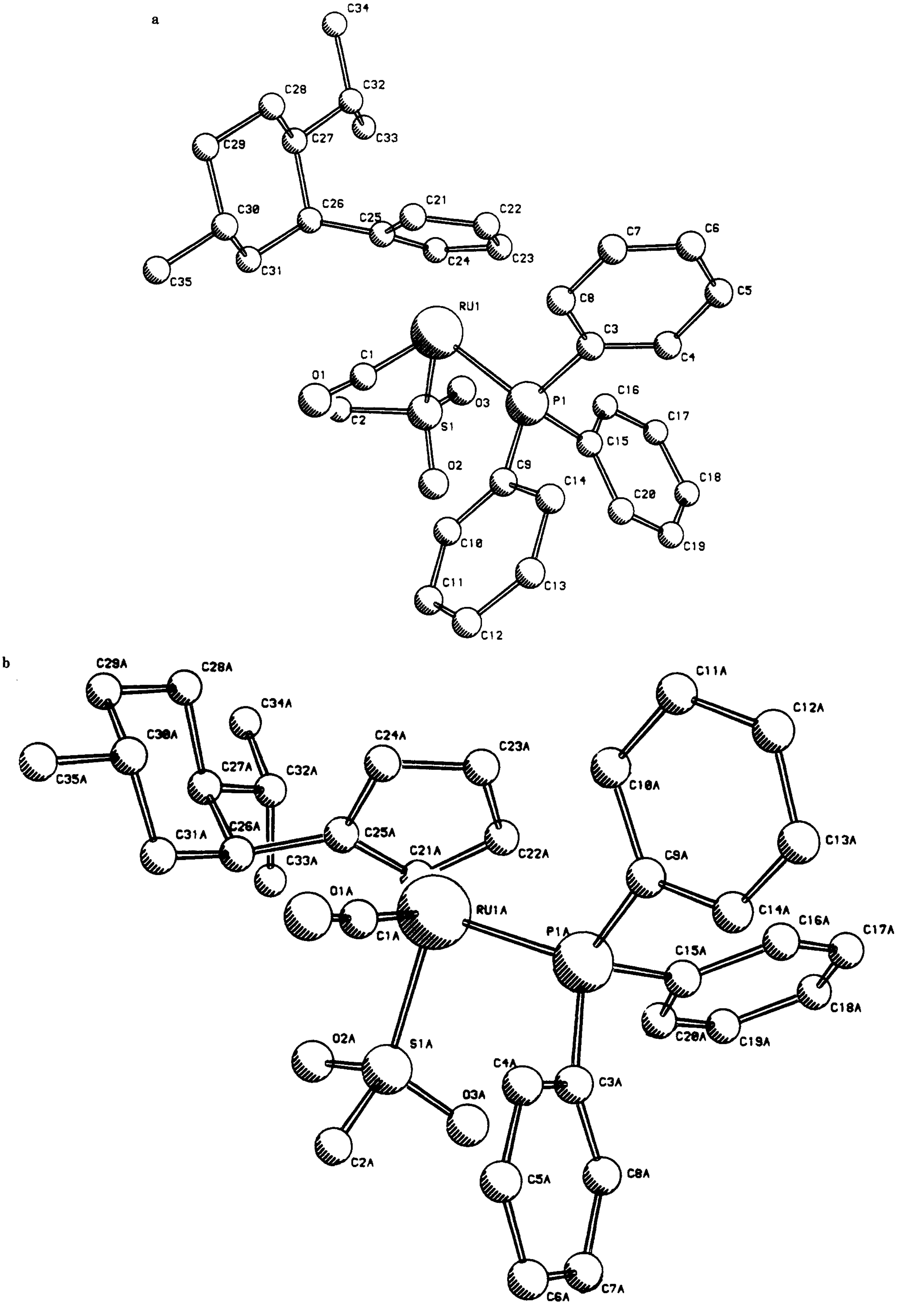

Figure 3. Molecular structures of the two crystallographically independent molecules of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)SO$_2$Me (**4**).

Scheme I. Proposed Mechanism for the Insertion of SO_2 into [Ru]Me ([Ru] = Ru(nmcp)(CO)(PPh$_3$))

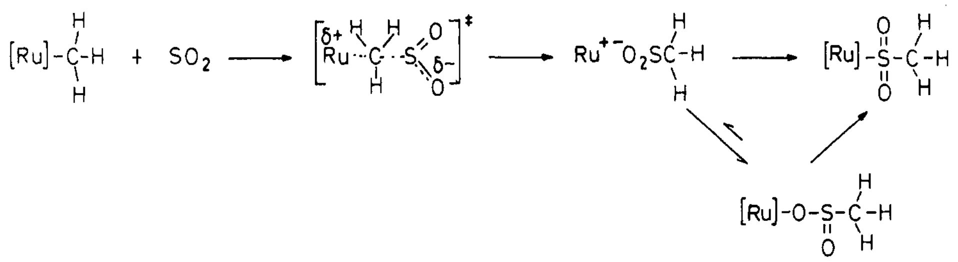

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) and Their Esd's

(*S*)-Ru(nmcp)(CO)(PPh$_3$)Me (**3**)

Ru-C(2)	2.165 (16)	Ru-C(1)	1.781 (15)	P-C(9)	1.834 (14)	P-C(15)	1.863 (14)
Ru-P	2.295 (7)	Ru-C(21)	2.291 (13)	C(21)-C(22)	1.428 (19)	C(22)-C(23)	1.515 (19)
Ru-C(22)	2.274 (14)	Ru-C(23)	2.278 (12)	C(23)-C(24)	1.467 (19)	C(24)-C(25)	1.440 (16)
Ru-C(24)	2.274 (12)	Ru-C(25)	2.323 (12)	C(25)-C(21)	1.443 (17)	C(1)-O	1.221 (19)
Ru-Cp[a]	1.92	P-C(3)	1.837 (13)				
P-Ru-C(2)	90.4 (4)	P-Ru-C(1)	90.2 (4)	Ru-P-C(15)	116.0 (6)	C(3)-P-C(9)	103.1 (6)
C(1)-Ru-C(2)	86.5 (6)	Ru-C(1)-O	176.1 (12)	C(9)-P-C(15)	101.9 (5)	C(15)-P-C(3)	101.4 (6)
Ru-P-C(3)	116.5 (4)	Ru-P-C(15)	115.7 (4)				

(*R*)-Ru(nmcp)(CO)(PPh$_3$)(SO_2Me) (**4**)

	molecule 1	molecule 2		molecule 1	molecule 2
Ru-P	2.363 (7)	2.342 (6)	Ru-S	2.306 (7)	2.344 (6)
Ru-C(1)	1.858 (18)	1.864 (18)	Ru-C(21)	2.256 (13)	2.203 (15)
Ru-C(22)	2.231 (16)	2.248 (18)	Ru-C(23)	2.215 (18)	2.209 (15)
Ru-C(24)	2.233 (16)	2.200 (12)	Ru-C(25)	2.293 (12)	2.219 (12)
Ru-Cp	1.903 (11)	1.875 (11)			
P-C(3)	1.829 (14)	1.805 (15)	P-C(9)	1.822 (17)	1.820 (14)
P-C(15)	1.818 (13)	1.854 (14)	S-C(2)	1.819 (16)	1.792 (21)
S-O(2)	1.437 (11)	1.447 (10)	S-O(3)	1.462 (13)	1.477 (11)
C(1)-O(1)	1.152 (23)	1.149 (23)	C(21)-C(22)	1.361 (19)	1.373 (18)
C(22)-C(23)	1.429 (18)	1.391 (23)	C(23)-C(24)	1.384 (19)	1.365 (19)
C(25)-C(21)	1.465 (16)	1.408 (20)	C(25)-C(26)	1.535 (16)	1.542 (16)

	molecule 1	molecule 2		molecule 1	molecule 2
S-Ru-P	90.8 (2)	95.2 (2)	Ru-P-C(3)	110.6 (4)	114.2 (4)
S-Ru-C(1)	90.4 (4)	91.8 (4)	Ru-P-C(9)	119.1 (5)	118.8 (4)
P-Ru-C(1)	92.4 (4)	91.3 (4)	Ru-P-C(15)	118.5 (4)	113.0 (4)
S-Ru-Cp	121.6 (4)	117.3 (4)	C(2)-S-O(2)	103.3 (8)	104.9 (7)
C(1)-Ru-Cp	125.5 (6)	125.9 (6)	C(2)-S-O(3)	103.7 (7)	103.1 (7)
P-Ru-Cp	125.9 (4)	126.6 (4)	O(2)-S-O(3)	113.6 (6)	112.7 (6)
Ru-S-C(2)	107.7 (5)	112.9 (5)	C(3)-P-C(9)	102.2 (7)	99.8 (7)
Ru-S-O(2)	116.5 (4)	109.5 (4)	C(3)-P-C(15)	101.1 (6)	107.4 (6)
Ru-S-O(3)	110.7 (6)	113.4 (4)	C(9)-P-C(15)	102.7 (6)	102.0 (6)
Ru-C(1)-O(1)	174.3 (11)	176.6 (11)			

[a] Cp indicates the center of the cyclopentadienyl ring.

Stirring (*RS*)-Ru(nmcp)(CO)(PPh$_3$)Me in refluxing sulfur dioxide at −10 °C for 1 h gave (*RS*)-Ru(nmcp)(CO)(PPh$_3$)SO_2Me. The sulfinate-*S* adduct was characterized by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy (Tables II and III) and by its mass spectrum. The sulfinate-*S* bonding mode was assigned from the sulfur–oxygen frequencies at 1176 and 1043 cm^{-1} in the infrared spectrum.[3a]

Similar treatment of epimerically pure (*S*)- and (*R*)-Ru(nmcp)(CO)(PPh$_3$)Me gave respectively (*S*)- and (*R*)-Ru(nmcp)(CO)(PPh$_3$)(SO_2Me) in essentially quantitative yield and with 99% stereoselectivity in each case (Figure 1).

That the reaction took place with retention of the ruthenium configuration was established by X-ray crystallography. Having determined the structure of $(S)_{Ru}$ methyl complex **3**, we naturally attempted to grow crystals of the sulfinate complex that originated from this $(S)_{Ru}$ epimer. Unfortunately, despite several attempts, we did not succeed in obtaining suitable crystals of this particular epimer; therefore, the crystal structure is of the sulfinate complex arising from the SO_2 insertion reaction of $(R)_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Me (Figure 3). Retention of the configuration at the metal center has also been reported for SO_2 insertion into the metal–alkyl bonds of Fe(C_5H_5)(CO)(PPh$_3$)CH_2CHMe_2[6] and Ti(C_5H_5){C_5H_4CH(Me)Ph}(Me)C_6F_5.[7] In the case of iron complexes, however, high (>95%) stereoselectivity was only observed when the reaction was carried out in organic solvents and, in contrast to the case for the ruthenium complex reported here, reaction in SO_2(l) proceeded with relatively low (79%) stereoselectivity.[15]

The currently accepted mechanism of these reactions involves backside attack on the alkyl group R by the electrophilic SO_2 and the formation of an the ion pair $[M]^+,^-O_2SR$, which rearranges to the product [M]-SO_2R (Scheme I). Pertinent to the present study is the finding that in the SO_2 insertion into Ru(C_5H_5)(CO)$_2$R (where R = Me, Ph, CH_2Ph) the ion pair rearranges to the sulfinate-*S* product via the sulfinate-*O* isomer.[16] The high stereoselectivity of the reaction of SO_2 with Ru(nmcp)(CO)(PPh$_3$)Me implies that the ion-pair intermediate

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(15) Attig, T. G.; Wojcicki, A. *J. Am. Chem. Soc.* **1974**, *96*, 262; **1979**, *101*, 619.

(16) Jacobsen, S. E.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *72*, 113.

Table V. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for (S)$_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)Me (3) and (*R*)$_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)SO$_2$Me (4)

atom	*x*	*y*	*z*	U_{eq}[a]	atom	*x*	*y*	*z*	U_{eq}[a]
(a) (*S*)-Ru(nmcp)(CO)(PPh$_3$)Me (**3**)									
Ru(1)	737 (1)	0	3681 (1)	42 (1)	C(17)	−5126 (16)	−904 (9)	1196 (10)	59 (5)
P(1)	−1055 (4)	718 (2)	2343 (2)	44 (1)	C(18)	−4939 (20)	−1102 (10)	165 (12)	70 (6)
O(1)	−2221 (13)	−820 (8)	4401 (8)	88 (5)	C(19)	−3601 (18)	−735 (11)	−224 (10)	65 (5)
C(1)	−1056 (17)	−463 (11)	4091 (8)	63 (5)	C(20)	−2467 (15)	−164 (10)	395 (9)	55 (5)
C(2)	688 (18)	−1130 (10)	2686 (11)	70 (6)	C(21)	2452 (15)	1149 (8)	4321 (9)	49 (4)
C(3)	−2472 (14)	1535 (8)	2736 (9)	45 (4)	C(22)	3302 (16)	631 (9)	3676 (10)	59 (5)
C(4)	−3946 (16)	1851 (8)	2076 (11)	56 (5)	C(23)	3594 (13)	−252 (7)	4192 (10)	52 (5)
C(5)	−4983 (16)	2453 (9)	2455 (12)	63 (5)	C(24)	2850 (15)	−195 (6)	5132 (9)	43 (4)
C(6)	−4589 (19)	2791 (10)	3429 (11)	70 (6)	C(25)	2177 (14)	661 (8)	5219 (8)	39 (4)
C(7)	−3094 (19)	2464 (11)	4121 (12)	74 (6)	C(26)	1498 (15)	1077 (8)	6125 (8)	48 (4)
C(8)	−2071 (18)	1862 (9)	3770 (10)	59 (5)	C(27)	2907 (16)	1115 (9)	7190 (9)	56 (5)
C(9)	−9 (14)	1314 (9)	1430 (9)	50 (4)	C(28)	3139 (16)	210 (9)	7711 (10)	66 (6)
C(10)	1295 (15)	934 (10)	1027 (8)	56 (5)	C(29)	1463 (18)	−171 (15)	7877 (9)	96 (8)
C(11)	2054 (17)	1314 (12)	261 (10)	71 (6)	C(30)	37 (17)	−240 (10)	6845 (11)	72 (6)
C(12)	1504 (22)	2132 (12)	−126 (10)	77 (7)	C(31)	−151 (17)	689 (11)	6377 (11)	63 (5)
C(13)	288 (25)	2552 (14)	288 (12)	83 (8)	C(32)	4619 (16)	1512 (9)	7051 (10)	59 (5)
C(14)	−515 (19)	2153 (10)	1056 (12)	72 (6)	C(33)	5908 (20)	1579 (11)	8130 (12)	91 (7)
C(15)	−2612 (11)	33 (13)	1425 (7)	44 (3)	C(34)	4404 (20)	2432 (9)	6536 (11)	75 (6)
C(16)	−3957 (15)	−329 (9)	1818 (10)	56 (5)	C(35)	−1635 (22)	−576 (15)	7085 (14)	110 (9)
(b) (*R*)-Ru(nmcp)(CO)(PPh$_3$)SO$_2$Me (**4**)									
Ru(1)	−1927 (1)	−250 (1)	−2186 (1)	36 (1)	C(30)	999 (16)	−3315 (13)	−3715 (10)	54 (6)
Ru(1a)	1924	241	2191	33 (1)	C(31)	540 (14)	−3508 (11)	−2571 (10)	49 (6)
P(1)	−3720 (3)	1553 (3)	−2565 (3)	42 (1)	C(32)	3032 (15)	−2477 (15)	−1622 (14)	67 (8)
P(1a)	243 (3)	1977 (3)	1548 (2)	36 (1)	C(33)	2783 (21)	−2741 (21)	−536 (15)	108 (12)
S(1)	−3194 (3)	−952 (3)	−815 (3)	48 (1)	C(34)	4531 (18)	−2779 (21)	−1870 (19)	119 (13)
S(1a)	825 (3)	18 (3)	3855 (2)	40 (1)	C(35)	541 (20)	−4034 (16)	−4260 (14)	88 (10)
O(1)	−2486 (11)	−1548 (11)	−3603 (9)	81 (6)	C(1a)	1256 (13)	−757 (11)	1775 (11)	47 (5)
O(2)	−4551 (9)	−615 (9)	−926 (7)	57 (4)	C(2a)	−446 (15)	−574 (16)	3934 (11)	68 (8)
O(3)	−2980 (11)	−727 (10)	149 (7)	67 (5)	C(3a)	−1380 (12)	1950 (11)	2013 (11)	45 (5)
O(1a)	904 (11)	−1396 (10)	1492 (9)	77 (6)	C(4a)	−1820 (13)	1210 (12)	1625 (11)	51 (6)
O(2a)	1729 (9)	−865 (9)	4537 (7)	57 (4)	C(5a)	−2974 (13)	1048 (14)	2003 (12)	57 (7)
O(3a)	126 (10)	1177 (8)	4242 (7)	63 (4)	C(6a)	−3714 (17)	1563 (17)	2836 (14)	77 (9)
C(1)	−2340 (12)	−1029 (12)	−3043 (10)	48 (5)	C(7a)	−3335 (13)	2344 (14)	3225 (12)	64 (7)
C(2)	−2588 (17)	−2596 (13)	−671 (12)	69 (8)	C(8a)	−2168 (11)	2500 (12)	2840 (11)	50 (6)
C(3)	−3152 (11)	2764 (11)	−3302 (10)	42 (5)	C(9a)	144 (13)	2335 (11)	170 (10)	44 (5)
C(4)	−3530 (17)	3899 (13)	−2992 (13)	68 (8)	C(10a)	1212 (16)	1753 (15)	−525 (11)	62 (7)
C(5)	−3026 (18)	4776 (16)	−3531 (13)	79 (8)	C(11a)	1082 (22)	2185 (20)	−1589 (14)	86 (11)
C(6)	−2211 (17)	4584 (13)	−4434 (12)	63 (7)	C(12a)	13 (25)	3093 (20)	−1947 (15)	92 (12)
C(7)	−1874 (14)	3506 (15)	−4764 (11)	60 (7)	C(13a)	−987 (26)	3580 (16)	−1255 (14)	95 (11)
C(8)	−2338 (12)	2581 (11)	−4218 (9)	42 (5)	C(14a)	−916 (18)	3196 (14)	−242 (12)	75 (8)
C(9)	−4885 (12)	1566 (13)	−3352 (10)	49 (6)	C(15a)	297 (11)	3392 (9)	1818 (9)	36 (4)
C(10)	−5386 (14)	645 (14)	−3146 (11)	58 (7)	C(16a)	132 (13)	4457 (12)	1095 (12)	56 (6)
C(11)	−6346 (15)	681 (17)	−3708 (14)	77 (9)	C(17a)	283 (15)	5486 (12)	1316 (12)	59 (7)
C(12)	−6823 (14)	1620 (21)	−4447 (14)	91 (10)	C(18a)	569 (16)	5449 (14)	2255 (15)	70 (8)
C(13)	−6341 (19)	2596 (21)	−4671 (14)	92 (10)	C(19a)	701 (16)	4426 (14)	2987 (14)	67 (8)
C(14)	−5388 (16)	2593 (16)	−4125 (11)	71 (8)	C(20a)	575 (15)	3428 (12)	2767 (11)	56 (7)
C(15)	−4774 (12)	2276 (11)	−1504 (9)	39 (5)	C(21a)	3567 (10)	150 (11)	2929 (11)	44 (5)
C(16)	−4225 (13)	2254 (13)	−659 (10)	53 (6)	C(22a)	3410 (13)	1101 (13)	2125 (11)	50 (6)
C(17)	−4993 (14)	2931 (12)	96 (10)	52 (6)	C(23a)	3619 (12)	617 (13)	1234 (11)	53 (6)
C(18)	−6282 (13)	3566 (11)	53 (10)	48 (6)	C(24a)	3946 (12)	−608 (11)	1502 (10)	43 (5)
C(19)	−6860 (14)	3562 (12)	−771 (9)	48 (6)	C(25a)	3914 (11)	−951 (11)	2569 (9)	41 (5)
C(20)	−6098 (12)	2925 (11)	−1540 (9)	42 (5)	C(26a)	4351 (11)	−2220 (10)	3232 (9)	38 (5)
C(21)	131 (12)	−482 (10)	−2936 (9)	38 (5)	C(27a)	5830 (12)	−2746 (12)	3287 (10)	46 (5)
C(22)	−414 (11)	617 (12)	−2622 (10)	44 (5)	C(28a)	6562 (16)	−3224 (13)	2311 (11)	66 (7)
C(23)	−699 (12)	408 (12)	−1527 (10)	47 (5)	C(29a)	6091 (18)	−4187 (15)	2114 (13)	76 (9)
C(24)	−297 (13)	−836 (12)	−1225 (10)	49 (6)	C(30a)	4641 (18)	−3725 (12)	2037 (13)	69 (8)
C(25)	216 (11)	−1451 (10)	−2045 (9)	36 (5)	C(31a)	3913 (13)	−3181 (11)	2975 (12)	58 (6)
C(26)	982 (12)	−2817 (11)	−1969 (10)	43 (5)	C(32a)	6317 (15)	−1876 (16)	3638 (14)	72 (8)
C(27)	2488 (11)	−3104 (12)	−2189 (11)	44 (5)	C(33a)	5771 (24)	−1643 (19)	4718 (14)	107 (12)
C(28)	2907 (14)	−2949 (14)	−3339 (12)	61 (6)	C(34a)	7764 (18)	−2314 (18)	3559 (19)	106 (12)
C(29)	2467 (15)	−3644 (14)	−3921 (11)	61 (7)	C(35a)	4175 (23)	−4738 (16)	1923 (17)	110 (12)

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

[Ru(nmcp)(CO)(PPh$_3$)]$^+$,$^-$O$_2$SMe, in contrast to the case for the related iron complexes above, is configurationally stable in SO$_2$(l) on the reaction time scale. One could just argue that the ruthenium is a tighter ion pair than its iron analogue; however, we do not see any good reason why this should be the case. Instead, we believe that the greater configurational stability of [Ru(nmcp)(CO)(PPh$_3$)]$^+$,$^-$O$_2$SMe is a reflection of a general trend that chiral ruthenium metal centers are configurationally more stable than their iron analogues. We see this trend, for example, in the halide complexes Fe(C$_5$H$_5$)(CO){PPh$_2$N(Me)CH(Me)Ph}X, which readily epimerize (e.g. for X = I, $t_{1/2}$ = 11 min at 70 °C),[17] whereas the analogous ruthenium complexes are exceedingly configurationally stable; e.g., (*R*)$_{Ru}$-Ru(nmcp)(CO)(PPh$_3$)I shows no tendency to epimerize after 24 h at 110 °C.[8]

Crystal Structures. The molecular structure of Ru(nmcp)(CO)(PPh$_3$)Me (**3**) is illustrated in Figure 2; the

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[17] Brunner, H.; Rackl, F. *J. Organomet. Chem.* **1976**, *118*, C19.

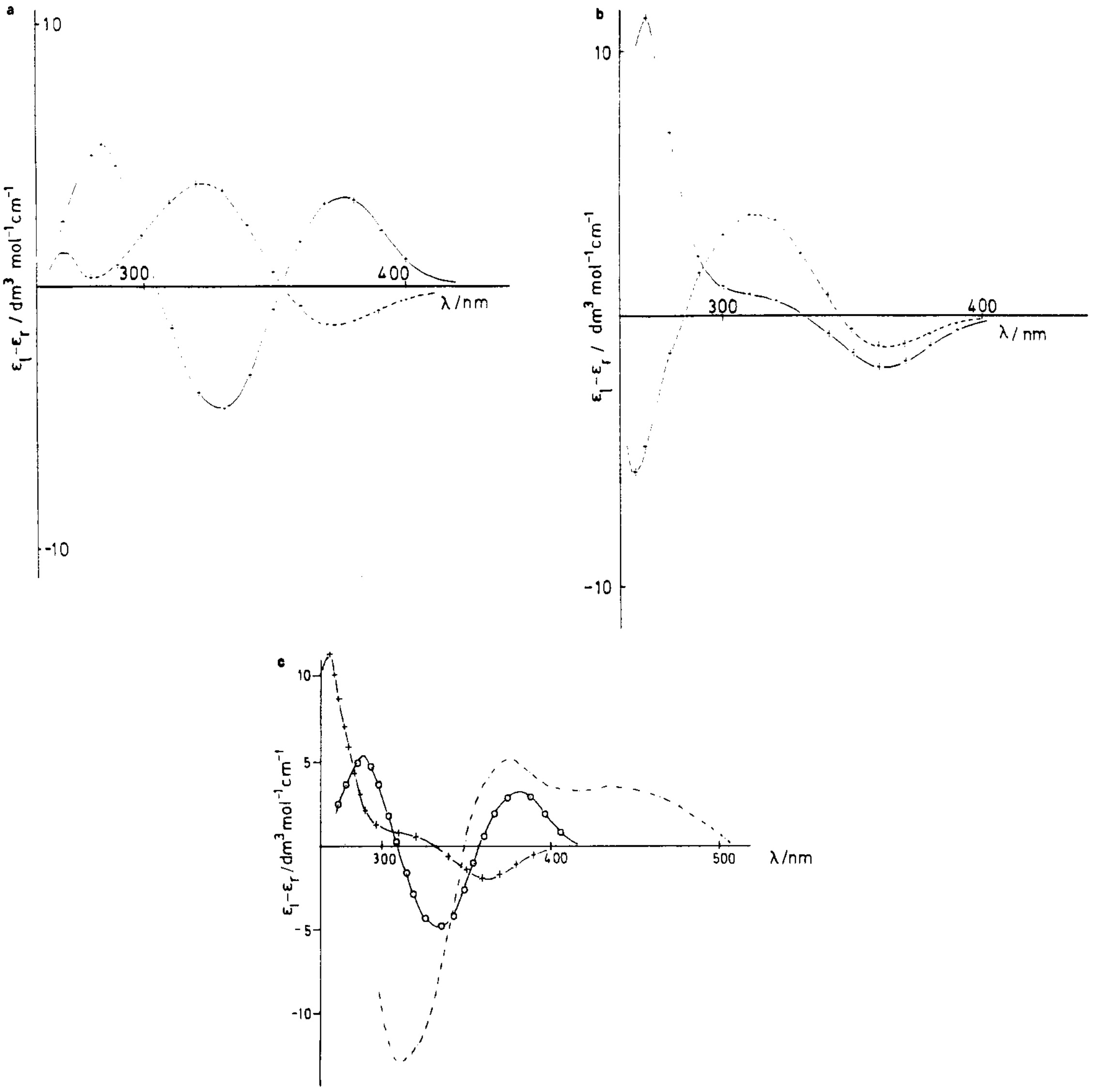

Figure 4. (a) CD spectra of Ru(nmcp)(CO)(PPh_3)Me: (---) $(R)_{Ru}$ epimer; (—) $(S)_{Ru}$ epimer. (b) CD spectra of Ru(nmcp)(CO)(PPh_3)SO_2Me: (---) $(R)_{Ru}$ epimer; (—) $(S)_{Ru}$ epimer. (c) CD spectra: (-·-) $(S)_{Ru}$-[Ru]Cl; (-⊙-) $(S)_{Ru}$-[Ru]Me; (-+-) $(S)_{Ru}$-[Ru]SO_2Me ([Ru] = Ru(nmcp)(CO)(PPh_3)).

sulfinate complex Ru(nmcp)(CO)(PPh_3)SO_2Me (4) crystallizes as two crystallographically independent molecules, and these are illustrated in parts a and b of Figure 3. Selected interatomic bond lengths and angles with estimated standard deviations for both compounds **3** and **4** are listed in Table IV. The final values of the positional parameters are given in parts a and b of Table V for **3** and **4**, respectively.

In Ru(nmcp)(CO)(PPh_3)Me the angles subtended by the monodentate ligands around the ruthenium atom are close to 90°, indicative of an octahedral geometry of the metal atom; the absolute configuration of the ruthenium center is *S*. The ruthenium(II) ion is symmetrically bonded to the η^5-neomenthylcyclopentadienyl ligand (rms deviation of five-membered-ring atoms from mean plane 0.006 Å, ruthenium atom 1.92 Å from the mean plane). There would appear to be a greater degree of ruthenium-carbonyl back-bonding in (*S*)-Ru(nmcp)(CO)(PPh_3)Me with respect to that in (*R*)-Ru(nmcp)(CO)(PPh_3)SO_2Me as reflected by the shorter Ru–CO distance and larger RuC–O of the former (Table IV). The Ru–Me bond length in (*S*)-Ru(nmcp)(CO)(PPh_3)Me (2.165 Å) is comparable to that reported for the similar complex $(S)_{Ru},(R)_C$-{Ru(η^5-C_5H_5)[$Ph_2PCH(Me)CH_2PPh_2$]Me} (2.169 Å).[14] The neomenthyl group is positioned such that the bulky isopropyl group is positioned remotely from the basal ligands, and there seem to be no significant interactions between the chiral neomenthyl substituent and the basal ligands (the shortest is C(31)···C(1) = 3.40 Å to the carbonyl). There is no evidence for disorder of the basal ligands of the type that has been seen in related structures.[18,19]

In Ru(nmcp)(CO)(PPh_3)SO_2Me (4) the metal has the *R* configuration and again the angles subtended by the monodentate ligands around the ruthenium atom are close to 90°. In each of the independent molecules, the ruthenium atom is approximately symmetrically bonded to a η^5 neomenthyl-substituted cyclopentadienyl ligand (rms deviations from mean ring planes 0.003 and 0.009 Å; ruthenium atoms lie 1.901 and 1.876 Å from the mean plane), a linear carbonyl, a triphenylphosphine, and to a methylsulfinate ligand. In both molecules, the phenyl groups are planar (rms deviations 0.015, 0.007, and 0.012 and 0.018, 0.014, 0.008 Å) and the triphenylphosphine, which is the most bulky basal ligand, lies trans to the neomenthyl substitution site on the cyclopentadienyl. The bonded neomenthyl carbon atoms (C(26) and C(26a)) are displaced

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(18) Bailey, N. A.; Jassal, V. S.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2815.

(19) Adams, H.; Bailey, N. A.; Browning, A. F.; Ramsden, J. A.; White, C. *J. Organomet. Chem.* **1990**, *387*, 305.

from the mean cyclopentadienyl planes by 0.270 and 0.175 Å in directions away from the ruthenium, and their orientations are such that the isopropyl group is remote from the ruthenium.

Unusually for molecules of this type, and in this space group, the two molecules are not related by approximate inversion symmetry; thus, correlation coefficients are low and the geometries are well determined. It is clear from Figure 3 that, although the molecules are of the same optically isomeric form, their conformations in the crystal lattice differ in a number of ways. The principal difference involves a twist about the ruthenium–phosphorus bond, and some associated P–C(phenyl) torsional twists. Comparable sets of O(C)–Ru–P–C(Ph) torsion angles are −112, +6, +132° and −64, +53, +176° for the molecules based on Ru(1) and Ru(1a), respectively. This must be solely a consequence of the crystal packing and thus has no significance for solution properties. A second, and perhaps consequential, change involves the orientation of the methylsulfinate group: the sets of P–Ru–S–X (X = O, C) torsion angles are +34, −98, +149° and −168, −41, +75° for the molecules based on Ru(1) and Ru(1a), respectively; in each case, the last value refers to X = C.

To the best of our knowledge, this is the first reported structure of a methylsulfinate ligand bound to a transition metal. However, apart from a short length for C(32)–C(33) and the rather long Ru–P distance, all bond lengths and angles are unexceptional and the structure may be compared to that of $(S)_{Fe}$-$Fe(C_5H_5)(CO)(PPh_3)SO_2CH_2CHMe_2$.[20] There are no significant intermolecular contacts.

CD Spectra. There is considerable interest in applying CD spectroscopy to assign the configuration of the metal in chiral complexes.[10] However, before this is possible it is necessary to compare the CD spectra of a wide range of chiral metal complexes of known absolute configurations in order to establish for which type of complexes the correlation between the CD spectrum and the configuration of the metal center holds. We have previously shown that in complexes of the type Ru(cp*)(CO)LX (where cp* = menthylcyclopentadienyl or neomenthylcyclopentadienyl, L = phosphorus donor ligand, and X = halide) the region 300–400 nm is diagnostic of the configuration of the metal center.[8,10] Therefore, we have recorded the CD spectra of the individual epimers of Ru(nmcp)(CO)(PPh_3)R (Figure 4a, R = Me; Figure 4b, R = SO_2Me) in order to test the generality of the above correlation.

In common with all other compounds of the type $[Ru(nmcp)(CO)(PR_3)(L')]^{n+}$ that we have prepared, the CD spectra of compounds **3** and **4** each exhibit a total of three maxima or minima in the region 260–500 nm. Figure 4c shows the CD spectrum of $(S)_{Ru}$-Ru(nmcp)(CO)(PPh_3)R (where R = Cl, Me, SO_2Me), and it is apparent from this figure that none of the maxima or minima correlate with each other in all three compounds, despite the fact that the configuration of the chiral ruthenium atom is the same in each case. Reluctantly we are therefore forced to conclude that there is no general correlation between the CD spectrum and the configuration of the metal center. As we have shown previously,[8,10] however, for compounds of the type $[Ru(nmcp)(CO)(PR_3)(L')]^{n+}$, minor changes in the nature of the PR_3 or L′ ligands do not lead to gross changes in the CD spectrum, and in such cases CD spectroscopy may be used to compare the configurations of the metal centers.

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Supplementary Material Available: Tables of complete bond lengths and angles, thermal parameters, and hydrogen atom positional parameters for 3 and 4 (9 pages); tables of observed and final calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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